

Using PANI–PPDA/Au composite films as cathode of lithium secondary battery

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Abstract

Polyaniline (PANI)–1,4-*para*-phenylenediamine (PPDA) composite films were prepared on Au plate with the cyclic voltammetry (CV) method and used as the cathode of lithium secondary battery. The polymerization rate increased with increasing the concentration of PPDA in the solution. When the PANI–PPDA/Au was prepared with cycle number of 10 in the presence of 0.1 M aniline and 10 mM PPDA and used as the cathode of Li secondary battery, the maximum discharge capacity was obtained to be 103.2 mAh g⁻¹ and the average fading rate was 0.147 mAh g⁻¹ cycle⁻¹ at charge/discharge rate of 0.4 mA.

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1. Introduction

Polyaniline (PANI) is readily prepared from aqueous acid solutions, and its conducting form exhibits the excellent environmental stability and high electrical conductivity [1]. Therefore, polyaniline has attracted much attention in the fields of the secondary batteries, capacitors and sensors. However, the considerable period is needed for obtaining a practical thickness, and this limits its applicability. The electropolymerization of PANI can be catalyzed and increased the electropolymerization rate in the presence of 1,4-*para*-phenylenediamine (PPDA) [2–11]. On the other hand, the polymerization rate of PANI is inhibited for the ratio of [PPDA]/[aniline] in the solution greater than 1/130 [3]. PPDA can also play a role of crosslinker and a dense and uniform polymer film is obtained by the addition of PPDA into the HCl solution containing aniline monomer [4]. The addition of PPDA into the polymerization solution has been proved to decrease the porosity, and increase the mechanical strength and the electrical conductivity of PANI–PPDA composite

film [5,6]. Nearly the studies of PANI–PPDA copolymerized composite films were mainly focused on the synthesis and properties of PANI–PPDA composite films [2–14]. However, using the PANI–PPDA composite film prepared by the electrochemical method as the cathode of lithium battery is seldom reported. It is interesting to prepare the PANI–PPDA composite film and use as the cathode of Li secondary battery. The electrochemical and charge/discharge properties of PANI film may be modified and promoted by the addition of PPDA as a composite film.

In this study, PANI–PPDA composite film was electropolymerized on the Au substrate by CV method in the presence of aniline and PPDA in the HCl aqueous solution. Using the preparing PANI–PPDA/Au as the cathode of lithium secondary batteries, the effect of the conditions for preparing the composite film and the charge/discharge conditions on the charge/discharge properties of battery were also investigated in this paper.

2. Experimental

2.1. Chemical and reagents

Aniline and PPDA used in this work were purchased from MERCK and TCI-EP, respectively. All of the chemicals in-

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cluding propylene carbonate (PC) (MERCK) and LiClO_4 (FERRO) were the reagent grade and used as received.

2.2. Preparation of PANI–PPDA/Au

A three-electrode cell was used to prepare PANI–PPDA/Au with the $\text{Ag}/\text{AgCl}/3\text{ M NaCl}$ aqueous solution and a platinum wire serving as reference and counter electrodes, respectively. Changing the cycle number and the concentration of PPDA in the solution, the PANI–PPDA conducting composite polymer was electrochemically deposited on the gold plate ($1\text{ cm} \times 1.2\text{ cm}$) with CV method in 30 ml 0.1 M aniline and 1.0 M HCl aqueous solution. The CV potential sweep was operated at a scan rate of 20 mV s^{-1} and a potential range of -300 to 1000 mV . The preparing composite films were rinsed by the distilled water for several times and dried in a vacuum oven at 80°C for 24 h and stored in the glove-box.

2.3. Characteristics and charge/discharge properties of PANI–PPDA/Au

The AC impedance was used to study the electric characteristics of PANI–PPDA composite film in 1.0 M LiClO_4 PC solution with the lithium foils used as counter and reference electrodes, respectively. The frequency range and the amplitude were set at 0.01–20,000 Hz and 5 mV.

The surface morphologies and the elemental compositions of PANI–PPDA composite films were analyzed with SEM (JEOL JXA-840) and element analyzer (HERAEUS CHN-O-RAPID), respectively. The weight of PANI–PPDA polymer prepared with different conditions around 0.1 g was collected and analyzed by gas adsorption (Micromeritics GEMINI-2375).

