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Preparation of Poly (*N*-Ether Group Substituted Pyrrole) Film-Coated Electrode Incorporating Microparticle Metals

Nobuhiro TAKANO*, Masahito NAKABAYASHI and Noboru TAKENO

Received July 17, 1995 ; Accepted August 23, 1995

1 INTRODUCTION

Recently the electrically conducting polymers having polyether chain have been attracted interest, because these polymers are expected for applications in ion-selective electrodes, membranes and ionic conductor of batteries¹. On the other hand, metal particles incorporated in the polymer-modified electrodes have been recognized to have potential applications in electrocatalytic reaction². We have previously reported the palladium microparticles incorporated poly (*N*-linear alkyl substituted pyrrole) film electrodes for electrocatalytic hydrogenation³. The introduction of ionic conductor into matrix is required to improve the ability of polymer electrode in electrocatalytic hydrogenation. We report herein the preparation and characterization of poly (*N*-ether group substituted pyrrole) film electrodes (2a and 2b) incorporating precious metals such as Pt, Pd, and Au.

2 EXPERIMENTAL

As shown in Scheme 1 the monomers, ether group substituted pyrrole 1a and 1b were prepared by the conventional methods. 1a : 90 °C / 1 torr (Kugelrolle), ¹H NMR(270 MHz, CDCl₃-DMSO-*d*₆) δ 3.20 (s, 1H, -OH), 3.51 (t, 2H, *J*=5Hz, -CH₂OH), 3.65 (t, 2H, *J*=5Hz, -CH₂O-), 3.74 (t, 2H, *J*=6Hz, -CH₂O-), 4.06 (t, 2H, *J*=5Hz, >NCH₂-), 6.11 (t, 2H, *J*=2Hz, Pyrrole), 6.71 (t, 2H, *J*=2Hz, Pyrrole). IR (neat) 3415, 2927, 2873, 1500, 1439, 1356, 1286, 1128, 1092, 1070, 731, 619 cm⁻¹. 1b: 130 °C / 2 torr (Kugelrolle), ¹H NMR (270 MHz, CDCl₃ - DMSO - *d*₆) δ 3.07 (s, 1H, -OH),

3.52 ~ 3.55 (m, 6H, >NCH₂CH₂O-, -OCH₂-CH₂OH), 3.58 ~ 3.73 (m, 4H, -OCH₂CH₂O-), 4.03 (t, 2H, *J*=5.6, >NCH₂-), 6.10 (t, 2H, *J*=2Hz, Pyrrole), 6.68 (t, 2H, *J*=2Hz, Pyrrole). IR(neat) 3433, 2873, 1500, 1456, 1352, 1286, 1120, 1090, 729, 619 cm⁻¹.

Scheme 1

The coating of polymer film 2a and 2b on glassy carbon disk (Area : 0.071cm²) was carried out by potential sweep between 0 and 1.1 V vs. SCE (saturated calomel electrode) or controlled-potential electrolysis at 1.1 V in CH₃CN containing 10 mmol dm⁻³ monomers and 0.1 mol dm⁻³ Bu₄NBF₄. The incorporation of metal in films was conducted according to the previously reported procedures³. The quantity of palladium metal in film was determined by the electroreduction method in 0.1 mol dm⁻³ KCl

Department of Applied Chemistry, Muroran Institute of Technology (27-1 Mizumoto-cho, Muroran 050, Japan)

Key Words: Metal Microparticles Incorporation, Polymer Film Electrode

solution. The current-voltage curves were measured by a linear sweep potential method.

3 RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms of prepared monomers, *N*-(5-hydroxy, 3-oxapentyl) pyrrole **1a** and *N*-(8-hydroxy, 3, 6-dioxaoctyl) pyrrole **1b** in CH_3CN containing Bu_4NBF_4 . These voltammograms show gradual increase in one redox peak couple at *ca.* 0.5 V in the successive cycles, as already observed for poly [*N*-(5-hydroxypentyl) pyrrole] film (PHPy)³. These couples corresponded to the anion BF_4^- doping-dedoping process. The resulting electropolymerized films exhibited considerable stability with slight decrease of peak current when cyclic potential sweep experiments were performed in the potential range of 0 to 0.8 V in an electrolyte solution free of monomer. The incorporation of catalytic metals into the polymer films which were prepared by the controlled-potential electrolysis method was performed by immersion treatment in a 50 mmol dm^{-3} Na_2PdCl_4 , K_2PtCl_4 , and KAuCl_4 solution and followed by the electrochemical reduction of permeated anions in films. The catalytic metals were more incorporated in film **2a** than **2b**. The amount of palladium metal was less than *ca.* 10 ~ 20 % compared with the case of PHPy.

