Conducting Polymer Film Electrodes with Immobilized Catalytic Sites

Fumio Mizutani,* Sei-ichiro Iijima, Yoshikazu Tanabe, and Keishiro Tsuda

Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan

Small particles (*e.g.* platinum black) or neutral molecules [*e.g.* cobalt(II) *meso*-tetraphenylporphine] have been immobilized as catalytic sites in a conducting polymer film electrode consisting of polypyrrole–poly(vinyl chloride) alloy.

Electrically conducting polymer films, such as polypyrrole (PPy) film, with immobilized catalytic sites have been attracting much interest in electrochemistry, since they are expected to exhibit unique characteristics as three-dimensional electrocatalysts.[1] However, there are only two methods for preparing such films: one based on electrochemical doping of anionic catalysts during the deposition of PPy[1,2] and that based on covalent attachment of catalysts onto PPy films.[3] We describe here a new method which is suitable for the immobilization of particles or molecules in the conducting polymer phase; the catalysts are first immobilized in poly(vinyl chloride) (PVC) film and, secondly, the insulating PVC matrix is converted into a conducting one of PPy–PVC alloy.

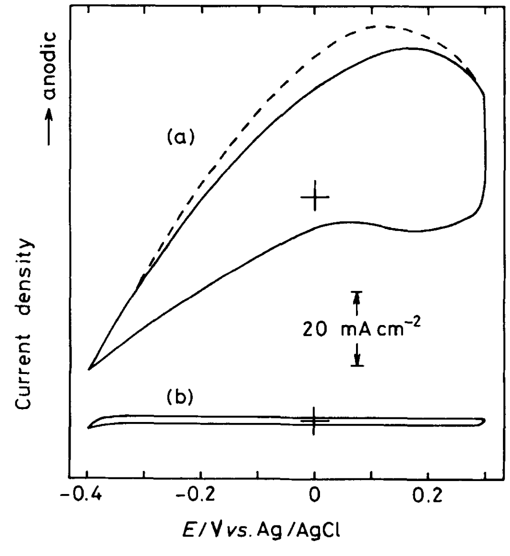

Figure 1. Cyclic voltammograms for proton–hydrogen redox system in 0.1 M $HClO_4$ of two types of electrode: (a) Pt black (2 mg cm^{-2})-containing PPy–PVC and (b) PPy–PVC. — in (a), Ar sat.; - - - in (a) H_2 sat.; — in (b), Ar or H_2 sat. Scan rate, 50 mV s^{-1}.

The catalysts employed in the present work are platinum black, cobalt(II) phthalocyanine (CoPc), and cobalt(II) *meso*-tetraphenylporphine (CoTPP). The catalysts (1—40 mg) were separately mixed with PVC solutions (1 mg of PVC in 1 ml of tetrahydrofuran), so as to form a dispersion (containing Pt black or CoPc) or a solution (containing CoTPP). The dispersion or solution (2—10 µl) was spread on a glassy carbon electrode (0.2 cm^2 in area) and then dried. In order to convert the PVC matrix into a conducting PPy–PVC alloy,[4] the glassy carbon electrode coated with the catalyst–PVC composite was used as a working electrode for the oxidative polymerization of pyrrole under the following conditions: electrolytic solution, acetonitrile containing 0.1 M pyrrole and 0.3 M $LiClO_4$; current density, 0.3 mA cm^{-2} for Pt black and CoPc, 1.0 mA cm^{-2} for CoTPP; charge passed, 0.1—0.2 C cm^{-2}. The higher current density in the case of CoTPP was employed in order to shorten the duration of electrolysis, since CoTPP dissolved slowly in the acetonitrile solution. The electrolysis caused a marked enhancement in conductivity of the film on the glassy carbon electrode. For example, an insulating CoPc-containing PVC film (conductivity $<10^{-9}$ S cm^{-1}) yielded a conducting system (*ca.* 10 S cm^{-1}).

Figure 1 shows cyclic voltammograms for the proton–hydrogen redox system on the glassy carbon electrodes coated with (a) Pt black-containing PPy–PVC and (b) PPy–PVC. The introduction of Pt black on the electrode caused it to become redox-active. The generation of hydrogen, which was observed if the potential of the electrode in (a) reached −0.3 V *vs.* Ag/AgCl, did not damage the film on the glassy carbon electrode.

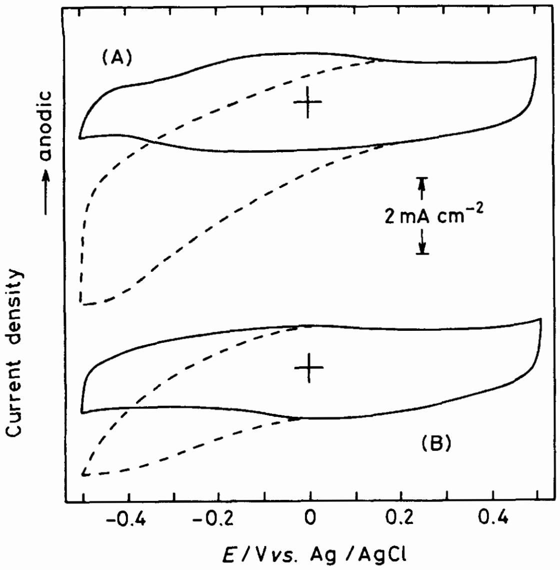

Figure 2. Cyclic voltammograms for oxygen reduction (—, Ar sat.; - - -, O_2 sat.) in 0.1 M $HClO_4$ of two types of electrode: (A) CoTPP (*ca.* 0.1 mg cm^{-2})-containing PPy–PVC and (B) PPy–PVC. Scan rate, 50 mV s^{-1}.

Figure 2 shows cyclic voltammograms for oxygen reduction on the glassy carbon electrode coated with (A) CoTPP-containing PPy–PVC and (B) PPy–PVC. The electrode in (A) showed a higher activity for oxygen reduction than that in (B). Reduction on the electrode in (A) was observed at a potential *ca.* 0.25 V higher than that on the electrode in (B).

The glassy carbon electrode coated with CoPc-containing PPy–PVC showed catalytic activity for various reactions, such as reduction of oxygen, reduction and oxidation of H_2O_2, and oxidation of –SH groups (*e.g.* mercaptoethanol).

In conclusion, we have developed a simple and widely applicable method for immobilization of catalysts in conducting polymer films.

Received, 30th July 1985; Com. 1122

References

1 R. A. Bull, F. R. Fan, and A. J. Bard, *J. Electrochem. Soc.*, 1984, **131**, 687.
2 K. Okabayashi, O. Ikeda, and H. Tamura, *J. Chem. Soc., Chem. Commun.*, 1983, 684.
3 M. V. Rosenthal, T. Skotheim, and J. Warren, *J. Chem. Soc., Chem. Commun.*, 1985, 342.
4 O. Niwa and T. Tamamura, *J. Chem. Soc., Chem. Commun.*, 1984, 817.