CHEMISTRY LETTERS, pp. 1757-1760, 1990.

Influence of Light Intensity on Photoelectroreduction of CO_2 at a p-GaP Photocathode

Hidetomo NODA,* Akio YAMAMOTO, Shoichiro IKEDA, Masunobu MAEDA,
and Kaname ITO
Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466

The influence of the light intensity on the photoelectroreduction of CO_2 was investigated at a p-GaP photocathode in 0.1 mol dm^{-3} $KHCO_3$ aqueous solution. The faradaic efficiencies for the formation of $HCOO^-$ and H_2 were strongly affected by the light intensity. The maximum faradaic efficiency for $HCOO^-$ production was close on 70 %. A mechanism of variation of the efficiencies with light intensity was discussed.

Recently, the photoelectroreduction of CO_2 at p-type semiconductor electrodes has been investigated by many authors from the viewpoint of the photovoltaic effect and the novel catalytic activities for CO_2 reduction, as reviewed recently.[1-3] In previous studies, however, the effects of light intensities on the photoelectroreduction of CO_2 have not been noted, and the intensities of the light irradiated on the semiconductor surfaces have only been reported on arbitrary scales which differ from one investigator to another. In the present work the effect of light intensity on the formation of $HCOO^-$ and H_2 at a p-GaP photocathode was examined.

A wafer of a p-GaP single crystal with the (111) face was purchased from Electronics and Materials Corporation, LTD. The ohmic contacts were made with an In-Ga alloy. The procedures for preparing the photoelectrode were described previously.[3] A bright Pt plate and an electrode of Ag-AgCl saturated with KCl served as an anode and a reference electrode, respectively. An aqueous solution of 0.1 mol dm^{-3}(M) $KHCO_3$ which had been pre-electrolyzed for 12 hours was used as the electrolyte. An H-type cell made of Pyrex equipped of a quartz window was employed. The catholyte was separated from the anolyte by a cation exchange membrane. The reaction gas was supplied from the same cyclic gas flow system as that shown previously.[3] The photoelectrolysis was potentiostatically performed by using a potentiostat (HA-301, Hokuto Denko), an electronic coulometer (HF-201, Hokuto Denko), and a Xe Lamp (Varian Corp., VX-300UV). The light intensity of the lamp was measured with a thermopile (The Eppley Laboratory, Inc.). The UV-cut filter (UV-37) and IR-cut filter (IRA-25S) were inserted between the light source and the cell. All the measurements were carried out at 298 K.

Products obtained by the photoelectrolysis were analyzed in the same manners as those described previously.[4] The products detected were $HCOO^-$, CO, and H_2. Hydrocarbons, aldehydes, alcohols, and other carbolic acid were not found.

Figure 1 shows the effect of the light intensity on the faradaic efficiencies for the formation of $HCOO^-$ and H_2 at -0.8, -1.0, -1.2, and -1.5 V. It is found that the efficiencies are affected by the variation of the light intensity even at constant potentials.

Figure 2 illustrates the potential dependencies of the faradaic efficiencies for $HCOO^-$ and H_2 formation at the light intensity of 320 mW cm^{-2}. The maximum efficiency for $HCOO^-$ production, which reaches about 70%, is obtained at -1.0 to -1.2 V. The efficiency for H_2 evolution increases as the electrode potential becomes either more positive or more negative than those potentials.

It is well known that the photocurrents at p-type semiconductor electrodes increase as the light intensity becomes stronger and/or the electrode potential becomes more negative. Therefore, it is expected that the magnitudes of photocurrents play an important role on the above effect.

Figure 3 shows the relationship between the total photocurrent density (I_t) and the partial current density (I_p) for the formation of $HCOO^-$. I_p is proportional to I_t, and the extrapolation to I_p = 0 gives I_t = ca. 0.4 mA cm^{-2} at the intercept. The slope is about 0.7.

