Electrocatalytic Reduction of Carbon Dioxide at Illuminated p-Type Silicon Semiconducting Electrodes

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Tetra-azamacrocyclic metal complexes catalyse the electrochemical reduction of carbon dioxide at illuminated p-Si at potentials approaching thermodynamic values.

Electrolytic reduction of carbon dioxide provides a possible means of converting it into useful fuels and organic compounds. The direct reduction of CO_2 at metal electrodes is well known.[1] The main problem with these systems is the large overpotential required for reduction. Several recent reports indicate that carbon dioxide can be electrocatalytically reduced.[2–6] These studies suggest that transition metal-based catalysts can be used to manipulate the electron-transfer kinetics and lessen the voltages required for reduction. Although the reported mediated reduction schemes lessen the overvoltages for CO_2 reduction, the required potentials are still in excess of reversible potentials predicted by simple thermodynamic considerations. We report here a system for the sustained photoelectrocatalytic reduction of CO_2 utilizing p-Si photocathodes at potentials approaching thermodynamic values.

We have shown previously that p-Si photocathodes can carry out the reduction of a variety of tetra-azamacrocyclic metal complexes at potentials significantly less than at metal electrodes such as Pt or Hg.[7] The optical energy utilization in these systems is reasonable compared to other p-type semiconductor-based cells. For example, a typical experiment using the $[(\mathrm{Me_6[14]aneN_4})\mathrm{Ni^{II}}]^{2+}$–$[(\mathrm{Me_6[14]aneN_4})\mathrm{Ni^{II}}]^{1+}$[†] couple in MeCN–$\mathrm{Bu^n_4NClO_4}$ solution gives a quantum yield for electron flow of 0.4—0.5 and an efficiency for light into electricity conversion of *ca.* 2.5% for a p-Si cathode illuminated with 752 nm light (*ca.* 400 μW/cm^2).[‡] The current efficiency for production of reduced macrocyclic compounds is in the range of 95—100%.[§] These systems can be used to effect the reduction of CO_2 at illuminated p-Si at potentials up to 0.6 V less than required at metal electrodes using catalysts such as $[(\mathrm{Me_6[14]aneN_4})\mathrm{Ni^{II}}]^{2+}$ (**1**), $[(\mathrm{Me_6[14]dieneN_4})\mathrm{Ni^{II}}]^{2+}$ (**2**), $[(\mathrm{Me_6[14]aneN_4})\mathrm{Co^{II}}]^{2+}$ (**3**), and $[(\mathrm{Me_8[14]dieneN_4})\mathrm{Ni^{II}}]^{2+}$ (**4**),[8][†] and up to 1.3 V less than required in an unmediated scheme.

Evidence for the electrocatalytic behaviour of these systems at p-Si is readily provided by an examination of the cyclic voltammograms of the complexes in the presence of CO_2. In the absence of CO_2, each of the complexes exhibits a single reversible redox wave in O_2-free MeCN–H_2O–$\mathrm{Bu^n_4NClO_4}$ (4 : 1 : 0.1 M) solution at illuminated p-Si in the potential range −0.8 to −1.3 V *vs.* S.C.E. The exact position of the redox wave is dependent on the light intensity and on the history of the electrode. The reduced form of the macrocycle readily reacts with CO_2, as shown by the disappearance of the corresponding oxidation wave in the cyclic voltammograms upon introduction of CO_2. Further evidence for CO_2 reduction is provided by controlled-potential electrolysis experiments. Data were obtained in a two-compartment cell utilizing a three electrode configuration consisting of a p-Si working electrode (*ca.* 2 cm^2) illuminated with a Pyrex filtered 750 W tungsten–halogen lamp, a S.C.E. as the reference, and a Pt counter-electrode. In a typical experiment, 1.8×10^{-2} moles of the complex were dissolved in 100 ml of CO_2-saturated O_2-free electrolyte solution (MeCN–H_2O–$LiClO_4$; 1 : 1 : 0.1 M), and the p-Si was held at a potential approximately 200 mV more negative than the reduction wave in the cyclic voltammograms.[¶] Gases were sampled periodically during the experiment and analysed by gas chromatography.

The best results were obtained using (**1**) as the electron-transfer mediator. Carbon monoxide and hydrogen are the principle products from electrolysis experiments with (**1**), and were consistently formed in a 2 : 1 molar ratio. The current efficiency for the production of CO exceeds 95 ± 5% for electrolysis times from 2 to >24 h. Complexes (**2**), (**3**), and (**4**) produce CO and hydrogen in *ca.* 1 : 1 ratio. However, current efficiencies for CO production are much lower (10—15%). Identical current efficiencies and product ratios are obtained at Hg with catalysts (**1**)—(**4**) under similar reaction conditions except that the required potentials are 400—600 mV more negative than at Si. The reduction reaction is solvent dependent. Highest current efficiencies were obtained in a 1 : 1 MeCN–H_2O solution. Aqueous Me_2SO and dimethylformamide solutions of the complexes show catalytic activity but with a lower efficiency (<5—50%) for CO formation.

In non-aqueous electrolyte solutions (MeCN–$\mathrm{Bu^n_4NClO_4}$) of (**1**), the reduction of CO_2 occurs at p-Si, but a potential of −1.3 V *vs.* S.C.E. is required for the reduction reaction. In the absence of water, no hydrogen is formed in the reaction, and equimolar amounts of CO and CO_3^{2-} are the only observed products. As the H_2O concentration increases, CO_3^{2-} production decreases. CO and CO_3^{2-} are formed at p-Si in the absence of an electron transfer catalyst in dry solvents, but the potentials required exceed −1.9 V *vs.* S.C.E. This compares with a value of −2.3 V *vs.* S.C.E. at Hg under similar conditions. In the presence of H_2O, without complex, hydrogen evolution is the predominant reaction at −1.9 V, although trace amounts of CO are still produced.

Although detailed kinetic data have not been obtained, the experimental results suggest that different reduction pathways occur in aqueous and non-aqueous electrolytes. The initial step in both solvent systems must involve transfer of an electron from the reduced metal complex to CO_2 and formation of $CO_2^{\cdot-}$. In aprotic solvents, $CO_2^{\cdot-}$ presumably reacts with a second molecule of carbon dioxide to form a radical dimer. This radical dimer is reduced in a subsequent step to form a dianion which disproportionates into CO and CO_3^{2-}. The

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[†] $\mathrm{Me_6[14]aneN_4}$ = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane. $\mathrm{Me_6[14]dieneN_4}$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. $\mathrm{Me_8[14]dieneN_4}$ = 2,5,7,7,9,12,14,14-octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene.

[‡] Data derived from equilibrium current–potential curves obtained in a one-compartment cell consisting of a p-Si cathode, a Pt anode, and a standard calomel electrode (S.C.E.) as the reference.

[§] The current efficiencies were determined from coulometry and from optical density measurements by monitoring a characteristic absorption band of $[(\text{tetra-azamacrocycle})\mathrm{M^{I}}]^{1+}$.

[¶] The potentials were held at −1.00 V for (**1**), −1.05 V for (**2**) and (**4**), and −1.30 V *vs.* S.C.E. for (**3**).

exact pathway in protic solvents is not certain. The reaction probably proceeds by protonation of $CO_2^{\cdot-}$ followed by a second reduction resulting in the overall reaction shown in equation (1). These suggestions are consistent with kinetic

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad (1)$$

data reported for the direct reduction of CO_2 at Hg in solvents of low proton availability.[9,10] The results of studies to elucidate the mechanistic details of the reduction process in both aqueous and non-aqueous solvents at illuminated p-Si will be reported separately.

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