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Water Enhancement of CO₂ Conversion on Silver in 1-Ethyl-3-Methylimidazolium Tetrafluoroborate

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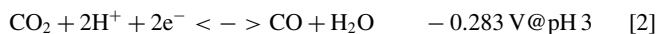
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Electrochemical recycling of carbon dioxide back to fuels and chemicals could be a viable method for CO₂ remediation if the efficiency of the process could be improved. One of the key challenges, though, is that the faradaic efficiency is low in the presence of water because water electrolysis is much easier than CO₂ electrolysis on most transition metal catalysts. Previous investigators have found that one can eliminate water conversion, by eliminating water from the system, but this has not proven to be practical. Here we present an alternate route, where EMIM-BF₄ is used to suppress water electrolysis. We observe that the addition of water to 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIM-BF₄) actually increased the efficiency of CO₂ conversion to CO. Indeed we find that little hydrogen is produced on silver in EMIM-Water solutions, provided the water concentration is no more than about 90% by mole. We observe an increase in rate of carbon monoxide (CO) production on silver and platinum as water is added to the electrolyte. We attribute this increase to the hydrolysis of tetrafluoroborate, which releases protons when mixed with water. Protons are shown to accelerate the reduction of CO₂ until a critical mole fraction of water is reached.

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Electrochemical recycling of carbon dioxide back to fuels and chemicals could be a viable method for CO₂ remediation, provided issues of catalyst activity, selectivity and energy efficiency could be overcome.¹⁻⁴ In this paper we consider a solution to one of the key problems in electrochemical CO₂ recycling: the low faradaic efficiency of CO₂ conversion in the presence of water. By way of background, carbon dioxide is among the most stable carbon based compounds under environmental conditions. While the equilibrium potential of CO₂ reduction in aqueous systems is similar to the hydrogen evolution reaction (HER), as shown in Equations 1 and 2, additional energy is required to drive the electrochemical conversion of CO₂.



The added energy due to thermodynamic barriers is known as overpotential. The overpotential is much larger for CO₂ reduction (Equation 2) compared to hydrogen evolution (Equation 1). We have shown in a previous paper⁵ that EMIM BF₄ can lower the overpotential of CO₂ reduction by forming low energy reduction intermediates. In the presence of protons one often finds that the faradaic efficiency for CO₂ conversion (i.e. the fraction of the electrons that react to yield the CO product) is low. Instead most of the electrons are wasted via reaction 1 or other undesired side reactions.

Previous investigators have tried to eliminate water electrolysis by eliminating water from the system but that has not proven to be practical. In dried 1-Butyl-3-Methylimidazolium Acetate, Barosse-Antle and Compton^{6,7} showed the onset of CO₂ reduction occurring at -1.4 V vs. a silver quasireference electrode. In this study, we report a novel solution to the water problem, where EMIM BF₄ is used to inhibit water hydrolysis so that CO₂ can be converted at high efficiency even in the presence of water. We find, in fact, that adding water to EMIM BF₄ increases the CO₂ reduction rate compared to dried EMIM BF₄.

Methods

Electrochemical cell.— Electrochemistry was performed using a Solatron SI 1287 attached to a PC using CorrWare software. All of the experiments described were conducted in a custom made glass

electrochemical cell shown schematically in Fig. S4. Prior to sparging any gases into an electrochemical cell, the gases were sent through a tube of Drierite, anhydrous calcium sulfate, in order to remove any residual moisture present in the gas streams. Working electrodes were silver or platinum nanoparticles supported by a 5 mm dia. silver or platinum slugs respectively. The particles were deposited onto the metal slugs by depositing a solution then evaporating the solvent using an infrared lamp. The counter electrode was made of a 25 × 25 mm piece of platinum gauze purchased through Alfa Aesar. The gauze was connected to a 5" 0.5 mm dia platinum wire. The reference electrode was an Ag/0.01 M Ag⁺ non aqueous reference electrode (BASi). The reference electrode was calibrated using ferrocene as an internal standard.

