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Potential Dependencies of the Products on Electrochemical Reduction of Carbon Dioxide at a Copper Electrode

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Potentiostatic electrochemical reduction of CO_2 was carried out at a Cu electrode in 0.1 mol dm^{-3} $KHCO_3$ aqueous solution at 298 K. As reduction products from CO_2, $HCOO^-$, CO, CH_4, C_2H_4, CH_3CHO, C_2H_5OH, C_2H_5CHO, n-C_3H_7OH etc. were detected and determined by gas chromatography and high performance liquid chromatography. The composition of these products changed drastically with a slight variation of electrode potential.

Recently, Hori et al. [1,2] have galvanostatically studied on the electrochemical reduction of CO_2 using a Cu electrode in $KHCO_3$ aqueous solution, and then they have reported that the principal products from CO_2 are CH_4 and C_2H_4 and that the composition of these products depends on the operating temperature. Furthermore, they [3] have studied on the electrochemical reduction of CO at a Cu electrode, and have also detected CH_4, C_2H_4, HCHO, C_2H_5OH, and n-C_3H_7OH as products.Therefore, they have suggested that the electrochemical reduction of CO_2 may proceed through CO or CO-derived intermediates formed on the Cu electrode. Cook et al. [4] also studied on the electrochemical reduction of CO_2 at in situ electrodeposited copper, and then they achieved high reaction rates and high faradaic efficiencies for CH_4 and C_2H_4 formations. Frese et al. [5] also studied potentiostatically at a Cu foil electrode in 0.5 mol dm^{-3} $KHCO_3$ aqueous solution, but they missed any products except for CO, CH_4, and C_2H_4. On the other hand, we have reported [6] that the electrode metals operate as catalysts for the electrochemical reduction of CO_2, i.e. in non-aqueous electrolyte, Hg, Pb, and Tl are available for selective formation of oxalic acid and In, Cu, Zn, Au etc. for selective formation of CO, and also in aqueous electrolyte, In, Hg, and Pb are available for selective formation of formic acid.

In the present work, the potentiostatic electrochemical reduction of CO_2 is precisely carried out at a Cu electrode in 0.1 mol dm^{-3} $KHCO_3$ aqueous solution under ambient temperature and pressure (298 K, pCO_2 = 104.4-107.4 kPa). It will be shown that $HCOO^-$, CO, CH_4, C_2H_4, C_2H_5OH, CH_3CHO, C_2H_5CHO, n-C_3H_7OH, and the trace amounts of C_2H_6, C_3H_8(propane), and C_3H_6(propylene) have been formed as products, and that the composition of these products depends on the electrode potentials and drastically changed with a slight variation of potential.

The electrode was prepared as follows, i.e. a Cu plate of 15 mm x 15 mm x 1 mm was cut off from a Cu ingot (99.9998%) donated by Sumitomo Electric Industries, Ltd. The surface was mechanically polished with 0.05 μm alumina powder, thereafter it was electrolytically polished in 60% H_3PO_4 aqueous solution and washed by twice distilled water before use. The electrolytic cell employed is the H shape Pyrex gas-tight cell which is separated into the cathode and anode chambers by a cation exchange membrane (Nafion-315). The electrolyte solution was prepared from twice distilled water and recrystallized $KHCO_3$ of reagent grade chemicals. Each amount of catholyte and anolyte used is 40 ml of 0.1 mol dm^{-3} $KHCO_3$.

Prior to the electrolytic experiments, purified CO_2 gas (CH_4 content < 50 nmol dm^{-3}) was supplied into the catholyte of the cell for 30 min, thereafter the gas flow system described previously [6] was closed to make it gas-tight. The reactant gas in the system was circulated by a mini-peristaltic pump with the flow rate of 0.02 dm^3 min^{-1}. The electrolytic reduction of CO_2 was potentiostatically performed for 50 coulombs by using a potentiostat, HA-301 (Hokuto Denko) connected with an electronic coulometer, HF-201 (Hokuto Denko). The electrode potentials are represented with respect to a KCl saturated Ag/AgCl reference electrode in this paper.

The qualitative and quantitative determinations of the products were performed by gas chromatography and high performance liquid chromatography. For H_2, CO, CH_4, air, C_2H_4, and CO_2 in gas phase, a gas chormatograph, GC-802 (Ohkura Riken), equipped with a TCD and the column of activated charcoal was employed, for CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8 in gas phase, GC-202 (Ohkura Riken), equipped with an FID and columns of Porapak-Q and Unipak-S, for CH_3OH, HCHO, C_2H_5OH, and n-C_3H_7OH in liquid phase, GC-103 (Ohkura Riken), equipped with an FID, a steam feeder, and a column of Porapak-T, for CH_3OH, CH_3CHO, C_2H_5OH, C_2H_5CHO, and n-C_3H_7OH in liquid phase, GC-103 (Ohkura Riken), equipped with an FID and a column of Porapak-Q, and for $HCOO^-$ in liquid phase, high performance liquid chromatograph, LC-5A (Shimadzu), equipped with UV and RI detectors and a column of Shodex Ion-Exchanger HC-125S.

