

Macromolecular Research

Volume 10, Number 4 August 31, 2002

© Copyright 2002 by The Polymer Society of Korea

Preparation and Comparative Test of Polypyrrole Electrodes for Direct Methanol Fuel Cell

Jae-Chan Park and Jeong Soo Kim*

Department of Polymer Science and Engineering, Chungnam National University, Yuseong, Taejeon 305-764, Korea

Doo Hwan Jung

Korea Institute of Energy Research (KIER), P.O.Box 103, Yuseong, Taejeon 305-343, Korea

Received Oct. 26, 2001 ; Revised June 5, 2002

Abstract: The displacement of carbon black to polypyrrole as a catalyst supporter in the fuel electrode of a direct methanol fuel cell was investigated. Polypyrrole was obtained as a black powder by the chemical polymerization of pyrrole with three different oxidants. The synthesized polypyrroles were pasted on carbon paper and transformed to the fuel electrodes with electrochemically deposited platinum. The prepared fuel electrode was assembled and mounted in a unit cell using a membrane and cathodic electrode film. In comparison with the carbon black fuel electrode, the performance of the unit cell was analyzed in relation to the state of the catalyst, the type of oxidant, and the morphology of the polypyrrole powder.

Keywords : polypyrrole electrode, direct methanol fuel cell (DMFC).

Introduction

Polymer electrolyte membrane fuel cells (PEMFC) including the direct methanol fuel cell (DMFC) is a promising power source for use as a portable electronic apparatus, electric vehicles, and transport applications, because they do not require any fuel processing equipment and can be operated with a higher efficiency at low temperatures. However,

there are still some challenging problems. These include their low electrocatalytic activities and potential poisoning of the catalysts at the anode by the adsorbed carboxyl species derived from the methanol oxidation.¹⁻³ Multi-component Pt-catalytic systems containing small amounts of Sn, Ru, or WO have been studied extensively in order to enhance the catalytic activities and lower the level of poisoning in the anodic catalysts. Another method to improve the catalytic power is to fabricate the electrodes by a dispersion of a precious metal in a polymer matrix.

Some conducting polymers such as polypyrrole (PPy),

*e-mail : jskim@cuvic.cnu.ac.kr

polyaniline and polythiophene are desirable systems to support highly dispersed platinum particles.⁴⁻⁶ Such conducting polymers used as supportors of catalyst in an electrode are usually conductive and have porous structure that can accommodate the dispersed catalyst with the large surface area that is necessary for efficient electrocatalysis.⁷ Recently, some studies have investigated the incorporation of transition metal (e.g., Pt, Pd, Ru, Sn) microparticles in a conducting polymer-coated electrode which exhibits enhanced electrocatalytic activities when compared to pure metal electrodes in the oxidation of small organic molecules.^{8,9} The increase in the catalytic activities is reported to be the result of a decrease in poisoning and the synergistic effects of a conducting polymer with metal microparticles. Other studies have reported the electrocatalytic activity of platinum microparticles dispersed in polyaniline and poly(N-methylpyrrole) composite films with Nafion on the electrooxidation of methanol.^{8,9}

In this paper, the electrocatalytic oxidation of methanol at polypyrrole electrodes containing platinum microparticles is reported. Polypyrrole was chemically polymerized by oxidants such as ferric chloride (FC, FeCl_3), ammonium persulfate (AP, $(\text{NH}_4)_2\text{S}_2\text{O}_8$), and oxygen (OX) in order to develop better electrode materials. The polypyrrole electrode layer where the platinum microparticles were dispersed was prepared by the electroreductive deposition of a platinum compound. The electrochemical oxidation of methanol at the electrode was observed using a cyclic voltammogram. Finally, a single cell was fabricated and the I-V characteristics for a direct methanol fuel cell were estimated.

Experimental

Materials. TGP-H-090 carbon paper from Toray was used as the supporting material for the polypyrrole powder. The air electrode used was a 60 wt% Pt/CB electrode from E-tek using Vulcan XC-72 carbon black (CB). H_2PtCl_6 (8 wt% solution) and perchloric acid were purchased from Aldrich. A poly(tetrafluoroethylene) (PTFE) suspension (60%) was added by preparing the electrode to enhance the water-repulsing property of the electrode. A perfluorinated ion-exchange resin (Nafion[®]) (5 wt%) was used for the binding of the polypyrrole slurry. The ferric chloride and ammonium persulfate, which were used as the oxidants for the chemical polymerization of pyrrole, were supplied as analytical grade by Aldrich. The pyrrole was a reagent grade from Aldrich. Propylene carbonate and methanol were obtained from Duksan, and were used without further purification. Water was purified by distillation and ion exchange.

