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# Photoelectrochemical Reduction of Carbon Dioxide at p-Type Gallium Phosphide Electrodes in the Presence of Crown Ether

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Reduction of carbon dioxide at p-type GaP photocathodes was investigated in lithium carbonate electrolytes. The reduction occurs in competition with hydrogen evolution and its current efficiency is enhanced by dissolving crown ether such as 15-crown-5 in the electrolyte. It is proposed that a chemical reaction pathway is involved in which the reduction of carbon dioxide is initiated by cathodically deposited lithium with formation of the anion radical of carbon dioxide.

Electrochemical reduction of carbon dioxide in aqueous solutions has been investigated by using metal cathodes of high hydrogen-overvoltage such as mercury and lead. Since Teeter and Rysselberghe(1) observed a cathodic wave due to reduction of carbon dioxide in polarograms, many investigators(2–6) have assumed that the electrochemical reduction of carbon dioxide is initiated by accepting single electron to give the anion radical of carbon dioxide. This view was confirmed by reflectance spectroscopy(5) and by measurement of photoemmission current of mercury cathodes in the presence of carbon dioxide.(6) The reduction product at mercury cathodes is in general exclusively formic acid(7) and high current yields for the reduction can be achieved by appropriate choice of electrolysis conditions.(1,4) However, the problem in using metal cathodes is that a large applied voltage of *ca.* 3 V seems to be required, as deduced from reported electrode potentials of the cathode.

Recently, photoelectrochemical reduction of carbon dioxide has been reported by Halmann(8) who used a p-type GaP photocathode to cut down the electrical energy input to a large extent. The photo-assisted reduction of carbon dioxide can also occur, even in the absence of electrical energy input, if heterogeneous reaction systems using semiconductor photocatalysts are employed,(9,10) although the rate of reduction is quite low in this case.

The present study was carried out with a view of elucidating the mechanism of the photoelectrochemical reduction of carbon dioxide at p-type GaP cathodes in lithium carbonate electrolytes. As will be reported in a separate paper,(11) lithium deposits onto illuminated p-type GaP cathodes to give $Li_xGaP$. This phenomenon is noticeable especially in the presence of crown ethers such as 15-crown-5 in the electrolyte. In this paper, it will be shown that the deposited lithium contributes to the reduction of carbon dioxide by providing a chemical reaction pathway in the initial stage of reduction to give the anion radical of carbon dioxide. A chemical reaction mechanism similar to this was postulated for the electrochemical reduction at mercury under a high cathodic bias in the presence of sodium cation, in which carbon dioxide reacts with sodium amalgam,(12) but no confirmative data has been presented. Rather, according to detailed studies by Park *et al.*,(4) such a mechanism is believed to be unlikely in general cases at metal electrodes.

## Experimental

Single crystal wafers of zinc-doped p-type GaP, donated by Sanyo Electric Co., were used as the electrode material. The acceptor concentration determined by the manufacturer was $4\times10^{17}$ cm$^{-3}$, and the (111) face was chosen as the electrode surface. The preparation of the electrode was etched in aqua regia for 2 min, and then washed with deionized water for 15 min.

Current-potential curves were obtained by employing the potential sweep method, in which a potentiostat (Hokuto Denko Model FG-2) and an X-Y recorder (Yokogawa Electric Model 3077) were used. Photoelectrolysis was carried out under potentiostatic control with the charge being measured with an electronic coulometer (Hokuto Denko Model HF-201). Techniques of anodic stripping voltammetry were used for cathodically prepolarized electrodes at a sweep rate of 0.7 V s$^{-1}$ by allowing the relay of the function generator to be excited whenever the cathodic polarization at a fixed potential was just enough to give a desired charge. An SCE served as the reference electrode.

Electrolysis experiments were usually carried out in a 3-compartment cell, and carbon dioxide was continuously bubbled into both the anode and cathode compartments after being saturated with water vapor. In order to collect reduction products, the effluent gas was passed through a trap which was cooled in a mixture of dry ice and acetone. In the case where the production of methane was to be investigated, a sealed 1-compartment cell was used under a carbon dioxide atmosphere.

