Short Communication

Electrochemical characteristics of polyaniline synthesized by various methods

Koji Nishio [a], Masahisa Fujimoto [a], Noriyuki Yoshinaga [a], Osamu Ando [b], Hitoshi Ono [b], Tetsuro Murayama [b]

[a] *New Materials Research Center, Sanyo Electric Co. Ltd., 1-18-13, Hashiridani, Hirakata, Osaka 573, Japan*
[b] *Yokohama Research Center, Mitsubishi Chemical Corporation, 1000 Kamoshida-cho, Aobaku, Yokohama 227, Japan*

Abstract

The influence of polymerization conditions on the electrochemical properties and morphology of polyaniline are studied. It is found that the charge/discharge performance of chemically synthesized polyaniline is greatly influenced by the oxidizing reagents used for the polymerization. $Cu(BF_4)_2$ and $Fe(ClO_4)_3$ are particularly suitable reagents. Protons in the reaction media exert a strong influence on the morphology and electrochemical properties of polyaniline in both chemical and electrochemical polymerization processes. A novel process for chemically synthesizing polyaniline is developed to obtain polyaniline with superior electrochemical properties. In this process, polyaniline/HBF_4 salt is oxidized with $Cu(BF_4)_2$/acetonitrile and produces fibrous polyaniline with good doping/undoping reversibility.

Keywords: Polyaniline; Conductive polymers

1. Introduction

Conductive polymers have been studied extensively as possible electrode materials for lithium secondary batteries. Among them, polyaniline has attracted much attention because of its high discharge capacity and good stability [1–3].

To date, electrochemical polymerization has been used for the synthesis of polyaniline as an electrode material [4–10]. By contrast, there have been fewer studies of the chemical synthesis of polyaniline [11–14]. In this research, chemical polymerization conditions are investigated to obtain polyaniline with good charge and discharge performances. Electrochemical polymerization is also studied to clarify the effect of protons in the polymerization media; the reaction conditions are controlled more easily here than in the chemical synthesis.

2. Experimental

Polyaniline was chemically synthesized with the use of potassium persulfate ($K_2S_2O_8$), ferric chloride ($FeCl_3$), ferric perchlorate ($Fe(ClO_4)_3$), and cupric tetrafluoroborate ($Cu(BF_4)_2$) as oxidizing reagents for the polymerization.

Each oxidizing reagent solution was added to the monomer that had been dissolved in water or acetonitrile. Crude polyaniline was purified by washing with water or organic solvents. The electrochemical properties of the chemically synthesized polyaniline were measured in the form of pressed pellets with a diameter of 10 mm.

Electrochemical polymerization was carried out on a stainless-steel plate (1 cm^2) in a solution containing perchloric acid ($HClO_4$) and an aniline monomer. A constant current of 0.5 mA cm^{-2} was used.

The surface of the polyaniline was observed by a scanning electron microscope (SEM) Hitachi, Model S-570.

A beaker-type test cell was employed for the electrochemical measurements. Propylene carbonate (PC) containing 1 M $LiClO_4$ or $LiBF_4$ was used as the electrolyte solution. Charging and discharging were conducted at constant current over a voltage range of 2.5 to 4.5 V. The cyclic voltammograms were measured at a sweep rate of 60 mV min^{-1}.

