

Controllable preparation of poly(aniline-co-5-aminosalicylic acid) nanowires for rechargeable batteries



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ABSTRACT

Poly(aniline-co-5-aminosalicylic acid) (poly(Ani-co-5-ASA)) nanowires were successfully prepared by controlling potentials during the copolymerization of aniline and 5-aminosalicylic acid in acidic solutions. Poly(Ani-co-5-ASA) nanowires were 40–100 nm in diameter and 2–3.5 μm length when deposited at $E = 0.95\text{ V}$ and 100–170 nm in diameter and 0.5–1.1 μm long when deposited at $E = 1.10\text{ V}$. The redox activity of poly(Ani-co-5-ASA) nanowires of smaller diameters was higher than that of nanowires of larger diameters, which could be taken as a strong evidence for the nanosize effect. The nanostructured poly(Ani-co-5-ASA) deposited on a graphite plate was used as a cathode in Zn-poly(Ani-co-5-ASA) rechargeable battery with $\text{ZnCl}_2/\text{NH}_4\text{Cl}$ aqueous electrolyte of pH 4.8. This battery showed a high energy density of 140.2 Wh kg^{-1} at a constant current discharge of 20 mA (5 mA cm^{-2}). The capacity density of the battery loses were 2.8% and 14.2% after 100 and 200 cycles, respectively.

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1. Introduction

Polyaniline in its polaronic form exhibits high conductivity, good redox reversibility and environmental stability [1,2]. Thus, this polymer can be used as a new material in electrocatalytic and energy storage applications. Electrochemical applications of polyaniline frequently involve exchange of protons and anions between the polymer film and the electrolyte being in contact with it. These processes are greatly facilitated for films of high surface area. This is why nanostructured polyaniline has received a great deal of attention. The preparation [3–5], morphology [6–8], properties [9,10] and formation mechanism [11,12] of nanostructured polyaniline has been studied extensively and has made great advancement during the past a score years. Clearly, the successful preparation of nanostructured polyaniline provides a wealth of information on preparing other nanostructured conduction polymers, such as poly(aniline-co-5-aminosalicylic acid), i.e., poly(Ani-co-5-ASA), described in this work.

Exploiting the good redox reversibility and stability of polyaniline in aqueous solutions, MacDiarmid et al. first employed polyaniline as a cathode in Zn/polyaniline batteries, which would

be charged and discharged reversibly in $\text{ZnCl}_2/\text{NH}_4\text{Cl}$ solution of $\text{pH} \sim 4$ [13]. Since then, many papers on the Zn/polyaniline batteries have been published which demonstrated significant improvement in the polymer synthesis, selection of the electrolytic medium etc. As a result, the energy density of the studied devices significantly increased [14–24]. In spite of this research effort, the Zn/polyaniline rechargeable batteries have not yet been commercialized because they still suffer from low energy density and other technological problems difficult to overcome. The main reason is that the redox activity of polyaniline strongly depends on pH, it decreases with increasing pH and even vanishes at pH 6 [2,25]. In addition, the energy density of polyaniline decreases with increasing its film thickness because only the outer layers of the active materials can contribute to charge-discharge processes [19]. An effective way for improving the pH dependence of polyaniline involves its sulfonation [26], or copolymerization of aniline with aniline derivatives containing pH-sensitive function groups [27]. The Zn-poly(aniline-co-*m*-aminophenol) battery with $\text{ZnCl}_2/\text{NH}_4\text{Cl}$ electrolyte of pH 4.7 shows so far the highest energy density [28]. Also, the Zn-poly(aniline-co-*N*-methylthionine) battery employing the same electrolyte shows the promising values of specific capacity and good charge-discharge characteristics [29]. To improve the energy density of polyaniline-based devices porous materials was used such as nickel foam-supported polyaniline with high specific surface area and others [24]. Most of the polyaniline

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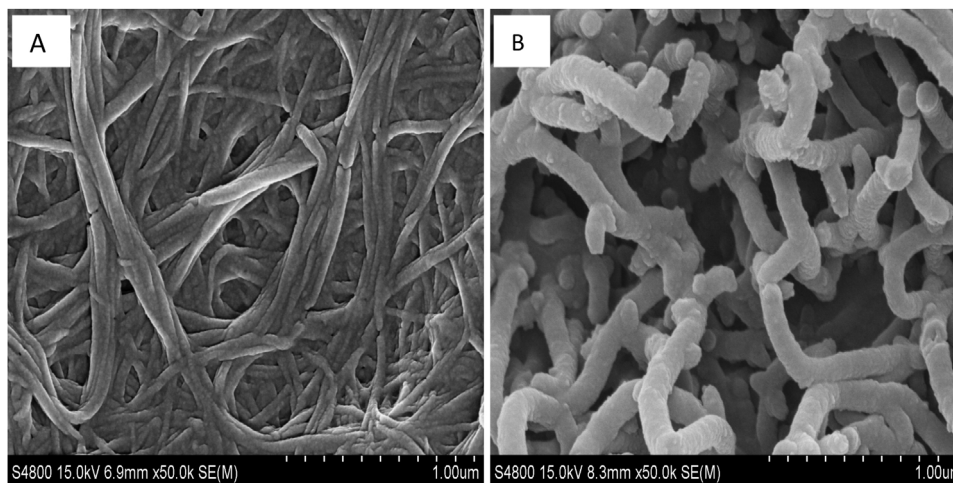


