

**PROTON AND HYDROXIDE CROSSOVER RATES AND ION
CONDUCTIVITIES OF ION-EXCHANGE MEMBRANES FOR REDOX
FLOW BATTERIES**

by

William Tytgat

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Chemical Engineering

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by

William Tytgat

Approved: _____
Yushan Yan, Ph.D.
Professor in charge of thesis on behalf of the Advisory Committee

Approved: _____
Abraham M. Lenhoff, Ph.D.
Chair of the Department of Chemical and Biomolecular 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

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NOMENCLATURE

RFB	Redox flow battery.
IEM	A generic ion-exchange membrane, either an AEM or a CEM.
AEM	An anion-exchange membrane in non-alkaline anion form (e.g., containing Cl^- anions).
CEM	A cation-exchange membrane in non-acidic form (e.g., containing Na^+ cations).
FES	Flywheel energy storage.
PHES	Pumped hydro energy storage.
CAES	Compressed air energy storage.
ECES	Electrochemical energy storage.
SHE	Standard hydrogen electrode.
HER	Hydrogen evolution reaction.
OER	Oxygen evolution reaction.
u	Ionic mobility [$10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$].
IEC	Ion-exchange capacity [mmol/g].
PEEK	Polyether ether ketone.
QNPPO	Quaternized Ammonium Poly(2,6-dimethyl-1,4-phenylene oxide).
PTFE	Polytetrafluoroethylene.
DS	Degree of substitution value for QN groups.
Z'	Real part of the impedance in a Nyquist plot.
Z''	Imaginary part of the impedance in a Nyquist plot.
σ	Ionic conductivity [mS/cm].

R_{membrane}	Overall membrane resistance [Ω].
l	Distance between the reference platinum electrodes [cm].
S	Cross-sectional area of the membrane [cm^2].
ASR	Area-specific resistance [$\Omega \text{ cm}^2$].
L	Mean membrane thickness [cm].
J	Molar flux [$\text{mol m}^{-2} \text{ s}^{-1}$].
D	Diffusion coefficient [$\text{m}^2 \text{ s}^{-1}$].
C	Concentration [mol L^{-1}].
C_A	Concentration of protons/hydroxide ions in the bulk phase of the enrichment side [mol L^{-1}].
C_B	Concentration of protons/hydroxide ions in the bulk phase of the deficiency side [mol L^{-1}].
C'_A	Concentration of protons/hydroxide ions at the interface between the membrane and the enrichment side [mol L^{-1}].
C'_B	Concentration of protons/hydroxide ions at the interface between the membrane and the deficiency side [mol L^{-1}].
x	Position [m].
t	Time [s].
K	Solubility partition coefficient [-].
P	Permeability coefficient [$\text{cm}^2 \text{ s}^{-1}$].
\bar{P}	Permeance [cm s^{-1}].
n_B	Moles of protons/hydroxide ions in the deficiency side [mol].
A	Effective area of the membrane [cm^2].
V_B	Volume of the deficiency side [cm^3].
LISICON	Li superionic conductor.
NASICON	Na superionic conductor.
E_a	Activation energy [J].
k_B	Boltzmann constant [J/K].
T	Absolute temperature [K].

ABSTRACT

A high selectivity and a low internal resistance are key performance properties for ion-exchange membranes in redox flow batteries. Here, the basic zinc-acidic iron double ion-exchange membrane redox flow battery is described. In order to find the best combination of an anion-exchange membrane and a cation-exchange membrane for this design, the H^+/OH^- permeabilities and the Cl^-/Na^+ conductivities of different anion-exchange membranes and cation-exchange membranes were characterized and compared. For the investigated anion-exchange membranes, the H^+ permeabilities were found to be in the order of Fumapem[®] FAA-3 > PTFE-QNPPO > QNPPO > Fumasep[®] FAB-PK-130, but the same order (from highest to lowest) is observed for the Cl^- conductivities. For the investigated cation-exchange membranes, the OH^- permeabilities were found to be in the order of Nafion[®] NR-212 > Fumasep[®] FKS-50 > Fumasep[®] FKE-50, while the same order (from highest to lowest) is observed for the Na^+ conductivities. Hence, the choice for a particular ion-exchange membrane in the redox flow battery design should be made based on a trade-off between a high selectivity (low crossover) and a high ion conductivity (low internal resistance).

Chapter 1

INTRODUCTION

The twentieth century saw a steep increase in the use of fossil fuels, due to population growth and continuing industrialization. Between 1980 and 2006, the worldwide annual growth rate was 2%. Nowadays, electric energy demand exceeds 20×10^3 TWh/year. Moreover it is still growing at approximately 3% per year. The exploitation of these resources in a relatively short amount of time puts a lot of pressure on the environment. CO₂ emissions need to be drastically reduced in order to restrict climate change. The continuous exhaustion of the available energy resources can lead to serious global energy crises. With the growing demand for energy and the increasing attention to environmental issues in mind, a surge of research effort is directed towards renewable energies, such as solar and wind power. Currently renewable energies, except hydropower, provide 4% of electricity production but that number is estimated to grow by more than 25% by 2030. Major challenges are presented by renewable energies due to their intermittency character, namely fluctuations in output and unavailability, since they cannot deliver a regular supply that is easily adjustable to consumption needs. Furthermore, integration of renewable energies in the design, control and management of the electric grid can cause problems, like voltage rises, surplus of the generated power and network load stability problems. Studies have suggested that the grid can become unstable if power from renewable sources exceeds 20% of the whole generated power. Therefore, energy storage technologies are indispensable. They can overcome the supply-demand imbalance as they are capable of accumulating energy during times when demand is low (peak shaving) and supplying it when demand is high, to ensure efficient energy handling (load leveling) [1, 2, 3, 4, 5, 6, 7].

1.1 Energy Storage Technologies

Energy storage technologies can be divided into three main categories, namely flywheel energy storage (FES) and supercapacitors, geological storage technologies and electrochemical energy storage (ECES) [1]. The performance parameters of the main energy storage systems are listed in Table 1.1 [3, 4].

Table 1.1: Characteristics of the main energy storage systems.

Energy Storage Technology	Top power [MW]	Energy density [Wh/kg]	Discharge time [h]	Response time	Round trip efficiency	Capital cost [\$/kWh]
PHES	3,000	0.3	>8	min	70-85	10-350
CAES	300	10-30	0.1-15	min	60	130-550
FES	20	11-30	0.1-1	ms	85	2,400
Supercapacitors	100	10-30	0.25	ms	95	4,600
Lead-acid battery	10-40	25-50	0.1-4	ms	75-85	130
Sodium-sulfur battery	34	150-250	1-10	s	85-90	550
Lithium-ion battery	16	100-200	0.1-1	ms	95	600
Redox flow battery	2-100	10-50	1-20	ms	85	900

1.1.1 Flywheel energy storage and supercapacitors

FES and supercapacitors are low-energy, high-power energy systems, mainly suited for power management (e.g., frequency regulation). Both FES and supercapacitors have a high round-trip efficiency, but only for short discharge times. The round trip efficiency would decrease considerably for longer times due to friction losses for FES and internal losses for supercapacitors. Therefore, long-term storage with these technologies is not feasible [1, 3, 4, 7].

1.1.2 Geological storage technologies

Geological storage technologies consist of pumped hydro energy storage (PHES) and compressed air energy storage (CAES). They are high-energy, high-power systems, suited for energy management. As they cannot respond to fast power demand, their

usefulness lies in long-time services. However, they need special geological and geographic requirements, besides the large capital and maintenance costs [1, 3, 4, 7].

1.1.3 Electrochemical energy storage technologies

Electrochemical energy storage technologies (ECES) consist of lead-acid batteries, lithium-ion batteries, sodium-based batteries and redox flow batteries (RFBs). ECES are the solution of choice for short-to-long-time scale, because they have major advantages like modularity, enabling wide scalability (applications ranging from a few kWh to several MWh), flexibility, cost and efficiency compared to the other energy storage technologies. It is clear from Figure 1.1, that ECES can be used in areas of the power/duration diagram where other energy storage technologies cannot reach. Additional advantages are that they can be sited everywhere (unlike PHES and CAES that have specific geographical and geological requirements) and that they have low environmental footprints, enabling them to be sited near residential areas [1, 3, 4, 7].

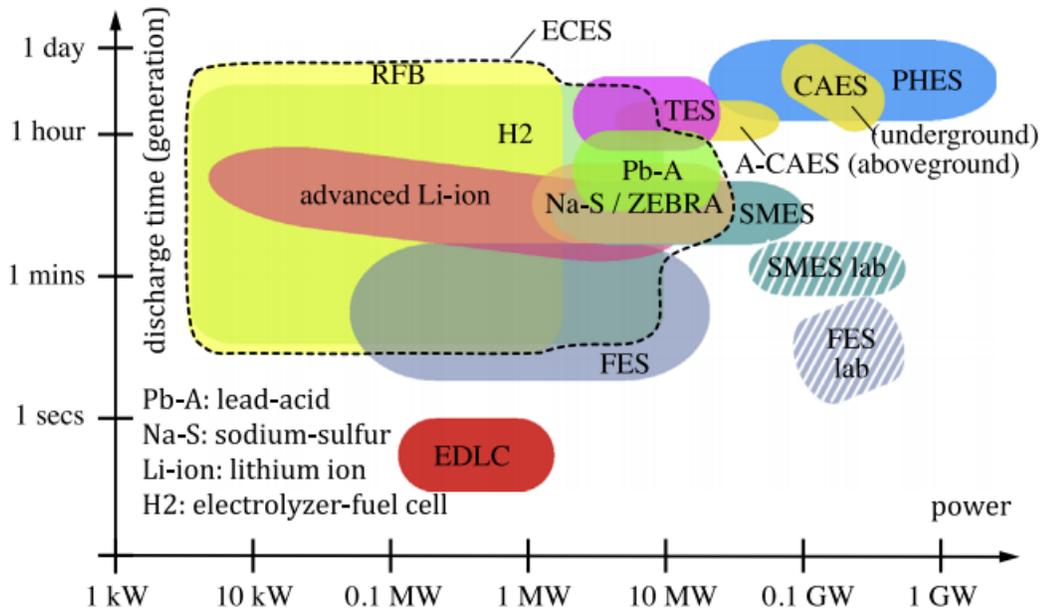


Figure 1.1: Power/duration diagram of energy storage systems.