The potential - photocurrent curves of the p-GaP electrode at different light intensities are shown in Fig. 4. The photocurrents increase exponentially with the potentials in the region of -0.5 to -0.7 V (region I), and then are inflected in the region of -0.7 to -0.85 V (region II). The currents in this region are close on ca. 0.5 mA cm^{-2}. In the range of -0.85 to -1.2 V (region III), the currents increase again exponentially. At the more negative potentials than about -1.2 V (region IV), the photocurrents finally reach saturation. In region I, the main product is H_2. This fact suggests that a preceding reaction may be the H_2 evolution reaction rather than the CO_2 reduction. The proton donor in this preceding reaction may not be H_2O but HCO_3^- or H_2CO_3. The detailed investigation of the preceding reaction is now in progress. The rate constants of a proton transfer reaction from HCO_3^- to OH^- is of $7x10^9$ dm^3 mol^{-1} s^{-1} at 298 K, that from H_2CO_3 of $8x10^6$ dm^3 mol^{-1} s^{-1}, and that from H_2O of $2.5x10^{-5}$ dm^3 mol^{-1} s^{-1}.(6) If the electrode is polarized cathodically and if it behaves in an anionic manner, the proton transfer from HCO_3^- and H_2CO_3 to the

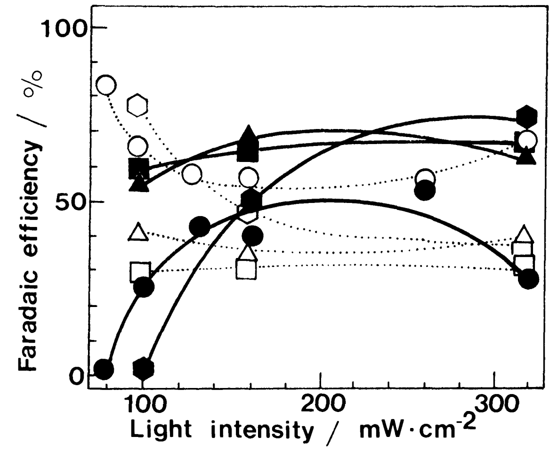

Fig. 1. The effect of the light intensity on the faradaic efficiencies for the formation of $HCOO^-$ and H_2 on a p-GaP electrode at -0.8(⬢ and ⬡), -1.0(■, □), -1.2(▲, △), and -1.5 V(●, ○) in 0.1 M $KHCO_3$ aq. solution.

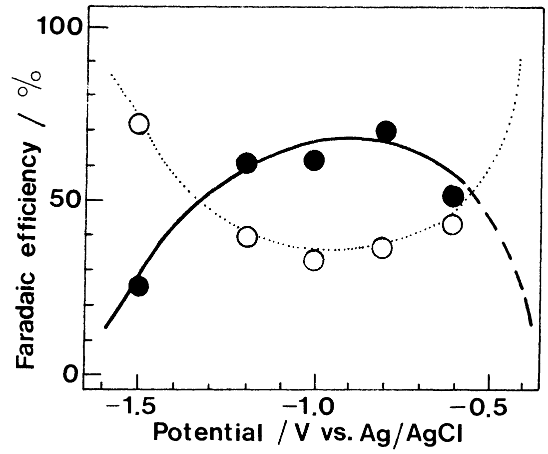

Fig. 2. The potential-faradaic efficiency curves for the formation of $HCOO^-$(●) and H_2(○) on a p-GaP electrode at the light intensity of 320 mW cm^{-2} in 0.1 M $KHCO_3$ aq. solution.

