

PHOTOELECTROCHEMICAL REDUCTION OF CO₂ USING SILICATE ROCK POWDER SUSPENDED IN WATER

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INTRODUCTION

Until now, numerous investigators have reported chemical fixation of carbon dioxide, such as electrochemical, photochemical and photoelectrochemical reductions (1-5). In these methods, relatively, a few studies on the photoelectrochemical conversion of CO₂ have been reported.

We have recently presented a photochemical reduction of carbon dioxide and hydrogen formation by using andesite sands as a photocatalyst under sunlight irradiation (6). At ambient temperature and atmospheric pressure, 6.5×10^{-2} ml g⁻¹ methane and 7.0×10^{-2} ml g⁻¹ of hydrogen were formed from carbon dioxide and water on the andesite.

This report presents the photoelectrochemical reduction of CO₂ using silicate rock (andesite) powder suspended in water.

EXPERIMENTAL

For photoelectrochemical reduction of CO₂, a home-made cell (Figure 1) with a platinum anode (30 mm x 10 mm i.d., 99.95% purity) and a copper cathode (30 mm x 10 mm i.d., 99.95% purity) was used. The cathode compartment was separated from the anode compartment with a Nafion 115 membrane. 0.1 M KHCO₃ solution as an electrolyte was placed in the cell. After andesite rock powder was added to the catholyte, carbon dioxide was bubbled into the catholyte for 5 min at a rate of 40 ml min⁻¹. Carbon dioxide in the cell was reduced at a constant potential, which was controlled by a potentiogalvanostats (Model HA-501, Hokuto Denko, Japan), as irradiating light. During the reduction, andesite rock powder was dispersed by stirring. A Xe lamp (Ushio Tech. Xebex Xe-ARC 160, 1kW) was used for the illumination. The electrochemical reduction of CO₂ was investigated at -1.0 to -2.5 V vs. SCE and at 0 to 60°C. The Faradaic efficiency of products was calculated from 50 C charge-passed at each potential. Products were analyzed by gas and liquid chromatography. Andesite rocks was shattered in an iron mortar and then the powder was sieved by stainless sieves to get 31.8-24.5 mm size. After washing with 1M-nitric acid and distilled-deionized water, the rock powder was dried by heating at 150 °C for 8 h in an oven. Trace contaminants (hydrocarbon, carbon monoxide, hydrogen, etc.) in carbon dioxide gas used in this study were checked.

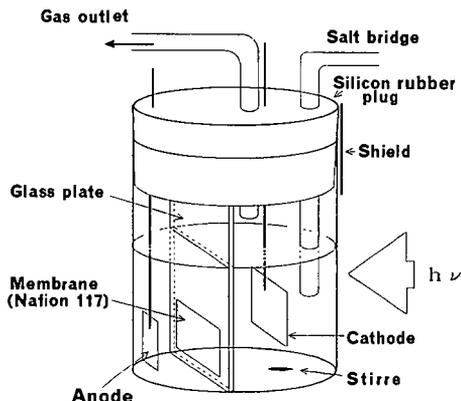


Figure 1. Cell for photoelectrochemical reduction.

RESULTS AND DISCUSSION

In previous study (6), it was found that under sunlight irradiation methane and hydrogen were formed from carbon dioxide and water on andesite sands at ambient temperature and atmospheric pressure. However, it needed the time of >10 h to obtain these products by the photochemical reduction. It was too long to obtain an adequate quantity of the products. Therefore, a photo-electrochemical reduction of CO_2 using andesite powder suspended in water was performed. First, the cyclic voltammograms in the electrolyte suspended andesite powder were measured with and without the irradiation. From the voltammograms, it was found that the electrochemical reduction of CO_2 occurred at -1.0 to -2.5 V vs.SCE and by the irradiation the current density increased about 1.5 times that obtained under no illumination.

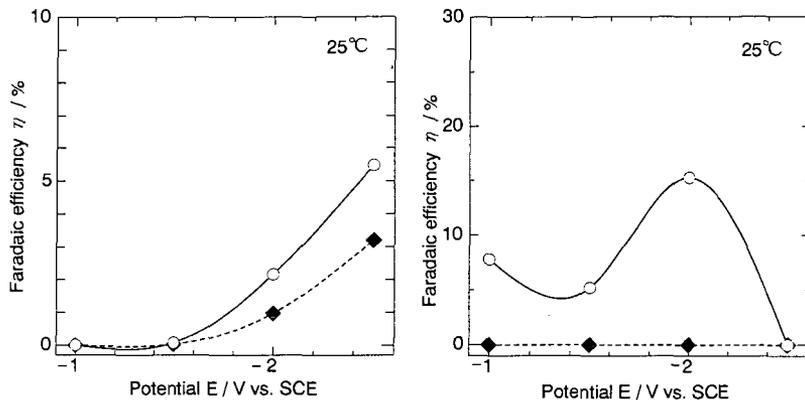


Figure 2. Faradaic efficiencies of CH_2 formation at Cu electrode saturated with CO_2 in 0.1 M KHCO_3 . ○ : Andesite suspension and illumination, ◆ : No andesite
 Figure 3. Faradaic efficiencies of CH_3OH formation at Cu electrode saturated with CO_2 in 0.1 M KHCO_3 . ○ : Andesite suspension and illumination, ◆ : No andesite