Quantitative analysis of formic acid, formaldehyde and methanol was carried out for both the electrolyte and residues in the cooled trap. Methanol was analyzed by gas chromatography using a Porapak Q column and a FID detector. Formic acid and formaldehyde were determined by a colorimetric analysis using chromotropic acid.(14) For the analysis of formaldehyde in sample solutions containing either crown ether or $CO_3^{2-}$ or both 4 cm$^3$ of HCl was added to 10 cm$^3$ of sample solution to make the solution acidic. In the case where the solution contained crown ether, it was then distilled to get rid of the crown ether.

Formic acid was indirectly determined by first reducing it to formaldehyde,(15) by which the formaldehyde in sample solutions was increased by the amount corresponding to that of formic acid, and then subtracting the original amount of formaldehyde from the total amount determined. For this purpose, 100 mg of Mg ribbons was dropped into 0.5 cm$^3$ of sample solution and then 0.05 cm$^3$ of HCl was added to the solution ten times at intervals of 1 min, to reduce formic acid to formaldehyde. Analysis of methane was carried out by gas chromatography using a Porapak Q column.

Current yields for the formation of the analyzed components were evaluated on the assumption that they are produced according to the following reduction schemes:

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH, \quad (1)$$

$$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O, \quad (2)$$

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O, \quad (3)$$

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O. \quad (4)$$

Spectroscopic measurements for the chemical reaction of carbon dioxide with lithium were carried out by using a Shimadzu MPS-5000 spectrophotometer. The cell used had a glass capillary through which carbon dioxide was bubbled.

A 500 W super high-pressure mercury arc lamp (Ushio Electric Model UXL-500) served as the light source. Light was collimated, passed through a Toshiba UV-37 filter which cut off lights of wavelengths shorter than 370 nm, and then focused so as to illuminate just the electrode surface. The intensity of the light effective for the excitation of electrode, which covered from 370 to 550 nm, was 0.05 W, as measured with a laser power meter (Coherent Radiation Model 201).

All the chemicals used were of reagent grade and no further purification was made except for the propylene carbonate, which was subjected to distillation under reduced pressure twice before use.

## Results and Discussion

*Current Efficiency for the Formation of Reduction Products.* Figure 1 shows current-potential curves for the illuminated p-type GaP electrode obtained under nitrogen atmospheres in 0.1 mol dm$^{-3}$ 15-crown-5. The crown ether seems to suppress the saturated photocurrent a little, but not to have any other noticeable effects on current-potential curves. A replacement of nitrogen with carbon dioxide in the bubbling gas brought about no marked change in current-potential curves.

The current efficiency for the production of formic acid, formaldehyde, and methanol was obtained with the same electrolytes as those given in Fig. 1 at three different electrode potentials, where photocurrents were greatly different in magnitude from one another. The electrolysis time chosen was 22 h. The results are shown in Fig. 2, from which it is noticed that the efficiency is enhanced by the addition of crown ether to the lithium carbonate electrolyte for all the three kinds of products. No enhancement in the current efficiency is brought about by any decomposition reactions of crown ether, because when an electrolysis was carried out under the same conditions but that an electrolyte of 0.1 mol dm$^{-3}$ LiOH containing 0.1 mol dm$^{-3}$ 15-crown-5 was used under a nitrogen atmosphere, no production of formic acid, formaldehyde, or methanol occurred.

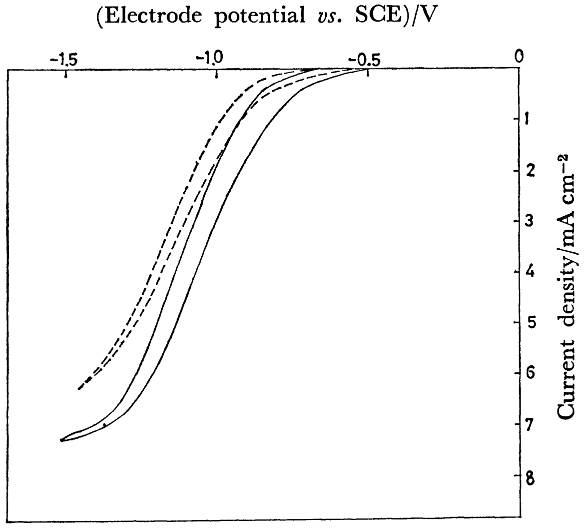

Fig. 1. Current-potential curves of an illuminated p-type GaP electrode under $N_2$ atmospheres in 0.1 mol dm$^{-3}$ $Li_2CO_3$.
- - -: In the presence of 0.1 mol dm$^{-3}$ 15-crown-5, ——: in the absence of the crown ether. Sweep rate: 0.1 V s$^{-1}$.

