Electrochemical Reduction of Carbon Dioxide to Carbon Monoxide at a Gold Electrode in Aqueous Potassium Hydrogen Carbonate

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CO_2 is electrochemically reduced to CO in 0.5 M aqueous $KHCO_3$ solution at a gold electrode at 18 °C, the reaction proceeding with markedly low overvoltage, starting at −0.8 V *vs.* normal hydrogen electrode (N.H.E.); the faradaic efficiency for CO formation is 91% at −1.10 V *vs.* N.H.E. with a partial current of 3.7 mA cm^{-2}, and the reaction probably proceeds *via* adsorbed intermediates.

The cathodic reduction of CO_2 at metal electrodes (Hg, Pb, Zn, Cd, Sn, and In) exclusively yields HCO_2^- with high overvoltages in aqueous inorganic salt solutions.[1] We previously reported the electroreduction of CO_2 at various metal cathodes in $KHCO_3$ aqueous solution.[2] Au and Ag cathodes gave CO as the major product. CH_4 and C_2H_4 were produced at Cu cathodes with high current efficiencies of 5—10 mA cm^{-2}. We now describe the effective electroreduction of CO_2 to CO at an Au cathode.

An Au electrode (99.99% purity), size 20 × 20 × 0.5 mm, welded to a gold wire (0.5 mm diameter), was etched with aqua regia for 1 min at ambient temperature, and then rinsed three times with doubly distilled water in an ultrasonic cleaning bath. A three-compartment Pyrex cell was employed in which two anode compartments faced each side of the cathode. The cathode compartment (36 mm inner diameter) was separated from the two anodes with sheets of cation exchange membrane (Selemion). The cathode was placed roughly at the centre of the electrolyte. The potential of the cathode was measured with respect to an Ag/AgCl electrode. The electrode potential was corrected for the *IR* drop between the Luggin capillary tip and the cathode. The aqueous electrolyte (0.5 M $KHCO_3$) was purified by pre-electrolysis with a 30 × 20 mm Pt black cathode at 2×10^{-2} mA cm^{-2} under purified N_2 gas for at least 20 h. The electrolyses were conducted under controlled electrode potentials at 18 °C with purified CO_2 bubbled into the solution (flow rate, *ca.* 140 ml min^{-1}). The electrolyte (60 ml) was vigorously stirred by a magnetic stirrer with a Teflon coated bar (20 mm long, 6 mm diameter) during electrolysis. The effluent gas from the cell was introduced to gas chromatographs, by which CO, H_2, CH_4, and C_2H_4 were analysed. The products which were soluble in the solution were analysed by ion chromatography and permanganate titration.

CO and H_2 appeared in the effluent gas after the beginning of the electrolysis; the concentrations remained constant during the electrolysis. No other gaseous product was detected. The only soluble product was formate ion. The pH of the electrolyte was *ca.* 7.5. Typical faradaic efficiencies are as follows, along with the electrode potentials with respect to normal hydrogen electrode (N.H.E.): −0.80 V, CO 77%, HCO_2^- 10%, H_2 10%; −0.98 V, CO 92%, HCO_2^- 1%, H_2 9%; −1.11 V, CO 90%, HCO_2^- 1%, H_2 11%. A plot of the partial current densities *i*(CO), *i*(H_2), and *i*(HCO_2^-), calculated from the analytical data, against the electrode potential (Figure 1) is curved, possibly because the rate of reaction is affected by the transport of CO_2 to the electrode, although the exact reason is not yet clear.

The standard potential for the cathodic reduction of CO_2 to CO is −0.52 V *vs.* N.H.E. at pH 7 and 25 °C, as calculated from thermodynamic data.[3] $CO_2^{\cdot -}$ is presumed to be an intermediate in the electrochemical reduction of CO_2.[4—7] The standard potential of $CO_2^{\cdot -}$ formation was reported to be −2.21 V *vs.* standard calomel electrode (S.C.E.) in dimethylformamide (DMF).[6] Thus, the reduction of CO_2 proceeds at more negative potentials than −1.5 V *vs.* N.H.E. at metal

