

Short communication

A new design for dry polyaniline rechargeable batteries

Hassan Karami^a, Mir Fazlollah Mousavi^{a,*},
Mojtaba Shamsipur^b

^aChemistry Department, Tarbiat Modarres University (TMU), P.O. Box 14115-111, Tehran, Iran

^bChemistry Department, Razi University, Kermanshah, Iran

Received 10 December 2002; accepted 28 January 2003

Abstract

Polyaniline powder of high conductivity is prepared by chemical polymerization of aniline in a solution of 0.10 M aniline, 2 M perchloric acid and 0.15 M ammonium persulfate at 5 °C. The powder is mixed with graphite and acetylene black to obtain the required conductivity and porosity. The mixed powder is compressed into a ring shape at a pressure of 2 t cm⁻² for use as positive electrodes (cathodes) in batteries. Zinc powder is mixed with magnesium oxide, zinc oxide and sodium carboxymethyl cellulose (CMC), and then compressed into a cylindrical shape at a pressure of 7 t cm⁻² for use as negative electrodes (anodes) in batteries. The battery electrolyte comprises 2 M Zn(ClO₄)₂, 1 M NH₄ClO₄, and 1.0 × 10⁻⁴ M Triton-X100 at pH 3. A 1 wt.% Optalloy powder is added to the negative-electrode composite to prevent the release of hydrogen gas. The assembled battery has an open-circuit voltage (OCV) of 1.64 V, a charge storage capacity of 125.43 m Ah g⁻¹, and a Coulombic efficiency greater than 95% during the first 100 charge–discharge cycles. Due to the low amount of electrolyte used, the battery is considered as a dry battery.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Polyaniline; Rechargeable; Dry battery; Conducting polymer; Zinc; Perchlorate

1. Introduction

In recent years, considerable interest has been shown in polyaniline as a conducting organic polymer [1,2]. It has been found that polyaniline film or polyaniline powder exhibit several redox couples in aqueous solutions. Polyaniline can be utilized in secondary batteries [3–5] and chemical sensors [6–8]. Recently, our research group have been involved in the application of polyaniline in rechargeable batteries [9] and ion-selective electrodes [10]. Fabrication of electrodes from polyaniline powder has been found to offer many advantages such as no limit to the amount of active material and no difficulties in electrode scale-up and electrode shape [1,2].

The majority of the previously reported rechargeable batteries which used polyaniline as the positive electrode (cathode) were typically wet batteries in which hydrochloric acid was used as a dopant acid and the corresponding electrolyte contained ZnCl₂ and NH₄Cl at pH of 4 or higher [11–15]. To the best of our knowledge, there have been no studies on the use of perchlorate as a dopant and electrolyte

in polyaniline batteries, although perchloric acid has been used for aniline polymerization [16–18].

In the work reported here, a dry rechargeable battery based on polyaniline doped with perchlorate ions and an electrolyte of Zn(ClO₄)₂, NH₄ClO₄, and Triton-X100 at pH of 3 is conducted. Optalloy was used in the battery preparation, the presence of which increases the overvoltage for reduction of H⁺ ions and, subsequently, prevents the formation of Zn–hydrogen local cells. Triton-X100 prevents the formation of dendrites during the charge process [16].

In order to increase the conductivity of polyaniline, graphite powder and acetylene black were added to polyaniline powder doped with perchlorate ions, then the mixed powder was compressed to enhance further the connectivity of polyaniline particles. The conductivity of the polyaniline rings was measured by means of the Van Der Pauw technique [1].

Zinc powder was mixed with magnesium oxide, zinc oxide and sodium carboxymethyl cellulose (CMC), and compressed at a pressure of 7 t cm⁻² in a global shape and used as the negative electrode (anode) of the battery. The presence of magnesium and zinc oxides effectively contribute to the reversibility of zinc, and CMC enhances the interconnection of the zinc particles.

* Corresponding author. Fax: +98-21-8006544.

E-mail address: mousavim@modares.ac.ir (M.F. Mousavi).

2. Experimental

2.1. Reagents and materials

Aniline, ammonium persulfate and zinc chloride were obtained from Aldrich. All other reagents such as hydrochloric acid, sodium hydroxide and other compounds were of analytical reagent grade (prepared from Fluka or Merck). Argon (99.999% purity) was purchased from Roham Gas Co. Doubly-distilled water was used in all experiments.

