

## Electrocatalysis of CO<sub>2</sub> Reduction in Brush Polymer Ion Gels

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**S** Supporting Information

**ABSTRACT:** The electrochemical characterization of brush polymer ion gels containing embedded small-molecule redox-active species is reported. Gels comprising PS–PEO–PS triblock brush polymer, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIm-TFSI), and some combination of ferrocene (Fc), cobaltocenium (CoCp<sub>2</sub><sup>+</sup>), and Re(bpy)(CO)<sub>3</sub>Cl (**1**) exhibit diffusion-controlled redox processes with diffusion coefficients approximately one-fifth of those observed in neat BMIm-TFSI. Notably, **1** dissolves homogeneously in the interpenetrating matrix domain of the ion gel and displays electrocatalytic CO<sub>2</sub> reduction to CO in the gel. The catalytic wave exhibits a positive shift versus Fc<sup>+0</sup> compared with analogous nonaqueous solvents with a reduction potential 450 mV positive of onset and 90% Faradaic efficiency for CO production. These materials provide a promising and alternative approach to immobilized electrocatalysis, creating numerous opportunities for application in solid-state devices.

Molecular catalysis of reactions pertinent to the synthesis of liquid fuels and other C1 building blocks from carbon dioxide is one of the most challenging problems in sustainable energy research today.<sup>1–5</sup> Though capable of producing C2 and C3 products, heterogeneous catalysis at metal surfaces has been consistently plagued with highly variable product distributions. CO<sub>2</sub> reduction beyond two-electron (CO and HCOOH) and four-electron (formaldehyde) processes has been a challenge with molecular electrocatalysts. While Fischer–Tropsch chemistry might increase the utility of CO<sub>2</sub> reduction to mixtures of CO and H<sub>2</sub>,<sup>6</sup> recent discoveries of homogeneous catalysts with selectivity for formaldehyde and systems with stoichiometric selectivity for methane using “preactivated” CO<sub>2</sub> and a supporting molecule have generated interest in leveraging inorganic complexes for molecular CO<sub>2</sub> reduction.<sup>7,8</sup> To date, the use of these homogeneous catalysts in industry has mostly been precluded by implementation difficulties.

Attempts at heterogenization of nominally homogeneous catalysts on electrode surfaces by covalent or non-covalent interactions have achieved limited success, with many systems producing stable catalysis for only hours to days.<sup>9</sup> Alternative strategies for stabilizing molecular catalysts in the solid state, maximizing catalyst efficiency, and preventing catalyst decomposition are clearly required.

Herein, we leverage physically cross-linked polymer networks to decouple the molecular interactions providing macroscopic

solidlike mechanical properties from the electrochemical activity of homogeneous small-molecule catalysts. This design captures the benefits of a solid support without the complexity associated with catalyst redesign and surface attachment.<sup>10–14</sup> This advance is afforded by the use of ABA triblock brush polymers infused with a B-selective ionic liquid (IL) as the matrix, a blend that forms physically cross-linked A-block micelles contained in a continuous matrix of B + IL.<sup>15–17</sup> We demonstrate that electroactive small molecules dissolved in the matrix domain are capable of undergoing redox reactions because of the high ionic conductivity and polarizability of the IL medium in which they are trapped. Incorporation of a well-established CO<sub>2</sub> reduction catalyst, Re(bpy)(CO)<sub>3</sub>Cl (**1**), provides a robust methodology capable of performing useful electrochemical reactions with homogeneous catalysts exhibiting macroscopic solidlike properties.

Little precedent exists for catalysis in a solid-state medium with facile catalyst diffusion through the structure. To our knowledge, reversible voltammetry has not been observed for ionic liquid–polymer gel electrolytes, aside from one report of a reversible Fc<sup>+0</sup> wave when a gel was still wet with casting solvent.<sup>18</sup>

