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Studies on New Type Current Collectors for Polyaniline Batteries

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Polyaniline (PANI) as active material of batteries possesses excellent electrochemical reversibility. It is a promising candidate for a rechargeable battery with a high performance. However, current collectors become a manufacturing bottleneck of PANI battery. In this paper, the effects of five current collectors: stainless steel (SS), conductive plastics (CP), aluminum foil (AF), lead foil (LF) and carbon fiber (CF) on the stability and electrical properties in the electrolyte (1M $ZnClO_4$/EC+DMC (volume ratio=1:1)) are studied by cyclic voltammetry, electrochemical impedance spectroscopy (EIS), galvanostatic polarization, monitoring of weight and scanning electron microscopy (SEM). Stainless steel (SS) and carbon fiber (CF) exhibit higher stability than the others which are corroded by immersion. But the charge transfer resistance of stainless steel (SS) loaded polyaniline is much higher. Charge-discharge of Zn/polyaniline battery applying carbon fiber (CF) as a current collector shows high stability, specific capacity and coulombic efficiency. So carbon fiber (CF) is considered to be one of the best current collectors for PANI secondary batteries in nonaqueous medium. The study provides an academic foundation and application prospect for developing PANI secondary battery.

Keywords: current collector, polyaniline, zinc, carbon fiber, nonaqueous medium, rechargeable battery

1. INTRODUCTION

Polyaniline (PANI) as active material of batteries possesses excellent electrochemical reversibility [1-3]. It is a promising candidate for a rechargeable battery with a high performance [4-9]. One of the major problems encountered today to develop PANI battery is the chemical and electrochemical stability of its current collector. The current collectors of PANI battery should be good conductors of electricity, sufficient mechanical strength, corrosion resistant and chemical and electrochemical stabilities etc [10-12]. Once corrosion or dissolution happened to current collectors, will the contact resistance between active material and current collector increase. In addition, dissolved metal ions will pollute electrolyte. These factors will cause battery performances decline. In general, gold (Au)/platinum (Pt), graphite plate and carbon nano tube are adopted as the current collectors of PANI batteries at present [13-17]. However, these materials suffer from either high price or fabrication trouble although they can meet above requirements. These current collectors are difficult to meet the requirement of mass commercial production. The normal current collectors (such as aluminum foil, copper foil, nickel foil and stainless steel) also don't apply to PANI batteries. Therefore, the problem of current collectors must be broken through to commercialize the PANI battery.

In this paper, by comparing the properties of different current collectors, the CF is considered as the best current collector for PANI battery duo to its chemical and electrochemical stability, sufficient mechanical strength, light weight and good adhesiveness. This will provide a commercial prospect for breaking through a manufacturing bottleneck of PANI battery.

2. EXPERIMENTAL

2.1. Materials

Five kinds of possible material as current collectors for PANI batteries were selected. Stainless steel (SS) was offered by Dongguan Mingnuo metal materials co., LTD. Aluminum foil (AF) was supplied by National medicine group chemical reagent co., LTD. Lead foil (LF) came from Qingdao Yongjiasheng industry and trade co., LTD. They were polished with abrasive paper to remove the oxidation layer on the surface before tested. Conductive plastics (CP) came from Shenzhen Xinrida technology co., LTD. Carbon fiber (CF) was supplied by Nantong Senyou carbon fiber co., LTD.

The monomer aniline offered by National medicine group chemical reagent co., LTD was distilled under reduced pressure and stored in refrigerator (about 4 °C) before use. The others were used as received without further treatment. Zinc perchlorate hexahydrate (reagent grade) was supplied by Alfa Aesar (Tianjin) chemical co., LTD. Ethylene carbonate (EC) was offered by Sigma-Aldrich chemie GmbH. Dimethyl carbonate (DMC), ammonium persulfate ($(NH_4)_2S_2O_8$), hydrochloric acid and ethanol were supplied by National medicine group chemical reagent co., LTD. 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) ionic liquid was synthesized according to literatures [18].

2.2. The preparation of electrodes

The typical procedure for the synthesis of PANI was as follows [19-21]: a solution containing monomer aniline, hydrochloric acid and EMIES with a certain concentration ratio was added into a beaker, followed by slowly adding $(NH_4)_2S_2O_8$ (as an oxidant) to the solution under stirring. After 4 h of continuously stirring, the precipitate of the PANI was separated by centrifugation and washed with ethanol firstly to remove the polymers with low-molecular weight, then with the electrolyte (1M $ZnClO_4$/EC+DMC (volume ratio=1:1)) to remove the polymers which can be dissolved in the electrolyte, and finally with doubly distilled water until the filtrate was colorless. EMIES used here is to increase the electrochemical activity in a wide range of pH. After drying at 65 ^oC under vacuum for 12 h, the product was obtained.

