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Photoelectrochemical reduction of carbon dioxide at p-type gallium arsenide and p-type indium phosphide electrodes in methanol

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Abstract

The photoelectrochemical reduction of carbon dioxide (CO_2) at p-type semiconductor electrodes, p-GaAs and p-InP, was studied in the methanol-based electrolyte. The main products from CO_2 were carbon monoxide and formic acid. The onset potentials of the photocathodic current in the methanol-based electrolyte were around −1.2 and −0.8 V versus Ag/AgCl (saturated KCl) with p-GaAs and p-InP electrodes, respectively. Since the onset photopotentials were more positive compared to those with normal metallic electrodes, the photo-aided electrolysis can save electrical energy corresponding to a potential shift of 0.3–1.0 V to less negative potentials. The maximum current efficiency for CO ($r_f = 41.5\%$) was obtained at −2.4 V for the p-InP photocathode. The current efficiencies for CO were better relative to those for formic acid at both p-GaAs and p-InP electrodes. The p-type indium phosphide electrode was found to be more effective than p-Si and p-GaAs for the photoelectrochemical reduction of CO_2 in methanol-based electrolyte.

Keywords: Photoelectrochemical reduction of CO_2; p-Type semiconductor; p-GaAs; p-InP; Methanol; Solar energy conversion

1. Introduction

Global warming caused by a remarkable increase of carbon dioxide (CO_2) emissions into the atmosphere is an important and urgent problem. On the other hand, hydrogen is one of the most promising energy carriers for future energy systems, consisting of the fuel-cell vehicles and the fuel-cell power-generation technologies. In the production of hydrogen from hydrocarbons, which are included in all kinds of fossil fuels, biomass, organic wastes, etc., gas products from the hydrocarbon gasification with water primarily contain not only hydrogen, but also carbon monoxide and CO_2. Therefore, for the development of CO_2 sequestration technologies including capture and secure storage, conversion methods has been of significant interest from the practical viewpoints [1–3]. The photoelectrochemical method with p-type semiconductor electrodes appears to be a very promising method for the conversion and reduction of CO_2, since it is one of the solar energy conversion technologies and can be regarded as an artificial model for photosynthesis in a natural plant [1–3].

Many investigations have been made on the photoelectrochemical reduction of CO_2 on p-type semiconductor electrodes including p-GaP, p-CdTe, p-GaAs, p-InP, p-SiC and p-Si and its diamond-coats [5–21]. Thus far, the CO_2 reduction has been exclusively examined in the aqueous solutions. Recently, the photoelectrochemical reduction of CO_2 in nonaqueous aprotic solvents such as propylene carbonate, acetonitrile, *N*,*N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) has been actively studied because organic solvents can dissolve much more CO_2 than water [5,19].

Methanol is a better solvent of CO_2 than water because the solubility of CO_2 in methanol is approximately five times higher (0.21 mol dm^{-3} in methanol and 0.048 mol dm^{-3} in water at 288 K) [22,23]. Therefore, methanol has been industrially used as a physical absorber of CO_2 in the Rectisol method [24]. Currently, over 70 large-scale plants apply the Rectisol process. Therefore, the direct photo/electrochemical reduction of CO_2 in methanol is an advantageous choice, especially when the process is performed under energetically efficient conditions. We have investigated the electrochemical reduction of CO_2 at various flat metallic electrodes using methanol as the solvent [25–35]. However, surprisingly only a few reports have dealt with the photoelectrochemical reduction of CO_2 in methanol at ambient pressure [36,37].

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In this study, the main results are reported for the photoelectrochemical reduction of carbon dioxide with p-type semiconductor electrodes, p-GaAs and p-InP, in methanol.

2. Experimental

The apparatus and experimental conditions for the photoelectrochemical reduction of CO_2 are shown in Table 1. The photoelectrochemical reduction of CO_2 was performed in a laboratory-made, divided H-type cell. An Aldrich Nafion 117-type ion exchange membrane (0.18 mm thickness) was used as the diaphragm. The photocathode potential was measured with respect to a Ag/AgCl, sat. KCl electrode that was connected by the catholyte through an agar salt bridge. The experimental procedures are shown in Fig. 1.