Synthesis of Polypyrrole. Since the polymerization of pyrrole with oxidants is a well-known method,¹¹ only the remarkable differences in the synthetic methods and procedures used here are described. To a solution of 56.33 g (0.35 mole) ferric chloride dissolved in 150 mL methanol, 10 g

(0.15 mole) of pyrrole was added dropwise for 30 minutes. The reaction slurry was filtered and washed with water and methanol followed by vacuum desiccation at 40°C. In using ammonium persulfate oxidant, 6.8 g (0.03 mole) of ammonium persulfate was dissolved in 300 mL water and then 10 g (0.15 mole) of the pyrrole was added dropwise. The other procedures were the same as the previous one. In the oxidation of pyrrole with oxygen, a catalytic amount of ferric chloride (4.2×10^{-3} mole) was dissolved in 200 mL of water and polymerization was performed in an oxygen atmosphere for 2 days.

Preparation of Pt/PPy Fuel Electrode. The carbon paper supporter of the polypyrrole powder was immersed in 5 wt% of PTFE suspension for 30 seconds, dried at room temperature for 1 day, and treated in a 350°C oven for 25 minutes. The polypyrrole (0.2 g) powder was stirred for 1 day in c.a. 2 mL of isopropyl alcohol containing 0.2 g of a 5 wt% Nafion solution. The prepared polypyrrole slurry was coated on carbon paper and dried at 80°C. A platinum catalyst was ankered at the polypyrrole film by electrochemical reduction in 1 M perchloric acid containing 5 mmole of H_2PtCl_6 .⁸

Preparation of Pt/CB Air Electrode. This cathode of membrane electrode assembly (MEA) was fabricated from 60 wt% Pt/CB catalyst and had 3.0 mg/cm² Pt loading.

Pretreatment of Nafion Membrane. Nafion 115 from Du Pont (130 μm thick and 1,100 g/eq) was selected as the separating proton conductor in MEA. This proton conducting membrane was treated by the well-known method.³

The Preparation of MEA. The fuel and air electrode were hot-pressed with a separating Nafion membrane at 135°C and 1,000 psi for 10 minutes.

SEM. The SEM images were obtained with XA 30S FEG from Philips.

Methanol Oxidation with Half Cell. Methanol oxidation with a fuel electrode was investigated with an electrochemical cell in 1 M perchloric acid, which was equipped with a SCE and Pt counter electrode and combined with an EG&G 273A electrochemical analyser.

I-V Characteristics of Unit Cell. The prepared MEA was inserted into the unit cell, mounted on a test station, and analyzed according to the conventional testing method. The methanol flow at the fuel electrode was set at 2 mL/min at 1 kg/cm² and the oxygen flow on the cathode was 300 mL/min at 1.5 kg/cm².

Results and Discussion

Conductive polymers as supporting materials for platinum catalysts in PEMFC have been reported in several articles in the last decade.^{2,3} The fabrication of conductive polymer films have usually been performed by the direct electrochemical polymerization on a supporter or by spin coating of a polymer solution. In this study, a more practical method was selected to prepare the electrodes where supporter films

were formed by a direct coating of the polypyrrole slurry. The polypyrrole powder was successfully obtained by polymerizing the pyrrole with different oxidants such as ferric chloride, ammonium persulfate, and oxygen.¹⁰ The polymer films morphology plays an important role in the catalytic power for fuel oxidation and the crossover of fuel such as methanol.

Pyrrole polymerization with chemical oxidants is a simple and conventional synthetic method.¹¹ The structures of the synthesized polypyrroles were confirmed by IR spectra and no significant differences were observed among the samples synthesized using different oxidants.