The Li/PANI–PPDA/Au battery was assembled in a glove-box by using a lithium foil and the PANI–PPDA/Au prepared in this work as the anode and the cathode, respectively. 1.0 M LiClO_4 PC solution was used as the electrolyte of the lithium battery. The Li/PANI–PPDA/Au battery was galvanostatically charged and discharged in the potential range of 4.0–2.5 V.

3. Results and discussion

3.1. AC impedance analysis of PANI–PPDA composite film

The scheme of the equivalent circuit model of PANI and PANI–PPDA composite film were illustrated in Fig. 1. The lines in Fig. 1 obtained by assigning the suitable parameters of the components in the equivalent circuit model were correlated well with the experimental data. The charge transfer resistance (R_{ct}) of PANI–PPDA ($5.47\ \Omega$) significantly less than that of PANI film ($43.55\ \Omega$) revealed that the electrochemical activity of PANI–PPDA was greater than that of

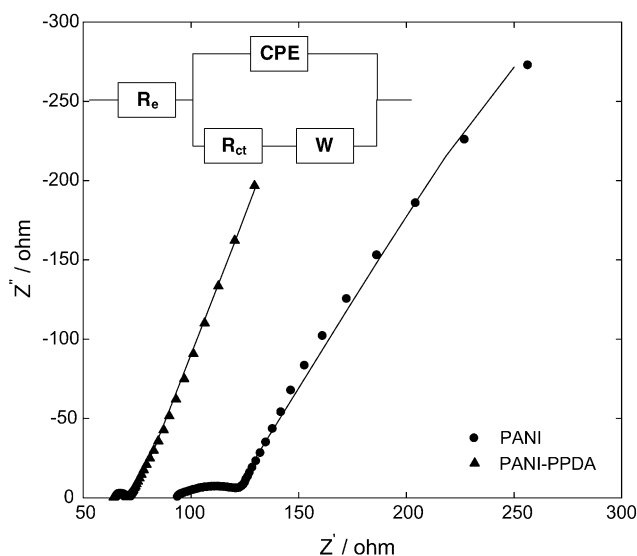


Fig. 1. The AC impedance diagrams of PANI and PANI–PPDA polymer films. Electrolyte: 1.0 M LiClO_4 PC solution; working electrode: PANI/Au (preparing conditions: [aniline] = 0.1 M, cycle number = 10, 1.0 M HCl aqueous solution) or PANI–PPDA/Au (preparing conditions: [aniline] = 0.1 M, [PPDA] = 10 mM, cycle number = 10, 1.0 M HCl aqueous solution); counter electrode: Pt wire and reference electrode: Li foil, amplitude = 5 mV, frequency = 0.01–20,000 Hz.

PANI. The parameter β (0–1) in the constant phase angle element ($\text{CPE} = 1/(j\omega C)^\beta$, where C was the capacity of the electric double layer) represented the roughness of the film surface. The β values of PANI and PANI–PPDA obtained from Fig. 1 were 0.77 and 0.85, respectively. The results indicated that the surface morphology of PANI–PPDA was denser and smoother than PANI. The similar results were also found from the SEM analysis.

3.2. Effect of the concentration of PPDA on the discharge properties of Li/PANI–PPDA/Au battery

Using PANI–PPDA composite films prepared in the presence of various concentrations of PPDA as cathodes, the discharge capacities increased with the cycle number (activation period) to a maximum discharge capacities (C_{max}) and then decreased with the cycle number as shown in the discharge curves of Fig. 2. The increase of the discharge capacity with the cycle number in the activation period might be due to the change of doping ions. The initial doping ion of PANI–PPDA was Cl^- because the conducting polymer was prepared in 1.0 M HCl aqueous solution. When PANI–PPDA polymer film was used as the cathode of Li battery with 1.0 M LiClO_4 as electrolyte, the doping ion would change from Cl^- to ClO_4^- and then the relative bulky ClO_4^- was finally instead by the smaller Li^+ .