Methanol (99%, Nacalai Tesque Inc., Kyoto, Japan) was purified by double distillation from metallic magnesium. Lithium hydroxide (98%, Merck, Germany) was used as the ionophore in the methanol-based catholyte. The pH of the catholyte was measured with a glass electrode for nonaqueous solvents, calibrated in water. The pH of 80 mmol dm^{-3} LiOH/methanol at 288 K was approximately 14, and after the saturation of the electrolyte with CO_2 the pH was 8.0. p-Type GaAs and InP wafers (SHOWA DENKO K.K.) were cut into pieces (about 1.0 cm × 1.0 cm in area), washed with a mixture of conc. HCl and HNO_3, etched in CP-4A (a mixture of 47% HF, 60% HNO_3, 99.7% CH_3COOH, and H_2O in a volume ratio of 3:5:3:22) and finally etched again with the mixture of concentrated acids to remove any organic contamination on the surface. Ohmic contact was made on the rear side of the piece with an indium alloy. A Pt foil was used as the counter electrode.

Table 1
Apparatus and experimental conditions

Electrochemical reduction	
Cell	H-type cell
Potentiostat/galvanostate	Hokuto HA-501
Coulometer	Integrator 1109 (Fusou Seisakujyo Inc., Japan)
Potential sweep	Hokuto HB-111 function generator
XY recorder	Graphtec WX1100
Working electrode	p-GaAs [(100), Zn-doped, 1–2 × 10^{17} cm^{-3}], p-InP [(100), Zn-doped, 5 × 10^{17} cm^{-3}]
Counter electrode	Pt foil (30 mm × 20 mm, 0.1 mm thickness, 99.98% purity)
Reference electrode	Ag/AgCl sat. KCl (Horiba, 2060A-10T)
Electrolyte	
Catholyte	80 mmol dm^{-3} LiOH in methanol
Anolyte	300 mmol dm^{-3} KOH in methanol
Carbon dioxide	99.9999% purity
Potential	−2.2 to −2.5 V vs. Ag/AgCl sat. KCl
Temperature	278, 283, 288 K (±0.5 K)
Product analysis	
Gas products	Gas chromatography TCD (GL Sciences GC-320, Molecular Sieve 5A; 13X-S, Ar and He carrier gas) FID (GL Sciences GC-353B, Porapak Q, N_2 carrier gas)
Liquid products	HPLC with UV detector (Hitachi L4000) TCD and FID gas chromatography

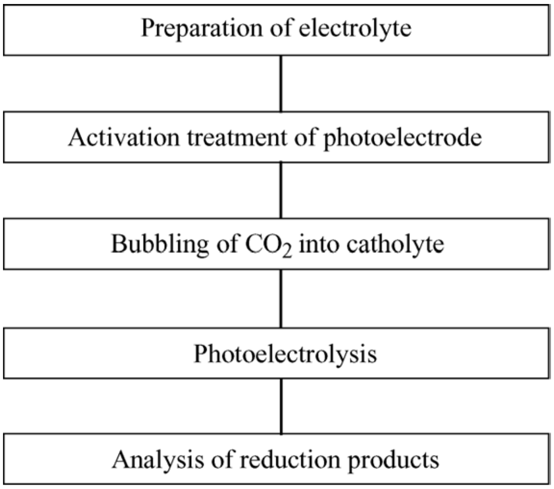


Fig. 1. Experimental procedures for the photoelectrochemical reduction of CO_2.

A 5000-W xenon lamp (Ushio, UXL-5000DK-B-O, Tokyo, Japan) was used to illuminate the semiconductor photocathode. Wavelengths shorter than 300 nm were filtered out by the cell wall. A discontinuous photoelectrochemical reduction procedure was used. First, CO_2 gas was bubbled into the methanol catholyte for 1 h at the rate of 30 ml min^{-1}. The CO_2-saturated solution was then reduced photoelectrolytically at cathodic polarizations in the range from −2.2 to −2.5 V versus Ag/AgCl, sat. KCl. In the potential region with p-InP and p-GaAs electrodes, the photocurrent density was in the range of 4.1–6.6 mA cm^{-2}. The catholyte was magnetically stirred. The Faradic efficiencies of formation for the main products were calculated from the total charge passed during batch electrolyses, which was set to 30 C. The reactions of the main products for the calculation of Faradaic efficiency were as follows:

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \quad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (2)$$

The gaseous products obtained during the photoelectroreduction were collected in a gas collector and analyzed by GC. Products soluble in the catholyte were analyzed by HPLC and GC.

3. Results and discussion

It was reported in the literature [22,23] that the solubilities of CO_2 in methanol and water are 4.6 and 1.07 cm^3 cm^{-3} at 298 K, respectively. In any case, the solubility of CO_2 in the system studied was much greater compared to that in water.

