Design and Optimization of Heterogeneous Catalyst Systems

for the Conversion of CO₂ to CO

by

Thomas Patrick Keane

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ABSTRACT

The electrochemical reduction of carbon dioxide is a critical step in the development of chemical storage systems for renewable energy. Practical implementation of such a system will require catalysts which are not only efficient, but which also can be fabricated from inexpensive and earth abundant materials. Ionic liquid (IL) mediated catalysis has enabled CO_2 reduction to be carried out using a variety of inexpensive, earth abundant cathode materials. The effects of the catholyte and cathode on the efficacy of catalysis were studied. A deeper understanding of the contributions of both of these components to IL mediated catalyst systems was developed which will allow for their continued improvement and innovation.

Chapter 1

INTRODUCTION

1.1 Global Energy: Production, Consumption, and Future

One of the hallmarks of modern industrial society is the consumption of large amounts of electricity. Global energy use has risen steadily since the advent of the industrial revolution, and in the year 2014 the average rate of global energy consumption was a massive 17.7 terawatts (TW).^{1–3} Two forces have historically driven trends in energy demand: human population and industrialization. As global population continues to increase, and as large portions of the world undergo development and industrialization, the amount of energy required to satisfy the global demand is also predicted to increase, with conservative estimates putting the total at 28 TW by 2050.^{4,5}

In order to meet the difference between current energy demands and those predicted for 2050, an additional 10 TW of power must be produced by some means. As can be seen in Figure 1.1, a large fraction of the global energy portfolio has been, and is currently, comprised of fossil fuels including coal, oil, and natural gas. While the use of fossil fuels could be expanded to fill the impending 10 TW energy gap,^{1,3} there are significant drawbacks to their use, as discussed in section 1.2, which warrant the consideration of other power sources.



Figure 1.1: Total global energy consumption from 1965 to 2014 showing contributions from various energy sources.¹

1.2 The Negative Impacts of Fossil Fuel Use

The preeminent use of fossil fuels over other energy sources (Fig 1.1) can be attributed to a number of factors. Historically, fossil fuels were the first energy sources employed on an industrial scale. The high gravimetric and volumetric energy density of coal and oil allows for these fuels to be easily stored and transported in ways that energy from other sources cannot.⁶ Finally, energy extraction from fossil fuels is relatively simple compared to other energy sources and the infrastructure necessary to extract, process, and distribute these fuels has been extensively developed, making fossil fuels both inexpensive and convenient.⁷

However, despite their convenience, the continued use of fossil fuels comes with significant consequences. The combustion of hydrocarbons to yield usable energy produces carbon dioxide gas, which is typically discharged directly into the atmosphere. In the year 2014 global CO_2 emissions totaled 35.7 billion tons.⁸ This in turn has led to sustained increases in atmospheric CO_2 concentration.⁹



Figure 1.2: Global average temperature and atmospheric CO₂ concentrations since 1880. Black line gives annual average CO₂ concentration, red and blue bars indicate temperatures above and below the 1901-2000 average, respectively.⁹

The increase in atmospheric CO_2 concentration over the past 100 years is concerning for a number of reasons. CO_2 is a greenhouse gas, and its accumulation in the atmosphere has been correlated with increasing global temperatures (Fig. 1.2), rising sea levels (Fig. 1.3), and ocean acidification.^{9,10}



Figure 1.3: Plot of sea level over time, demonstrating acceleration in the rate of sea level increase over the past 100 years.⁹

Given these considerations, as well as the projected increase in future energy demand, it would be prudent to begin the incorporation of greater amounts of carbonneutral and renewable energy sources into the global energy portfolio.

1.3 Solar Energy as an Alternative to Fossil Fuels

While a number of renewable energy alternatives to fossil fuels exist, solar power is the only source which is viable on the scale necessary to satisfy global energy demand.⁴ The average power density of solar radiation at the earth's surface ranges from 100 watts per meter squared near the poles up to 300 watts per meter at the equator.³ Thus, using a system with a 10% conversion efficiency, it would be possible to supply all 30 TW of the world's 2050 energy needs from a region between one and three million km² in size (For reference, the area of Alaska is around 1.7 million km²).

There are currently two major obstacles preventing the practical implementation of solar power. The first is cost. Currently, the average levelized cost of energy from a photovoltaic source is \$0.13 per kilowatt hour. In order to compete financially with fossil fuels, the cost of solar energy must be brought down to levels comparable to coal or natural gas, which are currently \$0.09 and \$0.07 per kilowatt hour, respectively.¹¹ The accomplishment of this goal will require not only the development of more efficient and inexpensive photovoltaics, but also the creation of a practical infrastructure for the distribution and utilization of energy generated by photovoltaics.

The second obstacle which must be addressed when considering solar power as a possible energy source is the need for a method of storing the energy produced. The diurnal cycle limits the hours of solar energy production in a given location, and results in a disjunction between the timeframe for solar power production, and demand for electricity. The ideal system would allow not only allow for energy storage, but would also enable the efficient distribution and transport of this power across long distances

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1.4 Heterogeneous CO₂ Conversion

One solution to the problem of solar energy storage involves storing energy generated from renewable sources in a chemical form. This process already occurs in nature, where plants use sunlight to convert H₂O and CO₂ into sugars. While the energy storing step in photosynthesis is the splitting of H₂O to form H₂ and O₂,^{12,13} the low volumetric energy density and difficulty in transporting H₂ suggests that a different reaction should be pursued. This work will instead focus on an energy storage scheme based on the electrochemical reduction of CO₂.

In the proposed scheme, electricity generated from a renewable source would be used to drive the energetically unfavorable conversion of CO_2 to more energy-rich compounds, such as formic acid, methane, or $CO.^{14,15}$ In the latter case, the water-gas shift reaction could then be used to convert CO and water into CO_2 and H_2 . CO and H_2 can then be used as feedstocks for Fischer-Tropsch chemistry in order to synthesize liquid fuels which can be readily integrated into existing infrastructure.^{16–18} These fuels, when burned, will release into the atmosphere only as much CO_2 as was used to create them, thus yielding a carbon-neutral fuel cycle (Fig 1.4).¹⁹



Figure 1.4: Scheme depicting proposed carbon neutral fuel cycle.

The practical implementation of such a system, however, requires a catalyst which can facilitate the efficient conversion of CO_2 into CO, a process described by the following equation:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
 Eq. 1.1

The ideal catalyst will drive the above reaction with a high energetic efficiency, described by equation 1.2, below.

$$\varepsilon_{energetic} = \left(\frac{E^0}{E^0 + \eta}\right) * FE$$
 Eq. 1.2

Here, $\varepsilon_{energetic}$ is the overall energetic efficiency of the catalyst, E^0 is the thermodynamic potential for equation 1.1, η (overpotential) is the difference between the applied potential and the thermodynamic potential, and *FE* (Faradaic efficiency) is

the percentage of current passed which goes towards the desired reaction. Therefore, catalysts with high faradaic efficiencies and low overpotentials are desired.

Heterogeneous catalysts for this purpose have been studied extensively. Currently, however, the best known catalysts for the above reaction are based on noble metals such as Au or Ag.^{20–27} If the proposed system is to become an economic reality, catalyst systems must be developed which can be fabricated from inexpensive and earth-abundant materials.

1.5 Ionic Liquid Catalysis and Bi-CMEC

Several advances have been made in recent years in response to the need for inexpensive CO₂ reduction catalysts. In 2011, Kenis and Masel demonstrated the capacity of imidazolium-based ILs to promote the selective conversion of CO₂ to CO at a silver cathode with overpotentials of less than 200 mV.²⁸ Several other groups have built upon this work, developing systems which use lower concentrations of ILs and less expensive cathode materials.^{29–32} Recently, Rosenthal and coworkers developed a bismuth-based heterogeneous catalyst which, in acetonitrile solutions containing low concentrations of ILs, comprised of appropriately substituted imidazolium cations such as [BMIM]⁺ or [EMIM]⁺ (Fig 1.5) could efficiently drive the conversion of CO₂ to CO with Faradaic efficiencies (*FEs*) and current densities (*j*) comparable to those observed with Au or Ag catalysts.²⁹ They described this catalyst as a "bismuth carbon monoxide evolving catalyst", or Bi-CMEC.