According to the results given in Fig. 2, the current efficiency for the production of every product de-

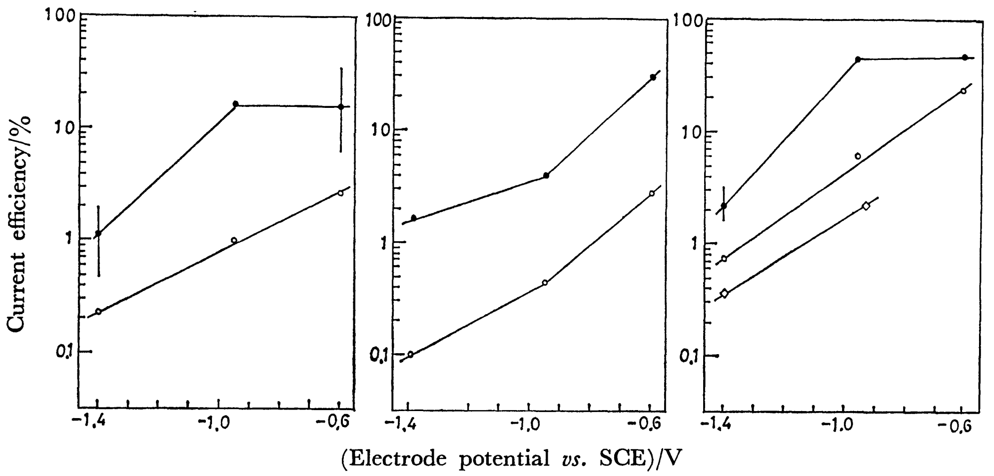

Fig. 2. The current efficiency for the production of formic acid (left), formaldehyde(middle), and methanol (right) as a function of electrode potentials.
—○—: 0.1 mol dm$^{-3}$ $Li_2CO_3$ under bubbling $CO_2$, —●—: 0.1 mol dm$^{-3}$ $Li_2CO_3$ containing 0.1 mol dm$^{-3}$ 15-crown-5 under bubbling $CO_2$, —◇—: 0.1 mol dm$^{-3}$ $Li_2CO_3$ containing 0.1 mol dm$^{-3}$ 15-crown-5 under bubbling $N_2$.

creases with an increase in the cathodic polarization. A replacement of the bubbling gas from carbon dioxide to nitrogen caused a decrease in the current efficiency for the formation of methanol by approximately one order of magnitude, as shown in Fig. 2, which confirms the well estabilished view that major electroactive species is not $CO_3^{2-}$ but $CO_2$.[16,17]

Besides the products given in Fig. 2, methane seems to be formed. Although no systematic investigation has been done, a current efficiency of *ca.* 5% was obtained for an electrolysis at −0.95 V *vs.* SCE in the presence of crown ether. It is characteristic of semiconductor photoelectrodes[8] and photocatalysts[9,10] that several reduction products are simultaneously formed.

Figure 3 shows effects of the concentration of 15-crown-5 on the production of formic acid, formaldehyde, and methanol. It is seen that the current efficiency for every product increases with an increase in the concentration of the crown ether. Since the crown ether affects the photodeposition of lithium in proportion to its concentration,[11] the results shown in this figure give an indication that the efficiency for the reduction of carbon dioxide is closely related to the feasibility of the lithium photodeposition.

*Current Efficiency Obtained in the Presence of 18-Crown-6.* Table 1 shows the current efficiency obtained in the presence of 18-crown-6, together with that obtained in the presence of 15-crown-5. It is seen that the current efficiency for the three kinds of products is higher in 15-crown-5 than in 18-crown-6. This difference seems to be caused by the feasibility of the lithium deposition which takes place in course of the cathodic polarization of electrode. As will be shown in detail in another paper,[11] the amount of deposited lithium increases with an increase in the cathodic charge and decreases with an increase in the molecular dimension of crown ethers. The kind of lithium salt electrolytes is not a problem for appearence of the phenomena. Typical examples of anodic stripping voltammetric waves of a cathodically prepolarized electrode in 0.2 mol $dm^{-3}$ LiOH are given in Fig. 4 for the presence of 15-crown-5 and 18-crown-6. The anodic peak observed in the voltammogram is due to oxidation of the deposited lithium.