Cyclic voltammograms of the polypyrroles containing platinum particles was investigated as shown in Figure 1 and Figure 2. At the sample codes in all the figures, the numerals coming after the Pt- denote the platinum loading levels ($\mu\text{g}/\text{cm}^2$) and the abbreviations after PPy- denote the oxidants used in the chemical synthesis of the polypyrrole. The Pt loading level calculated from the integrated current may differ from the exact analytical quantity of Pt on the electrode film. For the comparative test on the methanol oxidation performance, a conventional carbon black electrode containing platinum was prepared and used as the reference. As shown in Figure 3, the peak current through the oxidation of methanol was observed at 0.62 V in the anodic scanning region and 0.45 V in the cathodic scanning region, which are different in their strong asymmetric shape from usual cyclic voltammograms related to cyclic oxidation and reduction. The current increased with increasing platinum loading, which indicates the catalytic role of the platinum in methanol oxidation. As shown in Figure 1, the asymmetric cyclic voltammograms were also observed with the PPy-AP electrodes, although the currents were lower than the electrodes from the CB. The PPy-FC electrodes were analogous to the PPy-AP electrodes in terms of the cyclic voltammogram

shape and current density. However, the PPy-OX electrodes showed a much lower current than the PPy-AP electrodes, as shown in Figure 2, while strong asymmetrical cyclic voltammograms were also observed.

Figure 4 shows the cyclic voltammogram of different polypyrrole electrodes with the same Pt loading levels ($150 \mu\text{g}/\text{cm}^2$). The potentials for methanol oxidation were also similar to the prototype carbon black electrode, which shows a similar strong asymmetric oxidative current irrespective of the scanning direction. However, the current density of the polypyrrole electrode for methanol oxidation was much lower than that in the carbon black electrode. This inferiority of the synthesized polypyrrole electrode is thought to be the result of various factors including chemical and physical poisoning, defects, and the irregular morphology of the base powder. For a better understanding of this phenomenon, more detailed and reproducible experiments should be con-

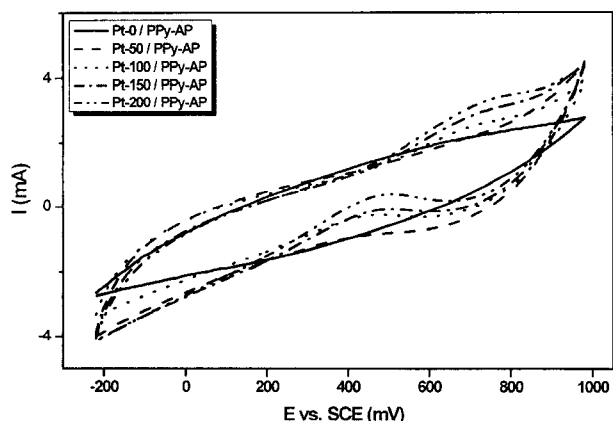


Figure 1. Cyclic voltammograms of a 1.0 M methanol + 1.0 M HClO_4 aq. solution on the polypyrrole electrode with different Pt loading levels ($\mu\text{g}/\text{cm}^2$) and at a scan speed of 25 mVs^{-1} . Polypyrrole was synthesized with ammonium persulfate as the oxidant.

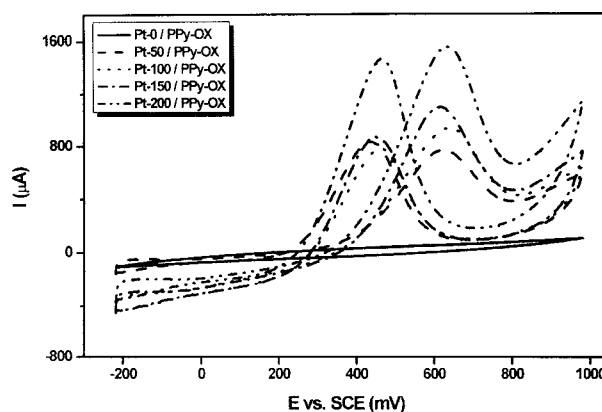


Figure 2. Cyclic voltammograms of a 1.0 M methanol + 1.0 M HClO_4 aq. solution on the polypyrrole electrode with various Pt loading levels ($\mu\text{g}/\text{cm}^2$) and at a scan speed of 25 mVs^{-1} . Polypyrrole was synthesized with oxygen as the oxidant.