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1.2 Redox Flow Batteries

RFBs are rechargeable batteries studied in detail in the following sections. First their operation principle is described, followed by a comparison of the RFB with other battery technologies, indicating their pros and cons. The importance of ion-exchange membranes (IEMs) in the RFB is highlighted, with special emphasis on a new double-membrane triple electrolyte design.

1.2.1 Main features

A RFB refers to an electrochemical system where redox couples, dissolved in the electrolytes, are used to store and release energy during the charge and discharge cycle of the battery, respectively. Reversible reduction-oxidation reactions take place in the two liquid electrolytes, which are separated by an IEM. The IEM is a crucial component of the RFB as it prevents cross-mixing of the positive and negative electrolytes while at the same time allowing the transport of ions to complete the circuit during the passage of current (to maintain electroneutrality). The two electrolytes are stored in separate tanks and circulated to the RFB by pumps [1, 3, 8].

1.2.2 Comparison of redox flow batteries with the other battery technologies

RFBs represent the most promising choice for large-scale energy storage for several reasons, including high efficiency, flexibility, cost, room temperature operation, extremely long charge/discharge cycle life and safety advantages, compared to the other ECES.

- Lead-acid batteries have a poor deep discharge performance, strongly affecting battery life. Furthermore, they cannot store large amounts of energy in a small volume (low energy density).
- Sodium-sulfur batteries are only operational at high temperatures, while at the same time there is a potential for fire.
- Lithium-ion batteries have a high energy density but also pose certain safety issues like potential fires and explosions. Moreover they are expensive to manufacture.

The most important advantage of RFBs is surely the ability to separate power and energy. The power is determined by the number of cells in the stack and the size of the electrodes, while the energy storage capacity depends on the concentration of the electroactive species (i.e., the solubility of the ions in the electrolytes) and the volume of the electrolytes. This is the case since the reactants in RFBs are dissolved in the electrolytes and stored in external tanks, whereas conventional batteries store the electrochemical reactants within the electrode itself (e.g., Li-ion batteries) [9]. Thus capacity is not fixed by cell dimensions, but by the size of the tanks [2]. By simply increasing the volume of the storage tanks, the energy storage capacity is increased. Hence, the incremental cost of each additional energy storage capacity unit is lower compared to other batteries. Since the cost per kWh of the system decreases substantially with increasing storage capacity, the RFB is especially appealing for long-time storage applications (in excess of 4-6 hours). Thus a RFB can be optimally designed to provide the specific power and energy requirements for each application. Drawbacks of RFBs are their small energy density, due to the low metal ion solubilities in the electrolytes, leading to the large electrolyte storage tanks, the necessity of pumping power to circulate the electrolytes to the cells and the toxicity of some of the electrolytes employed [1, 3, 4, 5, 9].

1.2.3 Single ion-exchange membrane configuration

Since their invention, RFBs employed a single-IEM configuration. However, there are some reservations about RFBs with a single-IEM configuration. First of all, only redox pairs with the same ion charge can be combined, since neither one single anion-exchange membranes (AEM) nor one single cation-exchange membrane (CEM) can effectively prevent the mixing of redox pairs with mixed ion charges [10]. Moreover combinations of two redox couples with a useful voltage and a reasonable solubility are seriously limited by hydrogen and oxygen evolutions in an aqueous system. Figure 1.2 illustrates the standard potentials versus SHE (standard hydrogen electrode) of known redox couples in aqueous systems (except the H₂ evolution potential that is

the overpotential on carbon electrodes) [11, 12]. The reversible voltage window of

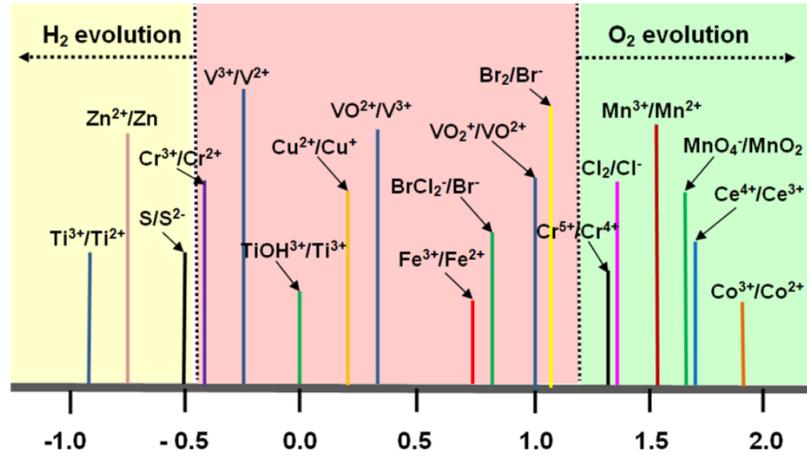


Figure 1.2: Standard potential versus SHE of redox couples in aqueous systems.
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water electrolysis is limited to 1.23 V, since the same pH has to be maintained in both negative and positive electrolytes. HER = 0 (hydrogen evolution reaction) versus OER = +1.23 V (oxygen evolution reaction) at pH = 0 or HER = -0.83 versus OER = +0.40 V at pH = 14. Figure 1.3 shows the two feasible options, an AEM isolating a cation-cation negative pair from a cation-cation positive pair (e.g., iron/chromium RFB) or a CEM isolating an anion-anion negative pair from an anion-anion positive pair (e.g., bromine/polysulphide RFB) [10].

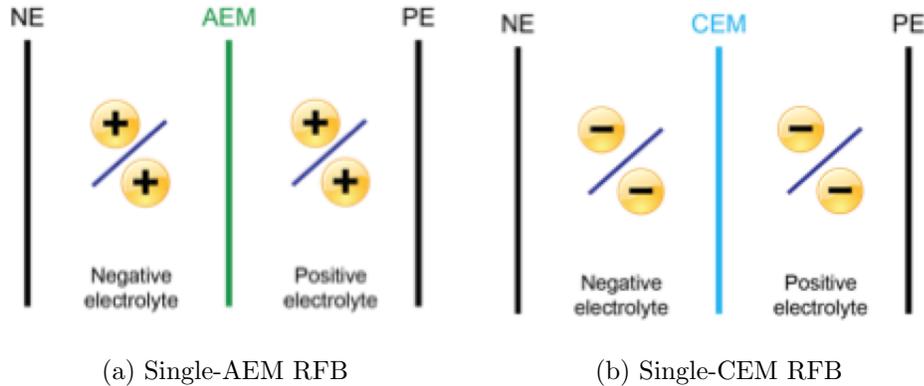


Figure 1.3: Two possibilities for single-IEM RFB configurations.

1.2.4 Double ion-exchange membrane configuration

However, freedom in choosing the redox pairs is nevertheless feasible by employing a double-IEM configuration as displayed in Figure 1.4.

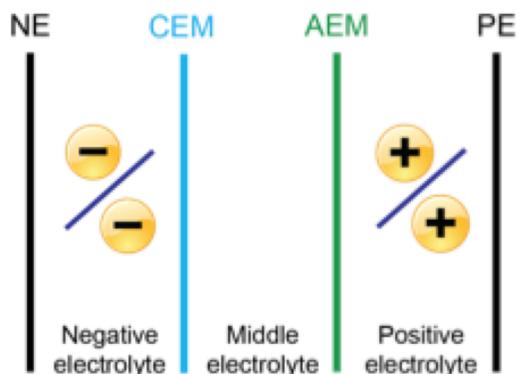


Figure 1.4: Double-IEM with redox pair combinations of mixed ion charges.

It consists of one AEM, one CEM and a middle electrolyte in between. Furthermore, a flexible choice of electrolytes is possible now, such as an acid electrolyte at one electrode and a base electrolyte at the other electrode, enabling a much larger reversible voltage window of water electrolysis of 2.06 V. HER = -0.83 V at pH = 14 versus OER = 1.23 V at pH = 0 [10]. One example is the basic zinc-acidic iron double-IEM RFB, displayed in Figure 1.5, with 1.99 V standard cell voltage. The redox reactions are the following (discharging reactions proceed from left to right and the reversed reactions happen for charging).

- At the negative electrode: $\text{Zn} + 4\text{OH}^- \longleftrightarrow \text{Zn}(\text{OH})_4^{2-} + 2\text{e}^-$ (-1.22 V) associated with a NaOH solution as the negative electrolyte.
- At the positive electrode: $\text{Fe}^{3+} + \text{e}^- \longleftrightarrow \text{Fe}^{2+}$ (0.77 V) associated with a HCl solution as the positive electrolyte.

The middle electrolyte is a NaCl salt solution that ionically connects the negative and positive electrolytes, in order to maintain the charge balance in each chamber.

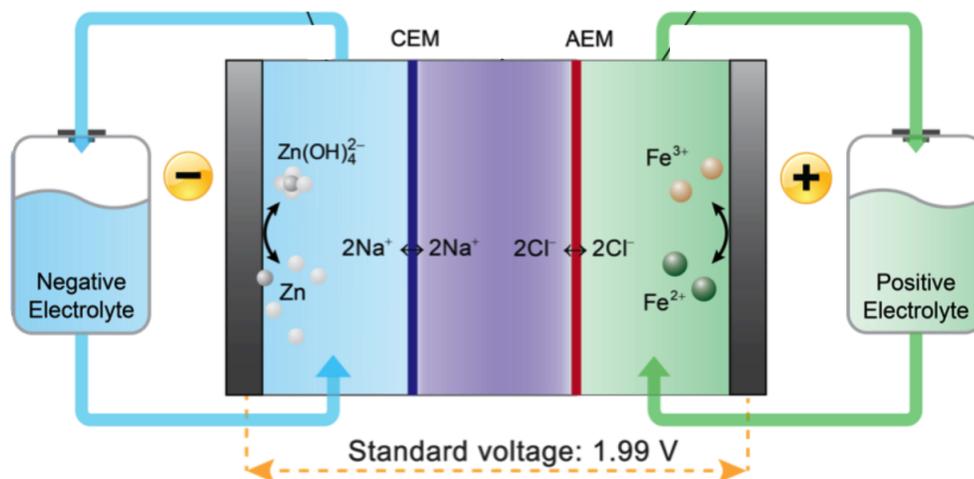


Figure 1.5: Zn/Fe double IEM-RFB

Other examples include a ultra-high voltage basic zinc-acidic cerium RFB with a 3.08 V standard cell voltage, combining the very negative redox potential from $\text{Zn}(\text{OH})_4^{2-}/\text{Zn}$ in base (-1.21 V) with the very positive redox potential from $\text{Ce}_2\text{O}^{6+}/\text{Ce}^{3+}$ in acid (+1.87 V) and an ultra-low cost sulfur-iron RFB with 1.22 V standard cell voltage, combining the $\text{S}_4^{2-}/\text{S}_2^{2-}$ anion redox pair (-0.45 V) with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cation redox pair (+0.77 V) [10].

