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Short Communication

Cheap and Eco-Friendly Synthesis of Polyaniline and Performance of Aqueous Zn-polyaniline Battery

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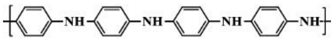
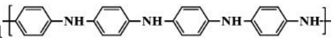
Polymerized from the abundant and cheap aniline monomer, polyaniline has high stability in air, water and other media, good redox reversibility, and advantages of easy synthesis, which has been widely studied in recent years. In this paper, a new synthesis method of polyaniline by adding trace ammonium persulfate into the conventional system of H_2O_2-Fe^{2+} was used, which achieves a yield of polyaniline higher than 90% in less than 5 hours. More importantly, the waste solution generated in the processes of filtering and washing of polyaniline products can be recovered and recycled for subsequent synthesis, which avoids the problem of waste liquid treatment existed in conventional synthesis route. The infrared absorption peaks of the as prepared polyaniline are consistent with that synthesized in conventional H_2O_2-Fe^{2+} system. The specific capacity of the zinc-polyaniline aqueous battery assembled by the polyaniline is as high as 80 mAh · g^{-1} when charged and discharged at 0.1C. The coulomb efficiency is higher than 93% when the battery is charged and discharged over 800 times at 0.3C. It shows that the battery has good redox reversibility and good charge discharge cycle performance. This work provides a low cost synthesis route of polyaniline, which inspires the further development of zinc polyaniline battery for commercial application.

Keywords: polyaniline·hydrogen peroxide·ferrous sulfate·cheap and eco-friendly synthesis·high yield

1. INTRODUCTION

Since MacDiarmid, Heeger and Shirakawa won the Nobel Prize for the discovery of conducting polymers in 2000, the synthesis, properties and applications of conducting polymers have been a research hotspot[1-3]. In view of the high stability of polyaniline in air, water and other media, excellent redox reversibility, rich and cheap aniline raw materials, and relatively easy synthesis method, polyaniline is the first choice for most conducting polymer researchers[4-6]. However, it is regrettable that the research of polyaniline is still at the stage of laboratory, and no large-scale commercial application of polyaniline products and reports have been found.

The study show that the theoretical specific capacity of polyaniline is about 147Ah · kg^{-1}, which is calculated from the complete reduction state to the semioxidation state according to the gain and loss of two electrons in the charge and discharge processes of each  (theoretical specific capacity is approximately 294 Ah · kg^{-1}, which is calculated from the complete reduction state to fully oxidized state according to the gain and loss of four electrons in the charge and discharge process of each. However, polyaniline in the fully oxidized state is prone to degradation). In fact, polyaniline has been used as the positive electrode material of zinc polyaniline aqueous battery since 1985 when MacDiarmid and others began to study polyaniline as conducting polymer again[7-8]. Mu[9] reported that in 1.0M $ZnCl_2$ and 2.0M NH_4Cl solution, the coulomb efficiency of zinc-polyaniline aqueous battery in 0.750-1.500V charging and discharging was 99.5%. After 1240 charging and discharging, its discharge capacity only decreased by about 13%, and the activity of polyaniline did not change significantly after 1000 charging and discharging. Our results show that the specific discharge capacity of the aqueous battery containing zinc chloride and ammonium chloride electrolyte is higher than 75mAh · g^{-1} under the charge-discharge condition of 0.1C. The main reason why there is no commercial application of zinc-polyaniline aqueous battery so far is that: first, the cost of polyaniline synthesized by existing chemical methods is too high (Only based on the current market price of raw materials, the production cost of chemically synthesized polyaniline is higher than ¥32 kg^{-1}， which is because the oxidant, ammonium persulfate, is too expensive), it does not have the price competitive advantage with conventional lead acid batteries, and there is an environmental pollution caused by waste synthetic liquid of polyaniline. Secondly, the hydrogen evolution corrosion of zinc anode, the formation of zinc dendrites and the corrosion of current collector during the process of battery charging and discharging caused by the weak acid electrolyte with high concentration of chloride ion in zinc-polyaniline aqueous battery are difficult to solve.

