# CARBON NANOTUBE MACROFILM-BASED NANOCOMPOSITE ELECTRODES FOR ENERGY APPLICATIONS

by

Zeyuan Cao

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering

Spring 2015

© 2015 Zeyuan Cao All Rights Reserved ProQuest Number: 3718322

All rights reserved

INFORMATION TO ALL USERS The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 3718322

Published by ProQuest LLC (2015). Copyright of the Dissertation is held by the Author.

All rights reserved. This work is protected against unauthorized copying under Title 17, United States Code Microform Edition © ProQuest LLC.

> ProQuest LLC. 789 East Eisenhower Parkway P.O. Box 1346 Ann Arbor, MI 48106 - 1346

# CARBON NANOTUBE MACROFILM-BASED NANOCOMPOSITE ELECTRODES FOR ENERGY APPLICATIONS

by

Zeyuan Cao

Approved:

Suresh G. Advani, Ph.D. Chair of the Department of Mechanical Engineering

Approved:

Babatunde A. Ogunnaike, Ph.D. Dean of the College of Engineering

Approved:

James G. Richards, Ph.D. Vice Provost for Graduate and Professional Education

Signed:	I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.
C	Bingqing Wei, Ph.D. Professor in charge of dissertation
	I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.
Signed:	Tsu-wei Chou, Ph.D. Member of dissertation committee
	I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.
Signed:	Ajay K. Prasad, Ph.D. Member of dissertation committee
	I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.
Signed:	Feng Jiao, Ph.D. Member of dissertation committee

#### ACKNOWLEDGMENTS

This dissertation would not have been possible without the assistance and support from a large number of people in the last five years; I may not name them all here, but I am grateful for their contributions.

First of all, I need to recognize my advisor, Professor Bingqing Wei, for guiding me enter the world of carbon nanotubes and energy storages, for providing the resources to support my research, for encouraging me to do independent research since the first day I started working in the lab, for allowing me to work at my own pace without much pressure, for discussing the research process with me always patiently, for improving written papers and for helping sort out career options.

Secondly, I would like to thank other members of my doctoral committee, Professors Tsu-wei Chou, Feng Jiao and Ajay K. Prasad for their time, insights, and constructive feedback to make the final defense possible. I also thank the previous committee members at UD, Professors Joshua L. Hertz and Jonghwan Suhr for their assistance and suggestions with my PhD proposal exam.

The group members in our lab made my PhD life full of persistence and fun with their strong motivation, friendly competition, helpful discussions, and termless laughs. Former members Dr. Qing Zhang, Dr. Jinwen Qin, Mr. Xin Li and Dr. Changsheng Shan taught me the first lab class covering not only the necessary stuff and skills to embark research but also the valuable optimistic attitudes. Without them I would not have been able to figure out how to follow the research progress step by step. I am also thankful to current group members Mr. Taoli Gu and Dr. Shihao Hu for their efforts in contributing to the same research field and creating an interesting research environment.

Next, thanks go to Dr. Fei Deng and Dr. Chaoying Ni for training me to use SEM, TEM, AFM, and FIB. I spent about at least 200 hours accumulated on these microscopies. I enjoyed the adventure with excitement every time when I communicated with these cold, bulky, and complicated machines. I want to thank Dr. Laurel L. Kegel, Dr. Jiaxin Ye, Dr. Zhongbin Zhuang, Dr. Xinran Zhou, Ms. Liang Gong, Dr. Nopporn Rujisamphan, and Mr. Trong Dinh Pham for their kindness to teach or help me use various characterizations such as Raman, RDE, TGA, *in-situ* tribology, BET, XRD, XPS, etc. I would appreciate the members in Prof. Jiao's group Dr. Qi Lu, Mr. Bryan Yonemoto, and Mr. Greg Hutchings who helped me a lot in electrochemical measurements. I also would like to thank Mr. Roger Stahl for assisting me with instrument problems and EHS issues in our lab as well as the administrative staff from Department of Mechanical Engineering at UD, especially Ms. Lisa M. Katzmire and Ms. Letitia Toto for their patience in answering my questions on both academia and campus life.

Outside of the lab, a small badminton community at UD provided me a new hobby and unforgettably happy time when playing with many friends: Mr. Zhen Cheng, Ms. Qing Sun, Mr. Jinlin Jiang, Mr. Zhen Shen who helped me release the pressure and renew my energy to be there. I want to thank all my dear friends, Mr. Jiayin Wang, Mr. Weida Shen, Mr. Yifei Zhang, Mr. Hang Yu, Ms. Wenjie Zhao, Ms. Yue Qiao, Ms. Zheyu Zhou, Ms. Shulin Wang, Mr. Jianbo He and so on for their accompaniment during my graduate life. Finally, I give my thanks to my family with no reservation. My fiancée Mengdan has simply made things better; I will always appreciate her love, patience, and productivity. The biggest thank you must go to my parents: "You raised me up. Without your undemanding love, care, trust, inspiration, and support, I could not go that far. Thank you!"

## DEDICATION

To my dearest mother, Xiaoqing Liu and father, Baishun Cao

LIST LIST LIST ABST	OF TA OF FI OF A TRAC	ABLES GURES BBREV F	S ATIONS		xiv xvi xxiv xxvii
Chapt	er				
1	INT	RODU	CTION		1
	1.1 1.2	Gener Carbo	al n Nanotul	be Macrofilms	1 4
		1.2.1 1.2.2	Direct sy Propertie	ynthesis by chemical vapor deposition es and energy application	6 9
	1.3	Recha	rgeable L	ithium-Ion Batteries	11
		1.3.1 1.3.2	Principle Nanocor	e nposite electrodes	
			1.3.2.1 1.3.2.2	Cathode materials Anode materials	15 16
		1.3.3	Battery	assembly and electrochemical tests	
			1.3.3.1	Cell components and tests set-up Electrochemical characteristics of batteries	
	1.4	Cataly	vsts for Ox	xygen Reactions	
		1.4.1 1.4.2 1.4.3 1.4.4	Principle Oxygen Nanocor Cell asse	e of fuel cells reduction and evolution reactions mposite catalysts embly and electrochemical tests	
			1.4.4.1 1.4.4.2	Rotating disk electrodes Electrocatalytic activity	
	1.5	Supero	capacitor.		
		1.5.1	Principle	е	
			1.5.1.1	Electric double layer capacitor	

## TABLE OF CONTENTS

			1.5.1.2	Pseudocapacitor	35
			1.5.1.3	Asymmetric supercapacitor	36
		1.5.2	Nanocor	nposite electrodes	36
		1.5.3	Cell asso	embly and electrochemical tests	38
			1.5.3.1	Three-electrode and two-electrode cells	39
			1.5.3.2	Electrochemical performance of supercapacitors	40
	1.6	Resear	rch Motiv	ation and Dissertation Scope	41
	REF	ERENG	CES		46
2	CAF NAN	RBON N NOCON	NANOTU /IPOSITE	BE MACROFILM-VANADIUM PENTOXIDE S AS CATHODES OF LITHIUM-ION BATTERIES	556
	2.1	Introd	uction		56
	2.2	Experi	imental		58
		2.2.1	$V_2O_5/SV$	WNT macrofilm preparation	58
		2.2.2	Characte	erization and electrochemical measurements	58
	2.3	Result	s and Dis	cussion	59
		2.3.1	Controll	able hydrolysis deposition of V <sub>2</sub> O <sub>5</sub>	59
		2.3.2	Mesopo	rous layer structure of nanocomposites and chemical	61
		2.3.3	Phase tr	ansition during lithiation and cyclic performance	61
		2.3.4	Rate cap	pability and electrochemical impedance spectroscopy.	70
	2.4	Concl	usions		75
	REF	ERENG	CES		77
3	CAF OXI LITI	RBON N DE NA HIUM-I	NANOTU NOCOM ION BAT	BE MACROFILM-LITHIUM MANGANESE POSITES AS STRETCHABLE CATHODES OF TERIES	81
	2 1	Tu tu a di			01
	3.1 3.2	Experi	imental		81
		3.2.1 3.2.2 3.2.3	<i>In situ</i> g Structur Potentio	rowth of LiMn <sub>2</sub> O <sub>4</sub> /SWNT by hydrothermal synthesis al and electrochemical characterizations static intermittent titration test	82 83 84

	3.3	Result	ts and Dis	cussion	85
		3.3.1	Demons	stration of bendable/stretchable electrodes and three-	05
			Uninensi Tutono oti	onal nanocomposite structure	00
		3.3.2	Flastra	ion between LINIn <sub>2</sub> O <sub>4</sub> and SWINI	89
		3.3.3	Electroc	iter and benavior and performance	92
		3.3.4	Diffusiv	ity analysis by PIII I	96
	3.4	Concl	usions		97
	REF	FEREN	CES		99
4	CAI	RBON I	NANOTU	BE MACROFILM-IRON OXIDE	
	NA	NOCON	<b>MPOSITE</b>	S AS ANODES OF LITHIUM-ION BATTERIES	101
	4.1	Introd	uction		101
	4.2	Exper	imental		103
		4.2.1	α-Fe <sub>2</sub> O <sub>3</sub>	/SWNT macrofilms preparation and hydrogen	
			annealin	I I Z Z	103
		4.2.2	Characte	erization and electrochemical measurements	104
		4.2.3	Galvano	ostatic intermittent titration test	105
	4.3	Resul	ts and Dis	cussion	106
		4.3.1	Sample	preparation, morphological and structural	
			characte	pristics of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT macrofilms	106
		4.3.2	Crystall	ine structure evolution of $Fe_2O_3$ to $Fe_3O_4$ nanocrysta	ls
			during F	$H_2$ annealing	112
			4.3.2.1	SEM and HRTEM characterization	112
			4.3.2.2	XRD and Rietveld fitting	114
			4.3.2.3	XPS and Raman spectroscopy	116
		4.3.3	Electroc	hemical characteristics of α-Fe <sub>2</sub> O <sub>3</sub> /SWNT	117
			4.3.3.1	Discharge-charge curves	117
			4.3.3.2	Electrochemical impedance spectroscopy	120
			4.3.3.3	Cyclic voltammetry analysis	122
			4.3.3.4	Cyclic performance and rate capability	123
			4.3.3.5	Effect of film thickness on Li <sup>+</sup> chemical diffusion	
				coefficient	125
		121	Enhonor	ad rate canability by Ha annealing	120
		4.3.4	Emance	the rate capability by m2 annealing	132

		4.3.5	Improve	d electrochemical kinetics by H <sub>2</sub> annealing	135
			4.3.5.1 4.3.5.2	Electrochemical impedance spectroscopy Galvanostatic intermittent titration test	135 136
	4.4	Concl	usions		139
	REF	FEREN	CES		141
5	TRA NAI APF	ANSITI NOTUE PLICAT	ON META BE MACR IONS	AL OXIDE NANOCOMPOSITES WITH CARBON OFILMS FOR ELECTROCHEMIAL	144
	5.1 5.2	Introd Exper	uction imental		144 146
		5.2.1 5.2.2 5.2.3	Syntheti nanocom Structura RDE pre	c route to $M_xO_y$ (M=Fe, Co, Ni)/SWNT macrofilm posites al characterization paration and ORR/OER electrochemical	146 147
		5.2.4 5.2.5	Lithium- Asymme	ion battery electrochemical testing etric supercapacitor electrochemical testing	. 147 149 150
	5.3	Result	ts and Dis	cussion	150
		5.3.1 5.3.2	Size, mo Electroc	rphology, and structure of $M_xO_y/SWNT$ atalytic properties of $M_xO_y/SWNT$	150 153
			5.3.2.1 5.3.2.2	ORR activity OER activity	153 157
		5.3.3 5.3.4	Battery j Supercaj	performance pacitor performance	. 158 160
	5.4	Concl	usions		163
	REF	FEREN	CES		164
6	A G ELE MA BAT	ENERA CTROI CROFI ITERIE	AL APPRO DES BY U LMS AS A S	DACH TO CONSTRUCT NANOCOMPOSITE JSING FRAGMENTED CARBON NANOTUBE ADHESIVE CONDUCTORS FOR LITHIUM-ION	168
	6.1	Introd	uction		168

6.2	Exper	imental			. 170
	6.2.1	Synthes	is of SWNT	macrofilms, LiMn <sub>2</sub> O <sub>4</sub> and Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	170
	622	nanocry Preparat	stais	-FCNT nanocomposite cathodes and LTC	.1/0 )-
	0.2.2	FCNT a	nodes		. 171
	6.2.3	<i>In situ</i> ti	ribology with	h wear track imaging force measurement	
		system s	set-up		. 172
	6.2.4	Characte	erization and	l electrochemical measurements	. 173
6.3	Result	s and Dis	cussion		. 174
	6.3.1	LMO-F	CNT half ce	lls	. 174
		6.3.1.1	General ch	aracterization of LMO-FNCT	. 174
		6.3.1.2	Electroche	mical performance of LMO-FCNT	. 176
				-	
			6.3.1.2.1	Specific capacity, rate capability, and	176
			62122	Cyclic stability of samples	.1/6
			0.3.1.2.2	mass loading of ECNT adhesive	
				conductors	179
			6.3.1.2.3	Microstructural evolution related to	
				capacity	. 182
		6.3.1.3	Adhesion s	strength of LMO-FCNT	. 184
	6.3.2	LTO-FO	CNT half cel	18	. 186
	0.0.2	21010			
		6.3.2.1	Structural of	characterization of LTO-FCNT	. 186
		6.3.2.2	Electroche	mical performance of LTO-FCNT	. 188
6.4	Concl	usions			. 190
REF	EREN	CES	•••••		. 191
CON	ICLUS	ION ANI	O FUTURE	WORK	. 194
7.1	Summ	ary of the	e Research C	Contributions	. 194
7.2	Future	Research	n Work		. 198
<b>D</b> ===					
REF	ERENC	CES			. 202

7

### Appendix

- A SCIENTIFIC AND TECHNICAL CONTRIBUTIONS DURING PH.D. .... 203

### LIST OF TABLES

Table 1.1	Electrochemical performance of some typical cathode materials and nanocomposites
Table 1.2	Electrochemical performance of some typical anode materials and nanocomposites
Table 1.3	Cell types with pros and cons for LIBs
Table 1.4	Catalytic activity of some typical metal oxides and nanocomposites for ORR
Table 1.5	Catalytic activity of some typical metal oxides and nanocomposites for OER
Table 1.6	Electrochemical performance of various carbon-metal oxide nanocomposites reported in the literature
Table 2.1	Binding Energy of the fitting peaks in XPS spectra shown in Figure 2.5
Table 2.2	The fitting values of the components in equivalent circuits shown in Figure 2.8c and 2.8d75
Table 4.1	Quantitative results of EDX spectra: weight percentage of Fe and C in FC_T, FC_N and FC_t110
Table 4.2	The fitting values of components in equivalent circuit for Figure 4.13a
Table 4.3	The fitting values of components in equivalent circuit for Figure 4.13b
Table 4.4	Li <sup>+</sup> chemical diffusion coefficients upon discharge determined by EIS and the intermediate parameters applied
Table 4.5	Li <sup>+</sup> chemical diffusion coefficients upon charge determined by EIS and the intermediate parameters applied
Table 4.6	Fitting parameters of the equivalent circuit for EIS data
Table 4.7	The crystal unit cell information and the calculated molar volumes for the two iron oxides

Table 4.8	The results of $\Delta E_s / \Delta E_t$ and $M_b$ items from calculation for the two iron	
	oxides1	38

### LIST OF FIGURES

Figure 1.1	Comparison of different batteries in terms of gravimetric energy density and volumetric energy density. Reprinted with permission from reference 6 ©2008, Macmillan Publishers Limited
Figure 1.2	Structural models of (a) CNTs; (b) C <sub>60</sub> ; (c) Graphene
Figure 1.3	Schematic of (a) SWNT and (c) MWNT; High-resolution TEM images of (b) SWNT bundles; (d) individual MWNT showing multi-layers and a closed tip
Figure 1.4	Illustration of CVD growth process of SWNT macrofilms and the photography of CVD products with SEM image showing the morphology of entangled CNT networks. Reprinted with the permission from reference 36 ©2007, Royal Chemical Society
Figure 1.5	<ul><li>(a) SWNT macro-film on the metal substrates is cut to various shapes.</li><li>(b) Free-standing SWNT macro-films. (c, d) Disk electrodes punched by SWNT macro-films on Cu foils</li></ul>
Figure 1.6	The schematic illustration of the working principle of Li-ion batteries13
Figure 1.7	Four major types of lithium-ion batteries: (a) schematic of cross section for a cylindrical cell, inset: popular 18650 cell cores; (b) schematic of cross section for a prismatic cell; (c) coin cells with schematic of cross section; (d) pouch cell
Figure 1.8	Assembly processes of a CR2032 coin cell in half-cell configuration followed by a PC programmed galvanostatic charge-discharge test21
Figure 1.9	Multi-channel potentiostat with a variety of accessories
Figure 1.10	Schematic of a PEM fuel cell
Figure 1.11	RDE system with the schematic of the cell construction and simple working mechanism
Figure 1.12	Hierarchical classification of supercapacitors
Figure 1.13	Schematic of the structure of (a) EDLC, (b) pseudocapacitor, and (c) asymmetric supercapacitor

Figure 2.1	Schematic illustration of the procedures to synthesize $V_2O_5/SWNT$ hybrid mesorporous films. (b) Ball-and-stick representation of the crystalline structure of layered $V_2O_5$ and SWNTs and the chemical interaction between them
Figure 2.2	SEM images showing the morphology of V <sub>2</sub> O <sub>5</sub> /SWNT hybrid mesoporous films annealed at 400 °C for 2h. (a) Photograph of the 400 °C annealed V <sub>2</sub> O <sub>5</sub> /SWNT hybrid film. (b) cross-section, (c) top view, (d) magnified top view from (c)
Figure 2.3	(a) TEM image of $V_2O_5$ nanoparticles anchorded firmly on SWNTs after 1 h sonication of the hybrid films. (b) High-resolution TEM image of an individual $V_2O_5$ nanoparticle grown on SWNT bundles 63
Figure 2.4	(a) X-ray diffraction pattern for 400 °C annealed hybrid films on an Al foil as current collector. (b) Raman spectrum at excitation of 532 nm
Figure 2.5	X-ray photoelectron spectrum for V <sub>2</sub> O <sub>5</sub> /SWNT hybrid mesoporous films showing the interaction between the slight function group of SWNT and V <sub>2</sub> O <sub>5</sub> nanoparticles. (a) survey-scan spectrum showing all C, O and V elements. (b) V 2p region with spin orbit splitting of $2p_{3/2}$ and $2p_{1/2}$ showing V <sup>5+</sup> state. (c) C 1s region of XPS spectrum deconvoluted to peaks indicating grahitic structure of SWNT and functional groups of SWNT macro-films. (d) Asymmetrical O 1s peak of XPS spectrum fitted with the predominant peak corresponding to O atoms in V <sub>2</sub> O <sub>5</sub> and the peak of hydroxyl groups in higher binding energy. 66
Figure 2.6	Electrochemical performance for $V_2O_5/SWNT$ hybrid mesoporous film in a half cell: (a) voltage profile of discharge-charge curves at 300 mAg <sup>-1</sup> after the 1 <sup>st</sup> , 2 <sup>nd</sup> , 10 <sup>th</sup> , 20 <sup>th</sup> , 30 <sup>th</sup> , 40 <sup>th</sup> cycle, (b) specific capacity retention for 40 cycles at the rate of 300 mAg <sup>-1</sup> , (c) discarhge charge curves at various rates for the same cell after the ending of the 40 <sup>th</sup> cycle of discharge-charge tests at the rate of 300 mAg <sup>-1</sup> , (d) high- rate capacities at various rates
Figure 2.7	The cyclic voltammetry of V <sub>2</sub> O <sub>5</sub> /SWNT hybrid mesoporous film at various scan rates from 1 mV/s to 50 mV/s for a half cell with 1 M LiPF <sub>6</sub> in EC:DEC (1:1 v/v) as electrolyte, consist with the excellent high-rate performance

Figure 2.8	Electrochemical Impedance Spectroscopy (EIS) data for V <sub>2</sub> O <sub>5</sub> /SWNT hybrid mesoporous film in the coin cell after cycling at rate of 300 mAg <sup>-1</sup> : (a) Nyquist plots before the 1 <sup>st</sup> cycle (orange curve) and after the 40 <sup>th</sup> cycle (purple curve), (b) Bode phase plots before the 1 <sup>st</sup> cycle (orange curve) and after the 40 <sup>th</sup> cycle (purple curve), (c) the equivalent circuit corresponding to the 1 <sup>st</sup> cycle, (d) the equivalent circuit corresponding to the 40 <sup>th</sup> cycle
Figure 3.1	From left to right: (1) picture of fully-flexible electrode fabricated by LMO-SWNT macrofilm coupled with PDMS; and their various flexible states of: (2) bending state; (3) stationary state without strain applied; and (4) stretching state
Figure 3.2	<ul> <li>(a) SEM image of LMO-SWNT macrofilm composite with a milled trapezoid trench showing the cross section (b) magnified SEM image of the marked top-view area in (a); (c) Cross-sectional view of LMO-SWNT macrofilm composite and (d) magnified image of the rectangular area in (c).</li> </ul>
Figure 3.3	<ul> <li>(a) XRD pattern of pristine LMO and freestanding LMO-SWNT macrofilm composite.</li> <li>(b) EDX spectrum and quantitative table of elements.</li> <li>(c) TGA curve of LMO-SWNT composite.</li> <li>(d) N2 isothermal</li></ul>
Figure 3.4	(a) SEM image of individual SWNTs with LMO nanoparticles for the LMO-SWNT macrofilm composite after intense ultrasonication; (b) contrast inversion of the identical image of (a). (c) TEM image of individual SWNTs with LMO nanoparticles for the LMO-SWNT macrofilm composite after intense ultrasonication; (d) HRTEM images showing the interaction area between SWNTs and LMO and (e) individual LMO nanoparticle with well-resolved lattice fringe 90
Figure 3.5	XPS spectra of (a) C 1s; (b) O 1s; (c) Mn 2p; and (d) Mn 3p with Li 1s peaks for the LMO-SWNT macrofilm composite
Figure 3.6	<ul><li>(a) Voltage profile between 3.5 and 4.5 V, inset: CR2032 half cell illustration;</li><li>(b) PITT results; and (c) CV curve of LMO-SWNT macrofilm composite.</li></ul>
Figure 3.7	(a) Capacity retention; and (b) Rate performance of LMO-SWNT macrofilm nanocomposite

Figure 3.8	(a) Potentiostatic intermittent titration curves for LMO-SWNT macrofilm composite at various delithiation composition, inset: the $Li^+$ diffusion coefficient with delithiation composition. (b) Q as a function of $t^{1/2}$ extracted from (a)
Figure 4.1	Microscopy images of SWNT macro-films before and after heat treatment at 450 °C in air for 30 min. (a) TEM image of Fe/SWNT macro-film before the heat treatment. (b) TEM image of $\alpha$ - Fe <sub>2</sub> O <sub>3</sub> /SWNT hybrid film and inset: diameter distribution for $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles. (c) SEM image of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT hybrid film. (d) Magnified SEM image of the dashed rectangular area in (c) with an inset: photograph of a brownish semi-transparent $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT hybrid film. 107
Figure 4.2	(a) XRD pattern of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT hybrid films (black) and the pure Fe <sub>2</sub> O <sub>3</sub> after removing SWNTs (red). (b) Raman spectra of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> free of SWNT (red) and $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT hybrid film (black) 109
Figure 4.3	(a) High-resolution TEM image of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT hybrid films. (b) High-resolution TEM image of dashed rectangular area in (a) with a higher magnification
Figure 4.4	(a, b, c) SEM images with insets: photographs of FC_T, FC_N and FC_t, $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT samples by sequence of film thickness from high to low. (d) The interferometer image of FC_T with the height information between A and B marked spots. (e, f) The corresponding AFM images of FC_N and FC_t with the roughness measured between A and B marked spots
Figure 4.5	(a, b) TEM images of iron oxide/SWNT hybrid films after H <sub>2</sub> annealing; (c) HRTEM image of Fe <sub>3</sub> O <sub>4</sub> nanocrystal in the hybrid films after H <sub>2</sub> annealing; (d) TEM image of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SWNT hybrid films before H <sub>2</sub> annealing; (e) HRTEM image of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanocrystals in the hybrid films before H <sub>2</sub> annealing; (f) SAED patterns of the hybrid films before (right) and after (left) H <sub>2</sub> annealing with the corresponding photographs inset in red and brownish on the same side
Figure 4.6	(a) SEM images of the iron oxide/SWNT macrofilm nanocomposites after H <sub>2</sub> annealing and (b) in a higher magnification

- Figure 4.9 Electrochemical performance comparison among the four samples: FC\_T, FC\_N, FC\_t and the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> free of SWNTs. (a) The galvanostatic discharge-charge curves for the three  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid film samples at the end of the 5<sup>th</sup> cycle and the first two cycles of the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample, all at the same current density of 100 mAg<sup>-1</sup>. (b) The histogram plot for the discharge specific capacities of all the samples during the five cycles. (c) The Nyquist plots of the asassembled fresh cells for all the samples. (d) The Nyquist plots of all the samples after 5 cycling discharge-charge tests at 100 mAg<sup>-1</sup>..........119

Figure 4.13	Electrochemical impedance spectra for FC_N. (a,b) Nyquist plots at various potentials and the corresponding fitting lines upon discharge and charge. (c) Equivalent circuit model employed in the curve fitting
Figure 4.14	Li <sup>+</sup> chemical diffusion coefficients of FC_N determined by GITT and EIS during charge and discharge processes
Figure 4.15	(a) The rate capabilities of the iron oxide/SWNT hybrid films after (top) and before (bottom) $H_2$ annealing; (b) The discharge/charge profiles for the hybrid films after $H_2$ annealing corresponding to the selected cycles at various rates
Figure 4.16	(a) Nyquist plots of the iron oxide/SWNT macrofilms before (red line) and after (black line) H <sub>2</sub> annealing with the inset equivalent circuit used for fitting; (b) the GITT discharge/charge curves for the two hybrid films distinguished by different colors in the plot; (c) the polarization curves at the plateau potential during charge processes for the two nanocomposites; (d) the polarization curves at the plateau potential during discharge processes for the two nanocomposites 137
Figure 5.1	Two-step synthetic route to M <sub>x</sub> O <sub>y</sub> (M=Fe, Co, Ni)/SWNT macrofilm nanocomposites
Figure 5.2	(a, b, d, e) TEM and (c, f) HRTEM images of (a, b, c) Co <sub>3</sub> O <sub>4</sub> /SWNT (200°C) and (d, e, f) NiO/SWNT. Insets: Histograms of the nanoparticle size distribution
Figure 5.3	<ul> <li>(a) XRD pattrens of Co-CNT (100°C), Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400°C).</li> <li>(b) XRD patterns of Ni-CNT and NiO/SWNT. (c) Raman spectra of Co-CNT (100°C), Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400°C), Ni-CNT, and NiO/SWNT.</li> </ul>
Figure 5.4	Electrocatalytic performance of $M_xO_y/SWNT$ under RDE measurements in O <sub>2</sub> -saturated 0.1 M KOH with scan rate of 5 mV s <sup>-1</sup> . (a) ORR polarization curves of Co <sub>3</sub> O <sub>4</sub> /SWNT (200, 400°C), NiO/SWNT, Fe <sub>2</sub> O <sub>3</sub> /SWNT, and Co-CNT (100°C) catalysts at a continuous electrode rotating speed of 1600 rpm. (b) ORR polarization curves of Co <sub>3</sub> O <sub>4</sub> /SWNT (200°C) at different rotation rates. (c) K-L plots from (b). (d) <i>iR</i> -corrected OER polarization curves of Co <sub>3</sub> O <sub>4</sub> /SWNT (200, 400°C), NiO/SWNT, Fe <sub>2</sub> O <sub>3</sub> /SWNT, and Co- CNT (100°C) at rotation rate of 2500 rpm. (e) Tafel plots from (d) 155

Figure 5.5	LIB performance of $M_xO_y/SWNT$ in half cells. (a) CV curves at a slow scan rate of 0.1 mV s <sup>-1</sup> , and (b) Galvanostatic discharge/charge voltage profiles at a constant current density of 50 mA g <sup>-1</sup> after CV tests of Co <sub>3</sub> O <sub>4</sub> /SWNT and NiO/SWNT. (c) Discharge/charge curves at the selected cycles, (d) Cycling performance of NiO/SWNT electrodes
Figure 5.6	(a) CV curves of NiO/SWNT at various scan rates. Inset: Specific capacitance as a function of the scan rates calculated from CV. (b) CV curves of an asymmetric supercapacitor composed of (+) NiO/SWNT-SWNT (-) at different scan rates between 5 - 200 mV s <sup>-1</sup> . Inset: Specific capacitance <i>vs.</i> scan rates. (c) Galvanostatic charge/discharge cyclic performance of the asymmetric supercapacitor within a voltage window of 1.5 V at a current density of 20 A g <sup>-1</sup> . Inset: charge/discharge curves. 162
Figure 6.1	Schematic illustration of preparing LMO-FCNT composite electrodes by ultrasound processing and drop casting
Figure 6.2	Schematic illustration of <i>in-situ</i> tribology combining adhesion force measurement and wear tracking images
Figure 6.3	(a) TEM and (b, c) high magnification TEM images of LMO-FCNT and (d) HRTEM image of LMO-FCNT showing individual LMO nanocrystal and FCNT mesh
Figure 6.4	<ul> <li>(a) GCD voltage profiles of LMO-FCNT composite electrodes cycled at 15 mAg<sup>-1</sup>.</li> <li>(b) CV curves of LMO-FCNT during the first 5 cycles.</li> <li>(c) Cycling performance of LMO-FCNT at 15 mAg<sup>-1</sup> for 50 cycles.</li> <li>(d) Comparison of rate capability between LMO-FCNT and LMO-PVDF-CB at different rates.</li> </ul>
Figure 6.5	(a) Galvanostatic charge/discharge voltage profiles of LMO-FCNT composite electrodes cycled at 150 mAg <sup>-1</sup> . (b) Cycling performance of LMO-FCNT at 150 mAg <sup>-1</sup> . Comparison of (c) voltage profiles for the 100 <sup>th</sup> cycle and (d) cycling performance between LMO-30 wt% FCNT, LMO-15 wt% FCNT and LMO-5 wt% FCNT at 150 mAg <sup>-1</sup> 180
Figure 6.6	Comparison of (a) Nyquist plot and (b) Bode phase plot between LMO-FCNT composites with different mass loading of FCNT
Figure 6.7	SEM images of LMO-FCNT composite before cycling (a, c, e) and (b, d, f) after cycling

Figure 6.8	(a) XRD patterns of pure LMO nanoparticles, LMO-FCNT composite before and after cycling. (b) FTIR spectrum of LMO-FCNT composite
Figure 6.9	Wear track images and adhersion strength of (a) LMO-30 wt% PVDF, (b) LMO-30 wt% FCNT before cycling, (c) LMO-30 wt% FCNT after cycling, (d) LMO-15 wt% FCNT before cycling, and (e) LMO-5 wt% FCNT before cycling. (f) Histogram of mean adhersion strength between LMO-30 wt% PVDF and LMO-FCNT with different mass loading of FCNT
Figure 6.10	(a) SEM image and (b) high magnification SEM image of LTO-FCNT nanocomposite. (c) XRD patterns of LTO nanoparticles before and after annealing in the Ar atmosphere and LTO-FCNT
Figure 6.11	(a) Galvanostatic discharge/charge voltage profiles of LTO-FCNT composite electrodes cycled at different rates. (b) Rate capabilities of LTO-FCNT. Comparison of (c) galvanostatic discharge/charge voltage profiles and (d) cycling performance for LTO-FCNT cycled at 1 C and 10 C
Figure 7.1	Illustrating other potential energy applications of CNT macrofilm- based nanocomposites

### LIST OF ABBREVATIONS

AFM	Atomic force microscopy
BET	Brunnauer-Emmett-Teller method
CE	Coulombic efficiency
CNT	Carbon nanotube
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DEC	Diethyl carbonate
EC	Ethylene carbonate
EDLC	Electrical double layer capacitors
EDX	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EV	Electric vehicles
FCNT	Fragmented carbon nanotube macrofilms
FIB	Focus ion beam microscopy
FTIR	Fourier-transform infrared spectroscopy
GC	Glassy carbon
GCD	Galvanostatic charge-discharge
GITT	Galvanostatic intermittent titration technique
HEV	Hybrid electric vehicles
HRTEM	High-resolution transmission electron microscopy
IHP	Inner Helmholtz plane
LIB	Lithium-ion battery
LMO	Lithium manganese oxides

LTO	Lithium titanate
МО	Metal oxides
MWNT	Multi-walled carbon nanotube
NMP	N-methyl-pyrrolidone
OCV	Open circuit voltage
OER	Oxygen evolution reaction
OHP	Outer Helmholtz plane
ORR	Oxygen reduction reaction
PANi	Polyaniline
PDMS	Polydimethylsiloxane
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
PEMFC	Proton exchange membrane fuel cells
PFM	Poly(9,9-diotylfluorene-co-fluorenone-co-methylbenzoic ester)
PHEV	Plug-in hybrid electric vehicles
PITT	Potentiostatic intermittent titration technique
PVDF	Polyvinylidene fluoride
RDE	Rotation disk electrode
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
SOD	State of discharge
SOFC	Solid oxide fuel cells
SWNT	Single-walled carbon nanotube
TEABF4	Tetraethylammonium tetrafluoroborate
TEM	Transmission electron microscopy

- TGA Thermogravimetric analysis
- TOF Turn of frequency
- XPS X-ray photoelectron spectroscopy
- XRD X-ray diffraction

#### ABSTRACT

Finding new electrode materials for energy conversion and storage devices have been the focus of recent research in the fields of science and engineering. Suffering from poor electronic conductivity, chemical and mechanical stability, active electrode materials are usually coupled with different carbon nanostructured materials to form nanocomposite electrodes, showing promising electrochemical performance. Among the carbon nanostructured materials, carbon nanotube (CNT) macrofilms draw great attention owing to their extraordinary properties, such as a large specific surface area, exceptionally high conductivity, porous structure, flexibility, mechanical robustness, and adhesion. They could effectively enhance the electrochemical performance of the incorporated active materials in the nanocomposites. In this dissertation, CNT macrofilm-based nanocomposites are investigated for rechargeable lithium-ion batteries, supercapacitors, and electrocatalysts of fuel cells.

The progressive research developed various nanocomposites from cathode materials to anode materials followed by a general nanocomposite solution due to the unique adhesive property of the fragmented CNT macrofilms. The *in-situ* synthesis strategy are explored to *in-situ* deposit unlithiated cathode materials V<sub>2</sub>O<sub>5</sub> and lithiated cathode materials LiMn<sub>2</sub>O<sub>4</sub> nanocrystals in the matrix of the CNT macrofilms as nanocomposites to be paired with metallic lithium in half cells. The presence of oxygen-containing functional groups on the surface of the CNT macrofilms after purification can enhance the association with the active materials to enable the facilitated transport of solvated ions to the electrolyte/electrode interfaces and increase the diffusion kinetics, consequently enhancing the battery performance in terms of high specific capacity, rate capability, and cycling stability.

It is also significant to demonstrate a reliable, low-cost, and effective route to synthesize the family of metal oxides ( $M_xO_y$  (M=Fe, Co, Ni)) with CNT macofilms as high performance anodes for rechargeable lithium-ion batteries and as catalysts for oxygen reduction/evolution (ORR/OER). All  $M_xO_y$ -CNT macrofilm nanocomposites inherit the high specific capacity and cycling stability for lithium-ion batteries. NiO/SWNT and Co<sub>3</sub>O<sub>4</sub>/SWNT (200 °C) have their specialized high catalytic activities for ORR and OER in alkaline solutions, respectively. NiO/SWNT also exhibits an excellent electrochemical performance in asymmetric supercapacitors with a high power and energy density. Experimental measurements on electrochemical kinetics such as potentiostatic/galvanostatic intermittent titration techniques (PITT/GITT) are depended to understand the underlying improved Li<sup>+</sup> diffusion behavior of nanocomposites. Critical effects of the film thickness have been identified. The CNT macrofilm with a thickness that is comparable to the characteristic diffusion length of 300~500 nm enables the nanocomposite with the highest Li<sup>+</sup> chemical diffusion coefficient and thus an optimal electrochemical performance.

The adhesive characteristic of CNT macrofilms is noticed for the first time after fragmentation by ultrasound that origins from irregular structures of laterally 2-D distributed CNT segments. The fragmented CNT macrofilms (FCNT) as "bifunctional" adhesive conductors promote a general approach to construct nanocomposite electrodes with both cathode and anode materials for lithium-ion batteries. An *in-situ* tribology method combining the wear track imaging and force measurement is employed to evaluate the adhesion strength of the adhesive FCNT conductors. The results show that the FCNT macrofilms have a higher adhesion strength than the conventional polymer binder polyvinylidene fluoride (PVDF). It is confirmed that the fabricated

nanocomposite electrodes exhibit high rate and retention capabilities, superior to the electrodes using PVDF and carbon black. Thus, FCNT is recognized to be a competent substitute for polymer binders to maintain mechanical integrity and meanwhile to improve electrical connectivity of active materials in the nanocomposite electrodes. In addition, this new electrode manufacturing technique avoids the utilization of toxic organic solvents and could provide a revolution to traditional battery industry.

### Chapter 1

#### **INTRODUCTION**

#### 1.1 General

Since the industrial resolution, particularly with the advent of electric era and the coming of contemporary information age, fossil fuels have been major energy resources to generate electricity for human. However, the massive consumption of irreproducible fossil fuels such as coals and natural gases leads to the dramatic increase of CO<sub>2</sub> emission, which is also the culprit of the global warming.[1] Thus, it is becoming urgent to seek alternatively renewable and clean energy resources (including hydrogen, wind and solar power) to alleviate the consumption of fossil fuels and even replace them. To take advantage of new energy resources to generate electricity, developing new energy conversion devices are also desired. Fuel cell is such a device that converts the chemical energy from a clean fuel such as hydrogen into electricity through a chemical reaction with oxygen.[2] Meanwhile, the increasing electricity productivity from these new energy resources accelerates the exploration of energy storage devices such as batteries and supercapacitors that serve as transducers with a reversible conversion between stored chemical energy and electrical energy.[3] Therefore, both the energy conversion and storage devices become attractive to global scientists and researchers.[4] As predicted by scientists, fuel cells and batteries could be effective strategies to reduce the carbon footprint if the inner combustion engines of the world's 800 million cars could be replaced by those electric "hearts".[4,5]

Fuel cells, batteries and supercapacitors have the common structure that consist of two electronically conductive electrodes and electrolyte as an inner, ionically conductive media. Although they have different working mechanisms, their voltage is limited by the potential difference and also the breakdown voltage of electrolyte. More specifically, fuel cell and battery voltage is determined by the difference of chemical potentials between the two electrodes (for fuel cell, they are H<sub>2</sub> and O<sub>2</sub>), which is dictated by Nerst Equation  $\Delta G$ =-nEF.[3] They all can supply power to the loadings such as electric appliances by connecting them with the two electrodes through an external circuit where electrode. Meanwhile, the charged ions are transported through the electrolyte via the inner circuit in the opposite direction to maintain the charge balance. Among all types of batteries, lithium-ion batteries have attract extensive attention due to the predominant advantage of high energy density (both gravimetric and volumetric, see Figure 1.1).[6]

The emergence and fast development of electric vehicles (EVs), hybrid EVs (HEVs) or plug-in hybrid EVs (PHEVs) and smart energy grids over the last two decades stimulate the increasing demand of these devices (fuel cells, lithium-ion batteries and supercapacitors) with higher electrochemical performance in terms of higher energy density, power density and long lifetime.[7,8] Electrode materials with high capacity/capacitance, rate capability and cyclic stability play a vital role in boosting the electrochemical performance[7,8]. Carbon-based nanomaterials have been extensively studied and widely used as electrode materials, due to their high conductivity, high surface area (up to  $2000 \text{ m}^2/\text{g}$ )[9], excellent anti-corrosion property, high temperature stability, controllable porous structure, compatibility in composite

materials, and relatively low cost.[10] They have structural diversity in different forms such as activated carbons,[11] templated carbons,[12] carbide-derived carbons,[13] activated carbon fabrics,[14] carbon fibers,[15] carbon aerogels,[16] carbon nanotubes (CNTs), [17, 18] carbon nanohorns,[19] carbon onions,[20] and the emerging graphene[21-23] or graphene composite[24-26] in recent research.



Figure 1.1 Comparison of different batteries in terms of gravimetric energy density and volumetric energy density. Reprinted with permission from reference 6 ©2008, Macmillan Publishers Limited.

Currently, they are the ideal substrates and electronically conductive additives to be coupled with active materials to form nanocomposite electrodes for energy conversion and storage devices.

#### **1.2** Carbon Nanotube Macrofilms

Among those diverse nanostructured carbon materials, CNT is one of carbon allotropes with a unique one-dimensional (1D) cylindrical nanostructure. CNTs are members of the fullerene (0D structure) structural family. CNTs have a long and hollow structure with two closed tips containing 12 pentagon carbon atoms and the walls containing one-atom-thick sheets of carbon expanded by millions of hexagons tiles as shown in the ball-stick models of Figure 1.2a. The closed tips are derived from fullerenes. The typical fullerene (Figure 1.2b), also called buckyball, is a molecule with 60 carbon atoms ( $C_{60}$ ) in the form of a hollow sphere which consists of 20 hexagons and 12 pentagons. The one-atom-thick carbon sheets forming the CNT walls are recognized as the basic constructive units called graphene with a 2D structure as illustrated in Figure 1.2c.



Figure 1.2 Structural models of (a) CNTs; (b) C<sub>60</sub>; (c) Graphene.

When the graphene sheets are stacked along the normal direction, they compose graphite, a well-known carbon allotrope as anodes of lithium-ion batteries.[27] As for CNTs, these sheets are rolled at specific and discrete ("chiral") angles, and the combination of chiral and radius dominates the properties of nanotubes; for example, whether the individual nanotube shell is a metal or semiconductor.[28] Based on the assembly of carbon patterns and number of rolled layers, CNTs are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).



Figure 1.3 Schematic of (a) SWNT and (c) MWNT; High-resolution TEM images of (b) SWNT bundles; (d) individual MWNT showing multi-layers and a closed tip.

SWNTs are visualized in Figure 1.3a and 1.3b with a cylindrical tube seamlessly wrapped by a single graphene sheet. The diameter of the SWNTs ranges from 1 to 5

nm.[29] MWNTs (Figure 1.3c and d) are composed of concentric tubes of graphene layers with an interlayer distance of approximately 3.4 Å. The outer diameter of the MWNTs ranges from 5 to 30 nm or even higher (~100 nm). Individual nanotubes (both SWNTs and MWNTs) naturally align themselves into bundles being held together by van der Waals forces via  $\pi$ -stacking.[30] Compared with other nanostructured carbon materials and regular CNTs in a powder form, CNT macro-films, in particular SWNT macro-films, with controllable web-like three-dimensional networks that are selfassembled by CNTs as building blocks show unique properties in terms of mechanical robustness, large specific surface area, thermal stability, and superior electrical conductivity  $(10^4 \sim 10^5 \text{ S/cm})$  in a more stable and flexible integrity, which is ideal as free-standing electrodes for energy applications including next-generation energy storage devices and electrocatalysts.[31] Large-scale fabrication of SWNT films with homogeneous and controllable size and porous structure could be achieved by various approaches including post-processing methods: LB technique, [32] vacuum filtration, [33] drying drop, [34] and direct synthesis: arc-discharge. [35] However, the complicated processing techniques and time-consuming shortcomings extremely limit the large yield of the products for practical use, although the multi-step post-treatment methods are usually capable of precisely controlling the desired orientation, morphology, and pore sizes of the SWNT films, Therefore, a more direct, simple and cost-effective strategy is highly needed and was successfully developed.[36]

#### **1.2.1** Direct synthesis by chemical vapor deposition

Chemical vapor deposition (CVD) is the most versatile technique available for large-scale fabrication of conformal CNTs compared with other available techniques such as arc-discharge and laser ablation. So does it become the top choice method for
the direct production of the CNT macro-films. The experimental setup for the CVD growth consists of a gas system to deliver the feedstock or create a desirable atmosphere and a heating system which is a ceramic tube furnace shown in Figure 1.4. The typical synthesis process is to use the solid volatile mixture of ferrocene/sulfur powders (atomic ratio Fe: S = 10: 1) as precursors by a modified floating CVD method. It has two separate phases: deposition and growth. During the deposition, the ferrocene with a relatively low sublimation point (~100  $^{\circ}$ C) is introduced with the carrier gas flow of argon (200 ml/min) into the central reaction zone of the furnace from the inlet of a ceramic tube. The ferrocene then starts pyrolysis at a high temperature to generate a carbon source and iron catalyst. The growth was carried out at 1150 °C with a mixed gas flow of argon (1500 mL/min) and hydrogen (150 mL/min). The temperature is a key factor to control nanotube growth by CVD. MWNTs are mainly produced at lower temperatures in the range 500-800 °C, whereas SWNTs require higher temperatures in the range of 600-1200 °C. Sulfur acts as an additive to promote SWNT growth as well as to enhance the growth rate of SWNTs. It was widely recognized that sulfur is predominant in controlling the wall number of CNTs. It is found that large-area SWNT macro-films (Figure 1.4) with uniformity (randomly homogeneous entanglement of SWNT bundles) and conformability (distribution of the nanotube diameter ranges from 0.8 to 1.3 nm) could be collected from the entire tube with a large diameter. This is the result of a reverse gas flow generated from the central hot zone to the cold endings due to the pressure difference between them. The thickness of the films can be tuned by controlling the amount of the precursor mixtures, substrate position in the tube, and reaction time.