Figure 1.5: Chemical Structures of [BMIM]⁺ and [EMIM]⁺. Here, X⁻ denotes the corresponding anion.

IL mediated heterogeneous catalyst systems, such as the Bi-CMEC, are interesting in that their properties depend not only on the cathode material used,^{31,32} but also on the composition of the catholyte.^{29,30} This work will seek to elucidate the effects of both of these components on the efficiency and nature of the resulting reaction.

Chapter 2

THE ROLE OF CATHOLYTE COMPOSITION IN IONIC LIQUID PROMOTED CATALYSIS

2.1 Introduction

The bismuth-based carbon monoxide evolving catalyst (Bi-CMEC) recently developed by Rosenthal and coworkers²⁹ represents an inexpensive alternative to current noble metal catalysts based on Au and Ag.

Work to date carried out on the Bi-CMEC system and other ionic liquid (IL) mediated systems has demonstrated that the identity of the catalyst surface and the composition of the catholyte are both critical to the nature and efficacy of catalysis.^{29–31} However, studies to date have only focused on the electrochemistry and catalysis of the Bi-CMEC system in the presence of $[BMIM]^+$ or $[EMIM]^+$ in MeCN based electrolytes. As such, we have sought to determine how varying the solvent composition of the catholyte solution might impact the ability of the Bi cathode to activate CO₂ and efficiently promote CO evolution. This chapter will examine the function of this system in several different solvents in order to determine the ideal system conditions for efficient CO production, and draw insights into the nature of IL-mediated electrocatalysis at the Bi-CMEC surface.

2.2 Experimental

2.2.1 **Bi-CMEC Preparation**

A glassy carbon electrode (Glassy carbon disk, 3.0 mm diameter) was polished with a slurry of 0.05 micron alumina powder in Millipore water. Residual alumina powder was rinsed off the electrode surface with additional Millipore water, and the electrode was then sonicated in Millipore water for 5 minutes. The polished glassy carbon electrode was then placed in an electrodeposition bath containing 20 mM bismuth (III) nitrate pentahydrate and 1.0 M hydrochloric acid. The glassy carbon electrode was preconditioned by cycling the applied potential (10 cycles) from 0 to – 0.65 V vs. SCE at a sweep rate of 100 mV/second. The electrode was then briskly agitated to remove any exfoliated material from the electrode surface. Controlled potential electrolysis (CPE) was initiated using this conditioned glassy carbon electrode in the quiescent Bi³⁺ solution at –0.30 V versus SCE until ~3 C/cm² of charge had been passed. The Bi-CMEC plated electrode was then rinsed first with Millipore water, then with the solvent being used for the particular experiment (In the case of the IL experiments, any remaining water was wiped off the electrode using a Kimwipe)

2.2.2 Electrochemical Measurements

Electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-720D bipotentiostat. Cyclic voltammetry experiments were performed using a standard three-electrode configuration. The working electrode was either a bare glassy carbon electrode (Glassy carbon disk, 3.0 mm diameter CH Instruments) or glassy carbon electrode onto which Bi-CMEC had been deposited. A piece of platinum gauze (Sigma 99.9%) was used as the counter electrode. Unless otherwise specified, all potentials were measured against a Ag/AgCl reference electrode (1.0 M KCl, CH Instruments) and converted to the SCE reference scale using $E_{SCE} = E_{Ag/AgCl} + 0.044$ V. Cyclic voltammograms were recorded at 100 mV/s with iR drop compensation.

2.2.3 CO₂ Reduction Electrolysis and Product Analysis

Current densities were determined by performing electrolysis in a gas-tight two-compartment cell. A Nafion (NRE-212) membrane separated the anode and cathode compartments. Both the anode and cathode compartments contained 100 mM [BMIM]OTf and 100 mM TBAPF₆ dissolved in 20 mL of solvent, and were sparged with CO₂ for at least 30 min. During electrolysis, the solution in the cathode compartment was stirred while a steady supply of CO₂ gas was delivered to the headspace of the cell at a rate of 5.0 cm³/min. The cathode compartment was vented directly into the sampling loop of a gas chromatograph (SRI Instruments, SRI-8610C). A GC acquisition was initiated every 11 minutes by placing the sampling loop in line with both a packed HeySep D column and a packed MoleSieve 5A column. Argon (Keen, 99.999%) was used as the GC carrier gas. The GC columns led directly to a thermal conductivity detector (TCD) to quantify hydrogen and a flame ionization detector (FID) equipped with a methanizer to quantify carbon monoxide. The partial current densities associated with production of CO and H₂ were calculated from the GC peak area as follows:

$$J_{CO} = \frac{Peak Area}{\alpha} \times Flow Rate \times \frac{2Fp_0}{RT} \times (Electrode Area)^{-1} \quad \text{Eq. 2.1}$$

$$J_{H_2} = \frac{Peak Area}{\beta} \times Flow Rate \times \frac{2Fp_0}{RT} \times (Electrode Area)^{-1} \quad \text{Eq. 2.2}$$

where α and β are the conversion factors based on calibration of the GC with standard samples of CO and H₂, respectively, F = 9.65 x 10⁴ C mo Γ^{1} , p₀ = 1 atm, R = 82.1 mL atm K⁻¹ mo Γ^{1} , and T = 273 K. Faradaic efficiencies for a given product were calculated by dividing these partial current densities by the total current density.

The same equipment and procedures were used for determining metrics in neat ILs, with one exception: instead of using a 2-compartment cell, a single-compartment cell was used, which housed a working electrode (Bi-CMEC), a counter electrode (Pt mesh), and a reference electrode (Ag wire); and contained 5 mL of the neat IL.

2.2.4 Tafel Analysis

Tafel plots were constructed using a Bi-CMEC plated glassy carbon stick electrode submersed in 10 mL of a CO_2 -saturated solution containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf. A stir bar was used to stir the solution throughout the experiment. For each point, a 20-50 second controlled potential experiment was allowed to run until the observed current plateaued. The final current for these experiments was then recorded, and the applied potential was plotted as a function of the log of the steady-state current.

2.3 **Results and Discussion**

It has previously been shown that Bi-CMEC electrodes in millimolar concentrations of imidazolium-based IL promoters solvated in acetonitrile engender efficient CO₂ reduction. This chapter will seek to examine whether the use of solvents other than acetonitrile might result in different reactivity for this process. The catholyte systems studied contained 100 mM tetrabutlyammonium hexafluorophospate (TBAPF₆) as a supporting electrolyte and 100 mM 1-butyl-3-methylimidazolium

trifluoromethanesulfonate ([BMIM]OTf) dissolved in several organic solvents under an atmosphere of CO₂. The solvents tested were all polar aprotic solvents including acetonitrile (MeCN), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and propylene carbonate (PC). Initial experiments employed Cyclic Voltammetry (CV) to probe the basic electrocatalytic response of the Bi-CMEC modified electrode in each of the electrolyte solutions described above. It was observed that in each case, the identity of the solvent did not have a significant effect on the onset potential of the catalytic wave, nor on the general shape of the CV (Fig 2.1). The peak current of the catalytic wave, however, did vary dramatically depending on the electrolyte solvent. In all cases, the catalytic peak current can be attributed to electrochemical CO₂ activation as repetition of the CV experiments in each solvent, but under an atmosphere of N₂, does not lead to a large catalytic wave in the potential region -1.75to -2.0 V (Fig 2.2).



Figure 2.1: Cyclic voltammograms recorded for Bi-CMEC modified GCEs in either MeCN, DMSO, DMF or PC containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf under 1 atm of CO₂.



Figure 2.2: Cyclic voltammograms recorded for Bi-CMEC modified GCEs in either MeCN, DMSO, DMF or PC containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf under 1 atm of N₂.

