CHEMISTRY LETTERS, pp. 1665-1668, 1987.

# Electrochemical Reduction of Carbon Monoxide to Hydrocarbons at Various Metal Electrodes in Aqueous Solution

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Electrochemical reduction of CO in an aqueous media was studied with voltammetric and coulometric measurements. The reduction did not proceed at Au and Pt electrodes. CO is appreciably reduced at Cu to hydrocarbons. Ni yielded products to some extent. The reaction was discussed in terms of the adsorption of CO or related intermediate species on the electrode.

Utilization of carbon monoxide is one of the most important subjects in chemistry. It is preferable to attempt conversion of carbon monoxide to other chemical substances in various ways. Electrochemical reaction of carbon monoxide is worth while to be studied, but few papers reported effective electroreduction of carbon monoxide. CO appears to be very inert to electrochemical reactions. The cathodic partial currents for electroreduction of CO did not exceed $5 \times 10^{-5}$ A cm$^{-2}$ according to previous publications.1) We previously reported an effective cathodic reduction of CO at a copper electrode to hydrocarbons and alcohols with appreciable current densities.2) This communication describes cathodic reductions of CO at various metal electrodes and compares the electrode activities for this reaction.

Sheets of Au (99.99%), Ni (99.99%), Pt (99.99%), and Cu (99.999%) were cut into 20 mm x 20 mm electrode with a lead strip of same metal attached. The Au electrode was etched in aqua regia before measurements. The other metal electrodes were electrolytically polished.3) Electrochemical measurements were conducted with a three compartment cell 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 potential of the cathode was measured with respect to an Ag/AgCl reference electrode. The electrode potential was corrected for the IR drop between the Luggin capillary tip and the cathode. The catholyte (60 ml), prepared from doubly distilled deionized water and reagent grade chemicals, was purified by preelectrolysis with a Pt black cathode under purified $N_2$ atmosphere at $2.5 \times 10^{-5}$ A cm$^{-2}$ for more than 15 h. CO (high purity grade, hydrocarbon content less than 0.5 ppm) was introduced to the catholyte after passing through KOH solution. The electrolytic cell was immersed in a water bath maintained at 19 °C.

Voltammetric measurements were conducted with electrolytes saturated with purified CO or $N_2$. Coulometric measurements at a constant current were conducted in 0.1 M $KHCO_3$ (1 M = 1 mol $dm^{-3}$) with CO bubbled into the catholyte (flow rate: ca. 70 ml $min^{-1}$); the catholyte was stirred vigorously with a magnetic stirrer. $CH_4$ and $C_2H_4$ in the effluent gas from the cell were analyzed by a gaschromatograph. $C_2H_5OH$ and n-$C_3H_7OH$ in the solution were also analyzed by a gaschromatograph after the electrolysis. The identification of the products by gaschromatographs was made with more than three columns for each substances. Formaldehyde in the solutions was determined by chromotropic acid colorimetric method. Other details were described in the previous reports.[3-5)]

Figure 1 shows voltammograms obtained at various metal electrodes in 0.1 M $KHCO_3$ saturated with $N_2$ and CO. The current voltage curve for the Au electrode showed an identical features both in CO and $N_2$ saturated solutions. However, the onsets of the cathodic current of the other electrodes are significantly shifted to the negative direction in the CO saturated electrolyte. Anodic oxidation of $CH_3OH$, as is well known, is markedly interfered with by some intermediate species formed in the reaction, e. g. CO adsorbed on electrodes or some other related species.[6)] Adsorption of CO or other intermediates may also prevent the $H_2$ evolution at the electrodes in the present study except Au.

Table 1 shows the faradaic yields of various products obtained in constant current (2.5 mA $cm^{-2}$) electrolysis. The total values of the faradaic efficiencies deviate a little from 100%, the deviations being still within the experimental error. CO is not reduced at the Au electrode, but only $H_2$ is formed. Reduction of CO appreciably proceeds at the Cu electrode, as already reported.[2)] $CH_4$ and $C_2H_4$ were major products at the Cu electrode. $C_2H_6$ was not detected. Ni yields products reduced from CO to some extent. A small amount of $C_2H_6$ was formed in addition to $CH_4$ and $C_2H_4$, distinguished from the Cu electrode. The electrochemical reduction of CO scarcely occurs at the Pt electrode.

CO or CO related species may be adsorbed on the electrode, as mentioned above. These adsorbed