3.1. Current–potential curves

First, the current–potential curves on the p-GaAs and p-InP photocathodes in the methanol-based electrolyte were recorded at 288 K. The potential was scanned at a sweep rate 50 mV s^{-1}. Figs. 2 and 3 show the typical current–potential curves with the p-type photoelectrodes. Under illumination, a relatively large

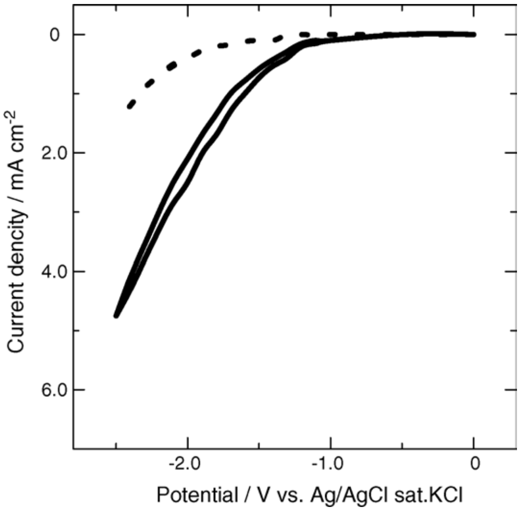


Fig. 2. Current–potential curves for p-GaAs photocathode in CO_2-saturated methanol at 288 K. Solid line, under illumination; dashed line, dark experiments. Catholyte: 80 mmol dm^{-3} LiOH/methanol; anolyte: 300 mmol dm^{-3} KOH/methanol.

photocurrent density was observed with the photocathodes. However, the dark current without illumination was relatively small (less than 1.5 mA cm^{-2}) at potentials down to −2.5 V. The onset potentials of the photocathodic current in the methanol-based catholyte were approximately −1.2 and −0.8 V with p-GaAs and p-InP photoelectrodes, respectively. It has been found in the previous work [36] that the onset potential at p-Si photoelectrode in methanol-based electrolyte was approximately −1.0 V versus Ag/AgCl sat. KCl. Taniguchi et al. [5] have stated that the onset photopotentials at the p-InP, p-Si and p-GaAs photocathodes in 0.1 M tetrabutylammonium perchlorate (TBAP)/DMF solution containing 5% water under CO_2 atmosphere were around −0.7, −1.0 and −1.1 V versus SCE, respectively. Hence, the relative ordering of the p-type semiconductor performances was very similar with their results. Under essentially the same conditions, the onset potentials of the cathodic current with metallic electrodes, such as Ag, In, Pb, Ti, and Zn were about −1.7, −1.7, −1.7, −1.8 and −1.5 V versus Ag/AgCl, respectively [26,28,29,31,33]. Therefore, photo-aided electrolysis can save electrical energy corresponding to a potential shift of 0.3–1.0 V to less negative potentials. Other workers have also shown similar comparison [5,7]. No voltammetric peak was observed in the potential range down to −2.5 V because further CO_2 reduction may proceed with increasing negative potentials.

After the onset photopotentials were determined from the polarization experiments, we investigated the reduction of CO_2 in CO_2-saturated methanol at cathodic polarizations exceeding the onset photopotential. The potentials for the p-GaAs and p-InP photocathodes were in the range −2.2 to −2.5 V versus Ag/AgCl sat. KCl.

3.2. *Effect of potential of the product Faradaic efficiency*

The results dealing with the effect of the potential on the current efficiencies for the products by the photoelectrochemical reduction of CO_2 on p-GaAs electrode in methanol at 288 K are illustrated in Fig. 4. CO and formic acid were detected as the reduction products from CO_2. The current efficiency of CO at the p-GaAs photocathode was convex and the maximum ($r_f = 24.9\%$) was observed at −2.4 V. On the other hand, the formation efficiency of formic acid was almost constant (approximately 14%). The maximum total current efficiency for the CO_2 reduction ($r_f = 40.5\%$) was observed at −2.4 V, which was superior to hydrogen formation efficiency ($r_f = 34.4\%$).

Fig. 5 presents the effect of the potential on the Faradaic efficiencies for the products by the photoelectrochemical reduction of CO_2 at p-InP photoelectrode in methanol at 278 K. First, the effect of temperature for p-InP electrode was investigated

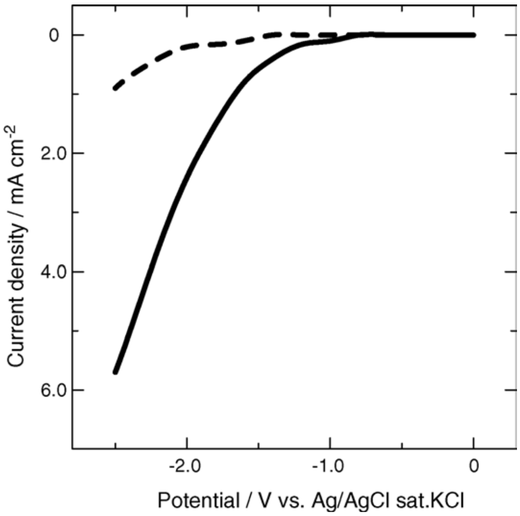


Fig. 3. Current–potential curves for p-InP photocathode in CO_2-saturated methanol at 288 K. Solid line, under illumination; dashed line, dark experiments. Catholyte: 80 mmol dm^{-3} LiOH/methanol; anolyte: 300 mmol dm^{-3} KOH/methanol.

