Ionic Liquid–Mediated Selective Conversion of CO₂ to CO at Low Overpotentials

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Electroreduction of carbon dioxide (CO₂)—a key component of artificial photosynthesis—has largely been stymied by the impractically high overpotentials necessary to drive the process. We report an electrocatalytic system that reduces CO₂ to carbon monoxide (CO) at overpotentials below 0.2 volt. The system continues producing CO for at least 7 hours at Faradaic efficiencies greater than 96%.

In the context of artificial photosynthesis (1–4), considerable progress has been made toward water-splitting technology that uses solar energy or solar-derived electricity, but CO₂ activation has proven to be more difficult (5–7). Although a few homogeneous catalysts show initial activity at overpotentials of 600 mV (6, 7), most quickly lose their activity under reaction conditions. Pyridine-catalyzed conversion may be an exception (8–10), although performance over an extended time has not been reported. A promising catalyst for efficient CO₂ conversion would need to exhibit both high energy efficiency (i.e., high Faradaic efficiency for CO production at low overpotential) as well as high current density (i.e., high rate or turnover number) (11).

Twenty years ago, Bockris and co-workers proposed that high overpotentials are needed to convert CO₂ (12, 13) because the first step in CO₂ reduction is the formation of a “CO₂” intermediate. (In this context, “CO₂” does not necessarily denote a bare CO₂ anion; instead, it is whatever species forms when an electron is added to CO₂.) The equilibrium potential for CO₂ formation is very negative in water and in most common solvents (12, 13). Consequently, it is necessary to run the cathode very negative (i.e., at a high overpotential) for the reaction to occur. This is very energy-inefficient (Fig. 1). The objective of the work described here was to develop a cocatalyst that would lower the potential for formation of the CO₂ intermediate, which then reacts with H⁺ on the silver cathode to produce CO (5). If Bockris’ proposal is correct, the overpotential for CO₂ conversion into useful products should decrease upon lowering the free energy of formation of the CO₂. For example, if a substance formed a complex with the CO₂ on the metal surface, then the reaction could follow the dashed line in Fig. 1. In that case, a complex between the solvent and the CO₂, labeled “EMIM-CO₂” in the figure, could form quickly. Although there would still be a barrier to form the final products of the reaction, the overall barrier to reaction would be reduced (14).

We chose 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) to test whether such a route was feasible. We first used cyclic voltammetry (CV) to characterize the reduction of CO₂ in an 18 mol % EMIM-BF₄ solution (see figs. S5 and S6 for CV diagrams of this process on a platinum and a silver working electrode, respectively). Barnes et al. (15) and Islam and Ohsaka (16) found that O₂⁻ forms a complex with the cation in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-NTf₂), moving the potential for O₂⁻ formation in the positive direction by 0.65 V. CO₂ is also known to form weak complexes with BF₄⁻ anions (17–21). We reasoned that if CO₂ and O₂⁻ form complexes with EMIM-BF₄ and BMIM-NTf₂, then CO₂ could do so as well, thereby shifting CO₂ conversion to less negative potentials, as suggested by Fig. 1. Also, the binding of CO₂ in EMIM-BF₄ is weaker than in many other ionic liquids. Ideally, the “CO₂” complex should be bound strongly enough to facilitate CO₂ reduction, but not so strongly that the “CO₂” is unreactive (14).

We tested whether the overpotential for CO₂ would be reduced as predicted. The experiments used a flow cell reported previously (22, 23) (fig. S1). The cell was constructed from a platinum anode and a silver cathode, with liquid in between. In such a setup, CO₂ flows into the cell, and the products present in the gaseous stream flowing out are analyzed by gas chromatography (GC). We previously ran the experiment, and we found that the platinum anode was quickly poisoned by CO created on the cathode, so we placed a Nafion 117 membrane between the anode and the cathode to isolate the anode from the ionic liquid (23).