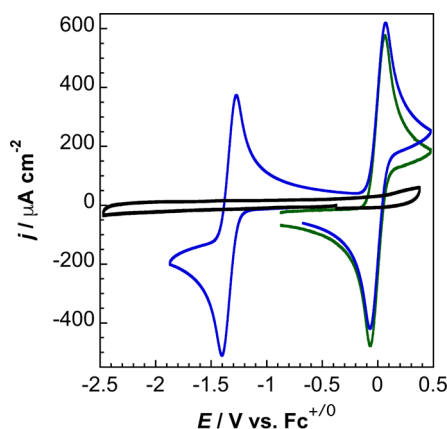
Ion gels were prepared by stirring polystyrene–poly(ethylene oxide)–polystyrene triblock brush polymer (*N*<sub>A</sub>:*N*<sub>B</sub>:*N*<sub>A</sub> = 15:119:15) with vacuum-dried 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIm-TFSI), dichloromethane (DCM) cosolvent, and optionally ferrocene (Fc) and/or CoCp<sub>2</sub><sup>+</sup> (to determine whether reversible redox couples could be observed).<sup>16,17</sup> The mixtures were stirred for 20 min and then allowed to dry in a nitrogen-filled glovebox for over 24 h. <sup>1</sup>H NMR spectroscopy confirmed the complete removal of DCM, and small-angle X-ray scattering suggested little change in gel structure with incorporation of electroactive species (see Figure S2). Electrochemical measurements were conducted in a nitrogen-filled glovebox by resting a glassy carbon working electrode on the surface of the gel and inserting a Pt wire counter electrode and a silver pseudoreference electrode into the gel.

Figure 1 displays potential sweeps for the blank gel, the gel with Fc, and the gel with both Fc and CoCp<sub>2</sub><sup>+</sup>. The thermodynamic separation between two redox standards, e.g., CoCp<sub>2</sub><sup>+</sup> and Fc, should be independent of the solvating medium. The *E*<sub>1/2</sub> of –1.33 V vs Fc<sup>+0</sup> for CoCp<sub>2</sub><sup>+0</sup> in the ion

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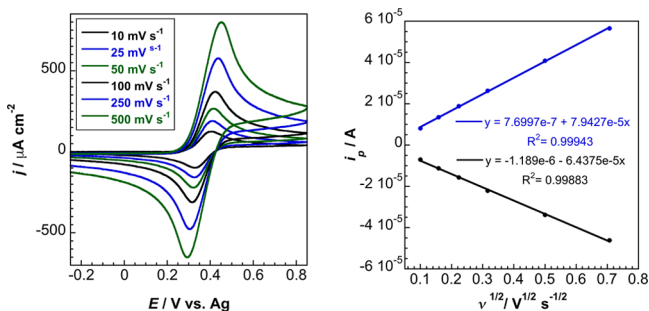
**Figure 1.** Cyclic voltammetry of blank ion gel electrolyte (black), ion gel with 14.3 mM Fc (green), and ion gel with 14.3 mM Fc and 15.3 mM CoCp<sub>2</sub><sup>+</sup> (blue).

gel is consistent with reported values for CoCp<sub>2</sub><sup>+0</sup> in ionic liquids as well as other electrolytes.<sup>19</sup>

In addition, to confirm the redox mechanism of the Fc<sup>+0</sup> and CoCp<sub>2</sub><sup>+0</sup> redox couples in the ion gel, diagnostic plots were obtained by Nicholson and Shain metrics, which confirmed the redox behavior of both couples as “case I”, corresponding to an electrochemically reversible redox process (see Figure S3).<sup>20</sup> The deviation of the Fc<sup>+0</sup> peak current ratio from 1 could be attributable to unequal diffusion coefficients for corresponding neutral and oxidized species in ionic liquids due to the charge effect of the medium.<sup>21,22</sup> The peak current, *i*<sub>p</sub>, of a reversible electron transfer in homogeneous electrochemistry is given by eq 1:

$$i_p = 0.4463n^{3/2}F^{3/2}AC_0^* \sqrt{\frac{D_0v}{RT}} \quad (1)$$

where *n* is the number of electrons (*n* = 1 for Fc oxidation and CoCp<sub>2</sub><sup>+</sup> reduction), *D*<sub>0</sub> is the diffusion coefficient of the electroactive species (in cm<sup>2</sup> s<sup>-1</sup>), *v* is the scan rate (in V s<sup>-1</sup>), *A* is the electrode surface area (*A* = 0.0707 cm<sup>2</sup>), and *C*<sub>0</sub><sup>\*</sup> is the bulk concentration of analyte (in mol L<sup>-1</sup>). The diffusion coefficient can be obtained from a plot of peak current versus *v*<sup>1/2</sup>.<sup>23</sup> In general, diffusion coefficients derived from voltammetric measurements tend to have high variability. However, we found good reproducibility in the values obtained from triplicate samples, and the diffusion coefficient of Fc in the ion gel is roughly one-fifth that for Fc in neat BMIm-TFSI. Figure 2 displays the scan rate dependence for the Fc<sup>+0</sup> redox couple and the corresponding linear fits (see Figures S4 and S5). Table