Having noted that the electrolyte solvent impacts the current associated with CO_2 reduction (i.e., reaction rate), we sought to further examine how the catholyte solvent impacted the reaction kinetics of this system and whether solvent choice affected the selectivity and efficiency of the CO_2 electrolysis. Controlled potential electrolysis (CPE) experiments were carried out for CO_2 -saturated solutions containing 100 mM [BMIM]OTf and 100 mM TBAPF₆ dissolved in each of the solvents employed for the voltammetry experiments of Figure 2.1. CPE was performed at -1.95 V and -2.05 V to probe the solvent dependency of Bi-CMEC catalysis at the foot and peak of the catalytic wave, respectively. The total current responses for representative CPE experiments are shown in Figure 2.3. Similar to the voltammetry in Figure 2.1, the CPE current is highly dependent upon the solvent choice, increasing in the order PC< DMSO< DMF< MeCN. This trend is observed at both -1.95 and -2.05 V with the latter providing a larger overpotential, resulting in the higher current densities observed in Figure 2.3b.



Figure 2.3: Total current density (j_{tot}) profiles for Bi-CMEC modified GCEs in either MeCN, DMSO, DMF or PC containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf under 1 atm of CO₂ at applied potentials of (a) E = -1.95 V versus SCE (b) E = -2.05 V versus SCE.

During electrolysis, gas chromatography was used to periodically sample the headspace of the cell and quantify any gaseous products formed. Quantification of the CO generated from $2e^{-}/2H^{+}$ reduction of CO₂ afforded the Faradaic efficiencies (FE_{CO}) and partial current densities (*j*_{CO}) for CO production for each of the catholyte solutions shown in Table 2.1. Consistent with the existing literature, electrolysis of IL solvated in MeCN at -2.05 V has a FE_{CO} of ~80%.²⁹⁻³¹ However, the FE_{CO} at -2.05 V decreases to ~71, 54, and 51 % when the catholyte contains DMF, DMSO, and PC, respectively, mirroring the kinetic trend observed for these solvents. For each of the catholyte solvents surveyed, CO was the only gaseous product formed and no solution products such as formic acid or oxalate were detectable

Solvent	Applied Potential (E)	$FE_{CO}(\%)$	j_{tot} (mA•cm ⁻²)	$j_{\rm CO}$ (mA•cm ⁻²)
MaCN	–1.95 V	70.0 ± 3.6	11.9 ± 0.4	8.5 ± 0.7
MECIN	–2.05 V	81.7 ± 1.9	22.1 ± 2.6	15.9 ± 0.3
DME	–1.95 V	62.1 ± 2.9	7.4 ± 1.6	4.5 ± 1.0
DMF	–2.05 V	71.0 ± 2.7	14.9 ± 1.4	10.9 ± 0.5
DMSO	–1.95 V	51.4 ± 6.6	5.0 ± 0.7	2.5 ± 0.4
DMSO	–2.05 V	54.1 ± 5.6	8.0 ± 1.3	3.8 ± 0.4
Propylene	–1.95 V	47.9 ± 7.0	2.2 ± 0.4	1.1 ± 0.02
Carbonate (PC)	-2.05 V	50.6 ± 7.1	6.3 ± 0.1	3.2 ± 0.4

Table 2.1: Metrics for CPE experiments performed with Bi-CMEC in CO₂ saturated solutions of the indicated solvents containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf at applied potentials of E = -1.95 V and -2.05 V (versus SCE).

The solvent employed for the CO_2 electrolysis experiments has a profound effect on both the kinetics and efficiency of CO evolution at Bi-CMEC. In an effort to understand which factors governed the differences in observed reaction rate and product selectivity for the various solvents studied, we initially worked to confirm that the CO evolution reaction occurred via the same rate determining process for each. CPE experiments were performed in order to determine the dependence of current density on applied overpotential for each of the solvents surveyed. Tafel analysis of the resulting data produced linear plots with slopes that ranged from 112–119 mV/dec (Fig 2.4). These Tafel slopes are all close to 118 mV/dec, and as such are consistent with a rate-limiting single electron transfer to CO_2 at the Bi-CMEC/catholyte interface.^{33,34}



Figure 2.4: Tafel plots for CO₂ reduction by a Bi-CMEC in solutions of 100 mM [BMIM]OTf and 100 mM TBAPF₆ dissolved in either (a)DMF, (b) DMSO, (c) MeCN, or (d) Propylene Carbonate.

With evidence suggesting that conversion of CO_2 to CO proceeds via the same fundamental rate determining process at Bi-CMEC in the presence of 100 mM [BMIM]OTf in each of the four solvents used in this study, we considered which solvent properties may be directing the disparate reactivity metrics shown in Table 2.1. Since charge transfer to CO_2 at the Bi-CMEC/catholyte interface is critical to catalysis, we hypothesized that differences in solvent polarity might impact the extent to which reduced CO_2 intermediates are stabilized at the electrode surface and manifest in the disparate rates and selectivities for CO production.³⁵ In order to correlate the current associated with CO₂ conversion with catholyte properties and to minimize complications stemming from analysis of electrode dynamics under manual convection, chronoamperometry was performed for Bi-CMEC films on glassy carbon submerged in quiescent solutions of each of the solvents of Figure 2.3 containing 100 mM [BMIM]OTf and 100 mM TBAPF₆ that were saturated under 1 atmosphere of CO₂ (i.e., the electrocatalytic conditions of Figures 2.3 and Table 2.1). Representative chronoamperometric traces recorded at applied potentials of E = -1.95 V and -2.05 V are reproduced in Figure 2.5 along with averaged steady state current densities obtained under these conditions. Plotting the average steady state *j_{tot}* values obtained in this way against either the dipole moment (D) or dielectric constant, (ϵ) of the four solvents studied showed a relatively weak correlation (See Figures 2.6a and 2.6b, respectively).³⁶ Both of these physical parameters are reproduced in Table 2 for each solvent studied herein. The absence of strong correlations in Figure 2.6 suggests that some other aspect of the solvent acts as the driving force for the observed kinetics in these systems.



Figure 2.5: Representative current traces for chronoamperometry experiments performed in either MeCN, DMSO, DMF or PC containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf under 1 atm of CO₂ at applied potentials of either (a) E = -1.95 V or (b) E = -2.05 V (black)



Figure 2.6: Steady state current density (j_{ss}) values for Bi-CMEC modified GCEs in either MeCN, DMSO, DMF or PC containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf under 1 atm of CO₂ at applied potentials of either E = – 1.95 V (red) or E = –2.05 V (black) are correlated versus (a) the dipole moments and (b) dielectric constants of the solvents studied.³⁶

Given that the Bi-CMEC is a heterogeneous catalyst, one would expect mass transfer effects to play a role in the system's performance. The general equation for a diffusion-limited steady-state current response is given by Equation 2.3, which is shown below:³³

$$j_{ss} = \frac{nFD_0 C_0^*}{\delta_0}$$
 Eq. 2.3

where j_{ss} is the steady-state current density, n is the number of electrons transferred in the reaction, F is Faraday's constant, D_O is the diffusion coefficient of the reactant(s), C_O^* is the bulk concentration of the reactant(s), and δ_O is the length of the diffusion layer, beyond which the concentration profile of the reacting species is approximately constant and equivalent to the bulk concentration. For conditions under which the diffusion layer thickness reaches a constant value due either to manual convection (i.e., in the CPE experiments), or to non-manual convection in the bulk solution as a result of density/concentration gradients (i.e., under quiescent conditions), one would expect a linear dependence of steady-state current on both D_O and C_O^* .

The Einstein-Stokes equation³⁷ (Equation 2.4), shown below, relates the solvent viscosity to the diffusion coefficient of a dissolved species (D_O)

$$D_O = \frac{k_b T}{6\pi\eta r_O}$$
 Eq. 2.4

Here, k_b is Boltzmann's constant, T is the solution temperature, η is the viscosity of the solvent, and r_0 is the approximate radius of the diffusing species.