3. Results and discussion

3.1. Influence of oxidizing reagents on the electrochemical behaviour of chemically synthesized polyaniline

The influence of the oxidizing reagent used for the chemical polymerization was investigated. A black powder of
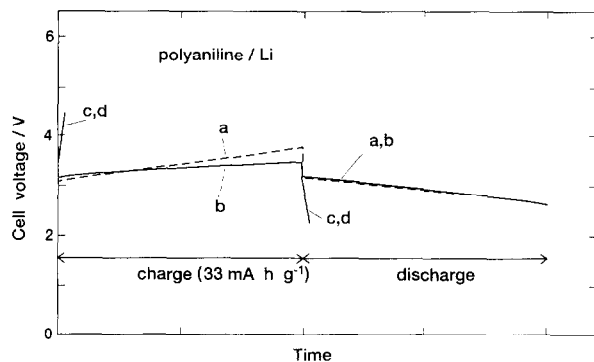
Fig. 1. Charge/discharge characteristics of polyaniline/Li cells using chemically synthesized polyaniline. Oxidizing reagent for polymerization: (a) $Fe(ClO_4)_3$; (b) $Cu(BF_4)_2$; (c) $K_2S_2O_8$; (d) $FeCl_3$. Electrolyte: 1 M $LiBF_4$/PC. Charge/discharge current density = 0.64 mA cm^{-2}.

polyaniline was obtained by using $K_2S_2O_8$, $FeCl_3$, $Fe(ClO_4)_3$, or $Cu(BF_4)_2$ as an oxidizing reagent. Fig. 1 shows the charge/discharge characteristics of test cells using polyaniline as a positive electrode, lithium as a negative electrode, and 1 M $LiClO_4$ in PC as an electrolyte. Polyaniline synthesized using $K_2S_2O_8$ or $FeCl_3$ has a very poor discharge capacity. On the other hand, polyaniline synthesized with $Fe(ClO_4)_3$ or $Cu(BF_4)_2$ delivers a high charge/discharge coulombic efficiency of 100% at 33 mAh g^{-1} of charge. All four types of polyaniline are partially soluble in the electrolyte solution; the solubility is higher for the polyaniline synthesized with $K_2S_2O_8$ or $FeCl_3$. The soluble component is presumed to be oligomers of aniline with a low degree of polymerization. To obtain an insoluble form of polyaniline, a more refined method is required.

3.2. Effect of protons in the electrochemical polymerization of aniline

Several researchers [5,13] have suggested that protons play an important role in the polymerization of aniline. Therefore, in order to obtain information on the influence of polymerization conditions — in particular, the influence of proton concentration in the polymerization solution on the morphology and electrochemical behaviour of the product — aniline was electrochemically polymerized in solutions with different $HClO_4$ concentrations.

Fig. 2 presents SEM photographs of polyaniline polymerized from solutions that contain 0.5 M aniline with (a) 0.5 M, (b) 1.0 M and (c) 2.0 M $HClO_4$. The morphology of the polyaniline is granular under condition (a), and fibrous under condition (c). The morphology under condition (b) is intermediate between (a) and (c). These results suggest that the proton concentration in the polymerization solution strongly influences the morphology of polyaniline. For the range of concentration examined here: the higher the proton concentration, the higher the degree of polymerization.

An examination has been made of the electrochemical properties of three types of polyaniline synthesized from the $HClO_4$ solutions (a), (b) and (c) above. Cyclic voltammo-

grams for these polyaniline samples in 1 M $LiClO_4$ in PC at a sweep rate of 60 mV min^{-1} are presented in Fig. 3. The charge/discharge behaviour of the same samples is given in Fig. 4.

The data reveal that fibrous polyaniline, obtained under conditions 2(b) and (c), has a better discharge performance than granular polyaniline. Taguchi and Tanaka [15] reported