The formula of PANI–PPDA conducting polymer might be expressed as $[(-\text{C}_6\text{H}_4\text{NH}-)_x(-\text{NHC}_6\text{H}_4\text{NH}-)_y]$, in which $(-\text{C}_6\text{H}_4\text{NH}-)$ and $(-\text{NHC}_6\text{H}_4\text{NH}-)$ denoted the aniline and PPDA units, respectively. The reactivity of aniline was different from PPDA; hence, the molar ratio of aniline and

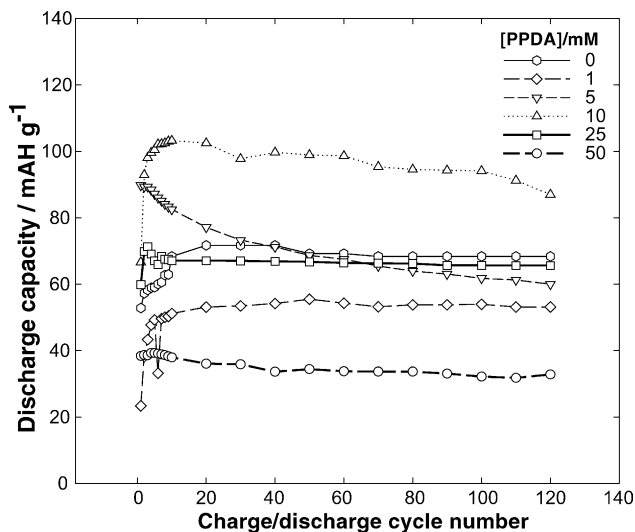


Fig. 2. The effect of charge/discharge cycle number on the discharge capacity of Li/PANI–PPDA/Au with the various concentrations of PPDA for preparing PANI–PPDA composite film. Electrolyte: 1.0 M LiClO₄ PC solution; anode: Li foil (1 cm × 1.2 cm); cathode: PANI–PPDA/Au (1 cm × 1.2 cm) (preparing cycle number = 10), potential range = 2.5–4.0 V, current = 0.4 mA.

PPDA (x/y ratio) was different from the initial molar ratio in the preparing solution. Increasing the concentration of PPDA added into the solution to prepare PANI–PPDA from 5 to 50 mM, the x/y ratio analyzed by the elemental analyzer and calculated based on the above formula decreased from 16.18 to 5.60 (Table 1). Compared with PANI the structure of PANI–PPDA became more fibrous and denser [5,8,11]. The BET surface area of PANI–PPDA polymer film increased from 14.5 to 27.8 m² g⁻¹ with the increase of PPDA concentration in the preparing solution from 1 to 10 mM (Table 1). Further increasing the concentration of PPDA to 50 mM the BET surface area decreased to 10.1 m² g⁻¹ due that the polymer film became too denser.

Increasing the concentration of PPDA for preparing PANI–PPDA from 0 to 10 mM increased the C_{\max} of the Li/PANI–PPDA/Au battery from 71.7 mAh g⁻¹ to the maximum value of 103.2 mAh g⁻¹. The value of C_{\max} decreased

Table 1

Effect of the concentration of PPDA in the preparing solution on the molar composition and BET surface area of PANI–PPDA

[PPDA] (mM)	Element molar composition		x/y^a	BET surface area (m ² g ⁻¹)
	C	N		
1	–	–	–	14.5
5	0.850	0.150	16.18	19.8
10	0.848	0.152	12.25	27.8
25	0.846	0.154	9.83	26.5
50	0.839	0.161	5.60	10.1

Electrolyte: 1.0 M HCl solution, [aniline] = 0.1 M, [PPDA] = 10 mM, WE: Au plate (1 cm × 1.2 cm); CE: Pt wire (0.6 cm²); RE: Ag/AgCl 3 M NaCl, scanning rate = 20 mV s⁻¹, room temperature.

^a The ratio of x/y is calculated based on the expression of PANI–PPDA polymer as [(-C₆H₄NH-)_x(-NHC₆H₄NH-)_y].

to 39.3 mAh g⁻¹ for further increase of the concentration of PPDA to 50 mM. The shorter activation period of battery found for the presence of PPDA in the composite film was due that the conductivity and the electrochemical kinetic of composite film were promoted by PPDA. When the concentration of PPDA for preparing composite film was greater than 10 mM, the oligomers formed in the composite film resulted in the decreased of the discharge capacity and the C_{\max} . The utility and the ions doping/undoping accompanied with the redox of composite film might also be decreased due to the denser and more compact structure for the concentration of PPDA greater than 10 mM. The effect of the PPDA concentration on discharge capacity of Li battery was correlated well with the results of BET surface areas analysis. The Coulomb efficiencies of Li/PANI–PPDA/Au batteries based on PANI–PPDA composite films preparing by various concentrations of PPDA were found to be greater than 97.3%.