2.2. Apparatus

All electropolymerization reactions were carried out with a BHP 2061-C electrochemical analyzer. Potential measurements were carried out with a Sa-Iran digital multimeter 8503 and pH measurements with Metrohm pH-meter model 691. A scanning electron microscope (Philips, X 30) was used for studying the surfaces of cathodes.

Charge and discharge experiments were performed on batteries with an automatic battery test unit (BPT Co., Tehran, Iran) and a PC computer with a A/C interface. All experiments were carried out at room temperature.

2.3. Method

Polyaniline was synthesized by chemical polymerization [1] from a solution of 0.10 M aniline, 2 M perchloric acid and 0.15 M ammonium persulfate at 5 °C. Argon gas was passed through the polymerization solution to remove dissolved oxygen and, during polymerization, the argon flow was passed across the surface of the solution to prevent oxygen diffusion. After 24 h, the mixture was filtered, washed with water and 2 M HClO₄ solution, and poured into tetrahydrofuran to separate the polyaniline small chains since these are soluble in tetrahydrofuran. It should be noted

that the presence of small chains decreases the conductivity of polyaniline. The mixture was then filtered and washed three times with a 2 M HClO₄ solution and water, respectively. The resulting polyaniline was dried under vacuum at 80 °C and powdered to particles with a diameter of 54–73 μm by using sieves of 200 and 270 mesh. Then, 80 g of this powder was mixed with 18 g of graphite and 2 g of acetylene black, and compressed into a ring shape under a pressure of 2 t cm⁻². The rings were used as cathodes in batteries. Zinc powder (93 g) was mixed with magnesium oxide (2 g), zinc oxide (4 g) and sodium carboxymethyl cellulose (CMC) (1 g), then compressed into a cylindrical shape at a pressure of 7 t cm⁻² anodes in batteries. The construction of the battery is shown schematically in Fig. 1. In this design, graphite is used as the cathodic current-collector, brass alloy as the anodic current-collector, and methyl polyacrylamide as the cover of battery.

3. Results and discussion

Due to the dependency of battery efficiency on the conductivity of the cathodic and the anodic materials, the use of polyaniline as a high conductive material is of critical importance. Meanwhile, the conductivity of polyaniline depends on various parameters such as the aniline concentration, the nature and concentration of oxidant (e.g. ammonium persulfate) and dopant acid in the synthesis solution, the temperature of polymerization, and the pressure and time used during compression of the polyaniline rings. Except for the pressure and time of compression, all other factors have been optimized and reported [1].

To investigate the effect of pressure on polyaniline conductivity, the pressure was varied from 0 to 8 t cm⁻². As shown by the data in Fig. 2, the conductivity of the polyaniline ring increases with increasing pressure until a

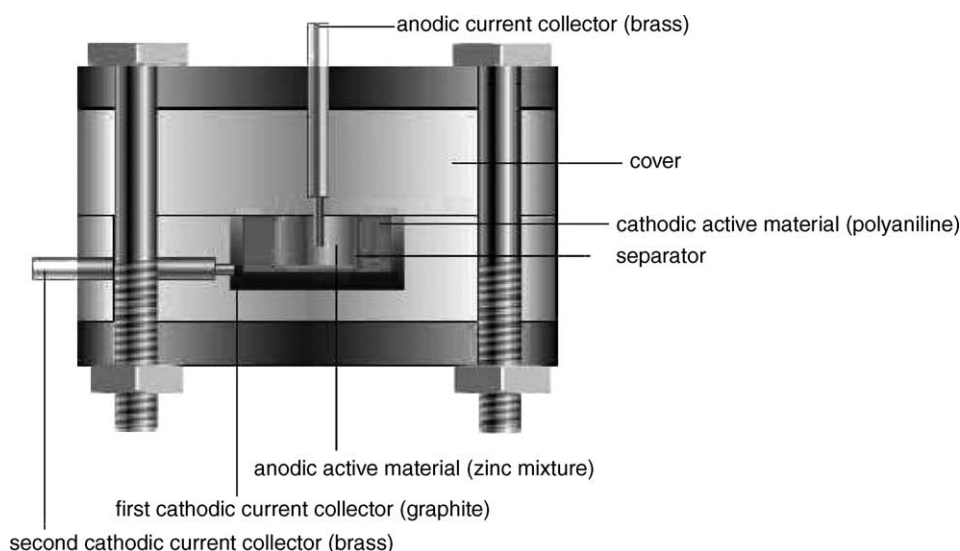


Fig. 1. Structure of proposed battery.

