CHEMISTRY LETTERS, pp. 1567-1570, 1989.

Nickel and Iron Modified Copper Electrode for Electroreduction of CO_2 by In-situ Electrodeposition

Yoshio HORI,* Akira MURATA, Shin-ya ITO,
Yuzuru YOSHINAMI, and Osamu KOGA
Department of Synthetic Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 260

Electroreduction of CO_2 was studied with a Cu electrode in 0.1M $KHCO_3$ aqueous solution added with a small amount of Ni^{2+} or Fe^{2+}. Ni or Fe was simultaneously electrodeposited on the electrode during the reduction of CO_2. Methane /ethylene product selectivity (C_1/C_2) increased in time with increase of electrodeposited Ni or Fe. The ratio C_1/C_2 was linearly correlated with hydrogen formation at the electrode, which would be a measure of atomic hydrogen concentration on the electrode.

Metallic copper is an effective electrocatalyst for reduction of CO and CO_2 to CH_4, C_2H_4, and alcohols as reported by the present authors.1-3) However, the product distribution is rather wide. New electrocatalysts of high selectivity are preferable from the view point of utilization of CO_2 by electroreduction.

We previously reported4) that methane ethylene product ratio depends upon the anion species of the electrolytes and their concentrations. CH_4 formation is more favorable than C_2H_4, when pH is low at the electrode.4) C_2H_4 production at 99.99% Cu cathode dropped to about one third that at 99.999% Cu cathode.2) The ethanol yield also decreased. The impurities responsible for the difference are unknown at present. These facts may suggest that methane formation preferentially proceeds when hydrogen production is favored. Methane may be easily formed on electrode surfaces where proton or some hydrogen species is more abundant.

Ni and Fe electrodes show much less electrocatalytic activity in reduction of CO and CO_2 as compared with Cu;1,3) H_2 is prevalently evolved at these electrodes in aqueous media. Deliberate modification of copper electrode with Ni or Fe may promote CH_4 production exclusively since hydrogen concentration will be increased. The present communication reports a significant change of the product selectivity as shown by nickel or iron modified copper electrodes formed by in-situ electrodeposition during electrochemical reduction of CO_2.

A copper sheet electrode (purity 99.999%, size 20 x 20 x 0.1 mm) 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) at a constant flow rate. A small amount of Ni^{2+} ($NiSO_4$) or Fe^{2+} ($FeSO_4$) solution was added to the electrolyte (0.1M $KHCO_3$); the concentration of Ni^{2+} or Fe^{2+} ranged between 0.1 to 1.0 micromole l^{-1}. The electrolyte was stirred vigorously by a magnetic stirrer. The electrolytic measurements were conducted at 18 °C. Ni or Fe will be deposited on the Cu electrode during the reduction of CO_2 (in-situ electrodeposition). The gaseous products in the effluent gas from the cell were analyzed at 5 min intervals by gaschromatographs. The time lags due to the dead volume between the cell and the gaschromatographs were corrected. The electrocatalytic properties will change in time with increase of deposited Ni or Fe. The variation of product distribution is immediately detected by gaschromatographs. Using this technique, one can continuously observe the variation of the catalytic features of the electrode modified with other metals. The soluble products were analyzed after electrolysis by an ion chromatograph and permanganate titration. Other experimental details were described previously.

Figure 1 shows the time course of the current efficiencies of gaseous products obtained in electrolysis at a constant current density (5 mA cm^{-2}) with the electrolyte added with 0.1 micromole l^{-1} Ni^{2+} (a) and 0.2 micromole l^{-1} Fe^{2+} (b). The current efficiencies of the gaseous products are virtually constant in the electrolysis without Ni^{2+} or Fe^{2+}. Thus the variation of current yields as shown in Fig. 1 may be attributed to the increase of deposited Ni or Fe on the Cu electrode during the reaction. At the time when the current yield of C_2H_4 begins to decrease, CH_4 still continues to increase. CH_4 remains constant (a) for 60 min or drops slowly (b). H_2 increases in time. The faradaic yield ratio of methane and ethylene (C_1/C_2) markedly increases during the reaction. Several electrolysis measurements were conducted at constant electrode potentials between -1.43 and -1.50 V vs. SHE. Identical features with Fig. 1 were observed. The soluble products, consisting of formate and ethanol, are not mentioned here in detail; the amounts of soluble products agreed with those reported previously.[1-4]

A coulometric measurement was also made with a Cu electrode on which Ni was deposited in a separate electrolytic cell in advance (pre-electrodeposition). The pre-electrodeposition was conducted in Ar atmosphere under the conditions equivalent to the in-situ electrodeposition (0.1 M $KHCO_3$ added with 0.3 micromole l^{-1} Ni^{2+}, 5 mA cm^{-2}, 30 min). The current yields of various products from CO_2 with pre-electrodeposited electrode remained constant during the electrolysis: CH_4 41%, C_2H_4 6%, and H_2 30%, in close agreement with the results obtained by an in-situ deposited Cu electrode at 5 mA cm^{-2} at 30 min in 0.1 M $KHCO_3$ added with 0.3 micromole l^{-1} Ni^{2+} with CO_2 sparged. Thus the product distribution is determined by the amount of deposited Ni or Fe.

