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Photoelectrochemical Reduction Products of Carbon Dioxide at Metal Coated p-GaP Photocathodes in Aqueous Electrolytes

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In order to increase the current efficiency of the photoelectrochemical reduction of CO_2 in aqueous electrolytes, metals such as Pb and Zn, which have a higher overpotential for the hydrogen evolution reaction, were coated on a p-GaP photocathode by sputtering and electroplating. Au was also coated by sputtering. Then, the photoelectrolytic experiments were carried out in a gas-tight cell with a cyclic gas-flow system. The products in a gas phase were determined as well as the products in the electrolyte. Accordingly, CO in addition to HCOOH as a reduction product of CO_2 was found to be produced as well as substantial amount of H_2 as a by-product. However, other products such as HCHO and CH_3OH were not found at all. In the case of the Pb coated p-GaP electrode, the current (faradaic) efficiency, η, for HCOOH formation was increased up to 48.2%, although in the case of bare p-GaP it was only 4.8% at maximum. On the other hand, the η for CO formation at the Zn-coated p-GaP electrode went up to 16.5%. While, in the case of an Au-coated p-GaP, the η for the CO_2 reduction was not so changed as for the bare p-GaP photocathode.

In a previous paper,[1] we reported that the some organic compounds such as formic acid, formaldehyde and methanol, which had been reported as photoelectrochemical reduction products of carbon dioxide (CO_2) by a few authors,[2,3] were also produced by the photolysis of cell materials such as electrolytes and epoxy resins. Also, the real reduction product of CO_2 at the p-GaP photocathodes in aqueous electrolytes was experimentally confirmed to be only formic acid, for which the current (faradaic) efficiency, η, was 4.8% at maximum.

The photoelectrochemical reduction of CO_2 is a competitive reaction with the reduction of water, *i.e.*, the hydrogen-evolution reaction (HER). Therefore, η for a CO_2 reduction may be increased if the electrode surface is covered with a thin layer of a metal such as Zn or Pb which have higher overvoltages for HER.

In the present paper, the discussed photoelectrolytic experiments were carried out in a gas-tight cell with a cyclic gas-flow system. The products in the gas phase were determined as well as the products in the electrolytes. In order to increase η for the CO_2 reduction, coatings using such metals as Au, Zn, and Pb were placed on the surfaces of p-GaP photocathodes and the effects on the reduction products and the characteristic properties as a photocathode were investigated. In this paper, mainly an analysis of the reduction products is reported. The properties of the metal-coated electrodes will be the subject of our next paper.

Experimental

Materials. The photocathode was prepared by molding a p-GaP wafer, Sanyo Electric Co. Ltd., Zn-doped 2.8—6.0×10^{17} cm^{-3}, of 1.0 cm^2 with epoxy resin, after an ohmic contact was made with an In-Zn (2%) alloy solder. It was etched in aqua regia for 1 min before use. In order to prevent the photolysis of the epoxy resin, the epoxy region of an electrode was shaved off only to the extent as not to cause a failure of the insulation (Fig. 1).

The electrolytes used were 0.1 mol dm^{-3} aqueous solutions of $(C_2H_5)_4NClO_4$ [TEAP], $(C_2H_5)_4NBr$ [TEABr], and $(n\text{-}C_4H_9)_4NBr$ [TBABr]. TEAP was synthesized with TEABr and perchloric acid.[4] The other reagents were all commercial grade and were used without further purification except for the case of TBABr, which was twice recrystallized with distilled water because it contained detectable amounts of methanol and ethanol.