Figure 1 shows the faradaic efficiencies for formations of $HCOO^-$, CO, C_2H_4 and CH_4 with respect to the electrode potential in the range of -1.35 to -1.75 V. The faradaic efficiency - potential curves for these products shift from relatively positive potential to negative in the order of $HCOO^-$, CO, C_2H_4 ,and CH_4 , and the maximum values are 32% at -1.40 V for $HCOO^-$, 33% at -1.52 V for CO, 41% at -1.58 V for C_2H_4, and 39% at -1.70 V for CH_4, respectively. These facts show that the composition of products on the electrochemical reduction of CO_2 at a Cu electrode in aqueous electrolytes depends on the electrode potential and changes with a slight variation of the electrode potential even in the range of -1.35 to -1.75 V.

Furthermore, it was found that CH_3CHO and C_2H_5CHO in addition to C_2H_5OH and n-C_3H_7OH were formed in liquid phase. However, CH_3OH and HCHO were not detected under all experimental conditions. The faradaic efficiency - potential curves for formations of CH_3CHO, C_2H_5OH, C_2H_5CHO, and n-C_3H_7OH are shown in Fig. 2. The maximum values are ca. 14% at -1.64 V for C_2H_5OH, 2% at -1.58 V for CH_3CHO, 4.5% at -1.58 V for n-C_3H_7OH, and 5% at -1.58 V for C_2H_5CHO, respectively. On the other hand, although the trace amounts of C_2H_6 (<0.12%), C_3H_6, and C_3H_8 were detected in gas phase, the results will be reported elsewhere.

Accordingly, as shown in Fig. 3, the sum of the total faradaic efficiencies

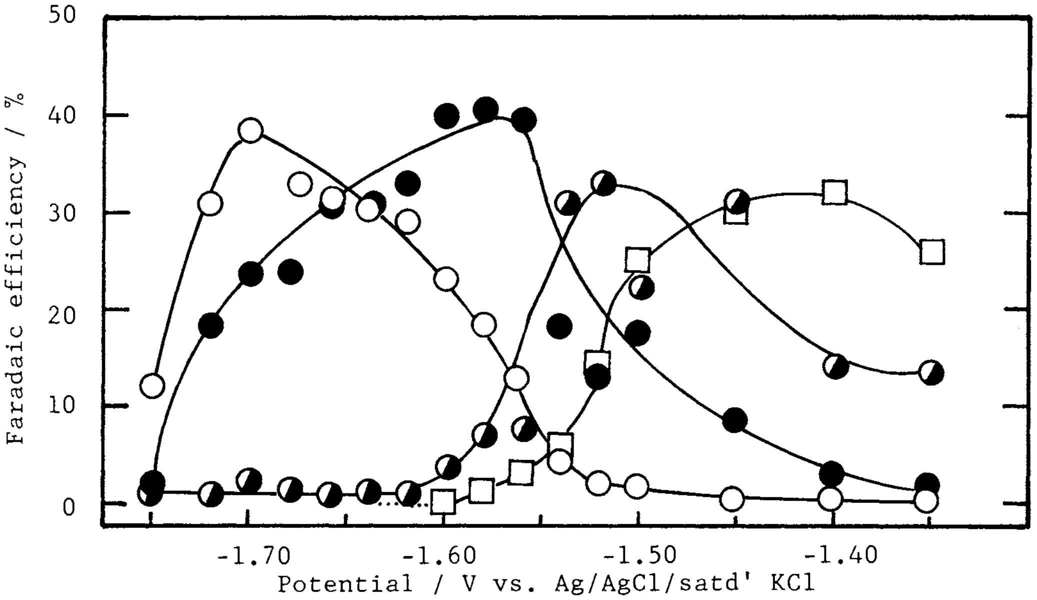

Fig. 1. The faradaic efficiency - potential curves for formations of $HCOO^-$ (□), CO (◐), C_2H_4 (●), and CH_4 (○) in 0.1 mol dm^{-3} $KHCO_3$ aq. solution at 298 K.