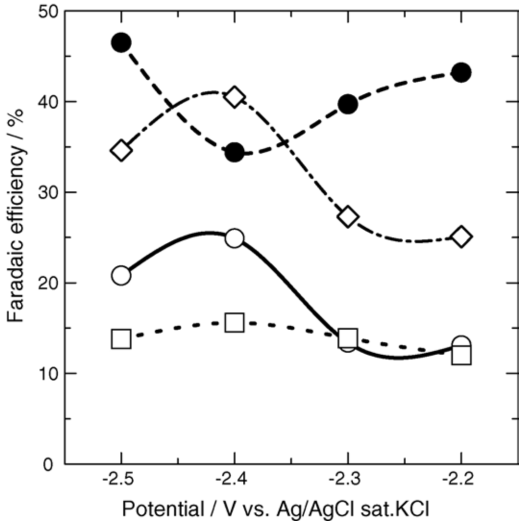


Fig. 4. Effect of potential on Faradaic efficiencies for the products by the photoelectrochemical reduction of CO_2 on p-GaAs photocathode in methanol at 288 K. CO (◯); HCOOH (☐); total CO_2 reduction (◊); H_2 (●); catholyte: 80 mmol dm^{-3} LiOH/methanol; anolyte: 300 mmol dm^{-3} KOH/methanol.

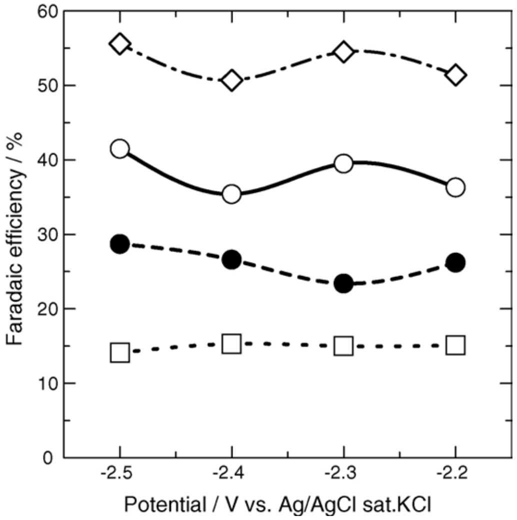


Fig. 5. Effect of potential on Faradaic efficiencies for the products by the photoelectrochemical reduction of CO_2 on p-InP photocathode in methanol at 278 K. CO (○); HCOOH (□); total CO_2 reduction (◇); H_2 (●); catholyte: 80 mmol dm^{-3} LiOH/methanol; anolyte: 300 mmol dm^{-3} KOH/methanol.

in the range of 278–288 K. Although the drastic effect was not observed in the temperature range tested, the total current efficiency for the CO_2 reduction tended to increase as lowering the temperature. Therefore, the potential effect was evaluated at 278 K. The main products from CO_2 were the same as those obtained at p-GaAs photocathode. The maximum current efficiency of CO was of 41.5% at −2.5 V. The formation efficiency of formic acid was nearly constant (r_f = about 15%). At all potentials tested, the total efficiency for CO_2 reduction was larger relative to those for hydrogen formation. Yoneyama et al. [7] have reported the photoelectrochemical reduction of CO_2 to CO and formic acid at the p-InP photoelectrode in water at 298 K. In the case of the inorganic supporting electrolytes, the Faradaic efficiencies for CO and formic acid were 8.6 and 17.5, 16.1 and 4.6, 10.7 and 2.3 and 13.7 and 24.2% in the 0.1 M Na_2CO_3, Na_2SO_4, Na_3PO_4 and $LiClO_4$ solutions, respectively. In the photoelectrochemical reduction of CO_2 at p-InP electrode in methanol, the current efficiencies for CO and formic acid was much better than those obtained in water [7] and the methanol using p-Si [36] and p-GaAs photocathodes. As illustrated in the current–potential curves, the required electrode potentials for the galvanostatic electrolyses were dependent upon the material type of semiconductor. The present work shows that the onset potential for the electrolyses using p-InP was more positive by 0.2–0.4 V than that with p-Si and p-GaAs photocathodes. Therefore, p-InP seems to be an effective material for the photoelectrochemical reduction of CO_2 in a methanol-based electrolyte compared with p-Si and p-GaAs photocathodes, since the CO_2 photoelectrochemical reduction proceeds both with good selectivity of the reduction product distribution and with a lower input potential.