This direct deposition of SWNT macro-films outperformed other synthetic methods with three advantages. First, the precursor only contains two solid state

components and no additional gaseous or liquid carbon source (e.g. methane,[37] hexane,[38] and xylene[39]) and prepared metallic catalytic layers (e.g. Fe, Co or Ni) on rigid substrates (e.g. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) are required. Second, the films are demonstrated that they can be deposited on various flexible substrates from metallic foils (e.g. stainless steel etc.) to polymer films which could be placed at both cold endings of the inner tube.



Figure 1.4 Illustration of CVD growth process of SWNT macrofilms and the photography of CVD products with SEM image showing the morphology of entangled CNT networks. Reprinted with the permission from reference 36 ©2007, Royal Chemical Society

Last but not the least, the as-deposited SWNT macro-film with up to 200 cm<sup>2</sup> area is easily peeled off from substrates without any damage and could also be transferred to current collectors (e.g. Cu, Al, Ni) and further cut into any desired shapes and sizes or maintained in a free-standing form when used as electrodes for electrochemical cells. (Figure 1.5)



Figure 1.5 (a) SWNT macro-film on the metal substrates is cut to various shapes. (b) Free-standing SWNT macro-films. (c, d) Disk electrodes punched by SWNT macro-films on Cu foils.

# **1.2.2** Properties and energy application

The original SWNT macro-films without any treatment after production have a porous structure with large specific surface area and contain impurities of amorphous carbon and iron catalysts derived from the pyrolysis of ferrocene. These characteristics make them a potential cathode catalyst for metal-air batteries. Meanwhile, the hydrophobic surface property of films could prevent organic electrolyte and some metal anodes such as lithium from deterioration by the water vapor in air and consequently will enhance the lifetime of cells.

The following post purification towards these SWNT macro-films can remove the impurities and transform the initial hydrophobic surface to hydrophilic by increasing hydroxyl, carboxyl, and other functional groups without damaging the integrity of the films. We have the purifying methods such as heat treatment in air at 450  $^{\circ}$ C for 0.5 ~1 h or slight oxidation by immersion in 30% H<sub>2</sub>O<sub>2</sub> solution for 72 h and rinsing with acid (37% HCl). The purified macro-films still maintain the porous structures. The presence of oxygen-containing functional groups could enhance the adhesion of the SWNT macro-films with current collectors and be coupled with other active energy nanomaterials such as V<sub>2</sub>O<sub>5</sub>, [40] Fe<sub>2</sub>O<sub>3</sub>, [41] LiMn<sub>2</sub>O<sub>4</sub>, [42] LiNi<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>O<sub>2</sub>, [43] LiFePO<sub>4</sub>, [44] RuO<sub>2</sub>, [45] MnO<sub>2</sub>, [46] and sulfur [47] to form nanocomposite electrodes for lithium-ion batteries, supercapacitors, and Li-S batteries. They could also be combined with many active catalysts such as noble metals (e.g. Pt,[48] Pd,[48] Au[49]) and metal oxides/hydroxides (e.g. IrO<sub>2</sub>, [50] Co<sub>3</sub>O<sub>4</sub>, [50] NiO [51] and Ni(OH)<sub>2</sub> [52]) in electrocatalysis reactions for fuel cells. The functionalization (oxidation) hardly impact the high electrical conductivity of the films. The thinnest SWNT film (< 50 nm) obtained with the extremely tunable growth rate of the CNT layers still has a sheet resistance of ~45  $\Omega/\Box$  with an optical transparency of as high as 80%.

When the films are chopped into tiny pieces under ultrasound, their intrinsic properties of sticky surface and web-like morphology are unchanged, making them a potential binder additive with high conductivity. In addition, SWNT macro-films exhibit excellent stretchability up to 50% pre-strain, and it is also notable that the electrical resistance experienced no remarkable change even under 50% tensile strain.

Combination of these unique properties including superior electrical conductivity, adhesive surface, hydrophobic-hydrophilic transformation, functionality

into nanocomposites as well as the high flexibility and deformability, awards the SWNT macro-films to open a promising field worth the investigation and research of their potential for energy applications, especially for energy storage and electrocatalysis.

## **1.3 Rechargeable Lithium-Ion Batteries**

Rechargeable Li-ion batteries (LIB) involve a reversible insertion/extraction of lithium ions, called the guest species, into/from a host matrix (electrode materials) which is a lithium insertion compound, during the charge/discharge processes. The brief history of LIB has experienced three major periods. [53] From 1972 to 1980, the concept of reversible electrochemical intercalation gave the birth of lithium batteries with layered dichalcogenides such as TiS<sub>2</sub> as a cathode, which serves the guest-host intercalation reactions for insertion and extraction of lithium ions, proposed by Whittingham et al. [54] The total electrochemical process is termed as the rockingchair process involving the cyclic transfer of lithium ions between the two electrodes since the lithium ions "rock" from one electrode side to the other. [55] However, the lithium dendrite formation during charging at the anodes composed of pure lithium metal, inevitably caused a catastrophic failure of a battery by shorting circuit between the two electrodes. Such a safety issue delayed the commercialization of LIB severely and was not resolved until metallic lithium was substituted by an alloy with Al. [56] In 1977-1979, Exxon realized the first marketed button cells with LiAl anodes and TiS<sub>2</sub> cathodes. Then the time moved to the era of layered oxides in 1980-1990 and the first surge of large commercialization arrived. In this period, LiCoO<sub>2</sub> stood out with a similar layered structure to that of the dichalcogenides and consequently recognized as an ideal cathode candidate with the similar Li-intercalation mechanism by Goodenough et al. [57] Meanwhile, with the discovery of the highly reversible, low voltage Li

intercalation–deintercalation process in carbonaceous material, e.g. graphite, SONY successfully made the first product of Li-ion battery by combining the LiCoO<sub>2</sub> cathode with a graphite anode. [58] Despite the dominant role of these two electrode combination choice promoted by SONY in the rechargeable lithium battery market, the limited availability and high price of cobalt and also their limited capacity restrict its applications. Seeking alternatives for large-scale applications is highly demanded, especially as envisioned for EV or HEV. Since 1990 to present, the second-generation Li-ion batteries have been extensively developed. Many electrode materials were investigated including the spinels, e.g. LiMn<sub>2</sub>O<sub>4</sub>, as cathode,[42] Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as the anode;[59] layered mixed-metal dioxides such as LiNi<sub>y</sub>Mn<sub>y</sub>Co<sub>1-2y</sub>O<sub>2</sub>, [43] transition metal compounds in olivine phase such as LiMPO<sub>4</sub> (M=Co, Fe, Mn, Ni), and a big family of metal oxides with the advantages of low cost, abundance and also environmentally benignity. [60]

## 1.3.1 Principle

A typical structure of a commercial LIB consists of a graphite anode, a cathode formed by lithium metal oxide such as  $LiCoO_2$ , and a separator embedded in an organic electrolyte containing a lithium salt (e.g. 1 M LiPF<sub>6</sub> in 1:1 of diethyl carbonate (DEC) and ethylene carbonate (EC) by volume). The schematic in Figure 1.6 illustrates the working principle of LIBs involving the electrochemical reactions at both electrodes in Equations 1.1 and 1.2:

$$\text{LiCoO}_{2} \xleftarrow{\text{charge}}{\text{Li}_{1-x}\text{CoO}_{2} + x\text{Li}^{+} + xe^{-1}} \qquad \text{Cathode} \qquad 1.1$$

$$6C + xLi^+ \xrightarrow{cnarge} Li_xC_6$$
 Anode 1.2



Figure 1.6 The schematic illustration of the working principle of Li-ion batteries.

The anode and cathode is the source and sink of the lithium ions, respectively. The electrolyte balances the charge transfer by promoting the ionic transport inside the cell, which is separated from the electronic transport that happens in the external circuit via electron flow for power supply. Throughout the charging process, lithium ions migrate from the cathode (LiCoO<sub>2</sub> in this case) through the electrolyte and are intercalated into the graphite anode (Li<sub>x</sub>C<sub>6</sub>). During discharge, the movement of lithium ions is in a reverse process: Li ions are extracted from the anode and intercalated into the cathode.

The open circuit potential  $V_{oc}$  of a LIB is decided by the difference in the Li<sup>+</sup> chemical potential between the cathode  $\mu_{cathode}$  and the anode  $\mu_{anode}$  as Nernst Equation (Equation 1.3) mentioned in Section 1.1 indicates:

$$V_{oc} = \frac{\mu_{cathode} - \mu_{anode}}{F}$$
 1.3

where *F* is the Faraday constant. The  $V_{oc}$  is given by the Gibbs free energy involved in both the electron transfer and the Li<sup>+</sup> transfer, which is related to the work functions of the cathode and anode. It is further governed by the crystal structure and the coordination geometry of the site for the Li<sup>+</sup> ions to be inserted and extracted back and forth [61].

## **1.3.2** Nanocomposite electrodes

Since 2000, nanotechnology has been involved in the design of next-generation LIB with electrode nanomaterials. [5] They have the potential to dramatically improve the electrochemical performance because of many emerging novel properties and reaction pathways under the nanoscale dimension. [5] As various morphologies and structures have been successfully synthesized such as nanoparticles, nanowires, nanotubes, and nanorods, the Li<sup>+</sup> diffusion length in these solid electrodes would be shortened to achieve fast Li<sup>+</sup> transport and a high power density. [62,63] However, the electrode kinetic issues including the low electronic and ionic conductivities related to most of electrode nanomaterials, such as the nanostructured metal oxides, still remain as the key challenge. [64] Thus, a concept of carbon-matrix nanocomposite has been proposed to overcome the problem by combining the nanomaterials with a highlyconductive carbon matrix in a nano-dimensional structure such as graphene, CNTs and SWNT macrofilms described in Section 1.2. It is recognized that the electrical, electrochemical, and mechanical properties of the nanocomposite will differ markedly from that of the component materials. The carbon matrix as scaffolds or substrates to be incorporated with electrode nanomaterials could exponentially enhance ionic and electronic conductivities. The enlarged surface area also increases the contact area between electrolyte and electrode and hence the number of active sites for

electrochemical reactions. The increased active area of an electrode in turn can reduce electrode polarization loss and improve energy density and efficiency. [5,63] The carbon matrix can also store extra Li ions on the surfaces, interfaces, and in the nanopores or tubes to boost the capacity. In addition, the nanocomposite electrodes also have an improved mechanical strength and structural integrity, which can improve the cyclic stability by efficiently accommodating irreversible volume or structural change during cycling and minimizing the capacity fading with the help of carbon supports as buffer layers. [65]

# **1.3.2.1** Cathode materials

Depending on the current anodes are whether carbonaceous such as graphitic carbons or a metallic lithium/lithium alloy, modern cathode materials for LIB are generally prepared in the lithiated state (source of Li<sup>+</sup> ions) paired with graphite anodes or in delithiated state paired with a lithium metal (source to provide Li<sup>+</sup> ions). It is worth noting that the paired cathodes should have higher average potentials versus Li/Li<sup>+</sup> than earlier materials such as TiS<sub>2</sub> for Li metal batteries to compensate for the graphite anodes with a penalty of approximately 0.1 V compared to Li metal, and also to maximize energy density. For ease of handling, it is desirable that the material be reasonably air-stable at room temperature. Moreover, the requirement for high specific capacity generally restricts our choices to compounds containing first-row transition metals (usually Mn, Fe, Co, and Ni) and vanadate containing V materials. [55] Today's technologically significant cathodes fall into two broad categories: metal oxides (e.g. LiMn<sub>2</sub>O<sub>4</sub> and V<sub>2</sub>O<sub>5</sub>) and polyanionic compounds (e.g. LiFePO<sub>4</sub>). [53] The electrochemical performance of various cathode materials and their corresponding

carbon-matrix nanocomposites reported in the literature are summarized in Table1.1 as follows:

		Capacit	y(mAh/g)	Curront	Voltago	Ref
Electrode materials	Function	Initial	After nth cycle	Density (mA/g)	versus Li <sup>+</sup> /Li (V)	ere nc e
$V_2O_5$ nanofilms	Cathode	~402	~240 (200th)	200	2-4	66
V₂O₅ nanowire- graphene nanocomposite	Cathode	~250	~250 (50th)	200	2-4	67
V <sub>2</sub> O <sub>5</sub> -CNT nanocomposite	Cathode	~450	~400 (20th)	560	1.5-4	68
LiMn <sub>2</sub> O <sub>4</sub> nanorods	Cathode	110	85 (100th)	148	3.5-4.3	69
LiMn <sub>2</sub> O <sub>4</sub> /CNT nanocomposite	Cathode	109	80 (50th)	148	3.2-4.3	70
LiMn <sub>2</sub> O <sub>4</sub> /reduced graphene oxides	Cathode	137	120 (100th)	1480	3.5-4.5	71

 Table 1.1
 Electrochemical performance of some typical cathode materials and nanocomposites

#### **1.3.2.2** Anode materials

Most of the improvements in anodes actually implemented over the last two decades have involved carbonaceous materials due to their extremely negative working voltage close to lithium and high Coulombic efficiency in concert with lithiated cathode materials. [55] The presence of them successfully solved the safety issues of lithium metals. However, the well-understood maximum intercalation mechanism of graphitic carbons to accommodate one lithium per six carbon atoms (x=1 in Li<sub>x</sub>C<sub>6</sub>) fails to break through the limitations of capacity. The short of satisfying needs for high power and/or

capacities in practical applications becomes the driving force for people to recheck the mechanism of lithium conversion reactions of interstitial-free 3d metal oxide structures (Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, NiO, and so on), which are ever believed unsuitable for intercalation chemistry. [55,64] Nevertheless they could exhibit large, rechargeable capacities in cells with lithium. The specific capacities of these materials can be as high as 1000 mA h  $g^{-1}$  (about three times those of commonly used graphitic carbons). [64] They, together with their corresponding carbon-matrix nanocomposites, are potential candidates for anode materials. The electrochemical performance of various such anode materials reported in the literature are summarized in the following Table1.2.

		Capacit	acity(mAh/g)		Voltago	Ref
Electrode materials	Function	Initial	After nth cycle	Density (mA/g)	versus Li <sup>+</sup> /Li (V)	ere nc e
Co₃O₄ nanoparticles	Anode	~1230	~200 (60th)	100	0.005-3	72
Co <sub>3</sub> O <sub>4</sub> nanowires	Anode	~1300	~200 (60th)	100	0.005-3	72
Co₃O₄/graphene hybrid	Anode	~1097	~935 (30th)	50	0.01-3	73
Mesorporous α- Fe <sub>2</sub> O <sub>3</sub>	Anode	~1730	~1293 (50th)	200	0.01-3	74
Fe <sub>2</sub> O <sub>3</sub> /single- walled carbon nanohorns	Anode	~1438	~950 (100th)	150	0.01-3	75
Fe <sub>2</sub> O <sub>3</sub> /reduced graphene oxide nanocomposites	Anode	~1693	~1100 (30th)	100	0.005-3	76
NiO nanowall	Anode	~1050	~638 (85th)	895	0.005-3	77

 Table 1.2
 Electrochemical performance of some typical anode materials and nanocomposites

NiO-graphene			~1031			
nanosheet	Anode	~1056	(40th)	71.8	0-3	78
composites			(4011)			

#### **1.3.3** Battery assembly and electrochemical tests

LIBs have to be assembled into specific construction no matter for commercial purpose or laboratory test use. Depending on various shapes available, they can generally be divided into four types as depicted in Figure 1.7 with respective pros and cons summarized in Table 1.3. [79] The coin cell, also known as button cell, with smallsize and compact design as well as low cost, is suitable for our research purpose in lab use.

Without any specification, all the cells under test in the following chapters are assembled in this type. Furthermore, the assembly of coin cells involves two configurations for LIBs, i.e., the half-cell and the full-cell configurations. To analyze the battery performance, it is also mandatory to have a preliminary knowledge of the electrochemical characteristics of the cathode and anode materials such as specific capacity and rate capability measured by employing a series of electrochemical testing methods.



Figure 1.7 Four major types of lithium-ion batteries: (a) schematic of cross section for a cylindrical cell, inset: popular 18650 cell cores; (b) schematic of cross section for a prismatic cell; (c) coin cells with schematic of cross section; (d) pouch cell.

Table 1.3	Cell	types	with	pros	and	cons	for	LIBs.
-----------	------	-------	------	------	-----	------	-----	-------

Cell Type	Pros	Cons	Usage
Cylindrical	good cycling ability; withstand high	heavy; low packaging density due to space	power tools, medical
	internal pressures without deforming;	cavities.	instruments and laptops
	economical		

Prismatic	improves space utilization and allows flexible design	expensive to manufacture; less efficient in thermal management and shorter cycle life	mobile phones, tablets and low- profile laptops
Pouch	simple; flexible and lightweight to battery design	no design standard; safety risk when exposure to high humidity and hot temperature	consumer, military and automotive applications; laboratory or company for research
Coin	small size, compact and inexpensive	not allow fast charging	cordless telephones, small medical devices; laboratory or company for research

# **1.3.3.1** Cell components and tests set-up

A standard CR2032 coin cell in the half cell configuration is typically assembled by a hydraulic assembly machine as illustrated in Figure 1.8 with the three primary functional components: two electrodes and one separator saturated in electrolyte. The working electrode could be either the cathode or anode material as positive electrodes across metallic lithium. Li metal in the half cell is the common reference material as negative electrodes to evaluate the Li<sup>+</sup> generation capability for the lithiated material e.g. LiCoO<sub>2</sub> and Li<sup>+</sup> insertion/extraction capability for the delithiated material e.g. graphite or V<sub>2</sub>O<sub>5</sub>. Whereas in the full cell configuration, anode materials with lower potential versus Li<sup>+</sup>/Li other than Li metal could also be used as negative electrodes by being paired with cathode materials with both lithiated state and higher potential as positive electrodes. The commercial batteries are all in full cell configuration. The Licontaining cathode material is able to generate lithium ions to insert into the anode material *via* electrolyte upon charging. The reverse process occurs during the discharge. The maximum capability of any specific cathode or anode materials that generate and store  $Li^+$  ions is usually determined in half cells under a constant current density testing mode, which is called galvanostatic charge-discharge (GCD) test. The exact amount of lithium ions that a cathode material generates for a given weight should match the amount of an anode material that can store effectively all the generated lithium ions by the cathode. For example, let us assume that the cathode material of  $LiCoO_2$  will deliver a charge capacity of 100 mAh/g in the half cell configuration across lithium metal.



Figure 1.8 Assembly processes of a CR2032 coin cell in half-cell configuration followed by a PC programmed galvanostatic charge-discharge test.

This means 1 unit (1 gram) of  $LiCoO_2$  can generate lithium ions pertaining to a maximum of 100 mA of capacity in a time unit (1 hour). Similarly, assuming that graphite anode material has a storage of the specific capacity of 372 mAh/g through Li<sup>+</sup> insertion and extraction in the half-cell configuration across lithium, then just 100/372

= 0.27 gram of the carbon anode material is required to match the 1 gram of LiCoO<sub>2</sub> cathode material for the full cell construction in order to achieve the optimum performance.

## **1.3.3.2** Electrochemical characteristics of batteries

As we emphasized in the last section, the reversible capacity of LIBs during charge and discharge is determined by the reversible  $Li^+$  transport between electrolyte and electrode. The theoretical specific capacity of the active electrode materials is the maximum  $Li^+$  that can be stored in the matrix of the materials per unit mass calculated by the maximum stoichiometry of the reversibly-lithiated products (e.g. the  $Li_xC_6$ ,  $x \le 1$ ). GCD is the most common method to evaluate the specific capacity, high-rate capability, and cyclic stability of LIBs at various constant current densities.

However, there is a tremendous amount of electrode materials with a considerable difference in theoretical specific capacity. Thus, in order to better implement the GCD measurements, it is convenient to take the current density as a reference rate denoted by 1C that enables one-time of charge or discharge completed within 1 h when it is applied to an arbitrary material, assuming with the theoretical specific capacity. For example, the theoretical specific capacity for SnO<sub>2</sub> is 781 mAhg<sup>-1</sup>, [80] so 1C is 781 mAg<sup>-1</sup> for the GCD test. This definition is widely adopted for both academic and industrial use.

In addition, the performance of any LIB is also tested by carrying out GCD tests at multiple current rates such as 0.1 C, 0.5 C, 1 C, 2C, 5C and even higher rates. The rate capability determines the specific capacity of the batteries at specific rate, at which they are charged and discharged. The LIB as power sources with better rate capability signifies a faster charging/discharging. It is an important requirement for EV or HEV, of which the drivers can recharge their batteries as easy and fast as they refill their gas tank of regular cars in a gas station. Apart from GCD, there are other two common electrochemical methods called cyclic voltammery (CV) and electrochemical impedance spectroscopy (EIS), which are also relied on to evaluate the electrochemical performance of LIB. CV and EIS are conducted on a multi-channel potentiostat with necessary accessories such as coin cells, test cells, and rotating disk electrodes, which will be introduced in the next section as shown in Figure 1.9.



Figure 1.9 Multi-channel potentiostat with a variety of accessories.

#### **1.4 Catalysts for Oxygen Reactions**

A fuel cell is also an electrochemical device, similar to a battery. The major difference is that fuel cell inherently is an energy conversion device that generates an electrical potential through the redox reaction of a fuel (e.g. H<sub>2</sub>) at an anode electrode and an oxidant (e.g. O<sub>2</sub>) at a cathode electrode rather than an energy storage device like LIB. While a variety of fuels may be available as fuels to provide electrons at the anode (including hydrogen, methanol, and etc.), the abundance of oxygen in the Earth's

atmosphere and the large thermodynamic driving force of the oxygen reduction reaction (ORR) make it the most appealing oxidant for fuel cell cathodes. [81] On the other hand, in contrast to LIB that must be recharged when the electrical energy stored are completely delivered or consumed, reactants are replenished or continuously supplied in a fuel cell. Thus, production of reactants by water splitting, which is electrolysis of water into oxygen and hydrogen, is vital to fuel cells too. [81] The oxygen generation process is also called oxygen evolution reaction (OER), which is a reverse process of ORR. It is well known that both ORR and OER catalyzed by enzymes are also the two most important reactions in life processes such as biological respiration and photosynthesis with a byproduct of hydrocarbons. [82] Similarly, for industry, the high efficient catalysts for oxygen reactions (both ORR and OER) are at the heart of fuel cells.

# **1.4.1 Principle of fuel cells**

There are many types of fuel cells, but their construction structure are similar to a battery: the anode and cathode are separated by an electrolyte that permits the masstransfer of ions between the electrodes. Direct current electricity is produced by electron flows between the electron source (anode) and the acceptor (cathode) through an external circuit. As the main discrimination among the different types is the electrolyte, fuel cells are classified by the type of electrolyte followed by the difference in startup time ranging from 1 second for proton exchange membrane fuel cells (PEM fuel cells, or PEMFC) to 10 minutes for solid oxide fuel cells (SOFC). [83]

The working principle of a typical PEM fuel cell is illustrated in Figure 1.10. On the anode side,  $H_2$  diffuses to the catalyst layer (usually Pt/C) where it dissociates into protons ( $H^+$  ions) and electrons. These protons exchange and react with oxidants at the

electrolyte interface, which is referenced as multi-facilitated proton membranes. The protons are conducted through the membrane to the cathode while the electrons are drawn in an external circuit to supply power because the membrane is electrically insulating. On the cathode side with specific catalysts such as Pt/C or alternative metal oxides, oxygen molecules react with the electrons (traveled from anode through external circuit) and protons to form water eventually.



Figure 1.10 Schematic of a PEM fuel cell.

## **1.4.2** Oxygen reduction and evolution reactions

ORR in aqueous electrolytes occurs mainly by two pathways: the direct 4electron reduction from  $O_2$  to  $H_2O$ , and the 2-electron reduction from  $O_2$  to hydrogen peroxide ( $H_2O_2$ ). These two reaction equations with different thermodynamic electrode potentials are listed in Equations 1.4 and 1.5. [84]

$$O_2 + 4H^+ + 4e^- \to H_2O$$
  $E^0 = 1.23 V$  1.4

$$O_2 + 2H^+ + 2e^- \to H_2O_2$$
  $E^0 = 0.67 V$  1.5

Although H<sub>2</sub>O<sub>2</sub> can further react with H<sup>+</sup> protons to become water  $(H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O, E^0 = 1.76 V)$ , Equation 1.5 is less desirable than 1.4 because of the lower efficiency and the generation of corrosive peroxide associated with it. When in non-aqueous aprotic solvents and/or in alkaline electrolytes, a third reduction pathway, that is 1-electron reducing O<sub>2</sub> to superoxide  $(O_2^{\bullet})$ , may also occur. Their potentials are strongly dependent on the solvent used. However, the ORR kinetics is normally very slow. The sluggish kinetics of the ORR are attributed to the strength of the O=O bond (498 kJ/mol) that must be broken in the course of the reaction. In order to speed up the ORR kinetics to reach a practical usable level in a fuel cell, a cathode ORR catalyst is highly needed by lowering the activation energy of the reaction and reducing the electrode overpotential. [84]

OER occurs in a reverse process of ORR *via* the electrocatalyzed oxidation of water to molecular oxygen and can be written as the following simplified chemical reaction (Equation 1.6): [85]

$$2H_2 0 \to 4e^- + 4H^+ + O_2 \tag{1.6}$$

The reaction requires the energy of four photons and electrons with a high activation energy, limiting the kinetics too. Hence, the highly-efficient catalysts for OER is also the current biggest bottleneck.

#### **1.4.3** Nanocomposite catalysts

At the current stage in nanotechnology, Pt-based nanomaterials are the most practical catalysts for ORR. However, because of the high cost and declining activity of Pt-based catalysts for making commercially viable fuel cells, extensive research over the past several decades has been focused on developing alternative catalysts to replace or reduce Pt catalysts. [83] These catalysts include other noble metals and alloys, carbon nanomaterials or hybrid carbon materials e.g. commercial carbon-supported Pt catalyst (Pt/C with 20wt% Pt on carbon Vulcan XC-72) [85] and transition metal oxides.

Although all carbon materials have a high stability and some electrocatalytic activity towards ORR in alkaline solutions, the activity are far comparable to Pt and the catalytic mechanisms vary widely depending on the type of carbon. For example, glassy carbon (GC) and pyrolytic graphite normally catalyze a 2-electron transfer oxygen reduction, producing  $H_2O_2$ . On an oxidized graphite electrodes, the  $H_2O_2$  can be further reduced to water at more negative potentials. [86] On CNTs, the O<sub>2</sub> reduction product is  $H_2O_2$  or a mixture of  $H_2O_2$  and OH<sup>-</sup>, which is also dependent of the preparation method and potential of the CNT-modified electrode [86]. In contrast to carbon materials, the low cost transition metal (Fe, Co, Ni) oxide nanomaterials have a preferred 4-electron ORR as desirable as Pt catalysts whereas their low electronic conductivity limits charge transfer process and consequently the electrocatalytic activity.[84] Similarly for OER, metal oxides such as  $RuO_2$  and  $Ir_2O_3$  in acidic conditions and first row spinel and perovskite metal oxides in alkaline conditions have been recognized with high catalytic activity and moderate over-potentials (< 400mV).[50]

Therefore, development of carbon-based nanocomposites that combine metal oxides with carbon nanomaterials such as CNT or graphene to optimize the ORR reduction pathway (4-electron transfer) and transport of all reactants ( $O_2$ ,  $OH^-$ ,  $H^+$ , and electrons) is a key direction deserving many efforts. The new nanocomposites can greatly increase catalytic active sites, enhance the electrode kinetics, and reduce overpotentials of reactions by relying on the synergistic contributions from both high-catalytic active metal oxides and carbon nanomaterials with a superior conductivity,

large specific surface area and high chemical stability. A variety of common metal oxides and their nanocomposites as catalysts for ORR and OER reported in the literature are summarized in Tables 1.4 and 1.5, respectively as follows:

Electrode materials/catalysts	Function	Electrolyte	ORR onset potential (V) <i>vs.</i> RHE	Current density (mA cm <sup>-</sup> <sup>1</sup> ) at 0.7 V <i>vs.</i> RHE	Ref ere nc e
Co₃O₄/rmGO nanocomposite	ORR	1 M KOH	0.83	12.3	84
Co₃O₄/N-rmGO	ORR	1 M KOH	0.79	52.6	84
Fe <sub>2</sub> O <sub>3</sub>	ORR	0.1 M KOH	0.85	2.77	87
Fe <sub>2</sub> O <sub>3</sub> /CNT	ORR	0.1 M KOH	0.88	3.89	87

 Table 1.4
 Catalytic activity of some typical metal oxides and nanocomposites for ORR

 Table 1.5
 Catalytic activity of some typical metal oxides and nanocomposites for OER

Electrode materials/catalysts	Function	Electrolyte	Overpotentia I (V)	Curren t densit y (mA cm <sup>-2</sup> )	Refe renc e
NiFe oxides	OER	1 M NaOH	1.51	0.5	88
Core-ring NiCo <sub>2</sub> O <sub>4</sub>	OER	1 M KOH	1.545	100	89
NiFe(OH)₂	OER	1 M NaOH	1.495	500	90
Co <sub>3</sub> O <sub>4</sub> /N-rmGO	OER	1 M KOH	1.54	10	84
NiFe-LDH/CNT	OER	1 M KOH	1.477	10	91

#### **1.4.4** Cell assembly and electrochemical tests

#### 1.4.4.1 Rotating disk electrodes

The most frequently applied method among oxygen electrocatalysis studies is rotation disk electrodes (RDE), which is used to analyze the catalytic activity of metal oxides (MO)/SWNT macrofilm nanocomposites in Chapter 5. The RDE system (Figure 1.11) consists of a conductive disk-shape electrode embedded in an inert nonconductive polymer or resin that can be attached to an electric motor with a panel that has a fine control of the electrode's rotation rate. The disk, like any working electrode, can be made of a noble metal or GC or any appropriate conductive material selected for specific needs. When the disk turns as shown in the schematic of Figure 1.11, the electrolyte solution in hydrodynamic boundary layer near the electrode surface is dragged by the spinning disk and the resulting centrifugal force flings these part of solution away from the center of the electrode. Then the solution underneath from the bulk electrolyte flows up vertical towards the electrode to reenter the boundary layer. The equilibrium result is forming a laminar flow of electrolyte towards and across the electrode. The rate of the laminar flow can be controlled by the electrode's rotating speed and calculated in a precise mathematic model. A final condition of steady-state current is achieved by the equilibrium flow rate. It has nothing with the diffusion. Thus, it is easier to investigate specific electrochemical behavior under such a condition only controlled by the amount of reactants supplied by the electrolyte flow with a certain rate rather than diffusion. [92] For example, a multi-electron transfer, the kinetics of a slow electron transfer, adsorption/desorption steps, and electrocatalysis mechanisms can be studied by running linear sweep voltammetry at various rotation rates.



Figure 1.11 RDE system with the schematic of the cell construction and simple working mechanism.

### **1.4.4.2** Electrocatalytic activity

The difference between the real electrode potential (*E*) and the equilibrium potential ( $E^0 = 1.23$  V) of the electrode reaction (Equation 1.4 and 1.6) is known as the overpotential,  $\eta = E \cdot E^0$ . When the electrode has a large overpotentials ( $\eta > 0.12$  V), the current of an electrochemical reaction is limited solely by the kinetics of reaction at the electrode surface.[83] That means at large overpotentials the current eventually becomes limited by Ohmic losses and by the mass-transport of oxygen to the electrode surface. The relationship between the current (*i*) and the overpotential is described by the Tafel equation (Equations 1.7 or 1.8: [83]

$$i = i_0 e^{-\frac{\alpha \eta F}{RT}}$$
 1.7

or 
$$\eta = \frac{RT}{\alpha F} lni_0 - \frac{RT}{\alpha F} lni$$
 1.8

where  $i_0$  is the exchange current,  $\alpha$  is the transfer coefficient, *T* is temperature; *R* and *F* are gas and Faraday's constants. At potential of E<sup>0</sup>, a dynamic equilibrium exists where the rate of the forward reaction (Equation 1.4) is equal to the rate of the reverse reaction (Equation 1.5), the exchange current ( $i_0$ ) describes the rate of these forward and reverse reactions which are equal in magnitude. Their sum results in zero net flow of current. The transfer coefficient ( $\alpha$ ) is the proportionality coefficient between the overpotential and the activation barrier. It is found from Tafel equation that increasing the overpotential lowers the activation barrier of the reaction linearly while at sufficient overpotentials, the current increases exponentially as a function of the overpotential.

Electrocatalysts act to increase the exchange current and therefore the increase current at the overpotentials where Tafel equation applies. Although the exchange current may be extrapolated from a Tafel plot, a plot of Equation 1.8with correlation of *lni* versus  $\eta$ , this extrapolation causes large uncertainties because the exchange current is too smaller (normally several orders of magnitude) than the observed currents. In practice, electrocatalysts are often compared in two ways: (1) comparing the observed current densities of the oxygen reactions at a given potential for two similar electrocatalysts, (2) comparing their onset potentials (E<sub>onset</sub>) or overpotential  $\eta$  versus equilibrium potential at E<sub>onset</sub>, where the onset potential is the potential at which a given (small) current density is reached, and that current density is chosen to roughly correspond the lowest value readily distinguished from zero.[83]

#### 1.5 Supercapacitor

Supercapaictor is also a significant energy storage device. The higher power density than rechargeable lithium-ion batteries makes it more favorable for applications requiring frequent and fast charge-discharge cycling rather than a long term compact energy storage.[93] They can be used in vehicles, heavy machinery and elevators for recovery energy from braking, short-term or burst-mode power delivery. Smaller units are applicable to memory backup such as static random-access memory.[94] A typical supercapacitor, normally assembled in a cell configuration similar to LIB for practical use (Figure 1.6), consists of two electrodes (positive and negative) immersed in electrolyte and a separator that electrically isolates them.

According to different charge storing mechanisms, supercapacitors are classified into two major types: electric double layer capacitors (EDLCs) and pseudo- or redoxcapacitors. The supercapacitor can also be constructed in a "half-and-half" configuration by pairing one EDLC electrode with one pseudo- electrode, which is called asymmetric or hybrid supercapacitors, differing from the symmetric one with two same electrodes. The hierarchical relation between these types of supercapacitor is illustrated in Figure 1.12.



Figure 1.12 Hierarchical classification of supercapacitors.

# 1.5.1 Principle

Unlike conventional dielectric capacitors, supercapacitors don't have a solid dielectric that separates the charges. They rely on electric double-layer capacitance (EDLC) or electrochemical pseudocapacitance (Pseudocapacitor) or a combination of both (Asymmetric supercapacitor) instead. Based on the types of electrolyte, the supercapacitors can be mainly classified to aqueous, including acidic solutions such as H<sub>2</sub>SO<sub>4</sub>,[95] neutral solutions (e.g. Na<sub>2</sub>SO<sub>4</sub>),[96] and alkali solutions (KOH),[83] and nonaqueous, including organic solutions such as tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) in polycarbonate (PC),[97] and ionic liquids.[98] The voltage window of a supercapacitor is determined by the electrolyte. The aqueous based supercapacitors usually have a very narrow voltage window as low as about 1.23 V, while it can be extended beyond 3 V by switching to an organic electrolyte.

### **1.5.1.1** Electric double layer capacitor

The EDLC is charged and discharged by the creation and release of the electrical double layers through the accumulation of electrolyte ions at the electrode/electrolyte interface. In EDLCs, the capacitance is contributed by electrostatic separation of charge at interfaces of electrodes and electrolytes with a few ångströms (0.3–0.8 nm), referenced as the Helmholtz double layer. [94] This order of separation is much smaller than in a conventional capacitor. Applying a voltage across the two electrodes of a supercapacitor will make both electrodes to generate double layers. Figure 1.13a shows the double layer structure on one electrode (positive). It consists of two layers of ions. One layer is of charge polarization in the surface lattice of the electrode. The other layer, with opposite polarity, emerges from solvated ions in the electrolyte. Between the two layers is a monolayer of solvent molecules, e. g. water molecules for aqueous electrolyte.

The monolayer forms the inner Helmholtz plane (IHP) effects as a molecular dielectric by physically adsorbing on the surface of the electrode and separating the oppositely polarized ions from each other. The amount of charge polarization in the electrode is matched by the magnitude of counter-charges in outer Helmholtz plane (OHP).



Figure 1.13 Schematic of the structure of (a) EDLC, (b) pseudocapacitor, and (c) asymmetric supercapacitor

The double layer capacitance, C<sub>dl</sub>, at the electrode interface is given by Equation

$$C_{dl} = \frac{\epsilon A}{4\pi t}$$
 1.9

where *A* is the interface area of the electrode with electrolyte,  $\epsilon$  the dielectric constant of the charge space, and *t* is the thickness of the double layer. It is the large surface-area (~2000 m<sup>2</sup>g<sup>-1</sup> for carbon-based) and the extremely short distance between the double layers that contribute to the high specific capacitance (50 Fg<sup>-1</sup>). [99] This is a non-Faradaic process, which means there is no charge transfer across the interface.

## 1.5.1.2 Pseudocapacitor

Pseudocapacitors can deliver a capacitance 10-100 times that of EDLCs because they not only store charges in the double layer but also take advantage of the charge transfer through the fast and reversible Faradaic reactions. [94] It requires that electrode materials have electrochemically redox activity with the electrolytes. This process is similar to the charge and discharge of batteries where the passage of Faradaic current occurs. In general, conductive polymers and the electroactive metal oxides are common electrode materials for this type of supercapacitors. [94]

A faradaic pseudocapacitance still only occurs together with a static doublelayer capacitance. The value of pseudocapacitance is determined by material, structure and the surface area of the electrodes. Taking the transition-metal oxide electrode on the positive side for example, the pseudocapacitance can originate when specifically adsorbed cations penetrate the double-layer, proceeding in several one-electron stages as shown in Figure 1.13b. During the faradaic processes, the electrons are transferred to or from valence-electron states (orbitals) of the redox electrode reagent. [100] When the electrons flow through the external circuit from the negative electrode to enter the positive electrode where a second double-layer with an equal number of cations has formed. But these cations don't "accept" the electrons. They remain on the electrode's surface in the charged state, and the electrons remain without being "swallowed" in the strongly ionized lattices of transition-metal ions of the electrode. [100] The storage capacity of such pseudocapacitance is a linear function of the surface coverage of the adsorbed cations which is potential-dependent. [100] The faradaic charge transfer as described involves three specific types: reversible redox system, electrosorption (underpotential deposition of metal adatoms) or intercalation system. [101] The adsorbed ions have no chemical reaction with the atoms of the electrode. No chemical

bonds forms but only a charge-transfer take place. When discharging pseudocapacitance, the charge transfer is reversed and the ions or atoms leave the double-layer and distribute randomly into the electrolyte. [100, 101]

#### **1.5.1.3** Asymmetric supercapacitor

More recently, asymmetric supercapacitors have been found to be an effective alternative approach to increase the energy density of supercapacitors. Figure 1.13c shows that these asymmetric supercapacitors consist of a battery-like pseudo-type electrode (e.g. metal oxides as the energy source) and an EDLC-type electrode (e.g. activated carbon as the power source). The asymmetric supercapacitors can make full use of the different potential windows of the two electrodes to extend the operation voltage across the maximum breakdown potential (~1.23 V) of aqueous electrolyte in the cell system, accordingly resulting in a greatly enhanced specific capacitance and significantly improved energy density (up to 10-20 Wh/kg). [102] Therefore, they simultaneously bears the advantages of both supercapacitors (high rate capability, extremely long life cycling stability) and LIB (high energy density).

#### **1.5.2** Nanocomposite electrodes

Since the amount of double-layer capaciatance and pseudocapacitance stored within one unit voltage is predominantly depended on the electrode surface area, therefore supercapacitor electrodes are typically made of porous, spongy carbon nanomaterial with an extraordinarily high specific surface area, such as activated carbon, carbide-derived carbon (also known as tunable nanoporous carbon), CNTs, and graphene. [102] Structurally, pore sizes in these carbons usually range from micropores (< 2 nm) to mesopores (2-50 nm). [102] However, pure carbon materials mainly exhibit

EDLC capacitance with a negligible pseudocapacitance. [102] Thus, two additional electrode materials including conductive polymer and metal oxides that have the ability of performing faradaic charge transfers are needed for pseudo- and asymmetric capacitors. Despite the high conductivity and highly reversible storage capacity the conductive polymers possess, it would unfortunately suffer swelling and shrinking during the redox process (ionic intercalation/deintercalation), resulting in the mechanical degradation of the polymer electrode and fading of electrochemical performance quickly.[103,104] In contrast, metal oxides have a better stability while undergoing longer cycles but worse conductivity, which compromises the fast electrochemical Faradaic reactions. [105] RuO<sub>2</sub>,[106, 107] MnO<sub>2</sub>,[108, 109]  $Co_3O_4$ ,[110] and NiO,[111], which have redox couples of transition metal ions and allow the facile ion interconversion of  $O^{2-} + R^+ \leftrightarrow OR^-$ , have been extensively investigated. To overcome the drawbacks of low conductivity and low power density, the concept of nanocomposite incorporating metal oxides with carbon nanomaterials, in particular CNTs, has been proposed and intensively studied. The CNTs have many significant effects in nanocomposites as follows:[100]

- The inherent superior conductivity of CNTs could greatly improve the electrical conductivity of nanocomposites.
- The large specific surface area of CNTs could favor the dispersion of metal oxide nanoparticles.
- That CNTs induce a high porosity to the nanocomposite electrode facilitates the charge transfer by providing more channels for electrolyte access and reducing the ion diffusion distance.

• The functional groups on the surface of CNTs could enable the transport of solvated ions to the electrolyte/electrode interfaces and increase the Faradaic reaction sites of metal oxides.

The electrochemical performance of various carbon-based nanocomposites reported in the literature is summarized in Table 1.6 as follows:

Table 1.6Electrochemical performance of various carbon-metal oxide<br/>nanocomposites reported in the literature

Metal oxides- Carbon Nanocomposites	Amount of metal oxides loading (%)	Specific capacitance based on composite electrodes (F/g)	Specific capacitance based on metal oxides alone (F/g)	Electroly te	Refer ences
RuO <sub>2</sub> /CNT	17	-	1192	0.5 M H₂SO₄	106
RuO <sub>2</sub> /Graphene	38.3	-	570	1 M H <sub>2</sub> SO <sub>4</sub>	107
MnO <sub>2</sub> /CNT/PED OT-PSS	60	-	129	1 M Na <sub>2</sub> SO <sub>4</sub>	108
MnO <sub>2</sub> /Graphene oxide	90.7	197.2	211.2	1 M Na <sub>2</sub> SO <sub>4</sub>	109
Co <sub>3</sub> O <sub>4</sub> /Graphene	24.4	-	243.2	6 M KOH	110
NiO/CNT	50	523.37	1037.74	6 M KOH	111
NiO/CNT	80	326.2	405.5	6 M KOH	111

# 1.5.3 Cell assembly and electrochemical tests

Similar to LIB (Figure 1.7), there are also four major types of supercapacitors depending on their cell assembly construction.[102] A cylindrical cell with wound

electrodes and a stack cell with the stacked electrodes as the name implies are mainly for practical use with good sealing, high pressure resistance and effective space utilization while the pouch cell and coin cell with compact size, low expense and easy assembly are more suitable for research use in the lab. As introduced in Section 1.3.3 for LIB, the two electrochemical testing techniques, CV and GCD, are also the two most common approaches to measure the specific capacitance, rate capability and cycling stability of supercapacitors.

# 1.5.3.1 Three-electrode and two-electrode cells

All the four types of supercapacitors in last section are commercially available and are in two-electrode cells, which can be easily fabricated. In addition, threeelectrode cell is also commonly used in electrochemical research and composed of a working electrode, a reference electrode, and a counter electrode in a multi-inlet cell (e.g. four-neck flask) as shown in Figure 1.11 without the rotating system. Threeelectrode cells differ from the packaged two-electrode cells in several important respects. In the three-electrode configuration, only one electrode, called the working electrode, is made of the active material being analyzed. The charge transfer under applied voltage across the single electrode are markedly different than that in a two-electrode cell configuration. For a three-electrode cell, the voltage potential applied to the working electrode is with respect to the particular reference electrode used and shown on the Xaxis of the CV plot. In contrast, the potential applied to each electrode, in a symmetrical two-electrode cell, are equal to each other and are one-half of the values shown on the X-axis of the CV plot. Therefore, for a given potential range on the X-axis of the CV, the working electrode of a three-electrode cell has the potential range twice as that is applied to either electrode in a two-electrode cell. This results in a doubling of the

calculated capacitance, which will be introduced in the next section. There are other differences between the two configurations as well. [112] The potential across counter electrode in a three-electrode cell is not controlled or measured, and is an order of magnitude or more lower (if the counter electrode is larger than the reference electrode) or can be approximately equal (in the case that the working and counter electrodes are of the same size and material.) The point of zero charge location on the CV also varies for each reference electrode/electrolyte/material combination. [112]

# **1.5.3.2** Electrochemical performance of supercapacitors

Specific capacitance  $C_s$  (F g<sup>-1</sup>) is usually considered in order to evaluate and compare the electrode materials for supercapacitors, which is calculated from Equation 1.10: [94]

$$C_s = \frac{C_i}{W}, \ i = p \ or \ n \tag{1.10}$$

where  $C_i$  is the electrode capacitance (i=p stands for positive and i=n stands for negative) and W is the mass of electrode materials. For the two-electrode cells, the average  $C_s(\overline{C_s})$ is calculated according to Equation 1.11 using CV:

$$\overline{C}_{S} = \frac{2 \int_{V_1}^{V_2} i(V) dV}{m \cdot v \cdot \Delta V}$$
1.11

where  $V_1$  and  $V_2$  (in unit of V) are the lower limit and upper limit of potential in a cyclic potential sweep, respectively;  $\Delta V = V_2 - V_1$ , is the voltage window; v is the scan rate (Vs<sup>-1</sup>); i(V) is the current as the function of voltage, and m is the total mass of both electrode materials. In the same system, the  $\overline{C_s}$  is worked out by GCD measurement from Equation 1.12: [94]

$$\overline{C}_s = \frac{4Q}{\Delta V \times m}$$
 1.12

where Q is the total capacity stored and released in a single cycle of charge and discharge;  $\Delta V$  is the voltage window pre-set for the cycling test, and m is the overall mass of electrode materials. (Except when specifically denoted, all of the specific capacitance results in Chapter 5 for the SWNT macrofilm-based supercapacitor are obtained by CV and GCD.)

