CHEMISTRY LETTERS, pp. 1231-1234, 1990.

Enhanced Evolution of CO and Suppressed Formation of Hydrocarbons in Electroreduction of CO_2 at a Copper Electrode Modified with Cadmium

Yoshio HORI,* Akira MURATA, and Shin-ya ITO
Department of Applied Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 260

Copper electrode modified with Cd was studied for reduction of CO_2 in 0.1 M $KHCO_3$ solution by in-situ deposition. Reduction of CO_2 to CH_4 and C_2H_4 is heavily prevented by a small amount of Cd with CO release significantly promoted. Anode stripping showed that Cd exists as adatoms.

Copper is an effective electrocatalyst for reduction of CO_2 to hydrocarbons and alcohols as firstly reported by the present authors.[1)] Cadmium is a metal of high hydrogen overvoltage and yields mainly formate in reduction of CO_2. The present paper reports an effect of modification of Cu electrode with a small amount of Cd with severe prevention of hydrocarbon formation and significant release of CO.

A copper sheet electrode (purity 99.999%, size 20 x 20 x 1 mm^3) was used in a three compartment cell in which two anode compartments faced each side of the Cu electrode. High purity carbon dioxide was sparged into the electrolyte (60 ml). A small amount of $CdCl_2$ solution was added to the electrolyte (0.1 M $KHCO_3$); the concentration of Cd^{2+} ranged between 0.2 to 10.0 μM. The electrolyte was stirred vigorously at 680 rpm by a magnetic stirrer. The electrolytic measurements were conducted at 18 °C. Cd^{2+} will be electrolytically deposited on the electrode during the reduction of CO_2 (in-situ electrodeposition).[2)] The gaseous products in the effluent gas from the cell were analyzed at 5 min intervals by gas chromatographs. The time lags due to the dead volume between the cell and the gas chromatographs were corrected. The electrocatalytic properties will change in time with the increase of deposited Cd. The variation of product distribution is immediately observed by the gas chromatographs. The soluble products were analyzed after electrolysis by an ion chromatograph and permanganate titration. Other experimental details were described previously.[1)]

The current efficiencies of the gaseous products, obtained in electrolysis at a constant current density (5 mA cm^{-2}), are shown in Fig. 1. The current efficiencies of the products are virtually constant in the electrolysis without Cd^{2+}. Thus the variation of current efficiencies (Fig. 1) results from the increase of deposited Cd on the electrode during the reaction. The current efficiencies of CH_4 and C_2H_4 are greatly suppressed in 20 min, CO becoming prevalent over the other products.

The limiting current densities of oxidation of $Fe(CN)_6^{4-}$ at various concentrations (2 to 10 mM) were measured with a smooth Pt electrode of the equal size under equivalent conditions. The diffusion layer thickness d was calculated; the values were between 0.024 and 0.027 mm. The average value of d was 0.025 mm. The concentration of Cd^{2+} is very low and the electrode potential is much negative of the Cd/Cd^{2+} standard potential. Thus Cd^{2+} must be electrodeposited under the limiting current conditions. The amount of electrodeposited cadmium q can be calculated from the equation $q = DCt/d$, where D is the diffusion coefficient of Cd^{2+} ($D = 0.81 \times 10^{-5}$ cm^2 s^{-1}),[4] C concentration, and t time. The apparent coverage of adsorbed Cd on Cu may be given simply by $S = qL_As$, where L_A and s are the Avogadro number and the cross sectional area of a Cd atom. The value of s may be taken as 7.7×10^{-16} cm^2 on the basis of the atomic radius in metal.[5] S is also marked in Fig. 1. The apparent coverage obtained in this manner is a rough measure, but it may still be valuable for discussion of electrocatalytic properties in wide range of modification.