Besides the freedom in choosing the redox pairs and the supporting electrolytes, the double-IEM configuration possesses also a significantly lower overall ion crossover rate between the negative and positive electrolytes than single-IEM RFBs (i.e., 15-143 times lower for double-IEM cells), enabling to reduce the thickness of both the AEM and CEM without compromising the coulombic efficiency. Hence, the middle electrolyte serves as an ion-crossover buffer while providing the electrolyte continuity [10].

1.3 Zn/Fe Double Ion-Exchange Membrane Redox Flow Battery

The double-IEM configuration for the Zn/Fe RFB has promising features. However, there are still some challenges with the Zn/Fe double-IEM RFB that need to be

addressed. There occurs H^+ crossover from the positive electrolyte through the AEM to the middle electrolyte, while at the same time OH^- crosses over from the negative electrolyte through the CEM to the middle electrolyte, leading to the formation of H_2O . This acid-base neutralization has a negative impact on the RFB, leading to a decrease in cell performance. Moreover the double-IEM configuration has two IEMs and three electrolytes contributing to the internal resistance, compared to only one IEM and two electrolytes in a single-IEM configuration. A reduction in internal resistance would improve the efficiency and the power density drastically. Therefore, the development of materials like electrodes and IEMs are critical [13].

1.4 Thesis Outline

Ideally, the best performance of the Zn/Fe double-IEM RFB is achieved when there is no H^+/OH^- crossover while at the same time the internal resistance is very small. However, in reality this is not the case, see Figure 1.6. On top of that, it is difficult to optimize both criteria at the same time. Decreasing the thickness of the IEMs reduces the internal resistance on the one hand, but increases H^+/OH^- crossover (i.e., acid-base neutralization) on the other hand. In order to find a good trade-off, the following data will be gathered in this work.

1. H^+ crossover rate through AEMs.
2. OH^- crossover rate through CEMs.
3. Cl^-/Na^+ conductivities of the AEMs/CEMs.

Chapter 2 gives an overview of the current knowledge about the transport mechanisms of protons and hydroxide ions in aqueous solutions, together with the basics on IEMs. While the details of the proton transport mechanism are well understood, the molecular-scale description of hydroxide ion transport is still controversial. Chapter 3 describes the experiments that are conducted in order to get the H^+/OH^- permeabilities and the Cl^-/Na^+ conductivities for different AEMs and CEMs. The results are discussed in Chapter 4. The conclusion of this work will be given in Chapter 5. Finally, some promising ideas will be highlighted for future work in Chapter 6.

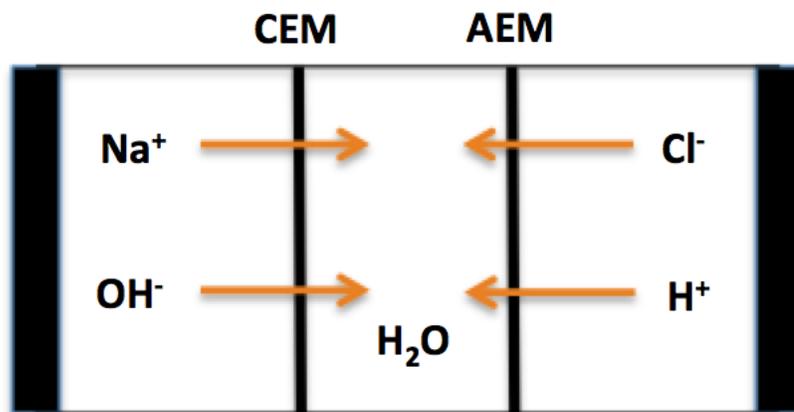


Figure 1.6: Acid-base neutralization and Cl^-/Na^+ conductivities in Zn/Fe double-IEM RFB.

Chapter 2

BACKGROUND

AEMs allow the selective transport of anions across the membrane, while ideally remaining impermeable to cations, whereas CEMs allow the selective transport of cations across the membrane, while ideally remaining impermeable to anions. However, protons and hydroxide ions exhibit an anomalously high mobility in aqueous solutions, compared to other ions, see Table 2.1 [14]. The ionic mobility of H^+ is about seven times that of Na^+ and approximately five times that of K^+ .

Table 2.1: Ionic mobilities in water at 298 K.

	u [$10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$]
H^+	36.23
OH^-	20.64
Na^+	5.19
K^+	7.62
Cl^-	7.91
Br^-	8.09

AEMs and CEMs swell in aqueous solutions, due to the presence of sorbed water. As a consequence, proton leakage through the AEM and hydroxide leakage through CEM occur [15]. Therefore, it is useful to get an understanding of the nature and transport of the protons and hydroxide ions in aqueous solution through IEMs. In the case of the protons, the transport mechanism is fairly well understood. Substantial research has led to a consistent theory, which has become textbook knowledge [14], described in Section 2.1. However, the situation is much less clear for the transport mechanism of hydroxide ions, as reported in Section 2.2. At last, Section 2.3 provides some basic knowledge about IEMs.

2.1 Proton Transport Mechanism in Aqueous Solution

The anomalously high mobility of protons in water can be explained by the “Grotthuss Mechanism”, also known as “structural diffusion”, since proton diffusion occurs via the migration of a structural defect (a topological defect) in the hydrogen-bonded network, not via migration as an individual proton H^+ . This proton-hopping kinetic mechanism involving the rearrangement of bonds in a group of water molecules [14, 16, 17] is illustrated in Figure 2.1.

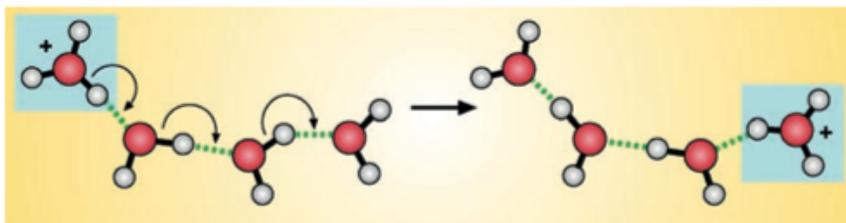
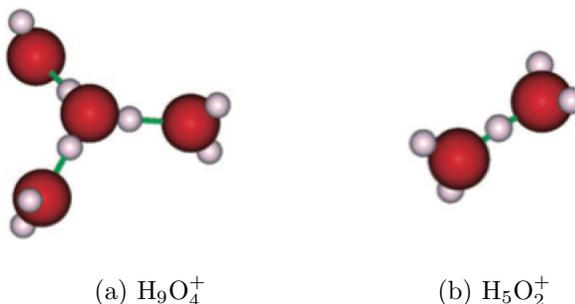


Figure 2.1: The Grotthuss Mechanism in proton diffusion.

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The Grotthuss Mechanism was unclear until fairly recently. It is considered to occur via an intricate interplay between the Eigen cation $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ or H_9O_4^+ , on the one hand and the Zundel cation, $[\text{H}_2\text{O}\cdots\text{H}\cdots\text{OH}_2]^+$ or H_5O_2^+ , on the other hand [18, 19]. In the Eigen cation, a hydronium core is solvated by accepting three hydrogen-bonded water molecules, while in the Zundel cation, the proton is shared equally between two water molecules via an ultrashort, centered hydrogen bond [17], see Figure 2.2.



(a) H_9O_4^+

(b) H_5O_2^+

Figure 2.2: The Eigen cation and the Zundel cation.

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The schematic mechanism in Figure 2.3 illustrates the sequence of transitions from the H_9O_4^+ to H_5O_2^+ to H_9O_4^+ hydrated complexes (a complete coordination shell is only shown for one of the first-solvation-shell waters). The rate-determining step is the hydrogen-bond cleavage of water molecules in the second solvation shell, since these hydrogen bonds are weaker than the ones in the first solvation shell. Then the proton migrates to the center of the bond to form a H_5O_2^+ cation. A new H_9O_4^+ cluster forms as other water molecules become members of the second solvation shell. The proton transfer is completed as a properly solvated H_3O^+ is located at a new site in the hydrogen-bond network. Note that the half-life of a solvated molecule during the proton transfer between two H_2O molecules is of the order of a few ps [14, 19, 20]. For a more detailed description of these steps, see reference [21].

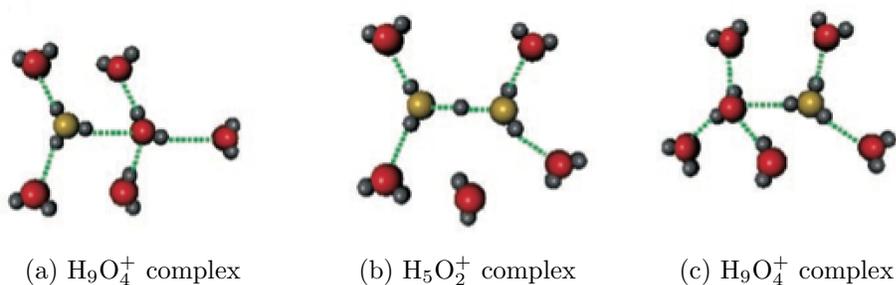


Figure 2.3: Structural diffusion mechanism: Intricate interplay between the Eigen ion and the Zundel ion.