It is then speculated that there is a chemical reaction between carbon dioxide and deposited lithium to give the anion radical of carbon dioxide as the initial step of carbon dioxide reduction:

$$Li + CO_2 \longrightarrow Li^+ + CO_2^{\cdot-}. \qquad (5)$$

In order to confirm this idea, the following experi-

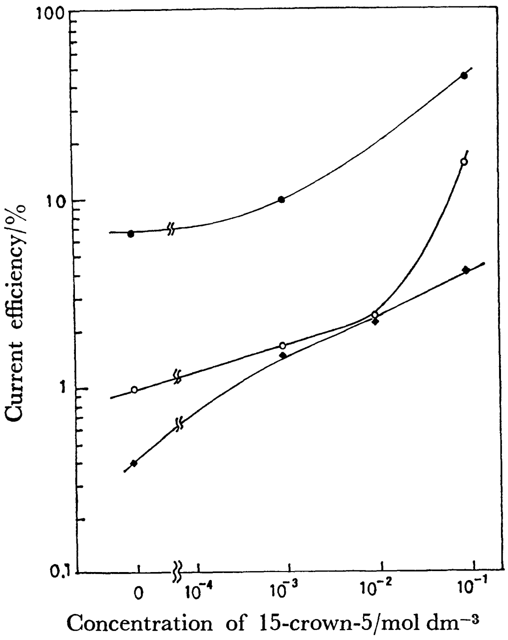

Fig. 3. Effects of the concentration of 15-crown-5 in 0.1 mol $dm^{-3}$ $Li_2CO_3$ on the current efficiency for the production of formic acid (—○—), formaldehyde (—◆—), and methanol (—●—).

TABLE 1. CURRENT EFFICIENCY FOR FORMATION OF FORMIC ACID, FORMALDEHYDE, AND METHANOL[a]

| Electrolyte | Current efficiency/% | | |
|---|---|---|---|
| | Formic acid | Formaldehyde | Methanol |
| 0.1 M[b] 15-Crown-5/ 0.1 M $Li_2CO_3$ | 15 | 4.0 | 44 |
| 0.1 M 18-Crown-6/ 0.1 M $Li_2CO_3$ | 4.8 | u. d.[c] | 6.5 |
| 0.1 M $Li_2CO_3$ | 1.0 | 0.5 | 6.5 |

a) The electrolysis was carried out at −0.95 V *vs.* SCE for 22 h. b) 1 M = 1 mol $dm^{-3}$. c) Undetermined.

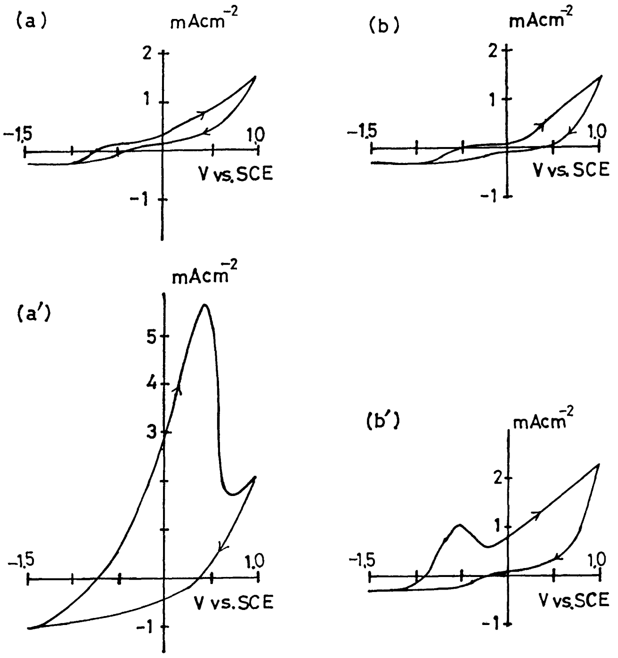

Fig. 4. Anodic stripping voltammograms of cathodically pre-polarized electrodes.
Electrolytes: (a) and (a′) 0.2 mol $dm^{-3}$ LiOH containing 0.1 mol $dm^{-3}$ 15-crown-5. (b) and (b′) 0.2 mol $dm^{-3}$ LiOH. Cathodic pre-polarization charge: (a) and (b) zero (no prepolarization was made), (a′) and (b′) 5.5 C $cm^{-2}$ at −1.5 V *vs.* SCE. Sweep rate: 0.7 V $s^{-1}$. The experiments were carried out under $N_2$ atmospheres.

ments were carried out.

