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Short communication

Effect of self-doped polyaniline on performance of secondary Zn–polyaniline battery

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Abstract

The characteristics of aniline and *m*-aminobenzoic acid (MABA) copolymer (self-doped polyaniline (PANi) (SDPA)) are studied in aqueous electrolytes. The SDPA films are deposited on a platinum electrode by means of cyclic voltammetry. The film is employed as a positive electrode (cathode) for a SDPA–Zn secondary battery that contains 1.0 M $ZnCl_2$ and 0.5 M NH_4Cl electrolytes at pH = 5. The cells are charged and discharged under constant current. It is found that the maximum capacity of the SDPA–Zn battery is 146.4 Ah kg^{-1} with a columbic efficiency of 97–100% over at least 200 cycles between 0.8 and 1.6 V. The specific energy is 172.8 Wh kg^{-1} and the SDPA cathode exhibits good recycleability.

Keywords: Rechargeable battery; Polyaniline; *m*-Aminobenzoic acid; Self-doped polyaniline

1. Introduction

During recent years, there has been an explosive growth of research in the field of conducting polymers because of their interesting electrical properties and their potential application in various fields such as electrochromic displays [1], electronic devices [2], batteries [3], and chemical sensors [4]. Polyaniline (PANi), due to its environmental stability, high degree of processability and interesting redox properties associated with its chain heteroatom, has been one of the most extensively studied electrochemical active polymers during the past 10 years [5,6].

PANi is a suitable material for PANi–Zn secondary batteries with aqueous electrolytes. A difficulty arises when zinc is the counter electrode, since zinc undergoes spontaneous dissolution in acidic media, while PANi is electroactive only in acidic media. In fact, it has been reported [7] that PANi loses its electrochemical activity as measured by cyclic voltammetry in solution of pH >4. This point is certainly a defect of PANi compared with other materials.Because of these two contradicting factors, it is necessary to seek for a co-polymer of aniline. Karyakin et al. [8] has reported that copolymerization of aniline with *m*-aminobenzoic acid (MABA) can exhibit electrochemical activity over a wide pH range even in basic solution.

In the present work, a copolymer of aniline and MABA is used as a cathodic active material for the PANi–Zn secondary battery. Results show that the performance of the SDPA–Zn rechargeable battery is better than that of a PANi–Zn rechargeable battery.

2. Experimental

Co-polymers of aniline with MABA were prepared by repeated potential cycling at a platinum plate electrode (5 cm × 4 cm) from −0.20 to 0.85 V (versus Ag/AgCl) at a sweep rate of 50 mV s^{-1}, in a solution containing 0.10 M aniline, 0.04 M MABA and 1.00 M hydrochloric acid. The self-doped PANi film at the Pt electrode was washed with distilled water and dried. This was used as the test electrode without any other treatment. The electrolyte in batteries was an aqueous solution of 1.0 M $ZnCl_2$ and 0.5 M NH_4Cl (pH = 5). The negative electrode consisted of a zinc plate with a working area of 16 cm^2.

An EG&G potentiostat–galvanostat 273A was used for the synthesis of SDPA. The instrument for the charge and discharge experiments of the batteries was an automatic battery test unit BTS12-100 (BPT Co., Tehran, Iran) and a 486 PC computer with a A/D interface. The batteries were

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charged and discharged between 0.80 and 1.60 V at a constant current density. All measurements were carried out at 25 °C.

3. Results and discussion

A typical voltage–time curve during the charging and the discharging periods is shown in Fig. 1. When the battery is charged, the voltage increases slowly and the reduced form of SDPA is changed to its oxidised form. The cell voltage increases rapidly when SDPA oxidation is completed and SDPA is degraded to its electrochemical inactive form [9]. There is a limit to the charge voltage, and if it is exceeded, the corresponding overcharge leads to irreversible changes in the chemical composition of the polymer, and strong degradation in cell performance. These changes have been attributed to an over-oxidation process in the polymer. In fact, when SDPA is subjected to rather positive voltages irreversible changes occur, which reduce the ability of the polymer to interact with anions. This behaviour is attributed to the oxidation of the monomeric units to *p*-benzoquinone (which in an acidic medium is oxidised to hydroquinone) that causes a break-down of the polymeric chains and increasing loss of the electrochemical activity properties of SDPA. This adversely affects the cycleability of the polymer [10]. Thus, changing is terminated when a cut-off voltage (COV) of 1.6 V is reached. The open-circuit voltage is 1.55 V under this condition.

When the cell is discharged, the voltage falls slowly until the SDPA reduced form is changed completely to its oxidised form. Thereafter, the voltage decreases rapidly. The discharge COV is 0.8 V. Below this voltage, gas is released at the cathode and the SDPA film becomes separated from the Pt collector electrode.