3.3. Effect of the cycle number for preparing PANI–PPDA composite film

Increasing the cycle number for preparing PANI–PPDA composite film from 5 to 10 increased the C_{\max} of the Li/PANI–PPDA/Au battery from 62.3 mAh g⁻¹ to a maximum value of 103.2 mAh g⁻¹ when the concentration of PPDA was 10 mM (Fig. 3). The value of C_{\max} decreased to 88.8 mAh g⁻¹ for further increase of the cycle number to 25. As shown in the overview of Fig. 4, the morphologies of PANI–PPDA polymer films became denser and more compact with the increase of the cycle number for preparation. The detail of Fig. 4 indicated that the fibrous structure of PANI–PPDA became clearly and thinner with the increase of the cycle number. The decrease of the fiber size resulted in the

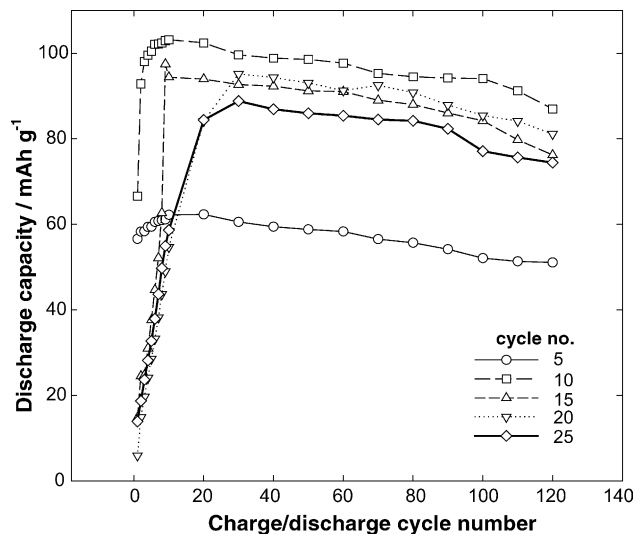


Fig. 3. The effect of charge/discharge cycle number on the discharge capacity of Li/PANI–PPDA/Au with the various cycle numbers for preparing PANI–PPDA composite film. Electrolyte: 1.0 M LiClO₄ PC solution; anode: Li foil (1 cm × 1.2 cm); cathode: PANI–PPDA/Au (1 cm × 1.2 cm) ([PPDA] = 10 mM), potential range = 2.5–4.0 V, current = 0.4 mA.