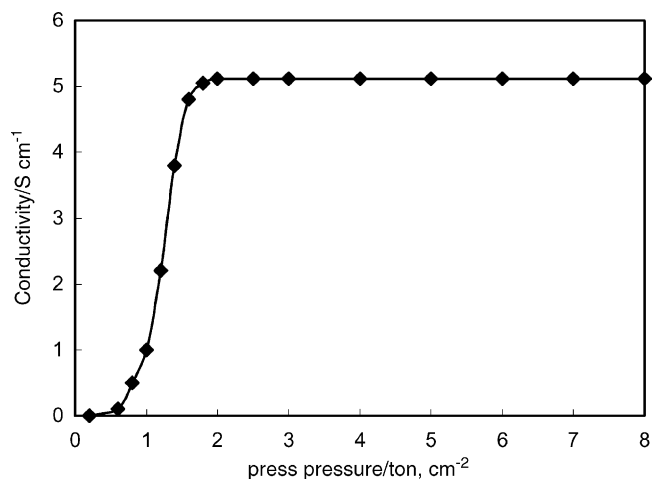


Fig. 2. Effect of press pressure on conductivity of polyaniline ring.

pressure of 2 t cm^{-2} is achieved, then the conductivity becomes independent of pressure. Nevertheless, the efficiency of the battery is decreased by increasing the press pressure. This is due to the decreased porosity of polyaniline at higher pressure which causes a reduction in the diffusion of battery electrolyte into the cathode rings.

Scanning electron micrographs of these cathode ring surfaces prepared under press pressures of 0.5, 1 and 2 t cm^{-2} are shown in Fig. 3. These clearly show the decreasing porosity of polyaniline on increasing the press pressure. The presence of graphite and, especially, acetylene black provides the required porosity in the compressed cathode.

The influence of press time, at a constant pressure of 2 t cm^{-2} , on the conductivity of polyaniline is presented in Fig. 4. As can be seen, an increase in press time improves the conductivity of polyaniline rings up to 3 min but, at longer periods, the polyaniline conductivity becomes independent of time. This is because of the proper orientation of polyaniline chains at about 3 min. This process improves the connectivity within chains and, subsequently, the conductivity of the rings. After this orientation of the chains, the ring conductivity will become independent of press time. The optimum conditions for preparing the polyaniline cathode rings of high conductivity are listed in Table 1.

To prepare the anode, zinc oxide and magnesium oxide were mixed with electrochemically-synthesized zinc powder

Table 1
Optimum conditions for polymerization and preparing of polyaniline ring

Optimized parameter	Optimum amount
Aniline concentration (M)	0.1
Ammonium persulfate concentration (M)	0.15
Perchloric acid concentration (M)	2
Synthesis temperature (°C)	5
Press pressure (t cm^{-2})	2
Press time (min)	3