The PANI was mixed with acetylene black and polytetrafluoroethylene (PTFE) in ethanol with a weight ratio of 80:10:10 to form slurry in an ultrasonic apparatus (KQ-100DB, Kunshan ultrasonic instrument co., LTD) for 3 h, then coated the slurry onto current collectors and dried for 2 h in an oven. The PANI battery consists of Zn slurry as anode, the PANI mixture as cathode, 1M $ZnClO_4$ / EC+DMC (volume ratio=1:1) as electrolyte and coated paper (Jiashan Yuhe Battery Industrial Co., Ltd.) as diaphragm. After assembling, the batteries were stored at room temperature for 24 h to ensure completely immersion of the active material and separators in the electrolytic solution.

2.3. Instrumentation and Characterization

Cyclic voltammetry (CV) performed on a CHI 660D electroanalysis apparatus and electrochemical impedance spectroscopy (EIS) powered by an electrochemical workstation (AutoLab, Nova 1.9, Metrohm) were used to compare the electrochemical activities of these current collectors before and after immersed in electrolyte for 40 days. The cyclic voltammograms were recorded in the solution of 1 M $ZnClO_4$ / (EC+DMC). A potential range was from -0.2 to 1.0 V at 0.05 V s^{-1}. The EIS spectra were taken in the same electrolyte. The superimposed sinusoidal voltage signal of 10 mV amplitude was applied. Data were collected within the frequency range of 10^5 to 10^{-2} Hz. The CV and EIS were carried out in a standard one-compartment three-electrode cell with a current collector as working electrode, and Pt foil as counter electrode. Saturated calomel electrode (SCE) served as a reference electrode. All potentials presented in this work refer to this reference electrode. The instrument for the charge and discharge experiments of the batteries was an automatic battery tester unit BTSDA (Shenzhen New ware). A Hitachi S-4800 scanning electron microscopy (SEM) was used to examine the surface morphologies of these current collectors before and after immersed in the electrolyte for 40 days. An analytical balance (Mettler Toledo) was applied to measure the weight of these current collectors before and after immersed in the electrolyte for 40 days.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry of blank current collectors

Figure 1 shows the cyclic voltammograms of the five blank current collectors before and after immersed in the previous electrolyte for 40 days. As shown in figure 1, there is some difference between the two curves of SS (A). The CV of stainless steel before immersed (curve 1) shows a broad hump at 0.2 V. However, the absence of the anodic broad hump after immersed in the electrolyte (curve 2) indicates that the surface of SS may be passivated in the electrolyte [22]. In figure B (CP), there are no redox peaks in two curves, which indicate the resistance and capacitance properties. But capacitive property in curve 2 is weaker than that of in curve 1, which is because the surface of CP is partly oxidized. So the superficial area of LF decreases. As to AF, the current value of the broad hump in curve 2 is much lower than that of in curve 1. It may be because that the decrease of conductivity for the aluminium oxide on AF surface after immersed, which shows AF is unstable in the electrolyte. According to LF, there are also no redox peaks in figure (D) and it only shows the property of resistance. The resistance value of LF after immersed is larger than that of before immersed. Fortunately, the CVs of the CF before and after immersed in the electrolyte in figure (E) maintain almost the same, which indicates that CF is stable in the electrolyte. Compared with other four current collectors, it can be seen that the CF as a current collector of PANI electrode is the best in the electrolyte.