The differences in behaviour of the PANi and SDPA cells may be explained by the incorporation of different anions in the PANi and SDPA layers. The dependence of PANi–Zn performance on the nature of the counter ion has been documented in previous work [9,11,12]. The anion in SDPA is $-COO^-$. The voltage characteristics of the SDPA–Zn battery is influenced by the doped anion and displays a higher value than other batteries [3].

The influence of current density on the coulombic efficiency of the charge–discharge cycles was studied in order to optimise the charge–discharge current density. The results are given in Fig. 2 and indicate that an increase in the charging current density results in a lowering of the coulombic efficiency. This is due to the fact that slow discharges allow the discharge of deeper zones of the SDPA layer, and this remains unvaried during charge–discharge cycling at higher current densities.

Discharge capacity was examined as a function of the charge capacity and the results are presented in Fig. 3. It is seen that the ratio is unity (dashed line) unless excess charging is applied. From these data, the maximum output capacity is determined to be 146.4 Ah kg^{-1} polymer. The corresponding specific energy for the average discharge voltage of 1.18 V is 172.8 Wh kg^{-1}. When the pH of cell electrolyte is increased to 5, the electrochemical activity of the PANi layer is decreased and the capacity of the PANi–Zn cell is reduced. In SDPA–Zn cells, however, the electrochemical activity of the SDPA layer is not decreased at pH = 5. This is due to the carboxylate anions present in the polymer fibres as well as the increased doping level in the polymer fibre in SDPA–Zn cells.

The results of the cell recycleability study are shown in Fig. 4. The deep charge–discharge process was carried out for 200 cycles. The coulombic efficiency and capacity values are given in Fig. 5. The coulombic efficiency of the cell remains over 97% after 200 complete cycles. The capacity of the SDPA–Zn cell decreases rapidly in the first 100 cycles and after that a slow decrease is observed. The average of capacity loss during 200 cycles is 0.19% per cycle. Similar to PANi [9], the capacity reduction of the cell during charge–discharge is due to the oxidative degradation of SDPA in aqueous media that decreases the active material. One way to reduce this effect is to decrease the charge COV of the cell.

An investigation was also made of the self-discharge reaction of the proposed cell. The results reveal that this cell behaviour is similar to that of the PANi–Zn cell previously reported in the literature. The reason for this behaviour has

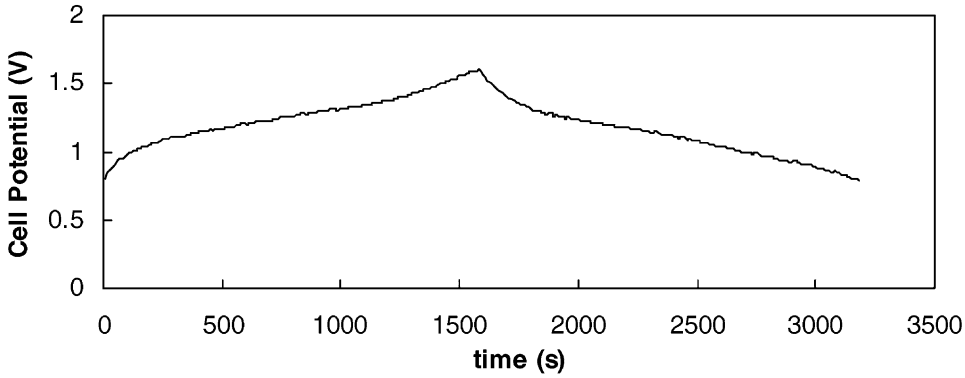

Fig. 1. Typical charge–discharge current density for SDPA–Zn cell at 1 mA cm^{-1} current density.

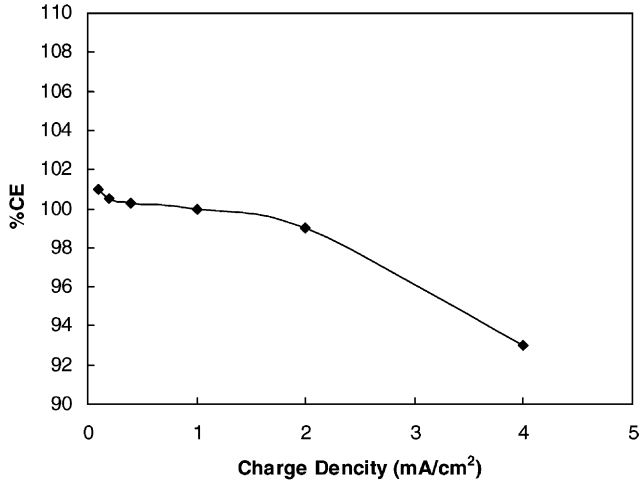

Fig. 2. Effect of charge–discharge current densities on coulombic efficiency.