Fig. 2. Electron micrographs of electrochemically synthesized polyaniline. Polymerization from 0.5 M aniline and (a) 0.5 M $HClO_4$, (b) 1.0 M $HClO_4$, and (c) 2.0 M $HClO_4$. Current density = 0.5 mA cm^{-2}.
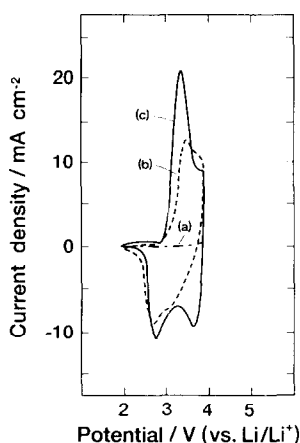
Fig. 3. Cyclic voltammograms for electrochemically synthesized polyaniline. Electrolyte: 1 M LiClO$_4$/PC. Sweep rate = 60 mV min^{-1}. Working electrode = 1 cm^2. Polymerization from 0.5 M aniline and (a) 0.5 M HClO$_4$, (b) 1.0 M HClO$_4$, and (c) 2.0 M HClO$_4$.
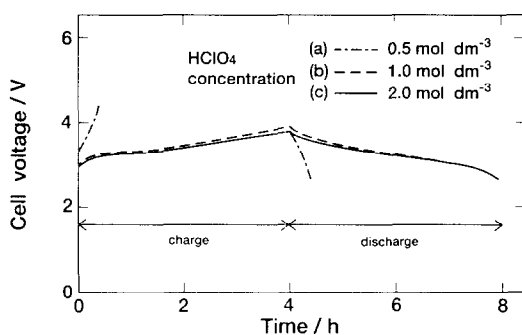

Fig. 4. Charge/discharge characteristics of test cells using electrochemically synthesized polyaniline as positive electrode. Charge/discharge current density = 0.5 mA cm^{-2}. Polymerization from 0.5 M aniline and (a) 0.5 M HClO$_4$, (b) 1.0 M HClO$_4$, and (c) 2.0 M HClO$_4$.

a similar finding, that is, granular polyaniline synthesized from a solution containing H$_2$SO$_4$ has a poorer discharge performance than fibrous polyaniline synthesized from a solution containing HClO$_4$. It was not possible to measure the mol. wt. distribution because the polyaniline was only partially soluble in the solvents. Nevertheless, based on the solubility in PC and the morphology, the degree of polymerization was presumed to decrease in the order: polyaniline (c) > polyaniline (b) > polyaniline (a) (refer (Fig. 2). It should be noted that polyaniline is considered to have a longer fibril with increasing degree of polymerization; this indicates a better acceptability of the dopants.

Genies et al. [16] investigated the electrochemical polymerization of aniline and proposed a mechanism in which the presence of protons is indispensable. Yonezawa et al. [17] pointed out that, under a high pH value, the aniline/anilinium ratio increases and the favourable head-to-tail reaction is suppressed. At a low pH value, dissolution of the intermediate product is believed to be suppressed and further polymerization is promoted.

3.3. New chemical polymerization process

In the electrochemical polymerization of aniline, the control of proton concentration is critical in determining the properties of the product. By analogy, the proton concentration is also assumed to be important in chemical polymerization. Therefore, in order to obtain fibrous polyaniline in chemical polymerization, the proton concentration has been controlled by the following method.

Aniline was first treated with HBF$_4$ to form a salt. The salt was dissolved in an acetonitrile solution that contained Cu(BF$_4$)$_2$. The subsequent reaction mixture was stirred for 7 h and left standing for 12 h. In this reaction process, the molar ratio of aniline:HBF$_4$:Cu(BF$_4$)$_2$:acetonitrile was 1:1:1:15.

