Ionic Liquid–Mediated Selective Conversion of CO_2 to CO at Low Overpotentials

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Electroreduction of carbon dioxide (CO_2)—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 CO_2 to carbon monoxide (CO) at overpotentials below 0.2 volt. The system relies on an ionic liquid electrolyte to lower the energy of the $(CO_2)^-$ intermediate, most likely by complexation, and thereby lower the initial reduction barrier. The silver cathode then catalyzes formation of the final products. Formation of gaseous CO is first observed at an applied voltage of 1.5 volts, just slightly above the minimum (i.e., equilibrium) voltage of 1.33 volts. The system continued 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 CO_2 activation has proven to be more difficult (*1*, *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 CO_2 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 CO_2 (*12*, *13*) because the first step in CO_2 conversion is the formation of a "CO_2^-" intermediate. (In this context, "CO_2^-" does not necessarily denote a bare CO_2^- anion; instead, it is whatever species forms when an electron is added to CO_2.) The equilibrium potential for $(CO_2)^-$ 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 CO_2^- intermediate, which then reacts with H^+ on the silver cathode to produce CO (*5*). If Bockris' proposal is correct, the overpotential for CO_2 conversion into useful products should decrease upon lowering the free energy of formation of the CO_2^-. For example, if a substance formed a complex with the CO_2^- 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 CO_2^-, labeled "EMIM-CO_2" 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-BF_4) to test whether such a route was feasible. We first used cyclic voltammetry (CV) to characterize the reduction of CO_2 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 $(O_2)^-$ forms a complex with the cation in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-NTf_2), moving the potential for $(O_2)^-$ formation in the positive direction by 0.65 V. CO_2 is also known to form weak complexes with BF_4 anions (*17–21*). We reasoned that if CO_2 and $(O_2)^-$ form complexes with EMIM-BF_4 and BMIM-BF_4, then $(CO_2)^-$ could do so as well, thereby shifting CO_2 conversion to less negative potentials, as suggested by Fig. 1. Also, the binding of CO_2 in EMIM-BF_4 is weaker than in many other ionic liquids. Ideally, the "CO_2^-" complex should be bound strongly enough to facilitate CO_2 reduction, but not so strongly that the "CO_2^-" is unreactive (*14*).

We tested whether the overpotential for CO_2 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, CO_2 flows into the cell, and the products present in the gaseous stream flowing out are analyzed by gas chromatography (GC). When we originally ran the experiment, 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-BF_4 in water at the same flow rate. Measurements indicated that the platinum anode had an electrochemical surface area of 500 cm^2 and the silver cathode had an electrochemical surface area of 6 cm^2. 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 the 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

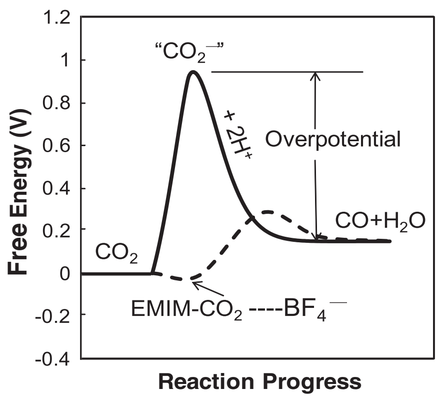

Fig. 1. A schematic of how the free energy of the system changes during the reaction $CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$ in water or acetonitrile (solid line) or EMIM-BF_4 (dashed line).

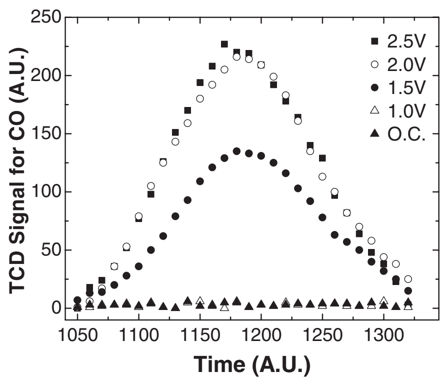

Fig. 2. The CO peak observed by gas chromatography as a function of the total potential applied to the cell (TCD, thermal conductivity detector; O.C., open cell). Gas-phase CO production is observed at an applied potential of 1.5 V (slightly above the equilibrium potential for the reaction, 1.33 V).

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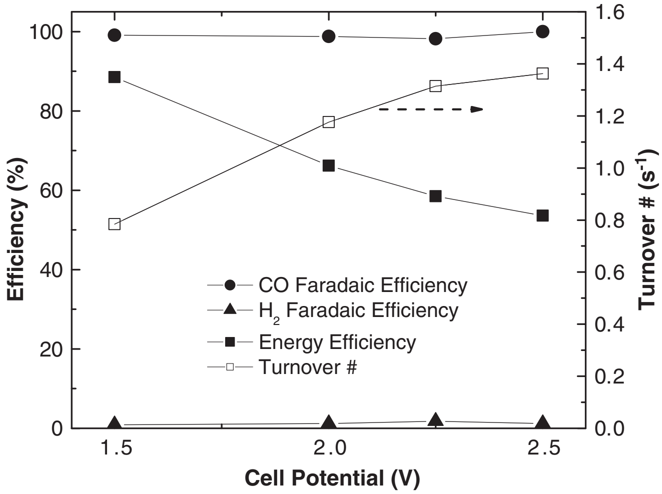

Fig. 3. A plot of the Faradaic efficiency of the process to form the desired CO and the undesired hydrogen, and the turnover rate as a function of applied cell potential.

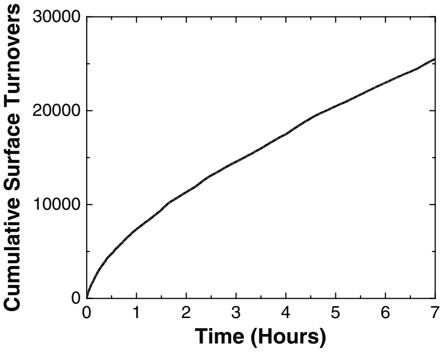

Fig. 4. The total number of turnovers accumulated on the catalyst as a function of time at an applied potential of 2.5 V. The curvature in the plot is due to a gradual increase in membrane resistance.

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

$$CO_2 \rightleftharpoons CO + {}^1/_2O_2 \qquad (1)$$

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 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

$$\text{energy efficiency} = \frac{\text{Faradaic efficiency} \times 1.33\ \text{V}}{\text{applied voltage}} \qquad (2)$$

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—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 cm^2, whereas commercial electrochemical cells for the chlor-alkali process have electrochemical surface areas on the order of 10^9 cm^2. 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.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/science.1209786/DC1
Materials and Methods
Figs. S1 to S7
References (*24–27*)

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