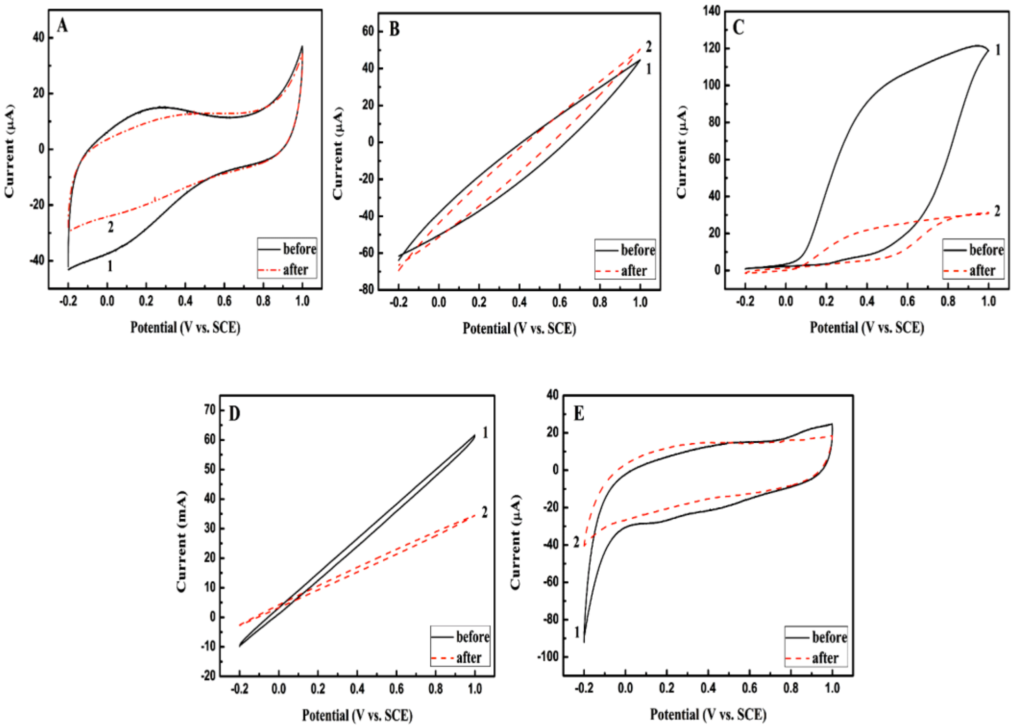

Figure 1. Cyclic voltammograms of current collectors before (1) and after (2) immersed in the electrolyte: (A): SS, (B): CP, (C): AF, (D): LF, (E): CF

3.2. Electrochemical impedance spectroscopy of blank current collectors

Figure 2 shows the electrochemical impedance spectra of the five current collectors before and after immersed in the electrolyte for 40 days. The electrochemical impedance spectra of SS, AF and CF illustrate straight lines without any semicircles, which reveal the electron transfer rate of the three current collectors is fast. However, after immersion the curves have changed more or less except CF. The difference of slope may be caused by the difference of surface morphology of electrode, which will be confirmed by SEM. The slope of straight lines after immersion decrease indicating the capacitive performance declines comparing with that of before immersion. The electrochemical impedance spectra of CP and LF show a compressed arc and an inclined straight line indicating that an ion diffusion process plays the primary role and there is no ion insertion reaction at the electrode/electrolyte interface [23]. But great changes have taken place by comparing the EIS curves of CP and LF before and after immersion (figure B and D). Compared with other four current collectors, it can also be seen that the CF as a current collector is the best in the electrolyte. These results are consistent with that of cyclic voltammetry.