#### **1.6 Research Motivation and Dissertation Scope**

Diverse aspects of CNT macrofilms right from CNT synthesis to their properties as well as the perspective applications in energy devices including rechargeable lithiumion batteries, catalysts for fuel cells, and supercapacitors are generally introduced in the above sections. It is believed that combining free-standing SWNT macro-films, which possess a high electric conductivity, large specific surface area, and tunable porous structure with active electrode materials, will enable the fabrication of high performance nanocomposite electrode materials for energy applications. This motivates us to focus on study of SWNT macro-films-based nanocomposite electrodes in this dissertation.

Previously, it was already demonstrated that flexible SWNT macrofilms itself is a good anode material for LIB. Nevertheless, little effort has been extended to the nanocomposites based on SWNT macrofilms with cathode materials and study their electrochemical behavior. In Chapter 2, a nanocomposite cathode for LIB, composed of  $V_2O_5$  nanoparticles and SWNT macrofilms ( $V_2O_5$ /SWNT) with mesoporous structures, are prepared by a controllably hydrolytic deposition method. The  $V_2O_5$ /SWNT assembled in half cells exhibits a high rate capability, which is attributed to the chemical interaction between the  $V_2O_5$  nanoparticle and the functional groups on the surface of SWNTs evidenced by a systematically structural characterization such as the HRTEM and XPS results. It is also conclusively elucidated with detailed electrochemical analysis that SWNTs can improve Li<sup>+</sup> diffusivity by several orders of magnitude to significantly facilitate lithium-ion transport, achieving an improved electrochemical performance for the nanocomposite cathode system.

Although  $V_2O_5/SWNT$  was successfully developed and demonstrated as cathode for LIB in a half-cell configuration, combining the lithiated cathode materials such as LiMn<sub>2</sub>O<sub>4</sub> (LMO) with SWNT macrofilms while maintaining the flexibility still remains a bottleneck for a stretchable LIB in a full cell with non-lithium anode. Thus, Chapter 3 presents a stretchable nanocomposite cathode fabricated by *in-situ* growth of LMO nanocrystals in the three-dimensional network of SWNT macrofilms via a low-temperature hydrothermal synthesis. It is demonstrated that the as-prepared composite cathode could be laminated with elastomeric substrate such as polydimethylsiloxane (PDMS) to form stretchable cathodes with full flexibility. This present work provides a necessarily preliminary examination on the electrochemical performance of such freestanding stretchable LMO-SWNT cathode in half-cells before developing the fully stretchable full cells in the future. The applied potential intermittent titration technique (PITT) also reveals that the Li<sup>+</sup> diffusivity of the freestanding composite is closely related to the electrochemical performance.

Compared to the graphitic carbon anodes, the extraordinary high capacities of transition metal oxides  $(M_xO_y)$  as anodes for LIB result from the conversion reactions of Li +  $M_xO_y \leftrightarrow M^0$  + Li<sub>2</sub>O in addition to the intercalation mechanism of Li ions into interstitial sites<sup>3</sup>. Among these oxides, iron oxides including Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> are considered as particularly promising electrode materials due to their natural abundance, low cost, environmental benignity, and low toxicity. In Chapter 4, we start an in-depth study of these conversional anode nanomaterial composites with SWNT macrofilms.
First, the composite films composed of SWNT macrofilms and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles in fine crystalline size (6-20 nm) are prepared by a simple heat treatment method. The SWNT macro-films can facilitate the charge transfer processes as well as accommodate the volumetric change of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles due to the convention reaction, enabling high specific capacities over 1000 mAhg<sup>-1</sup> and an excellent cyclic stability up to 100 cycles for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT. Experimental results and systematical analysis conclude that the thickness of the hybrid films has a significant impact on the diffusion coefficient of Li<sup>+</sup>.

However the low rate capabilities governed by the slow kinetics of Li-ion diffusion and the poor conductivity of the  $M_xO_y/M^0/Li_2O$  matrix still limit the performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT. To overcome this drawback, the second part of Chapter 4 involves a facile and effective hydrogen annealing method to significantly improve the poor rate capability *via* a thermal reduction of rhombohedral Fe<sub>2</sub>O<sub>3</sub> to cubic Fe<sub>3</sub>O<sub>4</sub> while maintaining the morphological integrity of the films. The enhancement of the electrochemical performance is attributed to the presence of highly-conductive Fe<sub>3</sub>O<sub>4</sub>, accelerated charge-transfer kinetics, and the increased Li<sup>+</sup> diffusivity confirmed by electrochemical impedance spectra and galvanostatic intermittent titration.

Based on the work in Chapter 4, the facile thermal treatment approach is expanded in Chapter 5 to be a general synthetic method to prepare a family of transition metal oxides ( $M_xO_y$  (M=Fe, Co, Ni))/SWNT macrofilm nanocomposites. The  $M_xO_y$ nanoparticles obtained are of 3-17 nm in diameter and homogeneously anchor on the free-standing SWNT macrofilms. A systematic investigation are performed to explore their electrochemical properties for ORR/OER, lithium-ion batteries and asymmetric supercapacitors. NiO/SWNT and Co<sub>3</sub>O<sub>4</sub>/SWNT favor ORR and OER, respectively with superior electrocatalytic activities in alkaline solutions. NiO/SWNT also exhibits a high specific capacitance of 400 F g<sup>-1</sup> and fast charge-transfer Faradaic redox reactions to achieve asymmetric supercapacitors with a high power and energy density. All  $M_xO_y$ /SWNT nanocomposites could deliver a high capacity beyond 1000 mAh g<sup>-1</sup> and show excellent cycling stability for lithium-ion batteries.

The adhesive characteristic of SWNT macrofilms have been noticed during the research work in Chapter 4 and 5 in preparing SWNT macrofilms with a small thickness (< 500 nm). It is expected that the adhesive and conductive SWNT could play a "bifunctional" role to replace the polymer binders such as poly(vinylidene fluoride) (PVDF) and conductive additives such as carbon black (CB), which are indispensable components in conventional electrode manufacturing for batteries. Thus, in Chapter 6, a concept of adhesive conductors employing fragmented SWNT macro-films (FCNTs) is proposed and demonstrated, for the first time, by constructing composite electrodes with both cathode and anode materials, LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>5</sub>Ti<sub>9</sub>O<sub>12</sub>. The adhesive FCNT conductors provide not only a high electrical conductivity but also a strong adhesive force, functioning simultaneously as both the conductive additives and the binder materials for lithium-ion batteries. Such composite electrodes exhibit superior high-rate and retention capabilities compared to the conventional electrodes using PVDF and CB. An *in-situ* tribology method combining wear track imaging and force measurement is used to evaluate the adhesion strength of the FCNT. It has a higher adhesion strength than PVDF. This strategy of adhesive conductors will contribute to be a more general approach to construct nanocomposite electrodes with any active materials.

Last, Chapter 7 concludes the dissertation with a summary and a brief outlook towards the future research on CNT macrofilms-based energy devices including lithium-sulfur batteries, metal-air batteries, sodium-ion batteries and photoelectrocatalysts.

### REFERENCES

- 1. Mokyr, J., The British Industrial Revolution: An Economic Prespective. 2nd ed.; *Westview Press*: **1999**.
- 2. Appleby, A. J. Fuel cell handbook. 7th ed.; *EG&G Technical Services, Inc.* **1988**.
- 3. Linden, D.; Reddy, T., Handbook of Batteries. 3rd ed.; *McGraw-Hill*: 2001.
- 4. Aricò, A. S., Bruce, P., Scrosati, B., Tarascon, J. M., Van Schalkwijk, W.. Nanostructured materials for advanced energy conversion and storage devices. *Nature Materials* **2005**, 4(5), 366-377.
- 5. Armand, M., Tarascon, J. M., Building better batteries. *Nature* **2008**, 451 (7179), 652-657.
- 6. Tarascon, J. M., Armand, M., Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, 414(6861), 359-367.
- 7. Morozan, A., Jousselme, B., Palacin, S. Low-platinum and platinum-free catalysts for the oxygen reduction reaction at fuel cell cathodes. *Energy & Environmental Science* **2011**, 4(4), 1238-1254..
- 8. Kim, T.-H., Park, J.-S., Chang, S. K., Choi, S., Ryu, J. H., Song, H.-K., The current move of lithium ion batteries towards the next phase. *Advanced Energy Materials* **2012**, 2(7), 860-872.
- 9. McCreery, Richard L. "Advanced carbon electrode materials for molecular electrochemistry." *Chemical Review* **2008**, 108(7), 2646-2687.
- 10. Pandolfo, A. G., Hollenkamp, A. F., Carbon properties and their role in supercapacitors. *Journal of Power Sources* **2006**, 157, 11-27.
- 11. Frackowiak, E., Beguin, F., Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* **2001**, 39, 937-950.
- 12. Fuertes, A. B., Lota, G., Centeno, T. A., Frackowiak, E., Templated mesoporous carbons for supercapacitor application. *Electrochimica Acta* **2005**, 50, 2799-2805.
- 13. Gogotsi, Y., Nikitin, A., Ye, H., Zhou, W., Fischer, J. E., Yi, B., Foley, H. C., Barsoum, M. W., Nanoporous carbide-derived carbon with tunable pore size. *Nature Materials* **2003**, 2, 591-594.

- 14. Hung, K., Masarapu, C., Ko, T., Wei, B., Wide-temperature range operation supercapacitors from nanostructured activated carbon fabric. *Journal of Power Sources* **2009**, 193, 944-949.
- Vix-Guterl, C., Frackowiak, E., Jurewicz, K., Friebe, M., Parmentier, J., Béguin, F., Electrochemical energy storage in ordered porous carbon materials. *Carbon* 2005, 43, 1293-1302.
- 16. Pekala, R. W., Farmer, J. C., Alviso, C. T., Tran, T. D., Mayer, S. T., Miller, J. M., Dunn, B., Carbon aerogels for electrochemical applications. *Journal of Non-crystalline Solids* **1998**, 225, 74-80.
- 17. Du, C., Yeh, J., Pan, N., High power density supercapacitors using locally aligned carbon nanotube electrodes. *Nanotechnology* **2005**, 16, 350.
- Lee, S. H., Park, J. S., Lim, B. K., Mo, C. B., Lee, W. J., Lee, J. M., Hong, S. H., Kim, S. O., Highly entangled carbon nanotube scaffolds by self-organized aqueous droplets. *Soft Matter* 2009, 5, 2343-2346.
- Yang, C. M., Kim, Y. J., Endo, M., Kanoh, H., Yudasaka, M., Iijima, S., Kaneko, K., Nanowindow-regulated specific capacitance of supercapacitor electrodes of single-wall carbon nanohorns. *Journal of the American Chemical Society* 2007, 129, 20-21.
- Pech, D., Brunet, M., Durou, H., Huang, P., Mochalin, V., Gogotsi, Y., Taberna, P., Simon, P. Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon. *Nature Nanotechnology* **2010**, 5, 651-654.
- Novoselov, K. S. A., Geim, A. K., Morozov, S., Jiang, D., Katsnelson, M., Grigorieva, I., Dubonos, S., Firsov, A., Two-dimensional gas of massless Dirac fermions in graphene. Nature 2005, 438, 197-200.
- 22. Yoo, E., Kim, J., Hosono, E., Zhou, H. S., Kudo, T., Honma, I., Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Letters* **2008**, 8, 2277-2282.
- 23. Lee, S. H., Kim, H. W., Hwang, J. O., Lee, W. J., Kwon, J., Bielawski, C. W., Ruoff, R.S., Kim, S. O., Three-dimensional self-assembly of graphene oxide platelets into mechanically flexible macroporous carbon films. *Angewandte Chemie International Edition* **2010**, 49, 10084-10088.

- 24. Choi, D., Wang, D., Viswanathan, V. V., Bae, I. T., Wang, W., Nie, Z., Zhang, J.-G., Graff, G. L., Liu, J., Yang, Z., Li-ion batteries from LiFePO<sub>4</sub> cathode and anatase/graphene composite anode for stationary energy storage. *Electrochemistry Communications* **2010**, 12, 378-381.
- 25. Lee, S. H., Lee, D. H., Lee, W. J., Kim, S. O., Tailored assembly of carbon nanotubes and graphene. *Advanced Functional Materials* **2011**, 21, 1338-1354.
- Lee, D. H., Kim, J. E., Han, T. H., Hwang, J. W., Jeon, S., Choi, S. Y., Hong, S. H., Lee, W. J., Ruoff, R. S., Kim, S. O., Versatile carbon hybrid films composed of vertical carbon nanotubes grown on mechanically compliant graphene films. *Advanced Materials* 2010, 22, 1247-1252.
- 27. Yazami, R., Surface chemistry and lithium storage capability of the graphite– lithium electrode. *Electrochimica Acta* **1999**, 45(1), 87-97.
- 28. Jasti, R., Bertozzi, C. R., Progress and challenges for the bottom-up synthesis of carbon nanotubes with discrete chirality. *Chemical Physics Letters* 2010, 494(1), 1-7.
- 29. Iijima, S., Ichihashi, T., Single-shell carbon nanotubes of 1-nm diameter. *Nature* **1993**, 363, 603-605
- 30. Cumings, J., Zettl, A, Low-friction nanoscale linear bearing realized from multiwall carbon nanotubes. *Science* **2000**, 289(5479), 602-604.
- 31. Zhu, H., Wei, B., Assembly and applications of carbon nanotube thin films. *Journal of Materials Science & Technology* **2008**, 24, 447.
- 32. Krstic, V., Duesberg, G. S., Muster, J., Burghard, M., Roth, S., Langmuir-Blodgett films of matrix-diluted single-walled carbon nanotubes. *Chemistry of Materials* **1998**, 10, 2338-2340.
- 33. Zhang, D., Ryu, K., Liu, X., Polikarpov, E., Ly, J., Tompson, M. E., Zhou, C. *Nano Letters* **2006**, 6, 1880-1886.
- 34. Duggal, R., Hussain, F., Pasquali, M, Self-assembly of single-walled carbon nanotubes into a sheet by drop drying. *Advanced Materials* **2006**, 18, 29-34.
- 35. Bonard, J. M., Salvetat, J. P., Stockli, T., de Heer, W. A., Forró, L., Châtelain, A., Field emission from single-wall carbon nanotube films. *Applied Physics Letters* **1998**, 73, 918-920.

- 36. Zhu, H. and Wei, B., Direct fabrication of single-walled carbon nanotube macrofilms on flexible substrates. *Chemical Communications* **2007**, 3042-3044.
- 37. Kong, J., Cassell, A. M., Dai, H., Chemical vapor deposition of methane for single-walled carbon nanotubes. *Chemical Physics Letters* **1998**, 292, 567-574.
- 38. Huang, S., Maynor, B., Cai, X., Liu, J., Ultralong, well-Aligned singl-walled carbon nanotube architectureson surfaces. *Advanced Materials* **2003**, 15, 1651-1655.
- 39. Zhu, H. W., Xu, C. L., Wu, D. H., Wei, B. Q., Vajtai, R., Ajayan, P. M. Direct synthesis of long single-walled carbon nanotube strands. *Science* **2002**, 296, 884-886.
- 40. Sathiya, M., Prakash, A. S., Ramesha, K., Tarascon, J. M., Shukla, A. K., V<sub>2</sub>O<sub>5</sub>anchored carbon nanotubes for enhanced electrochemical energy storage. *Journal of the American Chemical Society* **2011**, 133, 16291-16299.
- 41. Zhu, X., Zhu, Y., Murali, S., Stoller, M. D., Ruoff, R. S., Nanostructured reduced graphene oxide/Fe<sub>2</sub>O<sub>3</sub> composite as a high-performance anode material for lithium ion batteries. *ACS Nano* **2011**, *5*, 3333-3338.
- 42. Lee, H. W., Muralidharan, P., Ruffo, R., Mari, C. M., Cui, Y., Kim, D. K., Ultrathin spinel LiMn<sub>2</sub>O<sub>4</sub> nanowires as high power cathode materials for Li-ion batteries. *Nano Letters* **2010**, 10(10), 3852-3856.
- Ban, C., Wu, Z., Kirkham, M. J., Chen, L., Jung, Y. S., Payzant, E. A., Yan, Y., Whittingham, M. S., Dillon, A. C., Extremely durable high-rate capability of a LiNi<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode enabled with single-walled carbon nanotubes. Advanced Energy Materials 2011, 1, 58-62.
- 44. Muraliganth, T., Murugan, A. V., Manthiram, A., Nanoscale networking of LiFePO<sub>4</sub> nanorods prepared by a microwave-solvothermal route with carbon nanotubes for lithium-ion batteries. *Journal of Materials Chemistry* **2008**, 18, 5661-5668.
- 45. Hu, C. C., Chang, K. H., Lin, M. C., Wu, Y. T., Design and tailoring of the nanotubular arrayed architecture of hydrous RuO<sub>2</sub> for next generation supercapacitors. *Nano Letters* **2006**, 6(12), 2690-2695
- 46. Chen, S., Zhu, J., Wu, X., Han, Q., Wang, X., Graphene oxide-MnO<sub>2</sub> nanocomposites for supercapacitors. *ACS Nano* **2010**, 4(5), 2822-2830.

- 47. Zheng, G., Yang, Y., Cha, J. J., Hong, S. S., Cui, Y., Hollow carbon nanofiberencapsulated sulfur cathodes for high specific capacity rechargeable lithium batteries. *Nano Letters* 2011, 11, 4462-4467.
- 48. Lim, B., Jiang, M., Camargo, P. H., Cho, E. C., Tao, J., Lu, X., Zhu, Y., Xia, Y., Pd-Pt bimetallic nanodendrites with high activity for oxygen reduction. *Science* **2009**, 324(5932), 1302-1305.
- 49. Zhang, J., Sasaki, K., Sutter, E., Adzic, R. R., Stabilization of platinum oxygenreduction electrocatalysts using gold clusters. *Science* **2007**, 315(5809), 220-222.
- 50. Zhuang, Z., Sheng, W., Yan, Y., Synthesis of Monodispere Au@Co<sub>3</sub>O<sub>4</sub> coreshell nanocrystals and their enhanced catalytic activity for oxygen evolution reaction. *Advanced Materials* **2014**, 26(23), 3950-3955.
- 51 Sun, K., Shen, S., Cheung, J. S., Pang, X., Park, N., Zhou, J., Hu, Y., Sun, Z., Noh, S. Y., Riley, C. T., Yu, P., Jin, S., Wang, D., Si photoanode protected by a metal modified ITO layer with ultrathin NiO<sub>x</sub> for solar water oxidation. *Physical Chemistry Chemical Physics* 2014, 16(10), 4612-4625.
- 52. Gao, M., Sheng, W., Zhuang, Z., Fang, Q., Gu, S., Jiang, J., Yan, Y., Efficient water oxidation using nanostructured α-nickel-hydroxide as an electrocatalyst. *Journal of the American Chemical Society* **2014**, 136(19), 7077-7084.
- 53. Whittingham, M. S., Lithium batteries and cathode materials. *Chemical Reviews* **2004**, 104 (10), 4271-4302.
- 54. Whittingham, M. S., The role of ternary phases in cathode reactions. *Journal of The Electrochemical Society* **1976**, 123 (315).
- 55. Nazri, G. A., Pistoia, G., Lithium batteries: science and technology. *Springer Science & Business Media*. 2008
- 56. Rao, B. M. L.; Francis, R. W.; Christopher, H. A., Lithium-aluminium electrodes. *Journal of The Electrochemical Society* **1977**, (124), 1490-1492.
- 57. Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B., LixCoO<sub>2</sub>: A new cathode material for batteries of high energy density. *Materials Research Bulletin* **1980**, 15 (6), 783-789.
- 58. Nagaura, T., and K. Tozawa., Lithium ion rechargeable battery. *Progess in batteries and solar cells* **1990**, 9 (209).

- Sorensen, E. M., Barry, S. J., Jung, H. K., Rondinelli, J. M., Vaughey, J. T., Poeppelmeier, K. R., Three-dimensionally ordered macroporous Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>: effect of wall structure on electrochemical properties. *Chemistry of Materials* 2006, 18(2), 482-489.
- 60. Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B., Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *Journal of The Electrochemical Society* **1997**, 144 (4), 1188-1194.
- 61. Winter, M., Besenhard, J. O., Spahr, M. E., Novak, P., Insertion electrode materials for rechargeable lithium batteries. *Advanced Materials* **1998**, 10(10), 725-763.
- 62. Scrosati, B.; Garche, J., Lithium batteries: status, prospects and future. *Journal* of Power Sources **2010**, 195 (9), 2419-2430.
- 63.. Song, M.-K.; Park, S.; Alamgir, F. M.; Cho, J.; Liu, M., Nanostructured electrodes for lithium-ion and lithium-air batteries: the latest developments, challenges, and perspectives. *Materials Science and Engineering: R: Reports* **2011**, 72 (11), 203-252.
- 64. Taberna, P. L.; Mitra, S.; Poizot, P.; Simon, P.; Tarascon, J. M., High rate capabilities Fe<sub>3</sub>O<sub>4</sub>-based Cu nano-architectured electrodes for lithium-ion battery applications. *Nature Materials* **2006**, 5 (7), 567-573.
- 65. Rong, J.; Masarapu, C.; Ni, J.; Zhang, Z.; Wei, B., Tandem structure of porous silicon film on single-walled carbon nanotube macrofilms for lithium-ion battery applications. *ACS Nano* **2010**, 4 (8), 4683-4690.
- 66. Liu, Y.; Clark, M.; Zhang, Q.; Yu, D.; Liu, D.; Liu, J.; Cao, G., V<sub>2</sub>O<sub>5</sub> nanoelectrodes with high power and energy densities for thin film Li-ion batteries. *Advanced Energy Materials* **2011**, 1 (2), 194-202.
- 67. Liu, H.; Yang, W., Ultralong single crystalline V<sub>2</sub>O<sub>5</sub> nanowire/graphene composite fabricated by a facile green approach and its lithium storage behavior. *Energy & Environmental Science* **2011**, 4 (10), 4000-4008.
- 68. Chen, X., Zhu, H., Chen, Y. C., Shang, Y., Cao, A., Hu, L., Rubloff, G. W. MWCNT/V<sub>2</sub>O<sub>5</sub> core/shell sponge for high areal capacity and power density Liion cathodes. *ACS Nano* **2012**, 6(9), 7948-7955.
- 69. Kim, D. K., Muralidharan, P., Lee, H. W., Ruffo, R., Yang, Y., Chan, C. K., Peng, H. L. Huggins, R. A., Cui, Y., Spinel LiMn2O4 nanorods as lithium ion battery cathodes. *Nano Letters* **2008**, 8(11), 3948-3952.

- 70. Jia, X., Yan, C., Chen, Z., Wang, R., Zhang, Q., Guo, L., Wei, F., Lu, Y., Direct growth of flexible LiMn<sub>2</sub>O<sub>4</sub>/CNT lithium-ion cathodes. *Chemical Communications* **2011**, 47(34), 9669-9671.
- 71. Shaju, K. M.; Jiao, F.; Debart, A.; Bruce, P. G., Mesoporous and nanowire Co<sub>3</sub>O<sub>4</sub> as negative electrodes for rechargeable lithium batteries. *Physical Chemistry Chemical Physics* **2007**, 9 (15), 1837-1842.
- 72. Wu, Z.-S.; Ren, W.; Wen, L.; Gao, L.; Zhao, J.; Chen, Z.; Zhou, G.; Li, F.; Cheng, H.-M., Graphene anchored with Co<sub>3</sub>O<sub>4</sub> nanoparticles as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance. ACS Nano 2010, 4 (6), 3187-3194.
- 73. Xu, X.; Cao, R.; Jeong, S.; Cho, J., Spindle-like Mesoporous α-Fe<sub>2</sub>O<sub>3</sub> anode material prepared from MOF template for high-rate lithium batteries. *Nano Letters* **2012**, 12 (9), 4988-4991.
- 74. Wang, Z.; Luan, D.; Madhavi, S.; Hu, Y.; Lou, X. W., Assembling carboncoated α-Fe<sub>2</sub>O<sub>3</sub> hollow nanohorns on the CNT backbone for superior lithium storage capability. *Energy & Environmental Science* **2012**, 5 (1), 5252-5256.
- 75. Zhu, X.; Zhu, Y.; Murali, S.; Stoller, M. D.; Ruoff, R. S., Nanostructured reduced graphene oxide/Fe<sub>2</sub>O<sub>3</sub> composite as a high-performance Anode Material for Lithium Ion Batteries. *ACS Nano* **2011**, 5 (4), 3333-3338.
- Varghese, B., Reddy, M. V., Yanwu, Z., Lit, C. S., Hoong, T. C., Subba Rao, G. V., Chowdari B. V. R., Wee. A., Lim, C. T., Sow, C. H., Fabrication of NiO nanowall electrodes for high performance lithium ion battery. *Chemistry of Materials* 2008, 20(10), 3360-3367.
- 77. Zou, Y., Wang, Y. NiO nanosheets grown on graphene nanosheets as superior anode materials for Li-ion batteries. *Nanoscale* **2011**, 3(6), 2615-2620.
- 78. Types of battery cells. http://batteryuniversity.com/learn/article/types\_of\_battery\_cells
- Fuel cells: fundamentals and applications. Springer Science & Business Media,
   2006
- 80. Ferreira, K. N., Iverson, T. M., Maghlaoui, K., Barber, J., Iwata, S., Architecture of the photosynthetic oxygen-evolving center. *Science* **2004**, 303(5665), 1831-1838.

- 81. Basu, S. Fuel Cell Science and Technology. *Anamaya Publishers*, New Delhi, India. **2007**
- 82. Thorum, M. S., Oxygen reduction electrocatalysis (Doctoral dissertation, *University of Illinois at Urbana-Champaign*). **2011**
- 83. Liang, Y., Li, Y., Wang, H., Zhou, J., Wang, J., Regier, T., Dai, H., Co<sub>3</sub>O<sub>4</sub> nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nature Materials* **2011**, 10(10), 780-786.
- 84. Hudak, N. S., Gallaway, J. W., Barton, S. C., Formation of mediated biocatalytic cathodes by electrodeposition of a redox polymer and laccase. *Journal of Electroanalytical Chemistry* **2009**, 629(1), 57-62.
- 85. Gallaway, J., Wheeldon, I., Rincon, R., Atanassov, P., Banta, S., Barton, S. C., Oxygen-reducing enzyme cathodes produced from SLAC, a small laccase from Streptomyces coelicolor. *Biosensors and Bioelectronics* **2008**, 23(8), 1229-1235.
- 86. Gorlin, Y., Jaramillo, T. F., A bifunctional nonprecious metal catalyst for oxygen reduction and water oxidation. *Journal of the American Chemical Society* 2010, 132(39), 13612-13614.
- 87. Sun, M., Dong, Y., Zhang, G., Qu, J., Li, J., α-Fe<sub>2</sub>O<sub>3</sub> spherical nanocrystals supported on CNTs as efficient non-noble electrocatalysts for the oxygen reduction reaction. *Journal of Materials Chemistry A* **2014**, 2(33), 13635-13640.
- 88. Merrill, M. D., Dougherty, R. C., Metal oxide catalysts for the evolution of O2 from H<sub>2</sub>O. *The Journal of Physical Chemistry C* **2008**, 112(10), 3655-3666.
- 89. Cui, B., Lin, H., Li, J. B., Li, X., Yang, J., Tao, J., Core–ring structured NiCo<sub>2</sub>O<sub>4</sub> nanoplatelets: synthesis, characterization, and electrocatalytic applications. *Advanced Functional Materials* **2008**, 18(9), 1440-1447.
- 90. Indira L., Dixit M., Kamath P. V., Stabilized α-Ni(OH)<sub>2</sub> as electrode material for alkaline secondary cells. *Journal of Power Sources* **1994**, 52:93 174.
- 91. Gong, M., Li, Y., Wang, H., Liang, Y., Wu, J. Z., Zhou, J., Dai, H., An advanced Ni–Fe layered double hydroxide electrocatalyst for water oxidation. *Journal of the American Chemical Society* **2013**, 135(23), 8452-8455.
- 92. Hydrodynamic Voltammetry http://www.ceb.cam.ac.uk/research/groups/rgeme/teaching-notes/hydrodynamic-voltammetry

- 93. Wang, S., Yu, D., Dai, L., Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction. *Journal of the American Chemical Society* **2011**, 133(14), 5182-5185.
- 94. Conway, B. E. (1999). Electrochemical supercapacitors.
- 95. Schneuwly, A., Gallay, R., Properties and applications of supercapacitors: From the state-of-the-art to future trends. Rossens, Switzerland. 2011
- 96. Vivekchand, S. R. C., Rout, C. S., Subrahmanyam, K. S., Govindaraj, A., Rao, C. N. R., Graphene-based electrochemical supercapacitors. *Journal of Chemical Sciences*, **2008**, 120, 9-13.
- 97. Subramanian, V., Zhu, H., Wei, B., Nanostructured MnO<sub>2</sub>: hydrothermal synthesis and electrochemical properties as a supercapacitor electrode material. *Journal of Power Sources* **2006**, 159, 361-364.
- 98. Hung, K., Masarapu, C., Ko, T., Wei, B. Wide-temperature range operation supercapacitors from nanostructured activated carbon fabric. *Journal of Power Sources* **2009**, 193, 944-949.
- 99. Wang, G., Zhang, L., Zhang, J., A review of electrode materials for electrochemical supercapacitors. *Chemical Society Reviews* **2012**, 41, 797-828.
- 100. Conway, B. E., Pell, W. G., Double-layer and pseudocapacitance types of electrochemical capacitors and their applications to the development of hybrid devices. *Journal of Solid State Electrochemistry* **2009**, 7(9), 637-644.
- 101. Conway, B. E., Birss, V., Wojtowicz, J., The role and utilization of pseudocapacitance for energy storage by supercapacitors. *Journal of Power Sources* **1997**, 66(1), 1-14.
- 102. Supercapacitor. http://en.wikipedia.org/wiki/Supercapacitor#cite\_note-65
- 103. Meng, C., Liu, C., Chen, L., Hu, C., Fan, S., Highly flexible and all-solid-state paperlike polymer supercapacitors. *Nano Letters* **2010**, 10, 4025-4031.
- 104. Frackowiak, E., Khomenko, V., Jurewicz, K., Lota, K., Beguin, F., *Journal of Power Sources* **2006**, 153, 413-418.
- 105. Brousse, T., Taberna, P. L., Crosnier, O., Dugas, R., Guillemet, P., Scudeller, Y., Zhou, Y., Favier, F., Bélanger, D., Simon, P., *Journal of Power Sources* 2007, 173, 633-641.

- 106. Hu, C. C., Chang, K. H., Lin, M. C., Wu, Y. T., Design and tailoring of the nanotubular arrayed architecture of hydrous RuO<sub>2</sub> for next generation supercapacitors. *Nano Letters* **2006**, 6, 2690-2695.
- 107. Kim, I. H., Kim, J. H., Lee, Y. H., & Kim, K. B., Synthesis and characterization of electrochemically prepared ruthenium oxide on carbon nanotube film substrate for supercapacitor applications. *Journal of The Electrochemical Society* 2005, 152, A2170-A2178.
- 121. Kim, J. H., Lee, K. H., Overzet, L. J., Lee, G. S., Synthesis and electrochemical properties of spin-capable carbon nanotube sheet/MnO<sub>x</sub> composites for high-performance energy storage devices. *Nano Letters* **2011**, 11, 2611-2617.
- 122. Hou, Y., Cheng, Y., Hobson, T., Liu, J., Design and synthesis of hierarchical MnO<sub>2</sub> nanospheres/carbon nanotubes/conducting polymer ternary composite for high performance electrochemical electrodes. *Nano Letters* **2010**, 10, 2727-2733.
- 124. Chen, S., Zhu, J., Wu, X., Han, Q., Wang, X., Graphene oxide-MnO<sub>2</sub> nanocomposites for supercapacitors. *ACS Nano* **2010**, 4, 2822-2830.
- 125. Yan, J., Wei, T., Qiao, W., Shao, B., Zhao, Q., Zhang, L., Fan, Z., Rapid microwave-assisted synthesis of graphene nanosheet/Co<sub>3</sub>O<sub>4</sub> composite for supercapacitors. *Electrochimica Acta* **2010**, 55, 6973-6978.
- 126. Gao, B., Yuan, C. Z., Su, L. H., Chen, L., Zhang, X. G., Nickel oxide coated on ultrasonically pretreated carbon nanotubes for supercapacitor. *Journal of Solid State Electrochemistry* **2009**, 13, 1251-1257.
- 127. Chen, Z., Augustyn, V., Wen, J., Zhang, Y., Shen, M., Dunn, B., Lu, Y., Highperformance supercapacitors based on intertwined CNT/V<sub>2</sub>O<sub>5</sub> nanowire nanocomposites. *Advanced Materials* **2011**, 23, 791-795.
- Stoller, M. D., Ruoff, R. S., Best practice methods for determining an electrode material's performance for ultracapacitors. *Energy & Environmental Science* 2009, 3(9), 1294-1301.

### Chapter 2

# CARBON NANOTUBE MACROFILM-VANADIUM PENTOXIDE NANOCOMPOSITES AS CATHODES OF LITHIUM-ION BATTERIES

# 2.1 Introduction

Vanadium pentoxide  $(V_2O_5)$  with orthorhombic layered structure has been extensively studied as a potential cathode material for rechargeable LIBs owing to its inherent Li<sup>+</sup> intercalation mechanism, high specific capacity, abundance, and low cost.[1-3] Although the Li<sup>+</sup> intercalation potential versus Li<sup>+</sup>/Li of V<sub>2</sub>O<sub>5</sub> (~3 V) is lower than that of LiFePO<sub>4</sub> (3.4 V) and LiCoO<sub>2</sub> (3.7 V), [4-6] the two most commonly employed cathodes of LIBs in electric vehicles and portable electronic devices,  $V_2O_5$ exhibits higher energy and power densities as a result of its higher theoretical reversible capacity (~290 mAhg<sup>-1</sup>) and can easily be fabricated compared to LiFePO<sub>4</sub> (170 mAhg<sup>-1</sup>) <sup>1</sup>) and LiCoO<sub>2</sub> (140 mAhg<sup>-1</sup>). [7, 8] However, the low electrical conductivity and slow electrochemical kinetics of  $V_2O_5$  due to its low ionic conductivity restrict the lithiation and delithiation processes as well as charge transfer rate. [9] Its poor structural stability also seriously limits its cycle lifetime. [10] To overcome these challenges, reducing the size of V<sub>2</sub>O<sub>5</sub> structures to nanoscale, such as creating a mesoporous material with pore diameters from 2 to 50 nm, was demonstrated to increase the electrochemical kinetics by shortening the Li<sup>+</sup> diffusion distance and providing the nano-sized channels for fast Li ion transport. [10, 11] Recent years,  $V_2O_5$  nanomaterials in various structures have also been synthesized to improve their performance by using different processing methods: nanoparticles from xerogel deposition; [12, 13] nanotubes from hydrothermal method; [14] nanowires from CVD; [15] nanofibers from electrospinning, [16] and etc. However, a competing problem, i.e., the dissolution of such nanoscaled active material during the charge and discharge processes will occur, resulting in a limited cyclic stability and remaining as a major challenge. [17] Thus a strategy to employ mixed conductors such as applying carbon coatings e.g. CNTs for nanocomposite electrodes was proposed to enhance the conductivity of  $V_2O_5$ . [18-20]

The flexible SWNT macrofilms with a porous structure can be applied as a buffer layer between silicon films and current collectors to significantly improve the cyclic stability of silicon for LIB anodes. [28] Because of the interconnected electrical pathways within the macro-films, they can also be utilized as an anchoring substrate to improve the poor conductivity and electrochemical kinetics of nanostructured active materials. [29] In order to expand SWNT macrofilms to be composites with cathode materials i.e.  $V_2O_5$  and enhance the electrochemical performance of the cathode materials, in this chapter we present a facile approach for the synthesis of  $V_2O_5$ /SWNT hybrid macrofilms and demonstrate them as promising nanocomposite cathode materials for LIBs.

Because of the unique structure of the SWNT macro-films, the vanadium precursor is able to fully penetrate into the interior of the SWNT macro-films in order to form  $V_2O_5$  nanoparticles attached on the surface of SWNTs by a controllably slow hydrolysis. The resulting hybrid films exhibit highly reversible rate capacities: 548 mAhg<sup>-1</sup> at the discharge rate of 300 mAg<sup>-1</sup> (~1 C); 342 mAhg<sup>-1</sup> and 171 mAhg<sup>-1</sup> at high discharge rates of 1200 mAg<sup>-1</sup> (~4 C) and 2400 mAg<sup>-1</sup> (~8 C), respectively, achieving both high energy density and power density for LIBs. The high rate capacity is attributed to the compact affinity of  $V_2O_5$  nanoparticles to the surface of SWNTs through the functional groups such as hydroxyl groups, evidenced by detailed transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) characterizations. This hybrid cathode also holds a high coulombic efficiency and good cyclic stability.

approach provides a much easier and low-cost fabrication technique to deposit  $V_2O_5$  on carbon nanomaterials compared with other complicated processing methods reported.

#### 2.2 Experimental

# 2.2.1 V<sub>2</sub>O<sub>5</sub>/SWNT macrofilm preparation

SWNT macro-films were synthesized and purified by the method described in Section 1.2.1. Then, the films were transferred onto the aluminum foil (45  $\mu$ m thick) current collectors and then were punched to 1/2"-disc electrodes after dried in air.

In an Ar-filled glovebox (MBRAUN UNIIab),  $V_2O_5$  nanoparticles were deposited on the as-prepared SWNT macro-film electrodes by dropping 2 drops (2 µl) of vanadium (V) oxytriisopropoxide (99%, Acros Organics) and one drop (4 µl) of anhydrous ethanol (Fisher Chemical) on the pristine SWNT films using pipettes. The addition of ethanol is critical to assist the vanadium precursor liquid to spread and infiltrate into the SWNT films. Then the electrodes experienced a 24-hour hydrolysis reaction with a moisture (< 0.1 ppm) in the glovebox to form V<sub>2</sub>O<sub>5</sub>/SWNT hybrid mesorporous films. Afterwards, the hybrid films were annealed at 400 °C in the air for 2 h before they were assembled into battery coin cells for electrochemical measurements.

# 2.2.2 Characterization and electrochemical measurements

Morphology and structural characterizations were performed using scanning electron microscopy (SEM, JEOL JSM-7400F) and transmission electron microscope (TEM, JEOL JEM-2010F). X-ray diffraction (XRD, Philips X'Pert diffractometer with Cu K $\alpha$  radiation and a 2 $\theta$  range of 10 to 60 ° with 0.02 °/step and 1s/step) and Raman spectroscopy (Bruker SENTERRA with 573 nm laser excitation) were employed to verify the crystalline structure of the V<sub>2</sub>O<sub>5</sub> nanoparticles. The chemical interaction

between  $V_2O_5$  and the surface of SWNTs were investigated by X-ray photoelectron spectroscopy (EA 125 spectrometer with non-chromatic Al K $\alpha$  source (1486.5 eV)).

Before the cell assembly, the mass difference of electrodes before and after deposition of  $V_2O_5$  nanoparticles was weighed out using a micro/ultramicro balance (Mettler Toledo XP6) with 0.001 mg accuracy. Electrochemical tests were carried out on CR2032 coin cells with  $V_2O_5$ /SWNT hybrid mesoporous films as cathodes and lithium ribbons (0.38 mm thick, 99.9%, Sigma Aldrich) as anodes. The Celgard 2500 were chosen as separators and 1 M LiPF<sub>6</sub> dissolved in 1:1 v/v EC: DEC (Ferro Corporation) were used as electrolyte. All the half cells were assembled in the argon-filled glovebox. The cyclic voltammetry curves and electrochemical impedance spectra with a 10 mV AC signal employed from 100 kHz to 10 mHz were all collected by PARSTAT 2273 (Princeton Applied Research) potentiostat. The galvanostatic discharge-charge tests for the coin cells were carried out using BT-4 4-channel battery test equipment (Arbin Instrument, Itd.).

# 2.3 Results and Discussion

#### 2.3.1 Controllable hydrolysis deposition of V<sub>2</sub>O<sub>5</sub>

Preparation of the  $V_2O_5/SWNT$  hybrid films is schematically illustrated in Figure 2.1a.



Figure 2.1 Schematic illustration of the procedures to synthesize V<sub>2</sub>O<sub>5</sub>/SWNT hybrid mesorporous films. (b) Ball-and-stick representation of the crystalline structure of layered V<sub>2</sub>O<sub>5</sub> and SWNTs and the chemical interaction between them.

Vanadium (V) oxytriisopropoxide, an organic vanadium liquid which possesses an excellent wetting ability to the hydrophobic surface of SWNTs, was employed as the V precursor.[30] The precursor infiltrating into the interior of the SWNT macro-films were completely transformed into  $V_2O_5$  nanoparticles by controlling the hydrolysis rate in an argon-filled glovebox with  $H_2O < 0.1$  ppm and  $O_2 < 0.1$  ppm (Equation 2.1):

The  $V_2O_5$  nanoparticles with layered structures would attach on the SWNT surfaces through the functional groups, as schematic shown in Figure 2.1b.

### 2.3.2 Mesoporous layer structure of nanocomposites and chemical bonding

Figure 2.2a shows a photograph of such a dark yellowed film after being annealed at 400 °C in air for 2 hours. The film is semi-transparent due to the mesoporous structures. The SEM image in Figure 2.2b shows the cross section of the film with a multi-layered structure of  $V_2O_5$ -wrapped SWNTs, indicating the complete infiltration of the vanadium precursors into the mesh of the web-like SWNT macro-films. Figure 2.2c and 2.2d reveal the synthesized  $V_2O_5$  nanoparticles with a diameter of 5-150 nm. The bright particles below 20 nm and decorated on the SWNT surfaces suggest possibly chemical interactions between them and SWNTs. The TEM image also shows that smaller-sized  $V_2O_5$  particles with diameter of 5-20 nm are firmly attached on the SWNTs (Figure 2.3a), even after sonicating the hybrid film for 1 h, confirming the compact anchoring of  $V_2O_5$  on SWNTs. However, the obvious agglomeration of the smaller particles into larger particles or plates over 100 nm exists concurrently. The coexistence of different particle sizes implies that the functional groups on SWNTs could promote uniform nucleations of  $V_2O_5$  nanoparticle on the SWNT surfaces while this interaction is insufficient in the far regions from the SWNT surfaces.



Figure 2.2 SEM images showing the morphology of V<sub>2</sub>O<sub>5</sub>/SWNT hybrid mesoporous films annealed at 400 °C for 2h. (a) Photograph of the 400 °C annealed V<sub>2</sub>O<sub>5</sub>/SWNT hybrid film. (b) cross-section, (c) top view, (d) magnified top view from (c).

High-resolution TEM (HRTEM, Figure 2.3b) reveals the crystal structural information of a V<sub>2</sub>O<sub>5</sub> nanoparticle, showing the lattice feature of 3.39 Å, which corresponds to interplanar distance of (101) planes of V<sub>2</sub>O<sub>5</sub>. It agrees with the (101) peak in the X-ray diffraction (XRD) pattern presented below. The scheme in Figure 2.1b exhibits the possible chemical bonds between SWNTs and the layer-structured V<sub>2</sub>O<sub>5</sub>, which anchors on the SWNT surfaces. Despite the aggregation of the insulating V<sub>2</sub>O<sub>5</sub> nanoparticles, the films provide sufficient conductivity, large surface areas and favorable channels to facilitate the Li<sup>+</sup> diffusion and intercalation.



Figure 2.3 (a) TEM image of V<sub>2</sub>O<sub>5</sub> nanoparticles anchorded firmly on SWNTs after 1 h sonication of the hybrid films. (b) High-resolution TEM image of an individual V<sub>2</sub>O<sub>5</sub> nanoparticle grown on SWNT bundles.