*Spectroscopic Studies on the Chemical Reaction of Carbon Dioxide with Lithium.* If Reaction 5 occurs in aqueous electrolytes, the resulting anion radical will instantly react with water to give formate radical:[4,7]

$$\mathrm{CO_2}^{\overline{\cdot}} + \mathrm{H_2O} \longrightarrow \mathrm{HCO_2}\cdot + \mathrm{OH^-}. \qquad (6)$$

The occurrence of Reaction 5 was then investigated in propylene carbonate solutions by taking absorption spectra characteristic of the anion radical.[5] Figure 5 shows the results obtained with a solution into which carbon dioxide was continuously bubbled. A $CO_2$-saturated propylene carbonate containing 0.1 mol dm$^{-3}$ $LiClO_4$ shows no noticeable absorption in the UV region, but in the presence of lithium metal a strong absorption appeared at 265 nm which is due to $\sigma^* \leftarrow n^*$ transition of the anion radical,[5] confirming the occurrence of Reaction 5.

In order to obtain information on whether or not the deposited lithium can easily reduce formic acid to formaldehyde, similar experiments were carried out in propylene carbonate. Formic acid gave the absorption maxima at *ca.* 220 nm and formaldehyde at *ca.* 275 nm in a broad absorption band, as shown in Fig. 6. When a piece of lithium was dropped in propylene carbonate containing 64 mmol dm$^{-3}$ formic acid and shaken vigorously under an air-tight condition for 10 min, the resulting solution gave an enhancement of the broad absorption due to formaldehyde. Simultaneously, the absorption due to formic acid was weakened. When the propylene carbonate solution initially contained a small amount of water (0.025 cm$^3$/10 cm$^3$ propylene carbonate), the absorption at 275 nm was much stronger.

Judging from these results, the reduction of formic acid to formaldehyde with lithium is likely to occur in the course of photoelectrochemical reduction of $CO_2$ at illuminated GaP cathodes:

$$\mathrm{HCOO^-} + 2\mathrm{Li} + 2\mathrm{H_2O} \longrightarrow \mathrm{HCOOH} + 2\mathrm{LiOH} + \mathrm{OH^-}. \qquad (7)$$

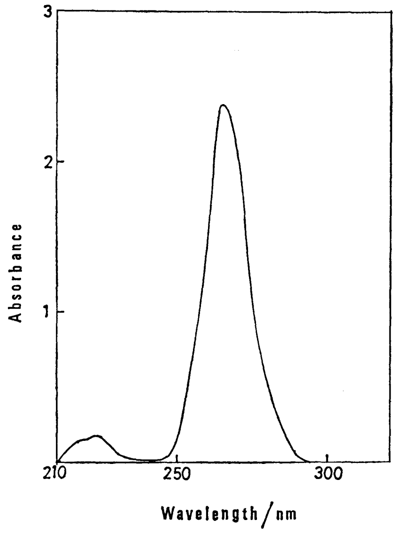

Fig. 5. An absorption spectrum showing the formation of $\mathrm{CO_2}^{\overline{\cdot}}$ by chemical reaction of $CO_2$ with lithium in propylene carbonate.