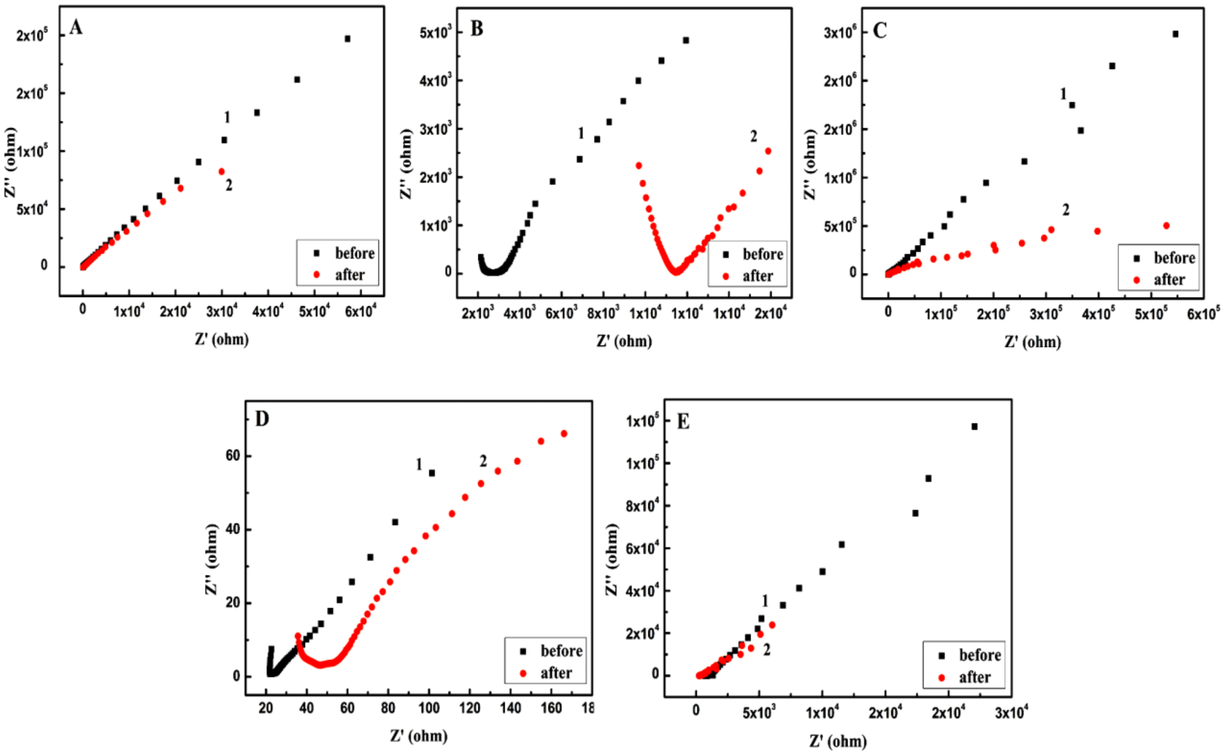

Figure 2. The electrochemical impedance spectra of current collectors before (1) and after (2) immersed in the electrolyte: (A): SS, (B): CP, (C): AF, (D): LF, (E): CF

3.3 Morphology of current collectors

Figure 3 shows the surface photographs of the five current collectors before and after immersed in the electrolyte for 40 days. It was seen from the Fig.3 that their morphologies have changed a lot after immersed except that of CF comparing with that of before immersed in the electrolyte. As to SS, the surface became a little rough after immersed in the electrolyte. The surface of the CP became rougher, loosened and porous obviously after immersed in the electrolyte, which is because the CP was partly dissolved in the electrolyte. The surface of AF after immersed in the electrolyte appears a lot of corrosion-pitting. LF after immersed in the electrolyte shows the flocculent morphology. However, the morphology of CF keeps almost the same before and after immersed in the electrolyte. The results show that the CF can remain stable in 1 M $ZnClO_4$ / (EC+DMC), which is consistent with that of CV and EIS.