XRD and Raman spectroscopy (Figures 2.4a and 2.4b) further identify the crystal structure of V<sub>2</sub>O<sub>5</sub>. The XRD pattern exhibits typical peaks of orthorhombic V<sub>2</sub>O<sub>5</sub> phase of the space group *Pmmn*, with lattice parameters a = 11.48 Å, b=4.36 Å, and c=3.55 Å, respectively. The peaks at 20.63°, 22.07°, 26.52°, 31.17°, 41.73°, and 47.45° can be indexed as (010), (110), (101), (400), (020), and (600) planes of V<sub>2</sub>O<sub>5</sub> (marked as "\*"), respectively except the two sharper peaks at around 38.69° and 45.03°, which are corresponding to (111) and (200) planes of the Al substrate as a current collector (JCPDS card No.01-075-0457).



Figure 2.4 (a) X-ray diffraction pattern for 400 °C annealed hybrid films on an Al foil as current collector. (b) Raman spectrum at excitation of 532 nm.

From the Raman spectrum, the two peaks at high frequency around 1353 cm<sup>-1</sup> and 1580 cm<sup>-1</sup> are the D band and G band of SWNTs (marked as " $\blacklozenge$ ") and all the remaining peaks are attributed to V<sub>2</sub>O<sub>5</sub> (marked as " $\ast$ "). The first peak at 994 cm<sup>-1</sup> corresponds to the inphase stretching vibration mode of all apical V-O bonds, resulting from *z*-displacement of O atoms. The second peak at 884cm<sup>-1</sup> is attributed to the antiphase stretching of the V-O<sub>3</sub> bonds, which are constructed by the triply coordinated oxygen atoms edge-shared by three pyramids. This  $B_{2g}$  symmetric mode forms the V-O<sub>3</sub>-V bridges. The third peak at 704 cm<sup>-1</sup> is assigned to the antiphase stretching mode of V-O<sub>2</sub> bonds between the central vanadium atom and the doubly coordinated oxygen atoms corner-shared by two pyramids. The  $A_g$  Raman-active mode at around 532 cm<sup>-1</sup> originates from the stretching of the V-O<sub>3</sub> bonds. Then follows the peak at 484.5 cm<sup>-1</sup>, which is ascribed to the bending vibrations of the V-O<sub>3</sub>-V bridges. The two Raman features at 403 cm<sup>-1</sup> and 283.5 cm<sup>-1</sup> can be characterized as the bending vibrations of the V-O<sub>3</sub> bonds. Two peaks in the

low-frequency region are assigned to the modes involving displacements of the V atoms. The one at 200 cm<sup>-1</sup> origins from  $A_g$  and  $B_{2g}$  modes, with the atoms oscillating along the *x* axis. The strongest peak at 149 cm<sup>-1</sup> is a mixture of signals coming from  $B_{1g}$  and  $B_{2g}$ . [32, 33] Note that the intensity of V<sub>2</sub>O<sub>5</sub> signal is comparable to that of G band belonging to SWNT. This confirms that the hybrid films consist of a high percentage of V<sub>2</sub>O<sub>5</sub>. Though few amount of SWNTs exist, their strong bonds in graphitic hexagons construct and ensure the relatively strong structural stability of the films.

XPS spectra further confirm the formation of  $V_2O_5$ . The survey spectrum (Figure 2.5a) indicates that all the elements detected are only vanadium, carbon and oxygen. Table 2.1 shows the XPS data for all the peaks. The binding energies for vanadium 2p<sub>3/2</sub> and 2p<sub>1/2</sub> at 516.8 eV and 524.2 eV as shown in the V 2p spectrum (Figure 2.5b) are consistent with those of  $V^{5+}$  in  $V_2O_5$ . [34] Notably, the central positions of  $2p_{3/2}$  and  $2p_{1/2}$  peaks shift to lower binding energies by 0.4 eV and 0.3 eV, respectively. [35] It is plausibly due to the affinity of V<sub>2</sub>O<sub>5</sub> to the SWNTs. The C 1s curve shown in Figure 2.5c could be deconvoluted into three peaks, indicating that carbon atoms are in three different chemical environments. The predominant peak at 284 eV derives from sp<sup>2</sup>-hybridized C=C bonds of the graphitic hexagons, which shifts to left by 0.4 eV as a result of the coupling between  $V_2O_5$  and SWNTs [35, 36]. The peak in the middle at 285.7 eV is assigned to single-coordinated C-O bonds in carboxyl groups and the smallest peak at 288.2 eV corresponds to the minimal carbonyl (C=O) groups. [36] These functional groups with a percentage of  $\sim 18\%$  play key roles in the electrochemical performance shown in the following section. The asymmetric peak in O 1s core-level spectrum (Figure 2.5d) can be fitted by two instinct O peaks.



Figure 2.5 X-ray photoelectron spectrum for V<sub>2</sub>O<sub>5</sub>/SWNT hybrid mesoporous films showing the interaction between the slight function group of SWNT and V<sub>2</sub>O<sub>5</sub> nanoparticles. (a) survey-scan spectrum showing all C, O and V elements. (b) V 2p region with spin orbit splitting of 2p<sub>3/2</sub> and 2p<sub>1/2</sub> showing V<sup>5+</sup> state. (c) C 1s region of XPS spectrum deconvoluted to peaks indicating grahitic structure of SWNT and functional groups of SWNT macro-films. (d) Asymmetrical O 1s peak of XPS spectrum fitted with the predominant peak corresponding to O atoms in V<sub>2</sub>O<sub>5</sub> and the peak of hydroxyl groups in higher binding energy.

The one at the position of 529.7 eV, which is 0.3 eV to 530 eV, belongs to the oxygen atoms of  $V_2O_5$ . [35] The other at 531.6 eV is attributed to hydroxyl groups (OH), consistent with the fitting peak of C 1s for carboxyl groups (C=O). [37] Overall, the existence of functional groups and peak shift towards lower binding-energy region by

 $0.3\sim0.4$  eV further imply that the V<sub>2</sub>O<sub>5</sub> nanoparticles could be bonded to the SWNT surfaces via V-O-C bonds or van der Waals forces. Thus, these results agree with the hypothesis that the compact association of V<sub>2</sub>O<sub>5</sub> nanoparticles with SWNTs can enhance the stability of these cathode materials for LIBs.

Peaks	Binding Energy (eV)	Bingding Energy (eV) in Ref. <sup>[34,35]</sup>	Shift (+: towards higher; -: towards lower energy)	C 1s peaks area	Functional groups percentage
V 2p <sub>3/2</sub>	516.8	517.2	-0.4	—	—
V 2p <sub>1/2</sub>	524.2	524.5	-0.3	—	—
C 1s (C=C)	284	284.4	-0.4	6240	
C 1s (C-O)	285.7	285.7	—	650	17.38%
C 1s (C=O)	288.2	288.2	—	435	
O 1s (V <sub>2</sub> O <sub>5</sub> )	529.7	530	-0.3	—	—
O 1s (OH)	531.6	531.6	—	—	

Table 2.1Binding Energy of the fitting peaks in XPS spectra shown in Figure 2.5.

#### **2.3.3** Phase transition during lithiation and cyclic performance

Electrochemical performance of the synthesized nanocomposite were evaluated in half-cell configuration that consists of the V<sub>2</sub>O<sub>5</sub>/SWNT hybrid mesoporous films as the cathodes and Li metal foils as the anodes. The cathodes has a loading mass of ca.0.3 mg V<sub>2</sub>O<sub>5</sub> material obtained by weighing out the mass increase of the films after deposition and annealing at 400 °C for 2 h of V<sub>2</sub>O<sub>5</sub> on pure SWNT macro-films using an ultramicro analytic balance as described in Sector 2.2.2. The discharge curves at a current density of 300 mAg<sup>-1</sup> (~1 C) (Figure 2.6a) show two flat plateaus at 3.5 V and 3.2 V since the 2<sup>nd</sup> cycle in the voltage profiles, corresponding to a gradual phase transition during the process of Li<sup>+</sup> intercalation into the pristine V<sub>2</sub>O<sub>5</sub>:  $\alpha$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase (x<0.1) (Equation 2.2) to  $\epsilon$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> (0.35<x<0.7) phase (Equation 2.3) and then to  $\delta$ - Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> (0.9<x<1) phase (Equation 2.4). The plateau at 2.3 V corresponds to the formation of  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> (Equation 2.5). [36] The  $\alpha \leftrightarrow \epsilon$  and  $\epsilon \leftrightarrow \delta$  transition processes are completely reversible because the structures of  $\alpha$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> and  $\epsilon$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phases are very similar to that of the pristine V<sub>2</sub>O<sub>5</sub> before Li-intercalation. [38]

$$xLi^{+}+V_2O_5+x\Theta \implies \alpha-Li_xV_2O_5 (x<0.1)$$
2.2

$$xLi^{+} V_2O_5 + x \ominus \implies \epsilon - Li_x V_2O_5 (0.35 < x < 0.7)$$
 2.3

$$xLi^{+}+V_2O_5+x \ominus \checkmark \delta-Li_xV_2O_5 (0.9 < x < 1)$$

$$xLi^{+}+V_2O_5+x\Theta \implies \gamma -Li_xV_2O_5 (1 < x < 2)$$

The open circuit voltage (OCV) value read from the first discharge curve is at 3.5 V, approaching to the equilibrium potential of  $\alpha \leftrightarrow \epsilon$  phase transition. Since 2<sup>nd</sup> discharge, all curves afterwards exhibit a higher potential than the initial potential at the first cycle due to the existence of the new phase,  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>, formed in the 1<sup>st</sup> discharge process.



Figure 2.6 Electrochemical performance for V<sub>2</sub>O<sub>5</sub>/SWNT hybrid mesoporous film in a half cell: (a) voltage profile of discharge-charge curves at 300 mAg<sup>-1</sup> after the 1<sup>st</sup>, 2<sup>nd</sup>, 10<sup>th</sup>, 20<sup>th</sup>, 30<sup>th</sup>, 40<sup>th</sup> cycle, (b) specific capacity retention for 40 cycles at the rate of 300 mAg<sup>-1</sup>, (c) discarding charge curves at various rates for the same cell after the ending of the 40<sup>th</sup> cycle of discharge-charge tests at the rate of 300 mAg<sup>-1</sup>, (d) high-rate capacities at various rates.

It was reported that the amount of  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase formed is directly determined by the state-of-discharge (SOD) during the preceding discharge cycles. The increasing amount of the  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> was formed in the electrode when the SOD of Li-intercalation increases during the first two cycles. [39] The  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> also has a partial irreversibility caused by puckering of the V<sub>2</sub>O<sub>5</sub> layers to accommodate the phase transition when more

than 1 mole of Li ions were intercalated into 1 mole of V<sub>2</sub>O<sub>5</sub>. [40] It is also noting that plateaus become less evident and are become a linear slope in the consecutive charge and discharge curves. This change is plausibly related to the formation of irreversible  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase (x > 2). The  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase experiences irreversible structural modification successively transited from  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> when per mole of V<sub>2</sub>O<sub>5</sub> is overinserted by 2 to 3 moles of Li ions, especially at high charging/discharging rates. [41] Thus, more  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase would form, leading to a higher storage capacity while at the expense of sacrificing the cyclic capacity retention if the limit of our current cutoff potential is lowered below 2 V versus Li<sup>+</sup>/Li for a deeper discharge. From the analysis above, it is deduced that the 6% loss of the initial capacity at 1 C after 40 cycles shown in Figure 2.6b may result from the increasing amount of irreversible  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase. Thus, drawing the cutoff potential up will benefit to extend the cyclic lifetime of the  $V_2O_5/SWNT$  hybrid films. The average discharge capacity for the 40 cycles in Figure 2.6b, is 548 mAhg<sup>-1</sup>. The higher capacity over the theoretical capacity is similar to the results presented in other reports. [3, 20] It is presumably attributed to the gradually irreversible processes such as the formation of solid-electrolyte-interface (SEI) layer, which also enables the excellent capacity retention as high as 94% at the end of the 40<sup>th</sup> cycle.

# 2.3.4 Rate capability and electrochemical impedance spectroscopy

Figure 2.6c presents charge and discharge curves for the V<sub>2</sub>O<sub>5</sub>/SWNT hybrid films at different rates. It is obviously found that the potential plateaus gradually disappear and become a sloped curve as the current density is raised, indicating that most of V<sub>2</sub>O<sub>5</sub> is transformed to the irreversible  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>.[42] Figure 2.6d shows rate capability of the V<sub>2</sub>O<sub>5</sub>/SWNT hybrid films (10 cycles at each rate) following the first 40 cycles after staying in OCV state for 24 h. The specific capacity remains as high as  $342 \text{ mAhg}^{-1}$  at the rate of about 4 C (1200 mAg<sup>-1</sup>). When the discharge rate reaches 8 C (2400 mAg<sup>-1</sup>), an average capacity of 171 mAhg<sup>-1</sup> during the corresponding 10 cycles is obtained. Afterwards, the capacity is still above 100 mAhg<sup>-1</sup> at the highest rate of 32 C (9600 mAg<sup>-1</sup>). In the last 10 cycles when it returns to the lower rate of 2 C (600 mAg<sup>-1</sup>), the capacity is able to recover to ~400 mAhg<sup>-1</sup>. These results demonstrate an excellent rate capability of the V<sub>2</sub>O<sub>5</sub>/SWNT hybrid structures. This is owing to the much improved electrochemical kinetics of V<sub>2</sub>O<sub>5</sub> with the involvement of SWNTs. In addition, the Coulombic efficiency (CE) (Figure 2.6d) is also improved beyond 90%. The stable CE values between the 10<sup>th</sup> and the 50<sup>th</sup> cycle from 4 C to 32 C remain in the range of 95%~97%, which are higher than the fluctuation in the range of 90%~92% at 1 C and 2 C rates. This is in agreement with the proved stability for  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>, the high portion of which makes the cell more stable at rates higher than 4 C.

Following the 40-cycle GCD tests at 300 mAg<sup>-1</sup> in Figure 2.6b, Figure 2.7 shows CV results for the nanocomposite cathode in the same cell. CV plots are within the potential window between 2 and 4 V versus Li<sup>+</sup>/Li at scan rates of 1, 5, 10, 20, and 50 mV/s. Three redox pairs at approximately 3.3 V/3.5 V, 3.1 V/3.2 V and 2.2 V/2.4 V are observed and can be attributed to the  $\alpha \leftrightarrow \epsilon$ ,  $\epsilon \leftrightarrow \delta$  and  $\delta \leftrightarrow \gamma$  reversible phase transitions, respectively. This is consistent with the previous analysis of the voltage profile plots. The CV curves also show that the peak separation of the redox pairs becomes larger and the peaks of the  $\delta \rightarrow \gamma$  pair become too broad to be evident as the scan rate increases. The former phenomenon results from the limit of kinetics while the latter is ascribed to the partial irreversibility of the  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase. This provides more evidence to support our discussion in the last section about the reason for capacity loss during cycling.

Moreover, it is worth noting that the peaks in the CV plots, even at 50 mV/s, is as discernable as that at a low scan rate of 100  $\mu$ V/s. This behavior is comparable to that of supercapacitors with a high power density, which further confirms the high rate capability of the V<sub>2</sub>O<sub>5</sub>/SWNT.



Figure 2.7 The cyclic voltammetry of  $V_2O_5$ /SWNT hybrid mesoporous film at various scan rates from 1 mV/s to 50 mV/s for a half cell with 1 M LiPF<sub>6</sub> in EC:DEC (1:1 v/v) as electrolyte, consist with the excellent high-rate performance.

EIS can reveal the information of conductivity, charge transfer and ionic diffusion and so it was performed to better understand the high rate capability. We compare the EIS plots (Figure 2.8a and 2.8b) of the as-assembled cell (before the 1<sup>st</sup> cycle) and at the end of the 40<sup>th</sup> cycle discharged under 1 C rate. The Nyquist plots are composed of a high-medium-frequency arc and a low-frequency Warburg tail as shown in Figure 2.8a, where the slopes of the Warburg tail for both curves are nearly equal to

1, indicating that the diffusion coefficients for the Li<sup>+</sup> intercalation and deintercalation are basically equal to each other (Equations 2.6, 2.7 and 2.8).[43, 44]

$$W' = \sigma \cdot \omega^{\frac{1}{2}}$$
 2.6

$$W'' = -\sigma \cdot \omega^{\frac{1}{2}}$$
 2.7

$$D = \frac{R^2 T^2}{2 \cdot A \cdot n^2 F^2 C^2 \sigma^2}$$
 2.8

Where the *W*' is the real part and *W*'' is the imaginary part of the Warburg impedance;  $\sigma$  is the Warburg factor indicating the Li-ion diffusing kinetics;  $\omega$  is frequency (< 1Hz); *A* is the surface area of the electrode (~1.2 cm<sup>2</sup>); *C* is the concentration of Li ions; *n* is the charge number in the transfer process, *i.e.* the Li<sup>+</sup> number during intercalation/deintercalation; *T* is temperature of testing condition (*T* = 25 °C); and the remaining parameters are all common physical constants. The typical frequency at the intersection of the semi-circle and sloped line represents the frequency response of electrode materials in various electrochemical energy storage devices. Its value is 15.20 Hz equally for both curves,

The Bode phase plot (Figure 2.8b) exhibits that the initial single peak (orange line) with a good symmetry at approximately 100 Hz becomes an asymmetrical major peak with a small shoulder at a high frequency over 10000 Hz after 40 cycles (purple line). Noting that the frequency position of the major peak for the 40<sup>th</sup> cycle still remains at 100 Hz and the minimum of the peaks for both curves are at around 10 Hz, which is in a good agreement with the above-mentioned 15.20 Hz. It implies that 100 Hz belongs to V<sub>2</sub>O<sub>5</sub>. The peak splitting is reflected in the corresponding equivalent circuits in Figure 2.8c and 2.8d. The initial peak in the first cycle (orange line) is assigned to the V<sub>2</sub>O<sub>5</sub>/SWNTs integration with a single parallel component in Figure 2.8c.



Figure 2.8 Electrochemical Impedance Spectroscopy (EIS) data for V<sub>2</sub>O<sub>5</sub>/SWNT hybrid mesoporous film in the coin cell after cycling at rate of 300 mAg<sup>-1</sup>: (a) Nyquist plots before the 1<sup>st</sup> cycle (orange curve) and after the 40<sup>th</sup> cycle (purple curve), (b) Bode phase plots before the 1<sup>st</sup> cycle (orange curve) and after the 40<sup>th</sup> cycle (purple curve), (c) the equivalent circuit corresponding to the 1<sup>st</sup> cycle, (d) the equivalent circuit corresponding to the 40<sup>th</sup> cycle.

The major peak and small shoulder (purple line) split from the initial peak can be fitted by a different equivalent circuit model (Figure 2.8d), which is composed of two parallel components in series. This splitting is probably ascribed to the dissociation of V<sub>2</sub>O<sub>5</sub> from the surface of SWNTs as forming new phases of Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> due to the relatively weak bonds between most V<sub>2</sub>O<sub>5</sub> particles in large sizes and SWNTs. The functionalized SWNTs cannot completely prevent the larger V<sub>2</sub>O<sub>5</sub> nanoparticles from dissociation into the electrolyte, which also cause the capacity decline of the V<sub>2</sub>O<sub>5</sub>/SWNT. Table 2.2 lists the values of key components in both equivalent circuit models. After 40 cycling tests, the charge transfer resistance of the initial films (*R<sub>mix</sub>*) as high as 227.40  $\Omega$  is divided to  $R_{mix}$  of 11.72  $\Omega$  assigned to the intimately-anchored V<sub>2</sub>O<sub>5</sub>/SWNT integrity and  $R_v$  of 24.99  $\Omega$  assigned to the larger V<sub>2</sub>O<sub>5</sub> particles. The lower charge transfer resistance may result from the stable SEI formation between electrolyte and the V<sub>2</sub>O<sub>5</sub>/SWNT.[13] Correspondingly, the Warburg resistance of the intimately-anchored V<sub>2</sub>O<sub>5</sub>/SWNT integrity is reduced from 16.03  $\Omega$  ( $W_{mix}$ ) to 0.01  $\Omega$  ( $W_{mix}$ ) after 40 cycles. However, Warburg resistance of the larger V<sub>2</sub>O<sub>5</sub> nanoparticles is 134.3  $\Omega$  ( $W_v$ ), which is much higher than 16.03  $\Omega$ , indicating that Li<sup>+</sup> diffusivity is decreasing during cycling. Nevertheless, the Li<sup>+</sup> diffusion coefficients (D<sub>Li</sub><sup>+</sup>) for both curves, the first cycle and the 40<sup>th</sup> cycle, are ca. 2.63x 10<sup>-7</sup> cm<sup>2</sup>/s and 7.505 x 10<sup>-10</sup> cm<sup>2</sup>/s, respectively, which are over 2 to 4 orders of magnitude improvement compared to that of the bulk V<sub>2</sub>O<sub>5</sub> (10<sup>-12</sup> cm<sup>2</sup>/s). Thus, it concludes that the high diffusion coefficient is a dominant factor in achieving the high rate capability of the cathodes, further confirming that SWNTs can enhance electrochemical performance of V<sub>2</sub>O<sub>5</sub> by accelerating the electrochemical kinetics.

Table 2.2The fitting values of the components in equivalent circuits shown in<br/>Figure 2.8c and 2.8d.

Components in EC	$R_{s}\left(\Omega ight)$	$R_{mix}\left(\Omega ight)$	$W_V$	$W_{mix}\left(\Omega ight)$	$R_{mix}(\Omega)$	$R_{v}\left( \Omega ight)$
1st cycle	11.95	227.40	_	16.03	_	—
40th cycle	7.22	—	134.3	0.01	11.72	24.99

### 2.4 Conclusions

In summary, we have successfully synthesized the layer-structured  $V_2O_5$  nanoparticle/SWNT nanocomposites with high rate capability and high CE as promising cathodes for lithium ion batteries. The chemical interaction between the  $V_2O_5$  particles and the SWNT surface through the functional groups has been verified, which enables

the fast electrochemical kinetics of V<sub>2</sub>O<sub>5</sub>. The resulting high Li-ion diffusion coefficient contributes to the excellent rate performance. SWNTs have also been demonstrated to enhance the cyclic stability of V<sub>2</sub>O<sub>5</sub> at high rates. The irreversibility of  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> and  $\gamma$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phases as well as the dissolution of V<sub>2</sub>O<sub>5</sub> nanoparticles during cycling account for the capacity loss. This work open a feasible path to involve SWNT macrofilm with more cathode materials *via* chemical bonding to achieve high performance nanocomposites for LIB.

# REFERENCES

- 1. Whittingham, M. S., Lithium batteries and cathode materials. *Chemical Reviews* **2004**, 104(10), 4271-4302.
- 2. Chernova, N. A., Roppolo, M., Dillon, A. C., Whittingham, M. S., Layered vanadium and molybdenum oxides: batteries and electrochromics. *Journal of Materials Chemistry* **2009**, 19(17), 2526-2552.3.
- 3. Zhou, S., Yang, X., Lin, Y., Xie, J., Wang, D., A nanonet-enabled Li ion battery cathode material with high power rate, high capacity, and long cycle lifetime. *ACS Nano* **2011**, 6(1), 919-924.
- 4. Ellis, B., Kan, W. H., Makahnouk, W. R. M., Nazar, L. F., Synthesis of nanocrystals and morphology control of hydrothermally prepared LiFePO<sub>4</sub>. *Journal of Materials Chemistry* **2007**, 17(30), 3248-3254.
- 5. Ferg, E., Gummow, R. J., De Kock, A., & Thackeray, M. M., Spinel Anodes for Lithium-Ion Batteries. *Journal of the Electrochemical Society* **1994**, 141(11), L147-L150.
- Wang, S., Lu, Z., Wang, D., Li, C., Chen, C., Yin, Y., Porous monodisperse V<sub>2</sub>O<sub>5</sub> microspheres as cathode materials for lithium-ion batteries. *Journal of Materials Chemistry* 2011, 21(17), 6365-6369.
- 7. Antaya, M., Dahn, J. R., Preston, J. S., Rossen, E., Reimers, J. N., Preparation and characterization of LiCoO<sub>2</sub> thin films by laser ablation deposition. *Journal of the Electrochemical Society* **1993**, 140(3), 575-578.
- 8. Yamada, A., Chung, S. C., Hinokuma, K.. Optimized LiFePO<sub>4</sub> for lithium battery cathodes. *Journal of the Electrochemical Society* **2001**, 148(3), A224-A229.
- 9. Tarascon, J. M., Armand, M., Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, 414(6861), 359-367.
- 10. Wang, S., Li, S., Sun, Y., Feng, X., Chen, C., Three-dimensional porous V<sub>2</sub>O<sub>5</sub> cathode with ultra high rate capability. *Energy & Environmental Science* **2011**, 4(8), 2854-2857.
- 11. Zhong, L. S., Hu, J. S., Liang, H. P., Cao, A. M., Song, W. G., Wan, L. J., Self-Assembled 3D flowerlike iron oxide nanostructures and their application in water treatment. *Advanced Materials* **2006**, 18(18), 2426-2431.

- 12. Liu, D., Liu, Y., Garcia, B. B., Zhang, Q., Pan, A., Jeong, Y. H., Cao, G, V<sub>2</sub>O<sub>5</sub> xerogel electrodes with much enhanced lithium-ion intercalation properties with N<sub>2</sub> annealing. *Journal of Materials Chemistry* **2009**, 19(46), 8789-8795.
- Liu, D., Liu, Y., Pan, A., Nagle, K. P., Seidler, G. T., Jeong, Y. H., Cao, G., Enhanced lithium-ion intercalation properties of V<sub>2</sub>O<sub>5</sub> xerogel electrodes with surface defects. *The Journal of Physical Chemistry C* 2011, 115(11), 4959-4965.
- 14. Petkov, V., Zavalij, P. Y., Lutta, S., Whittingham, M. S., Parvanov, V., Shastri, S., Structure beyond Bragg: Study of V2O5 nanotubes. *Physical Review B* **2004**, 69(8), 085410.
- 15. Chan, C. K., Peng, H., Twesten, R. D., Jarausch, K., Zhang, X. F., Cui, Y., Fast, completely reversible Li insertion in vanadium pentoxide nanoribbons. *Nano Letters* **2007**, 7(2), 490-495.
- Yu, D., Chen, C., Xie, S., Liu, Y., Park, K., Zhou, X., Zhang, Q., Li, J., Cao, G., Mesoporous vanadium pentoxide nanofibers with significantly enhanced Li-ion storage properties by electrospinning. *Energy & Environmental Science* 2011, 4(3), 858-861.
- Ng, S. H., Chew, S. Y., Wang, J., Wexler, D., Tournayre, Y., Konstantinov, K., Liu, H. K., Synthesis and electrochemical properties of V<sub>2</sub>O<sub>5</sub> nanostructures prepared via a precipitation process for lithium-ion battery cathodes. *Journal of Power Sources* 2007, 174(2), 1032-1035.
- Koltypin, M., Pol, V., Gedanken, A., Aurbach, D., The study of carbon-coated V<sub>2</sub>O<sub>5</sub> nanoparticles as a potential cathodic material for Li rechargeable batteries. *Journal of the Electrochemical Society* 2007, 154(7), A605-A613.
- 19. Thackeray, M. M., Thomas, J. O., & Whittingham, M. S., Science and applications of mixed conductors for lithium batteries. *MRS bulletin* **2000**, 25(03), 39-46.
- 20. Yamada, H., Tagawa, K., Komatsu, M., Moriguchi, I., Kudo, T., High power battery electrodes using nanoporous V<sub>2</sub>O<sub>5</sub>/carbon composites. *The Journal of Physical Chemistry C* **2007**, 111(23), 8397-8402.
- 21. Jia, X., Yan, C., Chen, Z., Wang, R., Zhang, Q., Guo, L., Wei, F., Lu, Y.. Direct growth of flexible LiMn<sub>2</sub>O<sub>4</sub>/CNT lithium-ion cathodes. *Chemical Communications* **2011**, 47(34), 9669-9671.
- 22. Zhou, Y., Wang, J., Hu, Y., O'Hayre, R., Shao, Z., A porous LiFePO<sub>4</sub> and carbon nanotube composite. *Chemical Communications* **2010**, 46(38), 7151-7153.
- Ban, C., Wu, Z., Kirkham, M. J., Chen, L., Jung, Y. S., Payzant, E. A., Yan, Y., Whittingham, M. S., Dillon, A. C., Extremely durable high-rate capability of a LiNi<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode Enabled with single-walled carbon nanotubes. *Advanced Energy Materials* **2011**, 1(1), 58-62.
- DiLeo, R. A., Ganter, M. J., Thone, M. N., Forney, M. W., Staub, J. W., Rogers, R. E., Landi, B. J., Balanced approach to safety of high capacity silicon-germanium-carbon nanotube free-standing lithium ion battery anodes. *Nano Energy* 2013, 2(2), 268-275.
- 25. Mukherjee, R., Krishnan, R., Lu, T. M., Koratkar, N., Nanostructured electrodes for high-power lithium ion batteries. *Nano Energy* **2012**, 1(4), 518-533.
- 26. Li, X., & Wei, B., Supercapacitors based on nanostructured carbon. *Nano Energy* **2013**, 2(2), 159-173.
- 27. Wu, Z. S., Zhou, G., Yin, L. C., Ren, W., Li, F., Cheng, H. M., Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy* **2012**, 1(1), 107-131.
- 28. Rong, J., Masarapu, C., Ni, J., Zhang, Z., Wei, B., Tandem structure of porous silicon film on single-walled carbon nanotube macrofilms for lithium-ion battery applications. *ACS Nano* **2010**, 4(8), 4683-4690.
- 29. Zhu, H., Wei, B., Direct fabrication of single-walled carbon nanotube macrofilms on flexible substrates. *Chemical Communications* **2007**, (29), 3042-3044.
- 30. Li, X., Wei, B., Facile synthesis and super capacitive behavior of SWNT/MnO<sub>2</sub> hybrid films. *Nano Energy* **2012**, 1(3), 479-487.
- 31. Patrissi, C. J., Martin, C. R., Sol-Gel-based template synthesis and Li-insertion rate performance of nanostructured vanadium pentoxide. *Journal of the Electrochemical Society* **1999**, 146(9), 3176-3180.
- 32. Baddour-Hadjean, R., Pereira-Ramos, J. P., Navone, C., Smirnov, M., Raman microspectrometry study of electrochemical lithium intercalation into sputtered crystalline V<sub>2</sub>O<sub>5</sub> thin films. *Chemistry of Materials* **2008**, 20(5), 1916-1923.

- 33. Lee, S. H., Cheong, H. M., Seong, M. J., Liu, P., Tracy, C. E., Mascarenhas, A., Pitts, J. R., Deb, S. K., Raman spectroscopic studies of amorphous vanadium oxide thin films. *Solid State Ionics* **2003**, 165(1), 111-116.
- Ibris, N., Salvi, A. M., Liberatore, M., Decker, F., Surca, A., XPS study of the Li intercalation process in sol-gel-produced V<sub>2</sub>O<sub>5</sub> thin film: influence of substrate and film synthesis modification. *Surface and Interface Analysis* 2005, 37(12), 1092-1104.
- 35. Sathiya, M., Prakash, A. S., Ramesha, K., Tarascon, J. M., Shukla, A. K., V<sub>2</sub>O<sub>5</sub>anchored carbon nanotubes for enhanced electrochemical energy storage. *Journal of the American Chemical Society* **2011**, 133(40), 16291-16299.
- 36. Moulder, J. F., Stickle, W. F., Sobol, P. E., Bomben, K. D., Handbook of Xray Photoelectron Spectroscopy, *Perkin Elmer, MN, USA* **1992.**
- 37. McCafferty, E., & Wightman, J. P., Determination of the concentration of surface hydroxyl groups on metal oxide films by a quantitative XPS method. *Surface and Interface Analysis* **1998**, 26(8), 549-564.
- 38. Whittingham, M. S., The role of ternary phases in cathode reactions. *Journal of The Electrochemical Society* **1976**, 123(3), 315-320.
- 39. Delmas, C., Cognac-Auradou, H., Cocciantelli, J. M., Menetrier, M., & Doumerc, J. P., The Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> system: An overview of the structure modifications induced by the lithium intercalation. *Solid State Ionics* **1994**, 69(3), 257-264.
- 40. Broussely, M., Labat, J., Bodet, J. M., Cocciantelli, J. M., Recent developments in rechargeable lithium batteries. *Journal of Power Sources* **1991**, 13, 429-436.
- Delmas, C., Brethes, S., & Menetrier, M., ω-Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>-a new electrode material for rechargeable lithium batteries. *Journal of Power Sources* **1991**, 34(2), 113-118.
- 42. Leger, C., Bach, S., Soudan, P., & Pereira-Ramos, J. P., Structural and electrochemical properties of  $\omega$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>( $0.4 \leq x \leq 3$ ) as rechargeable cathodic material for lithium batteries. *Journal of The Electrochemical Society* **2005**, 152(1), A236-A241.
- 43. Retter, U., Lohse, H., Electroanalytical Methods, *Springer, Verlag Berlin Heidelberg, Germany*, **2010**.
- 44. Bard, A. J., Faulkner, L. R., Electrochemical Methods-Fundamentals and Applications, *Wiley, Hoboken, NJ, USA* **2001**.

#### Chapter 3

# CARBON NANOTUBE MACROFILM-LITHIUM MANGANESE OXIDE NANOCOMPOSITES AS STRETCHABLE CATHODES OF LITHIUM-ION BATTERIES

#### 3.1 Introduction

We have demonstrated a  $V_2O_5$ /SWNT nanocomposite cathode in Chapter 2 under the guidance of the "in-situ" processing concept, which means creating chemical bonding between the active cathode materials and SWNT macrofilms. However, the unlithiated  $V_2O_5$  can only be paired with lithium metals in half cells. Thus, it is necessary to extend the nanocomposite cathode work by *in-situ* combining SWNT macrofilms with lithiated cathode materials via chemical bonding to pair with a graphitic anode instead of metallic lithium for most commercial LIBs in the full-cell configuration. What's more, the recent emerging human-interactive or human-assistant technology such as wearable electronics, [1,2] soft surgical tools, [3] flexible display devices, [4] and etc. also requires not only the integrated circuit but also the power sources, e.g. LIBs to be flexible. To achieve the flexibility, one of the key steps is to rely on flexible nanocomposite cathode materials suitable to accommodate the strains caused by deformation within a certain range with elastomeric substrates such as polydimethylsiloxane (PDMS).[5] Three major composite systems based on CNTcoating fabrics, [6] graphene foams [7] and conductive polymer matrix are usually employed.[8,9] However, most of these prototypes are only capable of bending but not stretching. The limited bendability sustaining the induced strains  $\leq 1\%$  is far insufficient for practical cases where the devices would experience more complicated and challenging stretching, which must accommodate a large strain deformation >>1%.[10] Hence, as stressed in Chapter 1 that SWNT has a unique property with high flexibility, it becomes extremely desirable to develop SWNT macrofilm based nanocomposites with lithiated cathode materials for both bendable and stretchable electrodes.

Whereas, how to integrate the cathode materials with the macrofilms meanwhile maintaining the flexible film structure without any destruction is always the biggest obstacle for us to extend to stretchable electrodes. A "grafting" technique by hydrothermal reaction is preferred due to the relatively mild reacting environment compared to other methods with rigor conditions.[11] This potential reactant systems have two desirable characteristics, low temperature and annealing-free, to keep the original SWNT macrofilms unbroken. In this chapter, we reported such a suitable hydrothermal synthesis realizing the *in-situ* growth of LiMn<sub>2</sub>O<sub>4</sub> (LMO) nanocrystals in three-dimensional SWNT macrofilms as stretchable composite cathodes for lithium-ion batteries. The bendable/stretchable electrodes prepared by assembling the LMO-SWNT macrofilms with PDMS flexible substrates show the full-flexibility. The electrochemical properties of the freestanding cathodes is also examined preliminarily in a half cell with lithium metal. This work is a good touchstone to demonstrate the feasibility for fabricating a stretchable battery employing such LMO-SWNT cathode and also sheds a light on the optimization of the cathode performance for our future work, which will be discussed in Chapter 7.

## 3.2 Experimental

#### 3.2.1 In situ growth of LiMn<sub>2</sub>O<sub>4</sub>/SWNT by hydrothermal synthesis

Direct CVD growth and purification of SWNT macro-films were described in details in Section 1.2.1. The freestanding films floating in the water after purification

were held up on a 2"  $\times$  2" square frame made of stainless steel and dried at room temperature overnight.

Then a modified hydrothermal method was adopted referenced to this article [12] to *in-situ* grow LMO nanoparticles on SWNT macrofilms. All the chemicals in the following were purchased from Sigma Aldrich and used as received without any treatment. Solution A is prepared by dissolving 0.22 g lithium hydroxide into 6 ml deionized water followed by adding 0.24 ml hydrogen peroxide (30 wt%). Then the asprepared freestanding SWNT macrofilms were immersed in the solution A. 0.69 g manganese acetate dissolved in 6 ml deionized water forms solution B. Solution A and B were blended with 20 ml methanol and stirred for 20 min. Then the resulting black-brownish slurry was transferred into a 40 ml Teflon-lined autoclave and hydrothermally reacted at 115 °C for 12 h. After the reaction was complete, the macrofilms were collected and washed several times with deionized water and ethanol. Finally, the freestanding LMO-SWNT macrofilms were dried under vacuum at 80 °C for 12 hr.

## 3.2.2 Structural and electrochemical characterizations

The morphology and structure were characterized by means of focus ion beam microscopy (FIB, Zeiss Auriga 60 FIB/SEM) and transmission electron microscopy (TEM, JEOL JEM-2010F). X-ray diffraction (XRD) patterns were recorded by Philips X'Pert diffractometer with Cu K $\alpha$  radiation. X-ray photoelectron spectra were acquired using a VG ESCALAB 220I-XL spectrometer. The X-ray source was monochromatic Al K $\alpha$  (1486.7eV) with a power of 105W (15 kV, 7 mA). The operating pressure in the main chamber was less than 1 × 10<sup>-8</sup> Torr. Nitrogen isothermal physisorption measurements were carried out using a Micromeritics ASAP 2020 physisorption analyzer. Samples were degassed by heating to 573 K under vacuum for 6 h prior to

measurement. N<sub>2</sub> was adsorbed on samples at 77 K to determine support surface area after cooling. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area from N<sub>2</sub> adsorption data over the  $p/p_0$  range of 0.06 – 0.30. Thermogravimetric analysis (TGA) was carried out on a high resolution TGA instrument (Mettler-Toledo, SDA851e) from 0 to 1000 °C at a heating rate of 10 °C/min in flowing air.

The mass of freestanding electrode was weighted by using a micro/ultramicro balance (Mettler Toledo XP6) with 0.001 mg accuracy. CR2032 coin cells were assembled in an argon-filled glovebox (MBRAUN UNIlab). Half cells consist of the LMO-SWNT macrofilms as the working electrode, a Celgard 2500 as the separator, and a lithium ribbon (0.38 mm thick, 99.9%, Sigma Aldrich) as the counter electrode in the 1 M LiPF<sub>6</sub> dissolved in 1:1 v/v EC: DEC as electrolyte (Ferro Co.). Galvanostatic discharge-charge tests were carried out on BT-4 4-channel battery testing equipment (Arbin CV Instrument, ltd.). was performed by PARSTAT 2273 potentiostat/galvanostat (Princeton Applied Research) with the scan rate of 0.05 mV/sbetween 3.8 and 4.3 V.

# **3.2.3** Potentiostatic intermittent titration test

The potentiostatic intermittent titration technique (PITT) is, together with its galvanostatic counterpart (GITT, which will be introduced in next chapter), one of the most used techniques to retrieve insights on the diffusion coefficient of the active electrode materials [1-3]. In a typical PITT measurement towards a half cell, for example, the experiment starts by recording the OCV of the battery ( $V_{ocv}$ ). Then, the cell was kept at  $V_{ocv}$  for 24 h. Afterwards, a positive potential increment of 20 mV is applied on  $V_{ocv}$  for at least 15 minutes, followed by a relaxation process for the cell at

switch-off state until the recorded signal of current density declines below C/50. The increment and relaxation processes constitute a step called intermittent titration. Then the same potential increment is consecutively applied to the previous step and the signal is recorded until the end of relaxation in current step. The potential pulses are applied until the upper limit of 4.5 V is reached. Each potential pulse is followed by relaxation time. Afterwards, a reverse intermittent titration process was driven by negative potential increments of -20 mV, which are consecutively applied starting from 4.5 V and followed by a relaxation process for the cell at switch-off state until the lower limit of 3.5 V is reached. During the 20 mV potential pulses, Li-ions are de-intercalated from the positive electrode and intercalated to the negative one. The reverse occurs during the negative discharging potential pulses, where the Li-ions are de-intercalated from the negative electrode and intercalated to the positive electrode. The PITT were carried out on a BT-4 4-channel battery testing equipment (Arbin Instrument, Itd.).

#### 3.3 **Results and Discussion**

# **3.3.1** Demonstration of bendable/stretchable electrodes and three-dimensional nanocomposite structure

The *in-situ* hydrothermal growth of LMO in SWNT macrofilms as the stretchable scaffolds without any post-processing is described in details in the above Experimental Sections. The as-prepared LMO-SWNT macrofilm was laminated tightly with a UV- or  $O_2$ -plasma-treated PDMS substrate and exhibits a stationary state, bending state, before and after stretching state from left to right in sequence in the pictures of Figure 3.1.



Figure 3.1 From left to right: (1) picture of fully-flexible electrode fabricated by LMO-SWNT macrofilm coupled with PDMS; and their various flexible states of: (2) bending state; (3) stationary state without strain applied; and (4) stretching state.

From the SEM images (Figure 3.2), we can observe the well-defined 3D structure of the LMO-SWNT macrofilms. The cross section was exposed in the trapezoid trench milled by a focused Ga<sup>+</sup> ion beam (Figure 3.2a).



Figure 3.2 (a) SEM image of LMO-SWNT macrofilm composite with a milled trapezoid trench showing the cross section (b) magnified SEM image of the marked top-view area in (a); (c) Cross-sectional view of LMO-SWNT macrofilm composite and (d) magnified image of the rectangular area in (c).

The magnified SEM image (Figure 3.2b) of labeled area in Figure 3.2a on the top view shows the LMO nanoparticles are homogeneously distributed in the entangled SWNT integrity. The high contrast cross section image in Figure 3.2c and the rectangular area with a higher magnification in Figure 3.3d indicate bright LMO nanoparticles are impregnated along the thickness of the macrofilms to construct the 3D composite structure. Figure 3.3a displays the XRD patterns of the LMO-SWNT macrofilm nanocomposite and the pure LMO nanoparticles prepared in the same way except

applying the SWNT macrofilm. The characteristic peaks which are identical in position to each other in both patterns are assigned to LMO nanoparticle with the Fd3m spinel structure.



Figure 3.3 (a) XRD pattern of pristine LMO and freestanding LMO-SWNT macrofilm composite. (b) EDX spectrum and quantitative table of elements. (c) TGA curve of LMO-SWNT composite. (d) N2 isothermal

The intensity of these peaks after LMO deposition is not distinctly attenuated, which implies a considerable LMO content in the composite. Energy-dispersive X-ray spectroscopy (EDX) in Figure 3.3b confirms the existence of three major elements C, O and Mn. SWNT is the carbon source and Mn entirely comes from LMO while the source of O is the most complicated including LMO and O-containing functional groups on SWNT. According to the quantitative report (table inset in Figure 3.3b) and considering the accuracy of EDX results, the weight percentage of SWNT macrofilms is approximately 44%. The mass loading of LMO is then 56% assuming the rest part of the composite are all LMO nanoparticles. Figure 3.3c presents the thermogravimetric analysis (TGA) curve for the LMO-SWNT composite. Typically, SWNTs are completely burnt out until 800 °C where the curve arrives at a stable phase. The weight percentage of remaining LMO nanoparticles is determined to be ~55% in a good agreement with the EDX results. The nanocomposite has a very high surface area of 160 m<sup>2</sup> g<sup>-1</sup> calculated by BET method (Figure 3.3d). Obviously, the high surface area and 3D structure are favorable for efficient electrolyte infiltration and confinement of Mn<sup>3+/4+</sup> ions from dissolving into electrolyte during the Li<sup>+</sup> intercalation/deintercalation processes.

## 3.3.2 Interaction between LiMn<sub>2</sub>O<sub>4</sub> and SWNT

In order to probe into the interaction between LMO nanoparticles and SWNTs in the 3D structure, we carried out TEM characterization for LMO-SWNT. The TEM sample was prepared by ultrasound processing towards the composite immersing in ethanol under a high frequency of 24 kHz and power of 200 W with continuous output amplitude for 2 hours. After intense ultrasonication, both individual SWNTs and LMO nanoparticles could be achieved in the dilute TEM sample and are clearly shown in the SEM images with normal and inverse contrast (Figure 3.4a and 3.4b). It is obviously seen that LMO was still firmly anchored on the surface of SWNTs and agglomerated at the crossing of nanotubes, although experiencing the strong forces generated by ultrasound.



Figure 3.4 (a) SEM image of individual SWNTs with LMO nanoparticles for the LMO-SWNT macrofilm composite after intense ultrasonication; (b) contrast inversion of the identical image of (a). (c) TEM image of individual SWNTs with LMO nanoparticles for the LMO-SWNT macrofilm composite after intense ultrasonication; (d) HRTEM images showing the interaction area between SWNTs and LMO and (e) individual LMO nanoparticle with well-resolved lattice fringe.