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In short, the Grotthus Mechanism is a proton-hopping kinetic mechanism, since a proton is exchanged between water molecules through hydrogen bonds that form and break. The simplified mechanism is visualized in Figure 2.4, emphasizing that the protons are passed along the hydrogen bonds [22].



Figure 2.4: The Grotthus Mechanism.

At high water contents, the Grotthuss Mechanism dominates proton conduction. In this case, protons are moving faster across the membrane than water. However, at low water contents, the Vehicle Mechanism is the dominating transport mechanism. Now the diffusion coefficients of protons and water are similar. As opposed to the Grotthuss Mechanism, bulk diffusion of a proton and its associated water molecules or “vehicle” in H_3O^+ , H_5O_2^+ etc. takes place, while the empty vehicles move in the opposite direction [22, 23], as illustrated in Figure 2.5 .



Figure 2.5: The Vehicle Mechanism.

2.2 Hydroxide Transport Mechanism in Aqueous Solution

OH^- mobility in aqueous solutions is only 57% of the H^+ mobility, as illustrated in Table 2.1. It would be nice to have a simple model to justify that OH^- moves in aqueous solutions at approximately half the speed of H^+ . However, while detailed investigations have led to a clear picture of the proton transport mechanism, the structural diffusion mechanism of hydroxide ions in aqueous environment is much less clear. The traditional view is that the mechanism of $\text{OH}^-(\text{aq})$ can be deduced from the proton structural diffusion mechanism, by invoking a pseudosymmetry argument. The underlying idea is that while H_3O^+ can be viewed as a water molecule with an excess proton, OH^- can be regarded as a water molecule missing a proton (“a proton-hole”). Assuming similar solvation shell topologies, the $\text{OH}^-(\text{aq})$ transport mechanism is deduced from the $\text{H}_3\text{O}^+(\text{aq})$ transport mechanism by reversing hydrogen bond polarities and the directions of the proton transfer, described in detail in reference [24]. However, as proposed by Tuckerman et al. [21], OH^- ions behave differently from excess protons in water, contrary to the “proton hole picture”. A complex and rich

picture for OH^- ion transport is proposed, in which the quantum-mechanical character of the OH^- ion plays a major role, using powerful simulation techniques as ab initio molecular dynamics simulations and ab initio path integrals [20]. As this discussion would lead us to far away from the real purpose of this thesis, the reader is referred to the references [17, 19, 21, 25, 26] for more information on the proposed $\text{OH}^-(\text{aq})$ transport mechanism.

2.3 Ion-Exchange Membranes

The IEM is one of the key components of RFBs. It allows the transport of ions to complete the electric circuit while preventing the cross-mixing of the positive and negative electrolytes. An ideal IEM exhibits the following characteristics [8].

- Good ionic conductivity, required to minimize the losses in voltage efficiency.
- High ion selectivity. The IEM should be permeable to the charge-balancing ions to complete the current circuit, while preventing the crossover of the active redox species to allow high coulombic efficiencies.
- Excellent chemical, mechanical and thermal stability.
- Low cost.

Optimizing the properties of IEMs is challenging, since opposing trends occur. For instance, increasing the mechanical strength of the IEM by applying a high degree of cross-linking in the membrane increases the electrical resistance (the ionic conductivity decreases) [27].

A high selectivity for IEMs is of utmost importance. The selectivity for Cl^- ions over H^+ ions and Na^+ ions over OH^- ions directly affects the current efficiency. Moreover the selectivity for Cl^- and Na^+ over multivalent ions delays fouling and increases the lifetime of the membrane [28].

Another important property of an IEM is the ion-exchange capacity (IEC), which is the number of functional groups per unit mass of polymer [29]. IEC is usually

expressed in meq/g (milliequivalents/g) or in mmol/g. An equivalent of an ion is defined as the quantity of that ion that contains one mole of charge. So one equivalent of an ion equals one mole of that ion divided by its valence. Hence, one equivalent of H^+ equals one mole of H^+ [30]. By varying the IEC of the IEM, it is possible to control both its ion conductivity and water uptake. Again opposing effects occur. Increasing the IEC enhances the ion conductivity, but at the same time excessive water uptake and swelling occur, compromising the mechanical properties of the IEM [31].

Chapter 3

EXPERIMENTAL WORK

This chapter provides detailed information on the experimental work. The first set of experiments, described in Section 3.1, is conducted to obtain the H^+/OH^- permeabilities across AEMs/CEMs. The purpose of the second set of experiments, described in Section 3.2, is to measure the Cl^-/Na^+ conductivities in AEMs/CEMs. An overview of the results and a discussion can be found in Chapter 4.

3.1 Determination of Proton and Hydroxide Permeabilities across Ion-Exchange Membranes

Figure 3.1 illustrates the equipment that is used to determine the H^+/OH^- permeabilities across AEMs and CEMs respectively.

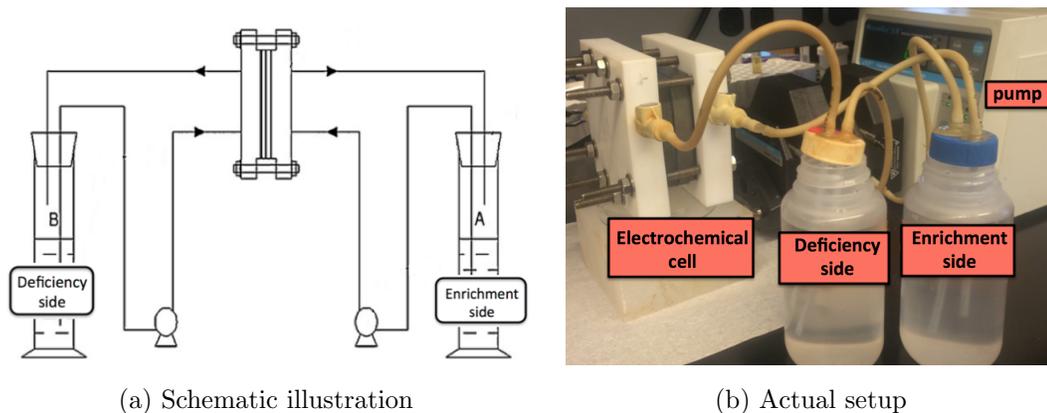


Figure 3.1: Setup for measuring the H^+/OH^- permeabilities.

Figure (a) reprinted with permission from Journal of Power Sources, ref. [32], Copyright 2009, Elsevier Ltd.

The setup consists of an electrochemical cell, two reservoirs and a peristaltic pump (Cole Parmer, Masterflex[®] L/S 600 rpm). The IEM is pressed between two

solid polytetrafluoroethylene (PTFE) blocks (electrolyte frames) with rubber gaskets on either side to prevent solution leakage. Eight bolts are torqued to 16 lbs to keep the cell together. The electrolyte flows through PTFE-lined rubber tubes (Cole Parmer, ChemDurance® #16) at a flow rate of 50 ml/min.

The solution in the right reservoir, the enrichment side (designated with letter A), contains 1.0 mol/L hydrochloric acid (HCl) in case the diffusion coefficient of protons through AEMs is investigated. For hydroxide ions permeability through CEMs, a solution containing 1.0 mol/L sodiumhydroxide (NaOH) is used. The left reservoir, the deficiency side (designated with letter B), is filled with 1.0 mol/L sodiumchloride (NaCl). Each reservoir contains 250 ml of solution. The Cl^- concentration for the H^+ diffusion experiment and the Na^+ concentration for the OH^- diffusion experiment are the same in both reservoirs, in order to eliminate the osmosis of the anions and cations respectively [32]. The IEM was immersed in distilled water before use. The effective area A of the IEM exposed to the solutions is 18 cm^2 . 1 ml solution of the deficiency side was sampled at a regular time interval. Determining the amount of protons/hydroxide ions crossing over from the enrichment side in function of time was done by measuring the pH of the sample.

H^+ crossover of the following AEMs was investigated.

1. **Fumapem® FAA-3**, a commercial, non-reinforced, alkaline stable AEM (Fumatech).
2. **Fumasep® FAB-PK-130**, a commercial PEEK-reinforced (polyether ether ketone) AEM which is developed for very low proton crossover with high selectivity, high mechanical stability and high stability in acidic and caustic environments (Fumatech).
3. **QNPPO**, $\text{DS}(x) = 14\%$, $\text{IEC} = 1.07 \text{ mmol/g}$, synthesized in the lab, see Figure 3.2 a. QNPPO stands for Quaternized Ammonium Poly(2,6-dimethyl-1,4-phenylene oxide) and the $\text{DS}(x)$ value indicates the degree of substitution value for QN groups.

4. **PTFE-QNPPO**, a polytetrafluoroethylene (PTFE) pore-filling membrane with $DS(x) = 14\%$, $IEC = 1.04$ mmol/g. It was synthesized in the lab, see Figure 3.2 b.

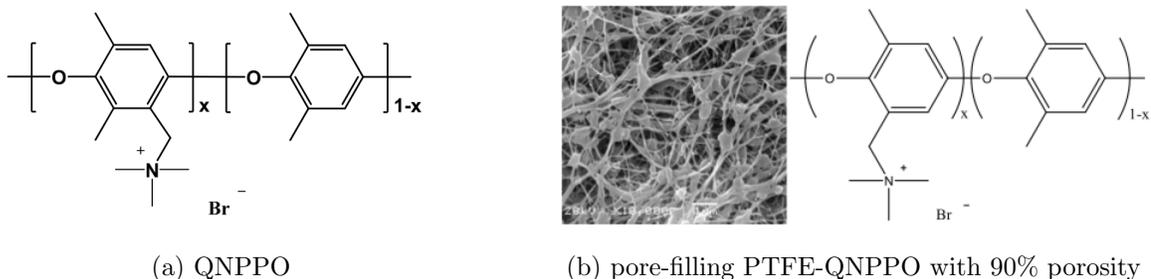


Figure 3.2: Chemical structures of the AEMs made in the lab.