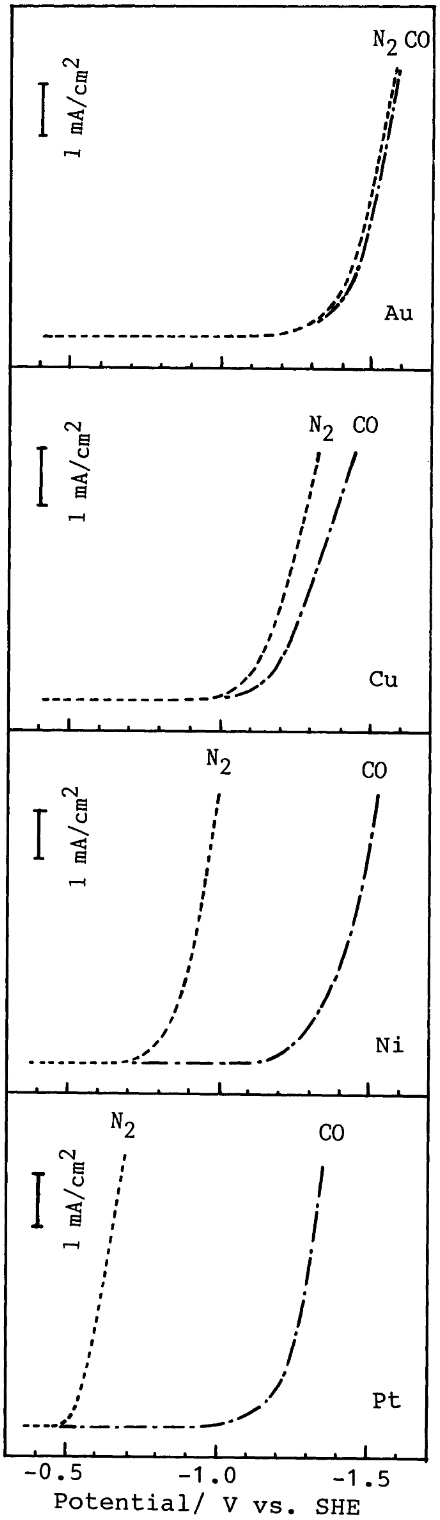

Fig. 1. Voltammograms for various electrodes obtained in 0.1 M $KHCO_3$ saturated with $N_2$ and CO.

Table 1. Faradaic efficiencies of the products from the electroreduction of CO at various electrodes in 0.1 M $KHCO_3$ (pH 9.6). (Temperature 19 °C)[a]

| Electrode | Potential/ V | Faradaic efficiency / % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_4$ | $C_2H_6$ | EtOH | PrOH | HCHO | $H_2$ | Total |
| Au | -1.49 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 101.6 | 101.6 |
| Cu | -1.40 | 16.3 | 21.2 | 0.0 | 10.9 | 1.5 | 0.1 | 45.5 | 95.5 |
| Ni | -1.46 | 2.6 | 0.3 | 0.6 | 0.1 | 0.0 | 0.0 | 94.2 | 97.8 |
| Pt | -1.29 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 96.8 | 96.9 |

a) Current density 2.5 mA $cm^{-2}$. Potential vs. SHE.

Table 2. The total faradaic yield of CO reduction and the negative potential shift of various electrodes

| | Au | Cu | Ni | Pt |
|---|---|---|---|---|
| Total faradaic yield of CO reduction[a]/ % | 0.0 | 49.9 | 3.6 | 0.1 |
| Negative potential shift[b]/ V | 0.01 | 0.10 | 0.50 | 0.65 |
| Heat of adsorption[c]/ kcal $mol^{-1}$ | 9 | 9 | 42 | 48 |

a) Constant current electrolysis at 2.5 mA $cm^{-2}$, electrolyte 0.1 M $KHCO_3$ (pH 9.6). Temperature 19 °C.
b) Negative potential shift: defined as the potential difference between CO and $N_2$ saturated solutions at 2.5 mA $cm^{-2}$.
c) Heat of adsorption: the value for gas phase adsoption of CO.

species themselves will probably be reduced at the Cu electrode at more negative potentials to yield hydrocarbons and alcohols. The adsorbed species at Ni and Pt are not easily reduced even at negative potentials. The negative potential shift is defined as the potential difference between CO and $N_2$ saturated solutions at a constant current (arbitrarily chosen 2.5 mA $cm^{-2}$) in Fig. 1. The negative potential shifts, tabulated in Table 2, will be affected by some factors, but still be closely related to the adsorption energy of intermediate species. Table 2 also presents the heats of adsorption of CO on the metals in gas phase.[7)] The magnitudes of the negative potential shift are in the same order as those of the heats of adsorption.

We thus attempt to elucidate the electrode activity in the electrochemical reduction of CO. Table 2 presents the total faradaic yields of CO reduction, the sum of $CH_4$, $C_2H_4$, $C_2H_6$, $C_2H_5OH$, n-$C_3H_7OH$, and HCHO. (1) The interaction of CO with Au is very weak, and the negative potential shift is small. CO is not reduced at Au, since CO is not effectively bound to the electrode. (2) CO is too strongly adsorbed on Pt, as is well-known in gas phase reaction.$^{7)}$ The negative potential shift is great. The adsorbed CO or CO related species are markedly stable, and will severely prevent hydrogen formation. The adsorbed species are not easily reduced at Pt despite of highly cathodic potential. (3) CO or CO related species are adsorbed at Cu with moderate strength. Adsorbed intermediate species suppress hydrogen formation at Cu to some extent. The adsorbed CO or related intermediates themselves are eventually reduced to hydrocarbons and alcohols due to highly reducible atmosphere at the electrode surface. Ni is an intermediate between Cu and Pt.

We previously reported electrochemical reduction of $CO_2$ at various electrodes.$^{3)}$ $CO_2$ is effectively reduced to hydrocarbons at Cu electrode. Only CO is formed at Au electrode. $CO_2$ is hardly reduced at Ni and Pt. $CO_2$ may probably be reduced to CO at these electrodes. Thus the selectivity of the products in this reaction would be revealed in the light of the electrochemical reduction of CO, as presented in this communication. The investigations in detail are now in progress, and will be published in near future.

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(Received May 9, 1987)