The corresponding TEM image (Figure 3.4c) also shows LMO nanoparticles are substantially connected by SWNTs. HRTEM in Figure 3.4d reveals the amorphous interaction area between each other in details. As denoted in the HRTEM of a single nanocrystal in Figure 3.4e, interplanar spacing of 4.86 Å could be assigned to the (111) planes of LMO, which is consistent with the XRD analysis. All these clues suggest the growth of LMO nanoparticles interact with SWNT macrofilms *via* chemical bonding, which means the *in-situ* growth of LMO. Then we rely on XPS to further confirm the

chemical bonding existence within the interaction between the LMO and SWNT. As shown in Figure 3.5a, C 1s peak could be deconvoluted to three independent peaks including the main peak with binding energy at 287.2 eV attributed to -C=C- sp<sup>2</sup> bonds of the SWNTs, -C-O- and -C=O peaks respectively shifting towards high-energy side by 0.8 eV and 2.8 eV, which are attributed to carboxyl and carbonyl groups on SWNTs. These functional groups come from the slight functionalization during acid purification. Similarly, the O 1s core-level peak (Figure 3.5b) is also a convolution of three subpeaks: the main peak at 532.5 eV assigned to Mn-O bonds constituting the framework of LMO, the peak at 533.6 eV attributed to -C-O-Mn bonds bridging the SWNT and LMO as well as the carbonyl groups of -C=O on SWNT surface at the 535.5 eV peak. However, it is worth noting that different from -C-O- part in C 1s peak with a lower relative area ratio (by integrating intensities) to the main peak *i.e.* C=C sp<sup>2</sup> of C 1s, the -C-O-Mn part in O 1s peak is more pronounced and its relative area ratio to the main peak of O 1s is obviously higher. This evidence implies the *in-situ* growth of LMO transits from an intermediate state of -C-O-Mn bonds to form the metal-oxide base, corresponding to the amorphous interaction area between LMO and SWNT and then LMO nanoparticles are growing *via* lithiation. In the Mn 2p core level spectrum (Figure 3.5c), Mn  $2p_{3/2}$  peak is located at 644.4 eV between two oxidation states Mn<sup>3+</sup>(644.3 eV) and Mn<sup>4+</sup>(646.3 eV). The energy separation between the Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$ peaks is 11.6 eV typically indicating the stoichiometric LMO has been synthesized as identified by C. V. Ramana et al. [13] Note that the peak position of both O 1s and Mn 2p shifts ~2.4 eV to a higher binding energy than pristine LMO with 530.1 eV and 641.9 eV for these two core levels. This coincidence strengthens the existence of chemical bonding between LMO and SWNT. Figure 3.5d shows the Mn 3p peak consisting of

 $Mn^{3+}/Mn^{4+}$  states and Li 1s peak with low intensity at 55 eV. It confirms the lithiation forming LMO as the previous implication reveals.



Figure 3.5 XPS spectra of (a) C 1s; (b) O 1s; (c) Mn 2p; and (d) Mn 3p with Li 1s peaks for the LMO-SWNT macrofilm composite.

# **3.3.3** Electrochemical behavior and performance

Electrochemical behavior of the freestanding LMO-SWNT macrofilm composite was investigated using lithium half-cells as demonstrated in the bottom picture of Figure 3.6a. The voltage profile versus the delithiated Li<sup>+</sup> composition as horizontal axis was plotted on the top of Figure 3.6a by PITT. As described in Section

3.2.3, the PITT was performed to measure the capacity storage or release at every single small voltage increment or decrement of 20 mV between the cutoff voltages of 3.5 V - 4.5 V as. When each voltage step ends, the current relaxation progresses until decay below the rate of C/50 meanwhile it provides the charge or discharge capacity available at that voltage.



Figure 3.6 (a) Voltage profile between 3.5 and 4.5 V, inset: CR2032 half cell illustration; (b) PITT results; and (c) CV curve of LMO-SWNT macrofilm composite.

The voltage profile exhibits a typical Li<sup>+</sup> insertion/extraction behavior of LMO with the corresponding potential plateaus between 3.9 and 4.2 V upon discharging and charging.

During these processes, no thermodynamic driving force is established for the phase transformation between LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>1-x</sub>Mn<sub>2</sub>O<sub>4</sub> until the potential for the two-phase coexistence of LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>0.2</sub>Mn<sub>2</sub>O<sub>4</sub> (denoted as "critical potential") is reached. [14, 15] For this reason, it is believed that the Li<sup>+</sup> diffusion instead plays a vital role in the lithiation and delithiation. Thus, PITT is a very useful tool for diffusivity analysis, which will be discussed in details in the next section. The PITT result in Figure 3.6b shows a continuous capacity accumulation below and above "critical potential" while two maximum specific capacities are located at around 4 V and 4.2 V. This is well consistent with the potential plateaus in Figure 3.6a. Combining the two plots together, the delithiation composition corresponding to two discharge capacity peaks is 26% and 51%. The shape of the curve linking the mean capacity at each voltage step shows a resemblance to the CV curve in Figure 3.6c. In the CV curve, the redox couple at 4.1 V/4.2 V is assigned to two-phase coexistence LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>0.2</sub>Mn<sub>2</sub>O<sub>4</sub>.

To evaluate the practical performance of such cathode in terms of cyclic stability and rate capability, long-term cycling and rate performance were examined by carrying out GCD measurement. Despite the poor electrical conductivity of LMO, because of the high conducting nature of SWNT macrofilm framework in the composite and *in-situ* chemical bonding between them for facilitated charge transfer, the charge capacity at the first cycle is 190 mAh g<sup>-1</sup> at the current density of 0.1 C (~ 15 mA g<sup>-1</sup>) as shown in Figure 3.7a, which is higher than those delivered by LMO/carbon black hybrid. The discharge capacity decays from initial 120 mAhg<sup>-1</sup> and stabilizes at 100 mAh g<sup>-1</sup> after over 250 cycles. The capacity retention maintains at 83% for such a long-term cycling with an average discharge capacity of 103 mAh g<sup>-1</sup>.



Figure 3.7 (a) Capacity retention; and (b) Rate performance of LMO-SWNT macrofilm nanocomposite.

The CE is increasing from the early-stage value as low as 70% to over 95% at the end of cycling. So it is obvious to observe that the gap between the charge and discharge curves is reduced gradually as the cycling progresses. The rate capabilities of the LMO-SWNT composite at high current densities of 1 C, 2 C and 4 C are shown in Figure 7b. At 4 C rate, LMO-SWNT composite is still able to deliver a discharge capacity of 70 mAh  $g^{-1}$ . A reversible capacity of 80 mAh  $g^{-1}$  could be rejuvenated at 2 C in the last 10 cycles after a continuous series of discharging, also demonstrating an excellent cyclic stability. The corresponding CE for 1 C, 2 C and 4 C is improved to 78%, 81% and 92% within less than 20 cycles at the early stage compared with the 70% for 0.1 C. This is not a unique but common phenomenon similar to the results in Chapter 2 and other reports and is attributed to parasitic reactions consuming charges such as the loss of Li ions for SEI growth during cycling. [16, 17] When the cells are cycled at lower rates, they need more time to complete such reactions and result in a lower CE.

#### **3.3.4** Diffusivity analysis by PITT

Since Li<sup>+</sup> diffusivity is a key factor determining the electrochemical performance of the composite, it is also definitely a significant factor related to SEI growth. As we mentioned previously that PITT is a useful method for diffusivity analysis, we can depend on its results to calculate Li<sup>+</sup> diffusion coefficient by Equation 3.1 and 3.2 as follows: [18]

$$Q = \frac{2FA\sqrt{D}}{\sqrt{\pi}} (C_0 - C_x)\sqrt{t}$$
3.1

$$C_x = \frac{1-x}{180g/mol} \times 4 \ g/cm^3 \ (C_0: x = 0)$$
3.2

In Equation 3.1, D is the diffusion coefficient, Q is the discharging coulombs per unit mass of active material due to potentiostatic charging or discharging, F is the Faraday constant, A is the specific surface area which has been determined by BET method,  $C_0$  and  $C_x$  are the concentrations of Li<sup>+</sup> at initial state and the real-time state after the voltage step, respectively, t is the elapsed time of relaxation for each voltage step. In Equation 3.2,  $C_x$  is a function of x which is the delithiation composition; 180 g  $mol^{-1}$  is the molecular weight of LMO; and 4 g cm<sup>-3</sup> is its density. The integration of current versus time in Figure 3.8a gives the values of Q. A series of specific values for x is selected at 13%, 26%, 51% and 76% where 26% and 51% corresponds to the potential plateaus, *i.e.* the two maximum peaks in the PITT plot (Figure 3.6b) upon discharging. Then D is determined from the slope of a linear plot with Q vs.  $\sqrt{t}$  at these x values (Figure 3.8b). It ranges from  $3.31 \times 10^{-17}$  cm<sup>2</sup>/s to  $0.216 \times 10^{-17}$  in a decreasing gradient with an increase from 13% to 76% as shown inset in Figure 3.8a. This decreasing tendency with the minimum diffusion coefficient at 76% of delithiation composition could be explained in that above the "critical potential" with the corresponding x over 51%, the thermodynamic driving force is applied and less

diffusivity is needed to drive the delithiation. However, the low order of magnitude of D significantly restricts the low CE and consequently the electrochemical performance. Therefore, we have to take our efforts to improve Li<sup>+</sup> diffusion coefficient for the future optimization work.



Figure 3.8 (a) Potentiostatic intermittent titration curves for LMO-SWNT macrofilm composite at various delithiation composition, inset: the Li<sup>+</sup> diffusion coefficient with delithiation composition. (b) Q as a function of  $t^{1/2}$  extracted from (a).

## 3.4 Conclusions

In conclusion, we fabricated a fully-flexible cathode material for lithium-ion batteries by *in-situ* growth of LiMn<sub>2</sub>O<sub>4</sub> nanocrystals in three-dimensional single-walled carbon nanotube mcacrofilms. We demonstrated both excellent bendability and stretchability of this composite material coupled with flexible substrates, *e.g.* PDMS in our case. Depending on various characterization including SEM, HRTEM and XPS, we have confirmed that the *in-situ* growth of the active materials was rendered by chemical

bonding between them and the carbon nanotube macrofilm scaffolds. The freestanding composite as cathode in half cells with lithium metal exhibits a satisfied average capacity of 103 mAh g<sup>-1</sup> and a satisfied cyclic stability with a high capacity retention of 83% over 250 cycles at the slow rate of 0.1 C. This electrochemical performance confirms that such composite cathode is a promising candidate for the stretchable lithium-ion batteries. The PITT results reveal that the Li<sup>+</sup> diffusion coefficient is a dominant factor limiting CE and sheds light on the optimization for future work to further improve such cathode performance. Overall, this preliminary work demonstrates the feasibility of the LMO-SWNT macrofilm nanocomposite before developing the fully-flexible lithium-ion battery based on such cathode materials in a full cell, e.g. with the pristine SWNT macrofilms as anode in the future.

## REFERENCES

- 1. Kim, D.-H.; Lu, N.; Ma, R.; Kim, Y.-S.; Kim, R.-H.; Wang, S.; Wu, J.; Won, S. M.; Tao, H.; Islam, A. Epidermal electronics. *Science* **2011**, *333*, 838.
- Xu, S.; Zhang, Y.; Jia, L.; Mathewson, K. E.; Jang, K.-I.; Kim, J.; Fu, H.; Huang, X.; Chava, P.; Wang, R., Bhole, S., Wang, L., Na, Y. J., Guan, Y., Flavin, M., Han, Z., Huang, Y., Rogers, J. A., Soft microfluidic assemblies of sensors, circuits, and radios for the skin. *Science* 2014, *344*, 70.
- 3. Kim, D.-H.; Lu, N.; Ghaffari, R.; Kim, Y.-S.; Lee, S. P.; Xu, L.; Wu, J.; Kim, R.-H.; Song, J.; Liu, Z., and et. al., Materials for multifunctional balloon catheters with capabilities in cardiac electrophysiological mapping and ablation therapy. *Natura Materials* **2011**, *10*, 316.
- Kim, S.; Kwon, H. J.; Lee, S.; Shim, H.; Chun, Y.; Choi, W.; Kwack, J.; Han, D.; Song, M.; Kim, S., Low - Power Flexible Organic Light - Emitting Diode Display Device. *Advanced Materials* 2011, *23*, 3511.
- 5. Khang, D. Y., Jiang, H., Huang, Y., Rogers, J. A., A stretchable form of single-crystal silicon for high-performance electronics on rubber substrates. *Science* **2006**, 311(5758), 208-212.
- Hu, L.; Pasta, M.; Mantia, F. L.; Cui, L.; Jeong, S.; Deshazer, H. D.; Choi, J. W.; Han, S. M.; Cui, Y., Stretchable, porous, and conductive energy textiles. *Nano Lett.* 2010, 10, 708.
- 7. Chen, Z.; Ren, W.; Gao, L.; Liu, B.; Pei, S.; Cheng, H.-M. Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nature Materials* **2011**, *10*, 424.
- 8. Hansen, T. S.; West, K.; Hassager, O.; Larsen, N. B., Highly stretchable and conductive polymer material made from poly (3, 4-ethylenedioxythiophene) and polyurethane elastomers. *Advanced Functional Materials* **2007**, *17*, 3069.
- 9. Sekitani, T.; Nakajima, H.; Maeda, H.; Fukushima, T.; Aida, T.; Hata, K.; Someya, T., Stretchable active-matrix organic light-emitting diode display using printable elastic conductors. *Nature Materials* **2009**, *8*, 494.
- Xu, S.; Zhang, Y.; Cho, J.; Lee, J.; Huang, X.; Jia, L.; Fan, J. A.; Su, Y.; Su, J.; Zhang, H., Rogers, J. A., Stretchable batteries with self-similar serpentine interconnects and integrated wireless recharging systems. *Nature Communications* 2013, *4*, 1543.

- 11. Yoshimura, M.; Byrappa, K., Hydrothermal processing of materials: past, present and future. *Journal of Materials Science* **2008**, *43*, 2085.
- 12. Lee, S.; Cho, Y.; Song, H. K.; Lee, K. T.; Cho, J., Carbon-coated single-crystal LiMn<sub>2</sub>O<sub>4</sub> nanoparticle clusters as cathode material for high-energy and high-power lithium-ion batteries. *Angewandte Chemie International Edition* **2012**, *51*, 8748.
- Ramana, C.; Massot, M.; Julien, C., XPS and Raman spectroscopic characterization of LiMn<sub>2</sub>O<sub>4</sub> spinels. *Surface and Interface Analysis* 2005, *37*, 412.
- Kim, D. K.; Muralidharan, P.; Lee, H.-W.; Ruffo, R.; Yang, Y.; Chan, C. K.; Peng, H.; Huggins, R. A.; Cui, Y., Spinel LiMn<sub>2</sub>O<sub>4</sub> nanorods as lithium ion battery cathodes. *Nano Letters* 2008, *8*, 3948.
- 15. Meethong, N.; Huang, H.; Speakman, S. A.; Carter, W. C.; Chiang, Y. M., Strain accommodation during phase transformations in olivine-based cathodes as a materials selection criterion for high-power rechargeable batteries. *Advanced Functional Materials* **2007**, *17*, 1115.
- 16. Smith, A.; Burns, J.; Dahn, J., A high precision study of the Coulombic efficiency of Li-ion batteries. *Electrochemical and Solid-State Letters* **2010**, *13*, A177.
- 17. Cao, Z., Wei, B., fragmented carbon nanotube macrofilms as adhesive conductors for lithium-ion batteries. *ACS Nano* **2014**, 8(3), 3049-3059.
- 18. Yu, P., Popov, B. N., Ritter, J. A., White, R. E., Determination of the lithium ion diffusion coefficient in graphite. *Journal of The Electrochemical Society* **1999**, 146(1), 8-14.

#### Chapter 4

# CARBON NANOTUBE MACROFILM-IRON OXIDE NANOCOMPOSITES AS ANODES OF LITHIUM-ION BATTERIES

## 4.1 Introduction

The development of rechargeable LIBs with a higher energy density and a longer lifetime doesn't only require high-performance cathode materials but also the anode materials with high performance. [1, 2] Nanostructured transition metal oxides  $(M_xO_y)$ have been extensively studied as the candidates for LIB anodes because of their shortening diffusion paths for lithium ions and high theoretical specific capacities. The extremely high capacity results from the reversible conversion reactions to accommodate over 6 moles of Li<sup>+</sup> insertion/extraction per mole of the oxides with the products of metal nanoparticles M<sup>0</sup> and Li<sub>2</sub>O. [3] Compared with common oxides such as SnO<sub>2</sub> [4], Co<sub>3</sub>O<sub>4</sub> [5] and TiO<sub>2</sub> [6],  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is a more promising anode material with a higher specific capacity over 1000 mAhg<sup>-1</sup>, three times that of commercial graphite (372 mAhg<sup>-1</sup>) anodes, as well as a lower cost, higher abundance and more friendliness to environment. [7] In spite of these evident advantages, drawbacks of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as anodes are also serious: they would experience structural collapses due to the large volumetric changes during lithiation/delithiation, causing severe capacity degradation and cyclic instability; their inherent low electronic conductivity and poor ionic conductivity owing to  $M_x O_v / M^0 / Li_2 O$  matrix deriving from the conversion reactions restrict their rate capability; a-Fe<sub>2</sub>O<sub>3</sub> also suffers from the limited electrochemical kinetics related to the solid-state diffusion of Li ions between electrolyte and electrodes, reflected by the voltage and capacity hysteresis between charge and discharge. [7-9] In order to circumvent these problems, many  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite with carbon nanomaterials to improve their performance have been developed using different synthetic methods. However, most of the methods have considerable manufacture cost and complicated processing involving several elaborate steps, such as hydrothermal syntheses and post-treatment processes including centrifuging, rinsing and vacuum infiltration, although the resulting excellent electrochemical performance of these nanocomposites are attractive. Hence, a more direct method to fabricate the nanocomposite integrating  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the carbon matrix is desired.

Based on the strategy in direct growth of SWNT macrofilms as described in Chapter 1, in this chapter we present a uniformly-dispersed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (<20 nm) /SWNT macrofilm nanocomposite by a simple heat treatment. The SWNT macro-films proves success in enabling fast charge transfer and serving excellent deformable and stretchable buffer layers with strong adhesion to current collectors to inhibit destruction of crystal structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by accommodating the large volumetric changes during the Li<sup>+</sup> intercalation and deintercalation. The nanocomposites as LIB anodes have shown increasingly high specific capacities over 1000 mAhg<sup>-1</sup> and remarkable cycling stability up to 100 cycles at different C-rates. We have further investigated the dependence of the Li<sup>+</sup> diffusivity on the film thickness by detailed calculations and analysis of the compatible results from GITT and EIS, and found that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films with a comparable thickness to the characteristic diffusion length of Li<sup>+</sup> ions shows the optimum electrochemical properties as a promising anode for LIBs.

However, the rate capability of such as-prepared  $Fe_2O_3/SWNT$  anodes at a high current density over 1 Ag<sup>-1</sup> is unsatisfactory. To further improve their electrochemical performance, we adopted a strategy of annealing in a reductive or inert atmosphere for two major reasons:

1. Annealing in an inert gas could induce surface defects of lower-state metallic ions and oxygen vacancies of the oxides. [10] The Li-ion insertion/extraction process could be facilitated due to the improved charge-transfer conductivity and modified surface thermodynamics with the presence of defects<sup>10</sup>. Meanwhile, the preservation of the integrity in the morphology of electrodes enables sustained recharge ability. [10]

2. The thermal treatment in a reductive gas, e.g.  $H_2$ , has been demonstrated to partially reduce the Fe<sup>3+</sup> in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to Fe<sup>2+</sup> in Fe<sub>3</sub>O<sub>4</sub>. [11] The hopping between Fe<sup>3+</sup> and Fe<sup>2+</sup> at the octahedral sites in the cubic inverse spinel structure of Fe<sub>3</sub>O<sub>4</sub> at room temperature renders it a half-metallic class with a high electronic conductivity (200 S/cm), which is only one order of magnitude lower than the minimum conductivity of a metal. [12]

Following this strategy, in the second part of this chapter we mainly discussed the conversion of  $Fe_2O_3/SWNT$  to  $Fe_3O_4/SWNT$  by  $H_2$  annealing. As expected, the iron oxide/SWNT after  $H_2$  annealing significantly enhance the rate capability and the cyclic stability at high rates. The reduced internal resistance and increased diffusivity of Li ions contribute to the improvement of their electrochemical performance.

#### 4.2 Experimental

#### 4.2.1 α-Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms preparation and hydrogen annealing

SWNT macro-films were synthesized by the modified floating CVD method described in the previous chapters. [13] Three samples with different thickness were prepared using 300 mg, 140 mg and 50 mg of the precursors, respectively. Here we name the thickest  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms as Sample FC\_T, the sample with

moderate thickness as FC\_N and the thinnest one as FC\_t. After 10-30 min CVD reaction, when the furnace were cooled down, all SWNT macrofilms containing Fe catalyst without purification were transferred to an annealing furnace for a simple heat treatment at 450 °C in air for 30 min to obtain the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilm nanocomposite. The H<sub>2</sub> annealing for the obtained  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films were carried out at 360 °C for 2 h in H<sub>2</sub> atmosphere to realize the thermal reduction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>.

# 4.2.2 Characterization and electrochemical measurements

The morphology and structure of the iron oxide/SWNT hybrid films were characterized by means of scanning electron microscopy (SEM mode, 3kV, Zeiss Auriga 60 FIB/SEM) and TEM (JEOL JEM-2010F). XRD patterns were recorded within a 2 $\theta$  range of 10 to 80° at 0.08°/step and 20s/step by Philips X'Pert diffractometer with Cu K $\alpha$  radiation. Rietveld fitting was performed using the GSAS and EXPGUI package to identify the crystalline lattice parameters of iron oxides and quantitatively calculate the mass ratio of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. [14] Raman spectroscopy (Bruker SENTERRA with 785 nm laser excitation) was employed to verify the crystalline structure of the iron oxides. XPS was conducted on the EA 125 spectrometer with a non-chromatic Al K $\alpha$  source (1486.5 eV). TGA was carried out on a high resolution TGA instrument (Mettler-Toledo, SDA851e) from 0 to 1000 °C at a heating rate of 10 °C/min in flowing air. The thickness of iron oxides/SWNT macrofilms was measured by optical interferometer (WYKO NT9100, Veeco instrument Inc.) and atomic force microscopy (AFM, Dimension 3100 Veeco instrument Inc.).

The electrodes were prepared by transferring the hybrid films onto the copper foil (9  $\mu$ m thick) current collectors with the aid of several drops of ethanol to enable a

solid adhesion, and then punching the Cu-supported films to discs with the diameter of 1/2" after they were dried in air. The mass of the hybrid films covering the disc-shaped electrodes was acquired from deducting the weight of bare Cu substrates using a micro/ultramicro balance (Mettler Toledo XP6) with 0.001 mg accuracy. The whole mass of the films are 0.25 mg by weighing. CR2032 coin cells were assembled in an argon-filled glovebox (MBRAUN UNIIab). A coin cell consists of the hybrid film as the working electrode, a Celgard 2500 as the separator, and a lithium ribbon (0.38 mm thick, 99.9%, Sigma Aldrich) as the counter electrode in the 1 M LiPF<sub>6</sub> dissolved in 1:1 v/v EC: DEC as electrolyte (Ferro Co.). The cyclic voltammetry curves and electrochemical impedance spectra with a 10 mV AC signal employed from 100 kHz to 10 mHz were all collected by PARSTAT 2273 (Princeton Applied Research) potentiostat/galvanostat. The galvanostatic discharge-charge tests were carried out on BT-4 4-channel battery testing equipment (Arbin Instrument, ltd.).

# 4.2.3 Galvanostatic intermittent titration test

As mentioned in Chapter 3, GITT is the counterpart of PITT as another most used technique to retrieve insights on the diffusion coefficient of the active electrode materials. In a typical GITT measurement, the procedure consists of a series of current steps. Each of steps is composed of a current pulse, followed by a relaxation time, in which no current passes through the cell. The current pulse is positive during charge and negative during discharge. Within a positive current pulse, the cell potential quickly increases from a lower limit of potential to reach a value proportional to the *iR* drop, where *R* is the sum of the uncompensated resistance  $R_{un}$  and the charge transfer resistance  $R_{ct}$ . Then, the potential increases slowly to maintain a steady concentration gradient under the constant charge pulse (galvanostatic). When the relaxation starts after current pulse ends, the composition of the electrode materials tend to become homogeneous driven by the Li-ions diffusion. Consequently, the potential first suddenly decreases to an *iR*-proportional value, and afterwards it slowly decreases until the electrode materials arrive at equilibrium again (*i.e.*, when  $dE/dt \sim 0$ ) meanwhile the OCV ( $V_{ocv}$ ) of the cell is reached. Then, a sequence of current steps applied to the previous step is repeated until the battery is fully charged to the higher potential limit. GITT were also carried out on BT-4 4-channel battery testing equipment (Arbin Instrument, ltd.). A series of current steps at 50 mAg<sup>-1</sup> (~0.05C) for 1 h, each followed by a 12 h relaxtion process between 0 and 3 V. The relaxation time of 12 h was to allow a full relaxation of lithium diffusion to reach equilibrium potential and to minimize selfdischarge during the test.

# 4.3 **Results and Discussion**

# 4.3.1 Sample preparation, morphological and structural characteristics of α-Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms

TEM demonstrates that the diameter of Fe<sub>2</sub>O<sub>3</sub> nanoparticles ranging from 6 to 20 nm (Figure 4.1b and right inset) are densely distributed into the SWNT-interwoven matrix of the Fe-containing SWNT macro-films after CVD growth (Figure 4.1a).



Figure 4.1 Microscopy images of SWNT macro-films before and after heat treatment at 450 °C in air for 30 min. (a) TEM image of Fe/SWNT macro-film before the heat treatment. (b) TEM image of α-Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid film and inset: diameter distribution for α-Fe<sub>2</sub>O<sub>3</sub> nanoparticles. (c) SEM image of α-Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid film. (d) Magnified SEM image of the dashed rectangular area in (c) with an inset: photograph of a brownish semitransparent α-Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid film.

Mean size and size distribution of the Fe<sub>2</sub>O<sub>3</sub> nanoparticles was determined by PEBBLES free software (http://pebbles.istm.cnr.it/) in automatic mode. The selected-area electron diffraction (SAED) patterns convince that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with hermatite structure are formed after oxidization of Fe catalysts that came from pyrolysis of

ferrocene during CVD reaction in the Fe-containing SWNT macrofilms. The size of nanoparticles becomes larger due to the crystal growth during the heat treatment process. SEM images in Figure 4.1c and Figure 4.1d in a higher magnification show the nanocomposites have a uniform morphology and distribution of nanosized Fe<sub>2</sub>O<sub>3</sub> particles with the entangled SWNTs. The inset photograph in Figure 4.1d presents the red/brown semi-transparent thin  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms.

Powder XRD pattern (Figure 4.2a) indicates that Fe catalysts are transformed to rhombohedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase in *R*-3*c* space group, with lattice parameters *a* =5.0347 Å, *b* =5.0347 Å, *c* =13.7473 Å and  $\alpha = \beta = 90$ °,  $\gamma = 120$ ° (JCPDS card No. 01-087-1164). The broad peaks are indicative of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles in delicacy crystalline sizes (10 nm on average) as fine as that observed in the TEM images. Raman spectra of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT (black curve) and the pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> after burning out SWNTs at above 700 °C (red curve) both show the featured peaks at 225, 248, 290, 400, 490, 600, and 1329 cm<sup>-1</sup> corresponding to Raman modes of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. [15] The similar peak positions of the two spectra further confirm the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The peak at 1589 cm<sup>-1</sup> in the black curve is attributed to G bands of SWNTs [13]. HRTEM (Figure 4.3) reveals the crystal lattice fringes of Fe<sub>2</sub>O<sub>3</sub> nanoparticles with interplanar distance of 2.69 Å and 3.62 Å, which are assigned to d-spacing of planes (104) and (012), respectively. They are also corresponding to the most intensive two peaks in the XRD pattern.



Figure 4.2 (a) XRD pattern of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films (black) and the pure Fe<sub>2</sub>O<sub>3</sub> after removing SWNTs (red). (b) Raman spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> free of SWNT (red) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid film (black).



Figure 4.3 (a) High-resolution TEM image of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films. (b) High-resolution TEM image of dashed rectangular area in (a) with a higher magnification.

Figure 4.4 (a)-(c) show SEM images with inset photographs of three samples, Cu-supported Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms with different thicknesses, prepared by controlling the precursors' amount and CVD deposition time (see details in Section 4.2.1). It is obvious to see that the thinnest film (Figure 4.4c) is almost transparent to expose the metal luster of the copper foil at the bottom. In contrast, the color of the thicker films becomes darker. From Figure 4.4a, the thickest FC\_T has the densest structure where it is scarcely to distinguish individual SWNTs or SWNT bundles. On the contrary, SWNTs cannot be recognized until the thickness of films is reduced to moderate thickness (FC\_N) shown in Figure 4.4b and it is easy to identify the long SWNTs entirely wrapped by Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the SEM image of the thinnest FC\_t (Figure 4c). The thinner films become sparser in particular for FC\_t. Therefore, the copper substrate underneath is visible. It implies that the concentration of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> it contains may increase as the hybrid films become thicker. This has been confirmed by the EDX mapping results within an equally-sized area of 5-µm scale for the three samples. Table 4.1 shows that FC\_T has the highest Fe/C mass ratio of 10.43:1 compared to 5.38:1 for FC\_t and 3.01:1 for FC\_N.

Table 4.1Quantitative results of EDX spectra: weight percentage of Fe and C in<br/>FC\_T, FC\_N and FC\_t.

Wt%	FC_T	FC_t	FC_N
С	6.47	6.02	6.26
Fe	67.53	32.42	18.84
Fe/C	10.43:1	5.38:1	3.01:1

Afterwards, we hypothesized that an optimal Fe/C weight ratio dependent on the film thickness, may have a significant impact on the electrochemical performance of  $Fe_2O_3$  nanocomposites as anodes. This hypothesis will be discussed and confirmed eventually in Section 4.3.3 focusing on the electrochemical analysis.



Figure 4.4 (a, b, c) SEM images with insets: photographs of FC\_T, FC\_N and FC\_t, α-Fe<sub>2</sub>O<sub>3</sub>/SWNT samples by sequence of film thickness from high to low.
(d) The interferometer image of FC\_T with the height information between A and B marked spots. (e, f) The corresponding AFM images of FC\_N and FC\_t with the roughness measured between A and B marked spots.

The measurement using optical interferometer in Figure 4.4d manifests that the thickness of FC\_T is about 5  $\mu$ m according to the average height difference along the line joining the spot marked by B near the edge of film and the flat surface of silicon

substrates at A-marked spot. It is worth to specify that the films are adhesively and flat transferred onto the silicon substrate without folding and overlapping by following the procedures to prepare electrodes (for details see Experimental Section). AFM images (Figure 4.4e and 4.4f) show that FC\_N and FC\_t hybrid films within an area of 5  $\mu$ m x 20  $\mu$ m are about 500 nm and 100 nm thick, respectively by averaging the roughness along the line between spot B on the film and spot A on the silicon surface.

# 4.3.2 Crystalline structure evolution of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> nanocrystals during H<sub>2</sub> annealing

## **4.3.2.1** SEM and HRTEM characterization

TEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilm nanocomposite after H<sub>2</sub> annealing (Figures 4.5a and 4.5b) and the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT before H<sub>2</sub> annealing (Figure 4.5d) all present a heterogeneous morphology of iron oxide nanocrystals with similar sizes (< 20 nm) distributed in the matrix of the entangled SWNT bundles. It is evident that the morphology of these nanocrystals is well maintained during the H<sub>2</sub> annealing. SEM images (Figure 4.6) also demonstrate the retention of morphology with a uniform distribution of nanocrystals except for the typical cubic shape of Fe<sub>3</sub>O<sub>4</sub> particles, which have a slightly more expanded volume than Fe<sub>2</sub>O<sub>3</sub>. This simply indicates the structural change during thermal reduction in H<sub>2</sub> atmosphere but more evidence from the following characterizations is needed. HRTEM images in Figures 4.5c and 4.6e show the detailed crystalline structure of the iron oxide nanocrystals in the nanocompsite macrofilms after and before H<sub>2</sub> annealing, respectively. The well-defined lattice fringe with d-spacing of 0.25 nm in Figure 4.5c is consistent with the interplanar distance of (311) planes for Fe<sub>3</sub>O<sub>4</sub>, whereas that of 2.69 Å and 3.62 Å in Figure 4.5e correspond to the (104) and (012) planes of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



Figure 4.5 (a, b) TEM images of iron oxide/SWNT hybrid films after H<sub>2</sub> annealing; (c) HRTEM image of Fe<sub>3</sub>O<sub>4</sub> nanocrystal in the hybrid films after H<sub>2</sub> annealing; (d) TEM image of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films before H<sub>2</sub> annealing; (e) HRTEM image of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocrystals in the hybrid films before H<sub>2</sub> annealing; (f) SAED patterns of the hybrid films before (right) and after (left) H<sub>2</sub> annealing with the corresponding photographs inset in red and brownish on the same side.

SAED patterns, showing two different well-resolved polycrystalline rings, in Figure 4.5f also reveal the conversion from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>. It is identified that the hametite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has a hexagonal close-packed (hcp) structure with the corresponding (104), (113), and (226) typical planes while after H<sub>2</sub> thermal reduction, the cubic close-packed (ccp) Fe<sub>3</sub>O<sub>4</sub> forms with the corresponding (533) and (311) planes. The conversion can also be visibly reflected on the films' color change from red (right inset photography in

Figure 4.5f) before  $H_2$  annealing to brownish (left inset photography in Figure 4.5f) after  $H_2$  annealing.



Figure 4.6 (a) SEM images of the iron oxide/SWNT macrofilm nanocomposites after H<sub>2</sub> annealing and (b) in a higher magnification.

# 4.3.2.2 XRD and Rietveld fitting

From the XRD pattern (Figure 4.7a) for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT after H<sub>2</sub> annealing, we can quantitatively assess the reduction degree of the initially pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> *i.e.* composition of nanocomposites. All the diffraction peaks could be indexed to two phases: the rhombohedral phase of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in *R*-3*c* space group (JCPDS No.01-087-1164) and the cubic phase of Fe<sub>3</sub>O<sub>4</sub> in *Fd*-3*m* space group (JCPDS No.01-075-0033). The co-existence of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> is in good agreement with the HRTEM results.


Figure 4.7 (a) XRD patterns and Rietveld fitting results of the iron oxide/SWNT hybrid films after H<sub>2</sub> annealing; (b) TGA curve of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films before H<sub>2</sub> annealing; (c) The crystalline structure models of cubic Fe<sub>3</sub>O<sub>4</sub> (left) and rhombohedral Fe<sub>2</sub>O<sub>3</sub> (right).

The transformation from rhombohedral phase to cubic phase involves the slip of atompacked planes from AB to ABC stacking. XRD refinement was analyzed by using the Rietveld fitting method to obtain the lattice parameters of the two phases: for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, a = b = 5.031705 Å, c = 13.743799 Å, and  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 120^{\circ}$ ; for Fe<sub>3</sub>O<sub>4</sub>, a = b = c= 8.387474 Å and  $\alpha = \beta = \gamma = 90^{\circ}$ , as depicted in their respective schematic crystal units (Figure 4.7c). The phase weight fraction of the two types of iron oxides was also quantitatively yielded: Fe<sub>2</sub>O<sub>3</sub>:Fe<sub>3</sub>O<sub>4</sub>=7.5%:92.5%, which in total constitute 75% of the nanocomposites evaluated by the TGA curve as shown in Figure 4.7b. The mean thickness of nanocomposite macrofilms is about 480 nm.

## 4.3.2.3 XPS and Raman spectroscopy

XPS results are presented in Figures 4.8a – 4.8e, confirming the conversion between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. In the survey spectrum (Figure 4.8a), the collected signal peaks are assigned to three elements of Fe (2s, 2p, 3p and LMM), O (1s and KLL) in the iron oxide states, and C (1s and KLL) coming from SWNTs. For the Fe<sub>2</sub>O<sub>3</sub>/SWNT without H<sub>2</sub> annealing, the peaks in Figure 4.8b at 711.45 eV and 725.1 eV are attributed to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>. The distinguishable peak at 719.9 eV is a featured satellite peak of Fe 2p<sub>3/2</sub> for Fe<sub>2</sub>O<sub>3</sub>. [16] As previously reported in other literature that there was no satellite peak for Fe 2p<sub>3/2</sub> of Fe<sub>3</sub>O<sub>4</sub>, [16] the absence of the satellite peak in Figure 4.8c clearly indicates the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> after H<sub>2</sub> annealing. Instead, only the Fe 2p<sub>3/2</sub> peak at 711.25 eV and the Fe 2p<sub>1/2</sub> peak at 724.95 eV are presented.

Raman spectrum (Figure 4.8d) of the nanocomposites after H<sub>2</sub> annealing also exhibits the mixed bands ranging from 400 cm<sup>-1</sup> to 1100 cm<sup>-1</sup> corresponding to Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanocrystals. SWNTs show the D band at around 1300 cm<sup>-1</sup>, G band at around 1600 cm<sup>-1</sup>, and the radial breathing mode (RBM) in the range of 200 ~ 300 cm<sup>-1</sup>. [17-19] The noticeable red spot marked in the optical microscopy image (Figure 4.8e) after Raman measurement shows a reverse phase transformation of black Fe<sub>3</sub>O<sub>4</sub> to be reoxidized to Fe<sub>2</sub>O<sub>3</sub> in red color caused by the accumulating heat of laser with a power of 10 mV. This provides another reliable evidence of the phase transformation between Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> due to the H<sub>2</sub> reduction.



Figure 4.8 (a) XPS survey spectrum of the hybrid films; (b) XPS spectrum of Fe 2p for the hybrid films before H<sub>2</sub> annealing. The presence of the satellite peak of Fe  $2p_{3/2}$  is the characteristics of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; (c) XPS spectrum of Fe 2p for the hybrid films after H<sub>2</sub> annealing. The absence of the satellite peak confirms the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> after H<sub>2</sub> annealing. (d) Raman spectrum of the iron oxide/SWNT hybrid films after H<sub>2</sub> annealing, the inset illustrates the details of the spectrum from 400 to 1100 cm<sup>-1</sup>; (e) the optical image snapshot showing the Fe<sub>3</sub>O<sub>4</sub> was reoxidized to Fe<sub>2</sub>O<sub>3</sub> as marked on the red spot.

#### 4.3.3 Electrochemical characteristics of α-Fe<sub>2</sub>O<sub>3</sub>/SWNT

## 4.3.3.1 Discharge-charge curves

The electrochemical characterizations were conducted for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms with the different thicknesses abovementioned in Section 4.3.1 as working electrodes in coin cells, which consist of a Li metal as the counter electrode and 1 M LiPF<sub>6</sub> in EC and DEC (1:1 by volume) as the electrolyte. In a control group, the

electrode was also prepared by simply mixing the pure  $Fe_2O_3$  nanoparticles with carbon black and PVDF binder in a weight ratio of 80:10:10.

Figure 4.9a exhibits the discharge-charge curves of FC\_T, FC\_N and FC\_t samples after 5 cycling tests between 3.0 V and 0.005 V at the current density of 100 mAg<sup>-1</sup>, compared with the control group during the first two cycles under the same condition. The voltage plateaus at around 1.5 V, 1.2 V and 0.78 V in the first-cycle discharge curve of the pure Fe<sub>2</sub>O<sub>3</sub> sample represent the conversional reactions, respectively in following Equations [7],

$$Fe_2O_3 + xLi^+ + x\Theta \longrightarrow \alpha - Li_xFe_2O_3$$
  
4.1

$$\alpha - \text{Li}_{x}\text{Fe}_{2}\text{O}_{3} + (2-x)\text{Li}^{+} + (2-x)\Theta \longrightarrow \text{Li}_{2}\text{Fe}_{2}\text{O}_{3}$$

$$4.2$$

$$Li_2Fe_2O_3 + 4Li^+ + 4\Theta \longrightarrow 2Fe^0 + 3Li_2O$$
4.3

The charge curve for the first cycle shows a sloping plateau from 1.5 V to 2.2 V, corresponding to the reverse reaction of  $Fe^{0} \rightarrow Fe(II)$  in Equation 4.4 [9]:

$$2Fe^{0} + 2Li_{2}O \iff 2Fe(II)O + 4Li^{+} + 4\Theta$$

$$4.4$$

where only 4 moles out of 6 moles Li ions are reversible during the whole cycle, accounting for only 420 mAhg<sup>-1</sup> charge capacity compared to 724 mAhg<sup>-1</sup> during the discharge process (based on the mass of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the mixture). The specific capacity of the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample in the second cycle decays to 405 mAhg<sup>-1</sup> which is only half of the initial capacity; that is partly because of the irreversibly structural transformation to co-existed hexagonal  $\alpha$ -Li<sub>x</sub>Fe<sub>2</sub>O<sub>3</sub> and cubic Li<sub>2</sub>Fe<sub>2</sub>O<sub>3</sub> during such phase transformations also deteriorate the capacity in the consecutive cycles.

Whereas for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT, the curves show a longer plateau at a higher voltage of 0.8~0.9 V with capacities over 750 mAhg<sup>-1</sup> (FC\_t) up to 825 mAhg<sup>-1</sup> (FC\_N) after 5 cycles (based on the total mass of the hybrid films).



Figure 4.9 Electrochemical performance comparison among the four samples: FC\_T, FC\_N, FC\_t and the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> free of SWNTs. (a) The galvanostatic discharge-charge curves for the three  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid film samples at the end of the 5<sup>th</sup> cycle and the first two cycles of the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample, all at the same current density of 100 mAg<sup>-1</sup>. (b) The histogram plot for the discharge specific capacities of all the samples during the five cycles. (c) The Nyquist plots of the as-assembled fresh cells for all the samples. (d) The Nyquist plots of all the samples after 5 cycling discharge-charge tests at 100 mAg<sup>-1</sup>.

The histogram in Figure 4.9b demonstrates that the SWNT macro-films would enhance the specific capacity and the cyclic stability of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> remarkably. On the contrary, pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> without SWNTs shows a quick capacity degradation dropping from the initial value of 724 mAhg<sup>-1</sup> to 332 mAhg<sup>-1</sup>, which retention for only five cycles is as low as 46%. Among the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT samples with different thicknesses of macrofilms, FC\_N has the highest discharge capacity and this is related to the thickness we will discuss later.

# **4.3.3.2** Electrochemical impedance spectroscopy

EIS analysis has been performed to provide the viewpoint of electrochemical kinetics in order to elucidate the difference of the electrochemical performance for the four samples in comparison in last section. The Nyquist plots of the fresh cells before the GCD testing in Figure 4.9c show that FC\_N has the smallest series resistance  $(R_s)$ involving the resistance of electrode, electrolyte and their contact interface in series. The smallest R<sub>s</sub> results from the lowest Fe/C ratio of FC\_N. All the nanocomposite samples show the semicircles with much shorter arc length than the pure  $Fe_2O_3$  sample. Compared with the pure Fe<sub>2</sub>O<sub>3</sub> sample, the nanocomposites have much smaller chargetransfer resistance (R<sub>ct</sub>), which is extrapolated from the real-impedance intersection of semicircle at an intermediate frequency of 35 Hz for FC\_N, 25 Hz for FC\_T and 21 Hz for FC\_t. [20] The decreased R<sub>ct</sub> indicates SWNTs contribute greatly to the improvement of the conductivity. The smallest  $R_{ct}$  at the highest frequency (35 Hz) for FC\_N means that it has the fastest charge-transfer process, which could be optimized by Fe/C weight ratio through controlling the thickness of α-Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films. From Figure 4.9c, we can also find that Warburg line of FC\_T with a slope of approximately 45 °is the longest probably due to the onset of finite length effects

originating from the highest concentration of Fe<sub>2</sub>O<sub>3</sub>. [21] Thus, depending on extrapolation at the intersection of the Warburg and capacitive lines to the real impedance axis in the Nyquist plot, FC\_T has the largest limiting resistance (R<sub>L</sub>) [21] The larger  $R_L$  to describe the Li<sup>+</sup> diffusion materials demotes the worse diffusive kinetics they possess. [21] The largest R<sub>L</sub> for FC\_T may come from the narrowing pore sizes of the densest architecture as shown in Figure 4.8a. Figure 4.9d shows that the  $R_s$ for all samples are increased after 5 cycles and the arc lengths of semicircles for all samples become shorter, i.e. a reduced R<sub>ct</sub>, as a result of the stable SEI formation. [11] The point connecting the semicircle with the Warburg line for the nanocomposites all shifts towards the lower frequency ( $\omega_{\rm C}$ ), indicating the kinetics become slower during cycling. This phenomenon also explains the capacity fading for FC\_N and FC\_t. Exclusively, FC\_T has electrochemical behavior differing from the other two nanocomposite samples. It is noting from the magnified high frequency part inset the Nyquist plot in Figure 4.9d that the initially single semicircle for FC\_T fresh cell is split into two ones connected at a high frequency of 1451 Hz after 5 cycling tests,. This is caused by the dissociation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles from the SWNT surfaces similar to the discussion in Chapter 2. [22] The major semicircle after splitting at a higher frequency is attributed to the intimately-anchored Fe<sub>2</sub>O<sub>3</sub>/SWNT integrity with a super high kinetics (1451 Hz), which could offset the diminishing of  $\omega_{\rm C}$  and stabilize the capacity of FC\_T with cycling continues. Overall, FC\_N with 500 nm thickness of a-Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms has shown the best electrochemical performance and was thoroughly investigated in the following sections.