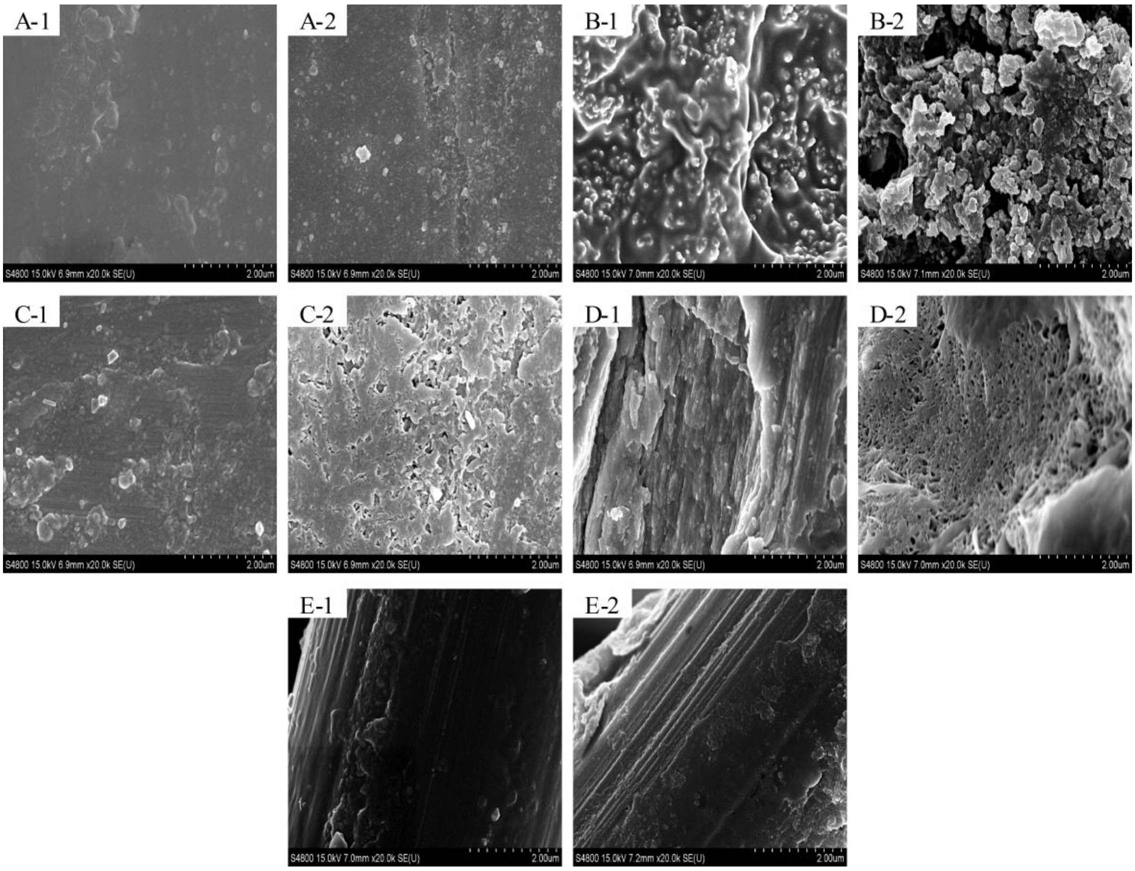

Figure 3. SEM photographs of current collectors: (A): SS, (B): CP, (C): AF, (D): LF, (E): CF (Before (1) and after (2) immersed in the electrolyte)

3.4 Tafel plots of current collectors

Tafel plot is an important indicator to characterize the anticorrosion of electrode material [24-26]. The left and right branches of Tafel plots in figure 4 are on behalf of cathodic and anodic polarization processes, respectively. It is seen from the figure 4 that the cathodic branches are under activation control and exhibit linearity in accord with Tafel relationship. The anodic branches are also consistent with Tafel law except AF and CF, which probably are duo to forming oxidation layer of AF film and swelling properties of CF film under higher positive potential. As is well-known, the higher the E_{corr} is, the better the anticorrosion of electrode material is [27]. Figure 4 shows Tafel plots of the five current collectors. Their E_{corr} before immersed in the electrolyte are -0.70V (SS), 0.55V (CP), -0.66V (AF), -0.66V (LF), -0.65V (CF), respectively. However, E_{corr} of CP (figure B) decreased greatly to -0.72V after immersed in the electrolyte for 40 days, which is because the CP is partly dissolved in the electrolyte. E_{corr} of the other four current collectors hardly change. So CP is unstable and not an appropriate current collector for PANI electrode in the electrolyte. E_{corr} of CF is higher and keeps stable both before and after immersion. CF may be an appropriate current collector for PANI electrode with potential application prospect.

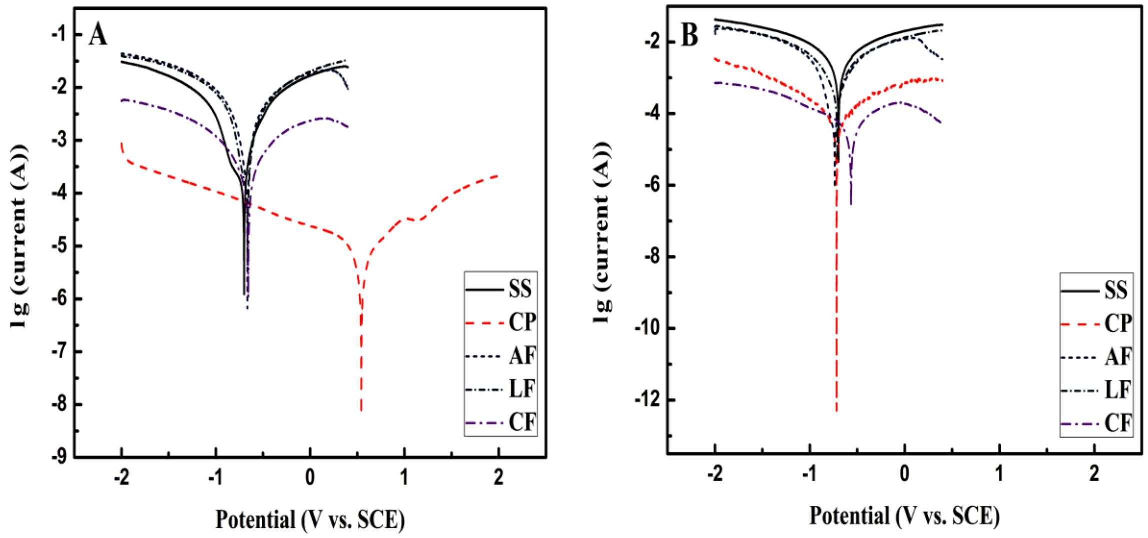

Figure 4. Tafel plots of current collectors: (Before (A) and after (B) immersed in the electrolyte)