Combining Equations 2.3 and 2.4 gives Equation 2.5, shown below, which describes the relationship between steady-state current density (j_{ss}) and solvent viscosity (η) and establishes a linear relationship between j_{ss} and C_0^*/η for systems with a constant diffusion layer thickness.

$$j_{ss} = \frac{nFk_b T C_0^*}{6\pi r_0 \delta_0 \eta} = \left(\frac{nFk_b T}{6\pi r_0 \delta_0}\right) \left(\frac{C_0^*}{\eta}\right)$$
Eq. 2.5

As such, we expect that the steady-state current obtained from the catalytic reduction of CO_2 to CO at the Bi-CMEC/catholyte interface should show a linear dependence on the bulk concentration of substrate(s)/reactant(s) and an inverse linear dependence on catholyte viscosity, assuming that the Einstein-Stokes equation holds over the range of solvents examined in this study.³⁸

Given that the rate limiting step for CO₂ reduction at the Bi-CMEC/catholyte interface is single electron transfer for each of the solvents studied herein, we first considered how variations in diffusion of CO₂ to the cathode surface may impact the disparate kinetics we observe for CO evolution in MeCN, DMF, DMSO and PC at both -1.95 and -2.05 V. Since the solubility of CO₂ (under 1 atm of CO₂) is different for each of the four solvents, C_{CO2}*/ η must take into account how the molarity of CO₂ ([CO₂]) and the ability of the dissolved gas molecule to diffuse to the electrode (η) varies for each catholyte solution.³⁹ Table 2.2 reproduces these values and Figure 2.7a plots the relation between j_{tot} and C_{CO2}*/ η for each of the solvents studied. Satisfyingly, a linear trend is observed, indicating that the current density observed for the Bi-CMEC catalyst system is limited by diffusion of CO₂, and that the reaction at the cathode surface is fast compared to mass transport.

The electrocatalytic conversion of CO_2 to CO and H_2O requires not only the transfer of $2e^-$ to CO_2 but also the transfer of $2H^+$.²¹ For the present Bi-CMEC/[BMIM]⁺ system, the $2H^+$ required to drive the reaction given in Equation 1.1 are provided by the [BMIM]⁺ cation via the process shown in Figure 2.8, which results in formation of the corresponding N-heterocyclic carbene (NHC), the conjugate base of the imidazolium.^{29,40} Reprotonation of this NHC with H⁺ generated at the anode and

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transferred by a Nafion PEM to the cathode compartment regenerates [BMIM]⁺ and ensures that carbene does not build up in the bulk catholyte solution.

Since diffusion to and availability of the imidazolium promoter at the electrode surface is critical to the efficient evolution of CO at Bi-CMEC, we also considered how j_{tot} values measured for each of the solvents at E = -1.95 and -2.05 V varied as a function of the ability of [BMIM]⁺ to diffuse to the cathode surface under electrocatalytic conditions (100 mM [BMIM]OTf and 100 mM TBAPF₆). These data are plotted in Figure 2.7c and once again show a linear correlation between current associated with CO₂ reduction and C_[BMIM]*/ η , demonstrating that the chemistry at Bi-CMEC which results in CO evolution is fast compared to transport of [BMIM]⁺ to the cathode/electrolyte interface. The dependence of j_{tot} on [BMIM]⁺ mass transport was further verified by measuring j_{tot} for solutions containing different concentrations of [BMIM]⁺ in a single solvent. Figure 2.9 plots j_{tot} versus C_[BMIM]*/ η for solutions containing 50 mM, 75 mM, 100 mM, and 150 mM [BMIM]⁺ in MeCN. As the value of C_[BMIM]* is changed independently of η , we continue to observe a linear dependence of j_{tot} on C_[BMIM]*/ η .

Table 2.2: Physical properties and j_{ss} values obtained for each of the solvents employed in this study. ^aConcentration of dissolved CO₂ in each solvent under 1 atm of CO₂. ^b j_{ss} values determined via chronoamperometry in CO₂ saturated solutions. Chronoamperometry experiments carried out in MeCN, DMF, DMSO or PC, contained 100 mM TBAPF₆ and 100 mM [BMIM]OTf.

Salvant	Dielectric	Viscosity	[CO ₂] ^{39,45,46} <i>a</i>	j_{ss} (mA•cm ⁻²) ^b	
Solvent	Constant $(\varepsilon)^{36,41}$	(ŋ) ^{36,42-44}		E = -1.95 V	E = -2.05 V
MeCN	36.6	0.37 cP	270	18.73 ± 6.3	25.61 ± 6.1
DMF	38.3	0.79 cP	186	7.05 ± 1.2	10.54 ± 0.5
DMSO	47.2	1.99 cP	129	3.12 ± 0.1	4.73 ± 0.1
PC	66.1	2.5 cP	144	2.30 ± 0.2	3.99 ± 0.1
neat [BMIM]OTf	13.1	76 cP	86	0.79 ± 0.1	1.14 ± 0.1
neat [EMIM]OTf	15.1	45 cP	74	1.01 ± 0.2	1.13 ± 0.2


Figure 2.7: Plots of (a) averaged steady state current density (j_{ss}) and (b) Faradaic Efficiency of CO production (FE_{CO}) for Bi-CMEC modified GCEs in either MeCN, DMSO, DMF or PC containing 100 mM TBAPF₆ and 100 mM [BMIM]OTf under 1 atm of CO₂ at applied potentials of either E = – 1.95 V (red) or E = –2.05 V (black) versus the product of the concentration of dissolved CO₂ and the inverse of the catholyte viscosity for each solvent studied. Panels (c) and (d) show how the same j_{ss} and FE_{CO} values correlate with the product of the concentration of dissolved [BMIM]OTf (100 mM) and the inverse of the catholyte viscosity for each solvent studied.

Having established that mass transport is a significant factor controlling the kinetics of CO_2 reduction by Bi-CMEC, we wondered whether similar phenomena

might be contributing to the disparate selectivities for CO evolution observed for the four solvents studied, which range from $FE_{CO} \sim 50\%$ for PC to $FE_{CO} \sim 80\%$ for MeCN. While a plot of observed FE_{CO} versus the ability of CO₂ to diffuse to the electrode surface (Fig 2.7b) does not provide a strong correlation, the corresponding plot constructed for [BMIM]⁺ clearly shows that as solvent viscosity decreases and the ability of [BMIM]⁺ to diffuse to the electrode increases, more selective CO generation is realized (Fig 2.7d).



Figure 2.8: Diagram depicting the transport of protons and protonated species from the anode to the cathode in a standard 2 cell setup.



Figure 2.9: Plot showing how averaged steady state current density (j_{ss}) recorded for a Bi-CMEC modified GCE varies as a function of the product of the concentration of dissolved [BMIM]OTf in MeCN and the inverse of the catholyte viscosity $(\eta^{-1} = 2.7 \text{ cP}^{-1})$ at applied potentials of either E = -1.95 V (red) or E = -2.05 V (black).

The results of Figures 2.7 and 2.9 suggest that transport and accumulation of the imidazolium promoter at the cathode surface is critical to achieving high selectivities and current densities for CO generation. With this in mind, we wondered how this system would operate if neat IL was used as the catholyte, which would ensure that a large concentration of imidazolium near the cathode surface is maintained during catalysis. CPE experiments were carried out at –1.95 V in either neat [BMIM]OTf or 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM]OTf) ILs. [EMIM]OTf was selected for its comparably low viscosity and structural similarity to [BMIM]OTf.^{43,44} Representative current density versus time

traces for these experiments are reproduced in Figure 2.10 and averaged current densities and selectivities for CO production are listed in Table 2.3. Consistent with a model in which accumulation of imidazolium at the cathode surface is critical to achieving high selectivities for CO evolution at Bi-CMEC, the CPE experiments conducted in neat IL delivered metrics of $FE_{CO} = 70.6 \pm 3.7$ and 82.6 ± 3.5 for [BMIM]OTf and [EMIM]OTf, respectively. This level of selectivity for CO is comparable to that observed for the least viscous solvents probed in this study (i.e., MeCN and DMF) in which the imidazolium can most readily diffuse and be supplied to the cathode surface. Although mass transport should be slow for neat [BMIM]OTf and [EMIM]OTf, which are relatively viscous, the high concentration of imidazolium (4.53 and 5.32 M for [BMIM]OTf and [EMIM]OTf, respectively) in the neat ILs ensures that the [BMIM]⁺ or [EMIM]⁺ promoter is always available at the Bi-CMEC surface to facilitate CO₂ reduction and ensure selective CO production.

Table 2.3: Metrics for CPE experiments performed with Bi-CMEC in CO_2 saturated solutions of the indicated imidazolium ILs (neat) at an applied potential of E = -1.95 V.