The addition of HBF$_4$ to form aniline/HBF$_4$ salt in the polymerization solution had a large influence on the morphology of the product. As shown in Fig. 5, polyaniline polymerized with HBF$_4$ addition was fibrous. On the other hand, polyaniline synthesized without HBF$_4$ addition was granular with a scale-like surface.
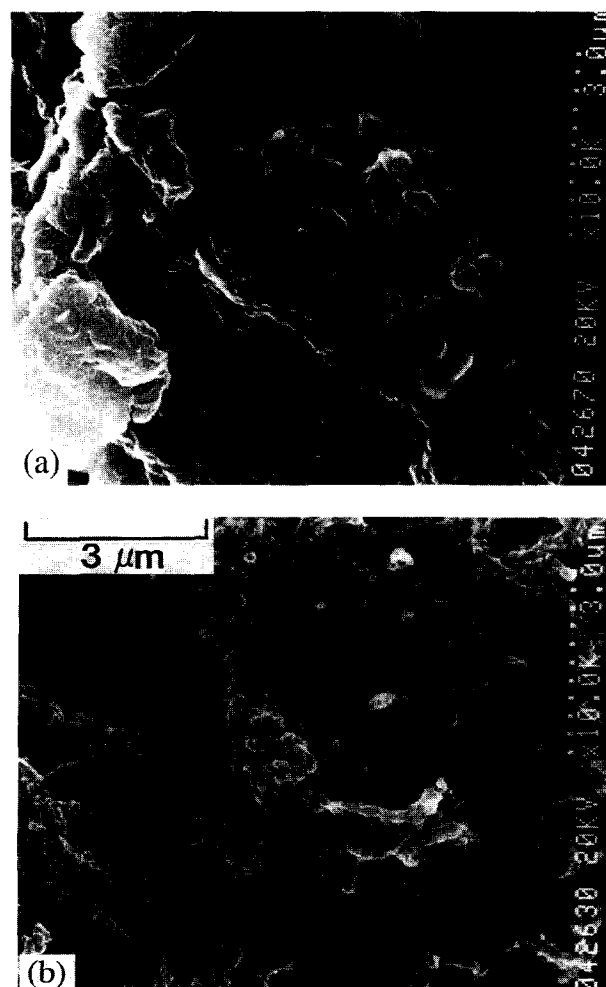

Fig. 5. Electron micrograph of chemically synthesized polyaniline. Oxidizing reagent for polymerization Cu(BF$_4$)$_2$: (a) without HBF$_4$ addition, and (b) with HBF$_4$ addition.
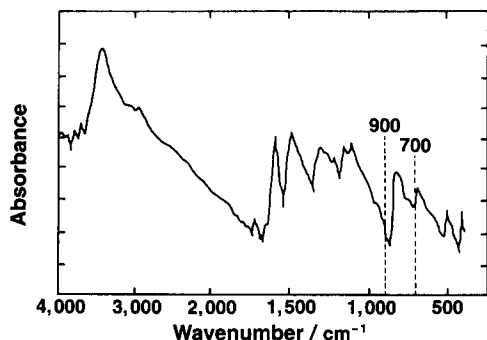
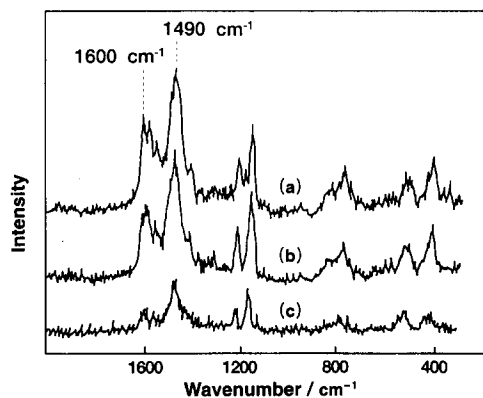Fig. 6. FT-IR spectra of chemically synthesized polyaniline. Oxidizing reagent is $Cu(BF_4)_2$.

Fig. 7. Raman spectra of chemically synthesized polyaniline. Oxidizing reagent: $Cu(BF_4)_2$. Excitation wavenumber: (a) 488 nm; (b) 514.5 nm, and (c) 632.8 nm.

Fig. 8. Cyclic voltammograms for chemically synthesized polyaniline. Oxidizing reagent for polymerization is $Cu(BF_4)_2$. Conductive additive: (a) none, and (b) acetylene black 16 wt.%. Sweep rate = 60 mV min^{-1}, electrolyte: 1 M $LiBF_4$/PC.

Figs. 6 and 7 show Fourier-transform infrared spectroscopy and Raman spectra of polyaniline synthesized with HBF_4 addition. This polyaniline was found to have a 1,4-substituted benzene structure, because only one peak was observed in the 700 to 900 cm^{-1} range in the FT-IR spectra. In the Raman spectra, peaks assigned to both 1,4-substituted benzene and C=N and C—C hybrid modes were observed at 1600 cm^{-1} and 1490 cm^{-1}, respectively.