# 4.3.3.3 Cyclic voltammetry analysis

CV was carried out in the potential window between 0 and 3 V at a scan rate of 100  $\mu$ V/s for 20 cycles. The curves of the first cycle, 2<sup>nd</sup>, 5<sup>th</sup>, 10<sup>th</sup>, and the last cycle are shown in Figure 4.10. The cathodic peak at 1.63 V in the 1<sup>st</sup> sweep starting with an OCV  $(V_{OCV}, 2.2 \text{ V})$  is ascribed to the single hexagonal phase induced by Li<sup>+</sup> insertion as shown in Equations 4.1. Another peak at 1.3 V is attributed to reaction of Equations 4.2 resulting in occurrence of lithiated phase, cubic  $Li_2Fe_2O_3$ . The sharp peak at 0.76 V with the highest cathodic current is assigned to the reduction of Fe(II) ions in Li<sub>2</sub>Fe<sub>2</sub>O<sub>3</sub> to Fe<sup>0</sup>, corresponding to Equation 4.3. In the anodic process of the first sweep, two adjacent anodic peaks at 1.6 V and 1.87 V are mirror-symmetrical to each other. This twin peaks derive from a two-step  $Li^+$  reversible charge reaction of  $Fe^0 \rightarrow Fe(II)$  as denoted in Equation 4.4. [9] In the following CV measurements from the second cycle up to 20 cycles, the cathodic peak at 1.63 V becomes more evident while the one at 1.3 V, well defined in the first cathodic sweep, is absent, probably owing to both the irreversibility of Equation 4.2 followed by the reduction from Li<sub>2</sub>Fe<sub>2</sub>O<sub>3</sub> to Fe<sup>0</sup> in Equation 4.3. [23] The irreversible phase transformation also makes the major cathodic peaks (Fe(II) $\rightarrow$  Fe<sup>0</sup>) all shift to a higher potential at 0.82 V with a lower current compared to the peak at 0.76 V in the first cycle. On the contrary, the twin anodic peaks remain at 1.6 and 1.87 V, indicating the good reversibility of  $Fe^{0} \rightarrow Fe(II)$ . The new-born anodic peak at 2.4 V may be attributed to a deeper oxidization of  $Fe(II) \rightarrow Fe(III)$ . [23] Generally, the welloverlapped curves after the first cycle manifest the good cyclic stability of FC N.



Figure 4.10 Selected cycle curves from cyclic voltammetry of the FC\_N (~500 nm thick)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid film sample between 0 and 3 V at a scan rate of 0.1 mV/s for 20 cycles. Numbers represent the cycle number. Potentials of peaks are also labeled.

## 4.3.3.4 Cyclic performance and rate capability

GCD cycling tests have been performed to evaluate the capacity retention and the cyclic stability of cell at various current densities of 100, 200, 500, and 1000 mAg<sup>-1</sup> for 100 cycles in total. The voltage profiles for the selected cycles in the 1<sup>st</sup>, 2<sup>nd</sup>, 10<sup>th</sup>, 20<sup>th</sup>, and 100<sup>th</sup> at the same rate of 100 mAg<sup>-1</sup> are shown in Figure 4.11a. The discharge curve for the 1<sup>st</sup> cycle shows a shortest voltage plateau at 1.7 V followed by the longer one at 1.3V and the longest at 0.8 V, which correspond to the respective processes from Equations 4.1 to 4.3. From the 2<sup>nd</sup> to the 20<sup>th</sup> cycle, the overlapped discharge curves have a sloped plateau at ~1.6 V and then an extended voltage plateau at elevated potential ~0.9 V compared to the 1<sup>st</sup> cycle. The charge curves for all the cycles have a similar potential between 1 V and 2.2 V. These results coincide well with the CV analysis discussed above. At the end of the 100<sup>th</sup> cycle, the sloped voltage plateau around 1.6 V is absent in the discharge curve. Instead, there is only a single voltage

plateau at 1 V, increasing 0.1 V compared to 0.9 V. Meanwhile, the charge potential of the 100<sup>th</sup> cycle is decreased by about 0.2 V compared to the rest of charge curves. The combined potential difference (0.1+0.2=0.3 V) results in a lower overpotential. Figure 4.11b shows the rate capability of FC\_N during 100 cycles at different rates. The cell was first cycled at 100 mAg<sup>-1</sup> for 20 cycles. An overall average capacity of 852 mAhg<sup>-</sup> <sup>1</sup> was achieved. In the first 20 cycles, the initial specific discharge capacity of 956 mAhg<sup>-</sup> <sup>1</sup> declines to 795 mAhg<sup>-1</sup> at the end of the 10<sup>th</sup> cycle and then rebounds constantly. Continuously, when the current density was increased to 200 mAg<sup>-1</sup>, the cell start being stabilized with the capacity of 927 mAhg<sup>-1</sup> and the CE is improved from the mean value of 91% within the first 10 cycles to 99.7% since the 20<sup>th</sup> cycle. The increase in capacity and CE is attributed to transition from Li<sup>+</sup> intercalation mechanism to the reversible  $Fe^{0} \leftrightarrow Fe(III)$  conversional reactions through the deeper oxidization of  $Fe(II) \rightarrow Fe(III)$ since the 10<sup>th</sup> cycle. The cell performance at 500 mAg<sup>-1</sup> shows a fluctuation around the average capacity of 850 mAhg<sup>-1</sup> and quickly drops below 200 mAhg<sup>-1</sup> at an even higher current density of 1000 mAg<sup>-1</sup>. The fluctuation is as a result of the sluggish kinetics of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and the severe structural transformation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> during Li<sup>+</sup> insertion and extraction at a high current density. After deep cycling at 1000 mAg<sup>-1</sup>, an increasing capacity over 1100 mAhg<sup>-1</sup> can be restored when returning the low rate of 100 mAg<sup>-1</sup>, which is indicative of an excellent cyclic stability. It is recognized that the capacity increase over the theoretical capacity in the last 15 cycles could result from the relaxation of electrochemical activation and the further reversible  $Fe^0 \leftrightarrow Fe(III)$ conversional reactions. [24]



Figure 4.11 Electrochemical measurements of a half-cell composed of FC\_N sample and Li. The specific capacities are based on the total mass of the hybrid films. (a) The galvanostatic discharge-charge curves at the same current density of 100 mAg<sup>-1</sup> for the 1st, 2nd, 10th, 20th and 100th cycle. (b) Capacity retention of FC\_N at various current densities. (c) The GITT curve of FC\_N plotted as voltage versus capacity.

# 4.3.3.5 Effect of film thickness on Li<sup>+</sup> chemical diffusion coefficient

In order to better understand the nature of the kinetic properties of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT for FC\_N, GITT is employed to analyze the Li-ion transport kinetics for the nanocomposite electrodes using small constant current pulses, and measuring potential changes as a function of time [25] (See details in Section 4.2.3).The GITT curve of FC\_N plotted as voltage versus capacity in Figure 4.11c, shows that the full

Li<sup>+</sup> diffusive reactions enable the specific charge and discharge capacity of FC\_N to reach 1200 mAhg<sup>-1</sup> given the relaxation time is sufficient to allow the system in equilibrium. Similar to the described GCD voltage profiles, the discharge process shows a voltage plateau at around 1 V due to the reduction of Fe(II) to Fe<sup>0</sup> and the inclined tail part below 0.5 V is contributed by SWNTs with a capacity of 380 mAhg<sup>-1</sup> considering the theoretical capacity of 372 mAhg<sup>-1</sup> for graphite. The equilibrium voltage upon charge shows a sharp slope up to 200 mAhg<sup>-1</sup>, which originates from SWNTs, followed by a longer increased slope from 1.2 V to 2.8 V, indicating that the reverse delithiation process might occur in a continuous Fe<sup>0</sup>  $\rightarrow$  Fe(II)  $\rightarrow$  Fe(III) reaction. These results are in good agreement with the analysis above in Section 4.3.3.1 and consequently confirm our hypothesis on the reasons for the capacity increment.

The effective Li<sup>+</sup> chemical diffusion coefficient can be determined by GITT, by Fick's law with the following equation (Equation 4.5) [25]:

$$D_{GITT} = \frac{4}{\pi \tau} \left( \frac{m_b V_M}{M_b S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (\tau \ll L^2 / D_{GITT})$$

$$4.5$$

where *L* is the characteristic length; *S* is the contact area between the electrode and electrolyte;  $V_M$  is the molar volume of the electrode material;  $M_b$  and  $m_b$  are the atomic weight of *b* and the mass of the component *b* in the sample, respectively;  $\Delta E_t$  is the total change of the cell voltage during the current pulse for the time  $\tau$ , neglecting the IR drop due to the current flux through the electrolyte and the interface; and  $\Delta E_s$  is the change of the steady-state voltage of the cell for the step in different potential range as illustrated and defined in Figure 4.12 (current steps at different potentials in the discharge-charge cycle). [25] Here the component *b* is  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and we simplify the  $V_M$  as the molar

volume of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> because of its high concentration over 90% in the nanocomposites. *V<sub>M</sub>* can be calculated from the Equation 4.6 as follows: [26]

$$V_M = N_A \frac{V_{cell}}{Z}$$

$$4.6$$

where  $V_{cell}$  is the unit cell volume;  $N_A$  is Avogadro constant and Z is the number of formula units in the unit cell.  $V_{cell}$  is calculated from a rhombohedral unit cell parameters for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

The polarization curves in Figure 4.12a and 4.12b are representative of each step at around 0.2 V and 1.5 V, respectively during the charge process. When the cell goes to a higher voltage upon charging, it needs more relaxation time to reach equilibrium. On the contrary when the cell is discharged to a lower voltage, the relaxation time would be delayed (Figure 4.12c and 4.12d). These phenomena reflect the change of lithium diffusion coefficients as a function of voltages during charge and different processes. The overpotential, *i.e.* the voltage difference between equilibrium potential at the end of relaxation and the potential at the end of the current pulse ( $\approx \Delta E_t - \Delta E_s$ , neglecting the IR drop), [27] increases as both charge and discharge proceed. Thus, the potential hysteresis could be maintained as shown by GITT in Figure 4.11c.

In the following analysis, we relied on EIS measurements to calculate the  $Li^+$  chemical diffusion coefficients at different potentials to make a comparison with those as determined by GITT. It is helpful to clarify the potential relationship between the film thickness and the  $Li^+$  diffusivity and consequently the difference in cell performance for the Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms with different thicknesses.



Figure 4.12 Polarized curves for current pulse steps from GITT data at various potentials in discharge and charge processes. (a,b) upon charge, 0~0.6 V and 1.5~1.7 V. (c,d) upon discharge, 1.8~1.4 V and 3~1.8 V.

Based on the EIS results for FC\_N with the thickness of 500 nm (Figure 4.13a and 4.13b), Li<sup>+</sup> diffusion coefficient can be calculated according to the following equations: [28]

$$D_{EIS} = \frac{t^2}{4\tau}$$

$$\tau = 2\left(\frac{Q_m \sigma dx}{dE}\right)^2 = 2C_{\text{int}}^2 \sigma^2$$
4.8



$$\sigma = \frac{1}{\omega^{-\frac{1}{2}}} \quad (\omega \to 0) \tag{4.10}$$



Figure 4.13 Electrochemical impedance spectra for FC\_N. (a,b) Nyquist plots at various potentials and the corresponding fitting lines upon discharge and charge. (c) Equivalent circuit model employed in the curve fitting.

where *t* is the film thickness;  $\tau$  is characteristic diffusion time and  $\sigma$  is the Warburg coefficient;  $Q_m$  is the total inserted Li ions and dE/dx is the slope of the Coulometric titration curve;  $C_{int}$  is capacitance for Li<sup>+</sup> diffusion; Z" is the imaginary impedance; and  $\omega$  is the angular frequency. [28]  $C_{int}$  is obtained by fitting the EIS data recorded during discharge (Figure 4.13a) and charge (Figure 4.13b) at various potentials with the corresponding equivalent circuit model as shown in Figure 4.13c. Table 4.2 and Table 4.3 show the fitting values of components in the equivalent circuit model. Warburg

coefficient  $\sigma$  is extrapolated by fitting the slope of curve (Z" versus the square root of  $\omega$  at a low frequency). The values of  $\sigma$  at various potentials are listed with the diffusion coefficients  $D_{EIS}$  in Tables 4.4 and 4.5.

The results of Li<sup>+</sup> chemical diffusion coefficients calculated from the EIS  $(D_{EIS})$  and GITT  $(D_{GITT})$  are shown in Figure 4.14.



Figure 4.14 Li<sup>+</sup> chemical diffusion coefficients of FC\_N determined by GITT and EIS during charge and discharge processes.

Both  $D_{EIS}$  and  $D_{GITT}$  is basically increasing with the charging and discharging. This is consistent with variation of Warburg impedance  $W_s$  (Table 4.2 and Table 4.3) and the results of polarization curves as described in Figure 4.12.  $D_{EIS}$  in the range of  $3\times10^{-12} \sim$  $7\times10^{-12}$  cm<sup>2</sup>/s is higher than  $D_{GITT}$  ranging from  $1\times10^{-12} \sim 4\times10^{-12}$  cm<sup>2</sup>/s probably due to the insufficient equilibrium confined by the characteristic diffusion length *L* for the EIS measurements. Therefore, the nanocomposite with the thickness of 300~500 nm, which is comparable to the characteristic diffusion length, *L*, may have the optimal electrochemical performance. If the Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilm was too thick or too thin, it would not benefit the maximization of Li<sup>+</sup> diffusivity for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Thus, it is no wonder that the cell with FC\_N films closest to 300~500 nm thick has the best performance in terms of the highest specific capacity and the cyclic stability. However the Li<sup>+</sup> chemical diffusion coefficient with a factor of -12 is still too low and is responsible for the inferior rate capability. This challenge remains unsolved until the H<sub>2</sub> annealing strategy is adopted, which will be discussed in the following section.

Potential at discharging (V)	Series resistance R₅ (Ω)	Charge transfer resistance R <sub>ct</sub> (Ω)	Warburg impedance Ws (Ω)	Constant phase element CPE (F)	Intercalation capacitance C <sub>in</sub> (F)
2	3.722	83.9	38.13	1.9054E-5	0.0050175
1.5	4.11	72.28	36.71	4.9431E-5	0.013473
1	4.351	70.15	39.74	5.1375E-5	0.015545
0.5	4.282	62.91	58.62	5.224E-5	0.026113
0.2	4.385	61.31	54.86	6.2949E-5	0.032586
0.05	4.51	72.19	62.21	7.6176E-5	0.061731

 Table 4.2
 The fitting values of components in equivalent circuit for Figure 4.13a.

Table 4.3The fitting values of components in equivalent circuit for Figure 4.13b.

Potential at discharging (V)	Series resistance R₅ (Ω)	Charge transfer resistance R <sub>ct</sub> (Ω)	Warburg impedance W₅ (Ω)	Constant phase element CPE (F)	Intercalation capacitance C <sub>in</sub> (F)
0.5	4.207	71.29	73.99	8.5774E-5	0.03205
1	5.184	62.13	53.81	6.0959E-5	0.029044
1.5	4.418	60	39.23	6.1094E-5	0.025756
2	4.479	68.64	53.91	5.9489E-5	0.013761
2.5	4.478	73.38	33.83	6.8308E-5	0.010591

Potential at discharging (V)	Intercalation Capacitance C <sub>in</sub> (F)	Warburg coefficient σ (Ω/s <sup>-1/2</sup> )	Characteristic diffusion time τ (s)	Diffusion coefficient D (cm²/s)
2	0.0050175	1305.01	85.75	7.287e-12
1.5	0.013473	510.31	94.54	6.610e-12
1	0.015545	447.24	96.67	6.465e-12
0.5	0.026113	287.89	113.03	5.530e-12
0.2	0.032586	240.92	123.26	5.070e-12
0.05	0.061731	169.67	219.40	2.850e-12

Table 4.4Li+ chemical diffusion coefficients upon discharge determined by EIS and<br/>the intermediate parameters applied.

Table 4.5Li<sup>+</sup> chemical diffusion coefficients upon charge determined by EIS and the<br/>intermediate parameters applied.

Potential at charging (V)	Intercalation Capacitance C <sub>int</sub> (F)	Warburg coefficient σ (Ω/s <sup>-1/2</sup> )	Characteristic diffusion time τ (s)	Diffusion coefficient D (cm²/s)
0.5	0.03205	257.85	136.60	4.575e-12
1	0.029044	279.69	131.97	4.735e-12
1.5	0.025756	332.74	146.89	4.255e-12
2	0.013761	532.52	107.40	5.820e-12
2.5	0.010591	799.63	143.44	4.357e-12

# 4.3.4 Enhanced rate capability by H<sub>2</sub> annealing

In order to enhance the rate capability of  $Fe_2O_3/SWNT$  macrofilms, annealing the nanocomposites in  $H_2$  atmosphere is considered an effective method based on several facts as described in Introduction Section. The electrochemical performance of the iron oxide/SWNT macrofilm nanocomposites after  $H_2$  annealing was thoroughly investigated. The comparison of the rate capabilities for the two samples before and after  $H_2$  annealing was performed by the continuous GCD measurements at a variety of current densities from 0.1 Ag<sup>-1</sup> up to 4 Ag<sup>-1</sup>. Figure 4.15a shows that the initial specific discharge capacity is 960 mAhg<sup>-1</sup> for the sample after H<sub>2</sub> annealing (denoted as "film AH" for the following use) at the constant current density of 0.1 Ag<sup>-1</sup>. Although it is found that this highest value starts to drop due to the irreversible capacity resulting from the formation of the SEI between electrolyte and anode, the average capacity of this sample is as high as 847 mAhg<sup>-1</sup> in the first 10 cycles at 0.1 Ag<sup>-1</sup>. The film AH also exhibits the enhanced rate capability during the following cycling tests: the mean discharge capacities are 890 mAhg<sup>-1</sup> and 861 mAhg<sup>-1</sup> corresponding to the cycles at 1 Ag<sup>-1</sup> and 2 Ag<sup>-1</sup>, respectively. When the current density as high as 4 Ag<sup>-1</sup> is applied, the capacity still stabilizes at 786 mAhg<sup>-1</sup> on average from the 40<sup>th</sup> to 60<sup>th</sup> cycle. It is also noted that the capacity is gradually increasing and retains 785 mAhg<sup>-1</sup>, which is 93% of that for the initial 10 cycles at the same current density for the last 10 cycles as the low current density of 0.1 Ag<sup>-1</sup> is back. On the contrary, only at the extremely low current densities of 0.1 Ag<sup>-1</sup> and 0.2 Ag<sup>-1</sup>, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT without H<sub>2</sub> annealing (denoted as "film BH") exhibits a specific capacity above 800 mAhg<sup>-1</sup> comparable to the film AH. Whereas, at the current density beyond 0.5 Ag<sup>-1</sup>, the capacity behavior of film BH is the same as described in Section 4.3.3.4: it fluctuates and fades quickly below 100 mAhg<sup>-1</sup>. The facilitated fading at a higher current density implies that the slow kinetics and diffusivity become more critical in limiting the performance of the nanocomposites. Meanwhile, the accumulated large volume change induced by conventional reactions in all the previous cycles may result in the dissociation of iron oxides from the entanglement of SWNTs where only the relatively weak interaction forces exist between them. This aggravates the fast fading of capacity. The remarkable improvement of the rate capability by  $H_2$  annealing suggests that the kinetic property of lithium-ion insertion/extraction could be enhanced by  $H_2$  annealing. In addition, the CE in the initial 10 cycles at 0.1 Ag<sup>-1</sup> for film BH is also lower with a remarkably larger gap between discharge and charge capacity than that of film AH. This is probably attributed to the lower conductivity of Fe<sub>2</sub>O<sub>3</sub> compared to that of Fe<sub>3</sub>O<sub>4</sub>.



Figure 4.15 (a) The rate capabilities of the iron oxide/SWNT hybrid films after (top) and before (bottom) H<sub>2</sub> annealing; (b) The discharge/charge profiles for the hybrid films after H<sub>2</sub> annealing corresponding to the selected cycles at various rates.

The discharge/charge curves for film AH at different rates in Figure 4.15b show a similar behavior of conversion reaction to the Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms. The voltage profiles have a well-defined potential plateau at around 1 V versus Li<sup>+</sup>/Li, corresponding to the phase reduction process of iron oxides (Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) into the Fe<sup>0</sup>/Li<sub>2</sub>O matrix. The well-overlapped curves before the 50<sup>th</sup> cycle with variation in the applied rates also reveal the excellent reversibility of the lithiation and delithiation processes. In contrast, it is worth noting that during the last several cycles when the rate is lowered to 0.1 Ag<sup>-1</sup>, the plateau length of the 70<sup>th</sup>-cycle discharge/charge profile, for example, becomes shortened due to the retarded reduction of the iron oxides, resulting in the capacity deterioration. However, with the full relaxation of lithium ion diffusion in the  $Fe_3O_4/Fe^0/Li_2O$  mixture, the following capacity is in an increasing trend as shown in Figure 4.15a. It is in coincidence with the phenomenon described previously. All these results demonstrate that H<sub>2</sub> annealing plays a significant role in enabling the high power densities for the conversion reactions of the iron oxide/SWNT macrofilm nanocomposites.

## 4.3.5 Improved electrochemical kinetics by H<sub>2</sub> annealing

In order to understand the electrochemical kinetics with respect to the enhancement of the rate capability, EIS and the GITT, which combines the transient and steady-state measurements to determine the  $Li^+$  chemical diffusion coefficient, were employed again to compare the variation of kinetic parameters of the two samples before and after H<sub>2</sub> treatment.

#### **4.3.5.1** Electrochemical impedance spectroscopy

The EIS results are presented in Figure 4.16a with the inset equivalent circuit used to fit the data. The Nyquist plots show a typical Randles-model behavior, [29] which consists of a semicircle at high-to-middle frequency (100 kHz to 1 Hz) and a linear Warburg tail at low frequency (<1 Hz). In the equivalent circuit model,  $R_s$  represents the series resistance of the electrodes, electrolyte, and the current collectors;  $R_{ct}$  is the charge-transfer resistance between electrode/electrolyte interface; *CPE* is the constant phase element; and *W* represents the Warburg impedance associated with the diffusion of the lithium ions. These parameters are calculated and presented in Table 4.6. All the resistances are decreased after H<sub>2</sub> treatment. The lower series resistance of

the film AH is benefitted from the high conductivity of Fe<sub>3</sub>O<sub>4</sub>. The nearly 50% drop of the charge-transfer resistance from 196.2  $\Omega$  to 112.6  $\Omega$  after H<sub>2</sub> treatment confirms the improved conversion reaction kinetics determined by the charge-transfer process. [30] Most importantly, the H<sub>2</sub> annealing causes *W* to sharply decrease to 14.93  $\Omega$  compared to the original 96.83  $\Omega$  for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms without annealing. This is vital to facilitate the lithium diffusion and enhances the rate capability.

	Series resistance $R_s$ ( $\Omega$ )	Charge-transfer resistance $R_{ct}$ ( $\Omega$ )	Warburg impedance W ( $\Omega$ )
After H <sub>2</sub> treatment	6.23	112.6	14.93
Before H <sub>2</sub> treatment	14.26	196.2	96.83

 Table 4.6
 Fitting parameters of the equivalent circuit for EIS data.

#### **4.3.5.2** Galvanostatic intermittent titration test

From the GITT curves of the two samples (Figure 4.16b) under the same conditions including the cutoff voltage, current pulse, and relaxation time, it is evident to observe that regardless of the  $H_2$  treatment, both possess a higher capacity of 1000 mAhg<sup>-1</sup> than the steady-state capacity measured at 0.1 Ag<sup>-1</sup> due to the full relaxation of Li<sup>+</sup> diffusion.



Figure 4.16 (a) Nyquist plots of the iron oxide/SWNT macrofilms before (red line) and after (black line) H<sub>2</sub> annealing with the inset equivalent circuit used for fitting; (b) the GITT discharge/charge curves for the two hybrid films distinguished by different colors in the plot; (c) the polarization curves at the plateau potential during charge processes for the two nanocomposites; (d) the polarization curves at the plateau potential during discharge processes for the two nanocomposites.

The plateau potential of the film AH is about 0.2 V higher than film BH, also supporting the structure transformation of the nanocrystals, from  $Fe_2O_3$  to  $Fe_3O_4$  *via* reduction during H<sub>2</sub> annealing. Another difference is that film AH has more GITT steps than film BH. In other words, the film AH reaches equilibrium faster for a single GITT step, which indicates higher transport kinetics after H<sub>2</sub> treatment. Li<sup>+</sup> chemical diffusion coefficients can be calculated from the polarization curves extracted during the plateau according to the Equation 4.5. Given the weight percentage of remaining Fe<sub>2</sub>O<sub>3</sub> after H<sub>2</sub> annealing is only 7.5% of the iron oxide mixture, it can be deduced that most of Fe<sub>2</sub>O<sub>3</sub> was converted to Fe<sub>3</sub>O<sub>4</sub>. Thus, for simplicity, we assume that after H<sub>2</sub> annealing, all the iron oxides become Fe<sub>3</sub>O<sub>4</sub>. The molar volume is calculated from Equation 4.6 by using the crystal lattice parameters from the Rietveld fitting results of the XRD data in previous analysis in Section 4.3.2.2. The unit cell information and the molar volumes of two iron oxides are listed in Table 4.7.

Table 4.7The crystal unit cell information and the calculated molar volumes for the<br/>two iron oxides.

	V <sub>cell</sub> (m <sup>3</sup> )	Z	V <sub>M</sub> (m³∙mol⁻¹)
Cubic Fe <sub>3</sub> O <sub>4</sub>	a <sup>3</sup> = 5.90e-28	4	8.88e-5
Rhombohedral Fe <sub>2</sub> O <sub>3</sub>	a <sup>2</sup> *c*sin60 °=3.01e-28	6	3.02e-5

Table 4.8 The results of  $\Delta E_s / \Delta E_t$  and  $M_b$  items from calculation for the two iron oxides.

	ΔE <sub>s</sub> /ΔE <sub>t</sub> on charge	$\Delta E_s / \Delta E_t$ on discharge	M₅ (g∙mol⁻¹)
Cubic Fe <sub>3</sub> O <sub>4</sub>	0.82	0.17	251.53
Rhombohedral Fe <sub>2</sub> O <sub>3</sub>	0.76	0.07	159.69

The polarization curves (Figures 4.16c and 4.16d) are representative of a single current step at plateau potential during the charge and discharge processes for two samples, respectively. The  $\Delta E_s / \Delta E_t$  items in Equation 4.5 calculated from the polarization curves and  $M_b$  are summarized in Table 4.8. Since the variation of  $m_b$  and

*S* could be neglected after H<sub>2</sub> annealing and  $\tau$  remains the same, we can figure out the ratio of  $D_{GITT}$  for film AH and film BH in the equation as follows:

$$D_{GITT}^{AH}: D_{GITT}^{BH} = \left(\frac{V_M^{AH}}{V_M^{BH}}\right)^2 \left(\frac{M_b^{BH}}{M_b^{AH}}\right)^2 \left(\frac{\Delta E_s^{AH}}{\Delta E_t^{AH}}\right)^2 \left(\frac{\Delta E_s^{BH}}{\Delta E_t^{BH}}\right)^{-2}$$

$$4.11$$

where the items with the superscripts AH and BH refer to the samples after H<sub>2</sub> annealing and before H<sub>2</sub> annealing, respectively. By substituting the items in Equation 4.11 with the data in Tables 4.7 and 4.8, the final  $D_{GITT}^{AH}/D_{GITT}^{BH}$  upon discharge at the plateau potential is calculated to be 10.30. The remarkable improvement of the Li<sup>+</sup> chemical diffusion coefficient is consistent with the decreased Warburg impedance as stressed in EIS analysis. Therefore, it is believed that the boost of  $D_{GITT}$  in particular during the discharge process contributes greatly to the excellent rate capability of iron oxides/SWNT macrofilm nanocomposites after H<sub>2</sub> annealing.

#### 4.4 Conclusions

Overall, in this chapter, we provide a strategy with systematic discussions on development of the nanocomposite based on iron oxides and SWNT macrofilms as high-performance anode materials for lithium-ion batteries.

First, we have demonstrated the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT with enhanced electrochemical properties in terms of high specific capacity and cycling stability compared to the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The SWNT macrofilms with a high conductivity and flexibility can remarkably facilitate the electrochemical kinetics and buffer the strains caused by Liintercalated phase transformation to improve the specific capacity and cyclic stability of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> anodes. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilm nanocomposites can take the best of reversible Fe<sup>0</sup> $\leftrightarrow$ Fe(III) conversional reactions to approach the theoretical capacity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> over 1000 mAhg<sup>-1</sup>. The effect of the thickness on the performance of  $\alpha$ -  $Fe_2O_3/SWNT$  macrofilms is investigated and well elucidated. The sample with the thickness that comparable to the characteristic diffusion length of 300~500 nm has the highest Li<sup>+</sup> chemical diffusion coefficient and thus possesses an optimal electrochemical performance.

Secondly, H<sub>2</sub> annealing method was developed for the purpose of improving the rate capability of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilm nanocomposites. The obtained products, iron oxide (Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>)/SWNT, after H<sub>2</sub> annealing exhibit an excellent cyclic stability and significantly enhanced rate capability with a high capacity of 786 mAhg<sup>-1</sup> at the high current density of 4 Ag<sup>-1</sup>. The electrochemical kinetic analysis by GITT and EIS characterization demonstrates the superior conductivity of Fe<sub>3</sub>O<sub>4</sub>, facilitated charge-transfer process, and the improved Li<sup>+</sup> chemical diffusion coefficient resulted from H<sub>2</sub> annealing, which enables the high-rate capability of the iron oxide/SWNT hybrid films. This thermal reduction strategy proves to be an efficient fabrication procedure to boost the power density of rechargeable lithium batteries.

## REFERENCES

- 1. Armand, M.; Tarascon, J. M., Building better batteries. *Nature* **2008**, 451(7179), 652-657.
- 2. Tarascon, J. M.; Armand, M., Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, 414(6861), 359-367.
- 3. Taberna, P. L.; Mitra, S.; Poizot, P.; Simon, P.; Tarascon, J. M., High rate capabilities Fe<sub>3</sub>O<sub>4</sub>-based Cu nano-architectured electrodes for lithium-ion battery applications. *Nature Materials* **2006**, *5*(7), 567-573.
- 4. Li, N.; Martin, C. R.; Scrosati, B., A high-rate, high-capacity, nanostructured tin oxide electrode. *Electrochemical and solid-state letters* **2000**, 3(7), 316-318.
- 5. Li, Y.; Tan, B.; Wu, Y., Mesoporous Co<sub>3</sub>O<sub>4</sub> nanowire arrays for lithium ion batteries with high capacity and rate capability. *Nano Letters* **2008**, 8(1), 265-270.
- Wang, D.; Choi, D.; Li, J.; Yang, Z.; Nie, Z.; Kou, R.; Hu, D.; Wang, C.; Saraf, L. V.; Zhang, J.; Aksay, I. A.; Liu, J., Self-assembled TiO<sub>2</sub>–graphene hybrid nanostructures for enhanced Li-ion insertion. *ACS Nano* 2009, 3(4), 907-914.
- 7. Chen, J.; Xu, L.; Li, W.; Gou, X., α–Fe<sub>2</sub>O<sub>3</sub> nanotubes in gas sensor and lithium-ion battery applications. *Advanced Materials* **2005**, 17(5), 582-586.
- Larcher, D.; Masquelier, C.; Bonnin, D.; Chabre, Y.; Masson, V.; Leriche, J.-B.; Tarascon, J.-M., Effect of Particle Size on Lithium Intercalation into α-Fe<sub>2</sub> O<sub>3</sub>. *Journal of The Electrochemical Society* 2003, 150(1), A133-A139.
- Reddy, M. V.; Yu, T.; Sow, C. H.; Shen, Z. X.; Lim, C. T.; Subba Rao, G. V.; Chowdari, B. V. R., α–Fe<sub>2</sub>O<sub>3</sub> nanoflakes as an anode material for Li-ion batteries. *Advanced Functional Materials* **2007**, 17(15), 2792-2799.
- Liu, D.; Liu, Y.; Pan, A.; Nagle, K. P.; Seidler, G. T.; Jeong, Y.-H.; Cao, G., Enhanced lithium-ion intercalation properties of V<sub>2</sub>O<sub>5</sub> xerogel electrodes with surface defects. *The Journal of Physical Chemistry C* 2011, 115(11), 4959-4965.
- Jiao, F.; Harrison, A.; Jumas, J.-C.; Chadwick, A. V.; Kockelmann, W.; Bruce, P. G., Synthesis of ordered mesoporous Fe<sub>3</sub>O<sub>4</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> with crystalline walls using post-template reduction/oxidation. *Journal of the American Chemical Society* 2006, 128(39), 12905-12909.

- 12. Coey, J.; Berkowitz, A.; Balcells, L.; Putris, F.; Parker, F., Magnetoresistance of magnetite. *Applied Physics Letters* **1998**, 72, 734.
- 13. Zhu, H.; Wei, B., Direct fabrication of single-walled carbon nanotube macrofilms on flexible substrates. *Chemical Communications* **2007**, (29), 3042-3044.
- 14. Toby, B. H., EXPGUI, a graphical user interface for GSAS. *Journal of Applied Crystallography* **2001**, 34(2), 210-213.
- Nasibulin, A.; Rackauskas, S.; Jiang, H.; Tian, Y.; Mudimela, P.; Shandakov, S.; Nasibulina, L.; Jani, S.; Kauppinen, E., Simple and rapid synthesis of α-Fe<sub>2</sub>O<sub>3</sub> nanowires under ambient conditions. *Nano Research* **2009**, 2(5), 373-379.
- 16. Yamashita, T.; Hayes, P., Analysis of XPS spectra of Fe 2+ and Fe 3+ ions in oxide materials. *Applied Surface Science* **2008**, 254(8), 2441-2449.
- 17. De Faria, D. L. A.; Venâncio Silva, S.; De Oliveira, M. T., Raman microspectroscopy of some iron oxides and oxyhydroxides. *Journal of Raman spectroscopy* **1997**, 28(11), 873-878.
- Aslan, S.; Loebick, C. Z.; Kang, S.; Elimelech, M.; Pfefferle, L. D.; Van Tassel, P. R., Antimicrobial biomaterials based on carbon nanotubes dispersed in poly (lactic-co-glycolic acid). *Nanoscale* 2010, 2(9), 1789-1794.
- 19. Maslar, J.; Hurst, W.; Bowers, W.; Hendricks, J.; Aquino, M., In situ Raman spectroscopic investigation of aqueous iron corrosion at elevated temperatures and pressures. *Journal of the Electrochemical Society* **2000**, 147(7), 2532-2542.
- 20. Bard, A. J., Faulkner, L. R., Electrochemical Methods-Fundamentals and Applications. *Wiley: Hoboken*, **2001**.
- 21. Ho, C.; Raistrick, I. D.; Huggins, R. A., Application of A-C techniques to the study of lithium diffusion in tungsten trioxide thin films. *Journal of The Electrochemical Society* **1980**, 127(2), 343-350.
- 22. Cao, Z., Wei, B. Q., V<sub>2</sub>O<sub>5</sub>/single-walled carbon nanotube hybrid mesoporous films as cathodes with high-rate capacities for rechargeable lithium ion batteries. *Nano Energy* **2013**, 2(4), 481-490.

- 23. Morales, J.; Sánchez, L.; Martín, F.; Berry, F.; Ren, X., Synthesis and characterization of nanometric iron and iron-titanium oxides by mechanical milling: Electrochemical properties as anodic materials in lithium cells. *Journal of The Electrochemical Society* **2005**, 152(9), A1748-A1754.
- 24. Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J. M., Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature* **2000**, 407(6803), 496-499.
- 25. Weppner, W.; Huggins, R. A., Determination of the kinetic parameters of mixed-conducting electrodes and application to the system Li<sub>3</sub>Sb. *Journal of The Electrochemical Society* **1977**, 124(10), 1569-1578.
- 26. Mills;, I.; Cvita;, T.; Homann;, K.; Kallay;, N.; Kuchitsu, K., Quantities, Units and Symbols in Physical Chemistry. 2nd ed.; *Blackwell Science Ltd: Oxford*, **1993**.
- Zhu, Y.; Wang, C., Strain accommodation and potential hysteresis of LiFePO<sub>4</sub> cathodes during lithium ion insertion/extraction. *Journal of Power Sources* 2011, 196(3), 1442-1448.
- Levi, M. D.; Salitra, G.; Markovsky, B.; Teller, H.; Aurbach, D.; Heider, U.; Heider, L., Solid-state electrochemical kinetics of Li-ion intercalation into Li<sub>1-x</sub>CoO<sub>2</sub>: simultaneous application of electroanalytical techniques SSCV, PITT, and EIS. *Journal of The Electrochemical Society* **1999**, 146(4), 1279-1289.
- 29. Randles, J., Kinetics of rapid electrode reactions. *Discussions of the Faraday Society* **1947**, 1, 11-19.
- Kang, Y.-M.; Song, M.-S.; Kim, J.-H.; Kim, H.-S.; Park, M.-S.; Lee, J.-Y.; Liu, H. K.; Dou, S., A study on the charge–discharge mechanism of Co<sub>3</sub>O<sub>4</sub> as an anode for the Li ion secondary battery. *Electrochimica Acta* 2005, 50(18), 3667-3673.

### Chapter 5

# TRANSITION METAL OXIDE NANOCOMPOSITES WITH CARBON NANOTUBE MACROFILMS FOR ELECTROCHEMIAL APPLICATIONS

## 5.1 Introduction

As we have illustrated in the last chapters, nanocomposites, consisting of a set of first-row transition-metal oxides such as Fe<sub>2</sub>O<sub>3</sub>,[1,2] Fe<sub>3</sub>O<sub>4</sub>,[3,4] CoO,[5] Co<sub>3</sub>O<sub>4</sub>,[6,7] NiO, [8,9] V<sub>2</sub>O<sub>5</sub>[10], and MnO<sub>2</sub>[11,12] in a variety of structures at nanoscale, and carbon nanomaterials such as CNTs and graphene, have been extensively explored for energy storage, in particular the LIBs.[13,14] One common strategy in designing such nanocomposites is coupling size-controllable nanaoparticles on the supporting carbon scaffolds to tailor surface area, conductivity and charge-transfer interaction in order to obtain the desired characteristics such as high energy and power density as well as excellent stability.[15-17] In this Chapter, following the analogous formation mechanism of the Fe<sub>2</sub>O<sub>3</sub>/SWNT nanocomposite, we not only generalize the efficient, and robust synthetic route developed in Chapter 4 to the family of  $M_xO_y$  (M=Fe, Co, Ni) with SWNT macrofilm nanocomposites but also expand their roles in energy applications to electrocatalysts and supercapacitors. The size of M<sub>x</sub>O<sub>y</sub> nanoparticles is successfully controlled within 3-17 nm and the desired morphology of electrically interconnected networks that associate metal oxides with SWNT is formed. We particularly discussed their electrocatalytic properties for OER and ORR and also the performance in asymmetrical supercapacitors and lithium-ion batteries. The results show different performance in specialized catalytic reactions but share equal energy storage capabilities in terms of high capacity and stability. NiO/SWNT outperforms other competitors with the highest OER activity while Co<sub>3</sub>O<sub>4</sub>/SWNT calcinated at a low temperature of 200 °C exhibits the best ORR activity. The optimized asymmetric

supercapacitor that consists of NiO/SWNT as the positive electrode and a pure CNT macrofilm as the negative electrode shows a high specific capacitance of 130 F g<sup>-1</sup> after a long-term discharge-charge duration of 5000 cycles. Both the NiO/SWNT and  $Co_3O_4$ /SWNT nanocomposites exhibit an exceptionally high capacity beyond 1000 mAh g<sup>-1</sup> in Li-ion batteries.

The general approach is composed of two steps to synthesize  $M_xO_y/SWNT$  macrofilms as schematically illustrated in Figure 5.1. First, bis(cyclopentadienyl)metal (MCp2, M=Fe, Co, Ni) and sulfur (with an atomic ratio of M/S = 10) were mixed as precursors to produce SWNT macrofilms by CVD. Taking NiO for example, nickelocene (NiCp2) is decomposed during the CVD reaction to Ni ions as catalysts and two parallel Cp rings as carbon source for SWNT formation. Sulfur is a predominant additive to control the wall number of CNTs so that to promote SWNT growth as well as to enhance the growth rate. The deposition lasted for 45 min at 1100 °C and the asprepared SWNT macrofilms were not achieved until cooled down to room temperature followed by the second step, calcination at selected temperature in air. The heat treatment resulted in the oxidation of the metal catalysts to metal oxides and also the growth of the oxides. The detailed synthetic procedures are described in the following Experimental section.



Figure 5.1 Two-step synthetic route to  $M_xO_y$  (M=Fe, Co, Ni)/SWNT macrofilm nanocomposites.

#### 5.2 Experimental

# 5.2.1 Synthetic route to M<sub>x</sub>O<sub>y</sub> (M=Fe, Co, Ni)/SWNT macrofilm nanocomposites

SWNT macrofilms containing metal catalysts were synthesized by the modified floating CVD method as described in Chapter 1 and the oxides conversion method was similar to that introduced in Chapter 4. In brief, a mixed precursor of MCp2, (M=Fe, Co, Ni) and sulfur (both from Sigma Aldrich) in a crucible boat was placed in the furnace, which then was pre-heated to 1100-1150 °C with an argon gas flow of 500 mL min<sup>-1</sup>. During the deposition, a mixed gas flow of Ar (1500 mL min<sup>-1</sup>) and H<sub>2</sub> (150 mL min<sup>-1</sup>) was delivered and the MCp2 then starts pyrolysis at such a high temperature to generate a carbon source and metal catalysts for CNT growth. After 45 min reaction, large-area SWNT macrofilms (M-CNT (M=Fe, Co, Ni)) containing metal catalysts could be collected from the entire furnace tube. The thickness of the films can be controlled by the amount of the precursor mixtures and reaction time. The M-CNT macrofilms were obtained when the furnace was cooled down followed by the direct thermal treatment in air for 30 min below the critical temperature that CNT began to

burn out (about 450 °C). During the calcination, metal catalysts were oxidized to metal oxide nanoparticles with fine sizes. Three samples of  $Co_3O_4/SWNT$  were prepared at different annealing temperatures: Co-CNT (100°C),  $Co_3O_4/SWNT$  (200°C) and  $Co_3O_4/SWNT$  (400°C) because of the more complicated phases than NiO/SWNT, which was obtained by annealing only at 400°C.

## 5.2.2 Structural characterization

Morphological and structural characterizations were performed using TEM and HRTEM on JEOL JEM-2010F field emission TEM operating at 200 kV. The crystalline phase of the samples were determined using XRD collected on a Philips X'Pert powder diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =0.15418 nm) operating at 45 kV and 40 mA. Raman spectroscopy (Bruker SENTERRA with 532 nm laser excitation) was employed to verify the transformation of metal catalysts to metal oxides. The TGA was carried out on a Mettler Toledo TGA/DSA 1 STARe System under air flow (20 mL min<sup>-1</sup>) with a heating rate of 5 °C min<sup>-1</sup>.

## 5.2.3 RDE preparation and ORR/OER electrochemical characterization

For RDE measurements, uniform thin film electrodes with active materials were prepared by casting inks containing  $M_xO_y$  (M=Fe, Co, Ni) /SWNT nanocomposites on GC electrodes (5 mm in diameter, Pine Instruments, polished to a mirror-finishing with 0.05 µm alumina). The catalyst inks were prepared by dispersing  $M_xO_y$  (M=Fe, Co, Ni)/SWNT (2 mg) in isopropanol (1 mL) with 0.05 wt % Nafion solution. The dispersion was fully sonicated for at least 30 min to form a homogeneous ink. Then 5 µL of catalyst ink was deposited on a GC electrode using a pipette and dried in air at room temperature. This procedure was repeated three more times so that a total amount of 20  $\mu$ L catalyst ink were loaded on the electrode, with a loading of 0.2 mg cm<sup>-2</sup>.

Electrochemical studies were carried out in a standard three-electrode system controlled by a multi-channel potentiostat (Princeton Applied Research). The modified-GC electrodes described above as the working electrodes, were mounted onto a rotator with rotation-speed control system (Pine Instruments) and was immersed into 0.1 M KOH solution. An Ag/AgCl electrode was used as the reference electrode and a Pt wire was used as the counter electrode. The  $M_xO_y$  /SWNT was cycled at least 30 times by CV at the scan rate of 50 mV s<sup>-1</sup> until a stable CV curve was reached before measuring polarization curves. Linear sweep voltammetry was carried out at 5 mV s<sup>-1</sup> for the polarization curves in an O<sub>2</sub>-saturated electrolyte. When comparing the ORR electrocatalytic activity among the  $M_xO_y$ /SWNT samples, the constant rotating speed was set at 1600 rpm. For the OER, the polarization curves were recorded at the rotation rate of 2500 rpm and corrected for solution resistance, which was measured using AC-impedance spectroscopy from 200 kHz to 100 mHz and a voltage perturbation of 10 mV. The overpotential of the  $M_xO_y$ /SWNT samples were referenced to Ag/AgCl electrode.