Solvent	Viscosity ^{43,44}	FE_{CO} (%)	j_{tot} (mA•cm ⁻²)	$j_{\rm CO}({ m mA}{ m \cdot cm}^{-2})$
[BMIM]OTf	76 cP	70.6 ± 3.7	2.22 ± 0.3	1.55 ±0.3
[EMIM]OTf	45 cP	82.6 ± 3.5	3.79 ± 0.2	3.12 ± 0.1



Figure 2.10: Representative current traces for chronoamperometry experiments in neat samples of [BMIM]OTf and [EMIM]OTf at (a) E = -1.95 V vs. SCE and (b) E = -2.05 V vs. SCE.

Chronoamperometry experiments carried out for CO₂ saturated solutions of neat [BMIM]OTf or [EMIM]OTf using a Bi-CMEC cathode polarized at -1.95 V or -2.05 V provide results that are consistent with the CPE experiments described above. Steady state current densities of $j_{ss} = 0.79 \pm 0.05$ mA/cm² and 1.14 ± 0.09 mA/cm² were recorded in [BMIM]OTf at -1.95 V and -2.05 V, respectively. Measured j_{ss} values were slightly higher for experiments conducted in neat [EMIM]OTf ($j_{ss} = 1.01$ ± 0.20 mA/cm² and 1.13 ± 0.22 mA/cm² at -1.95 V and -2.05 V, respectively) owing to the reduced viscosity of this IL compared to [BMIM]OTf. As such, the results of these experiments are consistent with those carried out in the various solvents of Figures 2 and 3 and support the observed connection between current density for CO production and solvent viscosity.

2.4 Conclusions

Clearly, acetonitrile functions as the best solvent for the Bi-CMEC. Of the solvents tested, it demonstrates both the fastest kinetics, as well as the highest faradaic efficiency for carbon monoxide production.

Furthermore, this work has demonstrated a strong correlation between the kinetics of reaction at the Bi-CMEC and the ability of reactants, both CO_2 and $[BMIM]^+$, to diffuse to the electrode surface. Additionally, it was determined that the selectivity of the Bi-CMEC system from CO production is dependent on the transport and availability of $[BMIM]^+$ at the electrode surface. In systems where $[BMIM]^+$ is made plentiful at the electrode surface, the selectivity for CO production is higher, while the selectivity for CO production decreases as the concentration of $[BMIM]^+$ at the electrode surface is depleted.

Chapter 3

DEVELOPMENT OF TRANSITION METAL CATALYSTS FOR CO₂ CONVERSION

3.1 Introduction

Heterogeneous CO_2 electrochemistry is a function of both cathode^{23,47–50} and catholyte²⁹ composition. In chapter 2 the identity of catholyte was found to affect Bi-CMEC catalysis by controlling the rates at which CO_2 and IL diffuse to Bi surfaces. Recently, the effect of cathode identity on IL mediated CO_2 reduction was investigated using similarly prepared Bi, Sn, Pb, and Sb surfaces.³¹ In catholyte solutions of identical composition, these surfaces displayed significantly different reactivity profiles, demonstrating the importance of cathode composition on reaction efficiency.

Thus far, only post-transition metals have been studied as electrodeposited cathode materials for IL mediated CO_2 catalysis. This chapter will seek to extend the scope of cathode materials studied for this type of system to include transition metals. Some of these metals have already been incorporated into in molecular CO_2 catalysts,^{51,52} while others are known to be active polycrystalline heterogeneous catalysts for CO_2 reduction.^{27,50}

Furthermore, in the case of bismuth, the addition of an imidazolium promotor is able to drastically change the nature of reaction at the electrode surface, shifting the major CO_2 reduction product from formic acid to CO, and engendering a large increase in reaction rate.^{21,29} With this in mind, it is plausible that even metals which

were previously catalytically inert to CO_2 reduction could become reactive in this new system.^{32,53}

3.2 Experimental

3.2.1 Electrodeposition of Fe, Ni, Cu, Zn, and Ag

A glassy carbon electrode (Glassy carbon disk, 3.0 mm diameter) was polished with a slurry of 0.05 micron alumina powder in Millipore water. Residual alumina powder was rinsed off the electrode surface with additional Millipore water, and the electrode was then sonicated in Millipore water for 5 minutes. The polished glassy carbon electrode was then placed in a N₂ saturated acetonitrile (MeCN) solution electrodeposition bath containing 100 mM TBAPF₆ and 20 mM of either Fe(OTf)₂, Ni(OTf)₂, Cu(OTf)₂, Zn(OTf)₂, or Ag(OTf). The glassy carbon electrode was preconditioned by cycling the applied potential (10 cycles) from +0.05 to -1.45 V versus the saturated calomel electrode (SCE; all potentials are referenced to this electrode) at a sweep rate of 100 mV/second for all metals except Ag, for which the applied potential was cycled between +0.55 to -0.35V at a sweep rate of 100 mV/second. The electrode was then briskly agitated to remove any exfoliated material from the electrode surface. Controlled potential electrolysis (CPE) was initiated using this conditioned glassy carbon electrode in the quiescent plating solution at -0.95 V for Fe, -1.15 V for Ni, -0.45 V for Cu, -0.85 V for Zn, and +0.30 V for Ag. In each case, electrolysis was continued until $\sim 3 \text{ C/cm}^2$ of charge had been passed. The electroplated carbon electrodes were rinsed with Millipore water, followed by MeCN prior to use or analysis.

3.2.2 Electrochemical Measurements and Product Analysis

Experimental procedures related to electrochemistry were the same as those outlined in section 2.2.2. Experimental procedures for controlled potential electrolysis and gaseous product analysis were identical to those outlined in section 2.2.3.

3.2.3 SEM and XPS Analysis

Scanning electron microscopy images and energy dispersive X-ray (EDX) spectra were acquired with a JEOL JSM 7400F Scanning Electron Microscope (SEM). X-ray photoelectron spectroscopy (XPS) was conducted using a VG ESCALAB 220I-XL spectrometer. The X-Rays used were nonmonochromatic Al K α X-rays (1486.7eV) with an applied power of 300 W applied. The operating pressure in the main chamber was less than 1×10^{-8} torr.

Initial XPS survey scans were collected at a pass energy of 100 eV using a step size of 1.0 eV. High-resolution XPS spectra were collected at a pass energy of 20 eV using a step size of 0.1 eV. All atomic ratios (X_i) were calculated from the high-resolution spectra and were determined using the equation:

$$X_i = \frac{\frac{A_i}{S_i}}{\sum_{i=1}^{A_i}}$$
Eq 3.1

where A_i is the area calculated with a Shirley-type baseline, and S_i is the relative sensitivity factor.

3.2.4 Infrared Spectroscopy

All infrared spectra were recorded using a Thermo / Nicolet Magna 750 spectrometer. Liquid samples were prepared under atmosphere, and were loaded into a liquid IR cell for analysis. Solid samples were prepared by mixing a small amount of analyte with powered KBr, crushing the mixture into a fine powder, and using a Carver manual pellet press to compress the mixture into a translucent disk, which was then analyzed.

3.3 Results and Discussion

3.3.1 Survey of Selected Transition Metals for Catalytic Activity

Following the discovery that imidazolium based ILs can promote the rapid and efficient conversion of CO_2 to CO at bismuth cathodes, it was of interest to determine whether this type of reactivity might also be observed when IL promotors were used with cathode materials other than bismuth. Recent literature has shown that the identity of the cathode surface plays a key role in directing the course of imidazolium-promoted CO_2 reduction.³¹ Additionally, the use of transition metal triffate precursors has been developed as a convenient method for electrodepositing metal species onto inexpensive carbon or metal substrates in organic solution.^{30,31} This procedure involved submersing a working electrode (e.g. glassy carbon) in an MeCN solution containing 20 mM of a triffate salt of the metal species of interest, and 100 mM of TBAPF₆ as a supporting electrolyte. A potential sufficiently negative enough to reduce the dissolved Mⁿ⁺ cations resulted in electrodeposition of a thin metal film onto the surface of the inert conducting substrate.³¹

Initially, five different transition metals were selected for which triflate salts were readily available. These included Fe(OTf)₂, Ni(OTf)₂, Cu(OTf)₂, Zn(OTf)₂, and Ag(OTf). For each metal, plating solutions were prepared, and thin films were electrodeposited onto a glassy carbon electrode. Preliminary investigations used cyclic voltammetry (CV) to probe the catalytic response of each metallic film towards CO₂ reduction. For each metal examined, a glassy carbon electrode containing an

electrodeposited layer of said metal was submersed in a solution containing 100 mM of [BMIM]OTf dissolved in MeCN under an atmosphere of CO_2 . The resulting current responses for each metal are shown in Figure 3.1, below:



Figure 3.1: Cyclic voltammograms recorded for surfaces composed of Ag, Zn, Cu, Fe, and Ni submersed in MeCN solutions containing 100 mM [BMIM]OTf under an atmosphere of CO₂. No additional supporting electrolytes were used in these experiments.



