CHEMISTRY LETTERS, pp. 539 - 542, 1985.

PHOTOELECTROCHEMICAL REDUCTION OF CARBON MONOXIDE ON IRON(II) TETRAPHENYLPORPHYRIN-COATED p-TYPE GaP ELECTRODES

Hiroshi YONEYAMA,* Koichi WAKAMOTO, Nobuyuki HATANAKA,
and Hideo TAMURA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-oka 2-1, Suita, Osaka 565

Reduction of CO to methanol was achieved with the current efficiency of ca. 10% at p-type GaP photocathodes coated with heat-treated 5,10,15,20-tetraphenylporphyrinatoiron(II).

Electrochemical reduction of CO does not easily occur in aqueous solutions: hydrogen evolution preferentially takes place under conventioanl electrolysis conditions. A low solubility of CO in the electrolyte solutions seems to be one of the principal causes for this. To our knowledge, any successful result has not been published yet.1) Referring to recent interests in C_1 chemistry and in the development of photoelectrochemical cells suitable for solar energy utilization, it will be of interest to find out a novel approach for photoelectrochemical reduction of CO to useful chemicals. In this communication, we would like to report one promising approach in which p-type GaP (p-GaP) as a photocathode was coated with 5,10,15,20-tetraphenylporphyrinatoiron(II) (Fe(II)TPP). It is well-known that Fe(II) in FeTPP binds CO reversibly.2) The use of FeTPP-coated electrodes will then be effective in enhancing the surface concentration of CO, resulting in high yields of the reduction products.

The electrode substrates used were p-GaP wafers and glassy carbon plates. One of their end faces was coated with a 10^{-2} mol dm^{-3} FeTPP/chloroform solution, and then the solvent was evaporated at room temperature. The procedure was repeated several times finally to give the total amount of the coated FeTPP of 5×10^{-7} mol cm^{-2}. In order to improve conductance of the coated film, the film-coated electrodes were heated at 500 °C in Ar for 10 min. The characterization of heat-treated porphyrins was already reported for cobalt porphyrins.3)

Electrolysis experiments were carried out in 0.5 mol dm^{-3} H_2SO_4 at a fixed current density of 0.5 mA cm^{-2} using a 2-compartment cell divided by an ion exchange membrane (Nafion). During the electrolysis, CO was bubbled into the catholyte, and the effuluent gases were fed first to a dry ice/acetone trap to collect methanol and formaldehyde, and then to a liquid nitrogen trap to collect methane. Analyses of the products were carried out both for these traps and for the catholyte. Methanol was determined by steam chromatography using a Porapak Q column at 150 °C. Gas chromatography with the use of an activated charcoal column at 60 °C was applied to determine methane. Formaldehyde was determined by colorimetry using chromotropic acid. A 500 W xenon lamp was used as a light source. The electrodes were illuminated with light of wavelengths longer than 390 nm.

Current-potential (I-E) curves of the prepared electrodes are shown in Fig. 1. The onset potential of cathodic photocurrents were different among the electrodes used and was positive in the following order; p-GaP > heat-treated FeTPP-coated p-GaP > unheated FeTPP-coated p-GaP > heat-treated FeTPP-coated glassy carbon. The improvement in the onset potential brought about by the heat-treatment is believed to be due to a decrease in resistance of the coated film. The photosensitization effect of p-GaP is remarkable from comparison of I-E curves of the FeTPP-coated p-GaP with those of FeTPP-coated glassy carbon. The heat-treated FeTPP film alone did not show any appreciable photosensitivity to the light from the xenon lamp, and the unheated film also made negligible contribution to the photosensitization.4)

If consecutive reduction of CO occurs, formaldehyde, methanol, and methane will be produced, but formaldehyde was not detected. Methane was always produced, but its amount was less than 1% of the current efficiency. As a result, methanol was exclusively produced. Table 1 summarizes the results on the methanol production. The current efficiency was determined by dividing the charge consumed in the methanol production with the total electrolysis charge on the assumption that the production of a methanol molecule required four electrons.