In details, the Koutecky–Levich (K–L) equation show the inverse current density  $(j^{-1})$  as a function of the inverse of the square root of the rotation speed  $(\omega^{-1/2})$  at different potential values. The number of electrons transfer in the reduction of per O<sub>2</sub> in the ORR on the catalysts is determined by the K-L equation:[18]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$
 5.1

where  $j_k$  represents the kinetic current and  $\omega$  is the electrode rotating speed. *B* is determined from the slope of the K–L plots ( $j^{-1}$  vs.  $\omega^{-1/2}$ ) based on the Levich equation:[18]

$$B = 0.2nFD_{O_2}^{2/3}\vartheta^{-1/6}C_{O_2}$$
 5.2

where *n* is the number of electrons transfer per O<sub>2</sub> reduction, *F* is the Faraday constant (*F*=96485 C mol<sup>-1</sup>),  $D_{O_2}$  is the diffusion coefficient of O<sub>2</sub> in electrolyte,  $\vartheta$  is the kinetic viscosity, and  $C_{O_2}$  is the bulk concentration of O<sub>2</sub>.

The turn of frequency (TOF) value is calculated from the following equation: [19]

$$\text{TOF} = \frac{jA}{4Fm}$$
5.3

where j is the current density at the overpotential of 0.3 V, A is the thin film electrode area, F is the Faraday constant, m is the moles of the active materials deposited on the GC electrode.

## 5.2.4 Lithium-ion battery electrochemical testing

The total mass of free-standing  $M_xO_y/SWNT$  films as working electrodes were weighed by a micro/ultramicro balance (Mettler Toledo XP6) with 0.001 mg accuracy. CR2032 coin cells were assembled under a half-cell system with lithium ribbons (0.38 mm thick, 99.9%, Sigma Aldrich) as both counter and reference electrodes in an argonfilled glovebox (MBRAUN UNIIab). Celgard 2500 were used as separators. Electrolyte is 1 M LiPF<sub>6</sub> dissolved in 1:1 (v/v) EC: DEC from Ferro Co. The CV curves were collected by PARSTAT 2273 (Princeton Applied Research) potentiostat. The galvanostatic discharge-charge tests were carried out using BT-4 4-channel battery test equipment (Arbin Instrument, Ltd.).

#### 5.2.5 Asymmetric supercapacitor electrochemical testing

Similarly, the free-standing NiO/SWNT macrofilms were employed as working electrodes. The CV tests of the NiO/SWNT electrodes were performed on the same PARSTAT 2273 potentiostat in a three-electrode cell. Pt wire was used as the counter electrode and Ag/AgCl electrode as reference electrode. The specific capacitance of the electrode can be calculated from the CV curves according to the Equation 1.11 in Chapter 1. To assemble an asymmetric supercapacitor, the loading mass ratio between NiO/SWNT (+) as positive electrode and purified SWNT (-) as negative electrode was estimated to be 0.25 from the equation:

$$\frac{m_+}{m_-} = \frac{c_-\Delta E_-}{c_+\Delta E_+} \tag{5.4}$$

where *m* is the mass, *C* is the specific capacitance and  $\Delta E$  is the potential window for electrode on each side. The subscripts of "+" and "–" represent the positive and negative electrodes, respectively. The electrochemical measurements of the asymmetric supercapacitor were carried out at room temperature under a two-electrode configuration in a CR2032 coin cell with a Whatman® glass microfiber filter as separator in 1M KOH aqueous electrolyte. The cycling performance was measured by GCD tests on the same equipment as used in last chapters. The specific capacitance could be also calculated by the Equation 1.12 in Chapter 1.

## 5.3 **Results and Discussion**

#### 5.3.1 Size, morphology, and structure of M<sub>x</sub>O<sub>y</sub>/SWNT

TEM images show size distribution of the  $Co_3O_4$  nanoparticles in the range of 5-17 nm (Figure 5.2a) and the NiO nanoparticles with a diameter of 3-10 nm (Figure 5.2d).


Figure 5.2 (a, b, d, e) TEM and (c, f) HRTEM images of (a, b, c) Co<sub>3</sub>O<sub>4</sub>/SWNT (200°C) and (d, e, f) NiO/SWNT. Insets: Histograms of the nanoparticle size distribution.

It is noted that the isolated-dispersed tiny particles in Figure 5.2a are Co catalysts, implying an incomplete oxidization at the low temperature of 200°C. In contrast, NiO has a better uniformity with a narrow size distribution due to that the Ni catalysts were fully converted to NiO nanoparticles at 400°C. It suggested and was confirmed that the Co residues in the Co<sub>3</sub>O<sub>4</sub>/SWNT sample (200°C) could be further oxidized when they were heated at 400°C in air. Figures 5.2b and 5.2e show similar morphologies of the  $M_xO_y$ /SWNT macrofilm nanocomposites. Metal oxide nanoparticles are coupled with the entangled serpentine CNT bundles. HRTEM images (Figures 5.2c and 5.2f) reveal the well-defined lattice fringes corresponding to face-centered cubic Co<sub>3</sub>O<sub>4</sub> and NiO, respectively. TGA demonstrates 23 wt.% CNT in the Co<sub>3</sub>O<sub>4</sub>/SWNT nanocomposite (200°C) while the NiO/SWNT nanocomposite contains only 12 wt.% carbon scaffold.

XRD and Raman spectroscopy further confirm the transformation from metal catalysts to metal oxides during calcination. The XRD patterns before and after heat treatments are shown in Figures 5.3a and 5.3b. The results indicate that the crystal structure of  $Co_3O_4$  is cubic phase with *Fd-3m* space group according to JCPDS No. 42-1467 and NiO is of the natural Brunsenite phase with *Fm-3m* space group (JCPDS No. 47-1049). This is in a good agreement with the HRTEM observations. Consistently, two distinct phases,  $Co_3O_4$  (marked by asteroid) and pure Co (marked by spade) are present in the XRD pattern of the  $Co_3O_4/SWNT$  sample (200°C). The absence of Co diffraction peaks in the  $Co_3O_4/SWNT$  sample (400°C) confirms the complete oxidation of the Co catalysts by annealing at 400°C. Raman spectra (Figure 5.3c) show the RBM features of single-walled CNT for all the samples at the wavenumber of ~ 100 cm<sup>-1</sup> as well as the typical D and G modes at 1350 cm<sup>-1</sup> and 1587 cm<sup>-1</sup>, consistent with the TEM results.[20]



Figure 5.3 (a) XRD pattrens of Co-CNT (100°C), Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400°C). (b) XRD patterns of Ni-CNT and NiO/SWNT. (c) Raman spectra of Co-CNT (100°C), Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400°C), Ni-CNT, and NiO/SWNT.

The presence of two small peaks,  $E_g$  (488 cm<sup>-1</sup>) and  $F_{2g}$  (522 cm<sup>-1</sup>) separate at each side of 500 cm<sup>-1</sup> with  $F_{2g}$  (618 cm<sup>-1</sup>) and the strongest peak  $A_{1g}$  (691 cm<sup>-1</sup>) are typically indicative of the Co<sub>3</sub>O<sub>4</sub> formation after the heat treatment.[21] Likewise, the first-order transverse optical (TO, 404 cm<sup>-1</sup>), longitudinal optical (LO, 564 cm<sup>-1</sup>), and two twophoton (2TO at 705 cm<sup>-1</sup>, 2LO at 1080 cm<sup>-1</sup>) peaks belong to NiO nanoparticles.[9,22]

# 5.3.2 Electrocatalytic properties of M<sub>x</sub>O<sub>y</sub>/SWNT

## 5.3.2.1 ORR activity

The electrocatalytic properties of  $M_xO_y/SWNT$  were investigated using a standard three-electrode system in an alkaline solution (see details in Experimental

section). The nanocomposites were uniformly cast onto a GC RDE (dia. 5 mm) with a mass loading of ca. 0.2 mg cm<sup>-2</sup> to study both ORR and OER activities. According to the TGA results, the actual loadings of Co<sub>3</sub>O<sub>4</sub> and NiO nanoparticles are 154 µg cm<sup>-2</sup> and 178 µg cm<sup>-2</sup>, respectively. Figure 5.4a shows the ORR polarization curves for the two Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400 °C) samples, NiO/SWNT, Fe<sub>2</sub>O<sub>3</sub>/SWNT, and Co-CNT macrofilms baked in air at 100 °C for 30 min (denoted as Co-CNT (100 °C) for only Co phase detectable in XRD pattern). The measurements were carried out in an O<sub>2</sub>-saturated 0.1 M KOH at a slow scan rate of 5 mV s<sup>-1</sup> to minimize capacitive current under a rotation rate of 1600 rpm. By analogy to other Fe-containing systems, Fe<sub>2</sub>O<sub>3</sub>/SWNT has two distinct shoulders, one at an onset potential of -0.25 V (*vs.* Ag/AgCl) and a half peak with an inflection point at -0.6 V, indicating that the ORR process is mainly a two-electron O<sub>2</sub> reduction mechanism according to the reaction:  $O_2 + H_2O + 2e^- \rightarrow HOO^- + OH^-$ .[23]



Figure 5.4 Electrocatalytic performance of M<sub>x</sub>O<sub>y</sub>/SWNT under RDE measurements in O<sub>2</sub>-saturated 0.1 M KOH with scan rate of 5 mV s<sup>-1</sup>. (a) ORR polarization curves of Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400°C), NiO/SWNT, Fe<sub>2</sub>O<sub>3</sub>/SWNT, and Co-CNT (100°C) catalysts at a continuous electrode rotating speed of 1600 rpm. (b) ORR polarization curves of Co<sub>3</sub>O<sub>4</sub>/SWNT (200°C) at different rotation rates. (c) K-L plots from (b). (d) *iR*-corrected OER polarization curves of Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400°C), NiO/SWNT, Fe<sub>2</sub>O<sub>3</sub>/SWNT, and Co-CNT (100°C) at rotation rate of 2500 rpm. (e) Tafel plots from (d).

The second shoulder can be assigned to the further electroreduction of  $H_2O_2$  (H00<sup>-</sup>) to H<sub>2</sub>O. Beyond -0.6 V to the more negative potential, the merely ORR active sites, Fe(II) ions, in Fe<sub>2</sub>O<sub>3</sub> play a predominant role binding both O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> to form OHOH adducts.[24] The strong bonding of H<sub>2</sub>O<sub>2</sub> to Fe(II) prevents it from leaving and thus provides a path for final reduction to water.[26] On the contrary, the polarization curves from both Co-CNT (100 °C) and Co<sub>3</sub>O<sub>4</sub>/SWNT (200°C) only have a single shoulder with a sharper current increase and reach quickly to a steady state, typically representing a four-electron reduction of O<sub>2</sub>  $(O_2 + 2H_2O + 4e^- \rightarrow 4OH^-)$ .[5] The ORR activity of NiO/SWNT is comparable with Co<sub>3</sub>O<sub>4</sub>/SWNT (400°C) because of their nearly identical ORR onset potentials. The well-defined peak (-0.5/0.6 V) on the curve of Co<sub>3</sub>O<sub>4</sub>/SWNT (400°C) is probably attributed to the surface effect related to ORR activity, which is similar to Au with variable activities on (100), (110) and (111) surfaces.[25] Notably, Co<sub>3</sub>O<sub>4</sub>/SWNT (200°C) exhibits a more positive half-wave potential of -0.216 V than Co-CNT (100 °C) with -0.271 V and Co<sub>3</sub>O<sub>4</sub>/SWNT (400°C) (-0.35 V). It suggests that the introduction of Co<sub>3</sub>O<sub>4</sub> phase with the retention of some Co catalysts in the  $Co_3O_4$ /SWNT sample (200°C) treated at a medium temperature leads to a significant enhancement in electrocatalytic performance for ORR. Compared with the graphene-Co/CoO nanoparticles, which shown an outstanding ORR activity reported by S. Sun et al., [5]  $Co_3O_4$ /SWNT (200°C) has a balanced performance with a higher steady-state current density (~6 mA cm<sup>-2</sup> vs. ~4 mA cm<sup>-2</sup>) offsetting the 40 mV difference in the half-wave potential. Additionally, polarization curves under different rotation rates (Figure 5.4b) reveal a function relation between the inverse of both limiting current density and the square root of rotation rate. Based on these data, three K-L plots at different potentials (Figure 5.4c) were obtained. The linearity at -0.3 V, -0.5 V and -0.7 V proves the first order reaction kinetics toward the concentration of  $O_2$  on  $Co_3O_4$ /SWNT (200°C).[5] The corresponding number of electrons involved per  $O_2$  in the ORR is determined between 3.8 and 3.9 from K-L and Levich equations.[7,26] It further confirms the four-electron ORR process of the sample.

## 5.3.2.2 OER activity

Figure 5.4d shows *iR*-corrected OER polarization curves (the solution resistance *R* is *ca.* 44  $\Omega$  by AC-impedance spectroscopy and see details in Section 5.2.2) for the same five samples in the ORR tests. During the measurements, the working electrode was rotating at 2500 rpm to remove the generated oxygen bubbles. Among all the samples, the NiO/SWNT catalyst shows the highest OER activity reflected by the lowest onset potential of OER and the sharpest current. The peak couple around overpotential of 0.1 V and 0.17 V is assigned to the Ni(II)/Ni(III or IV) redox process. Consistently, the Tafel slope (Figure 5.4e), 36 mV dec<sup>-1</sup>, of NiO/SWNT is much smaller than that of Co-CNT (100 °C) (53 mV dec<sup>-1</sup>), Co<sub>3</sub>O<sub>4</sub>/SWNT (200, 400 °C) (73 mV dec<sup>-1</sup>), and Fe<sub>2</sub>O<sub>3</sub>/SWNT (77 mV dec<sup>-1</sup>). Its overpotential of 0.30 V at a fixed current density of 10 A g<sub>catalyst</sub><sup>-1</sup> and Tafel slope of 36 mV dec<sup>-1</sup> are comparable with 0.28 V and 35 mV dec<sup>-1</sup> <sup>1</sup> of NiFe-layered double hydroxide (LDH)/CNT reported by H. Dai et al.[26] It indicates that NiO/SWNT has an OER activity as high as NiFe-LDH/CNT. In terms of these two values, NiO/SWNT has better OER performance than the highly OER active Au@Co<sub>3</sub>O<sub>4</sub> catalysts reported by Y. Yan *et al.*[27] The TOF of 0.604 s<sup>-1</sup> was also comparable to that of the most active perovskite-based catalyst, assuming all the metal sites were involved in the electrochemical reaction (See Section 5.2.2 for detailed calculations).[26] By summarizing the OER and ORR performance of the M<sub>x</sub>O<sub>y</sub>/SWNT

nanocomposites, we can conclude that each material system favors their own advantages in a specific reaction.

## **5.3.3** Battery performance

Besides electrocatalysis, the M<sub>x</sub>O<sub>y</sub>/SWNT nanocomposites are also an important family of energy storage materials particularly as high-capacity anodes for lithium-ion batteries. As an exemplary demonstration in Chapter 4, the electrochemical performance was studied in a half cell that consists of the free-standing M<sub>x</sub>O<sub>y</sub>/SWNT macrofilms as working electrodes and lithium metal as both counter and reference electrodes under a two-electrode configuration. CV was performed at an extremely slow scan rate of 0.1 mV s<sup>-1</sup> to adapt to the sluggish kinetics of lithiation/delithiation. The CV plot (Figure 5.5a) exhibits the first two cycles for  $M_x O_y/SWNT$  in fresh cells. The cathodic peaks at the potential higher than 1 V vs. Li<sup>+</sup>/Li on the first-cycle curves for both samples are ascribed to the formation of a SEI film.[9,28] The disappearance of them in the second cycle indicates the irreversible processes of SEI.[5] The peaks with a maximum current at 0.45 V and 0.87 V for NiO/SWNT and Co<sub>3</sub>O<sub>4</sub>/SWNT, respectively, are assigned to the reduction of M ions to  $M^0$  according to conversion reactions  $(2yLi + M_xO_y \leftrightarrow$  $xM + yLi_2O$  ).[29] Both the reactions shift to a more positive potential on the CV curves in the following cycle. The difference in the number of the cathodic peaks (one at 1 V for NiO/SWNT, two at 0.9 V and 1.36 V for Co<sub>3</sub>O<sub>4</sub>/SWNT) suggests the different reduction steps from the single oxidized state of Ni (II) in NiO and the multi-oxidized states of Co (II or III) in Co<sub>3</sub>O<sub>4</sub>, which agrees with the previously reported results of Fe<sub>2</sub>O<sub>3</sub>. Afterwards, the subsequent galvanostatic discharge/charge cycling measurements were carried out between 0.001-3 V at a constant current density of 50 mA g<sup>-1</sup> involving the same samples. Figure 5.5b shows their discharge/charge voltage

profiles. Consistent with the CV analysis, two plateaus at ~1.5 V and ~1 V on the discharge curve of Co<sub>3</sub>O<sub>4</sub>/SWNT were observed corresponding to the two cathodic peaks while NiO/SWNT has one plateau at ~1 V during discharge. A common discharge tail in the low voltage region between 0.8 V and 0.001 V with more inclined slope is present for  $M_xO_y/SWNT$ , which is attributed to the partial capacity contribution from SWNT macrofilms. Upon charging, there are two plateaus for both samples, which originate from the reverse processes of the conversion reactions from  $M^0$  to  $M_x O_v$ .[28] For Co<sub>3</sub>O<sub>4</sub>/SWNT, they (1.26 V and 2 V) correspond to the two anodic peaks at 1.28 V and 2 V on the CV curve. In contrast, NiO/SWNT has the higher ones at 1.32 V and 2.2 V corresponding to peaks (1.39 V and 2.22 V) in the CV plot. The continuous cycling results of NiO/SWNT over 80 cycles are selectively recorded in every 10 cycles as shown in Figures 5.5c and 5.5d. Basically, the discharge/charge curves are almost overlapped (Figure 5.5c), indicating a good cyclic stability. The discharge capacity maintains at 894 mAh g<sup>-1</sup> after 80 cycles with a retention as high as 88%. Compared with non-free-standing NiO/graphene (883 mAh g<sup>-1</sup> after 50 cycles) [9] and Co<sub>3</sub>O<sub>4</sub>/graphene (~935 mAh g<sup>-1</sup> after 30 cycles) [30] nanocomposites prepared by the cumbersome synthesis, to the best of our knowledge, the M<sub>x</sub>O<sub>y</sub>/SWNT nanocomposites (over 1000 mAh g<sup>-1</sup>) demonstrate one of the best electrochemical performance with an additional binder-free benefit among the reported hybrid anode materials.



Figure 5.5 LIB performance of  $M_xO_y/SWNT$  in half cells. (a) CV curves at a slow scan rate of 0.1 mV s<sup>-1</sup>, and (b) Galvanostatic discharge/charge voltage profiles at a constant current density of 50 mA g<sup>-1</sup> after CV tests of  $Co_3O_4/SWNT$  and NiO/SWNT. (c) Discharge/charge curves at the selected cycles, (d) Cycling performance of NiO/SWNT electrodes.

# 5.3.4 Supercapacitor performance

In spite of the higher energy density, LIBs usually suffer from a lower power density than supercapatiors. To take advantage of both virtues of these two energy storage devices, we compose the asymmetric supercapacitors with a battery-type Faradaic electrode (as the energy source) and a capacitor-type electrode (as the power source).[31] They can extend their operation voltages in the cell system with an aqueous electrolyte beyond the water splitting limit (~1.23 V) by making full use of the two

electrodes at different potential windows, consequently resulting in an enhanced specific capacitance and significantly improved energy density.[31] Figure 5.6a shows the typical CV curves of the NiO/SWNT nanocomposite at different scan rates in 1 M KOH aqueous solution. All the CV curves have a pair of strong redox peaks, which are representative of the pseudo-capacitive behavior due to Faradaic redox reactions. This is distinct from an approximately ideal rectangular shape of CV curves for electric double layer capacitors. The redox couple, for example, located at around 0.27 V (cathodic)/0.35 V (anodic) vs. Ag/AgCl at the scan rate of 50 mV s<sup>-1</sup>, is attributed to the reversible Faradaic redox reactions between NiO and NiOOH according to the equation:  $NiO + OH^- - e^- \leftrightarrow NiOOH$ . [32] The specific capacitance of the NiO/SWNT electrodes as a function of scan rates calculated from the CV curves (inset of Figure 5.6a) is stable at ~400 F g<sup>-1</sup>, suggesting the fast charge transfer in the Faradaic processes.[28] Purified SWNT macrofilms without metal oxide nanoparticles, which deliver a specific capacitance of ~40 F g<sup>-1</sup> as described in previous work,[33] are employed as negative electrodes to assemble the asymmetric supercapacitors in 1 M KOH aqueous electrolyte with the NiO/SWNT positive electrodes by carefully matching their mass ratio (See Section 5.2.3). Figure 5.6b exhibits the CV curves of the asymmetric supercapacitor at various scan rates from 5 to 200 mV s<sup>-1</sup> within an operation voltage window of 1.5 V. The specific capacitance of the asymmetric cell (based on the total mass of the two electrodes) maintains as high as 249 F g<sup>-1</sup> at 200 mV  $s^{-1}$  from 468 F  $g^{-1}$  at 5 mV  $s^{-1}$  as the scan rate increases.



Figure 5.6 (a) CV curves of NiO/SWNT at various scan rates. Inset: Specific capacitance as a function of the scan rates calculated from CV. (b) CV curves of an asymmetric supercapacitor composed of (+) NiO/SWNT-SWNT (-) at different scan rates between 5 - 200 mV s<sup>-1</sup>. Inset: Specific capacitance vs. scan rates. (c) Galvanostatic charge/discharge cyclic performance of the asymmetric supercapacitor within a voltage window of 1.5 V at a current density of 20 A g<sup>-1</sup>. Inset: charge/discharge curves.

The GCD curves at a current density of 20 A  $g^{-1}$  (inset of Figure 5.6c) show a good linear correlation of voltage with time, confirming a rapid I-V response of NiO/SWNT.[34] The nearly-equilateral triangular shapes demonstrate the excellent electrochemical reversibility. It is worth noting that at such a high current density, the specific capacitance approaches a steady state during long-life cycling up to 5000 cycles.

The performance above 130 F  $g^{-1}$  is sufficiently high to enable the asymmetric supercapacitor with qualified high energy and power density for durable and practical applications.

# 5.4 Conclusions

In the end, based on Chapter 4, we have demonstrated a general and facile strategy for synthesizing  $M_xO_y$  (M=Fe, Co, Ni)/SWNT macrofilm nanocomposites *via* CVD growth followed by a thermal treatment. We have also successfully demonstrated their promise in other energy applications including electrocatalysis and supercapacitors. NiO/SWNT and Co<sub>3</sub>O<sub>4</sub>/SWNT (200 °C) have high intrinsic OER and ORR electrocatalytic activities in alkaline solutions, respectively. NiO/SWNT also exhibits an excellent electrochemical performance in asymmetric supercapacitors with a high power and energy density. All  $M_xO_y$ /SWNT have shown a high specific capacity and cycling stability for lithium-ion batteries. We also uncovered that NiO/SWNT has a fast charge transport process in Faradaic redox reactions and the calcination temperature has an influence on the ORR activity of Co<sub>3</sub>O<sub>4</sub>/SWNT. This work proposed an important family of material candidates to serve industry. It may also stimulate the evolution of new technique involving production of many advanced, low-cost transitional metal oxide nanocomposites for energy applications.

# REFERENCES

- 1 Cao, Z., Wei, B. Q., α-Fe<sub>2</sub>O<sub>3</sub>/single-walled carbon nanotube hybrid films as high-performance anodes for rechargeable lithium-ion batteries. *Journal of Power Sources* **2013**, 241, 330-340.
- 2 Wang, Z., Luan, D., Madhavi, S., Hu, Y., Lou, X. W., Assembling carboncoated α-Fe<sub>2</sub>O<sub>3</sub> hollow nanohorns on the CNT backbone for superior lithium storage capability. *Energy & Environmental Science* **2012**, 5(1), 5252-5256.
- 3 Su, J., Cao, M., Ren, L., Hu, C., Fe<sub>3</sub>O<sub>4</sub>–graphene nanocomposites with improved lithium storage and magnetism properties *The Journal of Physical Chemistry* C 2011, 115(30), 14469-14477.
- 4 Cao, Z., Wei, B. Q., High rate capability of hydrogen annealed iron oxidesingle walled carbon nanotube hybrid films for lithium-ion batteries. *ACS Applied Materials & Interfaces* **2013**, 59(20), 10246-10252.
- 5 Guo, S., Zhang, S., Wu, L., Sun, S., Co/CoO nanoparticles assembled on graphene for electrochemical reduction of oxygen. *Angewandte Chemie International Edition.* **2012**, 124(47), 11940-11943.
- 6 Wu, Z.-S., Ren, W., Wen, L., Gao, L., Zhao, J., Chen, Z., Zhou, G., Li, F., Cheng, H.-M., Graphene anchored with Co<sub>3</sub>O<sub>4</sub> nanoparticles as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance. *ACS Nano* **2010**, 4(6), 3187-3194.
- 7 Liang, Y., Wang, H., Diao, P., Chang, W., Hong, G., Li, Y., Gong, M., Xie, L., Zhou, J., Wang, J., Regier, T. Z., Wei, F., Dai, H., Oxygen reduction electrocatalyst based on strongly coupled cobalt oxide nanocrystals and carbon nanotubes. *Journal of American Chemistry Society* **2012**, 134(38), 15849-15857.
- 8 Lee, J. Y., Liang, K., An, K. H., Lee, Y. H., Nickel oxide/carbon nanotubes nanocomposite for electrochemical capacitance. *Synthetic Metal* **2005**, 150(2), 153-157.
- 9 Zhou, G., Wang, D.-W., Yin, L.-C., Li, N., Li, F., Cheng, H.-M., Oxygen bridges between NiO nanosheets and graphene for improvement of lithium storage. ACS Nano 2012, 6(4), 3214-3223.
- 10 Cao, Z., Wei, B. Q., V<sub>2</sub>O<sub>5</sub>/single-walled carbon nanotube hybrid mesoporous films as cathodes with high-rate capacities for rechargeable lithium ion batteries. *Nano Energy* **2013**, 2(4), 481-490.

- Yu, G., Hu, L., Liu, N., Wang, H., Vosgueritchian, M., Yang, Y., Cui, Y., Bao,
  Z., Enhancing the supercapacitor performance of graphene/MnO<sub>2</sub>
  nanostructured electrodes by conductive wrapping. *Nano Letters* 2011, 11(10), 4438-4442.
- 12 Qin, J., Zhang, Q., Cao, Z., Li, X., Hu, C., Wei, B. Q., MnO<sub>2</sub>/SWCNT macrofilms as flexible binder-free anodes for high-performance Li-ion batteries. *Nano Energy* **2013**, 2(5), 733-741.
- 13 Xu, C., Xu, B., Gu, Y., Xiong, Z., Sun, J., Zhao, X., Graphene-based electrodes for electrochemical energy storage. *Energy & Environmental Science* **2013**, 6(5), 1388-1414.
- 14 Cao, Z., Wei, B. Q., A perspective: carbon nanotube macro-films for energy storage. *Energy & Environmental Science* **2013**, 6(11), 3183-3201.
- 15 Poizot, P., Laruelle, S., Grugeon, S., Dupont, L., Tarascon, J. M., Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature* **2000**, 407(6803), 496-499.
- 16 Li, J., Tang, S., Lu, L., Zeng, H. C., Preparation of nanocomposites of metals, metal oxides, and carbon nanotubes via self-assembly. *Journal of the American Chemical Society 2007*, 129(30), 9401-9409.
- 17 Grugeon, S., Laruelle, S., Herrera-Urbina, R., Dupont, L., Poizot, P., Tarascon, J.-M., Particle size effects on the electrochemical performance of copper oxides toward lithium. *Journal of The Electrochemical Society* 2001, 148(4), A285-A292.
- 18. Wang, S., Yu, D., Dai, L., Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction. *Journal of the American Chemical Society* **2011**, 133(14), 5182-5185.
- 19. Esswein, A. J., McMurdo, M. J., Ross, P. N., Bell, A. T., Tilley, T. D., Sizedependent activity of Co3O4 nanoparticle anodes for alkaline water electrolysis. *The Journal of Physical Chemistry C* **2009**, 113(33), 15068-15072.
- 20. Jorio, A., Pimenta, M., Souza Filho, A., Saito, R., Dresselhaus, G., Dresselhaus, M. Characterizing carbon nanotube samples with resonance Raman scattering. *New Journal of Physics* **2003**, 5(1), 139.
- 21. Hadjiev, V., Iliev, M., Vergilov, I., The Raman spectra of Co<sub>3</sub>O<sub>4</sub>. *Journal of Physics C: Solid State Physics* **1988**, 21(7), L199.

- 22. Wang, W., Liu, Y., Xu, C., Zheng, C., Wang, G., Synthesis of NiO nanorods by a novel simple precursor thermal decomposition approach. *Chemical Physics Letters* **2002**, 362(1), 119-122.
- 23. Grumelli, D., Wurster, B., Stepanow, S., Kern, K., Bio-inspired nanocatalysts for the oxygen reduction reaction. *Nature Communications* **2013**, 4, 2904.
- 24. Anderson, A. B., Sidik, R. A., Oxygen electroreduction on FeII and FeIII coordinated to N4 chelates. reversible potentials for the intermediate steps from quantum theory. *The Journal of Physical Chemistry B* **2004**, 108(16), 5031-5035.
- 25. Kim, J., Lee, S. W., Chen, S., Shao-Horn, Y., Synthesis and oxygen reduction reaction activity of atomic and nanoparticle gold on thiol-functionalized multiwall carbon nanotubes. *Electrochemical and Solid-State Letters* **2011**, 14(10), B105-B109.
- Gong, M., Li, Y., Wang, H., Liang, Y., Wu, J. Z., Zhou, J., Wang, J., Regier, T., Wei, F., Dai, H., An advanced Ni–Fe layered double hydroxide electrocatalyst for water oxidation. *Journal of the American Chemical Society* 2013, 135(23), 8452-8455.
- 27. Zhuang, Z., Sheng, W., Yan, Y., Synthesis of Monodispere Au@ Co<sub>3</sub>O<sub>4</sub> coreshell nanocrystals and their enhanced catalytic activity for oxygen evolution reaction. *Advanced Materials* **2014**, 26(23), 3950-3955.
- Varghese, B., Reddy, M., Yanwu, Z., Lit, C. S., Hoong, T. C., Subba Rao, G., Chowdari, B., Wee, A. T. S., Lim, C. T., Sow, C.-H., Fabrication of NiO nanowall electrodes for high performance lithium ion battery. *Chemistry of Materials* 2008, 20(10), 3360-3367.
- 29. Taberna, P. L., Mitra, S., Poizot, P., Simon, P., Tarascon, J. M., High rate capabilities Fe<sub>3</sub>O<sub>4</sub>-based Cu nano-architectured electrodes for lithium-ion battery applications. *Nature materials* **2006**, 5(7), 567-573.
- 30. Wu, Z.-S., Ren, W., Wang, D.-W., Li, F., Liu, B., Cheng, H.-M., High-energy MnO<sub>2</sub> nanowire/graphene and graphene asymmetric electrochemical capacitors. *ACS Nano* **2010**, 4(10), 5835-5842.
- 31. Yan, J., Fan, Z., Sun, W., Ning, G., Wei, T., Zhang, Q., Zhang, R., Zhi, L., Wei, F., Advanced asymmetric supercapacitors based on Ni(OH)<sub>2</sub>/Graphene and porous graphene electrodes with high energy density. *Advanced Functional Materials* **2012**, 22(12), 2632-2641.

- 32. Lu, Q., Lattanzi, M. W., Chen, Y., Kou, X., Li, W., Fan, X., Unruh, K. M., Chen, J. G., Xiao, J. Q., Supercapacitor electrodes with high-energy and power densities prepared from monolithic NiO/Ni nanocomposites. *Angewandte Chemie Internation Edition* **2011**, 123(30), 6979-6982.
- 33. Yu, C., Masarapu, C., Rong, J., Wei, B., Jiang, H., Stretchable supercapacitors based on buckled single-walled carbon nanotube macrofilms. *Advanced Materials* **2009**, 21(47), 4793-4797.
- 34. Fan, Z., Yan, J., Wei, T., Zhi, L., Ning, G., Li, T., Wei, F., Asymmetric supercapacitors based on graphene/MnO<sub>2</sub> and activated carbon nanofiber electrodes with high power and energy density. *Advanced Functional Materials* **2011**, 21(12), 2366-2375.

# Chapter 6

# A GENERAL APPROACH TO CONSTRUCT NANOCOMPOSITE ELECTRODES BY USING FRAGMENTED CARBON NANOTUBE MACROFILMS AS ADHESIVE CONDUCTORS FOR LITHIUM-ION BATTERIES

# 6.1 Introduction

Although the fabrication of nanocomposites combining a family of transition metal oxides (M<sub>x</sub>O<sub>y</sub>, M=Fe, Co, Ni) with SWNT macrofilms have been unified by a facile method in Chapters 4 and 5, a more general approach to construct nanocomposite electrodes with other active materials for practical use in industry is still desired. In conventional electrode design and manufacturing for any active materials, we usually divide the composite into three independent and indispensable components: active materials, conductive additives, and polymer binders and then fabricate them into composites. Acetylene carbon black, [1, 2] CNT, [3, 4] and graphene [5, 6] are three most common conductive additives that have been employed to construct a conductive matrix incorporating active materials spanning from cathode materials e.g. LiCoO<sub>2</sub> [7] and LiFePO<sub>4</sub> [8] to anode materials e.g. Fe<sub>2</sub>O<sub>3</sub> and Si. [9, 10] However, these conductive additives are barely used alone without any binder materials because it is commonly regarded that they cannot provide adhesive forces for the active materials to withstand long charge/discharge cycles. Thus, it is necessary to use polymer binders such as poly(vinylidene difluoride) (PVDF), [11, 12] phenol-formaldehyde (PF), [13] styrene butadiene rubber (SBR), [14] polyacrylic acid (PAA), [15] carboxymethylcellulose (CMC), [16] and *etc.* to maintain mechanical integrity of the composite electrodes. Although the polymer binders play crucial roles in electrode manufacturing, their electrochemical inactivity contributes nothing but impairs the specific capacity of the

whole electrodes. To overcome these challenges, a strategy to develop conductive binders such as poly(9,9-diotylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM), [17] polyaniline (PANi), [18] and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) [19] with "bifunctional" properties has been naturally proposed to replace both PVDF and carbon additives to improve the capacity and lifetime of batteries. However, these conductive polymers typically cannot provide a comparable electronic conductivity to the carbon additives. It also inevitably involves expensive and toxic organic solvents such as *N*-methyl-pyrrolidone (NMP). [20]

In parallel with this "bifunctional" concept, an adhesive conductor possessing both binding and conducting functions from pure carbon nanostructures is seldom reported. In fact, some specific forms of carbon such as the stretchy uncrumbled graphene sheets do bear adhesive properties and could act as both conductive additives and binders. [21] The irregular, laterally 2-D distributed CNT segments are also convinced to be able to enhance adhesion force of vertically-aligned CNT arrays, which could perform the mechanical binding function inspired from the gecko feet. [22] It is expected that these "bifunctional" adhesive conductors can not only provide an alternative to PVDF and carbon blacks to improve the battery performance but also is a revolution to electrode "Green" manufacturing by avoiding NMP and other toxic organic solvents. Thus, in this chapter, we demonstrate a most general approach to construct nanocomposite electrodes by applying fragmented CNT macro-films (FCNT) as adhesive conductors in two nanocomposite demo-systems: two half cells comprising cathode material, LiMn<sub>2</sub>O<sub>4</sub> (LMO) and anode materials, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) as working electrodes, respectively. The FCNT meshes are more like the cross-links in polymers to be entangled together with an adhesive property. They performs stronger adhesive strength and better electrochemical performance than conventional combination of PVDF and carbon blacks. To the best of our knowledge, this is the first-time report on the FCNT as a potential substitute of polymer binders and carbon additives for LIBs.

#### 6.2 Experimental

#### 6.2.1 Synthesis of SWNT macrofilms, LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanocrystals

First, SWNT macro-films were prepared according to the direct CVD method previously described in Chapter 1.

The LiMn<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized as Jaephil Cho *et al.* reported:[23] All the chemicals in the following were purchased from Sigma Aldrich and used as received. A solution is prepared by dissolving 0.22 g lithium hydroxide into 6 ml deionized water followed by adding 0.24 ml hydrogen peroxide (30 wt%). 0.69 g manganese acetate is dissolved in 6 ml deionized water. Blending the prepared solutions with 20 ml methanol and stirred for 20 min. Then the resulting black-brownish slurry was transferred into a 40 ml Teflon-lined autoclave and hydrothermally reacted at 115 °C for 12 h. After the reaction was complete, the solid precipitates were collected and washed several times with deionized water and ethanol. Finally, the black nanoparticles were dried in air at room temperature.

The Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanoparticles were synthesized by a similar hydrothermal method. Briefly, 1.7 ml of hydrogen peroxide was dispersed in 0.4 M lithium hydroxide with 40 ml methanol. Then 3 mM of titanium (IV) butoxide was added to the above solution. After stirring for 1 h, the solution was poured into a 40 ml Teflon-lined autoclave and the hydrothermal reaction was carried out at 130 °C for 12 h. Then the as-prepared white precipitates were washed *via* centrifugation with deionized water and ethanol for several times. After dried completely in air overnight, the sample was annealed in Ar atmosphere at 500 °C for 5h to obtain the final product, LTO nanoparticles.

# 6.2.2 Preparation of LMO-FCNT nanocomposite cathodes and LTO-FCNT anodes

The fabrication procedures of the LMO-FCNT composite electrodes can be completed within three steps as illustrated by the schematic in Figure 6.1.



Figure 6.1 Schematic illustration of preparing LMO-FCNT composite electrodes by ultrasound processing and drop casting.

Freestanding SWNT macrofilms and LMO or LTO nanoparticles are weighed by analytical balance (A&D weighing) microbalance. They are mixed in proper concentration with deionized water or ethanol solution (1:1 by volume) followed by ultrasonication generated from ultrasonic power (UP200S, hielscher ultrasound technology). The resulting ink solutions consisting of CNT fragments coupling with LMO or LTO nanoparticles was casted dropwisely on aluminum/copper disks with diameter of 1/2 inch as the current collectors. Then the electrodes were fabricated when the ink was naturally dried. No any organic solvents have been employed. Three samples of LMO-FCNT composite electrodes with desired mass loading of FCNT are prepared: 5 wt%, 15 wt%, and 30 wt%. The sample of LTO-FCNT with 30 wt% of FCNT is also prepared.

# 6.2.3 *In situ* tribology with wear track imaging force measurement system setup

The working mechanism of *in situ* tribology method is illustrated in the schematic in Figure 6.2.



Figure 6.2 Schematic illustration of *in-situ* tribology combining adhesion force measurement and wear tracking images.

A hemisphere probe with a radius of 3.174 mm exerts a preload of 2500 mN on the samples and starts sliding at the speed of  $25 \,\mu$ m/s on the sample films. The normal force

 $F_N$  and shear force  $F_f$  are tracked in a time-series chart; meanwhile the morphology of probe contact area is observed and imaged by an optical microscopy accessory. During the whole wear track, shear force  $F_f$  increases quickly to reach a steady state and stays for a long time until declining. The adhesion strength  $\sigma_A$  can be estimated by the equation,  $\sigma_A = F_f/A_c$ , where  $F_f$  is the critical shear force and  $A_c$  is the contact area equal to 0.13 mm<sup>2</sup> by the Hertzian model.[24]

#### 6.2.4 Characterization and electrochemical measurements

The morphology and structure of the LMO-FCNT and LTO-FCNT were characterized by means of SEM (SEM mode, 3kV, Zeiss Auriga 60 FIB/SEM) and TEM (JEOL JEM-2010F). XRD was carried out by Philips X'Pert diffractometer with Cu K $\alpha$  radiation within a 2 $\theta$  range of 10 to 80° at 0.02°/step and 2s/step. Fourier-transform infrared spectroscopy (FTIR, Thermo-Nicolet Nexus 670) was operated from 4000 to 400 cm<sup>-1</sup>. TGA was carried out on a high resolution TGA instrument (Mettler-Toledo, SDA851e) from 0 to 1000 °C at a heating rate of 10 °C/min in flowing air.

The mass of active materials was acquired by deducting the weight of bare Cu/Al substrates from the whole weight of electrodes using a micro/ultramicro balance (Mettler Toledo XP6) with 0.001 mg accuracy. CR2032 coin cells were assembled in an argon-filled glovebox (MBRAUN UNIIab). Half cells consist of the hybrid film as the working electrode, a Celgard 2500 as the separator, and a lithium ribbon (0.38 mm thick, 99.9%, Sigma Aldrich) as the counter electrode in the 1 M LiPF<sub>6</sub> dissolved in 1:1 v/v EC: DEC as electrolyte (Ferro Co.). The EIS was conducted on PARSTAT 2273 potentiostat (Princeton Applied Research) with a 10 mV amplitude of AC signal from 100 kHz to 10 mHz and GCD tests were performed on BT-4 4-channel battery testing equipment (Arbin Instrument, ltd.).

# 6.3 Results and Discussion

# 6.3.1 LMO-FCNT half cells

### 6.3.1.1 General characterization of LMO-FNCT

The entangled SWNT macrofilms are fragmentated to myriad small FCNT meshes by the strong ultrasound-generated impact. These FCNT meshes function as intermediate layers, which are similar to the cross-links linking polymer chains, connecting the LMO nanoparticles to the current collector. First, they can easily wrap the LMO nanopartilces primarily due to their flexbile mesh structures and large surface areas. The functional groups such as carboxylic (-C-O) and hydroxylic (-O-H) on the surface of FCNT may enhance the tight anchoring of the LMO nanoparticles. Secondly, the FCNT's sticky edges made of the SWNT bundle tips resemble the suckers of octopus with the "tentacles" on the surface of the current collector due to the rough contacts. TEM image of the as-prepared LMO nanoparticles in Figure 6.3a exhibits the agglormorate of cubic-shaped nanocrystals with the size in the range of 10-50 nm. TEM images in Figures 6.3b and 6.3c reveal that the LMO nanoparticles are tightly anchored on the entangled SWNT bundles in the LMO-FCNT nanocomposites as expected.



Figure 6.3 (a) TEM and (b, c) high magnification TEM images of LMO-FCNT and (d) HRTEM image of LMO-FCNT showing individual LMO nanocrystal and FCNT mesh.

HRTEM image (Figure 6.3d) clearly shows the fringes of lattice with d-spacing of 4.86 Å assigned to the (111) planes of an individual LMO nanocrystal, coupled with the visibly curved SWNTs in the interwoven FCNT meshes. Indexing of the XRD patterns in the following section confirms the spinel structure of LMO with Fd3m space group referenced to JCPDS 35-0782. The composition of the LMO-FCNT nanocomposite

sample prepared with 30 wt% SWNT macrofilms but casted on the glass slide is examined by EDS mapping. It shows that Mn element is homogeneously distributed in the carbon matrix. The quantitative analysis of the EDS spectrum also indicates that FCNT composes 27.5 wt% of the nanocomposites, containing neglectable amounts of impurities, Na, Si, Al, and S, which come from the glass slide substrate. The weight percentage of FCNT is in a good agreement with 27 wt% FCNT shown in the result of TGA. Note that the slight deviation (less than 3%) of mass loading from the initial input of 30 wt% justifies the desired uniform coupling of LMO with FCNT in compliance with the original weight ratios between LMO and the SWNT macrofilms.

## 6.3.1.2 Electrochemical performance of LMO-FCNT

## 6.3.1.2.1 Specific capacity, rate capability, and cyclic stability of samples

Electrochemical performance of the LMO-FCNT nanocomposite electrodes are evaluated in terms of specific capacity, rate capability, and cyclic stability using the half cells in the two-electrode configuration, which consists of the LMO-FCNT nanocomposites as working electrodes and lithium metal as counter electrodes. The sample with 30 wt% FCNT is a representative to exemplify the electrochemical performance of the LMO-CNT composite electrodes. The charge and discharge curves with selected cycle numbers (1<sup>st</sup>, 2<sup>nd</sup>, 10<sup>th</sup>, 20<sup>th</sup>, 30<sup>th</sup>, 40<sup>th</sup>, and 50<sup>th</sup>) at the current density of 15 mAg<sup>-1</sup> exhibit a typical delithiation/lithiation behavior of LMO with two featured potential plateaus at around 4 and 4.15 V (Figure 6.4a). They are consistent with the two reversible redox couples, *i.e.* 3.95 V/4.05 V and 4.1 V/4.2 V, which are indicative of the transformation between single cubic phases (LiMn<sub>2</sub>O<sub>4</sub>  $\leftarrow \rightarrow$ Li<sub>1-x</sub>Mn<sub>2</sub>O<sub>4</sub>) and coexistence of two phases (LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>0.2</sub>Mn<sub>2</sub>O<sub>4</sub>), respectively, as shown in the CV plots (Figure 6.4b). [25] These two processes can be distinguished by the shape difference of the two redox couples that the former one at the lower potential are broader while the latter at the higher potential are sharper. It is also worth noting that the potential plateaus during discharge rise above the initial curve as cycling. Correspondingly, the anodic peaks in the CV curves shift to higher potentials. Figure 6.4c reveals that the capacity retention remains as high as 94% of the initial discharge capacity *i.e.* 106 mAhg<sup>-1</sup>, after being charged and discharged for 50 cycles. Whereas, the average CE is only 88%, much lower than that at faster rates as shown in Figure 6.4d. Figure 6.4d also demonstrates the high rate capability of the LMO-FCNT. The lower CE at lower rates is caused by more time per cycle for parasitic reactions occurring and consuming charges, such as electrolyte oxidation and loss of Li ions for SEI growth. [26]

In contrast to the control electrodes with the same mass loading of LMO but 15 wt% of PVDF binders and 15 wt% of Super P carbon blacks instead (LMO-15 wt% PVDF-15 wt% CB, Figure 6.4d), LMO-FCNT outperforms with higher capacities at all testing rates of 15, 150, 300, 750, and 1500 mAg<sup>-1</sup>. Furthermore, this capacity difference becomes more evident as the rates increase. For examples, at the current density of 15 mAg<sup>-1</sup>, the capacity comparison at the 5<sup>th</sup> cycle is 109 mAhg<sup>-1</sup> *versus* 87 mAhg<sup>-1</sup> with the difference of 22 mAhg<sup>-1</sup> while it becomes 87 mAhg<sup>-1</sup> versus 49 mAhg<sup>-1</sup> at the 25<sup>th</sup> cycle when current density increases to 750 mAg<sup>-1</sup> and accordingly, the gap is enlarged to 38 mAhg<sup>-1</sup>. The remarkable improvement in capacity definitely benefits from the substantially decreased resistance of charge transfer by replacing the conventional PVDF and CB with the adhesive FCNT conductors. This is indicated in the results of

EIS (detailed discussion as follows), implying that the 2D FCNT mesh-bridged framework enables fast electronic and Li ionic transports.



