Visible Light-assisted Electrochemical Reduction of Oxygen at a Platinum Electrode Coated with Surface Active Cobalt(II) and Manganese(III) Porphyrins

By YOSHIO UMEZAWA* and TAKESHI YAMAMURA
(*Department of Chemistry, University of Tokyo, Hongo, Tokyo, Japan*)

Summary Visible light-assisted oxygen reduction with no applied potential was performed at a platinum electrode coated with surface active Co^{II} and Mn^{III} porphyrins.

CATALYTIC electrochemical reduction of oxygen is of importance for fuel cell applications. Some porphyrins, phthalocyanine complexes, and haem have been used for the catalytic electroreduction of oxygen.[1,2] Platinum is so far believed to be the most appropriate material for oxygen catalysis; the reduction of oxygen occurs at about $-0{\cdot}2$ V *vs.* the saturated calomel electrode (SCE) at a platinum electrode.

In this study, visible light-assisted electrochemical reduction of oxygen with no applied potential was performed using a platinum electrode coated with surface active Co^{II} and Mn^{III} porphyrins. As expected, the platinum electrode coated with surface active porphyrins was found to behave like a chemically modified electrode[3] having stable and novel photoactive characteristics.

The compounds used were the Co^{II} and Mn^{II} complexes of tetrakis-(*N*-stearylpyridinium)porphyrin tetraiodide monohydrate, $[M^{II}(stpy_4p)]I_4{\cdot}H_2O$ (M = Co or Mn), see Figure 1. The synthesis of these compounds has been described elsewhere.[4] In a typical experiment, about 1×10^{15} molecules of each compound were deposited on a clean polished Pt disc ($0{\cdot}2$ cm^2 in area) sealed in soft glass, by allowing 10 μl of a 5×10^{-4} M solution of the compound in MeOH–$CHCl_3$ (1 : 2 vol. %) to evaporate on the surface of the Pt disc. The Pt–$Co^{II}(stpy_4p)I_4$ and Pt–Mn^{III}-$(stpy_4p)I_4$ electrodes thus constructed were immersed in a $0{\cdot}1$ M aqueous solution of tetraethylammonium perchlorate (TEAP). The porphyrin layers on these electrodes were fairly stable with no indication of photodecomposition or of dissolution. The auxiliary electrode was a Pt coil. The reference electrode was a saturated calomel electrode (SCE) with an agar–KCl salt bridge. The oxygen content in the solution was measured by a TOA Model DO-IA oxygen

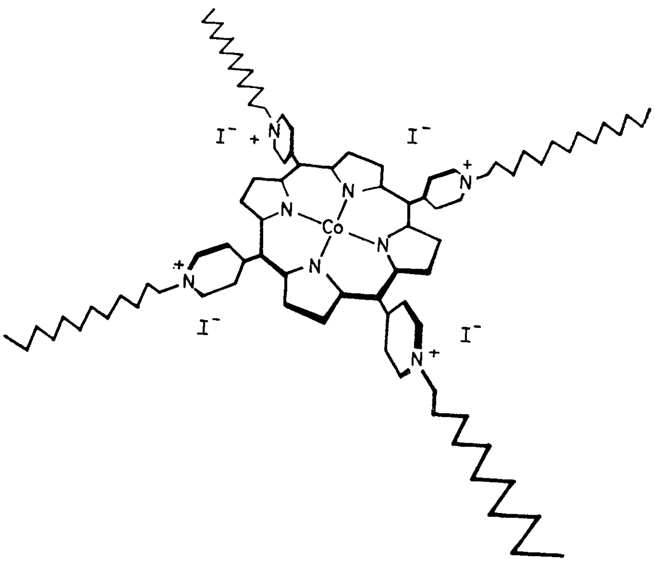

FIGURE 1. Structure of the surface active M^{II} porphyrins (see text) (M = Co or Mn). Double bonds have been omitted for clarity.

meter. When required, oxygen was completely eliminated by exhaustively degassing sample solutions with bubbling argon. Photocurrents were measured with a PAR Model 173 potentiostat and a Takeda Model TR-8651 electrometer. A focused light beam from a 750 W tungsten lamp was applied to the electrode surface through a quartz window underneath.

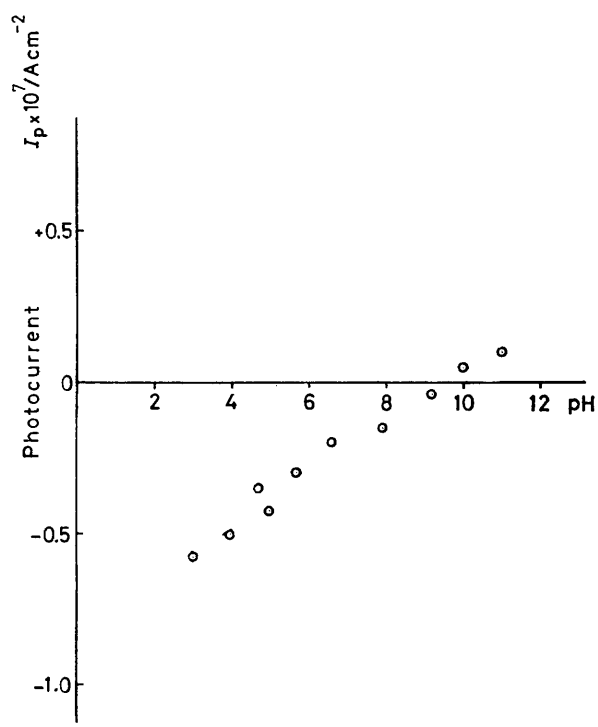

FIGURE 2. The pH dependence of photocurrents at the Pt–Co^{II}(stpy$_4$p)I_4 electrode at 0 V (SCE).