Apparatus and Procedure. A photoelectrolytic cell with a quartz glass window, (made of Teflon), was designed to separate the cathode and anode chambers with an ion-exchange membrane, Nafion-315, and to be able to operate with a small volume (*ca.* 5 ml) as a catholyte for the easy determination of products (Fig. 2). The cell was gas-tight and the gas, CO_2 or N_2, was supplied by a cyclic gas-flow system which was assembled with a mini peristaltic pump, a manometer and a gas sampler (Fig. 3). The cell and a UV-37 filter, which was used to cut off ultraviolet rays shorter than 370 nm in order to prevent the photolysis of

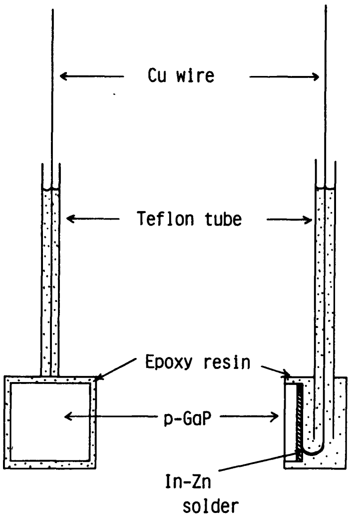

Fig. 1. Structure of p-GaP electrode.

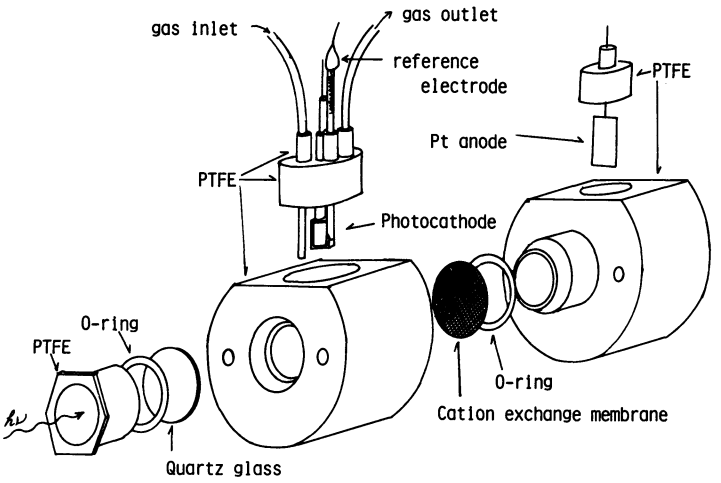

Fig. 2. Structure of photoelectrolytic cell.

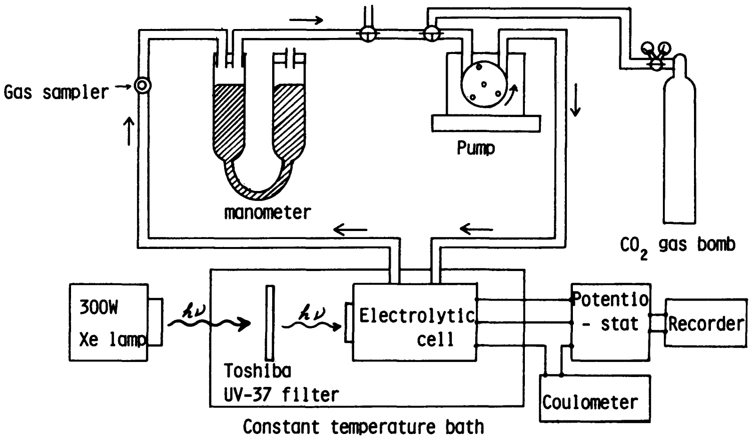

Fig. 3. Diagram of photoelectrolytic apparatus with cyclic gas flow system.

cell materials, were immersed in a water bath for the prevention of overheating due to illumination.

The photoelectrochemical reduction was carried out potentiostatically using a potentiostat and a xenon lamp, Model VIX-300; Varian Co. Ltd. The photocurrent was recorded using a conventional pen-recorder. The quantity of charge passed was monitored with an electronic coulometer, Model HF-102; Hokuto Denko Co. Ltd. After CO_2 or N_2 gas was blown into the cell from each cylinder and was exhausted through the cyclic gas-flow system for about 30 min, the line was closed to make it gas-tight. During the experiment, the gas in the system was circulated using a peristaltic pump with a rate of 1 ml/min.