For the OH^- crossover experiment, the next CEMs were employed.

1. **Nafion[®] NR-212**, a commercial CEM (Ion-Power, Inc.).
2. **Fumasep[®] FKE-50**, a commercial, non-reinforced CEM (Fumatech).
3. **Fumasep[®] FKS-50**, a commercial, non-reinforced CEM (Fumatech).

The IEC values for the commercial AEMs and CEMs are obtained from datasheets from Fumatech [33] and Ion Power [34]. The IEC values for the lab made AEMs, QNPPO and PTFE-QNPPO, are computed IEC values. They are listed in Table 3.1.

Table 3.1: IEC of the ion-exchange membranes

AEM	IEC [mmol/g]
Fumapem [®] FAA-3	1.9-2.1
Fumasep [®] FAB-PK-130	1.0-1.1
QNPPO	1.07
PTFE-QNPPO	1.04
CEM	IEC [mmol/g]
Nafion [®] NR-212	0.95-1.01
Fumasep [®] FKE-50	>1
Fumasep [®] FKS-50	>1

3.2 Ion Conductivities in Ion-Exchange Membranes

For the in-plane ion conductivity measurements, samples of the IEMs of ca. 7 cm × 1 cm are prepared. The thickness is measured at five locations with a digital micrometer (Mitutoyo American Corporation) and then averaged. They were submerged in 1.0 mol/L NaCl for 24 hours, since the purpose is to measure the Na⁺/Cl⁻ conductivity. After this treatment, the IEMs were repeatedly rinsed in deionized water. It is crucial that the IEMs are completely clean. As the ion conductivity on the IEMs is rather low, any presence of dissolved ions (Na⁺, Cl⁻) would influence the measurement considerably.

In order to determine the in-plane ionic conductivity of the IEM, the membrane resistance $R_{membrane}$ is calculated using an AC impedance method using four electrodes. The AC impedance measurements, carried out in the frequency region from 10000 Hz to 1 Hz, are performed using a computer-controlled impedance gain/phase analyzer (Solartron Instruments, model 1260) and electrochemical interface (Solartron Instruments, model 1287) measuring system, see Figure 3.3. The settings are specified in Table 3.2. Nyquist (Z' - Z'') plots were obtained and from the semicircles in the Nyquist plots, the $R_{membrane}$ can be determined for the different IEMs [35]. The in-plane ionic conductivity σ [mS/cm] can be calculated from the membrane resistance $R_{membrane}$ [Ω] using Equation (3.1)

$$\sigma = \frac{l}{R_{membrane}S} \quad (3.1)$$

where l is the distance between the reference platinum electrodes [cm], 1 cm in this case, and S is the cross-sectional area of the membrane (thickness x width) [cm²] [36, 37].



(a) 4-pole conductivity meter



(b) Solartron Instruments 1260 and 1287

Figure 3.3: Setup to measure the Cl^-/Na^+ conductivity of the IEMs.

Table 3.2: Settings for the Solartron Instruments 1260 and 1287

Frequency sweep	
Initial frequency [Hz]	10000
Final frequency [Hz]	1
Steps/Decade interval	10
Polarization	
DC potential [V]	0
AC amplitude [mV]	5

The area-specific resistance ASR [$\Omega \text{ cm}^2$] can subsequently be calculated from the ionic conductivity σ and the mean thickness L [cm] of the IEM σ with Equation (3.2).

$$ASR = \frac{L}{\sigma} \quad (3.2)$$

Chapter 4

RESULTS AND DISCUSSION

The H^+/OH^- permeabilities and the Cl^-/Na^+ conductivities in AEMs/CEMs are listed in Section 4.1 and Section 4.2. Section 4.3 summarizes and discusses all the gathered data.

4.1 Proton and Hydroxide Crossover in Ion-Exchange Membranes

The starting point to determine Equation (4.11) for calculating the permeability of protons and hydroxide ions across AEMs and CEMs respectively, are Fick's first law (4.1) and second law (4.2)

$$J = -D \frac{\partial C}{\partial x} \quad (4.1)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (4.2)$$

where J is the molar flux (i.e., the amount of moles per unit area per unit time) [$\text{mol cm}^{-2} \text{s}^{-1}$], D is the diffusion coefficient [$\text{cm}^2 \text{s}^{-1}$], C is the concentration of protons/hydroxide ions [mol L^{-1}], x is the position [cm] and t is the time [s]. Consider the experimental setup given in Chapter 3, Figure 3.1. Assume the case of steady-state diffusion, i.e., when there is a steady-state concentration profile across the membrane, see Figure 4.1. An equilibrium between protons/hydroxide ions is established on both surfaces of the IEM according to Henry's law, with a solubility partition coefficient K given by Equation (4.3)

$$K = \frac{C'_B}{C_B} = \frac{C'_A}{C_A} \quad (4.3)$$

where C_A and C'_A are the concentrations of protons/hydroxide ions in the bulk phase of the enrichment side and at the interface between the membrane and the enrichment

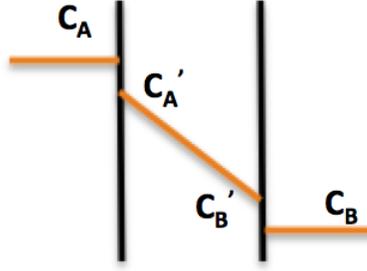


Figure 4.1: Concentration profile across the IEM in steady-state.

side respectively, while C_B and C'_B are the concentrations of protons/hydroxide ions in the bulk phase of the deficiency side and at the interface between the membrane and the deficiency side respectively. Note that the actual transmembrane concentration difference, $C'_A - C'_B$, is less than the overall concentration difference, $C_A - C_B$ [38].

The steady-state assumption is only valid if C_A and C_B are independent of time. Then Equation (4.4) is valid, so Fick's first law applies in this case [39].

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} = 0 \quad \longrightarrow \quad \frac{\partial C}{\partial x} = \text{constant} = \frac{C'_A - C'_B}{L} \quad (4.4)$$

$$J = D \frac{C'_A - C'_B}{L} = \frac{KD}{L} (C_A - C_B) = \frac{P}{L} (C_A - C_B) = \bar{P} (C_A - C_B) \quad (4.5)$$

where $P = KD$ is the permeability coefficient [$\text{cm}^2 \text{s}^{-1}$] and \bar{P} is the permeance [cm s^{-1}], defined as the ratio of P to L . From Equation 4.5, it is clear that the permeance of protons/hydroxide ions diffusing through a membrane of a given thickness is given by the flow rate of protons/hydroxide ions per unit cross-sectional area of membrane per unit driving force, i.e., the concentration gradient. Note that P is determined here rather than D since steady-state experiments do not allow to separate P into specific values for K and D [39, 40].

The value of C_A can be approximately regarded as a constant by employing a large volume (250 ml) of solution. However, the value of C_B will not remain constant

over time. C_B is 0 at $t = 0$ and will gradually increase as protons/hydroxide ions are permeating from the enrichment side to the deficiency side. Therefore, there is no constant gradient, so Fick's first law is not applicable. Since this situation represents unsteady-state diffusion, Fick's second law (4.2) should be solved instead.

However, a quasi-steady-state assumption can be made, since the membrane is so thin that the concentration within it may still be considered approximately linear, although changing in time, as visualized in Figure 4.2. As the transport rate at

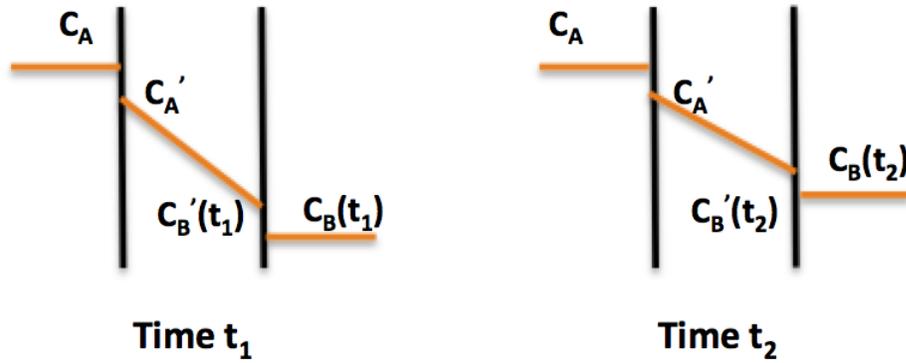


Figure 4.2: Approximately linear concentration profile in the quasi-steady-state approximation.

any time is equal to the steady-state flux at that specific moment time, Fick's first law is again applicable. Initially there are no protons/hydroxide ions in the deficiency side ($C_B = 0$ at $t = 0$). So n_B , the change in moles of protons/hydroxide ions in the deficiency side [mol], is related to the flux J of protons/hydroxide ions through the IEM and the effective area A of the membrane [cm^2], given by Equation (4.6) [39].

$$\frac{dn_B(t)}{dt} = JA \quad (4.6)$$

Combining Equation (4.6) with Equation (4.5) leads to Equation (4.7)

$$\frac{dn_B(t)}{dt} = P \frac{A}{L} (C_A - C_B(t)) \quad (4.7)$$

Equation (4.7) can be changed to Equation (4.9) by assuming that the volume V_B of the deficiency side [cm^3] is a constant. An assumption is also made that P is independent of concentration [41].

$$V_B \frac{dC_B(t)}{dt} = P \frac{A}{L} (C_A - C_B(t)) \quad (4.8)$$

$$\frac{dC_B(t)}{C_A - C_B(t)} = \frac{PA}{V_B L} dt \quad (4.9)$$

Given the initial condition $C_B = 0$ at $t = 0$, Equation (4.9) can be integrated and Equation (4.11) is obtained.

$$- \int_0^{C_B} \frac{d(C_A - C_B(t))}{C_A - C_B(t)} = \frac{PA}{V_B L} \int_0^t dt \quad (4.10)$$

$$\ln \left(\frac{C_A}{C_A - C_B} \right) = \frac{PA}{V_B L} t \quad (4.11)$$

It can be seen from Equation (4.11) that $\ln(C_A/(C_A-C_B))$ is proportional to the time t . Now the slope, corresponding to the value of $(PA/V_B L)$ can be obtained. Since A , V_B and L are known values, P can be calculated [32]. Note that P is independent of the thickness of the IEM.