Figure 2 shows the pH dependence of a steady photocurrent at a Pt–Co^{II}(stpy$_4$p)I_4 electrode in the absence of dissolved oxygen. In the acidic region, the photocurrent is cathodic and is roughly proportional to the pH values. In the alkaline region, the observed photocurrent is anodic and is roughly proportional to pOH. Figure 3 shows the dependence of photocurrent at a Pt–Co^{II}(stpy$_4$p)I_4 electrode on the concentration of dissolved oxygen. Initial anodic photocurrents decreased with oxygen concentration to become cathodic at [O_2] *ca.* 2 p.p.m. Similar behaviour was observed at a Pt–Mn^{III}(stpy$_4$p)I_4 electrode. At acidic pH values, the original cathodic photocurrent increased in proportion to the oxygen concentration.

Upon irradiation with visible light, charge separation occurs at the surface of the Co^{II} or Mn^{III} porphyrin layers, forming the cations and anions of these porphyrins, M–P$^+$ and M–P$^-$ [see equation (1)]. The species thus formed

$$2\text{M–P} \rightarrow \text{M–P}^+ + \text{M–P}^- \qquad (1)$$

may then react with redox systems in solution according to equations (2), (3), and (4). The accumulated charge of

$$2\text{M–P}^+ + OH^- \longrightarrow O_2 \text{ or } H_2O_2 + \text{M–P} \qquad (2)$$
(anodic photocurrent)

$$\text{M–P}^- + H^+ \longrightarrow H\cdot \text{ or } H_2 + \text{M–P} \qquad (3)$$
(cathodic photocurrent)

$$2\text{M–P}^- + O_2 \longrightarrow H_2O_2 + \text{M–P} \qquad (4)$$
(cathodic photocurrent)

opposite sign in the membrane during each reaction is neutralized by electron transfer from/to the counter electrode through the substrate Pt electrode. This results in continuous rather than transient photocurrents. In alkaline and acidic regions, reactions (2) and (3) respectively, become dominant. This may explain the result of Figure 2. Electron transfer from M–P$^-$ to oxygen molecules is allowed thermodynamically and takes place *via* reaction (4). The behaviour in Figure 3 is a result of competition between reactions (2) and (4).

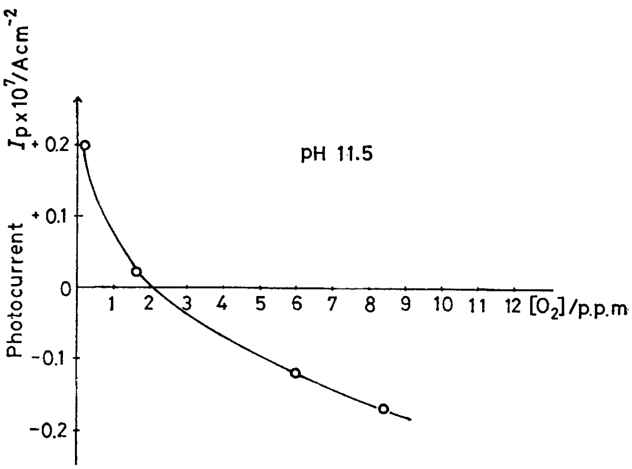

FIGURE 3. Dependence of photocurrent on the concentration of oxygen at the Pt–Co^{II} (stpy$_4$p)I_4 electrode at 0 V (SCE).

In conclusion, molecular oxygen was catalytically reduced at 0 V applied potential *via* reaction (4) on a Pt electrode coated with surface active Co^{II} and Mn^{III} porphyrins.

We thank Profs. S. Fujiwara and Y. Sasaki for their continuous encouragement and support.

(*Received*, *30th August* 1978; *Com.* 940.)

---

[1] For example, M. R. Tarasevich, K. A. Radiyschkina, and S. I. Androuseva, *Bioelectrochem. and Bioenerg.*, 1977, **4**, 18.

[2] C. F. Kolpin and H. S. Swofford, Jr., *Analyt. Chem.*, 1978, **50**, 920.

[3] For example, J. C. Lennox and R. W. Murray, *J. Amer. Chem. Soc.*, 1978, **100**, 3710; J. F. Evans, T. Kuwana, M. T. Henne, and G. P. Royer, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1977, **80**, 409, and references cited therein.

[4] T. Yamamura, *Chem. Letters*, 1977, 773.