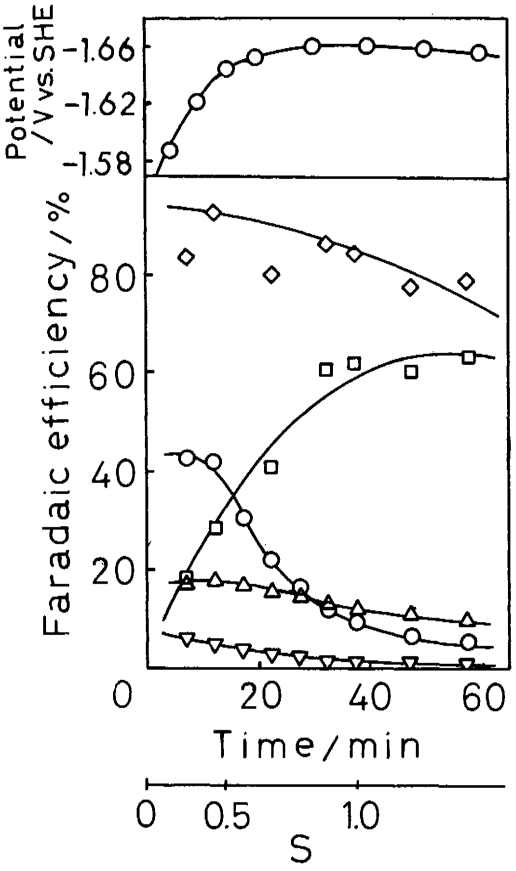

Fig. 1. Time course of electroreduction of CO_2 with 5 mA cm^{-2} at in-situ modified Cu electrodes with 0.5 μM Cd^{2+}. The total values are given for the gaseous products. ◇ : Total, □ : CO, ○ : CH_4, ▽ : C_2H_4, △: H_2.

Figure 2 shows that the current efficiency of CO is well correlated with the apparent coverage of Cd on Cu by a single curve irrespective of the concentration of Cd^{2+}. The CO formation reaches a maximum at $S = 1$, gradually dropping thereafter.

The total current efficiency of gaseous products gradually dropped during the reaction (Fig. 1). The concentration of $HCOO^-$ was analyzed after the electrolyses; the current efficiency values for $HCOO^-$ are average ones during the reactions. The current efficiency (%) for $HCOO^-$ agreed well with 100 - X, where X is the total current efficiency (%) of gaseous products for all the electrolysis time. Thus we assumed that the current efficiency of $HCOO^-$ is equal to 100 - X at any time during the reaction. The current efficiency for $HCOO^-$ estimated in this manner are also shown in Fig. 2.

Anodic strippings were carried out with the electrodes which were employed in electroreduction of CO_2 in 0.1 M $KHCO_3$ with Cd^{2+} added at 1.0 (a) and 5.0 (b) μM for 20 min. Anodic stripping measurements were conducted in the same electrolytes used for reduction of CO_2 immediately after the elctrolyses. Figure 3 presents the results. The voltammogram (a) has a small anodic peak at -0.47 V and another peak at -0.25 V; the voltammogram (b) also gives a higher peak at -0.47 V and a shoulder at -0.25 V. The equilibrium potential for Cd^{2+}/Cd with activity of Cd^{2+} 1 μM is -0.58 V, and the peak (-0.47 V) would be assigned to the anodic dissolution of metallic Cd on the surface. The peak height at -0.47 V of (b) is naturally much higher than (a), since greater amount of cadmium must have been deposited on the electrode in (b). A peak (a) and a shoulder (b) appear at -0.25 V with roughly equal height; the position is much positive of the potential for Cd/Cd^{2+}. Adatoms, as is well known, are anodically stripped at potentials much positive of equilibrium values. The potential difference of two peaks is 0.22 V, which agrees quite well with Kolb's correlation for underpotential shift ΔE_p versus the work function

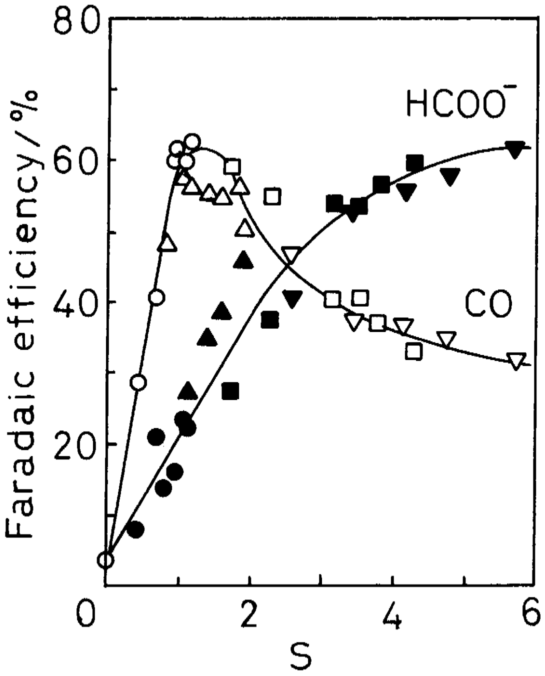

Fig. 2. Correlation between the faradaic yields of CO and $HCOO^-$ and the apparent coverage S of Cd on Cu (Cd^{2+} concentration in μM; ○ ●: 0.5,△▲: 1.0, □■: 2.0, ▽▼: 3.0).