electrode may occur more easily than that from H_2O. Such a consideration for this preceding reaction is also supported by the fact that a similar inflection is observed on the potential-photocurrent curve in a CO_2-free solution of 0.1 M $KHCO_3$ (Fig. 4). In addition, similar inflections are also observed at some metallic electrodes such as Cu and Ni in the same CO_2-free solution.7) The values of photocurrents in these inflection regions are in agreement with the value of the intercept (I_t=0.4 mA cm^{-2}) in Fig. 3 within experimental errors. The intercept in Fig. 3 may indicate the limiting current of the preceding reaction, and the slope (0.7) may correspond to the ratio of the partial current for the $HCOO^-$ production to the current which is obtained by subtracting the limiting current of the preceding reaction from the total current. CO_2 is predominantly reduced to $HCOO^-$ in region III, although H_2 evolution, the proton donor for which is H_2O, and the formation of a small amount of CO also occur. The preceding reaction may simultaneously proceed under a diffusion-limited condition in this region.7)

The phenomenon described above is tentatively explained by a schematic energy band model in Fig. 5. The photo-excited electron in p-GaP has practically the potential of ca. -1.6V in the present solution of pH=6.7,5) while the monitoring electrode potentials should be more positive, i.e., the electrode potentials indicate only the potentials of the Fermi level of the p-GaP. The bias voltage is now applied in order to prevent the recombination of the electron-hole pair with sufficient band bending. The photo-excited electron in p-GaP should be kept at the same energy level, even if the monitoring electrode potential and the light intensity should be changed, so that the activity of p-GaP for the CO_2 reduction would be kept constant. However, the apparent faradaic efficiencies are affected by the light intensity

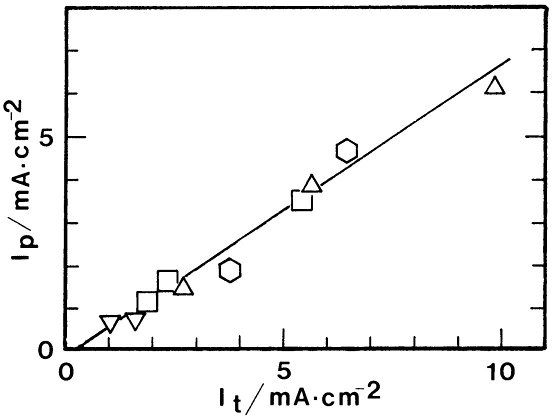

Fig. 3. The relationship between the total current density (I_t) and the partial current density (I_p) for $HCOO^-$ formation on a p-GaP electrode at different light intensities and electrode potentials.

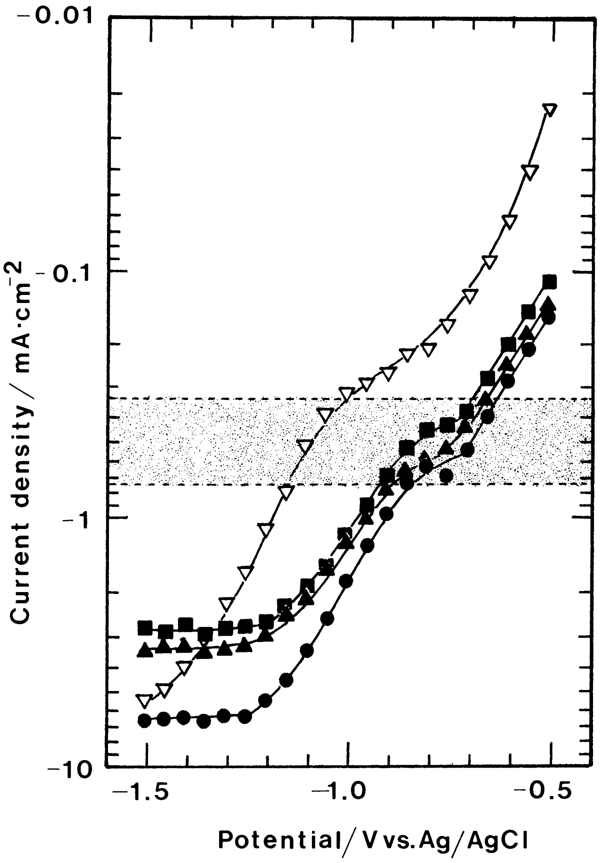

Fig. 4. The potential-photocurrent curves on a p-GaP electrode in 0.1 M $KHCO_3$ aq. solution saturated with CO_2(pH=6.7) at the light intensities of 100(■), 160(▲), 320 mW cm^{-2}(●) and in the same solution of CO_2- free(pH=9.1) at 200 mW cm^{-2}(▽).