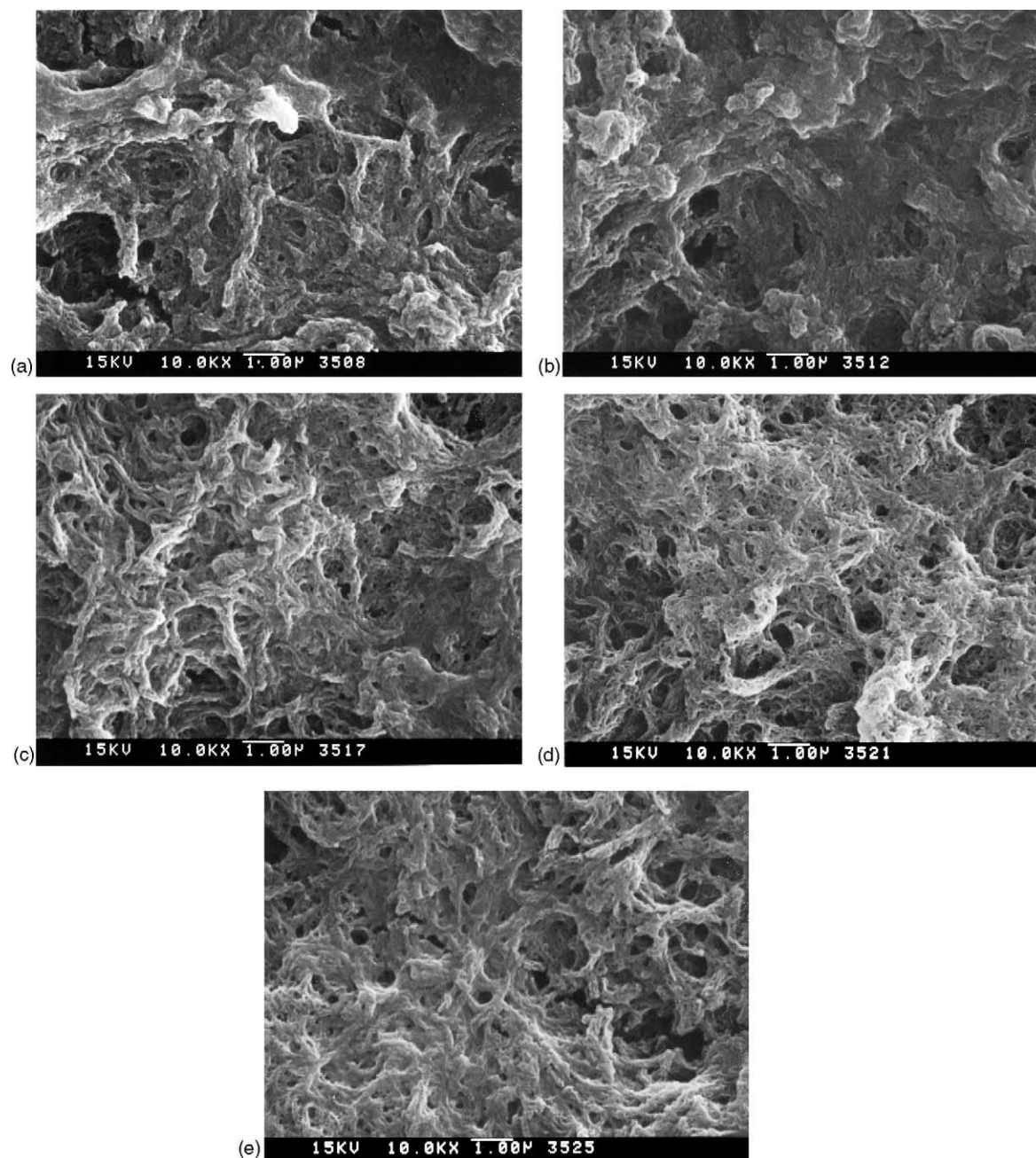


Fig. 4. SEM photographs of PANI-PPDA composite films. Cycle number for preparation: (a) 5, (b) 10, (c) 15, (d) 20 and (e) 25.

increase of the BET surface area. The experimental results indicated that the BET surface areas of PANI-PPDA polymers were obtained to be 13.9, 23.2, 31.6, 35.2 and 35.3 $\text{m}^2 \text{g}^{-1}$ for the preparing cycle number of 5, 10, 15, 20 and 25, respectively.

The increase of BET surface area from 13.9 to 23.2 $\text{m}^2 \text{g}^{-1}$ resulted in the increase of the discharge capacity C_{max} from 62.3 to 103.2 mAh g^{-1} when the cycle number for preparing PANI-PPDA as cathode of Li battery increased from 5 to 10. On the other hand, further increasing the cycle number to 25 the value of C_{max} decreased to 88.8 mAh g^{-1} although the BET surface area of PANI-PPDA increased to 35.3 $\text{m}^2 \text{g}^{-1}$.

The experimental results might be due to the decrease in the active sites for charging/discharging process.

As shown in the cyclic voltammograms for the electrosynthesis of PANI-PPDA polymers (Fig. 5), the redox peaks P_A and P_D were caused by the oxidation and propagation of polymer films. The second and third redox pairs, P_B and P_C , were believed to be the hydrolysis of amines on the polymers chain to benzoquinone/hydroquinone (BQ/HQ) [15,16,18] and the formation of *para*-aminophenol/benzoquinone-imine (PAP/QI) [15,17,19]. The results in Fig. 5 also revealed that the relative peak currents of P_B and P_C increased with the increase in cycle number for preparing PANI-PPDA.

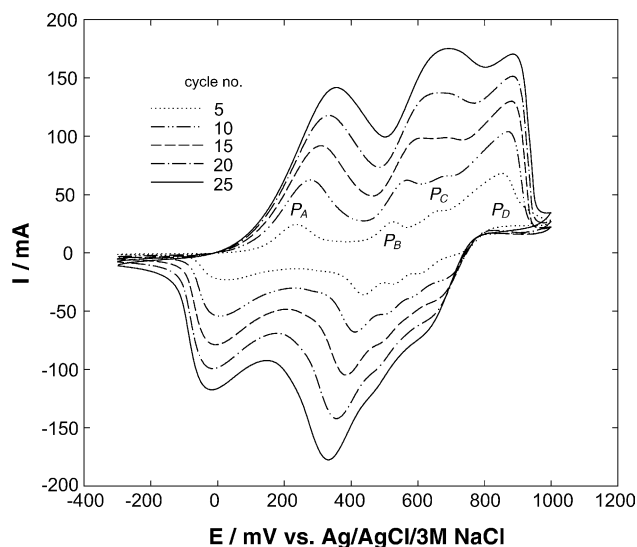


Fig. 5. Cyclic voltammograms for preparing PANI–PPDA/Au in various preparing cycle number. Electrolyte: 1.0 M HCl solution, [aniline] = 0.1 M, [PPDA] = 10 mM, WE: Au plate (1 cm × 1.2 cm), CE: Pt wire (0.6 cm²), RE: Ag/AgCl 3 M NaCl, scanning rate = 20 mV s⁻¹, room temperature.