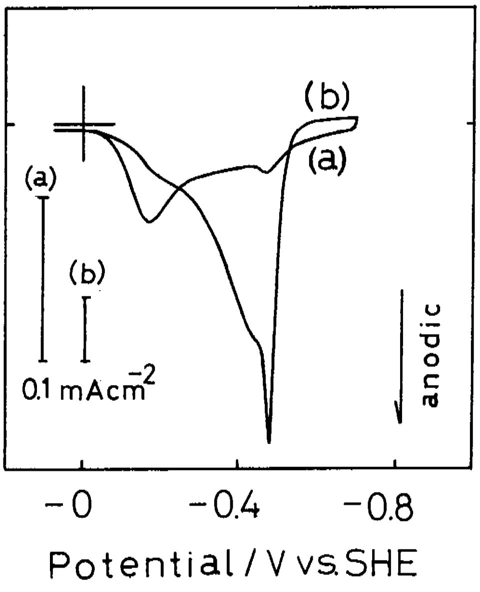

Fig. 3. Anodic stripping of Cd deposited on Cu electrode after the electroreduction of CO_2. Scan rate 50 mV s^{-1}. (a) 1.0 μM Cd^{2+}, in-situ electrodeposited for 20 min. (b) 5.0 μM Cd^{2+}, for 20 min.

difference.[6)] Thus the peak at -0.25 V in the present system is reasonably assigned to cadmium adatoms.

The charges of adatoms and bulk of cadmium on the electrode were roughly estimated by integration of the peak area (a) of Fig. 3. The peak area was tentatively divided at - 0.36 V, or the midpoint of the two peaks. The charge for adatom Cd was 0.23 mC cm^{-2}, and that for bulk Cd 0.14 mC cm^{-2}. In accordance with the limiting current deposition assumption, the total charge of deposited Cd should be 0.56 mC cm^{-2}. When the limiting current deposition of Cd^{2+} is conducted in sulfuric acid solution (pH = 2), the calculated charge of deposited Cd agrees well with the charge measured by the anode stripping technique. The anodic oxidation of Cd in 0.1 M $KHCO_3$ may lead to formation of $Cd(OH)_2$ film on the surface which partially protects further oxidation.

Apparent coverages of Cd for (a) is approximately 1.35 with assumption of the limiting current deposition; adatom Cd is likely formed on the electrode surface. The faradaic yield of CO is very low at both electrodes of elemental Cd and Cu.[1)] The electroreduction of CO_2 to hydrocarbons proceeds with intermediate formation of CO adsorbed on Cu electrode.[1,3)] The experimental facts described here support this mechanism. Cd adatoms likely prevent further reduction of CO to hydrocarbons and alcohols, and CO will be easily liberated from the electrode.

The apparent coverage of Cd on Cu (b) is ca. 6.7. The anodic stripping curve (Fig. 3) reveals that metallic cadmium is deposited on the electrode. Figure 2 suggests that formate ions will be predominantly produced at the electrode with S beyond 6. It is natural that the electrode (b) presents similar features with metallic cadmium.

References
1) Y. Hori, K. Kikuchi, and S. Suzuki, Chem. Lett., **1985**, 1695; Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, ibid., **1986**, 897; Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, J. Am. Chem. Soc., **109**, 5022 (1987); Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, J. Chem. Soc., Chem. Commun., **1988**, 17.
2) Y. Hori, A. Murata, S. Ito, and O. Koga, Chem. Lett., **1989**, 1567.
3) Y. Hori, A. Murata, and R. Takahashi, J. Chem. Soc., Faraday Trans. 1, **85**, 2309 (1989).
4) R. N. Adams, "Electrochmistry at Solid Electrodes," Marcel Dekker. New York (1969).
5) "Lange's Handbook of Chemistry," ed by J. A. Dean, 12th ed, McGraw-Hill, New York (1979).
6) D. M. Kolb, "Adv. Electrochem. Electrochem. Eng.," ed by H. Gerischer, and C. W. Tobias, Vol. 11, p. 125, John Wiley and Sons, New York (1978).
7) Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, Chem. Lett., **1987**, 1665.

(Received May 7, 1990)