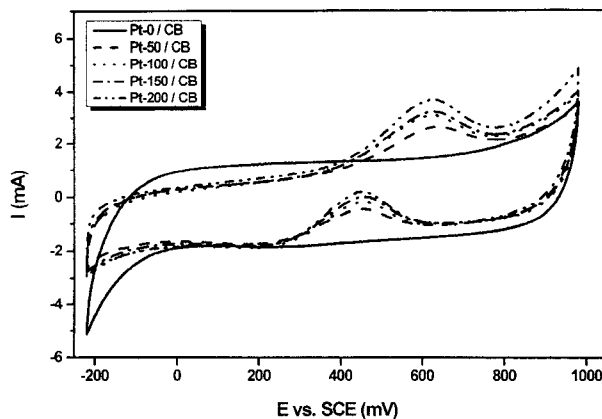


Figure 3. Cyclic voltammograms of a 1.0 M methanol + 1.0 M HClO_4 aq. solution on a conventional carbon black electrode with various Pt loading levels ($\mu\text{g}/\text{cm}^2$) and at a scan speed of 25 mVs^{-1} .

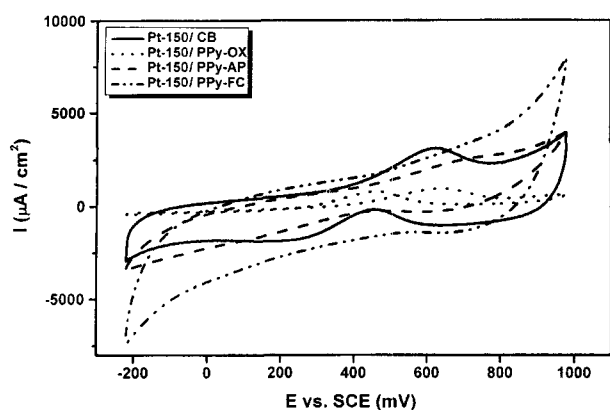


Figure 4. Cyclic voltammograms of a 1.0 M methanol + 1.0 M HClO₄ aq. solution on carbon black and polypyrrole electrodes that were synthesized with the different oxidants. The Pt loading level was held at a constant 150 μg/cm² and the scan speed was 25 mVs⁻¹.

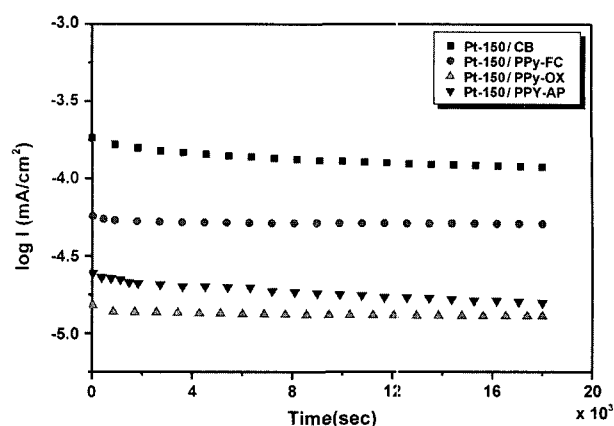


Figure 5. The stability of the current density for the oxidation of the 1.0 M methanol + 1.0 M HClO₄ aq. solution on various electrodes. The Pt loading level was held at a constant 150 μg/cm² and the applied potential was 500 mV.

ducted. The polypyrrole synthesized with oxygen as the oxidant showed a relatively lower activity when transformed to the fuel electrode supporter for methanol oxidation. Figure 5 shows the current stability of the prepared electrodes for methanol oxidation. The prepared polypyrrole electrode had a comparable stability with the conventional carbon black electrode, although it showed a lower current density.

The morphology of the electrode films was investigated using SEM. In this study, all the platinum particles were formed on carbon black or polypyrrole by electroreduction

of an aqueous solution of H₂PtCl₆. Figure 6 shows the SEM photomicrographs of the electrodes, which were used as the basic supporter of carbon black or the different polypyrroles. The diameters of the platinum particles in the electrodes were much larger than that of the commercially available catalyst, which has a diameter of 40-50 nm. The polypyrrole films were observed to have much rougher surface than carbon black irrespective of the oxidants used. In addition, the platinum catalyst particles at the polypyrrole films were also relatively larger than those at the carbon black, which were assumed to be cause of the lower catalytic activities of