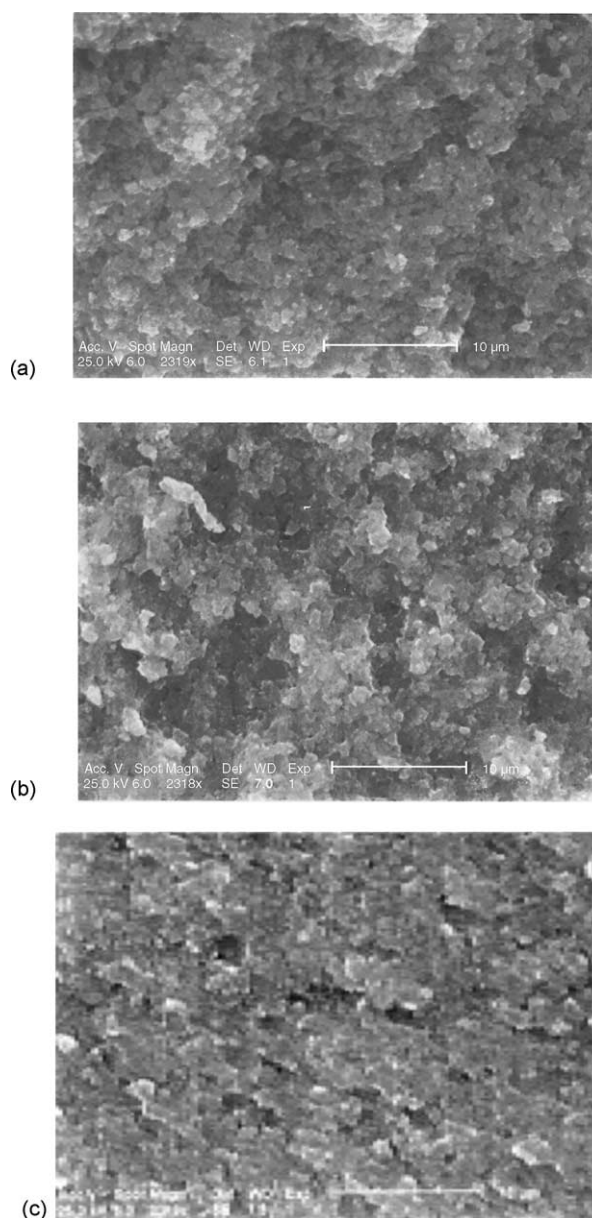


Fig. 3. Electron micrographs of polyaniline cathodes prepared at: (a) 0.5 t cm^{-2} ; (b) 1 t cm^{-2} ; (c) 2 t cm^{-2} .

to provide better porosity and to improve the charge–discharge characteristics of zinc. Carboxy methylcellulose was also added to provide fine connections between particles. The resulting mixture was pressed at 7 t cm^{-2} .

A solution of $2 \text{ M Zn}(\text{ClO}_4)_2$ and $1 \text{ M NH}_4\text{ClO}_4$ at pH 3 served as the battery electrolyte. At this pH, the reversibility of polyaniline is better than that at the higher values of pH used in previous reports [11,12,14,19].

A constant-current mode was chosen for charge–discharge cycling of the battery. The effect of current density on the voltage–time curve and Coulombic efficiency was investigated and the results are shown in Figs. 5 and 6, respectively. At current densities of 50 mA g^{-1} and lower, the charge and discharge times are equal (Fig. 5) and the

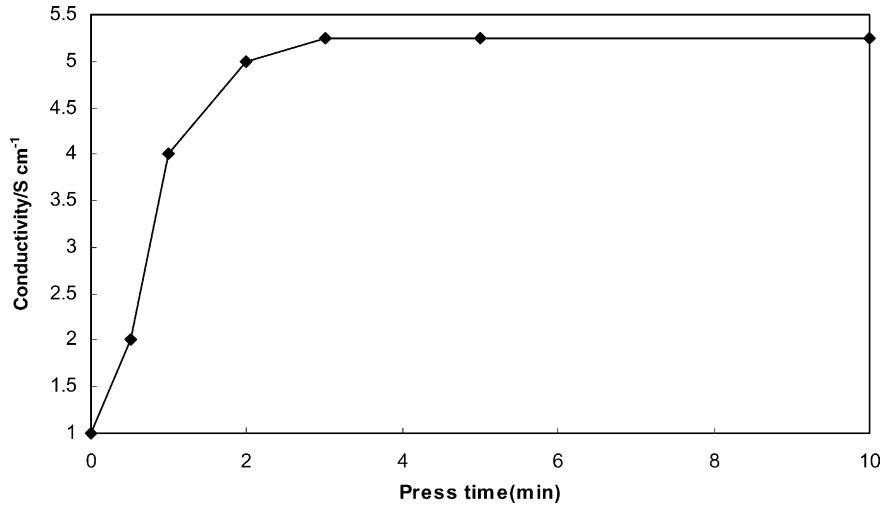


Fig. 4. Effect of press time on conductivity of polyaniline.

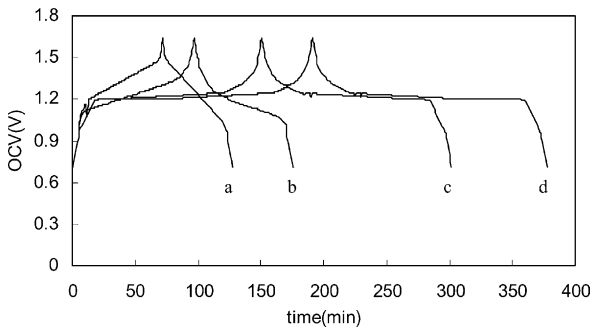


Fig. 5. Effect of current density on voltage–time curve of battery: (a) 80 mA g⁻¹; (b) 60 mA g⁻¹; (c) 50 mA g⁻¹; (d) 40 mA g⁻¹.

Coulombic efficiency is 100% (Fig. 6). If the current density is decreased, the corresponding charge and discharge times are increased. Thus, a current density of 50 mA g⁻¹ was selected.