In view of the low yield and time consuming of polyaniline synthesized by oxidation of aniline with ferrous sulfate-hydrogen peroxide up to now[10-12] , the production cost of polyaniline can be greatly reduced (Only based on the current market price of raw materials, the production cost is lower than ¥15 kg^{-1}) by using the improved ferrous sulfate-hydrogen peroxide oxidation method. At the same time, the problem of environmental pollution caused by waste liquid during the process of polyaniline synthesis by common methods is eliminated. It can create favorable price for large-scale commercial application of zinc-polyaniline aqueous battery.

2. EXPERIMENTAL

2.1. Reagents

Aniline (Shanghai Tiantan Technology Co., Ltd., China), hydrochloric acid (Sinopharm Group Chemical Reagent Co., Ltd., China), 30% hydrogen peroxide (Sinopharm Group Chemical Reagent Co.,Ltd.),ferrous sulfate heptahydrate (Sinopharm Group Chemical Reagent Co.,Ltd., China), potassium bromide (Sinopharm Group Chemical Reagent Co.,Ltd., China) (all reagents are analytical grade).

2.2. Instruments

SHZ-III circulating water vacuum pump (Jiangsu Nanjing Keer Instrument Equipment Co.,Ltd., China),electrothermal constant temperature blast drying oven (Shanghai Jinghong Experimental Equipment Co.,Ltd., China), EL-204 electronic balance [METTLER TOLEDO instrument (Shanghai) Co.,Ltd., China), Fourier transform infrared spectrometer (FTIR, tensor 27,Bruker,Germany).

2.3. Preparation of Polyaniline

First, a mixed solution of 50 mL containing 1.0M hydrochloric acid and 0.5M aniline was prepared at room temperature. Second, the calculated amount of solid ferrous sulfate and trace ammonium persulfate (about 1/3000 - 1/2000 of the actual concentration of hydrogen peroxide) was added into the above solution under magnetic stirring. Last, hydrogen peroxide was added slowly in 5 minutes' duration, and the polymerization was carried out. When the reaction is completed, the solid products were obtained by filtering the compounds in the beaker, and were washed by water for many times. Then the products were dried in an oven at 70 ^{o}C for 24 h, and weighed after naturally cooled. The filtering and washing solution could be recovered and recycled for subsequent synthesis by adjusting the concentration of aniline and hydrochloric acid to the required value.

2.4. IR characterization of Polyaniline

The synthetic products were measured by the method of potassium bromide compression in the range of 4000-400cm^{-1} using the German Brooke Tensor 27 Fourier infrared spectrometer (FTIR, Tensor 27, Bruker, Germany).

2.5. Structure of zinc-polyaniline aqueous battery

The structure of zinc-polyaniline aqueous battery is shown in Figure 1. First place 0.7mm-thick polyaniline sheets on both sides of the carbon paper, then wrap them with polyethylene membrane, then stack the zinc sheets, compress them and put them into plastic bags, finally add the electrolyte of zinc chloride-ammonium chloride with pH4.5 and seal them. After immersion for one day and night, the charge-discharge performances were measured by Neware's charge-discharge apparatus.

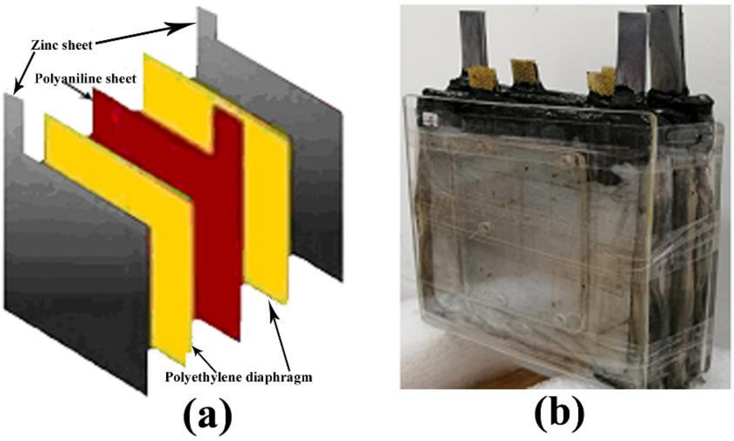


Figure 1. Structure scheme of zinc-polyaniline aqueous battery (a) Structure scheme of one zinc-polyaniline aqueous battery (b) Practicality picture of three zinc-polyaniline aqueous battery in series