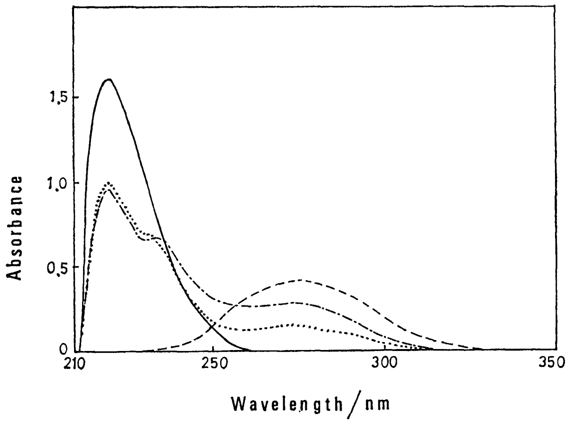

Fig. 6. Change in absorption spectra of formic acid in propylene carbonate by addition of a piece of lithium.
——: 64 mmol dm$^{-3}$ HCOOH, ······: after adding a piece of lithium to 64 mmol dm$^{-3}$ HCOOH, ----: after adding a piece of lithium and 0.025 µdm$^3$ of $H_2O$ to 10 cm$^3$ of 64 mmol dm$^{-3}$ HCOOH, — —: 30 mmol dm$^{-3}$ HCHO.

In this section, we have discussed chemical reaction paths for the production of analytically determined species. However, it seems important to stress here that the reduction of carbon dioxide by purely electrochemical processes[7] is not excluded, at least in cases where no crown ether is dissolved in the electrolyte.

*Energy Conversion Efficiency.* The energy conversion efficiency for the photoproduction of carbon dioxide was estimated for the results given in Fig. 2 by using the following equations:

$$\eta_{\mathrm{ph}} = \frac{[\Sigma n_i \Delta G_i^0 - VC]}{W_{\mathrm{ph}} t} \times 100, \qquad (8)$$

where $n_i$ is the number of moles of produced species $i$, $\Delta G_i$ have been evaluated as

$$\mathrm{CO_2} + \mathrm{H_2O} \longrightarrow \mathrm{HCOOH} + 1/2\mathrm{O_2} \qquad \Delta G^0 = 270.1\ \mathrm{kJ\ mol^{-1}}, \qquad (9)$$

$$\mathrm{CO_2} + \mathrm{H_2O} \longrightarrow \mathrm{HCHO} + \mathrm{O_2} \qquad \Delta G^0 = 521.7\ \mathrm{kJ\ mol^{-1}}, \qquad (10)$$

$$\mathrm{CO_2} + 2\mathrm{H_2O} \longrightarrow \mathrm{CH_3OH} + 3/2\mathrm{O_2} \qquad \Delta G^0 = 702.5\ \mathrm{kJ\ mol^{-1}}. \qquad (11)$$

$V$ is the applied voltage between the anode and cathode, $C$ is the amount of charge consumed in the electrolysis for 22 h, $W_{\mathrm{ph}}$ is the optical energy input which was 0.05 W for incident photons effective for the excitation of electrode, and $t$ the electrolysis time, 22 h. The experiments for Fig. 2 were carried out by controlling the photocathode potential but not the anode potential. In the present estimation of energy conversion efficiency, however, the anode potential needs to be evaluated, and this value was assumed here to be 0.52 V *vs.* SCE on the assumption of the oxygen overvoltage at the anode being 0.2 V, which will be achieved at the best anode (DSA) for the current density region chosen in the present study.

Table 2 gives calculated results for the total amount of formic acid, formaldehyde, and methanol produced.

TABLE 2. ENERGY CONVERSION EFFICIENCY FOR PHOTOELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE IN A CELL USING A p-TYPE GALLIUM PHOSPHIDE CATHODE[a)]

| Electrolyte | $E_{\text{cathode}}$ vs. SCE | $q$ | Appl. V[b)] | $VC$ | $\Sigma n_i \Delta G_i^0$ | $W_{\text{ph}}$ | $\eta_{\text{ph}}$ | $\eta_{\text{t}}$ |
|---|---|---|---|---|---|---|---|---|
| | V | C | V | J | J | J | % | % |
| 0.1 M 15-Crown-5/ 0.1 M $Li_2CO_3$ | −0.6 | 0.78 | 1.12 | 0.87 | 0.90 | 3960 | $9.1\times10^{-4}$ | $2.3\times10^{-2}$ |
| | −0.95 | 1.7 | 1.47 | 2.5 | 1.40 | 3960 | — | $3.5\times10^{-2}$ |
| | −1.40 | 37.4 | 1.92 | 71.6 | 3.20 | 3960 | — | $8.0\times10^{-2}$ |
| 0.1 M $Li_2CO_3$ | −0.6 | 0.93 | 1.12 | 1.04 | 0.59 | 3960 | — | $1.4\times10^{-2}$ |
| | −0.95 | 11.3 | 1.47 | 16.6 | 1.10 | 3960 | — | $2.8\times10^{-2}$ |
| | −1.4 | 134 | 1.92 | 257.4 | 1.50 | 3960 | — | $3.5\times10^{-2}$ |

a) The efficiency was obtained for the production of formic acid, formaldehyde, and methanol. b) Applied voltage between the anode and cathode. An overpotential of 0.2 V was assumed for the oxygen evolution reaction at the anode.