Flow cell electrolysis.— The flow cell (Fig. S1) was a sandwich style reactor in which there were two liquid channels containing the catholyte and anolyte, and one CO₂ gas channel. The gas channel was made of aluminum and was also the cathodic current collector. Just below the cathodic current collector was a piece of Sigracet graphite gas diffusion layer in which 10 mg of silver nanoparticles were made into an ink and painted onto an area of 1.5 cm². The ink was made by mixing 10 mg of silver nanopowder (40 nm diameter) with 600 μL of 18.2 MΩ ultra-pure water, 600 μL of isopropyl alcohol, and 10 μL of 1100 EW 5% Nafion solution (DuPont). This mixture was then sonicated for 2 min. The platinum anode ink was made the exact same way except using 5 nm platinum black nanoparticles (Alfa Aesar) in lieu of silver. Below the cathode was a Teflon liquid channel in which the ionic liquid mixtures could come in contact with the cathode. Below the top liquid channel was a 2 cm² piece of Nafion-117 membrane. Below the membrane is the lower liquid channel where 0.1 M H₂SO₄ passed over the anode. All liquids flowed through the cell at 0.5 mL/min, and CO₂ passed through the cell at 5 sccm. The gas channel exit was connected to a SRI Gas Chromatograph equipped with a 6-foot Molecular Sieve 5A column and a thermal conductivity detector (TCD). The column was kept at 100°C while the detector was at 110°C. The GC utilized a helium carrier gas with a flow rate of 25 sccm when analyzing the CO output. The carrier gas was switched to nitrogen for H₂ analysis.

Efficacy of water removal.— In order to establish a control, water was removed from the ionic liquid by heating the liquid *in vacuo* for 24 hours, followed by argon sparging at 150 sccm for an additional 24 hours. The water content was assessed quantitatively through a Karl-Fischer (KF) titration. The KF titrator was an Aquatest CMA made by Photovolt. The water content of the "dry" ionic liquid was measured to be 50 mM. The reagent kit was Photovolt's pyridine free

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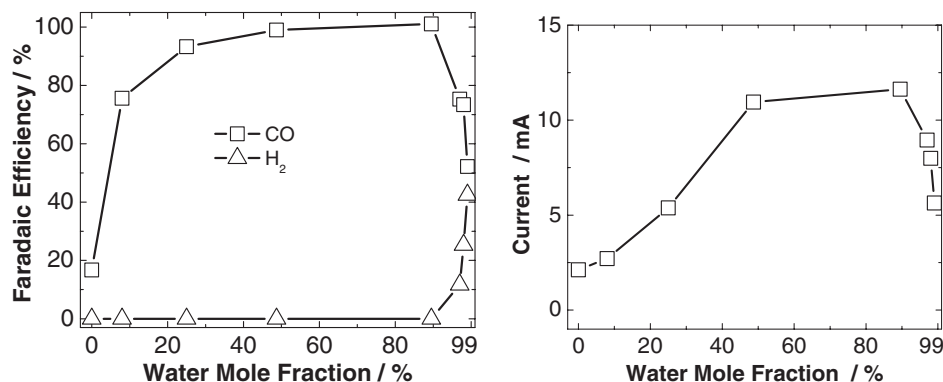


Figure 1. Effect of adding H₂O to EMIM BF₄ on the faradaic efficiency of CO₂ reduction to CO and H₂ (right) and on the flow cell current density (left) at a cell potential of 2.5 V. In the split flow cell electrolyzer, CO₂ flowed above the cathode gas diffusion layer (GDL). The gas outlet composition was measured by gas chromatography. The EMIM BF₄-water mixtures were made to flow adjacent to the cathode and 0.1 M H₂SO₄ was made to flow adjacent to the anode. See the supplementary material for more detail.

reagent kit. A KF titration is a coulometric titration used in analytical chemistry in order to detect trace amounts of water in dry solvents. The following is a brief description of the titration. The anode compartment is filled with both an alcohol (ROH) and a base (B) containing both sulfur dioxide and iodine. The overall reaction (Equations 3 and 4) is the oxidation of sulfur dioxide by iodine. One mole of iodine is consumed for each mole of water present. This can be converted back to current because there are 2 moles of electrons for every mole of water present.



CO Coverage/surface area measurements.— The carbon monoxide coverage on platinum was determined by integrating the area under the carbon monoxide stripping peak. The baseline for the carbon monoxide stripping peak was set by the profile of the second scan where the peak was no longer present due to the absence of carbon monoxide on the surface. Carbon monoxide stripping can help determine the coverage of carbon monoxide on platinum black using the conversion constant of 420 $\mu C/cm^2$.⁸

Cyclic voltammetry (CV) monitoring carbon dioxide reduction.— In order to monitor the reduction of carbon dioxide dissolved in the electrolyte solution, cyclic voltammograms were taken both before and after the addition of carbon dioxide to the electrolyte solution. In order to establish a control, the electrolyte was sparged (150 sccm) with UHP argon for 2 hours. During the control measurement, the ionic liquid was under an argon atmosphere (ca. 1 atm). Cyclic voltammetry measurements were taken at a scan rate of 10 mV/s in a stepped sweep mode with a 2 Hz low pass filter and ohmic loss compensation. The voltammetry experiments for the carbon dioxide saturated

experiments followed the same specifications as the blank, except the electrolyte was saturated with CO₂, and the head atmosphere which was also CO₂ rather than UHP argon.