The voltage–time variation at different cycle numbers (constant-current method) is shown in Fig. 7. The influence of cycle-life on battery capacity and Coulombic efficiency is given in Figs. 8 and 9, respectively. From these data, it is immediately obvious that the proposed battery possesses a high middle-point voltage of 1.2 V, a high capacity, and a high Coulombic efficiency at high cycle-life. Closer inspection, however, reveals that the battery capacity decreases slowly from 125.4 to 118.0 mAh g⁻¹, and the Coulombic efficiency from 100 to 96%, after 100 cycles. These results emphasize that the battery possesses a suitable efficiency.

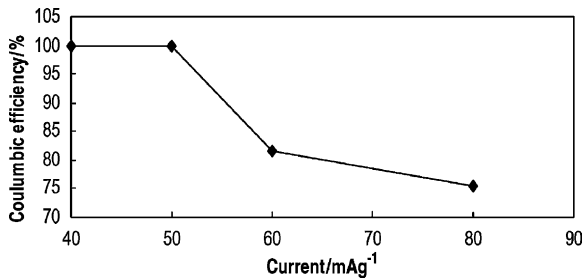


Fig. 6. Effect of current density on Coulombic efficiency of battery.

The battery stability was investigated after 40 days of standing without use. It was found that the battery experienced a self-discharge of less than 0.6% per day.

The open-circuit voltage (OCV) of the proposed battery is compared with that of several previously reported polyaniline batteries in Table 2. The proposed battery has the highest OCV.

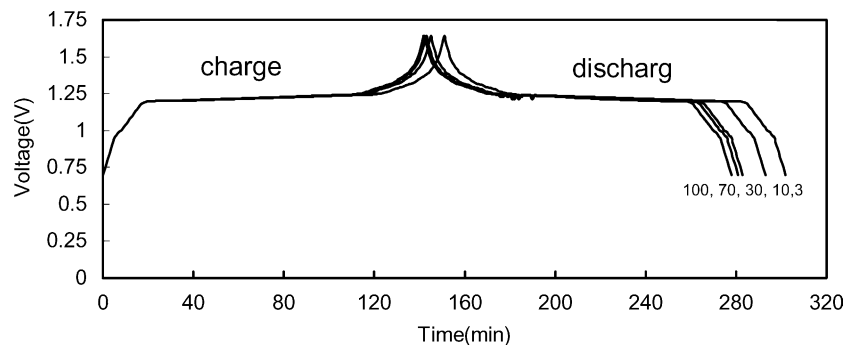


Fig. 7. Voltage–time curves of battery for different cycles at constant current (50 mA g⁻¹).

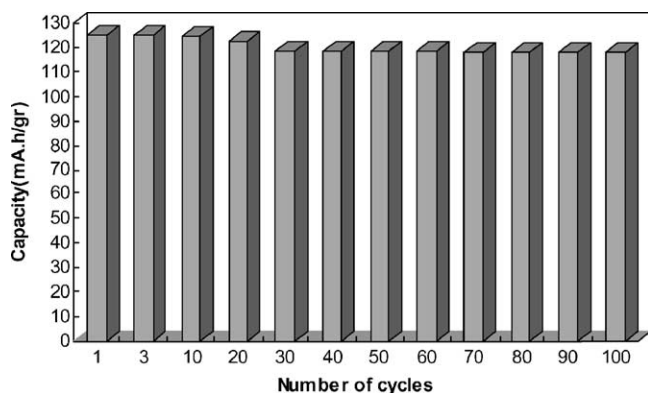


Fig. 8. Effect of cycle-life on battery capacity.

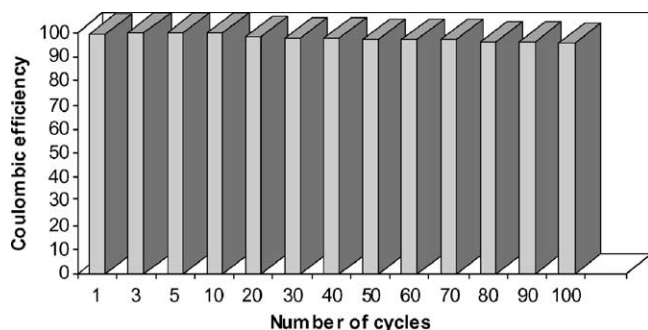


Fig. 9. Effect of cycle-life on battery Coulombic efficiency.

