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Electrochemical Methane Activation to C_2-Hydrocarbons Using Protonic Conductor

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Coupling of methane was performed using $SrCe_{0.95}Yb_{0.05}O_{3-x}$ as a solid electrolyte. The electrochemical hydrogen pump activated methane to C_2-hydrocarbons without forming carbon dioxide.

Advantage of electrochemical oxygen pump using stabilized zirconia over methane dimerization has been proposed by Otsuka et al.[1)] However, this reactor gave not only C_2-compounds (ethane and ethylene) but also carbon dioxide. On the other hand, we have previously reported that when $SrCe_{0.95}Yb_{0.05}O_{3-x}$ ceramic disc is exposed to hydrogen on one side and to Ar on another side, this becomes an almost pure protonic conductor.[2)] If such a protonic conductor is used in the electrochemical reactor for the methane coupling, this reactor will activate methane to C_2-compounds without forming carbon dioxide. In the present study, to confirm this possibility, we perform the methane coupling using $SrCe_{0.95}Yb_{0.05}O_{3-x}$ ceramic as a protonic conductor.

A one-end-closed ceramic tube of $SrCe_{0.95}Yb_{0.05}O_{3-x}$ (inside diameter: 0.5 cm, length: 1.5 cm and thickness: 0.1 cm) was used as a solid electrolyte (Fig. 1). The preparation of ceramic was described in detail elsewhere.[2)] As an electrode material, porous Ag were baked at 973 K on the inner and outer sides of the tube. The direct current was sent from galvanostat to reactor. The reaction was carried out at 1173 K under the atmospheric pressure. The flow rates of methane and Ar were 20 and 30 ml/min, respectively. Gas chromatography with porapak Q and molecular sieve 5A columns was employed in analyzing the products.

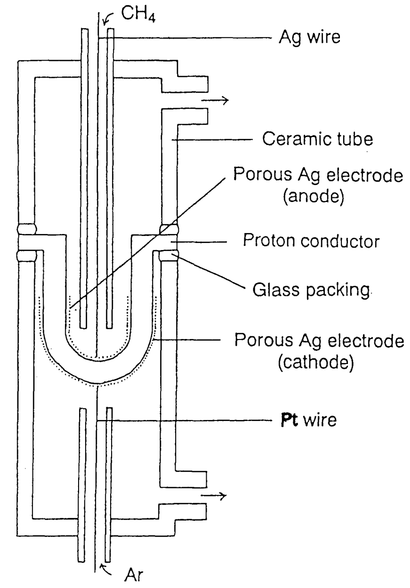

Fig. 1. Reaction cell configuration.

On introducing methane and Ar into the anode and the cathode, respectively, the electrochemical reactor gave a stable cell voltage (EMF) of 0.347 V. The conversion of methane was less than 1%. Hydrogen, ethane and ethylene were observed as the reaction products.

From the material balance before and after the reaction, the formation amount of the coke was found to be about 1.5 times the values of C_2-compounds. When the direct current was sent to the reactor, the formation rates of C_2-compounds, especially ethylene, were enhanced, as shown in Fig. 2. Furthermore, the formation rates of C_2-compounds were returned to the initial values by cutting off the direct current after the experiment.

On the other hand, hydrogen was evolved at the cathode, as shown in Fig. 3. At low current densities, the evolution rate of hydrogen was in agreement with the value calculated from Faraday's law, indicating that the protonic transport number was unity. However, at high current densities, the evolution rate of hydrogen reached a limiting value, probably due to a diffusion limit of hydrogen through the porous anode.

As described above, the present reactor enhanced C_2-formation in the methane dimerization without producing carbon dioxide. However, due to unsatisfied catalytic activity of Ag electrode, the considerable high reaction temperature was necessary. This resulted in the coking deposition. More detail investigations are required to improve the catalytic activity of Ag electrode.

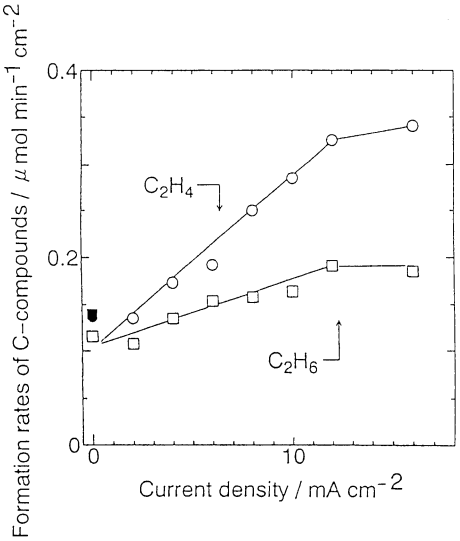

Fig. 2.

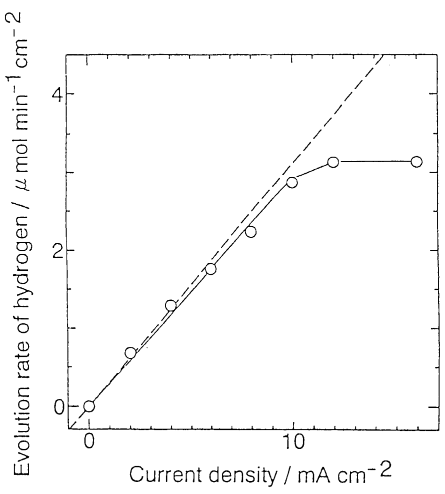

Fig. 3.

Fig. 2. Formation rates of C_2-compounds at the anode: Closed symbols show formation rates of C_2-compounds on cutting off direct current after experiment.

Fig. 3. Evolution rate of hydrogen at the cathode: Broken line shows theoretical evolution rate of hydrogen.

References

1) K. Otsuka, S. Yokoyama, and A. Morikawa, Chem. Lett., 1985, 319.

2) H. Iwahara, T. Esaka, H. Uchida, T. Yamauchi, and K. Ogaki, Solid State Ionics, 18/19, 1003 (1986).

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