3.5 Weight of current collectors

Table 1 is the weight of five current collectors after immersed in the electrolyte for different periods. There is almost no decrease of weight for SS and CF. But for CP, AF and LF, the decreases of weight are in varying degrees. The weights of CP and LF obviously decrease with increasing of immersion time. The color of the electrolyte turned from colorless and transparent into claret-colored when CP had been immersed for one month approximately. And when the immersion time reached 2736 h, CP has been completely dissolved in the electrolyte. So CP and LF are very easy to be corroded. The weight of AF maintains constant till immersed for 1512 h. But it is obvious that the weight of AF decreases when immersion time reached to 2736 h, which indicates that corrosion has also happened. But there is no obvious corrosion to SS and CF after immersed for 2736 h. It is seen that SS and CF may be two kinds of current collector for PANI electrode with higher stability.

Table 1. the weight of five current collectors after immersed in electrolyte for different periods

Weight / g	SS	CP	AF	LF	CF
0 h	0.0727	0.0168	0.0641	0.3541	0.0061
24 h	0.0729	0.0145	0.0641	0.3470	0.0061
48 h	0.0729	0.0139	0.0641	0.3388	0.0060
288 h	0.0730	0.0129	0.0641	0.3155	0.0060
528 h	0.0729	0.0130	0.0640	0.3052	0.0060
1512 h	0.0730	0.0117	0.0641	0.3002	0.0060
2736 h	0.0729	------	0.0633	0.2362	0.0060

3.6. Cyclic voltammetry of polyaniline deposited on current collectors

Cyclic voltammograms of polyaniline deposited on the five current collectors are shown in figure 5. As to the cyclic voltammogram of the polyaniline-coated CF, two pairs of redox peaks are more pronounced than that of the other four. Two main anodic peaks at 0.18 and 0.77 versus SCE correspond to the conversions between leucoemeraldine and emeraldine and between emeraldine and pernigraniline, respectively [28-30]. Two main cathodic peaks at -0.05 and 0.44 correspond to the reverse process, respectively. And the current values of redox peaks of the polyaniline-coated CF are the highest in the five current collectors. Only one pair of redox peaks appears for the polyaniline-coated AF, and the anodic peak moves to the right compared with the curve of CF. The curve for the polyaniline-coated SS shows two cathodic peaks and one broad anodic peak which may be the incorporation of two anodic peaks mentioned above. The curve for the polyaniline-coated CP and the insert of the polyaniline-coated LF both show no redox peaks, which indicates the electrochemical performance of the polyaniline-coated CP and the polyaniline-coated LF are not as good as others. This is because the electrochemical activity of polyaniline depends on the properties of current collector. By comparison, the CF current collector is the one with most application prospect among the five current collectors, which is in great agreement with the results of the above.

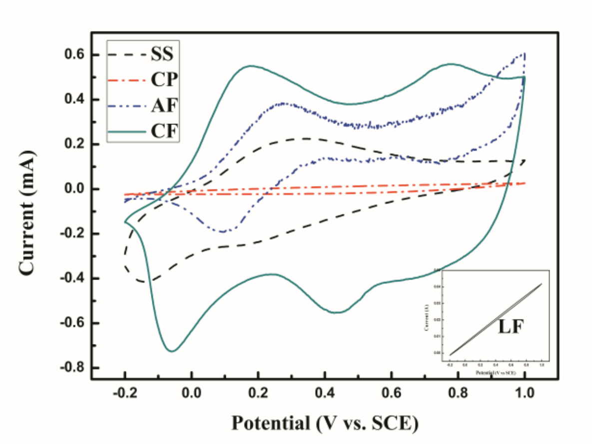

Figure 5. Cyclic voltammograms of polyaniline deposited on current collectors: (sanning speed = 1mV s^{-1}, the insert is about LF)

3.7. Electrochemical impedance spectroscopy of polyaniline deposited on current collectors

Figure 6 illustrates the Nyquist plots of polyaniline deposited on current collectors which obviously include two different regions [31-32]: a semicircle in high frequency region and a straight line in low frequency range. The semicircle in high frequency region stands for charge transfer resistance and double-layer capacitance. The straight line is on behalf of Warburg impedance of PANI, which indicates the reaction is controlled by interface diffusion between the electrolyte and electrode. The charge transfer resistances (R_{ct}) of polyaniline deposited on SS and CP are much higher than the other three. The possible reasons are as follows. First, high R_{ct} may be attributed to a poor current collector/active material contact: the surface contact is not optimum, due to a lack of adhesion of the active layer onto the current collector surface [33]. Second, the poor conductivity of the CP may be another reason. Therefore, SS and CP are not appropriate current collectors for polyaniline batteries.