3. RESULTS AND DISCUSSION

The polymerization of aniline has the characteristics of self catalyzed free radical reaction [13-14]. Polyaniline can be synthesized as long as the formation of free radicals of aniline can be promoted by adding an appropriate amount of initiator in the initial stage of aniline polymerization.

Under the catalysis of Fe^{2+}, H_2O_2 can promote the formation of Fe^{3+} and highly oxidized hydroxyl radicals ($HO\cdot$), and H_2O_2 can also react with Fe^{3+} to generate Fe^{2+}. The whole reaction process realizes the cycle between Fe^{2+} and Fe^{3+}, and continuously produces living free radicals ($HO\cdot$ and $HO_2\cdot$). The reaction process is as follows [15-16]:

$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + HO\cdot$ (1)

$Fe^{3+} + H_2O_2 = Fe^{2+} + H^+ + HO_2\cdot$ (2)

Aniline is autocatalytic polymerized by producing aniline radicals initiated by active radicals ($HO\cdot$ and $HO_2\cdot$). However, the initial stage of aniline free radical produced by the oxidation of only H_2O_2-Fe^{2+} is slow, while the initial rate of aniline free radical produced by the oxidation of ammonium persulfate is very fast. In view of this, we add a small amount of ammonium persulfate into the mixed solution of 0.5M aniline and 1.0M hydrochloric acid to explore the influence of the amount of ferrous sulfate, the amount of hydrogen peroxide and the reaction time on the yield of polyaniline, so as to realize the purpose of eco-friendly and cheap synthesis of high yield polyaniline.

3.1. Effect of the amount of ferrous sulfate on the yield of polyaniline

Figure 2 shows the effect of the amount of ferrous sulfate on the yield of polyaniline under the condition of adding trace ammonium persulfate into the mixed solution of 0.5 M aniline, 1.0 M hydrochloric acid and 4.1 ml hydrogen peroxide.

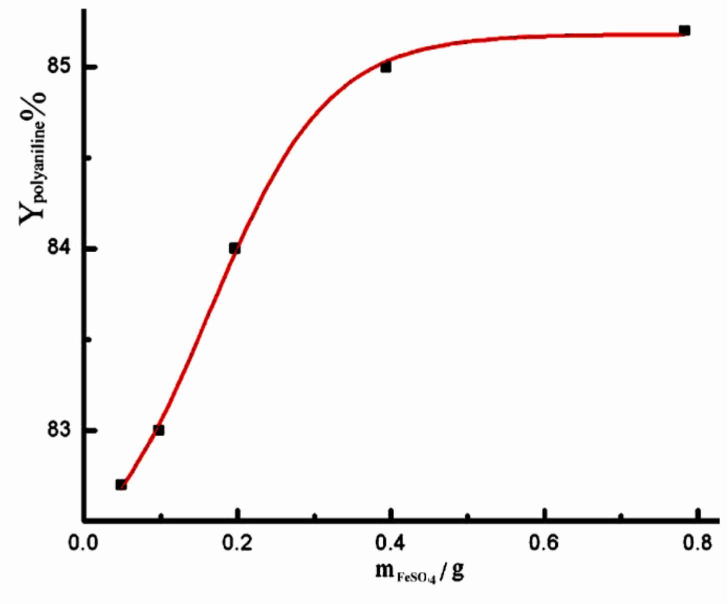


Figure 2. Effect of the amount of ferrous sulfate on the yield of Polyaniline. The mixed solution containing 0.5M aniline, 1.0M hydrochloric acid, 4.1ml hydrogen peroxide and trace ammonium persulfate