Fig. 1. SEM images of poly(Ani-co-5-ASA), prepared at 0.95 V (A) and 1.10 V (B).

batteries were constructed of a polyaniline cathode and a zinc anode with $\text{ZnCl}_2/\text{NH}_4\text{Cl}$ aqueous electrolyte, as indicated above. In this case, the electrochemical activity of polyaniline is limited by the pH value of the electrolyte solution, since the zinc electrode easily undergoes corrosion in solutions of lower pH. This has a very negative effect on the battery performance. To protect zinc against corrosion, the pH value of the electrolyte solution in the battery must be raised. One way to overcome this problem is to use aniline copolymers instead of polyaniline as already mentioned. Among aniline copolymers, poly(Ani-co-5-ASA) shows good redox activity from pH < 1 to pH 12 [30,31]. In the research described here, poly(Ani-co-5-ASA) deposited on a graphite plate is used as a cathode in a Zn-poly(Ani-co-5-ASA) rechargeable battery. In addition graphite plate is used as a substrate for poly(Ani-co-5-ASA) instead of Pt [18,29], Ni [24] or TiO_2 [18], because it is cheap, stable and combines high conductivity with good mechanical properties [20]. In addition, the used graphite plate has a rather rough surface which improves nanowires adhesion.

We report the controllable preparation of the long and uniform nanowires of poly(Ani-co-5-ASA) exhibiting the nanosize effect. We also demonstrate the feasibility of this polymer application in Zn-poly(Ani-co-5-ASA) rechargeable batteries with a $\text{ZnCl}_2/\text{NH}_4\text{Cl}$ electrolyte of pH 4.8.

2. Experimental

5-aminosalicylic acid (5-ASA) was purchased from Fluka Company. Other chemicals used were received from Sinopharm Chemical Reagent Company (Shanghai) and were of analytical grade. The pH values of the solutions were determined with a PXD-12 pH meter.

A conventional three-electrode cell, consisting of a graphite plate working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE), was used for the electrochemical experiments that were performed on a CHI 407 workstation. The area of the graphite plate is 2 cm^2 ($0.8 \text{ cm} \times 2.5 \text{ cm}$). A solution consisting of 18 mM 5-ASA, 0.2 M aniline and 0.6 M H_2SO_4 was used to prepare poly(Ani-co-5-ASA) at different potentials. The morphology of poly(Ani-co-5-ASA) film was measured on a field emission scanning electron microscopy (SEM) S-4800 II FE-SEM instrument. The impedance measurements of poly(Ani-co-5-ASA) deposited on a graphite plate were performed on an Autolab Nova 1.8 instrument. Frequency sweeps extended from 10^4 to 0.1 Hz using a sinusoidal perturbation signal of 10 mV, peak-to-peak.

3. Results and discussion

3.1. Controllable preparation of poly(Ani-co-5-ASA) nanowires and nanosize effect

The electrochemical oxidative polymerization of aniline for the preparation of polyaniline nanostructures has relatively easy controllability compared to that of the chemical method because the electrochemical polymerization rate can be controlled by applied potentials. The polymerization rate of aniline is related to the formation rate of polyaniline nuclei on the electrode surface; hence polyaniline nanostructures prepared using the electrochemical method are affected by the applied potentials [5,10]. In this case, to control the nanostructures of poly(Ani-co-5-ASA), which was synthesized at differently applied potentials. Fig. 1A and B shows the SEM images of the copolymers when synthesized at $E = 0.95$ and 1.10 V (vs. SCE), respectively. As can be seen in Fig. 1A, the copolymer nanostructures are composed of numerous intercrossing nanowires that exhibit the diameter ranging from 40 to 100 nm and the lengths varying from 2 to 3.5 μm . Fig. 1B indicates that the wires are 100–170 nm in diameter and 0.5–1.1 μm in length. Comparison of Fig. 1A and B shows that nanowire diameter of the copolymer synthesized at 0.95 V is much smaller than that of the copolymer synthesized at 1.10 V; however, the nanowire length of the copolymer synthesized at 0.95 V is much longer than that prepared at 1.10 V. This difference is caused by the applied potential in the synthesis of the copolymer; the copolymerization rate of aniline with 5-ASA at 1.10 V is faster than that at 0.95 V. In that case, the reactants cannot be supplied enough fast to the electrode surface, which inhibits the elongation of nanowire growth. Thus, the copolymer grows on nanowire itself as the electrolysis proceeds, which makes nanowire become thicker and shorter. The result shown in Fig. 1 demonstrates that the sizes and lengths of the nanowires are strongly affected by the applied potentials and easy controlled by the applied potentials in the copolymerization processes of aniline and 5-ASA.

Fig. 2A and B shows the effect of pH on the cyclic voltammogram (CV) of poly(Ani-co-5-ASA) when synthesized at $E = 0.95$ and 1.10 V, respectively. There are three redox couples on curve 1 that was recorded in 0.20 M H_2SO_4 solution. The first redox couple at the lowest potentials corresponds to redox reaction between leucoemeraldine and emeraldine; the third redox couple at the highest potentials corresponds to the redox reaction between emeraldine and pernigraniline accompanied with the exchange of protons between the copolymer film and the solution as well as

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