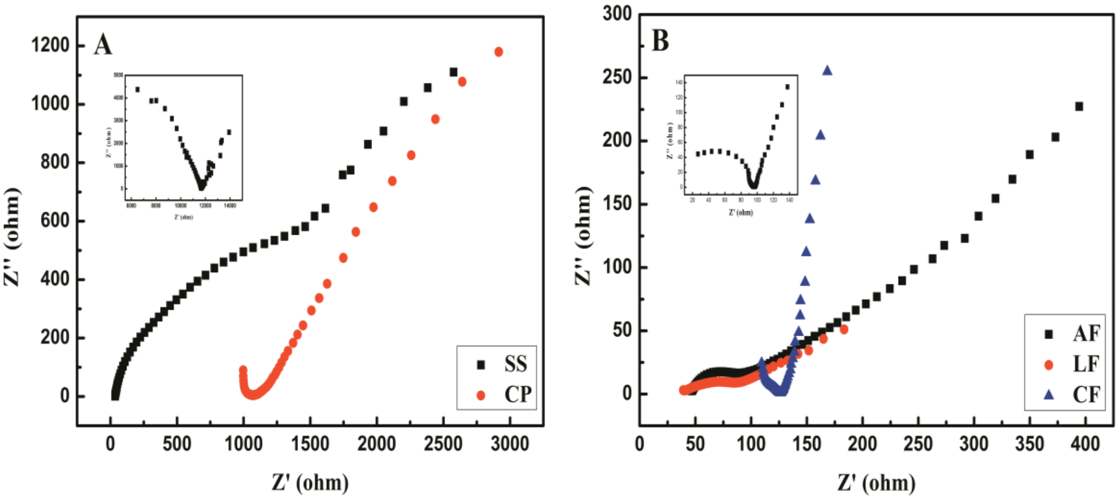

Figure 6. The electrochemical impedance spectra of polyaniline deposited on current collectors: ((A): SS (1), CP (2); (B): AF (3), LF (4), CF (5), the insets in (A) and (B) are EISs of PANI coated on CP and CF respectively with frequency range from 1MHz to 0.01Hz)

3.8 Galvanostatic charge-discharge measurement of Zn/PANI battery

The zinc slurry as anode and PANI deposited on the current collectors as cathode was cycled at a current density of 50 mA g^{-1} over 100 cycles to test the electrochemical properties. Figure 7 is the charge and discharge profiles of the Zn/polyaniline batteries at the 10th, 50th and 90th cycles. When cycled between 0.7 and 1.5V, the batteries exhibit symmetrical oblique lines except LF and AF. There are not any plateaus in discharge process that can be observed in lithium batteries [34], which is the characteristic discharge property of polyaniline [35]. As to figure A and B, with the increase of cycling numbers, both the potential range of charge-discharge processes and specific capacity diminished. But neither have happened to CF (figure E) which exhibits steady growing specific capacity although a slightly decline happened until the 90th cycle. The batteries can't carry through charge-discharge processes for LF and AF for the low open circuit potential (curves C and D). AF performs as anodic polarization at a constant current. As to LF, it has performed what AF dose for 77 h. Then the potential declined to zero sharply, which may attribute to short circuit. Therefore, CF performs better than the others.