It can be seen from Figure 2 that after other conditions are determined, the yield of polyaniline increases with the increase of ferrous sulfate content. When the dosage of ferrous sulfate reaches 0.4g, the yield of polyaniline does not increase further with the further increase of ferrous sulfate content. This is because ferrous sulfate mainly acts as a catalyst in the polymerization of aniline, and a small amount of Fe^{2+} and hydrogen peroxide can combine to form Fenton system. Under the action of Fe^{2+}, H_2O_2 reacts to produce OH^- and HO· (hydroxyl radical), which has strong oxidation ability and can quickly initiate aniline reaction. At the same time, Fe^{2+} is converted into Fe^{3+}, Fe^{3+} can also oxidize aniline, which promotes the polymerization of aniline. Only a small amount of Fe^{2+} and Fe^{3+} in the system can make the polymerization of aniline continue.

3.2. Effect of the amount of hydrogen peroxide on the yield of the product

Figure 3 shows the relationship between the amount of hydrogen peroxide and the yield of polyaniline under the condition of adding trace ammonium persulfate into the mixed solution of 0.5M aniline, 1.0M hydrochloric acid and 0.195g ferrous sulfate.

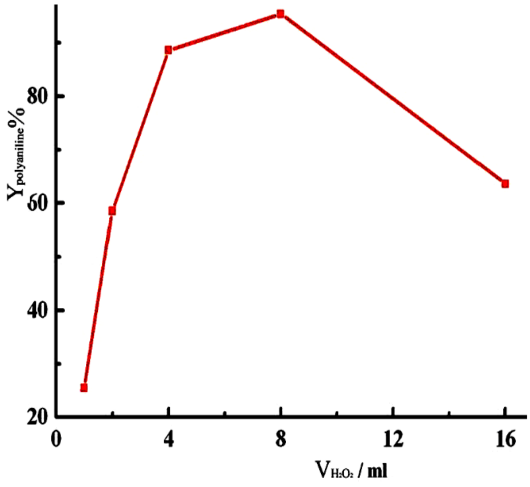


Figure 3. Effect of the amount of hydrogen peroxide on the yield of the product. The mixed solution containing 0.5M aniline, 1.0M hydrochloric acid, 0.195g ferrous sulfate and trace ammonium persulfate

As shown in Figure 3 that, if other factors are constant, the yield of polyaniline first increases with the increase of the amount of hydrogen peroxide.

It can be seen from Figure 3 that, if other factors are the same, the yield of polyaniline first increases with the increase of the amount of hydrogen peroxide. When the amount of hydrogen peroxide is 4-10 ml, the yield of polyaniline is more than 90%. When the amount of hydrogen peroxide is 8 ml, the yield of polyaniline is as high as 95.4%. However, when the amount of hydrogen peroxide is 16 ml, the yield of polyaniline is less than 70%. This is because the formation of polyaniline is formed by the cationic free radical oxidation polymerization of aniline monomer [17]. With the increase of the amount of oxidant, the concentration of hydroxyl free radical increases, which promotes the polymerization of aniline. However, if the amount of oxidant is too large, the polyaniline chain will be oxidized and the polyaniline will be degraded into water-soluble oligomer, which will reduce the yield of polyaniline [18]. It can be seen that the polyaniline product with high yield can be obtained when 8 ml hydrogen peroxide is added to the mixed solution of 0.5M aniline, 1.0M hydrochloric acid and 0.195g ferrous sulfate with a small amount of ammonium persulfate.

3.3. Effect of reaction time on product yield

Figure 4 shows the effect of reaction time on the yield of polyaniline by adding trace ammonium persulfate into the mixed solution of 0.5M aniline, 1.0M hydrochloric acid, 4.1ml hydrogen peroxide and 0.195g ferrous sulfate.