The limited 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 estimated; the values were between 0.024 and 0.027 mm. The average value of d was 0.025 mm. In the in-situ electrodeposition conditions, the concentration C of Ni^{2+} or Fe^{2+} is very low and the electrode potential is much more negative, as compared with the Ni/Ni^{2+} for Fe^{2+} standard potentials. Thus Ni^{2+} or Fe^{2+} must be electrodeposited under limited current conditions. The amount of electrodeposited metal q can be calculated from the equation $q = DCt/d$, where D is the diffusion coefficient

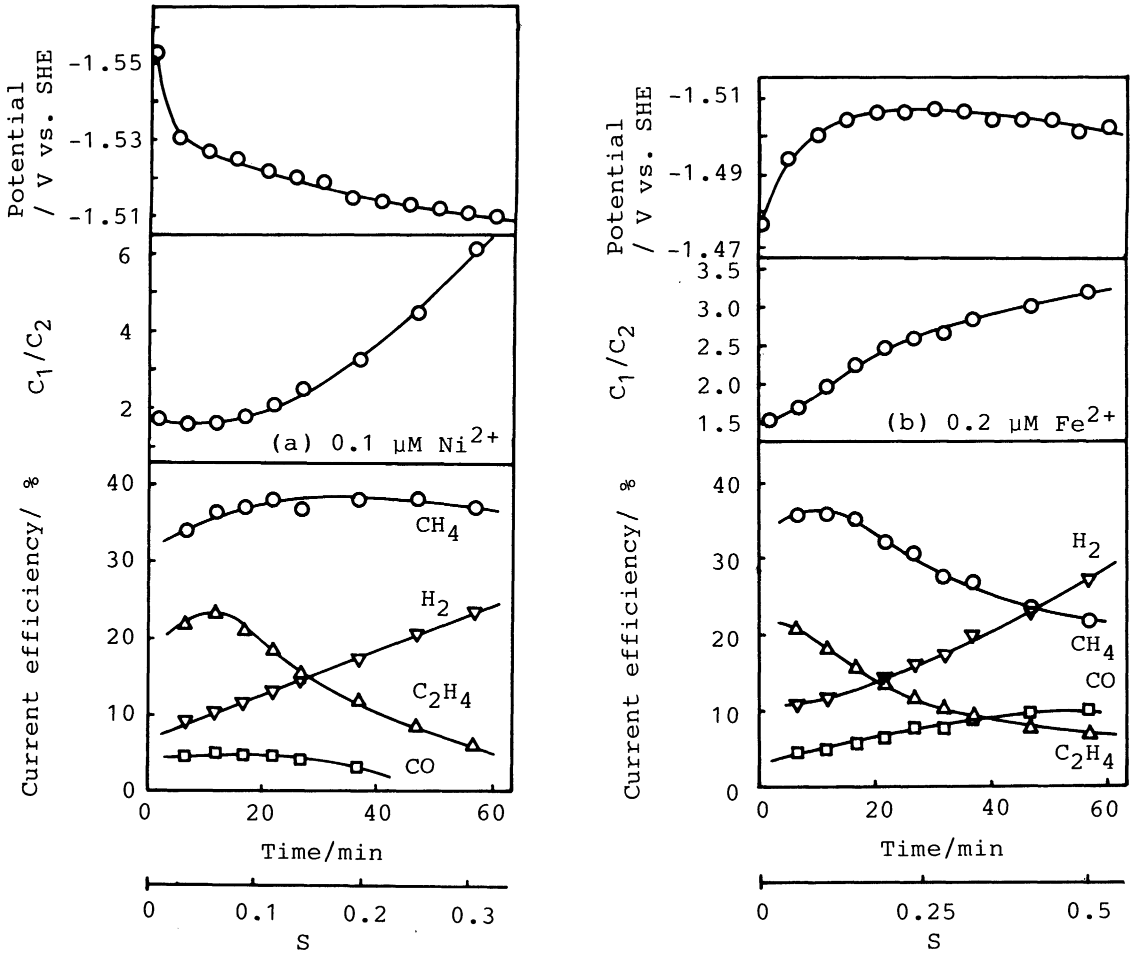

Fig. 1. Time courses of electroreduction of CO_2 with 5 mA cm^{-2} at in-situ modified Cu electrodes with 0.1 micromole l^{-1} Ni^{2+} (a) and 0.2 micromole l^{-1} Fe^{2+} (b). Apparent coverage S of Ni and Fe on the electrodes is also indicated.

(Ni^{2+}; 0.705 x 10^{-5} cm^2/s5)), Fe^{2+}; 0.53 x 10^{-5} cm^2/s6)) and t time. The apparent coverage of adsorbed Ni or Fe 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 Ni atom. The value of s may be taken as 5.4 x 10^{-16} cm^2 (Ni) and 5.8 x 10^{-16} cm^2 (Fe) on the basis of the atomic radius in metal.7) The apparent coverage calculated in this manner is just a rough measure, but it may still be valuable for discussion of electrocatalytic properties of metal adsorbed Cu electrode in wide range of modification.