4.1.1 Proton permeability across anion-exchange membranes

Figure 4.3 shows the plots of $\ln(C_A/(C_A-C_B))$ versus time for the four different AEMs and these plots are all put together in one plot in Figure 4.4. The proton permeability for each AEM is determined from the value of the slope $(PA/V_B L)$ and is listed in Table 4.1.

Table 4.1: H^+ crossover rates in anion-exchange membranes.

AEMs	L [μm]	V_B [ml]	A [cm^2]	Slope $\frac{PA}{V_B L}$ [min^{-1}]	P_{H^+} [cm^2/s]
Fumapem [®] FAA-3	35	250	18	0.0091	7.4×10^{-6}
Fumasep [®] FAB-PK-130	130	250	18	6×10^{-5}	1.8×10^{-7}
QNPPO	35	250	18	0.0003	2.4×10^{-7}
PTFE-QNPPO	55	250	12.2	0.0005	9.4×10^{-7}

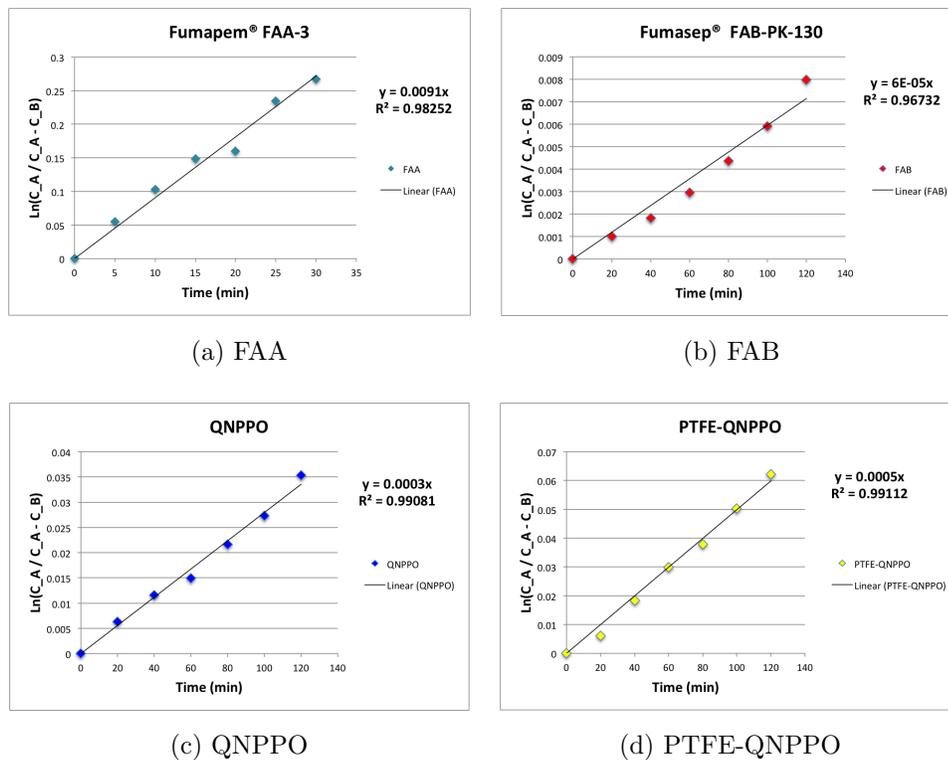


Figure 4.3: Plots of $\ln(C_A/C_{A-C_B})$ vs t for different AEMs.

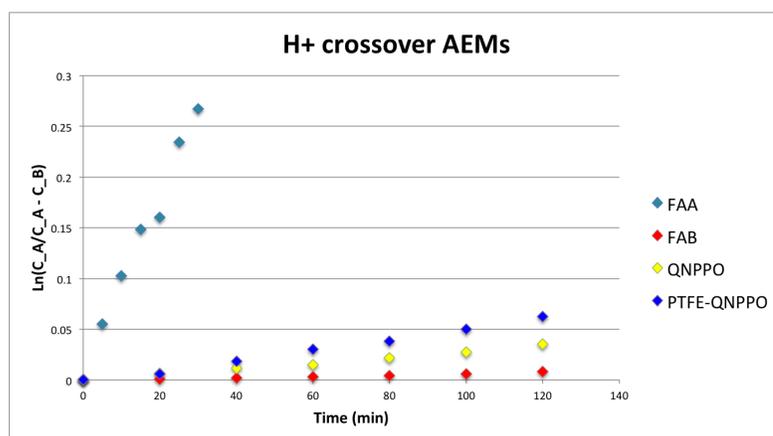


Figure 4.4: Comparison of the H^+ crossover rates in AEMs.

It is clear that the proton permeability across Fumapem[®] FAA-3 is the largest one, whereas proton permeabilities across the three other AEMs are substantially

smaller. The proton permeability of PTFE-QNPPO is slightly higher than that of QNPPO, with Fumasep[®] FAB-PK-130 possessing the lowest proton permeability.

4.1.2 Hydroxide permeability across cation-exchange membranes

Plots of $\ln(C_A/(C_A-C_B))$ versus time for the three different CEMs are shown in Figure 4.5 and Figure 4.6. Table 4.2 lists the values for the hydroxide permeability for each CEM, obtained from the value $(PA/V_B L)$ of the slope.

Table 4.2: OH⁻ crossover rates in cation-exchange membranes.

CEMs	L [μm]	V _B [ml]	A [cm^2]	Slope $\frac{PA}{V_B L}$ [min^{-1}]	P _{OH-} [cm^2/s]
Nafion [®] NR-212	50	250	18	5×10^{-5}	5.8×10^{-8}
Fumasep [®] FKE-50	50	250	18	1×10^{-5}	1.2×10^{-8}
Fumasep [®] FKS-50	50	250	18	2×10^{-5}	2.3×10^{-8}

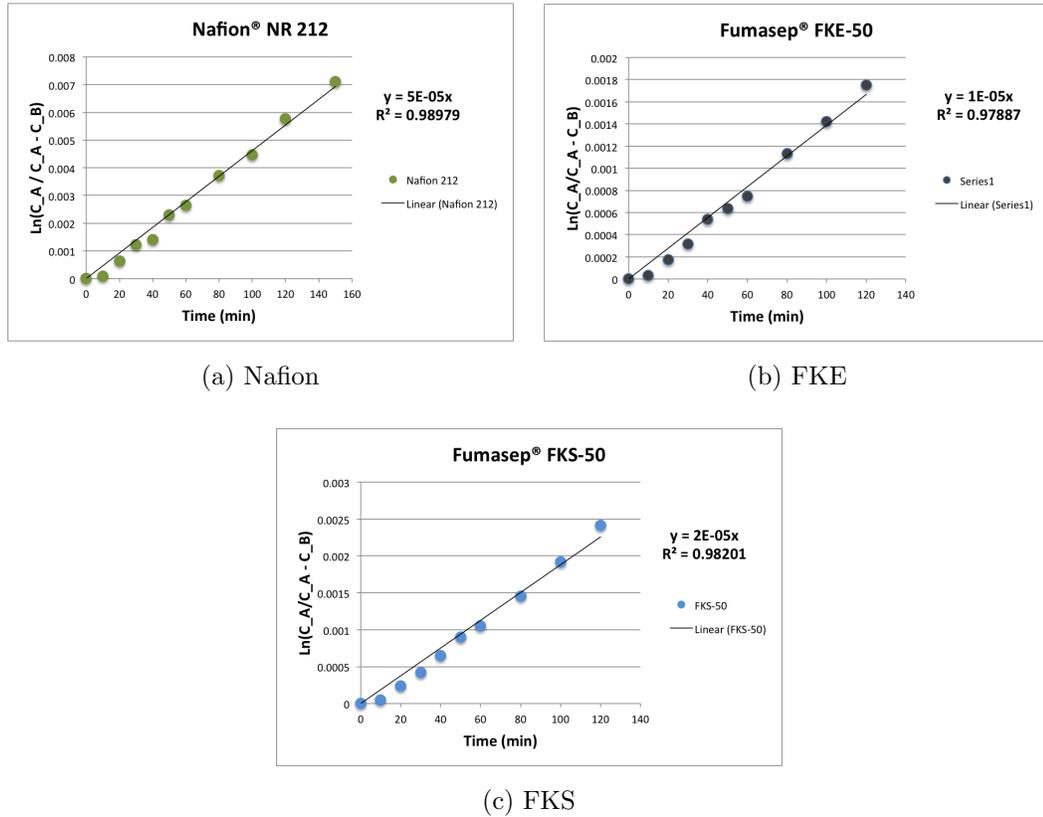


Figure 4.5: Plots of $\ln(C_A/C_A-C_B)$ vs t for different CEMs.

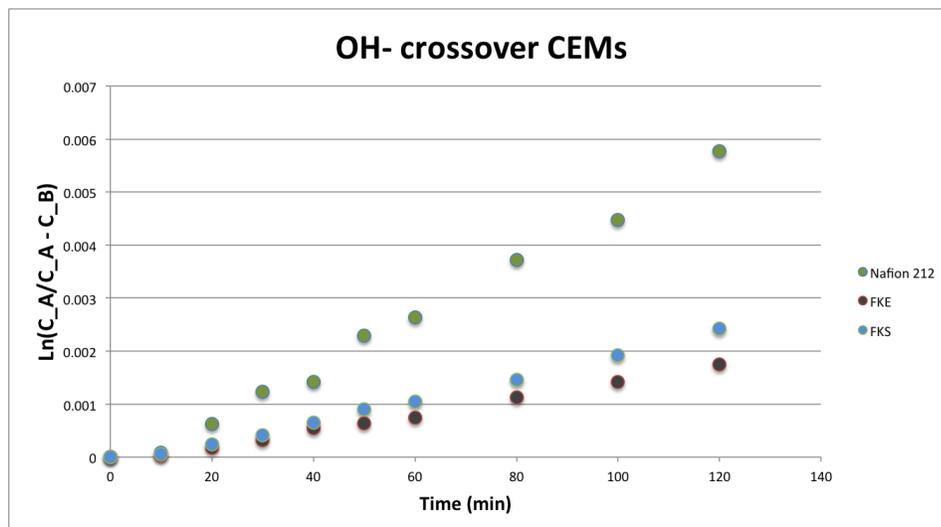


Figure 4.6: Comparison of the OH⁻ crossover rates in CEMs.

