

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 5×10^{-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 N₂ atmosphere at 2.5×10^{-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 N₂. Coulometric measurements at a constant current were conducted in 0.1 M KHCO₃ (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. CH₄ and C₂H₄ in the effluent gas from the cell were analyzed by a gas chromatograph. C₂H₅OH and n-C₃H₇OH in the solution were also analyzed by a gas chromatograph after the electrolysis. The identification of the products by gas chromatographs 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 KHCO₃ saturated with N₂ and CO. The current voltage curve for the Au electrode showed an identical features both in CO and N₂ 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 CH₃OH, 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 H₂ 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 H₂ is formed. Reduction of CO appreciably proceeds at the Cu electrode, as already reported.²⁾ CH₄ and C₂H₄ were major products at the Cu electrode. C₂H₆ was not detected. Ni yields products reduced from CO to some extent. A small amount of C₂H₆ was formed in addition to CH₄ and C₂H₄, 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

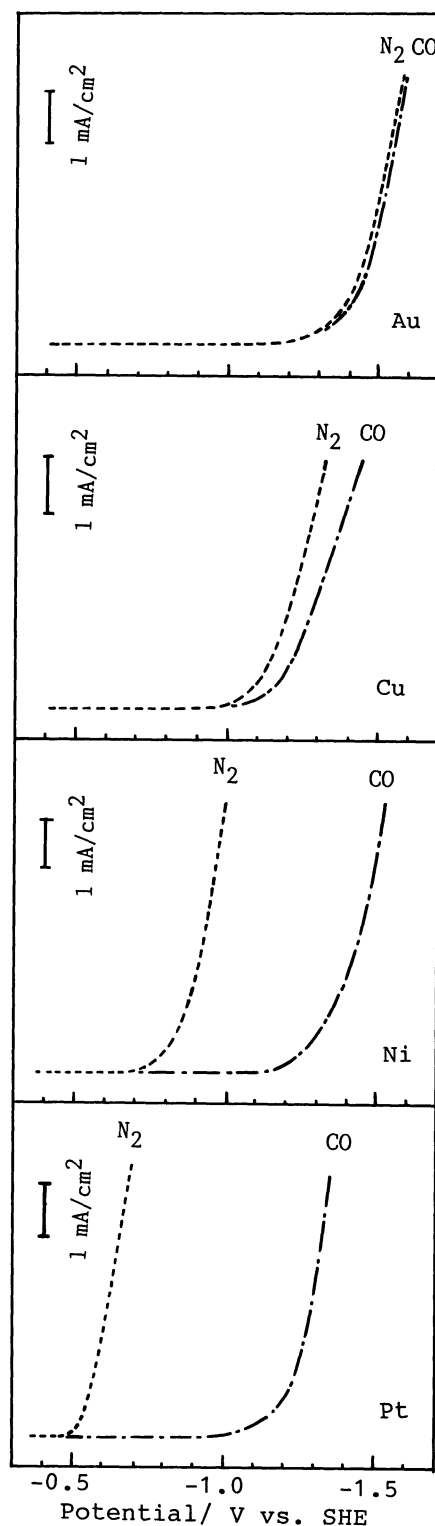


Fig. 1. Voltammograms for various electrodes obtained in 0.1 M KHCO₃ saturated with N₂ and CO.

Table 1. Faradaic efficiencies of the products from the electroreduction of CO at various electrodes in 0.1 M KHCO₃ (pH 9.6). (Temperature 19 °C)^{a)}

Elec- trode	Poten- tial/V	Faradaic efficiency / %							
		CH ₄	C ₂ H ₄	C ₂ H 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 KHCO₃ (pH 9.6). Temperature 19 °C.

b) Negative potential shift: defined as the potential difference between CO and N₂ saturated solutions at 2.5 mA cm⁻².

c) Heat of adsorption: the value for gas phase adsorption 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 N₂ 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 CH₄, C₂H₄, C₂H₆, C₂H₅OH, n-C₃H₇OH, 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 CO₂ at various electrodes.³⁾ CO₂ is effectively reduced to hydrocarbons at Cu electrode. Only CO is formed at Au electrode. CO₂ is hardly reduced at Ni and Pt. CO₂ 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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