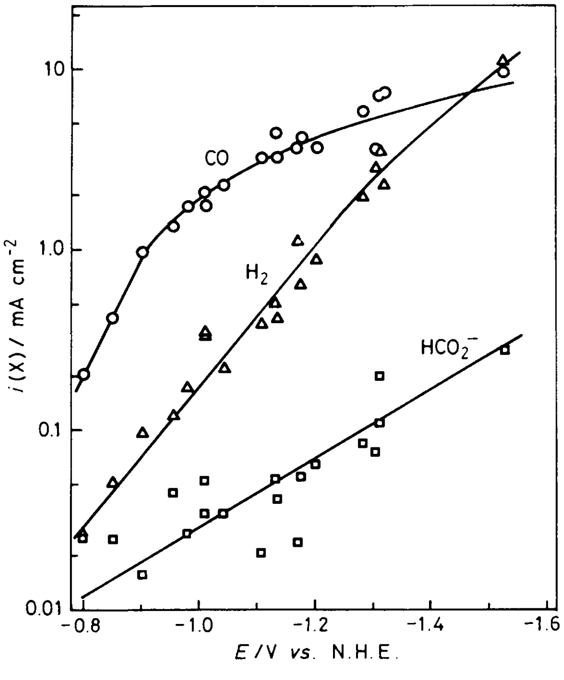

Figure 1. Partial current densities of the products, *i* (X), *vs.* electrode potential, *E* (0.5 M $KHCO_3$, 1 atm CO_2, 18 °C).

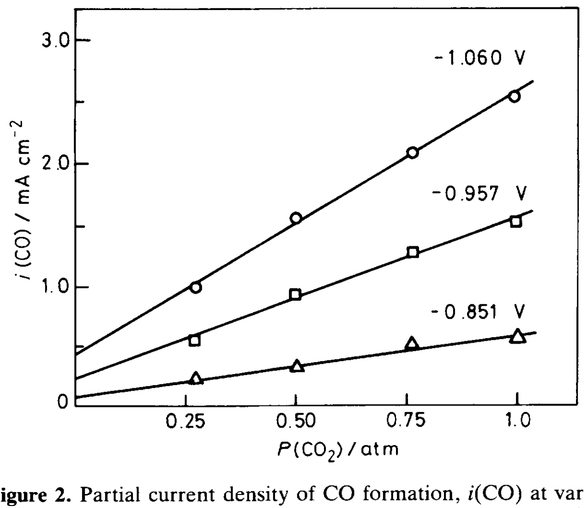

Figure 2. Partial current density of CO formation, *i*(CO) at various CO_2 pressures, $P(CO_2)$ (0.5 M $KHCO_3$, 18 °C). The potentials refer to N.H.E.

electrodes such as Hg, Cd, In, Sn, Pb, and Zn. The present results indicate that the CO is formed at markedly low cathodic potentials, −0.8 to −1.2 V *vs.* N.H.E. $CO_2^{\bullet -}$ appears to be stabilized significantly by adsorption to the electrode surface.

$i(CO)$ was measured with various CO_2 partial pressures by using mixtures of CO_2 and N_2 as the flow gas. Figure 2 shows that $i(CO)$ depends linearly on $P(CO_2)$ at various electrode potentials. However, the intercepts extrapolated to the ordinate are not equal to zero. These intercepts numerically agree well with the cathodic currents associated with the reduction of CO_2 which is supplied by the dissociation of HCO_2^- in the electrolyte solution.[8] Thus, it can be reasonably concluded that $i(CO)$ is proportional to $[CO_2]$, the concentration of CO_2 in the solution.

Amatore and Savéant studied the mechanism of the electroreduction of CO_2 at Pb and Hg in media of low proton availability (H_2O–DMF solutions).[7] They proposed a scheme for production of CO, HCO_2H, and $(CO_2H)_2$ in terms of intermediate species which contain two carbon atoms. They derived the rates of formation, R, for HCO_2^- and CO as functions of the experimental parameters. Their equations may easily be transformed into the simple form of equation (1) provided $i_0 \ll i_l$, where i_0 denotes the electrolysis current density and i_l the limiting current density.

$$R(HCO_2^-)/R(CO) = \text{const.} \times [H_2O]/[CO_2] \qquad (1)$$

Ryu *et al.* and Kapusta *et al.*[4] reported that the electroreduction of CO_2 to HCO_2^- in aqueous media at Hg, Sn, and In is a first-order reaction with respect to $P(CO_2)$ or $[CO_2]$. Thus, it is reasonable that $R(HCO_2^-)$ is proportional to $[CO_2]$. If Amatore and Savéant's scheme is valid for the CO formation, $R(CO)$ will be proportional to $P(CO_2)^2$ according to equation (1). However, the present results indicate that $i(CO)$ is proportional to $[CO_2]$. Hence, the formation of CO at the Au cathode proceeds by a different mechanism, probably *via* adsorbed species; CO and CO_2 adsorbed species have been discussed.[9] Detailed investigations are in progress.

It was recently reported that some transition metal complexes catalyse the cathodic reduction of CO_2 to CO with low overvoltages.[10] The partial currents for CO production can be estimated from these reports; the values range between 0.5 and 1.2 mA cm^{-2} with the electrode potential between −0.91 and −1.25 V *vs.* N.H.E. The present results show that the partial current for CO formation varies from 3.7 mA cm^{-2} at −1.1 V *vs.* N.H.E. to 10 mA cm^{-2} at −1.5 V. Thus the activity of Au electrode is remarkably high.

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