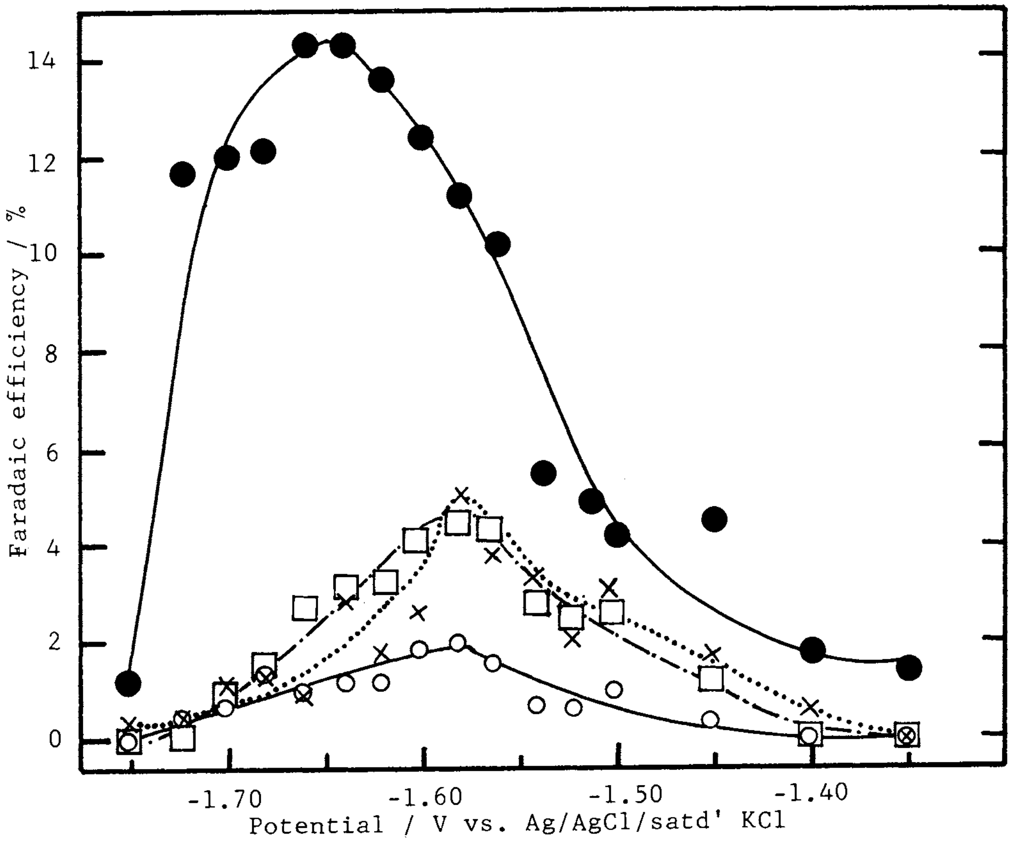

Fig. 2. The faradaic efficiency - potential curves for formations of CH_3CHO (○), C_2H_5OH (●), C_2H_5CHO (×), and n-C_3H_7OH (□) in 0.1 mol dm^{-3} $KHCO_3$ aq. solution at 298 K.

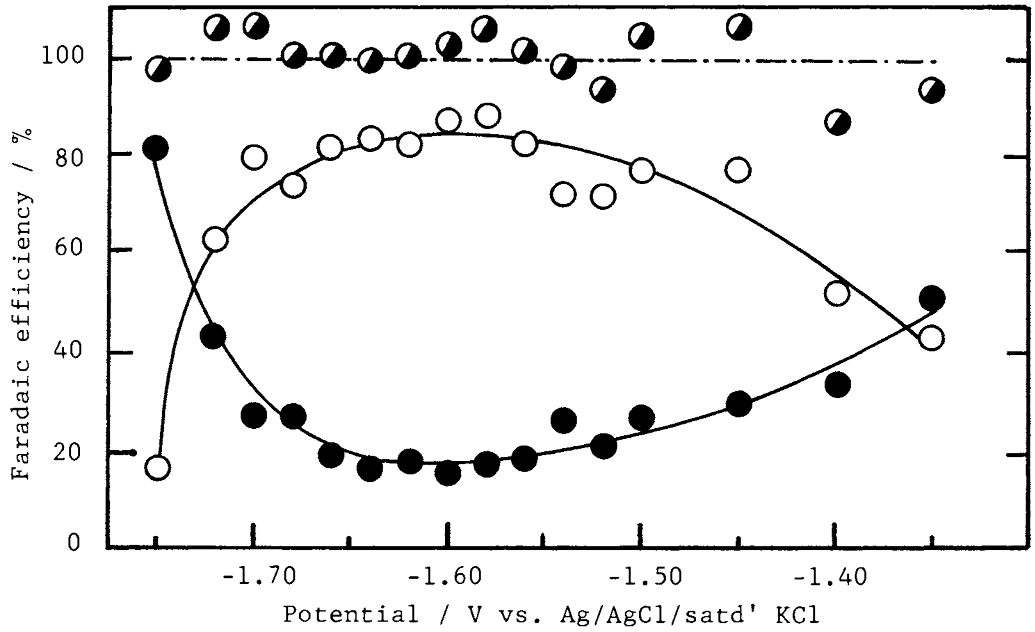

Fig. 3 The faradaic efficiency - potential curves for CO_2 reduction (○), for H_2 evolution (●), and the sum of them (◐) in 0.1 mol dm^{-3} $KHCO_3$ aq. solution at 298 K.

for all products from CO_2 and the faradaic efficiency for H_2 evolution become almost ca. 100% in the potential range of -1.35 to -1.75 V, although there is a trace amount of unidentified C_3 or C_4 product in liquid phase. This fact means that total analysis for the products on the electrochemical reduction of CO_2 have been achieved, so that the results obtained will play a part to clarify the reaction mechanism on the electrochemical reduction of CO_2. The mechanism will be disscussed elsewhere.

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