Figure 6.4 (a) GCD voltage profiles of LMO-FCNT composite electrodes cycled at 15 mAg<sup>-1</sup>. (b) CV curves of LMO-FCNT during the first 5 cycles. (c) Cycling performance of LMO-FCNT at 15 mAg<sup>-1</sup> for 50 cycles. (d) Comparison of rate capability between LMO-FCNT and LMO-PVDF-CB at different rates.

Subsequently, cyclic stability measurement at a higher rate of 150 mAg<sup>-1</sup> for a longer time of 100 cycles is conducted. The voltage profiles in Figure 6.5a show a similar behavior as described above. The potential plateau during discharge is increasing meanwhile the potential plateau upon charge is decreasing as the cycles continue. This

indicates a lower polarization and a higher efficiency. The result is also consistent with the reverse shift of the redox couple at 4.1 and 4.2 V to opposite direction in the CV plots. The corresponding capacity retention in Figure 6.5b confirms a perfect performance with no deterioration as well as that CE is approaching 100% since the 20<sup>th</sup> cycle when it reaches equilibrium.

# 6.3.1.2.2 Effect of different content and optimum mass loading of FCNT adhesive conductors

The GCD results for three samples with 5 wt%, 15 wt%, and 30 wt% of FCNT at the current density of 150 mAg<sup>-1</sup> for 100 cycles are present in Figures 6.5c and 6.5d, showing the effect of different FCNT contents in the nanocomposites on the electrochemical performance of the LMO-FCNT. From their GCD curves (Figure 6.5c), there is no difference except for the extending length of potential plateau with increasing weight percentage of FCNT. Similar to each other in the trend of specific capacity retention as shown in Figure 6.5d, all the three samples' capacities are increasing till the 20<sup>th</sup> cycle, since when the samples with 5 wt% and 15 wt% FCNT start fading while the LMO-30 wt% FCNT nanocomposite electrode maintains stable till the end. The capacity of LMO-5 wt% FCNT decreases faster with the decay slope of 0.15 mAhg<sup>-1</sup>/cycle than LMO-15 wt% FCNT with 0.05 mAhg<sup>-1</sup>/cycle. It can be inferred by linear interpolation method that when the weight of FCNT additives is increased to 20 wt% and above, the decay slope would become ~zero, which means no capacity fading. This inference is experimentally confirmed by the nanocomposite sample containing 30 wt% FCNT.



Figure 6.5 (a) Galvanostatic charge/discharge voltage profiles of LMO-FCNT composite electrodes cycled at 150 mAg<sup>-1</sup>. (b) Cycling performance of LMO-FCNT at 150 mAg<sup>-1</sup>. Comparison of (c) voltage profiles for the 100<sup>th</sup> cycle and (d) cycling performance between LMO-30 wt% FCNT, LMO-15 wt% FCNT and LMO-5 wt% FCNT at 150 mAg<sup>-1</sup>.

Thus, it is supposed that the electrochemical performance is determined by the resistance of charge transfer and the integrity of nanocomposites. EIS result in Figure 6.6a shows the Nyquist plots of four composite electrodes in fresh cells before cycling, including LMO-15 wt% PVDF-15 wt% CB, LMO-5 wt% FCNT, LMO-15 wt% FCNT, and LMO-30 wt% FCNT for comparison. All the samples show a common Randles behavior with a typical semicircle, of which the radius on real-axis is assigned to the resistance of charge transfer, in mid-frequency area. [27] Hence, without fitting curves by equivalent circuit, it can be easily estimated that LMO-15 wt% PVDF-15 wt% CB

has the largest charge-transfer resistance over 600  $\Omega$ . The charge-transfer resistance of the LMO-FCNT is decreased from 250  $\Omega$  to 150  $\Omega$ , and to 100  $\Omega$  as the corresponding FCNT content increases from 5 wt% to 15 wt%, and then 30 wt%. The Bode phase plots (Figure 6.6b) could reveal the information on the integrity of the nanocomposite electrodes. For the LMO-5 wt% FCNT sample, an evident separation of the two distinct peaks at 641 Hz and 16681 Hz in the range of high frequency indicates the amount of FCNT is insufficient to integrally bind the LMO nanoparticles together. So is the curve for LMO-15 wt% PVDF-15 wt% CB where a protruded shoulder at 148 Hz can be deconvoluted from the main peak at 5336 Hz. By contrast, LMO-15 wt% FCNT and LMO-30 wt% FCNT have a good integrity with no phase separation in the Bode phase curves. Therefore, combination of the best integrity, the best conductivity, and the lowest charge-transfer resistance results in the best electrochemical performance of the LMO-30 wt% FCNT sample out of the four samples.



Figure 6.6 Comparison of (a) Nyquist plot and (b) Bode phase plot between LMO-FCNT composites with different mass loading of FCNT.

## 6.3.1.2.3 Microstructural evolution related to capacity

*Ex-situ* SEM is implemented to compare the microstructures before and after the cycling measurements in order to understand the correlation between the capacity retention of the LMO-FCNT nanocomposites and their microstructural evolution during GCD cycling. In left column of Figure 6.7, from *a* to *c* and *e*, the images of fresh electrode is by the sequence of increasing magnification. They show the porous structures, which consists of the LMO-nanoparticle "islands" in the area of high brightness entangled with the FCNT meshes in gray and dark area. Basically, the effective ultrasound treatment makes the LMO particles uniformly distributed in the FCNT frameworks. After cycling for 100 cycles at 150 mAhg<sup>-1</sup>, the pores are filled up by the SEI layers or residual electrolytes as shown in the right column of Figures 6.7 from *b*, to *d* and *f*. The condensed morphology and structure enable a consolidated association between LMO and SWNT, effectively inhibiting the LMO nanoparticles from dissolving into electrolyte.

The corresponding *ex-situ* XRD results are present in Figure 6.8a with the same patterns except that only the slightly decreasing intensity is detectable at the featured peaks assigned to LMO, indicating a possible tiny loss of LMO nanoparticles after cycling. In addition, it is believed that the functional groups on SWNT may enhance the binding of LMO with FCNT meshes. Figure 6.8b is the FTIR spectrum of the LMO-FCNT nanocomposite electrode disassembled after cycling. The two absorption peaks below 600 cm<sup>-1</sup> are ascribed to the Mn-O vibrating modes of LMO. [28] The two peaks at 1100 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> derive from -C-O stretching and conjugation of -C=O with C=C of SWNT, respectively.<sup>32</sup> A broad peak with a weak intensity in the range of 3100~3300 cm<sup>-1</sup> is assigned to -O-H stretching on the surface of SWNT. [29]



Figure 6.7 SEM images of LMO-FCNT composite before cycling (a, c, e) and (b, d, f) after cycling.

Thus, taking all the factors discussed above into account, the cyclic stability of the LMO-FCNT nanocomposite primarily benefits from the solid integral structures of LMO-FCNT.



Figure 6.8 (a) XRD patterns of pure LMO nanoparticles, LMO-FCNT composite before and after cycling. (b) FTIR spectrum of LMO-FCNT composite.

## 6.3.1.3 Adhesion strength of LMO-FCNT

The adhesion strength of the samples on current collectors, is the most important mechanical property for binders and adhesive conductors. It is quantitatively evaluated by an *in-situ* tribology method combining the wear track imaging and force measurement. The working principle and setting up have been introduced in Experimental section. The value of adhesion strength  $\sigma_A$  is delimited within a range whose lower and upper limits are determined by two critical  $F_f$  corresponding to the occurrence of a large scale failure and the steady state that a large area of substrate underneath is exposed as shown in Figure 6.9. The wear track images of LMO-30 wt% PVDF (Figure 6.9a) show not only an adhesive failure at the interface between the sample film and current collector but also a cohesive failure generated inside the sample film by the  $F_f$  beyond the shear strength of the PVDF binders. Whereas in Figure 6.9b, there only occurs an adhesive failure for LMO-30 wt% FCNT because SWNTs can hardly be tore up because of their entangled feature and extremely high tensile strength over 10 GPa, far exceeding the 50~57 MPa for PVDF. [30] It is also found that the

failure area of LMO-30 wt% FCNT becomes disconnected after cycling as shown in Figure 6.9c, which seemingly implies a weakened destruction and retarded failure. However, the directional coherence of the scratches indicates a cohesive failure. In fact, due to the brittleness of the SEI layer, the adhesion strength is therefore decreased from 7~10 MPa to 3.05~6.5 MPa after cycling. By analogizing the correlation between charge-transfer resistances and different weight percentage of FCNT for the LMO-FCNT nanocomposites, it is anticipated that the adhesive strength is also in a positive correlation with the FCNT mass. Figures 6.9d and 6.9e for both LMO-5 wt% FCNT and LMO-15 wt% FCNT samples confirm this correlation when the large scale failures occur immediately without a transition through a threshold of failure. The mean values of the adhesive strength for the three LMO-FCNT samples and LMO-30 wt% PVDF are summarized in the histogram (Figure 6.9f), where the upper limit and the lower limit of the adhesive strength for each sample is taken as the error limits denoted.

The average adhesive strength of LMO-FCNT declines from the maximum value of 8.5 MPa to 2.36 MPa and to the minimum, 1.07 MPa as we decrease FCNT amount correspondingly from 30 wt% to 15 wt% and then 5 wt%. The 8.5 MPa for LMO-30 wt% FCNT also overpasses 7.15 MPa for LMO-30 wt% PVDF, justifying FCNT a promising adhesive conductor overwhelming the conventional binders. Such a high adhesion strength of FCNT is mainly attributed to the mechanical interlock of the nanotubes at the asperities on the current collectors. [22]



Figure 6.9 Wear track images and adhersion strength of (a) LMO-30 wt% PVDF, (b) LMO-30 wt% FCNT before cycling, (c) LMO-30 wt% FCNT after cycling, (d) LMO-15 wt% FCNT before cycling, and (e) LMO-5 wt% FCNT before cycling. (f) Histogram of mean adhersion strength between LMO-30 wt% PVDF and LMO-FCNT with different mass loading of FCNT.

# 6.3.2 LTO-FCNT half cells

# 6.3.2.1 Structural characterization of LTO-FCNT

To further verify the general roles of FCNT as an adhesive conductor to construct nanocomposite electrodes, we extend the use of FCNT with anode materials. Here we choose LTO, which has a theoretical specific capacity of 175 mAhg<sup>-1</sup> (1 C), as an example because their compatible capacity with that of LMO (~150 mAhg<sup>-1</sup>) is important for pairing them to construct a full cell with two electrodes in a balanced
weight.[31] The synthesis of LTO is similar to that of the spinel LMO nanocrystals using a low-temperature hydrothermal method described in Section 6.2.1. The electrode preparation is also the same except using Cu instead of Al as the current collectors. All details can be found in Experimental Section. The morphology of the LTO-FCNT nanocomposite is also similar to that of LMO-FCNT as shown in Figures 6.10a and 6.10b.



Figure 6.10 (a) SEM image and (b) high magnification SEM image of LTO-FCNT nanocomposite. (c) XRD patterns of LTO nanoparticles before and after annealing in the Ar atmosphere and LTO-FCNT.

The SEM images show a porous structure framed by the FCNT meshes. LTO nanoparticles in large size or aggregation are incorporated in the FCNT networks while

those in smaller size are anchored on the SWNT bundles. It is also worth noting that unlike the preparation method for LMO where no heat treatment is needed to obtain the final LMO products in spinel structure, annealing the LTO precipitates collected from hydrothermal reaction in Ar atmosphere at 500°C for 5h is indispensable to obtain the final spinel  $Li_4Ti_5O_{12}$  through phase transition from intermediate product of Li-intercalated rock-salt type LiTiO<sub>2</sub>. This is identified by indexing the XRD data (Figure 6.10c) according to JCPDS 49-0207 and JCPDS 16-0223.

### 6.3.2.2 Electrochemical performance of LTO-FCNT

The electrochemical performance of the LTO-FCNT nanocomposite electrodes is also investigated in half cells with Li metal by a series of GCD measurements. In Figure 6.11a, the voltage curves for selected cycles at varied rates from 1 C to 20 C, show the well-defined long and flat discharge and charge potential plateaus at around 1.5 V and 1.6 V *versus* Li<sup>+</sup>/Li, indicating the reversible Li<sup>+</sup> insertion and extraction processes (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> $\leftarrow$ →Li<sub>7</sub>Ti<sub>5</sub>O<sub>12</sub>).[31] The corresponding rate capabilities in Figure 6.11b show that the specific discharge capacity decays from initial 182 to 125 mAhg<sup>-1</sup> at the end of the 10<sup>th</sup> cycle at 1C rate and retains at 120 mAhg<sup>-1</sup> at 5 C for the following 10 cycles. As it continues from the 20<sup>th</sup> to the 30<sup>th</sup> cycle at 10 C, the capacity retains in a steady state of 100 mAhg<sup>-1</sup> followed by no more capacity fading within the last 10 cycles. CE is approaching 100% since the first cycle. The cyclic performance of LTO-FCNT is tested at 1 C and 10 C, respectively for 200 cycles. By merging the GCD curves at 1C (bottom Figure 6.11c) and 10 C (top Figure 6.11c), it clearly exhibits the discharge potential plateaus shift -0.1V from 1.5 V to 1.4V while the charge plateaus shift +0.1V from 1.6 V to 1.7 V. As a result, the polarization becomes evident at higher current rate

of 10 C with the enlarged 0.2 V potential gap between the two plateaus upon charge and discharge.



Figure 6.11 (a) Galvanostatic discharge/charge voltage profiles of LTO-FCNT composite electrodes cycled at different rates. (b) Rate capabilities of LTO-FCNT. Comparison of (c) galvanostatic discharge/charge voltage profiles and (d) cycling performance for LTO-FCNT cycled at 1 C and 10 C.

This is the same case with LMO-FCNT described above. The capacity retention in Figure 6.11d is consistent with the rate capability results. It shows a steady capacity of around 125 mAhg<sup>-1</sup> at 1 C after a substantial fading during the first several cycles. At 10 C, the capacity dropped from 125 mAhg<sup>-1</sup> at the first cycle and then retains at 100

mAhg<sup>-1</sup> since the 3<sup>rd</sup> cycle. CE also maintains as high as 100%. Overall, the excellent electrochemical performance of the LTO-FCNT nanocomposites also proves the success application of FCNT as the adhesive conductors for anodes in lithium ion batteries.

#### 6.4 Conclusions

In summary, a concept of adhesive conductors is proposed with bifunctional roles as both conductive additive and binder for LIBs. The fragmented carbon nanotube macrofilms are such adhesive conductors that can be coupled with active electrode materials to construct nanocomposite electrodes. They are assembled by a simple ultrasound processing and the drop casting method. The electrochemical performance are exemplified by involving FCNT in the cathode materials LMO and anode materials LTO to form their respective half cells with lithium metal. Compared with conventional PVDF binders, the adhesive FCNT conductors can significantly improve the rate capability and cyclic stability of LMO, which are derived from the superior conductivity and solidly framed matrix in a porous structure, providing highly conductive pathways for electrons and fast transport channels for lithium ions. The tribology experimental results show that LMO-30 wt% FCNT has a higher adhesive strength over PVDF with the same mass loading. The successful uses of FCNT in both cathode and anode materials demonstrate that the adhesive conductor is an efficient and general strategy to substitute conventional binders to construct nanocomposite electrodes for LIB.

### REFERENCES

- 1. Oh, S. M., Oh, S. W., Yoon, C. S., Scrosati, B., Amine, K., Sun, Y. K., Highperformance carbon-LiMnPO<sub>4</sub> nanocomposite cathode for lithium batteries. *Advanced Functional Materials.* **2010**, 20(19), 3260-3265.
- 2. Li, Y., Tan, B., Wu, Y., Mesoporous Co<sub>3</sub>O<sub>4</sub> nanowire arrays for lithium ion batteries with high capacity and rate capability. *Nano Letters* **2008**, 8(1), 265-270.
- 3. Wang, W., Kumta, P. N., Nanostructured hybrid silicon/carbon nanotube heterostructures: reversible high-capacity lithium-ion anodes. *ACS Nano* **2010**, 4(4), 2233-2241.
- 4. Wen, Z., Wang, Q., Zhang, Q., Li, J., *In Situ* growth of mesoporous SnO<sub>2</sub> on multiwalled carbon nanotubes: a novel composite with porous-tube structure as anode for lithium batteries. *Advanced Functional Materials* **2007**, 17(15), 2772-2778.
- 5. Paek, S.-M., Yoo, E., Honma, I., Enhanced cyclic performance and lithium storage capacity of SnO<sub>2</sub>/graphene nanoporous electrodes with three-dimensionally delaminated flexible structure. *Nano Letters* **2008**, 9(1), 72-75.
- Wang, H., Yang, Y., Liang, Y., Cui, L. F., Sanchez Casalongue, H., Li, Y., Hong, G., Cui, Y., Dai, H., LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> nanorods grown on graphene sheets for ultrahigh-rate-performance lithium ion batteries. *Angewandte Chemie International Edition* 2011, 123(32), 7502-7506.
- 7. Antaya, M., Dahn, J. R., Preston, J. S., Rossen, E., Reimers, J. N., Preparation and characterization of LiCoO<sub>2</sub> thin films by laser ablation deposition. *Journal of the Electrochemical Society* **1993**, 140(3), 575-578.
- 8. Zaghib, K., Shim, J., Guerfi, A., Charest, P., Striebel, K., Effect of carbon source as additives in LiFePO<sub>4</sub> as positive electrode for lithium-ion batteries. *Electrochemical and Solid-State Letters*. **2005**, 8(4), A207-A210.
- 9. Cao, Z., Wei, B., α-Fe<sub>2</sub>O<sub>3</sub>/Single-walled carbon nanotube hybrid films as highperformance anodes for rechargeable lithium-ion batteries. *Journal of Power Sources* **2013**, 241, 330-340.
- 10. Yu, C., Li, X., Ma, T., Rong, J., Zhang, R., Shaffer, J., An, Y., Liu, Q., Wei, B., Jiang, H., Silicon thin films as anodes for high-performance lithium-ion batteries with effective stress relaxation. *Advanced Energy Materials* **2012**, 2(1), 68-73.

- 11. Liu, G., Zheng, H., Simens, A., Minor, A., Song, X., Battaglia, V., Optimization of acetylene black conductive additive and PVDF composition for high-power rechargeable lithium-ion cells. *Jouranl of the Electrochemical Society* **2007**, 154(12), A1129-A1134.
- 12. Maleki, H., Deng, G., Kerzhner-Haller, I., Anani, A., Howard, J. N., Thermal stability studies of binder materials in anodes for lithium-ion batteries. *Journal of the Electrochemical Society* **2000**, 147(12), 4470-4475.
- Liu, G., Xun, S., Vukmirovic, N., Song, X., Olalde-Velasco, P., Zheng, H., Battaglia, V. S., Wang, L., Yang, W., Polymers with tailored electronic structure for high capacity lithium battery electrodes. *Advanced Materials* 2011, 23(40), 4679-4683.
- 14. Buqa, H., Holzapfel, M., Krumeich, F., Veit, C., Novak, P., Study of styrene butadiene rubber and sodium methyl cellulose as binder for negative electrodes in lithium-ion batteries. *Journal of Power Sources* **2006**, 161(1), 617-622.
- Li, J., Le, D.-B., Ferguson, P., Dahn, J., Lithium polyacrylate as a binder for tincobalt-carbon negative electrodes in lithium-ion batteries. *Electrochimica Acta* 2010, 55(8), 2991-2995.
- 16. Kim, G., Jeong, S., Joost, M., Rocca, E., Winter, M., Passerini, S., Balducci, A., Use of natural binders and ionic liquid electrolytes for greener and safer lithiumion batteries. *Journal of Power Sources* **2011**, 196(4), 2187-2194.
- 17. Xun, S., Song, X., Battaglia, V., Liu, G., Conductive polymer binder-enabled cycling of pure tin nanoparticle composite anode electrodes for a lithium-ion battery. *Journal of the Electrochemical Society* **2013**, 160(6), A849-A855.
- 18. Zhang, H., Cao, G., Yang, Y., Carbon nanotube arrays and their composites for electrochemical capacitors and lithium-ion batteries. *Energy & Environmental Science* **2009**, 2(9), 932-943.
- 19. Yu, G., Hu, L., Liu, N., Wang, H., Vosgueritchian, M., Yang, Y., Cui, Y., Bao, Z., Enhancing the supercapacitor performance of graphene/MnO<sub>2</sub> nanostructured electrodes by conductive wrapping. *Nano Letters* **2011**, 11(10), 4438-4442.
- 20. Lee, K., Chromey, N., Culik, R., Barnes, J., Schneider, P., Toxicity of *N*-methyl-2-pyrrolidone (NMP): teratogenic, subchronic, and two-year inhalation studies. *Fundamental and Applied Toxicology* **1987**, 9(2), 222-235.

- 21. Luo, J., Jang, H. D., Huang, J., Effect of sheet morphology on the scalability of graphene-based ultracapacitors. *ACS Nano* **2013**, 7(2), 1464-1471.
- 22. Hu, S., Xia, Z., Gao, X., Strong adhesion and friction coupling in hierarchical Carbon nanotube arrays for dry adhesive applications. *ACS Applied Materials and Interfaces* **2012**, 4(4), 1972-1980.
- 23. Lee, S., Cho, Y., Song, H. K., Lee, K. T., Cho, J., Carbon-coated single-crystal LiMn<sub>2</sub>O<sub>4</sub> nanoparticle clusters as cathode material for high-energy and high-power lithium-ion batteries. *Angewandte Chemie International Edition* **2012**, 51(35), 8748-8752.
- 24. Schwarz, U. D., A generalized analytical model for the elastic deformation of an adhesive contact between a sphere and a flat surface. *Journal of Colloid Interface Science* **2003**, 261(1), 99-106.
- 25. Kim, D. K., Muralidharan, P., Lee, H.-W., Ruffo, R., Yang, Y., Chan, C. K., Peng, H., Huggins, R. A., Cui, Y., Spinel LiMn<sub>2</sub>O<sub>4</sub> nanorods as lithium ion battery cathodes. *Nano Letters* **2008**, 8(11), 3948-3952.
- 26. Smith, A., Burns, J., Dahn, J., A high precision study of the coulombic efficiency of Li-ion batteries. *Electrochemical Solid-State Letters* **2010**, 13(12), A177-A179.
- 27. Randles, J., Kinetics of rapid electrode feactions. *Discussion of the Faraday* Society **1947**, 1, 11-19
- Chitra, S., Kalyani, P., Mohan, T., Massot, M., Ziolkiewicz, S., Gangandharan, R., Eddrief, M., Julien, C., Physical properties of LiMn<sub>2</sub>O<sub>4</sub> spinel prepared at moderate temperature. *Ionics* **1998**, 4(1-2), 8-15.
- 29. Kim, U. J., Furtado, C. A., Liu, X., Chen, G., Eklund, P. C., Raman and IR spectroscopy of chemically processed single-walled carbon nanotubes. *Journal of the American Chemican Society* **2005**, 127(44), 15437-15445.
- 30. IDEMAT Materials Selection Guide, http://www.idemat.nl/
- 31. Feckl, J. M., Fominykh, K., Döblinger, M., Fattakhova-Rohlfing, D., Bein, T., Nanoscale porous framework of lithium titanate for ultrafast lithium insertion. *Angewandte Chemie International Edition* **2012**, 51(30), 7459-7463.

### Chapter 7

#### **CONCLUSION AND FUTURE WORK**

#### 7.1 Summary of the Research Contributions

This dissertation covers the original works in the area of carbon nanotube macrofilm-based nanocomposite electrodes for energy applications, in particular rechargeable lithium-ion batteries as well as fuel-cell catalysts and asymmetrical supercapacitors. Progressess in these energy conversion and storage devices are built on the successful material synthesis and the manufacturing technology for the nanocomposites electrodes. Thus, a reliable, low-cost and effective route to synthesize high performance electrodes becomes more significant. The progressive research on developing various nanocomposites based on CNT macrofilms evolving from cathode materials in Chapters 2 and 3 to anode materials in Chapters 4 and 5, followed by a general nanocomposite solution in Chapter 6 demonstrates the unique properties of CNT macrofilm frameworks, including the inherent superior conductivity, large specific surface area, porous structure, stretchability, robustness, and adhesion could be fully taken to enhance the electrochemical performance of the incorporated active materials in the nanocomposites. Understanding the underlying improved electrochemical behavior of nanocomposites is also necessary and critical to the optimization of the synthetic method and techniques for the practical applications. Significant effects of functional groups and film thickness have been observed and investigated in-depth. The presence of oxygen-containing functional groups on the surface of the SWNT macrofilms after purification can enhance the association of the SWNT films with the active materials to enable the transport of solvated ions to the electrolyte/electrode interfaces and increase the diffusion kinetics. The CNT macrofilm with thickness that comparable to the characteristic diffusion length of 300~500 nm could afford the nanocomposites the highest Li<sup>+</sup> chemical diffusion coefficient and thus possesses an optimal electrochemical performance. The noticed adhesive characteristic of SWNT macrofilms as "bifunctional" adhesive conductors promotes a general approach to construct nanocomposite electrodes with both cathode and anode materials.

Specifically, in Chapter 2, a facile method to prepare  $V_2O_5/SWNT$  macrofilms composed of SWNT macrofilm with nanostructured vanadium oxides are developed and their electrochemical behavior as Li-ion battery cathodes have been systematically studied. The nanocomposites are synthesized by a simple controllable hydrolysis in-situ deposition of the active materials in SWNT macrofilms. They are carefully characterized by means of SEM and TEM microscopy, X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy combined with electrochemical measurements including galvanostatic discharge/charge, cyclic voltammetry and electrochemical impedance spectrum analysis for the  $V_2O_5/SWNT$  hybrid film as cathode in a coin cell with 1M LiPF<sub>6</sub> in EC:DEC (1:1 v/v) electrolyte. It exhibits an excellent high-rate capacity, high Coulombic efficiency and reasonable cyclic stability. Then this *in-situ* synthesis strategy stimulates the fabrication of stretchable nanocomposite materials by *in-situ* growth the lithiated cathode materials such as LiMn<sub>2</sub>O<sub>4</sub> nanocrystals in SWNT macrofilms as discussed in Chapter 3. The freestanding nanocomposite as cathode in half cells with lithium metal exhibits a satisfied average capacity of 103 mAh g<sup>-1</sup> and a satisfied cyclic stability with a high capacity retention of 83% over 250 cycles at the slow rate of 0.1 C. This electrochemical performance confirms that such composite cathode is a promising candidate for the stretchable lithium-ion batteries. The PITT results reveal Li<sup>+</sup> diffusion coefficient is a dominant factor limiting the Coulombic efficiency and sheds light on the optimization as future work to further improve such cathode performance. This work demonstrated the feasibility of the LMO-SWNT macrofilm nanocomposite for developing the fullyflexible lithium-ion battery based on such cathode materials in couple with the pristine SWNT macrofilms as anode in the future.

The CNT macrofilm-based nanocomposites with anode materials has been further developed in Chapter 4. The work focuses on discussing the nanocomposites of iron oxides with SWNT macrofilms as anodes for rechargeable lithium-ion batteries. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT hybrid films, which are composed of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles in fine crystalline size (6-20 nm) incorporated in the matrix of SWNT macrofilms, are prepared by an oxidizing transformation from the original Fe-containing SWNT macro-films via a simple heat treatment. We have investigated the dependence of the Li<sup>+</sup> diffusivity on the film thickness by detailed calculations and analysis of the compatible results from GITT and EIS, and found that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilms with a comparable thickness to the characteristic diffusion length of Li<sup>+</sup> ions could obtain the optimum electrochemical properties. These nanocomposites exhibit an excellent high capacity and cyclic stability but a poor rate capability. Then a hydrogen annealing method has been demonstrated to enhance the rate capability. The phase transformation involved in the thermal reduction of rhombohedral  $Fe_2O_3$  to cubic  $Fe_3O_4$  during  $H_2$  annealing are thoroughly investigated by SEM and TEM microscopy, Rietveld fitting of XRD data, XPS and Raman spectroscopy. The  $H_2$ -annealed nanocomposites have a higher capacity of 786 mAhg<sup>-1</sup> at 4000 mAg<sup>-1</sup> with a prolonged lifetime compared to the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SWNT. The electrochemical kinetic analysis are also performed by EIS and the GITT results further confirm that the enhancement of the rate capability is attributed to the presence of highly-conductive  $Fe_3O_4$ , accelerated charge-transfer kinetics, and the increased Li<sup>+</sup> diffusivity.

By expanding the work of iron oxides above to the family of metal oxides ( $M_xO_y$  (M=Fe, Co, Ni)), in Chapter 5, we demonstrated the  $M_xO_y$ /SWNT macrofilm nanocomposites for OER/ORR electrocatalysis, lithium-ion batteries and asymmetric supercapacitors. It is concluded that all  $M_xO_y$ /SWNT macrofilm nanocomposites inherit the high specific capacity and cycling stability for lithium-ion batteries, similar to the results for iron oxides in Chapter 4. NiO/SWNT and Co<sub>3</sub>O<sub>4</sub>/SWNT (200 °C) have their specialized strength for OER and ORR in alkaline solutions, respectively with high catalytic activities. NiO/SWNT also exhibits an excellent electrochemical performance in asymmetric supercapacitors with a high power and energy density. We also elucidated that NiO/SWNT has a fast charge transport process in Faradaic redox reactions and the calcination temperature has an influence on the ORR activity of Co<sub>3</sub>O<sub>4</sub>/SWNT.

Finally, Chapter 6 presents a new concept of adhesive conductors using fragmented CNT macro-films (FCNTs) with irregular structures of laterally 2-D distributed CNT segments to construct nanocomposite electrodes as a general approach. The adhesive FCNT conductors provide not only a high electrical conductivity but also a strong adhesive force, functioning simultaneously as both the conductive additives and the binder materials for lithium-ion batteries. This adhesive conductor role of FCNT is verified by constructing the electrodes with both cathode and anode materials. An *insitu* tribology method combining the wear track imaging and force measurement is employed to evaluate the adhesion strength of the adhesive FCNT conductors. The results show that the adhesive FCNT conductors exhibit a higher adhesion strength than

PVDF. It is also confirmed that the fabricated nanocomposite electrodes exhibit superior high-rate and retention capabilities compared to the electrodes using conventional PVDF and carbon black. Thus, FCNT is recognized to be a competent substitute for polymer binders to maintain mechanical integrity and meanwhile to improve electrical connectivity of active materials in the nanocomposite electrodes. In addition, this new electrode manufacturing technique avoids toxic organic solvent and could provide a revolution to traditional battery industry.

### 7.2 Future Research Work

Although this dissertation follows up a research route to develop nanocomposites based on CNT macrofilms with various materials from cathode to anode by a variety of synthetic methods for energy application, and basically realizes a general nanocomposite-construction approach, there are many optimization that needs to be continued towards specific works. For example, even though we have demonstrated the potential of LMO-SWNT macrofilm nanocomposites as the flexible LIB cathodes in Chapter 3, the low Li<sup>+</sup> chemical diffusion coefficient still limits their performance. The optimization to improve the Li<sup>+</sup> diffusivity of such cathode nanocomposites is highly desired for pairing with the pristine SWNT macrofilms as anodes to construct the full stretchable cells in the future. This research would be an exciting direction to benefit the development of wearable electronics such as smart watches, which requires fully-flexible power sources.

Those conclusions we have obtained between the chapters can definitely shed light on each other for optimization work in the future. For example, the annealing strategy in the atmosphere of  $H_2$  to enhance the rate capability of Fe<sub>2</sub>O<sub>3</sub>/SWNT macrofilm nanocomposites could also be relied on to reduce V(V) in V<sub>2</sub>O<sub>5</sub> to lower states such as V(IV) in  $VO_2$  to further improve the electrochemical performance of the  $V_2O_5/SWNT$  macrofilm nanocomposites as developed in Chapter 2.

It is also significant to start with some phenomena observed in the research work to extend investigation of key factors such as temperature, pressure, functional groups and etc. in terms of their effects on the device performance. As we discussed in Chapter 5 that calcination temperature has an influence on the ORR activity of  $Co_3O_4$ /SWNT, the continued fundamental research of probing in-depth the correlation between the catalytic activity and calcination temperature as well as the causality could provide vital information for designing high efficient nanocomposite catalysts for ORR with desired activity. Based on the adhesive properties of the fragmented CNT macrofilms observed in Chapter 6, it is necessary to theoretically and experimentally investigate the stickiness origin of such FCNT meshes and their working mechanisms as "bifunctional" adhesive conductors in nanocomposite electrode fabrication. This study will help us to understand and disclose the fundamental physics, chemistry and mechanics for the inherent adhesion of adhesive conductors and accordingly bring light to design new adhesive conductors. By following this direction, we could also pioneer in creating a new evaluation method and standard for measuring the adhesive mechanical behavior of adhesive conductors.

Last but not the least, it is also meaningful to expand CNT macrofilms' role in nanocomposites with other active materials for potential energy conversion and storage devices beyond the discussion scope of this dissertation such as sodium-ion batteries, lithium-sulfur batteries, metal-air batteries, and photocatalysts as illustrated in Figure 7.1. Sodium-ion batteries are a type of rechargeable battery that is the same as lithiumion battery except using sodium-ions as its charge carriers. The sodium salts used in the electrolytes are highly abundant, much more so than those of equivalent lithium salts, making them both cheap and easily obtainable. However, inferior cycling performance limits the ability of non-aqueous Na-ion batteries to compete with commercial Li-ion cells. [1] We can depend on SWNT macrofilms combining with potential Na-ion active materials as nanocomposite electrodes to overcome the challenge. Rapid progress of electric vehicle technologies also demands innovation of new battery chemistry beyond Li-ion systems and the promising alternatives are focusing on Li-S and metal-air batteries such as Li-air batteries with capacity over at least a factor of 5-fold higher than that of LIBs. [2, 3] It is envisioned that SWNT macro-film/S nanocomposite could be developed by the *in-situ* deposition of sulfur. The oxygen-containing functional groups of the SWNT macro-films after purification could provide more sites to fasten highlydispersed sulfur at a high percentage. Such nanocomposites can be used directly as the cathode for Li-S batteries to enhance the electrochemical performance. Similarly, it is expected that the SWNT macrofilms with a tunable micro-to-meso-porous structure and hydrophobic surface hold the potential to be an ideal supporting materials that are "Direct" composited with ORR catalysts as breathable air cathode. photoelectrocatalysis at a solid-liquid junction is one of the predominant strategies for water splitting. [4] It requires that the photoelectrode has not only suitable light absorption characteristics to generate a photovoltage sufficient to split water (> 1.23 V)but also surface stability and good electronic properties. The use of SWNT macrofilms with photocatalytic active materials can be a good nanocomposite as photoelectrocatalyst to reduce the overpotential required for a given redox reaction to take place, and in some cases promotes separation and diffusion of carrier species.



Figure 7.1 Illustrating other potential energy applications of CNT macrofilm-based nanocomposites.

### REFERENCES

- 1. Slater, M. D., Kim, D., Lee, E., Johnson, C. S., Sodium-ion batteries. *Advanced Functional Materials* **2013**, 23(8), 947-958.
- 2. Bruce, P. G., Hardwick, L. J., Abraham, K. M., Lithium-air and lithium-sulfur batteries. *MRS bulletin* **2011**, 36(07), 506-512.
- 3. Lee, J. S., Tai Kim, S., Cao, R., Choi, N. S., Liu, M., Lee, K. T., Cho, J., Metal–air batteries with high energy density: Li–air versus Zn–air. *Advanced Energy Materials* **2011**, 1(1), 34-50.
- 3. Maeda, K., Teramura, K., Lu, D., Takata, T., Saito, N., Inoue, Y., Domen, K., Photocatalyst releasing hydrogen from water. *Nature* **2006**, 440(7082), 295-295.

### Appendix A

### SCIENTIFIC AND TECHNICAL CONTRIBUTIONS DURING PH.D.

Published Papers:

- 1. **Cao, Zeyuan**, and Bingqing Wei. "A general facile route to metal oxides and single-walled carbon nanotube macrofilms nanocomposites for energy storage" **Frontiers in Materials**, 2, (2015): 40
- 2. Lu, Qi, Gregory S. Hutchings, Weiting Yu, Yang Zhou, Robert V. Forest1, Runzhe Tao, Jonathan Rosen, Bryan T. Yonemoto, **Zeyuan Cao**, Haimei Zheng, John Q. Xiao, Feng Jiao, Jingguang G. Chen. "Highly porous nonprecious bimetallic electrocatalysts for efficient hydrogen evolution" **Nature Communication**, 6, (2015): 6567
- 3. Liang, Kun, Taoli Gu, **Zeyuan Cao**, Xianzhong Tang, Wencheng Hu, and Bingqing Wei. "In-situ synthesis of SWNTs@MnO<sub>2</sub>/polypyrrole hybrid film as binder-free supercapacitor electrode." **Nano Energy** 9, (2014), 245-251
- 4. Zhang, Qing, Kathryn Scrafford, Mingtao Li, **Zeyuan Cao**, Zhenhai Xia, Pulickel M. Ajayan, and Bingqing Wei. "Anomalous Capacitive Behaviors of Graphene Oxide Based Solid-State Supercapacitors." **Nano Letters** 14, 4 (2014): 1938-1943.
- 5. **Cao, Zeyuan,** and Bingqing Wei. "Fragmented carbon nanotube macrofilms as adhesive conductors for lithium-ion batteries." **ACS Nano** 8, 3 (2014): 3049-3059.
- 6. Liu, Zhikun\*, Zeyuan Cao\*, Biwei Deng, Yuefeng Wang, Jiayi Shao, Prashant Kumar, C. Richard Liu, Bingqing Wei, and Gary J. Cheng. "Ultrafast and scalable laser liquid synthesis of tin oxide nanotubes and its application in lithium ion batteries." Nanoscale 6, 11 (2014): 5853-5858. (\*: contribute equally)
- 7. **Cao, Zeyuan**, and Bingqing Wei. "α-Fe<sub>2</sub>O<sub>3</sub> single-walled carbon nanotube hybrid films as high-performance anodes for rechargeable lithium-ion batteries." **Journal of Power Sources** 241 (2013): 330-340.
- Shan, Changsheng, Wenjie Zhao, X. Lucas Lu, Daniel J. O'Brien, Yupeng Li, Zeyuan Cao, Ana Laura Elias et al. "Three-dimensional nitrogen-doped multiwall carbon nanotube sponges with tunable properties." Nano Letters 13, 11 (2013): 5514-5520.

- 9. Xu, Ping, Taoli Gu, **Zeyuan Cao**, Bingqing Wei, Jianyong Yu, Faxue Li, Joon-Hyung Byun, Weibang Lu, Qingwen Li, and Tsu-Wei Chou. "Carbon nanotube fiber based stretchable wire-shaped supercapacitors." **Advanced Energy Materials** 4, 3 (2014).
- 10. **Cao, Zeyuan,** and Bingqing Wei. "High rate capability of hydrogen annealed iron oxide–single walled carbon nanotube hybrid films for lithium-ion batteries." **ACS Applied materials & interfaces** 5, 20 (2013): 10246-10252.
- 11. Qin, Jinwen, Qing Zhang, **Zeyuan Cao**, Xin Li, Changwen Hu, and Bingqing Wei. "MnO<sub>x</sub>/SWCNT macro-films as flexible binder-free anodes for high-performance Li-ion batteries." **Nano Energy** 2, 5 (2013): 733-741.
- 12. **Cao, Zeyuan,** and Bingqing Wei. "V<sub>2</sub>O<sub>5</sub>/single-walled carbon nanotube hybrid mesoporous films as cathodes with high-rate capacities for rechargeable lithium ion batteries." **Nano Energy** 2, 4 (2013): 481-490.
- 13. **Cao, Zeyuan,** and Bingqing Wei. "A perspective: carbon nanotube macrofilms for energy storage." **Energy & Environmental Science** 6, 11 (2013): 3183-3201.
- Liang, Kun, Ni Wang, Mei Zhou, Zeyuan Cao, Taoli Gu, Qing Zhang, Xianzhong Tang, Wencheng Hu, and Bingqing Wei. "Mesoporous LaNiO<sub>3</sub>/NiO nanostructured thin films for high-performance supercapacitors." Journal of Materials Chemistry A 1, 34 (2013): 9730-9736.

Submitted Papers:

1. Ping Xu, Bingqing Wei, **Zeyuan Cao**, Jie Zheng, Ke Gong, Faxue Li, Jianyong Yu, Qingwen Li, Weibang Lu, Joon-Hyung Byun, Byung-Sun Kim, Yushan Yan, and Tsu-Wei Chou. "Stretchable wire-shaped asymmetric supercapacitors based on pristine and MnO<sub>2</sub> coated carbon nanotube fibers" submitted.

Filing Patents:

- 1. Bingqing Wei, and **Zeyuan Cao**. "Fragmented Carbon Nanotube Macro-Films as Adhesive Conductors for Lithium-Ion Batteries" U.S. provisional patent application, under serial number 61/968,407. Mar. 2014
- 2. Tsu-Wei Chou, Ping Xu, Bingqing Wei, Taoli Gu and **Zeyuan Cao**. "Carbon Nanotube Fiber Based Stretchable Wire-Shaped Supercapacitors" U.S. provisional patent application, under serial number 61/945,876. Feb. 2014

### Appendix B

### AWARDS DURING PH.D.

- 1. Guest Lecture, MRS Chapter at Stevens Institute of Technology
- 2. Professional Development Award for Graduate Student, University of Delaware (2014)
- 3. Awarded Student Membership, the Electrochemical Society (2014)

### Appendix C

### PERMISSION FOR USING COPYRIGHTED MATERIALS

#### 1. Reprinted permission for Figure 1.1 NATURE PUBLISHING GROUP LICENSE TERMS AND CONDITIONS

Mar 20, 2015

This is a License Agreement between Zeyuan Cao ("You") and Nature Publishing Group ("Nature Publishing Group") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Nature Publishing Group, and the payment terms and conditions.

# All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3593181041504
License date	Mar 20, 2015
Licensed content publisher	Nature Publishing Group
Licensed content publication	Nature
Licensed content title	Issues and challenges facing rechargeable lithium batteries
Licensed content author	JM. Tarascon and M. Armand
Licensed content date	Nov 15, 2001
Volume number	414
Issue number	6861
Type of Use	reuse in a dissertation / thesis
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Figures	Figure 1 Comparison of the different battery technologies in terms of volumetric and gravimetric energy density. The share of worldwide sales for Ni–Cd, Ni–MeH and Li-ion portable batteries is 23, 14 and 63%, respectively. The use of Pb–acid batteries is restricted mainly to SLI (starting, lighting, ignition) in automobiles or standby applications, whereas Ni–Cd batteries remain the most suitable technologies for high-power applications (for example, power tools ).
Author of this NPG article	no
Your reference number	None
Title of your thesis / dissertation	CARBON NANOTUBE MACROFILM-BASED NANOCOMPOSITE ELECTRODES FOR ENERGY APPLICATIONS
Expected completion date	Apr 2015
Estimated size (number of	235

### 2. Reprinted permission for Figure 1.4

Mar 20, 2015

This is a License Agreement between Zeyuan Cao ("You") and Royal Society of Chemistry ("Royal Society of Chemistry") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Royal Society of Chemistry, and the payment terms and conditions.

## All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3593190390782
License date	Mar 20, 2015
Licensed content publisher	Royal Society of Chemistry
Licensed content publication	Chemical Communications (Cambridge)
Licensed content title	Direct fabrication of single-walled carbon nanotube macro-films on flexible substrates
Licensed content author	Hongwei Zhu,Bingqing Wei
Licensed content date	Apr 20, 2007
Issue number	29
Type of Use	Thesis/Dissertation
Requestor type	academic/educational
Portion	figures/tables/images
Number of figures/tables/images	1
Format	print and electronic
Distribution quantity	1
Wil you be translating?	no
Order reference number	None
Title of the thesis/dissertation	CARBON NANOTUBE MACROFILM-BASED NANOCOMPOSITE ELECTRODES FOR ENERGY APPLICATIONS
Expected completion date	Apr 2015
Estimated size	235
Total	0.00 USD

Terms and Conditions

This License Agreement is between {Requestor Name} ("You") and The Royal Society of Chemistry ("RSC") provided by the Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by the Royal Society of Chemistry, and the payment