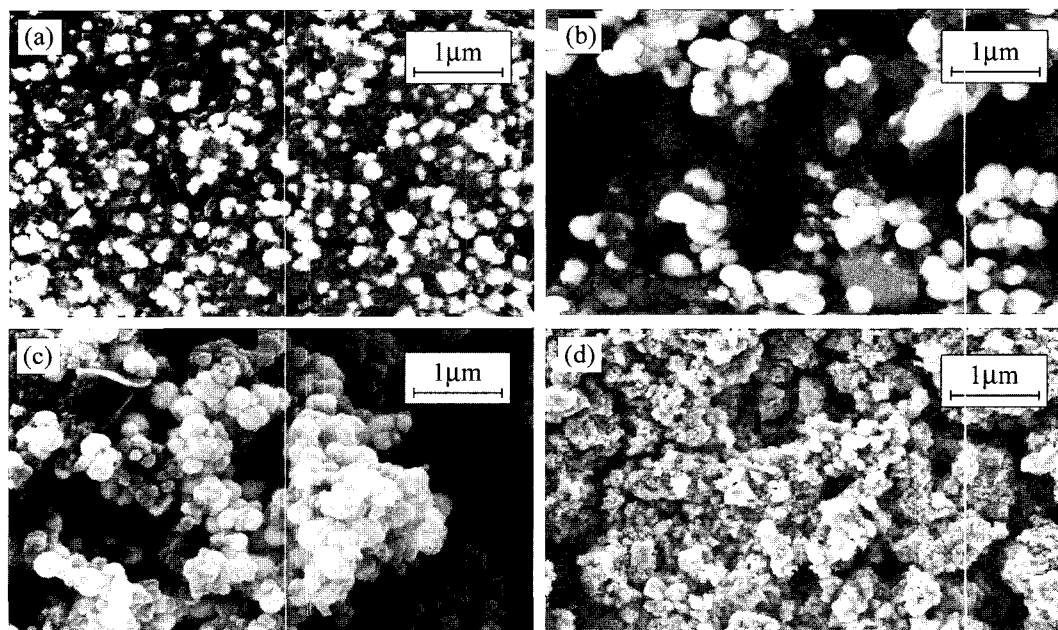


Figure 6. SEM micrograph of the carbon black electrode and polypyrroles; (a) Pt-150/CB, (b) Pt-150/PPy-AP, (c) Pt-150/PPy-FC, and (d) Pt-150/PPy-OX.

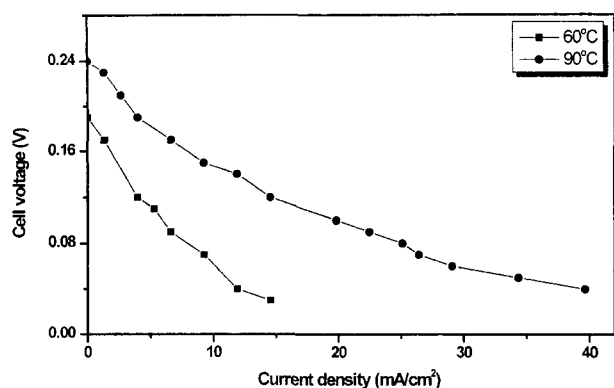


Figure 7. I-V plot of the direct methanol unit fuel cell fabricated with a carbon black electrode Pt-1000/CB. The other operating conditions are detailed in the experimental section.

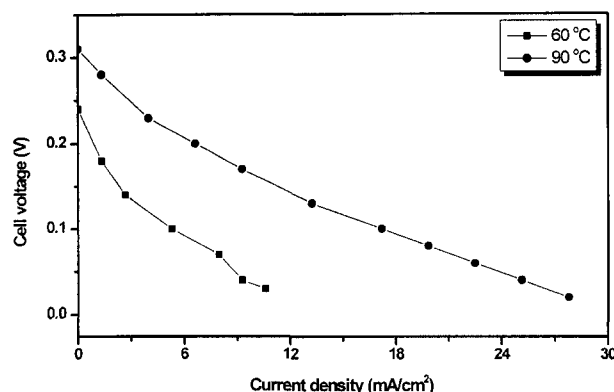


Figure 8. I-V plot of the direct methanol unit fuel cell fabricated with the prepared polypyrrole electrode Pt-1000/PPy-FC. The other operating conditions are detailed in the experimental part.

the polypyrrole electrodes compared to the carbon black electrode.

The electrodes prepared from the polypyrrole using oxygen as the oxidant exhibited a different surface shape. We could not find any spherical particles of platinum on the electrode surfaces, as shown in (d) of Figure 6, although they showed very weak catalytic activities for methanol oxidation. From these observations, it is deduced that shape of the platinum in the electrodes plays a dominant role on the catalytic activity.