Analysis. The products in the gas phase were determined qualitatively and quantitatively by gas chromatography, Model GC-3AH, Shimadzu Corp., having a TC detector on a column of activated charcoal 60/80, 3 mm×3 m, at 100 °C using He gas as a carrier with a rate of 13 ml/min. The products in the electrolyte were sampled after the line was exposed to the atmosphere and were then determined by high-performance liquid chromatography. The equipment used was a Model HSLC-022; Atto Corp., with RI and UV detectors with 225 nm on a column of Shodex HC-125S using 1% H_3PO_4 aqueous solution at 1.0 ml/min and 35 °C as an elueant. An analysis was also performed using steam chromatography, SSC-1 Model 103; Ohkura Riken, with a FID on a column of Chromosorb 101, 2 mm×3 m, at 120 °C using steam as a carrier at 8.6 ml/min (5.4 µl/min as water) for the determination of alcohols and aldehydes, although they were not detected at all in the present work.

Metal Coating. The molded p-GaP electrode was coated with a thin layer of Au, Pb, or Zn by sputtering and electroplating methods. The sputtering was carried out at DC 700 V under *ca.* 1 Pa air using an ion cleaner, Model IB-1; Eiko Co. Ltd., where the coverage was controlled by the sputtering time *i.e.*, 7, 15 or 20 min. Au of 99.99%, Pb of 99.99% and Zn of 99.9999% were used as the target metal. Typical weights of coated metals measured by weighing method were 0.06, 0.07, and 0.02 mg cm^{-2} in the cases of Au, Pb and Zn, respectively, for 10-min sputtering.

The electroplating method under photo-illumunation was also used for the coating of Pb and Zn. The electroplating was carried out potentiostatically usig an H-type Pyrex cell with a quartz window under the illumination of a xenon lamp. The amounts of the coated metals were monitored with a coulometer connected in series between the anode and the potentiostat.

In the case of Pb plating, 0.5 mol dm^{-3} of lead acetate was used as an electrolyte, and a p-GaP electrode, a Pb sheat

(99.99%) electrode and a Ag/AgCl/sat'd KCl electrode served as a cathode, an anode and a reference electrode, respectively. The electroplating was carried out at a potential of −0.4 V *vs.* Ag/AgCl/sat'd KCl, during which almost a uniformly deposited gray film of Pb was obtained.

In the case of Zn coating, the electrolyte was a solution of zinc sulfate (300 g) and ammonium chloride (20 g) dissolved into 1 dm^3 of distilled water; a zinc plate (99.9999%) served as an anode. Electroplating was carried out at −0.2 V, and a uniform film of Zn was deposited.

Under these experimental conditions, no hydrogen evolution was observed at all, so that the deposited amounts per coulomb should correspond to 1.0 mg C^{-1} and 0.33 mg C^{-1} for Pb and Zn, respectively. Therefore, the amounts of metals coated on the p-GaP electrodes were controlled by the quantities of electricity passed.

In the present paper, these metal coated p-GaP electrodes are named as Au(s)-p-GaP, Pb(s)-p-GaP, and Zn(s)-p-GaP prepared by sputtering and Pb(e)-p-GaP and Zn(e)-p-GaP by electroplating, respectively.

Results and Discussion

Photoelectrochemical Reduction Products of CO_2. The photoelectrochemical reduction products of CO_2, when metal coated p-GaP electrodes by sputtering were used as a photocathode and the photoelectrolysis was carried out at −1.2 V up to 100 C in various aqueous solutions, are summerized in Table 1. This table demonstrates that the reduction products are only formic acid in the electrolytes and hydrogen and carbon monoxide in the gas phase. No products such as other carboxilic acids, alcohols or aldehydes were observed at all, although these organic compounds had been reported as photoelectroreduction products by some authers.2,3,5)

In the case of the metal-coated p-GaP electrodes prepared by electroplating (Table 2), the products were also formic acid, carbon monoxide and hydrogen. The current efficiency for CO production increased up to about 16.5% at the Zn(e)-P-GaP

Table 1. Photoelectrochemical reduction products of CO_2 on bare and metal coated p-GaP photocathodes, prepared by sputtering method, at −1.2 V *vs.* Ag/AgCl/sat'd KCl. Quantity of electricity; 100 C.