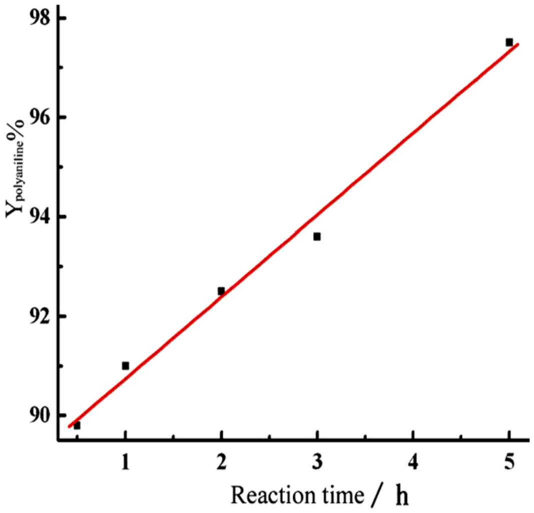


Figure 4. Effect of reaction time on product yield. The mixed solution containing 0.5M aniline, 1.0M hydrochloric acid, 4.1ml hydrogen peroxide, 0.195g ferrous sulfate and trace ammonium persulfate

It can be seen from Figure 4 that under this experimental condition, the yield of polyaniline increases with reaction time. The yield of polyaniline has reached 97.5% after 5 hours, which is far higher than the yield of polyaniline synthesized in H_2O_2-Fe^{2+} system reported in the existing literature[10, 19-23]. This may be related to the increase of the initial rate of aniline radicals caused by the addition of trace ammonium persulfate.

3.4. IR characterizations of products

Figure 5 is the infrared spectra of polyaniline products obtained by oxidative polymerization of H_2O_2-Fe^{2+} without (a) and with (b) trace ammonium persulfate, respectively.

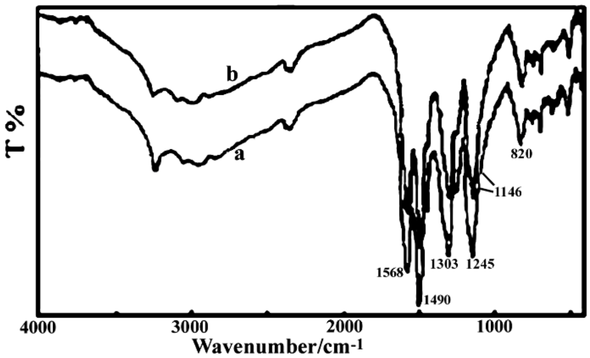


Figure 5. IR characterizations of products (a) Without trace ammonium persulfate in the synthesis system (b) With trace ammonium persulfate in synthesis system

In Figure 5, 3520-3000 cm^{-1} peak is caused by -NH- or $-NH_2$ group of polyaniline chain; 1568 cm^{-1} peak belongs to the stretching vibration of quinone structure (N=Q=N), while 1490 cm^{-1} peak is caused by benzene structure (N=B=N) (Q represents quinone ring, B represents benzene ring); 1303 cm^{-1} peak and 1245 cm^{-1} peak correspond to QBQ and BBB respectively. The peak of 1146 cm^{-1} is caused by the bending vibration of N=Q=N, and the peak of 820 cm^{-1} belongs to the out of plane bending vibration of C-H on 1,4-disubstituted benzene ring. The infrared spectra show that both of the polyanilines, which are synthesized without (a) and with (b) trace ammonium persulfate, have basically the same vibrational properties.

3.5. Performance of zinc-polyaniline aqueous battery

Figure 6 is a diagram of the relationship between the specific capacity and the charge-discharge ratio of the zinc polyaniline aqueous battery with the structure of Figure 1(b). The discharge specific capacity of the battery at 0.1 C can reach the designed theoretical specific capacity (80 mAh · g^{-1}); the discharge specific capacity of the battery at 5 cycles of 0.3 C is stable at 59 mAh · g^{-1}. After repeated charge-discharge cycles of 0.5 C and 0.8C, the discharge specific capacity of the battery at 0.3 C remain stable at 60 mAh · g^{-1}. The results show that the zinc-polyaniline aqueous battery composed of polyaniline synthesized by this method has better rate characteristics.