Results

Figure 1 shows the faradaic efficiency of CO and H₂ from the gas exit stream of the flow cell measured using a flow cell CO₂ electrolyzer. The cell potential was held at 2.5 V for all of the data points in this figure.

We find that in nearly dry ionic liquid electrolytes, the faradaic efficiency is low, because of leakage currents and other current losses in the cell. We have found evidence of corrosion on some of our flow cell components, and while this effect is small, its contribution to the calculation of faradaic efficiency was larger when the overall current was also small. The faradaic efficiency to CO increased when water was added to the dry EMIM BF₄ electrolyte reaching nearly 100% at 89.5 mol% water. The 89.5% water mixture contains 49.7 moles/liter of water. At higher water concentrations, evolution began; consequently the faradaic efficiency of CO dropped. Figure 2 shows the steady state performance of the flow cell. The steady state current was measured at the two proton concentrations showing the highest performance from Figure 1. Table I shows the pH of various EMIM BF₄-H₂O mixtures, as well as an EMIM BF₄-0.1 M H₂SO₄ mixture. Notice how the hydrolysis of the BF₄ anion causes the pH of EMIM BF₄-H₂O mixtures to form a global minimum. From Figure 1, we see that an EMIM BF₄-water mixture with a pH of 3.2 showed the highest performance. We made an electrolyte mixture of 10.3 mol% 0.1 M H₂SO₄ in EMIM BF₄, which is also at pH 3.2. Figure 2 shows that the steady state currents for both the 89.5 mol% water mixture and the 10.3 mol% 0.1 M H₂SO₄ mixture overlapped. This demonstrates the dependence on proton availability of the CO₂ reduction rate.

Figure 3 shows the cyclic voltammetry for the reduction of carbon dioxide on silver nanoparticles in EMIM BF₄. In dry EMIM BF₄, CO₂ reduction began at -0.7 V vs. SHE. As water was added, we measured an increase in the CO₂ reduction current relative to the dry ionic liquid, consistent with Figures 1 and 2. We also observe the

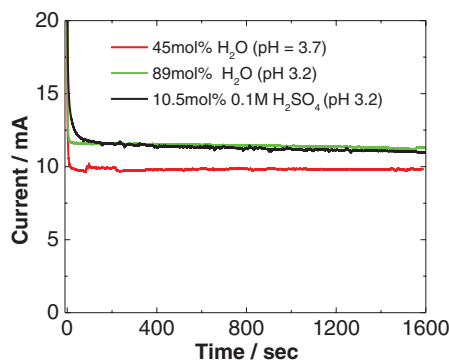


Figure 2. Steady state performance of flow cell with silver cathode at -0.7 vs. SHE. Note that the steady state current for CO₂ reduction depends on the proton concentration.

Table I. The pH of EMIM BF₄ mixed with various amounts of water and 0.1 M H₂SO₄.

Solution Composition	pH
EMIM BF ₄ +	
0 mol% H ₂ O	5.54
8 mol% H ₂ O	4.99
25.0 mol% H ₂ O	4.87
48.7 mol% H ₂ O	3.76
89.5 mol% H ₂ O	3.20
96.4 mol% H ₂ O	4.92
98.0 mol% H ₂ O	7.61
10.3 mol% 0.1 M H ₂ SO ₄	3.20

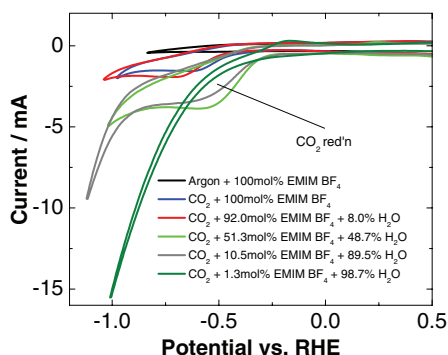


Figure 3. Effect of adding H₂O to EMIM BF₄ on carbon dioxide reduction on a silver nanoparticle cathode ($v = 50$ mV/s).

onset potential of CO₂ reduction moving to more positive potentials. The onset potential for CO₂ reduction increased from -0.6 V to about -0.45 V vs. SHE, as the pH dropped from 5.54 to 3.2, consistent with the Nernst equation. The earliest onset potential, as well as the largest reduction current, was observed at a pH of 3.2, 89.5 mol% water and 10.5 mol% EMIM BF₄. In addition to pH effects mentioned above, the mass transport resistance to the electrode is considerably lowered as water is added due to the lower viscosity.