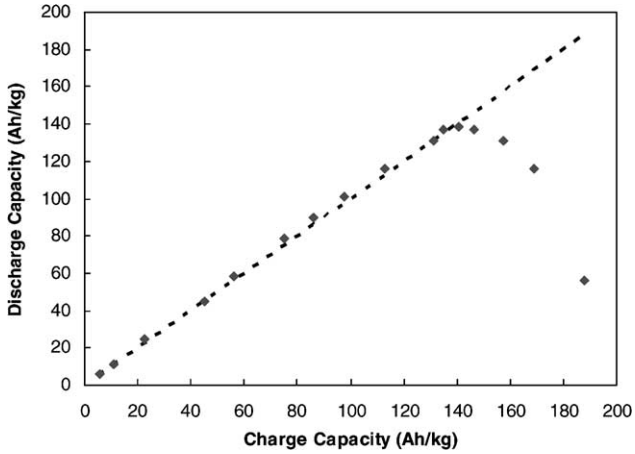

Fig. 3. Relationship between charge–discharge capacity, dotted line corresponds to 100% coulombic efficiency.

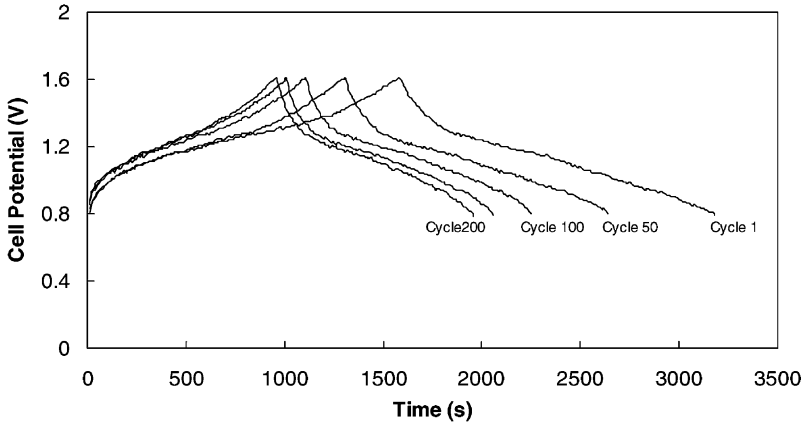

Fig. 4. Charge–discharge curves for SDPA–Zn cell after various cycles. Cell charged and discharged at a constant current density of 1 mA cm^{-2}.

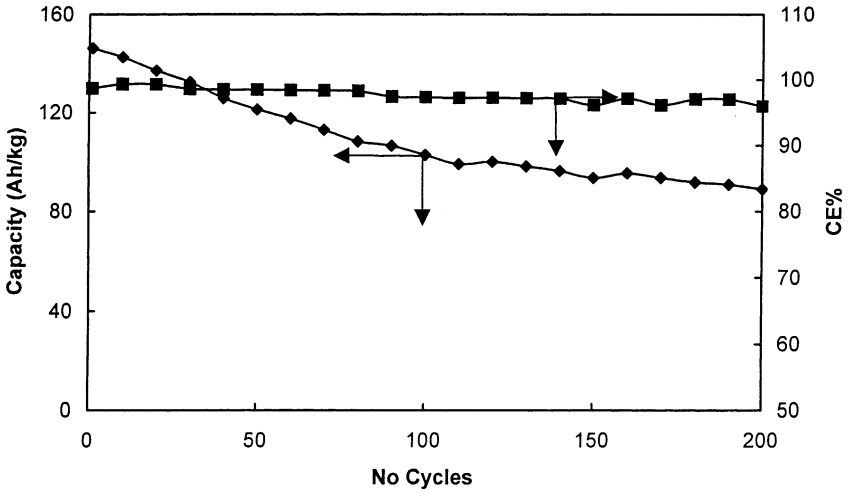

Fig. 5. Discharge capacity and coulombic efficiency vs. cycle number for SDPA–Zn cell at a constant current density of 1 mA cm^{-2}. Working voltage range from 1.6 to 0.8 V.

already been discussed by Trinidad et al. [13]. We believe that this behaviour can be attributed to a Zn^{2+}-induced change in the electronic properties of PANi, as suggested by Anand et al. [14].

4. Conclusions

Studies on the SDPA–Zn cell clearly demonstrate the viability of using this conductive co-polymer as an active electrode material. In general, the performance of the cell is better than that of the PANi–Zn cell (in terms of electrolyte pH, voltage characteristics, coulombic efficiency, capacity, specific energy). Similar to PANi, the recycleability of SDPA is affected by the charge and discharge COV and this parameter must be optimised for SDPA–Zn cells.

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