The coating of p-GaP with heat-treated FeTPP was found to be effective in enhancing the methanol production. The current efficiency of ca. 10% was achieved. The obtained values of the current efficiency, however, suggest that the major reaction was not CO reduction but hydrogen evolution. The heat-treated film was porous, allowing hydrogen evolution at the p-GaP surface, and accumulated hydrogen bubbles at the film/GaP interface caused the removal of the coated film which led to the disappearence of the effect of FeTPP coating. An increase in the photocurrents with repeating potential sweeps, which is shown in Fig. 1 for the heat-treated FeTPP-coated p-GaP electrode, is also related to the removal of the coated film with potential sweep cycles.

The current efficiency at the unheated FeTPP-coated p-GaP was comparable with that obtained at the bare p-GaP, suggesting that the electrode reactions took place preferentially at the GaP substrate surface with involvement of the electrolyte solution that was supplied there by penetration through the film. The coated film in that case had so high a resistance as to block the transport of photo-

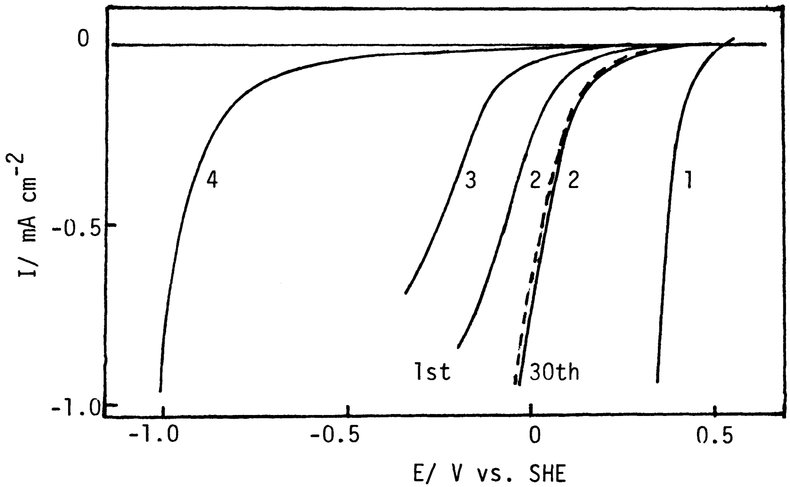

Fig. 1. I-E curves in 0.5 mol dm^{-3} H_2SO_4 at 0.1 V s^{-1} in the presence (—) and absence (– –) of CO. Electrode: bare p-GaP (1), heat-treated FeTPP-coated p-GaP (2), unheated FeTPP-coated p-GaP (3), and heat-treated FeTPP-coated glassy carbon (4). The cycle number of the potential sweeps is given for the electrode (2).

Table 1. Electrochemical reduction of carbon monoxide to methanol on p-type GaP and glassy carbon electrodes with and without coated FeTPP film

Electrode Coated film/Substrate	Charge consumed in electrolysis	Potential vs. SHEa)		Current efficiency
		Initial	Final	
	C	V		%
p-GaP	30	0.35	0.40	3.2
FeTPP/p-GaP	30	-0.23	0.25	3.5
FeTPP/p-GaP	5			4.2
(ht)FeTPP/p-GaPb)	30	-0.05	0.25	10.9
(ht)FeTPP/p-GaP	9			10.9
(ht)FeTPP/p-GaP	3			8.3
(ht)CoTPP/p-GaP	30	-0.05	0.25	2.4
(ht)FeTPP/glassy carbon	30	-0.90	-0.95	5.5
glassy carbon	30	-0.90	-0.95	1.2

a) The electrode potential in an initial stage and a final stage of the constant current electrolysis at 0.5 mA cm^{-2}. b) The notation (ht) denotes the heat-treatment.

generated electrons to the outermost surface of the coated FeTPP. As shown in the table, the heat-treated CoTPP-coated p-GaP gave a poor activity for the methanol production. The result seems to be reasonable from the viewpoint that CO does not make any definite interaction with Co in CoTPP.5)