The effect of water enhanced CO₂ reduction is also seen on metals with very low hydrogen overpotentials such as platinum. This effect is particularly interesting because it would be expected that metals like platinum would produce only hydrogen upon the addition of protons. Figure 4 shows CO stripping from a platinum surface after it was held at -0.7 V vs. SHE for 5 min. Because CO irreversibly adsorbs on platinum at room temperature, the area under the stripping peak is a measure of how much CO was produced during the electrolysis step. The stripping peaks can be found in Figure S3 in the supplemental section. We observe a similar trend on platinum and silver in that there is a peak in CO production at an intermediate mole fraction of water. This critical mole fraction, where the CO production reaches a maximum, occurs at a smaller water concentration on platinum compared to silver. This is because the overpotential of hydrogen on platinum is lower compared to silver. The result is that the surface is covered by H₂ at a lower water fraction on platinum compared to silver.

Discussion

It is useful to compare the results here to those from the previous literature. Tomita et al.⁹ examined the effects of water additions on CO₂ electrolysis in acetonitrile-water mixtures, and found that

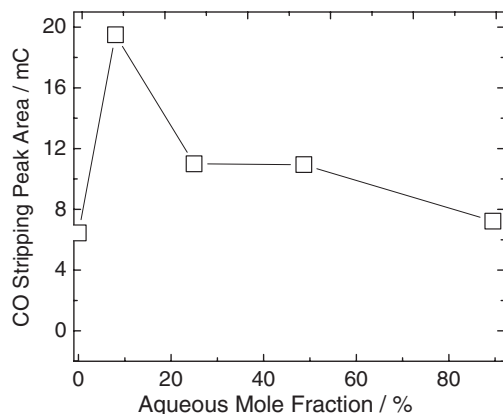


Figure 4. Effect of adding H₂O to the CO stripping peak area after the electrode was held at a reducing potential of -0.7 V vs. SHE for 5 min.

they could observe significant hydrogen formation when as little as 0.01 moles/liter of water is added to a dry acetonitrile solution. Hydrogen formation dominates at water concentrations of 1 moles/liter or more. Here we find little hydrogen formation when the water concentration is about 25 moles/liter and only start to observe significant hydrogen formation at water concentrations above 30 moles/liter. Interestingly, we produce about the same amount of hydrogen at a water concentration of 37 moles/liter as Tomita et al. report at a water concentration of 0.03 moles/liter. Clearly, the EMIM-BF₄ can inhibit hydrogen formation.

We can speculate how this occurs. Previous workers¹⁰⁻¹² have found that amines can inhibit hydrogen formation, although the effects were smaller than those observed here. While the mechanism is not clear, we previously showed¹³ that on platinum, EMIM covers the surface. We speculate that the EMIM layer blocks hydrogen adsorption. For example Figure S6 shows that 1 mol% EMIM BF₄ in 0.1 M H₂SO₄ completely inhibited the UPD hydrogen peaks on a platinum cathode. Clearly, there is a significant effect.

Our other key observation is that water lowers the overpotential for CO₂ conversion. This is also a surprising result. Of course, water additions also lower the pH of the EMIM-BF₄ solution. This is due to the hydrolysis of BF₄⁻ to form HF and anions such as [BF₃OH]⁻, [BF₂(OH)₂]⁻, [BF(OH)₃]⁻, and [B(OH)₄]⁻.^{14,15} At room temperature, Wamser et al.¹⁶ found that approximately 13% of the BF₄ anions in HBF₄ hydrolyze.

The overall reaction on the cathode is



Therefore, we propose that the decrease in the pH of the system as water is added to the mixture leads to a greater proton availability, which according to the Marcus equation should lower the barrier to the reaction and enhance the rate.

This result shows that the addition of water to EMIM BF₄ can in fact accelerate the desired CO₂ reaction, while the EMIM cation could inhibit the H₂ evolution expected upon water addition, even at high water concentrations.

Acknowledgments

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