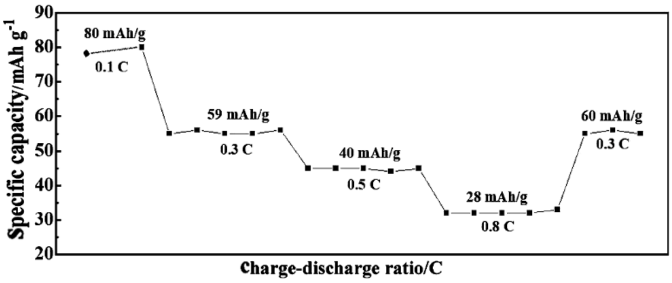


Figure 6. Relationships between the specific capacity and the charge-discharge ratio of the zinc polyaniline aqueous battery with the structure of Figure 1(b)

Figure 7 and Figure 8 are the relationship between the voltage and time of the zinc-polyaniline aqueous battery with the structure shown in Figure 1(b) and the relationship between the coulomb efficiency and the number of cycles, respectively. Figure 7 shows that the charge and discharge curve symmetry over 800 cycles is very good when the battery composed of the polyaniline synthesized by this method is charged and discharged at 0.3C. The high coulomb efficiency of the battery is consistent with that of Figure 8. It can be seen that the battery has good redox reversibility and good charge discharge cycle performance.

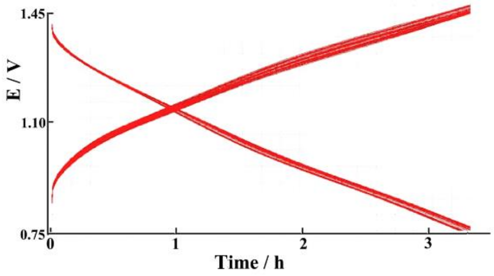


Figure 7. Relationships between the voltage and time of the zinc-polyaniline aqueous battery with the structure of Figure 1(b)

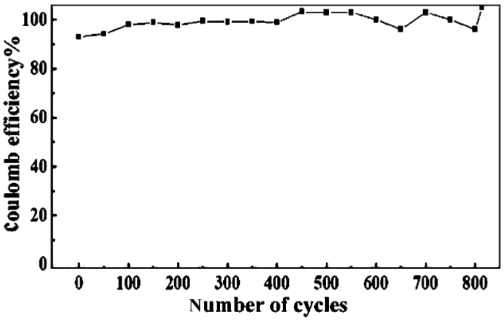


Figure 8. Relationships between the coulomb efficiency and the number of cycles of the zinc-polyaniline aqueous battery with the structure of Figure 1(b)

4. CONCLUSION

In this paper, a new method of polyaniline synthesis is proposed. By adding a small amount of ammonium persulfate (about 1/3000 - 1/2000 of the actual concentration of hydrogen peroxide) into the system of H_2O_2-Fe^{2+} polyaniline synthesis, the yield of polyaniline (the system in 50 ml 0.5 M aniline + 1.0 M hydrochloric acid + 4-10 ml 30% hydrogen peroxide + 0.195 g) is greatly improved with a short reaction time. The yield of polyaniline is more than 90% by using this method. Since the filtering and washing solution of this method can be recycled completely and then used as the reaction solution for the synthesis of polyaniline after the concentration of aniline and hydrochloric acid is adjusted appropriately according to the amount of precipitated solid product, the method of self-cycle synthesis can completely avoid the problem of waste liquid treatment caused by conventional synthesis of polyaniline.

The infrared spectrum shows that there is no obvious difference between the structure of the polyaniline synthesized by this method compared to that synthesized in H_2O_2-Fe^{2+} system..

The zinc-polyaniline aqueous battery with a thickness of 0.7mm has a high specific capacity (80 mAh · g^{-1} when charged and discharged at 0.1 C). The battery is charged and discharged at 0.3 C, and its discharge coulomb efficiency over 800 cycles is higher than 93%. It shows that the battery has good redox reversibility and good charge discharge cycle performance.

This work provides a low cost synthesis route of polyaniline, which inspires the further development of zinc polyaniline battery for commercial application.

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