Figure 3.2: Cyclic voltammograms recorded for surfaces composed of Ag or Zn submersed in MeCN solutions containing 100 mM [BMIM]OTf under an atmosphere of N₂. No additional supporting electrolytes were used in these experiments.

From the preliminary cyclic voltammetry experiments, it can be observed that the identity of the metal surface used has a profound effect on the resulting current response. Based on these experiments, Cu, Fe, and Ni appear to be catalytically inactive for CO₂ reduction even in the presence of [BMIM]OTf at potentials as negative as -2.25 V. These metals do not show any significant current response in the potential region where CO₂ reduction is typically observed. In contrast to these metals, both Ag and Zn display significant increases in current at potentials more negative than -1.6 V, consistent with an electrocatalytic process. Upon repetition of these experiments under an atmosphere of N₂, no such peaks are observed, indicating that these peaks are a result of CO₂ reduction processes and not reduction of the imidazolium cation (Fig 3.2).

Following CV experiments, CPE experiments were performed to further characterize the catalytic ability of these metal cathodes and to identify the CO_2 reduction products produced in these systems. These CPE experiments were carried out at an applied potential of -1.95 V, and were coupled to gas chromatographic analysis of the electrolysis headspace. To determine the effect of [BMIM]⁺ on each catalyst, CPEs for each substrate were carried out in MeCN solutions containing either 100 mM [BMIM]OTf or 100 mM TBAPF₆. Representative current traces for each of these experiments are reproduced in Figure 3.3, and metrics for each electrodeposited catalyst substrate under the above described conditions are provided in Table 3.1.

Table 3.1: Metrics for CPE experiments performed with transition metal surfaces in CO_2 saturated MeCN solutions containing 100 mM of either [BMIM]OTf or TBAPF₆ at an applied potential of E = -1.95 V

Metal	Conditions	FE_{CO} (%)	j_{tot} (mA•cm ⁻²)	$j_{\rm CO}$ (mA•cm ⁻²)
Ea	TBAPF ₆	0	0.69 ± 0.03	0
ге	[BMIM]OTf	37.7 ± 18.3	0.30 ± 0.04	0.11 ± 0.05
N	TBAPF ₆	10.6 ± 6.3	0.42 ± 0.03	0.04 ± 0.02
INI	[BMIM]OTf	20.5 ± 3.7	0.37 ± 0.02	0.08 ± 0.02
Cu	TBAPF ₆	15.0 ± 17.7	0.43 ± 0.09	0.08 ± 0.10
Cu	[BMIM]OTf	0	0.33 ± 0.07	0
7n	TBAPF ₆	102.2 ± 8.0	6.42 ± 1.81	6.49 ± 1.62
ZII	[BMIM]OTf	97.1 ±2.8	7.47 ± 0.73	7.26 ± 0.83
٨	TBAPF ₆	46.7 ± 13.9	0.51 ± 0.06	0.24 ± 0.06
Ag	[BMIM]OTf	80.8 ± 16.8	1.44 ± 0.20	1.18 ± 0.40



Figure 3.3: Representative current traces for Fe, Ni, Cu, Zn, and Ag under an atmosphere of CO_2 , submerged in MeCN solution containing either (a) 100 mM [BMIM]OTf or (b) 100 mM TBAPF₆.

The data in Figure 3.3 and Table 3.1 both illustrate the catalytic inactivity of the Fe, Ni and Cu surfaces for CO_2 reduction. The CPE experiments also reveal some interesting properties of the Ag and Zn based cathodes. Despite showing a promising current response in preliminary cyclic voltammetry experiments, the activity of the Ag cathode quickly deteriorates in the presence of [BMIM]OTf, though its selectivity for CO production remains relatively high throughout the experiment. This particular phenomenon is examined in greater detail in section 3.3.3.

Interestingly, CPE experiments demonstrated that surfaces electrodeposited from Zn(OTf)₂ salts were able to catalyze efficient CO production with high current densities both in the presence or absence of [BMIM]OTf. In both cases, the Zn cathode is nearly quantitatively selective for CO production. This Zn catalyst system is examined in greater detail in section 3.3.2.

3.3.2 A Novel Zinc-Based CO₂ Reduction Catalyst

In the previous section, a Zn film electrodeposited from MeCN solutions of $Zn(OTf)_2$ was shown to efficiently and selectively drive the conversion of CO_2 to CO at an applied potential of -1.95 V. Remarkably, the Zn cathode is able to drive this reaction either in the presence of the [BMIM]⁺ or TBA⁺ based electrolytes. The reactivity of the Zn cathode in several conditions is summarized in figure 3.4, below. Given the promising metrics demonstrated by this catalyst system, further investigation into the mechanism of its function was pursued.



Figure 3.4: Summary of Reactivity with the Zn cathode. (a) Linear sweep voltammograms for a Zn cathode submersed in MeCN solution containing 100 mM of either TBAPF₆ or [BMIM]OTf under an atmosphere of either CO₂ or N₂. (b) Current traces and FE_{CO} for CPEs performed at -1.95 V with Zn cathode in solutions containing 100 mM of either TBAPF₆ or [BMIM]OTf under an atmosphere of CO₂

First, the long-term stability of the Zn catalyst system was tested by performing CPE at -1.95 V for over 12 hours. Multiple CPE experiments were performed for three variations of this system, with an MeCN catholyte solution

containing either 100 mM [BMIM]OTf only, 100 mM TBAPF₆ only, or 100 mM of both [BMIM]OTf and TBAPF₆. The results of these experiments are given in Figure 3.5, below.



Figure 3.5: Current and Faradaic efficiency traces for long term CPE experiments with Zn plated glassy carbon electrode in CO₂ saturated MeCN solutions containing (a) 100 mM [BMIM]OTf only, (b) 100 mM TBAPF₆ only, or (c) 100 mM [BMIM]OTf and 100 mM TBAPF₆

These long term CPE experiments reveal that while the Zn catalyst system is stable for short time scales, over longer periods of time both total current density and selectivity decline significantly before stabilizing. The chemical composition and surface morphology of the Zn catalyst system were also examined. XPS was used to analyze the chemical composition of the Zn catalyst, and to determine which surface species might be responsible for its catalytic activity. High resolution XPS spectra were obtained for several relevant atomic regions, including the Zn 2p, O 1s, and N 1s regions (Figs A.5-7). While the rapid oxidation of zinc under atmospheric conditions makes analysis of surface species somewhat ambiguous, we were able to determine which Zn species were present on the electrode surface prior to and following electrolysis. Based on the observation of Zn $2p_{3/2}$ peaks at a binding energy of ~1022.7 eV, and LMM auger peaks observed at a kinetic energy of ~986.5 eV, it was determined that the Zn species present on the electrode surface is primarily Zn(OH)₂ (Fig 3.6).⁵⁴



Figure 3.6: XPS and auger spectra taken of Zn catalyst surface (a) prior to electrolysis,
(b) following electrolysis in a CO₂ saturated 100 mM [BMIM]OTf solution in MeCN, and (c) following electrolysis in a CO₂ saturated 100 mM TBAPF₆ solution in MeCN.