Therefore, increasing the cycle number the molar fraction of electrochemical inactive substances within PANI–PPDA increased and then the specific discharge capacity of PANI–PPDA used as cathode of Li battery decreased when the cycle number for preparing PANI–PPDA was greater than 10.

4. Conclusions

The charge transfer resistances of PANI and PANI–PPDA composite film in 1.0 M LiClO₄ PC solution were evaluated to be 43.55 and 5.47 Ω, respectively. The C_{\max} of Li/PANI–PPDA/Au increased from 71.7 mAh g⁻¹ to the maximum value of 103.2 mAh g⁻¹ by increasing the concentration of PPDA from 0 to 10 mM. For the concentration of PPDA greater than 10 mM the decrease in the discharge capacity of the composite film was due to the increase in the content of oligomers in the composite film, and the decrease in the utility of composite film. Changing the cycle

number for preparing PANI–PPDA composite film the maximum value of C_{\max} was obtained for the cycle number of 10. Therefore, the discharge capacity of PANI–PPDA was significantly affected by the content of the oligomers and the structure of the composite film.

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References

- [1] E.M. Genies, A. Boyle, M. Lapkowski, C. Tsintavis, *Synth. Met.* 36 (1990) 139.
- [2] Y. Wei, G.W. Jang, C.C. Chan, K.F. Hsueh, R. Hariharan, S.A. Patel, C.K. Whitecar, *J. Phys. Chem. B* 94 (1990) 7716.
- [3] H. Tang, A. Kitani, S. Maitani, H. Munemura, M. Shiotani, *Electrochim. Acta* 40 (1995) 849.
- [4] C. Mailhe-Randolph, J. Desilvestro, *J. Electroanal. Chem. Interfacial Electrochem.* 262 (1989) 289.
- [5] J. Desilvestro, W. Scheifele, *J. Mater. Chem.* 3 (1993) 263.
- [6] C.H. Yang, T.C. Wen, *J. Electrochem. Soc.* 144 (1997) 2078.
- [7] Y. Wei, G.W. Jang, K.F. Hsueh, R. Hariharan, S.A. Patel, C.C. Chan, C. Whitecar, *Polym. Mater. Sci. Eng.* 61 (1989) 905.
- [8] J.C. Michaelson, A.J. McEvoy, N. Kuramoto, *React. Polym.* 17 (1992) 197.
- [9] J. Stejskal, P. Kratochvil, M. Spirkova, *Polymer* 36 (1995) 4135.
- [10] R. Mazeikiene, A. Malinauskas, *React. Funct. Polym.* 45 (2000) 45.
- [11] L. Duic, M. Kraljic, S. Grigic, *J. Polym. Sci., Part A: Polym. Chem.* 42 (2004) 1599.
- [12] Y. Wei, G.W. Jang, R. Hariharan, C.C. Chan, K.F. Hsueh, *Polym. Mater. Sci. Eng.* 61 (1989) 911.
- [13] J. Trlica, P. Saha, O. Quadrat, J. Stejskal, *Eur. Polym. J.* 36 (2000) 2313.
- [14] O. Starykov, J. Prokes, I. Krivka, J. Stejskal, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* 385 (2002) 33.
- [15] D.E. Stilwell, S.M. Park, *J. Electrochem. Soc.* 135 (1988) 2254.
- [16] D.E. Stilwell, S.M. Park, *J. Electrochem. Soc.* 135 (1988) 2491.
- [17] S.K. Dhawan, D.C. Trivedi, *J. Appl. Electrochem.* 22 (1992) 563.
- [18] E.M. Genies, M. Lapkowski, J.F. Penneau, *J. Electroanal. Chem.* 249 (1988) 97.
- [19] R.L. Hand, R.F. Nelson, *Electrochim. Acta* 125 (1978) 1059.