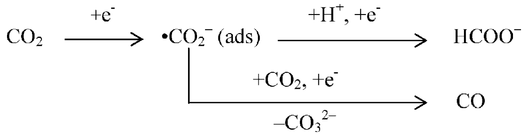
Generally, during the photo/electrochemical reduction of CO_2 in water, hydrogen formation simultaneously occurs with the CO_2 reduction. Therefore, the depression of hydrogen formation is very significant because the applied energy is wasted on hydrogen evolution instead of being used for the CO_2 reduction. The current efficiency for hydrogen formation on the p-InP photocathode in a methanol-based catholyte could be suppressed to less than 29%. For the photoelectrochemical reduction of CO_2 at the p-InP photocathode in water with the inorganic supporting salts at 298 K, the hydrogen formation efficiency was of 61.8% [7]. For the electrochemical reduction of CO_2 with various metal electrodes in methanol, it has been found that methanol as a catholyte was more efficient in decreasing the hydrogen formation [25–35]. Hence, during the photoelectrochemical reduction process, the methanol-based catholyte was suitable for suppressing hydrogen formation.

3.3. Reduction mechanism

The mechanism for the photoelectrochemical reduction of CO_2 in methanol-based electrolyte was investigated at p-type semiconductor electrodes. A GC-MS study with deuterated methanol catholyte demonstrated that no reduction product was produced from methanol [35]. Under a nitrogen atmosphere, electrolysis yields exclusively hydrogen. Consequently, the required products were obtained by the photoelectrochemical reduction of CO_2.

Amatore and Savéant [38] investigated the electrochemical reduction of CO_2 in media of low proton availability, in which three competing pathways were proposed. (1) oxalate production through self-coupling of $^{\bullet}CO_2^{-}$; (2) CO production via oxygen–carbon coupling of $^{\bullet}CO_2^{-}$ with CO_2; and (3) formate production through protonation of $^{\bullet}CO_2^{-}$ by residual or added water followed by an electron transfer occurring in the solution, the electron source being $^{\bullet}CO_2^{-}$ itself. The CO production mechanism was thought to contain the coupling of CO_2 and $^{\bullet}CO_2^{-}$ radical anion, where the complex radical anion can be shown as $(CO_2)_2^{\bullet -}$. These species then can undergo either the electrochemical reduction, or chemical reduction via $^{\bullet}CO_2^{-}$, and the resulting dianion can then decompose into CO and carbonate.

The experimental data in the present work and literature reports [4–21,25–37] suggest that the pathway by which formic acid and CO are formed is as follows.



In this reduction system, the usual pathway involving a one-electron reduction is assumed. This step is followed by a second electron transfer/protonation to yield formic acid and then by parallel disproportionation of the $^{\bullet}CO_2^{-}$ radical anions to neutral CO molecules and dinegative carbonate ions.

The reduction of CO_2 to CO can be expected to proceed more efficiently in a hydrophobic environment, relative to formic acid formation [37]. In the present study, since the ΔG_f° value for In_2O_3 (−410.9 kJ mol^{-1} [39]) is less negative than that for Ga_2O_3 (−496.2 kJ mol^{-1} [40]), p-InP would be considered to be more hydrophobic than p-GaAs. p-Si will be considered to be highly hydrophilic due to the very negative value (−798.7 kJ mol^{-1} [41]).

4. Conclusion

The photoelectrochemical reduction of CO_2 at p-GaAs and p-InP electrodes was investigated in the methanol-based electrolyte. A predominant formation of CO on p-InP photocathode was observed in the potential range of −2.2 to −2.5 V versus Ag/AgCl, and the best current efficiency for CO was of 41.5% at −2.4 V. The Faradaic efficiencies of formic acid were in the range of 12–15% at both p-type photocathodes. Carbon monoxide is one of the raw materials in the hydroformylation reaction, which plays an important role in the chemical industry. Formic acid has been industrially used in various processes including textile dyeing and finishing, leather tanning and electroplating. Since methanol is widely used in industry as a CO_2 absorbent in the Rectisol process [24], the synthesis of useful substances by electrochemical reduction of CO_2 may be of practical interest in connection with the removal of CO_2 from the atmosphere, storage of solar energy and the production of raw materials for the chemical industry.

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