The performance of the unit cell using the anodic supporter of polypyrrole was comparatively investigated with the I-V characteristics. Figure 7 and Figure 8 show the I-V characteristics of the unit cell that was assembled with a fuel electrode from the carbon black and PPy-FC respectively. Both unit cells show a typical current shape, which is characterized by an increasing current density with decreasing cell voltage and increasing temperature. Figure 9 shows a summarized performance of the unit cells composed of the

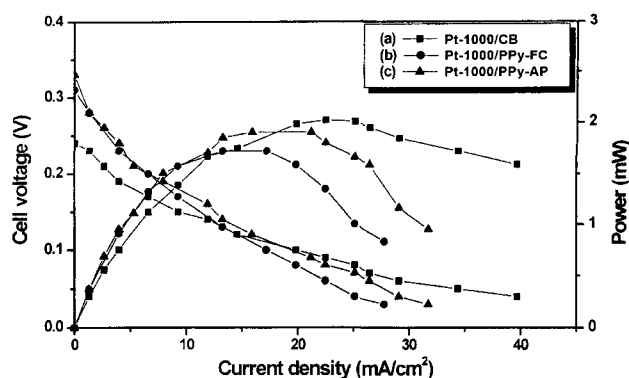


Figure 9. I-V and output power plot of the direct methanol unit fuel cell fabricated with carbon black and various polypyrrole electrodes. The anode was (a) Pt-1000/CB, (b) Pt-1000/PPy-FC, and (c) Pt-1000/PPy-AP. The other operating conditions are detailed in the experimental part.

fuel electrodes that were based on carbon black and the synthesized polypyrroles.

The performance of the unit cell fabricated from the prepared polypyrrole was inferior in current density and power output to the conventional carbon black. The inferiority of polypyrrole as an electrode base material in DMFC resulted mainly from the narrow surface area of the synthesized polymer and the large particle size of platinum that was electrodeposited on the synthesized polypyrrole. These drawbacks are expected to be overcome with a more precise and controlled synthesis and electrodeposition of the platinum catalyst.

Conclusions

The conducting polypyrrole can be easily polymerized and prepared in a powder form by the chemical oxidation of pyrrole, which was applied as the supporting material in the PEMFC or DMFC fuel electrodes. The platinum catalyst was electrodeposited directly on the supporting polymer. The performance of the fuel electrode is critically dependent on the morphology of the supporting polymer and the physicochemical state of the catalyst deposited on it. The smooth and high porous polymer matrix with a small and uniform platinum catalyst dispersed over its surface is recommended in order to enhance the performance of the MEA.

References

- (1) A. R. Landgrebe, R. K. Sen, and D. J. Wheeler, *Direct Methanol-air Fuel Cells*, The Electrochemical Society Inc., Pennington, 1992.
- (2) S. Gottesfeld, G. Halpert, and A. Landgrebe, *Proton Conducting Membrane Fuel Cells I*, The Electrochemical Society Inc., Pennington, 1995.

- (3) S. Gottesfeld and T. F. Fuller, *Proton Conducting Membrane Fuel Cells II*, The Electrochemical Society Inc., Pennington, 1999.
- (4) F. T. A. Vork, L. J. J. Janssen, and E. Barendrecht, *Electrochim. Acta*, **31**, 1569 (1986).
- (5) S. Holdcroft and B. L. Funt, *J. Electroanal. Chem.*, **240**, 89 (1988).
- (6) K. S. Ryu, S. H. Chang, S.-K. Kwon, Y.-H. Kim, and D.-H. Hwang, *Macromol. Res.*, **10**, 40 (2002).
- (7) J.-S. Park and J. S. Kim, *Korea Polym. J.*, **9**, 179 (2001).
- (8) H. Laborde, J.-M. Léger, and C. Lamy, *J. Appl. Electrochem.*, **24**, 219 (1994).
- (9) P. O. Esteban, J.-M. Léger, and C. Lamy, *J. Appl. Electrochem.*, **19**, 462 (1989).
- (10) S. Machida, S. Miyata, and A. Techagumpuch, *Synthetic Metals*, **31**, 311 (1989).
- (11) J. Rodríguez, H.-J. Grande, and T. F. Otero, in *Organic Conductive Molecules and Polymers*, H. S. Nalwa, Eds., John Wiley & Sons, Chichester, 1997, Vol. 2, pp 416-442.