Table 2

Comparison of open-circuit voltage (OCV) of different batteries

Electrolyte	OCV (V)	Reference
ZnSO ₄ (1 M)	1.18	[4]
ZnCl ₂ (2 M) + NH ₄ Cl (0.5 M)	1.35–1.5	[5]
ZnCl ₂ (sat.) + NH ₄ Cl (1 M)	1.1	[11]
ZnCl ₂ (1 M) + NH ₄ Cl (0.5 M)	1.3	[12]
ZnCl ₂ (1 M) + NH ₄ Cl (0.5 M) + NaBF ₄ (0.1 M)	1.4	[13]
ZnBr ₂ (2 M) + NH ₄ Cl (1 M)	1.5	[14]
ZnI ₂ (1.5 M) + NH ₄ Cl (1 M)	1.2	[14]
Zn(ClO ₄) ₂ (2 M) + NH ₄ ClO ₄ (1 M)	1.64	This work

4. Conclusions

It is found that chemically-synthesized polyaniline powder can be used as a cathode in dry rechargeable batteries. Addition of graphite and acetylene black to polyaniline powder and compressing the resulting mixture improves the conductivity of the cathode and, consequently, the battery efficiency. The use of perchlorate dopant increases

both the open-circuit voltage and the efficiency of battery. The use of compressed, electrochemically-synthesized, zinc powder mixed with MgO, ZnO and carboxymethyl cellulose, as a stable anode, improves the rechargeability of battery. The reduction of electrolyte pH to 3 in the presence of ClO₄⁻ as dopant increases the reversibility of the redox reaction of polyaniline. Optalloy is successful in preventing evolution of hydrogen. These observations suggest the possibility of commercial polyaniline rechargeable batteries.

Acknowledgements

The authors are grateful for support from the National Research Council of I.R. Iran (National Project No. 4652) and Tarbiat Modarres University (TMU) Research Council.

References

- [1] A.A. Syed, M.K. Dinesan, *Talanta* 38 (1991) 815.
- [2] P. Novak, K. Muller, K.S.V. Santhanam, J. Haas, *Chem. Rev.* 97 (1997) 207.
- [3] A. Kitani, M. Kaya, K. Sasaki, *J. Electrochem. Soc.* 133 (1986) 1069.
- [4] N.L.D. Somasiri, A.G. MacDiarmid, *J. Appl. Electrochem.* 18 (1988) 92.
- [5] G. Mengoli, M.M. Musiani, D. Pletcher, S. Vaicher, *J. Appl. Electrochem.* 17 (1987) 515.
- [6] M. Kanungo, A. Kumar, A.Q. Contractor, *J. Electroanal. Chem.* 528 (2002) 46.
- [7] T. Lindfors, A. Ivaska, *Anal. Chim. Acta* 437 (2001) 171.
- [8] A.N. Ivanov, L. Lukachova, G.A. Evtugyn, E.E. Karyakina, S.G. Kiseleva, H.C. Budnikov, A.V. Orlov, G.P. Karpacheva, A.A. Karyakin, *Bio. Anal. Chem.* 55 (2002) 75.
- [9] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 110 (2002) 229.
- [10] M.F. Mousavi, M. Shamsipur, S. Riahi, M.S. Rahmanifar, *Anal. Sci.* 18 (2002) 137.
- [11] B. Wang, G. Li, F. Wang, *J. Power Sources* 24 (1988) 115.
- [12] F. Trinidal, M.C. Montemayor, E. Fatas, *J. Electrochem. Soc.* 138 (1991) 3186.
- [13] A.G. MacDiarmid, J.C. Chiang, M. Halpern, W.S. Huang, J.R. Krawczyk, R.J. Mammone, S.L. Mu, N.L.D. Somasiri, W. Wu, *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* 25 (1984) 248.
- [14] G. Mengoli, M.M. Musiani, D. Pletcher, S. Valcher, *J. Appl. Electrochem.* 17 (1987) 525.
- [15] W. Boachen, L. Gi, L. Changzhi, W. Fosong, *J. Power Sources* 24 (1988) 115.
- [16] E.M. genies, P. Noel, *J. Electroanal. Chem.* 310 (1991) 89.
- [17] Z. Mandic, L. Duic, F. Kovacicck, *Electrochim. Acta* 42 (1997) 1389.
- [18] S. Mu, J. Kan, *Synth. Met.* 98 (1998) 51.
- [19] J. Kan, H. Xue, S. Mu, *J. Power Sources* 74 (1998) 113.