Among the three CEMs, Nafion[®] NR-212 has the highest hydroxide permeability, whereas Fumasep[®] FKE-50 has the lowest.

4.2 Ion Conductivities in Ion-Exchange Membranes

The results of the ion conductivity test, described in Section 3.2, are summarized in Table 4.3. Note that the resistance of deionized water was measured to be 94000 Ω.

Table 4.3: Cl⁻/Na⁺ conductivities in ion-exchange membranes.

AEMs	L [μm]	Chloride conductivity σ_{Na^+} [mS/cm]	Area-specific resistance ASR [Ω cm ²]
Fumapem [®] FAA-3	35	13	0.27
Fumasep [®] FAB-PK-130	130	0.8	16.3
QNPPO	45	2.6	1.7
PTFE-QNPPO	30	6.6	0.45
CEMs	L [μm]	Chloride conductivity σ_{Cl^-} [mS/cm]	Area-specific resistance ASR [Ω cm ²]
Nafion [®] NR-212	50	14.2	0.35
Fumasep [®] FKE-50	50	4.2	1.2
Fumasep [®] FKS-50	50	5.3	0.94

4.3 Discussion

Ideally, an IEM should possess both a low H^+/OH^- crossover (i.e., a high selectivity of Cl^-/Na^+ over H^+/OH^-) and a high ionic conductivity (a low ASR). To compare the investigated IEMs, the experimental data from Tables 4.1, 4.2 and 4.3 are summarized in Table 4.4. A trend between the H^+/OH^- crossover and the ionic conductivity is observed. Fumapem[®] FAA-3 has by far the highest ionic conductivity, but also the highest H^+ crossover of all the considered AEMs. On the contrary, Fumasep[®] FAB-PK-130 has the lowest ionic conductivity as well as the lowest H^+ crossover. QNPPO and PTFE-QNPPO have moderate values for both of the parameters. The same trend is observed for the CEMs. Nafion[®] NR-212 has the highest ionic conductivity, while also having the highest OH^- crossover of the three CEMs. On the other hand, Fumasep[®] FKE-50 has the lowest ionic conductivity and the lowest OH^- crossover. Clearly the experimental data shows that a trade-off should be made, since both a low H^+/OH^- crossover (high selectivity) and a high ionic conductivity (low ASR) cannot be achieved at the same time for the presented IEMs.

The thickness L of IEMs plays an important role in both the ASR and the ion crossover. First of all, it links both ASR and σ , see Equation 3.2.

$$ASR = \frac{L}{\sigma} \quad (3.2)$$

Furthermore, it links the permeance \bar{P} to the permeability P , as given by Equation 4.12. \bar{P} is also calculated and listed in Table 4.4. Since \bar{P} contains the thickness L of the IEM, \bar{P} is a property for an IEM with a given thickness, not for the IEM itself.

$$\bar{P} = \frac{P}{L} \quad (4.12)$$

For any given membrane, the product of \bar{P} and ASR is irrelevant of membrane thickness, as can be seen by Equation 4.13.

$$\bar{P} \times ASR = \left(\frac{P}{L}\right) \times \left(\frac{L}{\sigma}\right) = \frac{P}{\sigma} \quad (4.13)$$

Therefore, it is instructive to calculate the conductivity/permeability ratio σ/P , listed in Table 4.5. Since the H^+/OH^- crossover should be as low as possible and the ionic conductivity should be as high as possible, the parameter σ/P should be as high as possible for the best performance of an IEM. It is clear that σ/P is almost two orders of magnitude higher for CEMs than for AEMs. This is primarily due to the lower OH^- crossover in CEMs compared to H^+ crossover in AEMs. The AEMs are thus the bottleneck for the design of double-IEM RFBs.

Also the influence of the IEC on both parameters should be noted. A high IEC gives rise to a high ionic conductivity. However, it also enhances the water uptake of the membrane, increasing the H^+/OH^- crossover. The proton permeability and ionic conductivity of Fumapem[®] FAA-3 are clearly higher than those of Fumasep[®] FAB-PK-130, QNPPO or PTFE-QNPPO, as Fumapem[®] FAA-3 possesses a higher IEC.

Table 4.4: Comparison of the H^+/OH^- crossover rates and Cl^-/Na^+ conductivities in ion-exchange membranes.

AEMs	L [μm]	IEC [mmol/g]	P_{H^+} [cm^2/s]	$\bar{\text{P}}_{\text{H}^+}$ [cm/s]	σ_{Cl^-} [mS/cm]	ASR [$\Omega \text{ cm}^2$]
Fumapem [®] FAA-3	35	1.9-2.1	7.4×10^{-6}	2.1×10^{-3}	13	0.27
Fumasep [®] FAB-PK-130	130	1.0-1.1	1.8×10^{-7}	1.4×10^{-5}	0.8	16.3
QNPPO	35	1.07	2.4×10^{-7}	6.9×10^{-5}	/	/
QNPPO	45	1.07	/	/	2.6	1.7
PTFE-QNPPO	55	1.04	9.4×10^{-7}	1.7×10^{-4}	/	/
PTFE-QNPPO	30	1.04	/	/	6.6	0.45
CEMs	L [μm]	IEC [mmol/g]	P_{OH^-} [cm^2/s]	$\bar{\text{P}}_{\text{OH}^-}$ [cm/s]	σ_{Na^+} [mS/cm]	ASR [$\Omega \text{ cm}^2$]
Nafion [®] NR-212	50	0.95-1.01	5.8×10^{-8}	1.2×10^{-5}	14.2	0.35
Fumasep [®] FKE-50	50	>1	1.2×10^{-8}	2.4×10^{-6}	4.2	1.2
Fumasep [®] FKS-50	50	>1	2.3×10^{-8}	4.6×10^{-6}	5.3	0.94

Table 4.5: Conductivity/Permeability ratio

AEMs	$\sigma_{\text{Cl}^-}/\text{P}_{\text{H}^+}$ [(mS s)/ cm^3]
Fumapem [®] FAA-3	1.8×10^6
Fumasep [®] FAB-PK-130	4.4×10^6
QNPPO	1.1×10^7
PTFE-QNPPO	7.0×10^6
CEMs	$\sigma_{\text{Na}^+}/\text{P}_{\text{OH}^-}$ [(mS s)/ cm^3]
Nafion [®] NR-212	2.4×10^8
Fumasep [®] FKE-50	3.5×10^8
Fumasep [®] FKS-50	2.3×10^8

Chapter 5

CONCLUSION

This thesis focuses on the IEMs of the basic zinc-acidic iron double-IEM RFB. The advantages from the double-IEM configuration over the single-IEM configuration are highlighted. Challenges of this Zn/Fe double-IEM RFB are the H^+/OH^- crossover and the high internal resistance, caused by the two IEMs and the middle electrolyte, leading to acid-base neutralization and a decrease in cell performance. An overview of the current knowledge about proton and hydroxide transport mechanisms in aqueous solutions is given. The H^+/OH^- crossover and the Cl^-/Na^+ of several AEMs (Fumapem[®] FAA-3, Fumasep[®] FAB-PK-130, QNPPO, PTFE-QNPPO) and CEMs (Nafion[®] NR-212, Fumasep[®] FKE-50, Fumasep[®] FKS-50) were measured. A general trend was observed between the H^+/OH^- crossover and the Cl^-/Na^+ conductivity, where the H^+/OH^- crossover decreases (selectivity increases) as the Cl^-/Na^+ conductivity decreases (internal resistance increases). Therefore, in the selection of IEMs for the Zn/Fe RFB, a trade-off between a low H^+/OH^- crossover (high selectivity) and a high ionic conductivity (low internal resistance) should be made. It was also shown that the conductivity/permeability ratio is almost two orders of magnitude higher for CEMs than for AEMs. Hence, AEMs are the bottleneck of the double-IEM configuration. Further research should focus on finding IEMs with both a high selectivity and a low internal resistance to improve the performance of the Zn/Fe double-IEM RFB.

Chapter 6

FUTURE WORK

6.1 Introduction

Currently the Zn/Fe double-IEM RFB utilizes polymer IEMs owing to their low electrical resistance and mechanical flexibility. But their main drawback is the low selectivity and fouling, reducing efficiency and life [42]. H^+/OH^- crossover occurs, which gradually changes the pH values in the anode and cathode compartments while also leading to acid-base neutralization in the middle compartment.

To circumvent the H^+/OH^- crossover issue, it is worthwhile to look into alternatives to polymer IEMs. Super-selective ceramic membranes are an interesting and highly promising choice. The focus is on ceramic LISICON/NASICON (Li superionic conductor/Na superionic conductor) materials. Superionic conductors are also referred to as “fast ion conductors” or “solid electrolytes” [43]. As the name suggests, these are highly selective membranes, i.e., they only permit Li^+/Na^+ ions to pass through the membrane.

6.2 Super-Selective Ceramic Membranes

6.2.1 Polymeric ion-exchange membranes versus super-selective ceramic membranes

It is instructive to compare the characteristics from a polymer IEM, for instance Nafion, with a ceramic LISICON/NASICON membrane [44].

- Nafion shows a high chemical stability, but a low ion selectivity. It does not inhibit the crossover of H^+ . The ion conductivity is rather high, approximately 100 mS/cm for protons [45] and 14 mS/cm for Na^+ ions at room temperature.

- The water-stable LISICON/NASICON membrane only permits Li^+/Na^+ ions to pass through, so it effectively inhibits the H^+ crossover. However, the ion conductivity is rather low, approximately 0.1 mS/cm [44, 46], leading to a low power density.