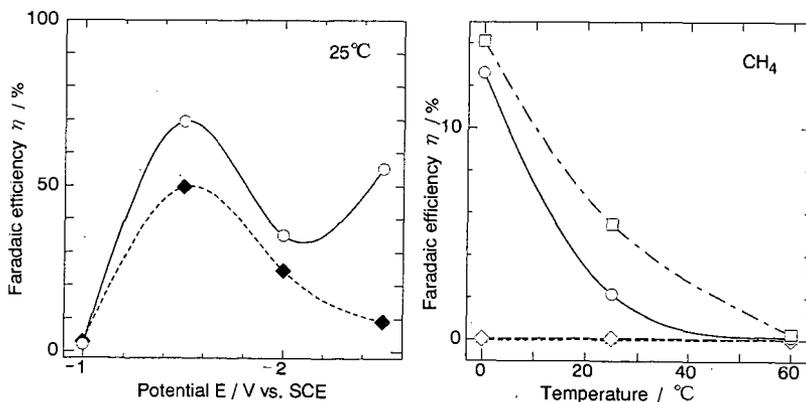


Figure 4. Faradaic efficiencies of H_2 formation at Cu electrode saturated with CO_2 in 0.1 M KHCO_3 . ○ : Andesite suspension and illumination, ◆ : No andesite
 Figure 5. Effect of temperature on the efficiency at Cu electrode saturated with CO_2 in 0.1 M KHCO_3 (Andesite suspension and illumination).

△ : -1.0 V, ◇ : -1.5 V, ○ : -2.0 V, □ : -2.5 V,

Effects of illumination and potential.

The effects of illumination and potential on Faradaic efficiency of products were investigated at 25°C. The products were

hydrogen, methane, methanol, ethylene, carbon monoxide and formic acid. By illumination, the amounts of methane, methanol and hydrogen formed were larger than those of these products obtained without andesite, as shown in Figure 2-4. Furthermore, the Faradaic efficiencies for these products under irradiation were large, compared with the efficiencies obtained in the case of andesite addition and no illumination. These facts prove the large effect of andesite addition and illumination.

However, by the addition of andesite and the illumination the formations of ethylene, carbon monoxide and formic acid decreased. The Faradaic efficiency of methane increased as the potential became negative. The outstanding effect of andesite and illumination was observed in the case of methanol formation. The maximum was obtained at -2.0 V. The maximum hydrogen generated at -1.5 V.

At 0°C , the illumination and andesite affected on the formations of hydrogen, carbon monoxide and formic acid. Especially, the effect was outstanding for the formation of formic acid at -2.0 V. At 60°C , the effect by the addition of andesite and the illumination was not observed the formation of those products except for hydrogen formation.

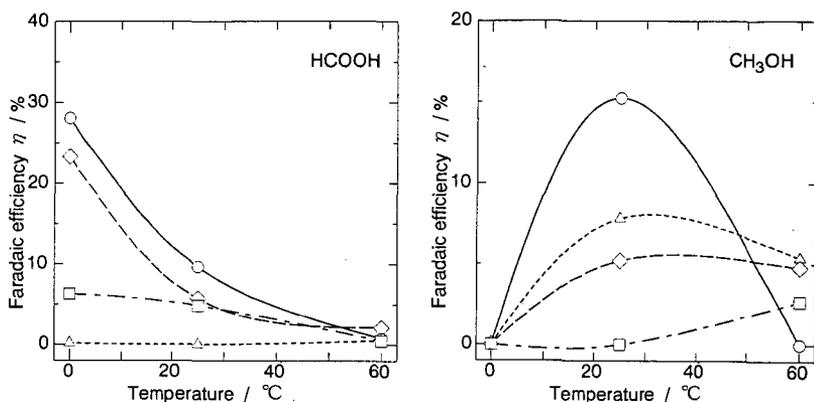


Figure 6. Effect of temperature on the efficiency at Cu electrode saturated with CO_2 in 0.1 M KHCO_3 (Andesite suspension and illumination).

Δ : -1.0 V, \diamond : -1.5 V, \circ : -2.0 V, \square : -2.5 V,

Figure 7. Effect of temperature on the efficiency at Cu electrode saturated with CO_2 in 0.1 M KHCO_3 (Andesite suspension and illumination).

Δ : -1.0 V, \diamond : -1.5 V, \circ : -2.0 V, \square : -2.5 V,

Effects of temperature

The effect of temperature on Faradaic efficiency of products was investigated at -1.0 , -1.5 , -2.0 and -2.5 V. The results for methane, methanol, and formic acid are shown in Figure 5-7. The Faradaic efficiencies of methane, ethylene and formic acid decreased with temperature. The maximum formation of methanol was obtained at 25°C . In the case of monoxide formation, the maximum efficiency was observed at 0°C and -2.0 V and the formation was almost independent of temperature. Hydrogen formation increased with temperature. The efficiency of hydrogen formation was beyond 100% at 60°C .

Under optimal experimental conditions, the Faradaic efficiencies of hydrogen, methane, methanol, ethylene, carbon monoxide, and formic acid were 120% at -2.5 V and 60°C , 14% at -2.5 V and 0°C , 15% at -2.0 V and 25°C , 2.7% at -2.5 V and 0°C , 0.88% at -2.0 V and 0°C , and 28% at -2.0 V and 0°C , respectively.

In described above, the effects of light irradiation and the addition of andesite are evident. Accordingly, X-ray diffraction signal of the andesite was measured for getting a key of the mechanism. The components of the andesite were multiple oxides consisting of SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MnO , MgO , CaO , Na_2O , K_2O , H_2O , P_2O_5 , etc. Therefore, the reducing power may be due to an active site such as TiO_2 on the andesite and the semiconductivity. Something like free electron generated on

andesite probably gives desirable electrochemical reduction of CO₂. However, the detail mechanism could not be made clear.

Consequently, it was found that this method with andesite had effect on formic acid and methanol formation and hydrogen formation by the catalyzed photoelectric dissociation of water. Since silicate rock catalyst such as andesite is easy and cheap to get, the carbon dioxide reduction system developed may be able to have the economic feasibility in large scale hydrogen, methane, formic acid and methanol productions.

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