Electrode	Electrolyte	Time	HCOOH		CO		H_2		$\eta_1+\eta_2$	$\eta_1+\eta_2+\eta_3$
		min	n_1/μ mol	$\eta_1/\%$	n_2/μ mol	$\eta_2/\%$	n_3/μ mol	$\eta_3/\%$	%	%
p-GaP	TEAP	560	65	12.6	17	3.3	350	68	15.9	83.9
	TEABr	805	52	10.1	30	5.8	340	66	15.9	81.9
	TBABr	345	11	2.2	5.3	1.0	480	92	3.2	95.2
Au(s)-p-GaP	TEAP	255	28	5.4	14	2.7	460	88	8.1	96.1
	TEABr	570	62	12.1	26	5.0	370	72	17.1	89.1
	TBABr	235	68	13.1	24	4.5	430	84	17.6	101.6
Zn(s)-p-GaP	TEAP	555	44	8.4	17	3.3	350	68	11.7	79.7
	TEABr	455	74	14.4	34	6.6	360	70	21.0	91.0
	TBABr	300	26	4.9	11	2.2	470	91	7.1	98.1
Pb(s)-p-GaP	TEAP	825	60	11.5	13	2.5	360	69	14.0	83.0
	TEABr	625	63	12.1	22	4.2	290	56	16.3	72.0
	TBABr	775	53	10.3	21	4.1	340	66	14.4	80.4

η_1, η_2, and η_3 are current efficiencies for HCOOH, CO, and H_2, respectively.

Table 2. Photoelectrochemical reduction products of CO_2 on metal coated p-GaP photocathodes, prepared by electroplating method, at −1.2 V *vs.* Ag/AgCl/sat'd KCl in 0.1 M† TEABr aq

Electrode	Q_e	Q	Time	HCOOH		CO		H_2		$\eta_1+\eta_2$	$\eta_1+\eta_2+\eta_3$
	C	C	min	n_1/μ mol	$\eta_1/\%$	n_2/μ mol	$\eta_2/\%$	n_3/μ mol	$\eta_3/\%$	%	%
Zn(e)-p-GaP	0.06	20	610	14	13.2	11	10.9	64	62	24.1	86.1
	0.07	20	870	15	14.7	15	14.9	68	66	29.6	95.6
	0.08	20	655	26	25.1	17	16.5	49	47	41.6	88.6
	0.09	20	460	15	14.7	15	14.7	63	63	29.4	92.4
Pb(e)-p-GaP	0.06	100	710	87	16.7	8.2	1.6	350	67	18.3	85.3
	0.07	50	605	95	36.5	8.5	3.3	120	48	39.8	87.8
	0.08	20	310	50	48.2	5.0	4.8	33	31	53.0	84.0
	0.09	20	360	49	47.2	4.1	3.9	41	40	51.1	91.1

Q_e; quantity of electricity for electroplating. † 1 M = 1 mol dm^{-3}.

electrode and that for formic acid production increased up to 48.2% at Pb(e)-p-GaP electrode. These results suggest that formic acid is effectively produced at the Pb(e)-p-GaP photocathode, as the side reactions such as HER is depressed by coating the metal with a high overpotential for HER. These results are thought to be due to the fact that the metal is deposited preferably onto the active sites of the p-GaP electrode. Thus, the metal plays the role more effectively than that deposited by sputtering.

In the case of a Pb(s)-p-GaP photocathode, the surface changed to a silvery color upon the reduction of lead during the photoelectrolysis. Figure 4 shows the current efficiencies for HCOOH and CO production plotted with respect to the quantity of charge passed. At the point of 25 C (coulomb), where the surface was not silvery, current efficiencies for HCOOH and CO were as small as 5.6% and 1.0%, respectively, while, over the point of 50 C, they became about twice a large as before. In order to clarify this situation, the gas in the cyclic gas-flow system was progresively analysed while watching the surface state of the Pb(s)-p-GaP. The results are shown in Fig. 5. The open triangle in that figure represents the point where the surface became silvery. The formation of H_2 became smaller and, in contrast to this, that of CO became larger after this point. The content of CO_2 gradually decreased with the passage of current and air gradually penetrated into the line. Although the products in the electrolytes were not analyzed, the current efficiency for HCOOH formation may be estimated to increase after this point by the depression of HER.

