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Selective Electrocatalytic Reduction of Carbon Dioxide to Methanol on Ru-modified Electrode

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CO_2 was electrochemically reduced to CH_3OH in aqueous Na_2SO_4 solution on a Ru-modified glassy carbon electrode. Ru was fixed on poly(hydroquinone/p-benzoquinone) prepared by electropolymerization of mercaptohydroquinone. The reduction of CO_2 proceeded with markedly low overvoltage, starting at -0.5 V vs. SCE at room temperature. The current efficiency for CH_3OH formation attained ca. 100% at -0.7 V vs. SCE with a current density of ca. 0.2 mA/cm^2.

In recent years the electrochemical reduction of CO_2 has attracted considerable interest from the viewpoint of useful fuel generation from abundant CO_2. The reduction products of CO_2 are influenced by the kind of electrolytes and metal species of working electrodes.[1)] To date, many works have been reported on the reduction of CO_2 to CH_3OH using semiconductors,[2)] metals,[3)] and metal complex modified electrodes.[4)] Ru is known as a catalyst for the gas-phase conversion of CO_2 to CH_4. Recently, Frese et al.[5)] performed the CO_2 reduction using an electroplated Ru and a teflon-supported Ru electrode and obtained CH_4, CO, and CH_3OH.

In previous papers we reported the preparation of poly(hydroquinone/p-benzoquinone) which is a conductive polymer[6)] and the fixation of various transition metals on the conductive polymer by means of mercaptide formation.[7)] Ru-modified electrode used here was prepared by forming the mercaptide as follows: the conductive polymer was prepared on a glassy carbon disk (3 mm in diameter, Tokai Carbon Co.) sealed in a glass tube with epoxy resin and on a glassy carbon rod (5 mm in diameter, Furuuchi Kagaku Co.) by electrochemical polymerization of mercaptohydroquinone (4 mM, 1 M = 1 mol dm^{-3}) at +0.5 V vs. a saturated calomel electrode (SCE) for 30 min in a Britton-Robinson buffer solution (pH 5.0) containing 20 volume percent ethanol. The former was used for voltammetric measurements and the latter was used for controlled potential electrolysis. After the mercapto group was attached to the quinone ring as described in the previous paper,[7] these two electrodes were soaked in 1 mM $RuCl_3$ aqueous solution for ca. 6 h. Formation of Ru-mercaptide was judged from the complementary experimental result that mercaptohydroquinone precipitates in aqueous solution on addition of $RuCl_3$. Finally, all electrodes were thoroughly rinsed with deionized water. Electrolysis of CO_2 saturated in electrolytes was carried out in a closed system consisting of a ca. 1 dm^3 CO_2 reservoir, a teflon circulation pump, and an electrolysis cell. The anode and cathode compartments were separated by a saturated KCl/agar bridge. The surface area of Ru-modified electrode immersed into the CO_2-saturated solution was ca. 6.5 cm^2. Electrolyte was prepared from reagent grade Na_2SO_4 and deionized water. High purity N_2 gas was passed through the catholyte (50 ml) containing 0.2 M Na_2SO_4 for 30 min to remove dissolved O_2. The current efficiency for CH_3OH under the irradiation of vissible light was observed to go up to over 100% though the mechanism of this excessive current efficiency is obscure now. All measurements and electrolyses reported here were, therefore, carried out in the dark in order to remove the complication arised from the light irradiation. A Toho technical research 2001 potentiostat and a Yanagimoto P-1000 voltammetric analyser were used for controlled potential electrolyses and voltammetric measurements, respectively. Product analysis, mainly on CH_3OH and CH_4, was carried out with a Shimazu GC-8A gaschromatograph equipped with Porapak Q and PEG 20M columns.

Current-potential curves for the Ru-modified electrode in CO_2 aqueous solution containing 0.2 M Na_2SO_4 are shown in Fig. 1. Limiting currents resulted from the CO_2 reduction were observed over the pH region 5 to 10, while any cathodic wave based upon the CO_2 reduction was not observed on the polymer-coated electrode having no Ru-mercaptide. Relationship between the wave height of the limiting currents and CO_2 concentration[8] is shown in the inset in Fig. 1. This result shows that CO_2 saturated in 0.2 M Na_2SO_4 aqueous solution can be reduced with high current efficiency by the controlled potential electrolysis over the potential range -0.6 to -0.8 V vs. SCE. Table 1 shows the data obtained from the controlled potential electrolysis of CO_2 at -0.7 V vs. SCE using a CO_2-saturated 0.2 M Na_2SO_4