SEM was employed to characterize the surface morphology of the Zn catalyst prior to and following CPE. Prior to electrolysis, the surface of the electrodeposited Zn catalyst appears uniform and highly microstructured, consisting of numerous "plateletlike" structures (Fig 3.7a). Following electrolysis, both the uniformity and microstructure of the catalyst surface decrease slightly (Fig 3.7b). Over extended periods of time, the accumulation of these changes to the catalyst surface structure may account for the decreases in both activity (decrease in surface area) and selectivity (decrease in active site population) observed for long term electrolysis experiments.



Figure 3.7: SEM images (a) before and (b) after CPE at -1.95 V vs. SCE using a Zn electrode in 100 mM [BMIM]OTf solution in CO₂ saturated MeCN. Large images were taken at 2,500x magnification, and insets are taken at 10,000x magnification.

Having characterized both the reactivity and surface composition of the Zn catalyst system, we next sought to elucidate the mechanism by which CO_2 reduction proceeded at the Zn surface. The continued efficient function of this system in the

absence of an IL promotor implies that the mechanism for this system likely differs from that of the Bi-CMEC platform.

It has been previously suggested that one of the roles played by the IL promotor in the Bi-CMEC system is the delivery of protons necessary for CO_2 to undergo proton-coupled electron transfer,⁵¹ as illustrated by equation 1.1.²⁹ The fact that CO_2 reduction at the Zn catalyst surface occurs in an aprotic solvent in the absence of [BMIM]OTf implies that one of two things must be true. Either (1) there must exist an alternative source of protons in the catholyte being used, or (2) The overall reaction occurring at the electrode surface must be different than that described in equation 1.1.

Initially, we sought evidence to either support or refute possibility (1), that an alternate proton donor species was present in the reaction catholyte. Other than the supporting electrolyte, TBAPF₆, the only other species which might be present in the catholyte would be trace H₂O. The MeCN used in these experiments was purchased from VWR and had a maximum allowed H₂O content of 0.30% by volume, equivalent to a potential 167 mM of H₂O present in solution. If H₂O were acting as a proton donor in this reaction, it is conceivable that this amount could provide the protons necessary for the reduction of CO₂ to CO to occur. To test this possibility, CV was performed using a Zn plated glassy carbon surface submersed in solutions containing 100 mM TBAPF₆ and varying concentrations of H₂O (Fig 3.8). Additionally, CPE experiments were performed for systems containing either 200 mM, 300 mM or 500 mM of added H₂O, as well as systems in which molecular sieves had been added to the catholyte in an effort to eliminate any H₂O which might be initially present in trace amounts (Table 3.2).



Figure 3.8: Cyclic voltammograms for Zn-plated glassy carbon electrode submersed in MeCN solution containing 100 mM TBAPF_6 , with varying amounts of added H_2O .

Table 3.2: j_{tot} , j_{CO} , and FE_{CO} values for Zn catalyst systems containing different concentrations of H₂O

Conditions	$FE_{CO}(\%)$	j_{tot} (mA•cm ⁻²)	$j_{\rm CO}$ (mA•cm ⁻²)
Mol Sieves (~0 mM H ₂ O)	104.1 ± 1.7	6.20 ± 1.84	6.39 ± 1.94
No H ₂ O added	102.2 ± 8.0	6.42 ± 1.81	6.49 ± 1.62
200 mM H ₂ O added	100.1 ± 24.3	6.54 ± 1.22	6.36 ± 1.14
300 mM H ₂ O added	109.6 ± 15.4	3.92 ± 0.82	4.34 ± 1.15
500 mM H ₂ O added	98.0 ± 28.3	6.91 ± 0.63	6.66 ± 1.59

From Figure 3.8 and Table 3.2, it can be seen that varying the concentration of H_2O in the system has little to no effect on the selectivity or rate of CO production. Particularly significant is the fact that the catalysis is almost entirely unaffected in the experiments where molecular sieves are used to nearly eliminate the presence of any trace H_2O contamination.

With strong evidence against explanation (1) for the continued effectiveness of the Zn catalyst system in the absence of [BMIM]OTf, we next investigated possibility (2); that the reduction of CO_2 in this system proceeds via a pathway distinct from that described by equation 1.1. Equation 3.2 has been put forward as a potential pathway for CO_2 reduction in environments of low proton availability.²⁰

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$$
 Eq. 3.2

If Equation 3.2 is the route by which CO_2 reduction occurs in this system, one would expect to observe the production of carbonate (CO_3^{2-}) concurrent with CO in the cell cathode. Thus, IR spectroscopy was used to probe for the presence of CO_3^{2-} in the catholyte of the cell (Fig 3.10) as well as in the Zn film (Fig 3.9). For each component studied, spectra were taken before and after a one hour CPE experiment at -1.95 V, in a CO₂ saturated 100 mM TBAPF₆ solution and compared to carbonate standards. The spectra collected of the catholyte do not show any major change over the course of the electrolysis, which is likely a result of carbonate's low solubility in organic solvents.⁵⁵ The IR spectrum of the film, however, provides strong evidence for the generation of carbonate during the reaction. Spectra taken following electrolysis display a set of absorption features at 1379 cm⁻¹ and 1450 cm⁻¹, which correspond to features observed in a potassium carbonate standard. These features are absent in spectra recorded of films immediately following plating, and films which had been subjected to electrolysis conditions at open circuit potential, demonstrating the carbonate present is a product of electrolysis, and is not due to spontaneous reactions within the catholyte.



Figure 3.9: IR spectra of Zn films immediately following plating (Pre Electrolysis, green), after soaking for 1.5 hours in a CO_2 saturated 100 mM TBAPF₆ MeCN solution(orange), and following a 1 hour CPE at -1.95 V (red). Also included is a standard spectrum of solid K₂CO₃ (black).



Figure 3.10: IR spectra of electrolysis solution containing 100 mM TBAPF₆ dissolved in CO₂ saturated MeCN prior to and following a 1 hour CPE at -1.95 V with a Zn-plated carbon plate (Surface area: 2.5 cm^2).

3.3.3 Passivation of Silver in the Presence of [BMIM]OTf

In section 3.3.1, a Ag surface was electrodeposited from an MeCN precursor solution containing 100 mM Ag(OTf) and 100 mM of TBAPF₆ as a supporting electrolyte. Preliminary cyclic voltammetry experiments showed promising results for the use of these surfaces as CO_2 reduction catalysts. However, during CPE experiments, the Ag surface quickly became passivated and displayed a sharp decrease in total current density. This is a particularly interesting phenomenon, as metallic Ag is known to function as a robust CO_2 catalyst in aqueous, organic, and IL solutions.^{20–}

^{22,26–28} Investigation of the observed passivation under these conditions will hopefully yield insights into the behavior of system components throughout the process of IL promoted catalysis.

In order to better understand the passivation process which occurs during CPE with these Ag surfaces, we characterized the chemical and morphological properties of the Ag catalyst surface prior to and following electrolysis.

SEM experiments were carried out in order to detect any changes to the surface morphology which might be occurring over the course of the experiment, and determine whether these might be contributing to the catalyst deactivation over the course of CPE. Prior to electrolysis, the surface appears to consist of highly crystalline Ag deposits distributed across the glassy carbon substrate surface (Fig 3.11a). Following electrolysis, both the crystallinity and density of Ag deposits appear to have decreased slightly, with larger portions of the underlying substrate visible (Fig 3.11b). These changes, however, are relatively minor.



Figure 3.11: SEM images of electrodeposited Ag Surface (a) before and (b) after CPE at -1.95 V. Large images were taken at 2,500x magnification and insets are taken at 10,000x magnification.

X-ray photoelectron spectroscopy (XPS) was used to characterize changes in the surface chemical composition of the Ag catalyst over the course of the catalytic process. Spectra were taken of a Ag surface at three stages of the catalysis process: Immediately following the plating procedure; after subjecting the Ag-covered plate to the chemical conditions of an hour-long CPE, but with no external potential applied; and following an hour-long CPE experiment, during which a potential of -1.95 V was applied.