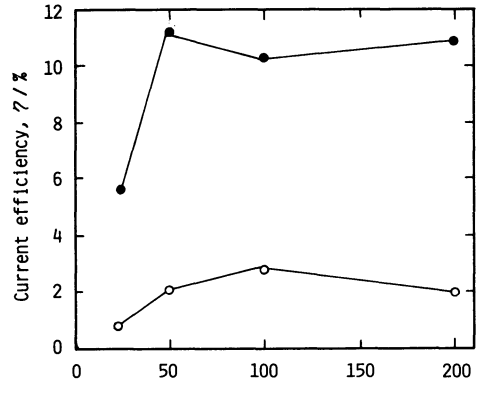

Fig. 4. Current efficiencies, η, for HCOOH (●) and CO (○) formations with respect to quantity of electricity, Q, at Pb(s)-p-GaP (7 min) electrode in 0.1 M TEABr aq.

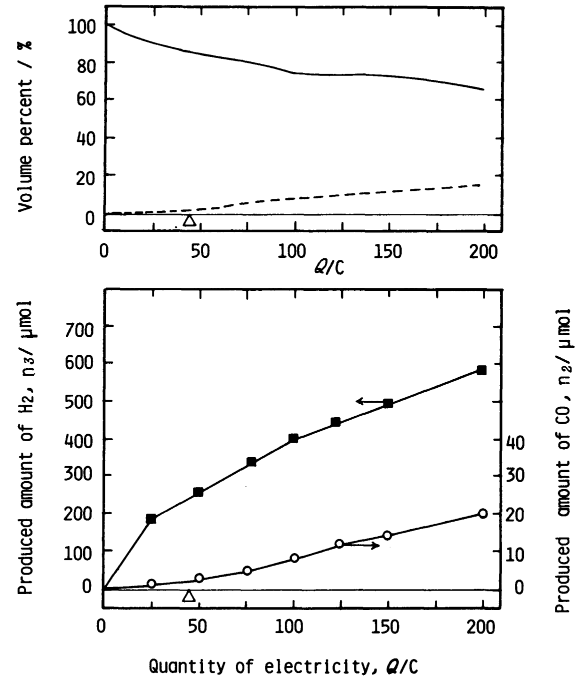

Fig. 5. Amount of products, CO (○) and H_2 (■), and contents of CO_2 (——) and air (----) in gaseous phase with respect to quantity of electricity, Q, when photoelectrochemical reduction of carbon dioxide was performed at Pb(s)-p-GaP (7 min) electrode in 0.1 M TEABr aq. Triangle represents the point where the surface of the electrode became silvery.

Table 3. Photoelectrochemical reduction products of CO_2 at -1.2 V *vs.* Ag/AgCl/sat'd KCl. Quantity of electricity for electroplating Zn and Pb on p-GaP; 0.07 coulomb

Electrolyte	Electrode	Q	t	HCOOH		CO		H_2		$\eta_1+\eta_2$	$\eta_1+\eta_2+\eta_3$
		C	min	n_1/μ mol	$\eta_1/\%$	n_2/μ mol	$\eta_2/\%$	n_3/μ mol	$\eta_3/\%$	%	%
TEAP	p-GaP	100	500	65	12.6	17	3.3	350	68	15.9	83.9
	Zn(e)-p-GaP	14	640	19	26.5	6.5	8.9	48	64	35.4	99.4
	Pb(e)-p-GaP	50	645	118	45.5	10	4.0	95	37	49.4	86.5
TEABr	p-GaP	100	805	52	10.1	30	5.8	340	66	15.9	81.9
	Zn(e)-p-GaP	20	375	32	31.0	7.5	7.2	55	53	38.2	91.2
	Pb(e)-P-GaP	50	605	95	36.5	8.5	3.3	120	48	39.8	87.7
TBABr	p-GaP	100	345	11	2.2	5.4	1.0	480	92	3.2	95.2
	Zn(e)-p-GaP	20	745	19	18.6	9.0	8.7	39	37	27.3	64.3
	Pb(e)-p-GaP	40	715	42	20.0	11	5.1	110	54	25.1	79.5