Fig. 1 Cyclic voltammograms of 10 mmol dm^{-3} **1a** (a) and **1b** (b) on glassy carbon disk electrode in 0.1 mol dm^{-3} Bu_4NBF_4 - CH_3CN solution. Scan rate 100 mV s^{-1} .

The amount of metals incorporated in film **2b**, which was formed under the polymerization electricity $Q = 0.14 \text{ C cm}^{-2}$, increased in order of Au ($14 \mu\text{g cm}^{-2}$), Pd ($7.0 \mu\text{g cm}^{-2}$), and Pt ($4.4 \mu\text{g cm}^{-2}$) and was proportional to the thickness of films. These behaviors show that the ether oxygen atoms in chains dose not greatly contribute to the incorporation of anions. The penetrations of the metal chloride anions, PdCl_4^{2-} , PtCl_4^{2-} , and AuCl_4^- into film may be interfered by the electron-repulsion between them and lone paired electrons of oxygen atoms.

As shown in Figure 2, when the current-voltage curves for metals incorporated polymer film **2b** electrode in a 0.1 mol dm^{-3} HClO_4 aqueous solution were measured, steep rise in cathodic currents based on hydrogen evolution were observed at *ca.* -0.4 ~ -0.5 V. The potentials of the H^+ reduction to H_2 for catalytic film electrodes were shifted in order of Pt, Pd, and Au to cathodic potential side. This order agreed with that of hydrogen overvoltage of metals in aqueous solution. It is of interest that using these catalytic film electrodes H^+ was

Fig. 2 Cathodic current-voltage curves for hydrogen evolution of metal incorporated polymer film **2b** electrodes in 0.1 mol dm^{-3} HClO_4 solution. Scan rate 20 mV s^{-1} . a) : Pt ($4.4 \mu\text{g cm}^{-2}$), b) : Pd ($7.0 \mu\text{g cm}^{-2}$), c) : Au ($14 \mu\text{g cm}^{-2}$) incorporated film electrode, d) : film electrode.

reduced at lower potential in spite of the metals were less incorporated in the film.

The current-voltage curves for palladium metal incorporated polymer film **2a**, **2b**, and

Fig. 3 Cathodic current-voltage curves for hydrogen evolution of Pd metal incorporated polymer film electrodes in 0.1 mol dm⁻³ HCl buffer solution (pH=1) containing 50 % ethanol. Scan rate 100 mV s⁻¹. a) : **2a** (8.4 μg cm⁻²), b) : **2b** (7.0 μg cm⁻²), c) : PHPy (9.3 μg cm⁻²) film electrode.

PHPy electrodes in 0.1 mol dm⁻³ HCl buffer solution (pH = 1) containing 50 % ethanol are shown in Fig. 3. The current-voltage characteristics similar to those measured in the HClO₄ solution were observed. The film **2a** and **2b** electrodes showed highly catalytic activity compared with PHPy. This result suggests that the migration of proton as hydrogen source is enhanced by the presence of etheral chains in matrix film.

Further research is in progress in our laboratories for development of an electrocatalytic hydrogenation for organic compounds using these catalytic film electrodes.

This work was supported by Grant-in-Aid for Scientific Research on Priority Area (No.236) from the Ministry of Education, Science and Culture of Japan.

REFERENCES

- 1) J. Roncali, R. Garreau, D. Delabouglise, F. Garnier and M. Lemaire, *J. Chem. Soc., Chem. Commun.*, **1989**, 679; J. Roncali, H. K. Youssoufi, R. Garreau, F. Garnier and M. Lemaire, *J. Chem. Soc., Chem. Commun.*, **1990**, 414.
- 2) W-H. Kao and T. Kuwana, *J. Am. Chem. Soc.*, **106**, 473 (1984); D.E. Bartak, B. Kazee, K. Shimazu and T. Kuwana *Anal. Chem.*, **58**, 2756 (1986); T. Yamada, T. Osa and T. Matsue, *Chem. Lett.*, **1987**, 1611.
- 3) N. Takano, M. Nakabayashi and N. Takeno, *Denki Kagaku*, **62**, 1238 (1994).