High resolution spectra were recorded for the P 2p, S 2p, C 1s, N 1s, O 1s, Ag 3d, and F 1s regions (Table A.1). Analysis of these spectra reveals the presence of TBA^+ , PF_6^- , and OTf^- ions adsorbed to a Ag^0 surface immediately following deposition, assigned from standard spectra obtained from TBAPF₆ and Ag(OTf).. After soaking in a CO₂ saturated electrolyte solution containing 100 mM [BMIM]OTf, only adsorbed [BMIM]⁺ and OTf⁻ are observed on the Ag⁰ surface. Following electrolysis, several significant changes to the catalyst surface are observed. First, the binding energies for all spectra are observed to increase by ~1.25 eV, which we attribute to charging effects resulting from an insulating surface.^{56,57} Second, the ratio of adsorbed OTf⁻ to [BMIM]⁺ decreases, something which is likely a result of the cathodic potential applied to the working electrode (which would result in the repulsion of anions and attraction of cations). Third, following electrolysis, a significant feature in the O1s region appears at a binding energy of ~530.6 eV. This feature, while not conclusively identified, could indicate the formation of a layer of some metallic oxide species on the electrode surface, possibly silver carbonate or silver oxide.⁵⁶ Such a layer of insulating oxide species could potentially account for the deterioration in current density observed during electrolysis.⁵⁷



Figure 3.12: High resolution XPS spectra of the O1s region for a Ag surface electrodeposited onto a carbon plate (a) immediately following plating, (b) following a 1 hour soak in a CO₂ saturated MeCN solution containing 100 mM [BMIM]OTf, and (c) Following a 1hr CPE at -1.95 V vs. SCE in a CO₂-saturated MeCN solution containing 100 mM [BMIM]OTf.

Having identified potential explanations for the rapid degradation of Ag's catalytic efficiency in the presence of [BMIM]OTf, we next sought to develop solutions to this problem. The fact that the plating procedure for the Ag surface is performed in organic solution allows for the possibility of an in-situ plating procedure, in which the deposition of the catalyst and the process of CO₂ reduction occur simultaneously, as has been demonstrated previously for other electrodeposited catalysts.^{30,31,58} An MeCN solution was prepared containing 1 mM of Ag(OTf) and 100 mM [BMIM]OTf, acting as both a supporting electrolyte and a co-catalyst. A glassy carbon electrode was then submersed in this solution, and a potential of –1.95 V was applied to the system. Remarkably, despite the rapid deactivation previously observed for the ex-situ plated Ag catalyst, the in-situ procedure displays high current density and selectivity over an extended period of time (Fig 3.13). The change in catalyst efficacy observed between these two methods is likely due to the ability of the in-situ plated Ag surface to continually renew itself throughout the experiment,

counteracting the surface oxide layer which forms during electrolysis of the ex-situ plated catalyst.



Figure 3.13: Current density and faradaic efficiency traces for GCE in MeCN solution containing 1 mM Ag(OTf) and 100 mM [BMIM]OTf under 1 atm of CO₂ at an applied potential E = -1.95 V versus SCE.

3.4 Conclusions

Several transition metals have been studied for use as cathodes in IL mediated CO_2 reduction catalyst systems. While Fe, Cu and Ni surfaces were found to be relatively inactive towards CO_2 reduction, these studies have also led to the identification of Zn and Ag as two cathode materials with interesting activity towards CO_2 reduction.

Zn surfaces electrodeposited in MeCN solution from $Zn(OTf)_2$ precursors were found to be active towards CO_2 reduction in both the presence and absence of the IL promotors necessary for Bi-CMEC catalysis. This unique reactivity can be attributed to the reduction of CO_2 via a different method with this catalyst than for the Bi-CMEC.

Ag surfaces prepared through similar methods have also shown interesting reactivity patterns of a different nature. Whereas polycrystalline Ag surfaces have been shown to be active CO_2 reduction catalysts, the Ag surface in an IL mediated system is quickly deactivated during electrolysis. This loss of activity was attributed to the formation of a nonconductive oxide layer on the Ag surface during electrolysis, and was corrected through the use of in-situ electrodeposition and catalysis procedures.

These studies have expanded the scope of heterogeneous IL mediated catalysis to transition metal cathodes, and have demonstrated the importance of cathode choice in the development of future IL mediated catalyst systems.

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Appendix

SUPPLEMENTARY DATA AND FIGURES

Table A.1: Tabulated XPS data from representative experiments with a Ag-plated carbon plate. "Pre" denotes an electrode taken immediately from plating solution, "Soak" denotes an electrode which has been submerged in a CO₂ saturated 100 mM [BMIM]OTf solution in MeCN for 1.5 hours, and "Post" denotes an electrode examined following a 1 hour CPE at –1.95 V in a CO₂ saturated 100 mM [BMIM]OTf solution in MeCN.

	F	Pre		Soak		Post, Corrected	
Name	Peak BE	Atomic %	Peak BE	Atomic %	Peak BE	Atomic %	
P2p3/2	135.92	3.00					
P2p1/2	136.89	2.94					
S2p3/2	167.98	1.61	168.27	4.85	168.10	1.20	
S2p1/2	169.25	1.57	169.48	4.75	169.12	1.18	
C1s A	284.84	32.10	284.97	17.17	284.89	24.41	
C1s B	286.13	16.44					
C1s C			286.51	25.08	286.19	18.59	
C1s D			289.00	1.39	288.57	2.98	
C1s E			292.38	4.12	291.84	4.15	
C1s F					294.47	1.77	
Ag3d5/2 A					366.97	20.79	
Ag3d5/2 B	368.20	15.34	368.24	5.59			
Ag3d5/2 C					370.68	0.16	
N1s A	399.32	0.87			399.47	1.89	
N1s B	400.82	0.38	399.82	0.57			
N1s C			401.82	7.25	401.35	6.63	
N1s D	402.09	2.59					
O1s A					530.58	9.62	
O1s B	531.91	4.41	531.86	13.35	531.95	2.93	
O1s C	533.75	0.58	533.37	2.03	533.23	0.77	
F1s A	686.41	12.42	686.40	0.40			
F1s B	688.31	5.74	688.36	13.44	688.20	2.94	

Table A.2: Table containing relative abundance at the electrode surface of selected species for "Pre", "Soak", and "Post" conditions. Relative abundances are determined based on relative atomic % of elements composing each species.

	Relative Abundance, %		
	Pre	Soak	Post
TBA^+	11.38	0.00	0.00
PF_6^-	9.79	0.34	0.00
OTf	7.48	32.36	5.89
$[BMIM]^+$	0.00	26.16	12.64
Ag	71.35	41.13	53.42
Oxide	0.00	0.00	28.05



Figure A.1: Cyclic voltammograms at various scan rates of Zn plated glassy carbon electrode in a CO_2 saturated 100 mM TBAPF₆ solution in MeCN. First sweep of CVs are shown here.



Figure A.2: Cyclic voltammograms at various scan rates of Zn plated glassy carbon electrode in a CO_2 saturated 100 mM TBAPF₆ solution in MeCN. Second sweep of CVs are shown here.


Figure A.3: Cyclic voltammograms at various scan rates of Zn plated glassy carbon electrode in an N_2 saturated 100 mM TBAPF₆ solution in MeCN. First sweep of CVs are shown here.



Figure A.4: Cyclic voltammograms at various scan rates of Zn plated glassy carbon electrode in an N_2 saturated 100 mM TBAPF₆ solution in MeCN. Second sweep of CVs are shown here.



Figure A.5: High resolution XPS spectra taken of C 1s region for Zn catalyst surface
(a) prior to electrolysis, (b) following electrolysis in a CO₂ saturated 100 mM [BMIM]OTf solution in MeCN, and (c) following electrolysis in a CO₂ saturated 100 mM TBAPF₆ solution in MeCN.



Figure A.6: High resolution XPS spectra taken of N 1s region for Zn catalyst surface
(a) prior to electrolysis, (b) following electrolysis in a CO₂ saturated 100 mM [BMIM]OTf solution in MeCN, and (c) following electrolysis in a CO₂ saturated 100 mM TBAPF₆ solution in MeCN.



Figure A.7: High resolution XPS spectra taken of O 1s region for Zn catalyst surface
(a) prior to electrolysis, (b) following electrolysis in a CO₂ saturated 100 mM [BMIM]OTf solution in MeCN, and (c) following electrolysis in a CO₂ saturated 100 mM TBAPF₆ solution in MeCN.