as well as the electrode potential. The effect of the light intensity on the efficiency is explained as follows. The preceding reaction of H_2 evolution would occur more easily than the CO_2 reduction and proceed mainly in regions I and II. The photo-electroreduction of CO_2 is performed mainly in regions III and IV, where the preceding reaction may proceed under a diffusion-limited condition. In these regions the stronger the light intensity becomes, the relatively larger becomes the ratio of the efficiency for $HCOO^-$ production to that for the preceding reaction. However, if the photocurrent becomes larger and the mass transfer of CO_2 is limited, the efficiency of H_2 evolution, the proton donor for which is H_2O, is increased.

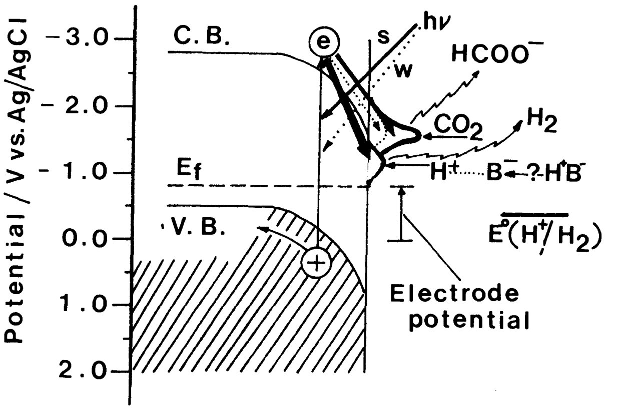

Fig. 5. The schematic energy band model in the photoelectroreduction of CO_2 at a p-GaP electrode in 0.1 M $KHCO_3$ aq. solution
s: strong light intensity, w: weak light intensity, B^-: HCO_3^- or CO_3^{2-}.

In conclusion, it may be said that the light intensity irradiated on the p-GaP photocathode affects the apparent faradaic efficiency for the formation of $HCOO^-$ and H_2 in aqueous $KHCO_3$ medium, because the variation of the intensity leads to the change of the photocurrent and results in the variation of the ratio between the partial current for $HCOO^-$ production and that for the preceding reaction of H_2 evolution which occur more easily than the CO_2 reduction. It is also suggested that the proton donor of the preceding reaction may be HCO_3^- or H_2CO_3.

This work was partially supported by Grant-in-Aid for Energy Research on Priority Areas (No. 01603521) from the Ministry of Education, Science and Culture.

References

1) I. Taniguchi, "Modern Aspects of Electrochemistry No.20," ed by J. O'M Bockris, R. E. Conway, Plenum (1989), and references cited therein.
2) S. Ikeda, M. Yoshida, and K. Ito, Bull. Chem. Soc. Jpn., **58**, 1353 (1985).
3) S. Ikeda, Y. Saito, M. Yoshida, H. Noda, M. Maeda, and K. Ito, J. Electroanal. Chem., **260**, 335 (1989).
4) H. Noda, S. Ikeda, Y. Oda, and K. Ito, Chem. Lett., **1989**, 289.
5) Y. Nakato, S. Tonomura, and H. Tsubomura, Ber. Bunsenges. Phys. Chem., **80**, 1289 (1976).
6) G. M. Panchenkov and V. P. Lebedev, "Chemical Kinetics and Catalysis," Mir Publishers (1976).
7) H. Noda, S. Ikeda, Y. Oda, A. Yamamoto, K. Imai, M. Maeda, and K. Ito, in preparation.

(Received July 9, 1990)