The production of methane was neglected in this case, but this is not serious for the present purpose of estimating a rough order of conversion efficiency, because the methane production is believed to be minor. According to the obtained results which are given in Table 2, storage of optical energy was achieved only for one case where the electrolysis was carried out at −0.6 V *vs.* SCE in the presence of 15-crown-5. The estimated conversion efficiency in this case was as low as $9.1\times10^{-4}\%$, which has no practical significance. In the other cases, the electrical energy input was found to exceed the sum of chemical energies produced.

Then, another measure for the total energy conversion efficiency was defined by Eq. 12, which gives the ratio of stored chemical energy to total energy input consumed for obtaining the chemicals in question:

$$\eta_t = \frac{\Sigma n_i \Delta G_i^0}{VC + W_{\text{ph}} t} \times 100. \tag{12}$$

Results obtained by applying this equation are also shown in Table 2, which indicates that the efficiency is still low even if estimated in this measure.

As indicated in Table 2, the principal cause responsible for such low conversion efficiencies is low utilization of optical energy in producing cathodic photocurrents. The low utilization is, of course, inevitable for the electrolysis at potentials where saturated photocurrents are not attained. Judging from the results shown in Fig. 1, the electrolysis at −0.6 V, for example, will give a relative utilization of optical energy of less than one twentieth that at −1.4 V. Furthermore, a gradual decrease in photocurrent, which occurs in the course of electrolysis, is very serious. If one estimates the average photocurrent in the electrolysis by dividing the amount of measured charges by the electrolysis time (22 h), the following values are obtained: 27.6 μA $cm^{-2}$ at −0.6 V, 62.9 μA $cm^{-2}$ at −0.95 V, and 1.38 mA $cm^{-2}$ at −1.4 V *vs.* SCE. If these values are compared with those given in Fig. 1, it will be noticed that the degradation of electrode is serious. The major cause for bringing about such degradation is believed to be due to the incorporation of lithium which causes a noticeable decrease in quantum yield of photocurrent in the intrinsic absorption region.[11)] Similar degradation, though to a less extent, is in general caused to occur at p-type GaP photocathodes by impregnation of hydrogen.[13)] In order to achieve a high conversion efficiency of optical energy, such unstable behavior of photocathodes should be avoided.

Judging from the results given in Fig. 2, the sum of the current efficiencies for the production of formic acid, formaldehyde, and methanol is less than 100%, indicating that a hydrogen evolution took place competitively. Since hydrogen is a useful fuel which can store optical energy, $\eta_t$ was again calculated for the whole cathodic reactions including the hydrogen evolution from the results shown in Table 2 on the assumption that 100% efficiency will be attained for the production of formic acid, formaldehyde, methanol, and hydrogen. The results obtained in the presence of the crown ether were $2.55\times10^{-2}$, $5.4\times10^{-2}$, and 1.1% for the cathodic potentials −0.6, −0.95, and −1.4 V, respectively, while in the absence of the crown ether $\eta_t$ was $2.5\times10^{-2}$, 0.35, and 3.9% at −0.6, −0.95, and −1.4 V, respectively. The observed increase in $\eta_t$ with an increase in the cathodic polarization in this case simply reflects the tendency that both the quantum yield of cathodic photocurrents and the current efficiency for the hydrogen evolution will increase with increasing cathodic polarization.

In the present study, unsatisfactory results were obtained in the point of energy conversion efficiency for the reduction of carbon dioxide. The results obtained, however, have revealed that carbon dioxide can be reduced at −0.6 V *vs.* SCE at p-type GaP photocathodes with current efficiency enhanced by addition of crown ether to lithium salt electrolyte. This implies that replacement of conventional metal cathodes by the present systems can save us more than 1 V of electrical energy input for the carbon dioxide reduction.

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