In order to check the mechanism of CO formation, a blank test was carried out using a Pb(s)–p-GaP electrode in an 0.1 mol dm^{-3} TEABr aq solution previously containing 0.01 mol dm^{-3} HCOOH under N_2 atomsphere for 100 C at −1.2 V *vs.* Ag/AgCl. The product was only hydrogen and CO was not observed. Also, the concentration of formic acid did not change. Therefore, it may be concluded that the CO obtained in the above-mentioned experiments was not obtained through HCOOH from CO_2 but was produced by the direct reduction of CO_2.

Table 3 shows the effect of the supporting electrolyte on the current efficiencies for the reduction products when bare p-GaP, Zn(e)–p-GaP, or Pb(e)–p-GaP were used as photocathodes. In the cases of TEAP and TEABr, the current efficiencies, η, for HCOOH, CO and H_2 productions were not so much affected by the electrolytes, but were largely affected by the coating metals. The η for CO_2 reduction became about 50% at Pb(e)–p-GaP photocathode in TEAP aq. In the case of TBABr, however, a bare p-GaP electrode showed extremely lower η for HCOOH or CO production. The η for CO was up to the same values in the former electrolytes by coating of Pb or Zn. The η for HCOOH, however, was only recovered up to half values. These results indicate that the η for CO_2 reduction is affected not by an anion but the cation size of the supporting electrolytes. The favorable formation of nonaqueous circumstance by large cation of tetrabutylammonium salts on the electrode surface may depress the effect of a lead or zinc coating.

Reduction Mechanism. The photoelectrochemical reduction of CO_2 starts from the formation of a carbon dioxide anion radical, $\cdot CO_2^{-}$, by the electron acceptance of a CO_2 molecule,[6] and the anion radical is thought to be adsorbed on the electrode surface. The HER also takes place on the same electrode surface and becomes adsorbed atomic hydrogen as follows.[7]

$$CO_2 + e^- \rightarrow \cdot CO^{-}_{2\,ad} \qquad (1)$$

$$H^+ + e^- \rightarrow H_{ad} \qquad (2)$$

Now, formic acid, the main reduction product of CO_2 in aqueous electrolytes, is produced according to Reactions 3 and/or 4.

$$\cdot CO^{-}_{2\,ad} + H_{ad} \rightarrow HCOO^- \qquad (3)$$

$$\cdot CO^{-}_{2\,ad} + H^+ + e^- \rightarrow HCOO^- \qquad (4)$$

Hydrogen is produced by HER as follows.

$$H_{ad} + H^+ + e^- \rightarrow H_2\uparrow \qquad (5)$$

$$H_{ad} + H_{ad} \rightarrow H_2\uparrow \qquad (6)$$

By coating the electrode surface with metals such as Pb and Zn having a higher overpotential for the HER, the rates of Reactions 5 and 6 become slow and the HER is suppressed. Concequently, the rate of formic acid formation by Reaction 3 or 4 through Reaction 1 becomes larger.

On the other hand, carbon monoxide is produced by the disproportionation reaction of the CO_2 anion radical according to Reaction 7.[8]

$$\cdot CO^{-}_{2\,ad} + \cdot CO^{-}_{2\,ad} \rightarrow CO + CO_3^{2-} \qquad (7)$$

This reaction is thought to be competitive with Reaction 3 or 4. In the case of the Pb(e)–p-GaP electrode, the rates of Reaction 3 and/or 4 are larger than that of Reaction 7. Thus, the formic acid is the predominant product from CO_2. For the case of the Zn(e)–p-GaP electrode, the rate of Reaction 7 is approximately equal to that of Reaction 3 or 4, so that substantial amounts of formic acid and CO are produced.

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