**Figure 2.** Scan rate dependence of Fc<sup>+0</sup> in ion gel electrolyte (14.3 mM Fc).

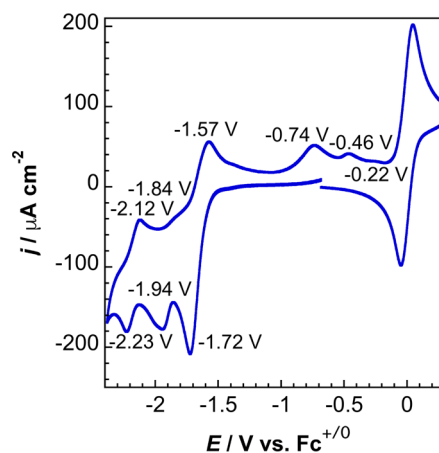
1 gives average values of the diffusion coefficients of Fc and CoCp<sub>2</sub><sup>+</sup>.

**Table 1. Diffusion Coefficients Obtained by Randles–Sevcik Analysis and Literature Data for Fc, CoCp<sub>2</sub><sup>+</sup>, and Re(bpy)(CO)<sub>3</sub>Cl in IL and Gel**

| species                        | <i>D</i> <sub>0</sub> in gel (10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ) | <i>D</i> <sub>0</sub> in neat BMIm-TFSI (10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ) |
|--------------------------------|--|---|
| Fc                             | 0.81 ± 0.04  | 3.89 <sup>a</sup> ± 0.05  |
| CoCp <sub>2</sub> <sup>+</sup> | 0.53 ± 0.04  | 2.22 <sup>a</sup> ± 0.03  |
| Re(bpy)(CO) <sub>3</sub> Cl    | 0.42 <sup>b</sup> ± 0.01   | 1.94 ± 0.02   |

<sup>a</sup>Literature value.<sup>19</sup> <sup>b</sup>Calculated by multiplying the diffusion coefficient in BMIm-TFSI by the change in peak current ratio observed for ferrocene.

Polymer ion gels were subsequently investigated as media capable of supporting homogeneous electrocatalytic reactions.<sup>24–26</sup> CO<sub>2</sub> reduction studies were pursued with **1** because of its well-characterized product distribution and kinetics in nonaqueous electrolytes.<sup>27–31</sup> Additionally, a recent report has shown dramatic improvement in catalytic activity and a positive shift in the onset potential of **1** in EMIm-TCB, a low-viscosity ionic liquid.<sup>32</sup> The increased CO<sub>2</sub> reduction activity observed in ionic liquids is likely a cation effect, where the imidazolium of the ionic liquid hydrogen-bonds to the halide ligand to generate the catalytically active form of the complex at a more positive potential.<sup>33</sup> Our finding of enhanced activity of **1** in EMIm-EtSO<sub>4</sub> and EMIm-OTf agrees with this hypothesis. The redox behavior of **1** in ionic liquid media is more complex than that in organic solvents. Rather than two one-electron reductions corresponding to bipyridine-centered and metal-centered reductions, the electrochemistry in both the gel and neat BMIm-TFSI exhibits three separate reduction waves (the waves at -1.94 V overlap) and an additional reversible redox process near the edge of the electrochemical window, as shown in Figure 3. This behavior may arise from ligand exchange of the chloride for the TFSI anion. TFSI is present in high concentration and is a π-donor ligand like Cl<sup>-</sup>, which makes ligand exchange at negative potentials feasible.<sup>34</sup> The three peaks were observed in ultramicroelectrode experiments as three separate steady-state currents (see Figures S6 and S7),

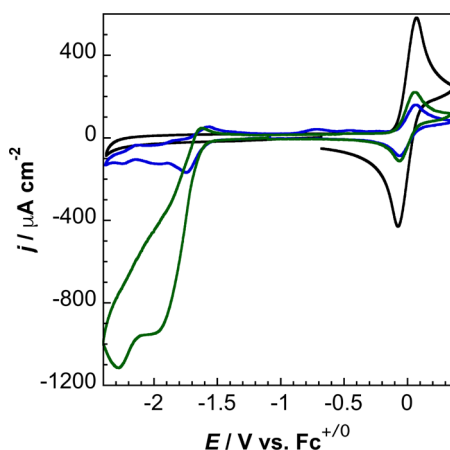


**Figure 3.** Cyclic voltammetry of the ion gel electrolyte with 14.3 mM Re(bpy)(CO)<sub>3</sub>Cl and 5 mM Fc. Potentials have been shifted relative to the half-wave potential of Fc<sup>+0</sup>.

and the expected current ratios suggest the presence of two forms of the catalyst. The additional, reversible redox process is proposed to correspond to a second bipyridine reduction, which has been observed for analogous complexes.<sup>35</sup>