S is also indicated in Fig. 1. It is remarkable that C_1/C_2 for Ni deposited Cu electrode varies from 1.7 to 6 for small difference of the apparent coverage 0 to 0.3. If Ni and Fe adatoms are agglomerated three dimensionally as nuclei on the electrode surface, C_1/C_2 will not change to such a great extent. It is likely that Ni and Fe adatoms are uniformly dispersed on the surface.

The faradaic yield of H_2 is plotted against the apparent Ni coverage in Fig. 2. The data are scattered, but they can still be correlated by a single curve irrespective of the concentration of Ni^{2+} in the electrolyte. The hydrogen formation is chiefly determined by the apparent Ni coverage on the electrode.

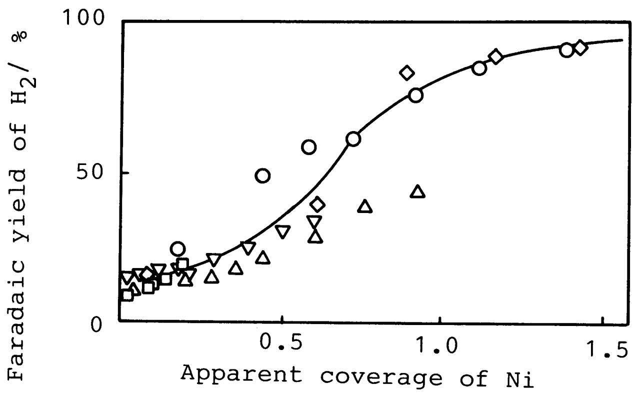

Fig. 2. Correlation between the Faradaic yield of H_2 and the apparent coverage of Ni on Cu. (Ni^{2+} concentration in micromole l^{-1}; □: 0.1, ▽: 0.2, △: 0.3, ○: 0.5, ◇: 1.0).

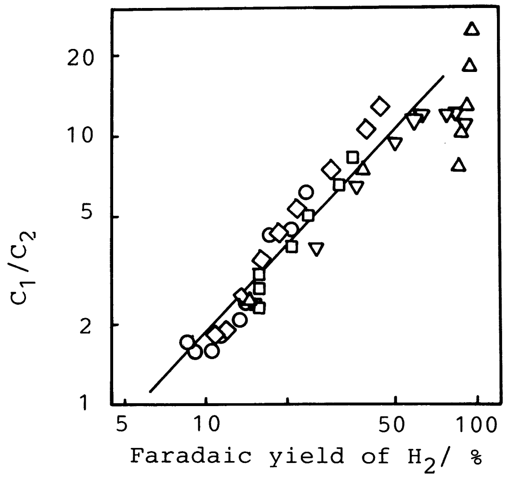

Fig. 3. Correlation between C_1/C_2 and the Fadadaic yield of H_2. (Ni^{2+} concentration in micromole l^{-1}; ○: 0.1, □: 0.2, ◇: 0.3, ▽: 0.5, △: 1.0).

Both C_1/C_2 and hydrogen formation vary in time as shown in Fig. 1. Figure 3 presents the logarithmic relation between C_1/C_2 and hydrogen formation for Ni modified electrode. The correlation is given by a straight line with slope unity irrespective of Ni^{2+} concentration for H_2 formation below 60%. The faradaic yields of CH_4 and C_2H_4 are low for high H_2 formation conditions, C_1/C_2 scattering widely. The extent of hydrogen formation will be strongly related with the concentration of atomic hydrogen adsorbed on the surface. Thus the ratio C_1/C_2 will be determined by the H atom concentration on the surface. The identical results were obtained for Cu electrodes modified with Fe. The values of C_1/C_2 for Ni modified electorde are higher than those for Fe modified electrode as shown in Fig. 1; the reason is unknown at present. As a concluding remark, modifications of Cu electrodes with other metals evidently control the product selectivity.

The present work was partially supported by Japan Securities Scholarship Foundation.

References

1) Y. Hori, K. Kikuchi, and S. Suzuki, Chem. Lett., 1985, 1695.
2) Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, Chem. Lett., 1986, 897.
3) Y. Hori, A. Murata, R. Takahashi and S. Suzuki, Chem. Lett. 1987, 1665.
4) Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, J. Chem. Soc., Chem. Commun., 1988, 17.
5) A. L. Horvath, "Handbook of Aqueous Electrolyte Solutions," Ellis Horwood Limited, Chichester (1985), p. 290.
6) R. N. Adams, "Electrochmistry at Solid Electrodes," Marcel dekker. New York (1969).
7) J. A. Dean, ed. "Lange's Handbook of Chemistry," 12th ed, ed by J. A. Dean, McGraw-Hill, New York (1979).

(Received June 9, 1989)