The NASICON ceramic membrane is more suited for use in the Zn/Fe RFB, since Na^+ is used as a charge carrier instead of Li^+ . Nasicon is attracting attention because of the abundant availability of Na^+ and because the costs of Li^+ are expected to rise strongly as the resource availability decreases [46]. Since NASICON only permits Na^+ to pass through, the double-IEM configuration, originally introduced to combine redox pairs with mixed ion charges with flexible choices of electrolytes, could be changed for a single-IEM configuration, provided NASICON is stable in between an acid electrolyte and a base electrolyte.

6.2.2 Structure of NASICON materials

It is informative to take a better look at the structure and the conduction pathway of NASICON materials. Reports of Hong and Goodenough [47, 48] mentioned NASICONs for the first time in 1976. In search for skeleton structures for fast alkali-ion transport, the system $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, with $0 \leq x \leq 3$, was discovered and analyzed. The NASICON structure consists of linked ZrO_6 polyhedra connected to $(\text{P}/\text{Si})\text{O}_4$ tetrahedra. Figure 6.1 shows the conduction channels, which allow the passage of Na^+ [49]. Thanks to their unique structural features, NASICONs exhibit many useful properties [43].

- **High thermal and chemical stability.** Since NASICONs are strong, covalently bonded 3-dimensional frameworks, their melting points are quite high (> 1650 °C).
- **Low thermal expansion**, attributed to the strongly bonded framework structure. Also the corner sharing octahedra, rather than edge-sharing, lead to an open framework with structural holes, providing the octahedra some freedom for rotational motion.
- **Ionic conductivity.** The ionic conductivity of a NASICON material depends on the composition. The maximum conductivity at room temperature, 0.67 mS/cm, occurs for $\text{Na}_2\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ($x = 2$) [46].

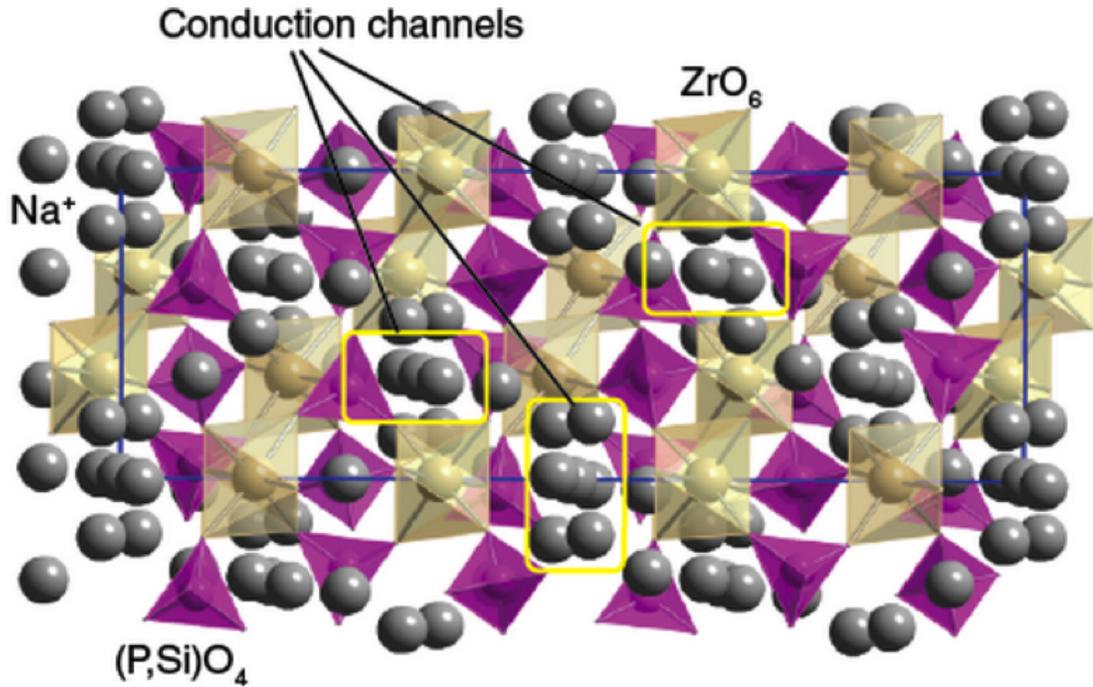


Figure 6.1: The structure of NASICON.

6.2.3 Ionic conductivity in solid electrolytes

The ion conductivity for solid electrolytes depends basically on four factors.

1. The concentration of charge carriers.
2. The temperature of the crystal.
3. The availability of vacant-accessible sites, controlled by the density of defects in the crystal.
4. The ease with which an ion can jump to another site, controlled by the activation energy.

The activation energy indicates the free energy barrier an ion has to overcome for a successful jump between the sites. It is thus the energy to make the ions move. It is of great importance since the dependence is exponential. The activation energies can be deduced using the Arrhenius expression, given by Equation (6.1),

$$\sigma = \frac{A}{T} \exp\left(\frac{-E_a}{k_B T}\right) \quad (6.1)$$

where σ is the ionic conductivity, T is the absolute temperature [K], k_B is the Boltzmann constant [J/K], E_a is the activation energy [J] and A is the pre-exponential factor, containing all the remaining factors mentioned earlier, i.e., other than the activation energy, that influence the ionic conductivity.

Ions move through a crystal by hopping from an occupied site to a vacant site. Hence, defects must be present for ion conductivity to occur. Two types of point defects are the Schottky defect and the Frenkel defect, see Figure 6.2 [50]. A Schottky defect is a defect in which a pair of ions, one cation and an anion, are missing in the crystal, leaving their position vacant. A Frenkel defect occurs when a single ion is missing from its regular position and is located at an interstitial site in the crystal [43].

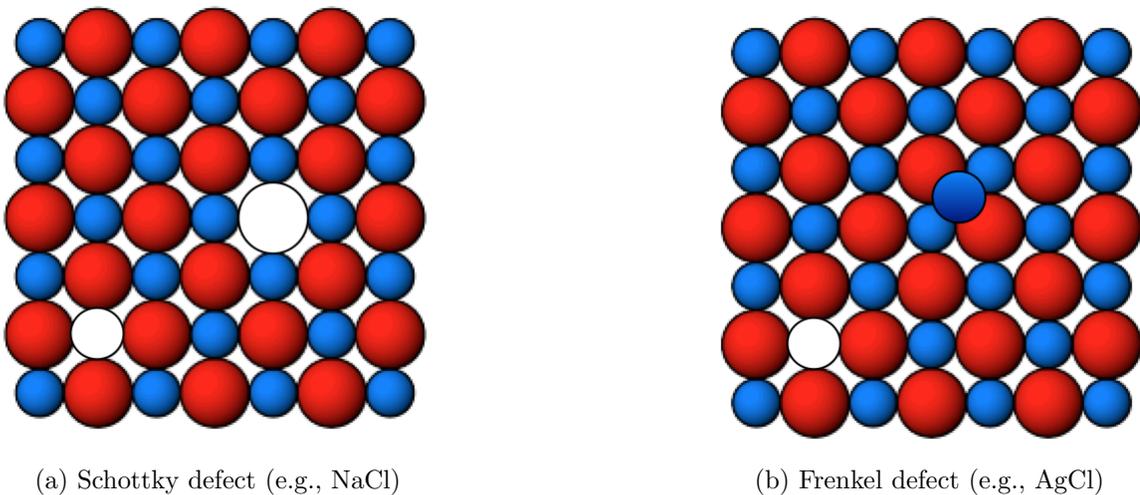


Figure 6.2: Point defects: The Schottky defect and the Frenkel defect.

There are three different conduction mechanism, using the vacant sites generated by both the Schottky and Frenkel defects [43, 51].

1. **Vacancy migration:** Diffusion which occurs between vacancies.
2. **Interstitial migration:** Diffusion which occurs between interstitials.
3. **Interstitialcy mechanism:** Diffusion which occurs when an interstitial atom displaces another atom from its original substitutional site.

6.3 Composite Ceramic Membranes

So the general idea is to replace the double-IEM configuration with polymeric IEMs with a single-IEM configuration employing a ceramic NASICON membrane. However, the major concern is the low ionic conductivity of NASICON, approximately 0.1 mS/cm, compared to the ionic conductivities of polymer IEMs, drastically limiting the power density. In order to obtain high current densities, it is necessary to produce thin components, reducing the resistance. However, the thickness required for self-supporting ceramic membranes leads to a high resistance and increases the energy consumption to unacceptable levels. There is a trade-off to make. Reducing the membrane thickness increases the battery energy and power density (since the cell resistance decreases), but at the same time lowers the mechanical strength. With the ionic conductivity σ fixed at that value, it can be seen from Equation (3.2) that by decreasing the thickness of the membrane d , an acceptable area-specific resistance ASR can be obtained. For instance, to achieve a value of $2 \Omega \text{ cm}^2$

$$d = ASR \times \sigma = 2 \Omega \text{ cm}^2 \times 0.1 \times 10^{-3} \frac{\text{S}}{\text{cm}} = 0.0002 \text{ cm} = 2 \mu\text{m} \quad (6.2)$$

a thickness of $2 \mu\text{m}$ is required, but this low thickness compromises the mechanical strength of the membrane considerably.

Both the polymeric IEMs and the ceramic NASICON membranes have their strengths and weaknesses. By employing a composite membrane, formed by a ceramic NASICON thin film deposited onto an appropriate polymeric membrane or ceramic membrane, the advantages of both polymeric IEMs (the mechanical flexibility and the low electric resistance) and ceramic membranes (the high selectivity, due to the ability to inhibit H^+ crossover) can be combined [28, 42].

6.4 Future Work

In this chapter, the idea of using a composite membrane, where a ceramic NASICON thin film is deposited onto a polymeric membrane or a ceramic membrane, is proposed. To go further down this road, it is crucial to investigate

1. If the ceramic NASICON membrane is indeed super-selective. In other words, an experiment needs to be conducted to make sure no H^+/OH^- crossover occurs across the membrane.
2. If the composite membrane is stable for a long time in acid-base aqueous solution.
3. If the mechanical strength of the composite membrane is sufficient.

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