Previous research has suggested that the coalescence of the two waves observed for the Re catalyst in BMIm-TFSI is a result of two-electron transfer to the complex as supported by analysis of **1** in ionic liquid media.<sup>32</sup> The exchange of TFSI for Cl<sup>-</sup> correlates with the observation of both waves for **1** with exchanged anion due to slower dissociation of TFSI. Other complexes with axial ligands also exhibit analogous behavior. For example, voltammetry of Co[5,10,15-tris(perfluorophenyl)-corrole](pyridine)<sub>2</sub> (selected for its labile axial ligands) in BMIm-TFSI revealed a doubling of redox events, suggesting two redox-active forms of the complex (see Figure S8).<sup>36</sup>

The electrochemistry of (1) the ion gel with Fc under 1 atm CO<sub>2</sub>, (2) the ion gel with **1** and Fc under an inert atmosphere, and (3) the ion gel with Fc and **1** under 1 atm CO<sub>2</sub> is shown in Figure 4. Under CO<sub>2</sub>, a catalytic wave is observed. Analogous to

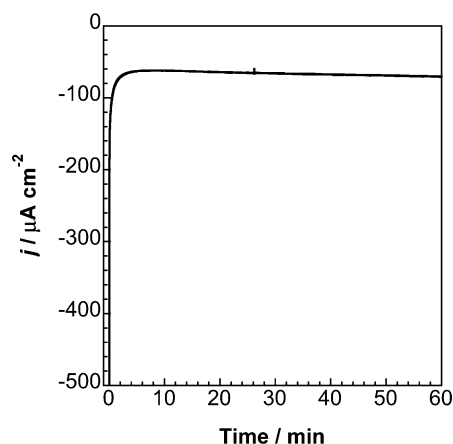


**Figure 4.** Cyclic voltammetry of the ion gel electrolyte with 14.3 mM Fc and 1 atm CO<sub>2</sub> (black), with 5 mM Fc and 10 mM Re(bpy)(CO)<sub>3</sub>Cl (blue), and with 7.1 mM Fc, 14.3 mM Re(bpy)(CO)<sub>3</sub>Cl, and 1 atm CO<sub>2</sub> (green).

neat BMIm-TFSI, the potential needed for reduction of CO<sub>2</sub> with Re(bpy)(CO)<sub>3</sub>Cl is shifted 450 mV positive of its value in nonaqueous systems.

Figure 5 reports controlled-potential electrolysis of the ion gel with embedded catalyst using a glassy carbon plate working electrode; results for both the ion gel and ionic liquid control are summarized in Table 2. The current density for **1** in the ion gel is smaller than that observed for **1** in the ionic liquid or nonaqueous solvent because of slower diffusion and lack of an embedded proton source.<sup>9,27,28</sup>

The materials described herein reflect a general strategy that bridges the divide between homogeneous solution-state catalysis and heterogeneous solid-state catalysis. Decoupling the time scales associated with macroscopic flow and local molecular reorganization enables the formulation of materials with solidlike properties containing small molecules that respond to electrochemical stimuli with near-liquidlike kinetics. We have demonstrated that this new class of materials is capable of electrocatalytically reducing CO<sub>2</sub> with a well-defined small-molecule catalyst historically used in homogeneous solutions. The catalytic enhancement and high CO<sub>2</sub> solubility imparted by the ionic liquid results in a significant decrease in



**Figure 5.** Controlled-potential electrolysis of the ion gel electrolyte with 7.1 mM Fc and 1 mM Re(bpy)(CO)<sub>3</sub>Cl under 1 atm CO<sub>2</sub>.

**Table 2. Controlled-Potential Electrolysis of 1 mM Re(bpy)(CO)<sub>3</sub>Cl in IL and in Ion Gel<sup>a</sup>**

| medium    | onset potential (V vs Fc <sup>+0</sup> ) | electrolysis potential (V vs Fc <sup>+0</sup> ) | Faradaic efficiency for CO (%) |
|-----------|--|---|--------------------------------|
| BMIm-TFSI | -1.55                                    | -1.9  | 92 ± 5                         |
| ion gel   | -1.60                                    | -2.1  | 90 ± 5                         |

<sup>a</sup>Results are averages of triplicate measurements.

CO<sub>2</sub> reduction potential compared with typical nonaqueous electrolytes. Since physical cross-links imbue mechanical properties, reversible gelation is thermally accessible with an appropriately tuned upper critical solution temperature or through good solvent addition. Extraction of electrochemical reaction products, reformulation of the composition, and macroscopic shape adjustment should thus be possible. Further implementation of these ion gel composites in solid-state devices is currently underway.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08795.

Materials and methods and additional electrochemistry data (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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