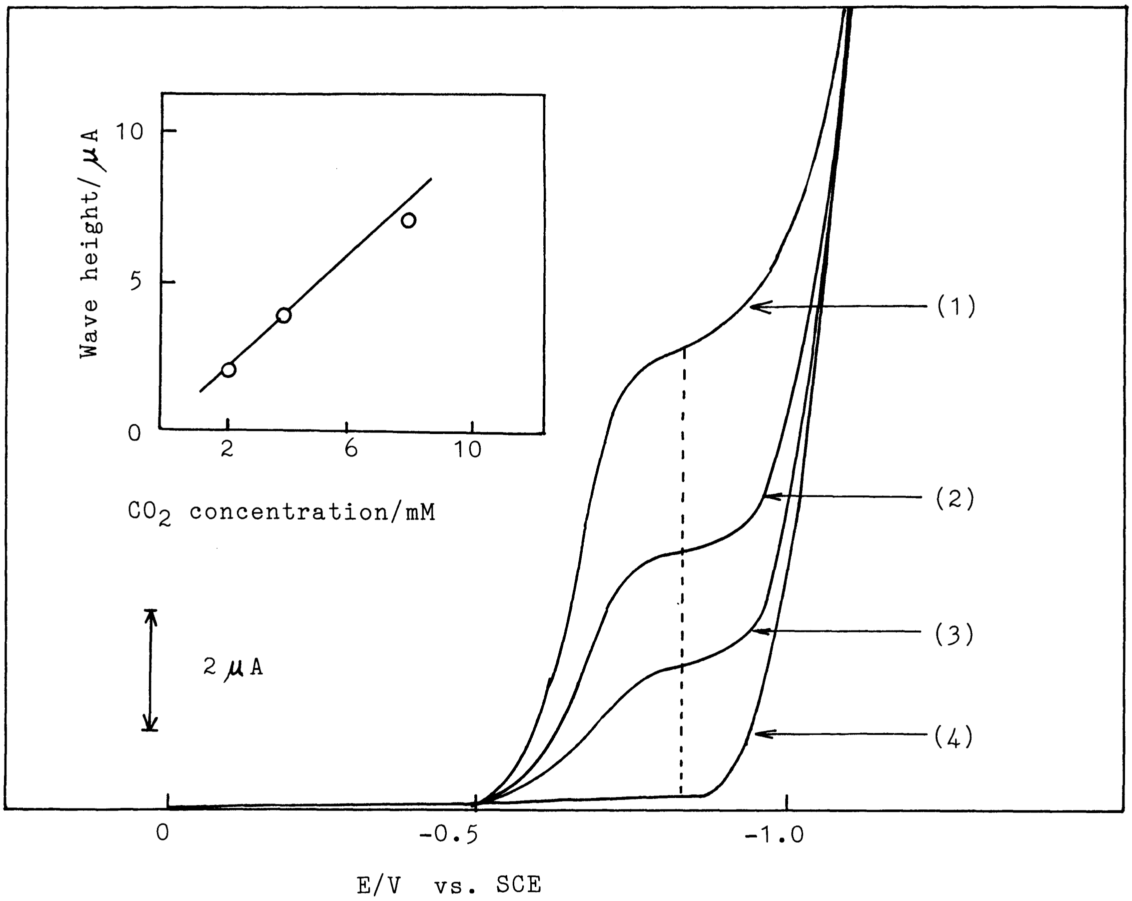

Fig. 1. Current-potential curves in CO_2-dissolved 0.2 M Na_2SO_4 solutions for a Ru-modified electrode at room temperature. Inset shows limiting currents as a function of CO_2 concentration.
Scan rate : 5 mV s^{-1}. Electrode : 3 mm in diameter.
CO_2 concentration : (1) 8 mM, (2) 4 mM, (3) 2 mM, (4) without CO_2.

Table 1. Reduction products and current efficiency for CH_3OH on Ru-modified electrode at -0.7 V vs. SCE for 8 h[a)]

Products	Amounts / mol dm^{-3}	Charge / C	Current density[b)] / mA/cm^2	Current efficiency / %
CH_3OH	ca. 1.2×10^{-3}	33.6—37.4	0.18—0.20	97—99
CH_4, CO	(trace)	HCOOH, (COOH)$_2$	(N.D.)[c)]	

a) All data were obtained from ten trials or above.

b) The current density remained constant throughout the experimental period.

c) N.D. = not detected.

aqueous solution. The faradic efficiency for CH_3OH became almost ca. 100% on the Ru-modified electrode in the potential range of -0.6 to -0.8 V vs. SCE. The present result is different from Frese's result[5] with regard to the selectivity of the reduction products. This difference suggests that the selectivity and the species of the CO_2 reduction products were seriously influenced by the fixing form or state of Ru on a substrate electrode.

Returning to Fig. 1, the current-potential curves for the CO_2-dissolved 0.2 M Na_2SO_4 aqueous solution (ca. pH 5.0) revealed that CO_2 can be reduced to CH_3OH on this Ru-modified electrode at the potential nearly equal to the standard potential (-0.536 V vs. SCE, pH 4.2) for $CO_2+6H^++6e \rightleftharpoons CH_3OH+H_2O$.[9] The electrode potential initiating the CO_2 reduction was less negative by ca. 500 mV than that observed on a n-GaAs electrode[10] where CH_3OH was obtained in ca. 100% yield for current density of 0.14 mA/cm^2.

As described above, this Ru-modified electrode possesses excellent functions for the selective CO_2 reduction to CH_3OH. Further investigation on detailed electrode process of the CO_2 reduction on this Ru-modified electrode under the vissible light irradiation is now undertaken.

References

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8) CO_2 concentration was estimated by adding a known excess of an aqueous stock solution of $Ba(OH)_2$ which was back-titrated with standard oxalic acid (phenolphthalein indicator) to each CO_2-dissolved solution.
9) Quoted from Ref. 3.
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