The anode compartment contained 100 mM aqueous sulfuric acid flowing at 0.5 ml/min. The cathode compartment contained 18 mol % EMIM-BF₄ in water at the same flow rate. Measurements indicated that the platinum anode had an electrochemical surface area of 500 cm² and the silver cathode had an electrochemical surface area of 6 cm². The procedures for the surface area measurements of both the anode (CO stripping) and cathode (underpotential deposition of lead) can be found in the supporting online material.

During the experiments, we held the voltage on the cell constant, and measured the products of the reaction by GC. We observed only three products: hydrogen and CO on the cathode and oxygen on the anode. Other products may have been present at concentrations below 3 parts per million, the GC detection limit.

Figure 2 shows how the CO peak in the GC trace varies with the applied voltage, in experiments in which we held the voltage constant and waited until we found steady performance. We began to see CO at an applied potential of 1.5 V. By comparison, when we ran the cell under identical conditions but in the absence of...
Faradaic efficiency was always greater than 96%. We did observe a little hydrogen formation from electrolysis of water, but the hydrogen formation was always less than 3% of the Faradaic efficiency. Figure 3 also shows the energy efficiency of the process, calculated from the equation

\[
\text{energy efficiency} = \frac{\text{Faradaic efficiency} \times 1.33 \text{ V}}{\text{applied voltage}} \tag{2}
\]

The energy efficiency is 87% at low voltage (1.5 V) and drops as voltage increases because of energy loss due to resistive losses in the membrane and solutions.

To ascertain the catalytic rate and robustness, we ran the cell for 7 hours and obtained about 26,000 turnovers in which the turnovers were calculated according to the electrochemical surface area of our cathode catalysts. The plot of the data in Fig. 4 exhibits some curvature because the membrane resistance is increasing over time, but clearly the setup is capable of many turnovers.

The one weakness of the system at present is that our observed rates are lower than what is needed for a commercial process. Typically, commercial electrochemical processes run at a turnover rate of about 1 to 10 per second, in contrast with the rate of 1 per second or less that we observe here. Further development of the reactor configuration and exact operating conditions—e.g., for example, to overcome some mass transport issues—is expected to increase the turnover number. Indeed, we observed a rate of 60 turnovers per second with a rotating-disk electrode at a cathode potential equivalent to that observed when the cell potential is about 2 V (Fig. S7).

Also, scale-up needs to be done. At present, our cathode has an electrochemical surface area of only 6 cm², whereas commercial electrochemical cells for the chlor-alkali process have electrochemical surface areas on the order of 10^4 cm². At 2 V, our cell produces CO at a rate of only ~1 μmol/min, whereas commercial processes require thousands of moles per minute per cell.

Fig. 3. A plot of the Faradaic efficiency of the process to form the desired CO and the undesired hydrogen, and the turnover rate as a function of applied cell potential.

Fig. 4. The total number of turnovers accumulated on the catalyst as a function of time at an applied potential of 2.5 V. The curvature in the plot is due to a gradual increase in membrane resistance.

The ionic liquid, CO was not detected until a cell potential of 2.1 V was applied. This control experiment was carried out using 500 mM KCl electrolyte. The CO peak grew slightly as we increased the potential, but the increases were small because the membrane resistance to mass transfer was large, hence the current was mass transfer limited. The data in Fig. 2 show that most of the increased potential went toward polarizing the membrane or anode, rather than polarizing the cathode. To put the data in perspective, the equilibrium potential for the reaction

\[
\text{CO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO} + \text{H}_2 \tag{1}
\]

is 1.33 V, so the fact that we could observe gas phase CO formation at an applied potential of 1.5 V implies that we could form CO with a cell overpotential of only 0.17 V. Normally, an anode overpotential would also have to be accounted for, but in our cell the electrochemical surface area of the anode is about 80 times that of the cathode.

We also used GC to measure the Faradaic efficiency of CO formation (i.e., the fraction of the electrons going to the CO product, as opposed to the hydrogen by-product); the results are shown in Fig. 3. We found that the
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