Cyclic voltammograms for polyaniline both without and with a conducting additive (acetylene black 16 wt.%) are presented in Fig. 8(a) and (b), respectively. A 1 M solution of $LiBF_4$ in PC was used as the electrolyte. The polyaniline electrodes showed good doping and undoping reversibility. From the cyclic voltammograms, the doping amount was calculated as 90 mAh g^{-1} for polyaniline with conducting additives.

4. Conclusions

1. Protons in the reaction media have a remarkable influence on the morphologies and electrochemical properties of polyaniline for both chemical and electrochemical polymerizations.

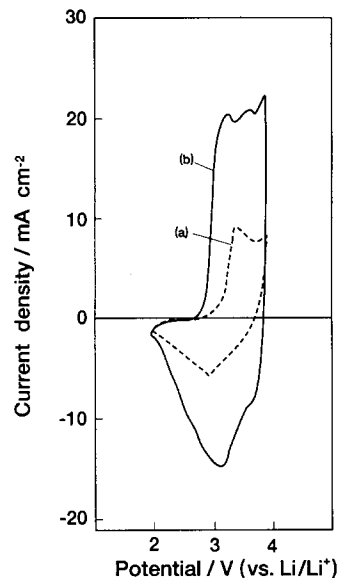2. A novel process for the chemical synthesis of polyaniline has been developed. In this process, aniline is treated first with HBF_4 to form a salt, and then oxidized with $Cu(BF_4)_2$/acetonitrile. This chemical polymerization method successfully produces fibrous polyaniline. The obtained polyaniline displays good doping/undoping reversibility in a non-aqueous electrolyte and has a discharge capacity of 90 mAh g^{-1}.

References

[1] A.G. MacDiarmid, J.C. Chiang and M. Halpern, Mol. Cryst. Liq. Cryst., 121 (1985) 173.
[2] A. Kitani, J. Izumi, Y. Hiromoto and K. Sasaki, Bull. Chem. Soc. Jpn., 57 (1984) 2254.
[3] T. Boschi, M.L. Di Vona, P. Tagliatesta and G. Pistoia, J. Power Sources, 24 (1988) 185.
[4] A. Kitani, M. Kaya, Y. Hiromoto and K. Sasaki, Denki Kagaku, 53 (1985) 592.
[5] F. Goto, K. Abe, K. Okabayashi, T. Yoshida and H. Morimoto, J. Power Sources, 20 (1987) 243.
[6] N. Oyama, Y. Ohnuki, K. Chiba and T. Ohsaka, Chem. Lett., (1983) 1759.
[7] T. Kobayashi, H. Yoneyama and H. Tamura, J. Electroanal. Chem., 177 (1984) 293.
[8] D.E. Stillwell and S.-M. Park, J. Electrochem. Soc., 135 (1988) 2497.
[9] K. Hyodo and M. Nozaki, Electrochim. Acta, 33 (1988) 165.
[10] K. Hyodo, M. Omae and Y. Kagami, Electrochim. Acta, 36 (1991) 357.
[11] W. Baochen, L. Gi, L. Changzhi and W. Fosong, J. Power Sources, 24 (1988) 115.
[12] E. Genies, P. Hany and Ch. Santier, Synth. Met., 28 (1989) C647.
[13] E.M. Genies, P. Hany and Ch. Santier, J. Appl. Electrochem., 18 (1988) 751.
[14] M. Mizumoto, M. Namba, S. Nishimura, H. Miyadera, M. Koseki and Y. Kobayashi, Synth. Met., 28 (1989) C639.
[15] S. Taguchi and T. Tanaka, J. Power Sources, 20 (1987) 249.
[16] E.M. Genies, A.A. Syed and C. Tsintavas, Mol. Cryst. Liq. Cryst., 121 (1985) 181.
[17] S. Yonezawa, K. Kanamura and Z. Takehara, J. Electrochem. Soc., 140 (1993) 629.