The CO reduction is thought to proceed with a scheme shown in Fig. 2 which is based on a well-established view on the charge transport mechanism in redox polymer-coated electrodes.6) The postulated reaction scheme will be valid when the following energetic correlations are fulfilled : the potential of the bottom of the conduction band is more negative than the redox potential of Fe(II)TPP/Fe(III)TPP, and the latter is negative of the electrode potential of CO/CH_3OH. In Fig. 3, the energetic correlation of electrochemical reactions, the coated film, and the GaP substrate is shown, from which it is noticed that the energetic requirement for the methanol production is met at the FeTPP-coated p-GaP electrodes. It seems important, however, to describe here the assumptions taken in illustating Fig. 3. The redox potential of Fe(II)TPP/Fe(III)TPP is assumed to be equal to that obtained at meso-tetrakis(4-sulfonatophenyl)porpyrin-iron dissolved in aqueous solutions.7) This assumption will not contain any serious error unless the heat-treatment causes a dramatic change in redox chemistry of FeTPP, because the redox potential of metal ions coordinated to the porphyrin ring is not greatly different among a variety of porphyrinato ligands.8) The standard electrode potential of CO/CH_3OH shown in the figure is that derived from calculation based on ΔG^0 of CO and methanol. The interaction of CO with FeTPP will cause some

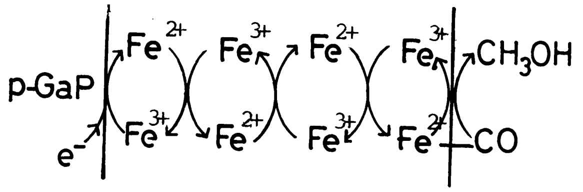

Fig. 2. Redox mechanisms involved in reduction of CO at FeTPP-coated p-GaP electrode.

change in the electrode potential of CO/CH_3OH, but if its change is not large enough to upset the energetic correlation shown in Fig. 3, the CO reduction is then said to be energetically feasible.

It is possible to construct a photoelectrochemical cell using a heat-treated FeTPP-coated p-GaP as a cathode and a hydrogen electrode as an anode. The maximum open circuit photovoltage to be expected, however, is as small as 0.35 V for the photon energy input greater than 2.3 eV, giving no practical significance. What we would like to stress here is that the results obtained in this study have significance in showing one promising approach for electrochemical reduction of CO. A higher current efficiency for the methanol production than those shown in this paper will be achieved if one find a novel method to prepare more adhesive and more tight FeTPP coating.

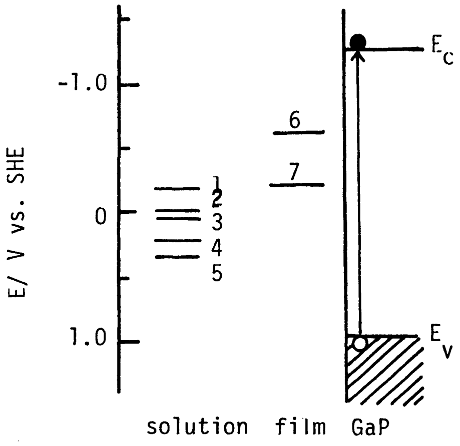

Fig. 3. Energetic correlation of electrochemical reactions concerned with CO reduction, coated porphyrin film, and p-GaP. Standard electrode potentials: CO/ HCHO (1), H^+/H_2 (2), CO/CH_3OH (3), CH_3OH/CH_4 (4). HCHO/ CH_3OH (5), Fe(II)TPP/ Fe(III)TPP (6), and Co(II)TPP/ Co(III)TPP (7). E_c and E_v denote the bottom of the conduction band and the top of the valence band, respectively.

This work was supported by a Grant-in-Aid for Scientific Research, No. 59550551, from the Ministry of Education, Science and Culture.

References

1) J-P. Randin, "Encyclopedia of Electrochemistry of the Elements," ed by A. J. Bard, Dekker, New York (1978), Vol. VII , p. 152.
2) B. K. James, "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1978), Vol. V, p. 209.
3) K. Weisner and A. Fuhrman, Z. Phys. Chem. (Leipzig)., 261, 411 (1980); K. Okabayashi, O. Ikeda, and H. Tamura, Chem. Lett., 1982, 1659.
4) H. Yoneyama, H. Shiota, and H. Tamura, J. Electroanal. Chem., 159, 361 (1983).
5) B. M. Hofman, T. Szymaski, and F. Basolo, J. Am. Chem. Soc., 97, 673 (1975); B. B. Wayland, J. Minkiewicz, and M. E. Abd-Elmageed, ibid., 96, 2795 (1974).
6) R. W. Murray, "Electroanalytical Chemistry," ed by A. J. Bard, Dekker, New York (1984), Vol. 13, p. 191.
7) O. Ikeda, K. Okabayashi, N. Yoshida, and H. Tamura, To be published.
8) R. H. Helton, "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1978), Vol. V, p. 52.

(Received December 8, 1984)