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PRODUCTION OF METHANE AND ETHYLENE IN ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE AT COPPER ELECTRODE IN AQUEOUS HYDROGENCARBONATE SOLUTION

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The electrochemical reduction of CO_2 was studied with galvanostatic (5 mA cm^{-2}) electrolysis at a copper electrode between 0 and 40 °C. The production of CH_4 and C_2H_4 was confirmed by GC with 4 different columns. The faradaic efficiency of CH_4 formation was about 65% at 0 °C and dropped with an increase of temperature, whereas that of C_2H_4 formation rose to ca. 20% at 40 °C.

The present authors reported the electrochemical reduction of CO_2 in aqueous $KHCO_3$ electrolytes at various metal cathodes.[1)] CO was chiefly produced at Au and Ag cathodes. Appreciable amount of CH_4 was formed at Cu cathodes. However, the total value of the faradaic efficiency for the Cu cathode (87-92%) was appreciably less than 100%. The difference seemed to suggest that some unidentified substances might be produced in the process. The previous experiments were carried out at ambient temperature without any regulation. We found that the variation of the room temperature affected the product distribution for the Cu cathode. We consequently attempted to make total analysis of the products in more detail and to reveal the temperature dependence of the product distribution.

The experimental procedures were described in the previous communication.[1)] Only the alterations are mentioned here. A three compartment cell was employed which had two anode compartments. A copper sheet (purity 99.999%, Sumitomo Metal Mining Co.) was cut into 20 x 20 mm electrode attached with a lead strip (3 x 50 mm) of the same metal. The anode compartments faced each side of the Cu cathode. The two platinum sheet anodes (20 x 20 mm) were connected in parallel to a galvanostat, and the currents to both anodes were virtually equal. Thus the current density will be uniform at both sides of the cathode. The temperature was regulated within ± 0.5° with a water bath in which the cell was immersed.

The galvanostatic electrolysis experiments were conducted at a constant current 5 mA cm^{-2} for 30 min. Purified CO_2 was bubbled into the solution at ca. 150 ml min^{-1} at the atmospheric pressure. The electrode potential ranged between -1.33 and -1.39 V vs. SHE, and became less negative with an increase of temperature. The gaseous products appeared after the electrolysis started. The gaseous products contained a considerable concentration of C_2H_4 as well as CH_4, CO, and H_2. The formation of CH_4 and C_2H_4 was confirmed with 4 types of columns of gas chromatography; activated alumina, Porapak N and Q, and silica gel. C_2H_6 was not detected. The concentration of the products remained constant in the exhaust gas during the electrolysis conducted below 20 °C. The concentration of C_2H_4 gradually dropped after 15 min in the experiments at 30 and 40 °C. Typical values of concentration in the exhaust gas were as follows; CH_4 260 ppm and C_2H_4 40 ppm in the experiments at 16 °C.

Figure 1 presents the temperature dependence of the product distribution in the electrolysis at constant current density 5 mA cm^{-2} in 0.5 M $KHCO_3$ (1 M = 1 mol dm^{-3}). The data for C_2H_4 at 30 and 40 °C were taken from the measurements at 10 min. The current efficiency of CH_4 was ca. 65% at 0 °C, but significantly dropped with temperature. The faradaic efficiency of C_2H_4 rose to ca. 20% at 40 °C. CO and H_2 increased with temperature, and $HCOO^-$ remained constant. The total values of the faradaic efficiency ranged between 95 and 101%. The electrolytic experiments were also made at 10 mA cm^{-2}. The product distributions at 10 mA cm^{-2} at various temperatures were similar to those at 5 mA cm^{-2}. The measurements were made with another Cu cathode (99.99% Furuuchi Kagaku). The faradaic efficiencies for CH_4 formation were approximately equal for both electrodes at various temperatures. However, those for C_2H_4 formation at the 99.99% Cu cathode dropped to about one third those at the 99.999% Cu cathode.

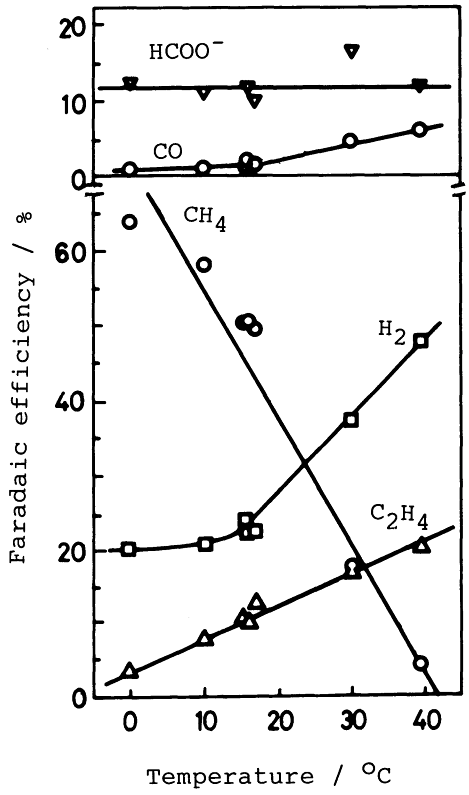

Fig.1. Faradaic efficiencies for products from electrochemical reduction of CO_2.

Previous papers reported formation of CH_4 at relatively slow rates at semiconductor electrodes or photocatalysts.[2)] However, production of C_2H_4 has not yet been reported in the cathodic reduction of CO_2. It is remarkable that hydrocarbons are produced from electrochemical reduction of CO_2.

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