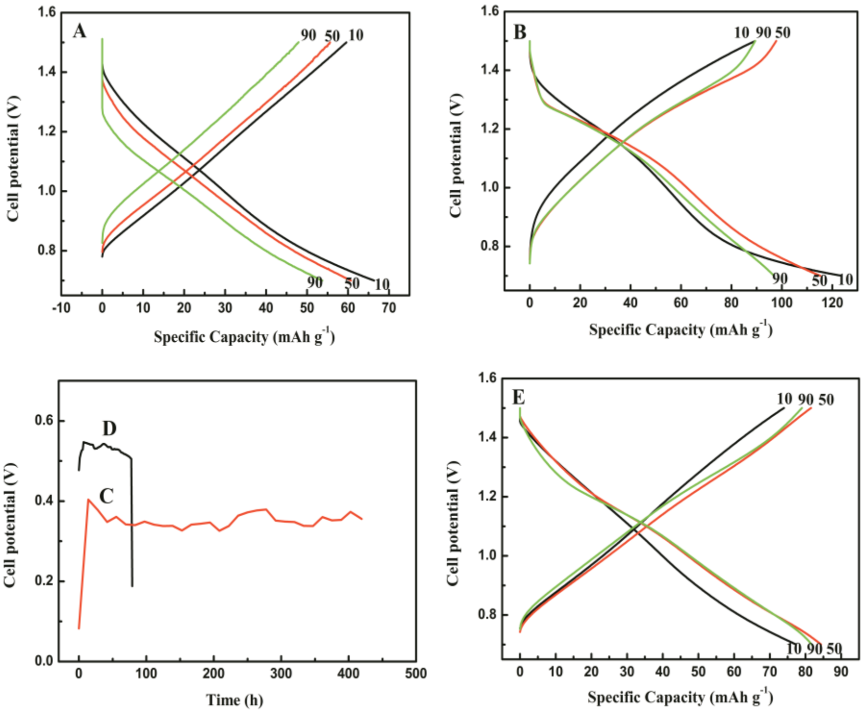

Figure 7. Charge and discharge profiles of Zn/polyaniline batteries at a current density of 50 mA g^{-1}: (A): SS, (B): CP, (C): AF, (D): LF, (E): CF

The cycle life of the Zn/PANI battery is shown in Figure 8. The figure only includes the dates of SS, CP and CF as current collectors because the batteries using AF and LF as current collectors can't carry through charge-discharge processes for the low open circuit potential (Figure 7(C-D)). There are obvious increases of the reversible capacity during initial several cycles. This is perhaps due to the activation process, which makes the electrolyte penetrate into the electrodes [36]. As to SS and CF as current collectors, the cycle efficiency maintains at approximate 100% or a little higher, which may well be related to the oxidization of part electrochemical reduced PANI by the oxygen in air. The discharge capacity of PANI for CF can keep stable at about 85.0 mAh g^{-1}. After 80 cycles, the discharge capacity slightly decreases with respect to cycle number but remains as high as 78.7 mAh g^{-1} at the 100th cycle losing only 7.4% of its beginning discharge capacity. The data demonstrates the excellent capacity retention with coulombic efficiency above 98%. The discharge capacity of PANI for SS decreases from 68.9 mAh g^{-1} to 51.1 mAh g^{-1} losing 25.8% of its beginning discharge capacity in the range of 100 cycles. So the specific capacity of PANI for SS decreases more quickly despite the coulombic efficiency is high. As to CP, the discharge capacity and coulombic efficiency of first few cycles reach up to above 130 mAh g^{-1} and 130%, respectively. Then they all decline quickly, which may attribute to that the component of CP includes some active substance which takes part in reactions. The CP is unstable in the electrolyte although the specific capacity and the coulombic efficiency are higher than the other two. So CF is the appropriate current collector for PANI electrode, which is in good agreement with the conclusion of the above.

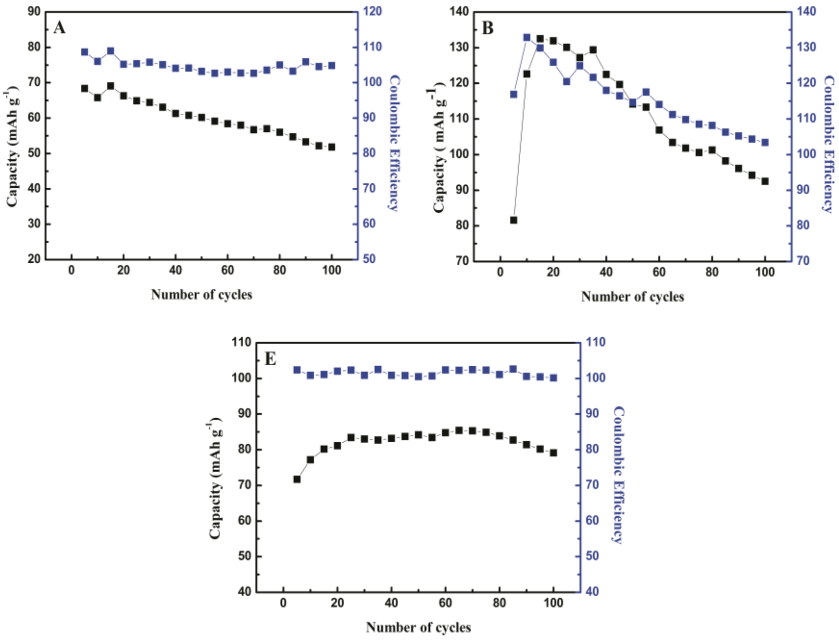

Figure 8. Cycle life data of Zn/polyaniline batteries at a current density of 50 mA g^{-1}: (A): SS, (B): CP, (E): CF

3.9 Morphology of current collectors after charge-discharge processes

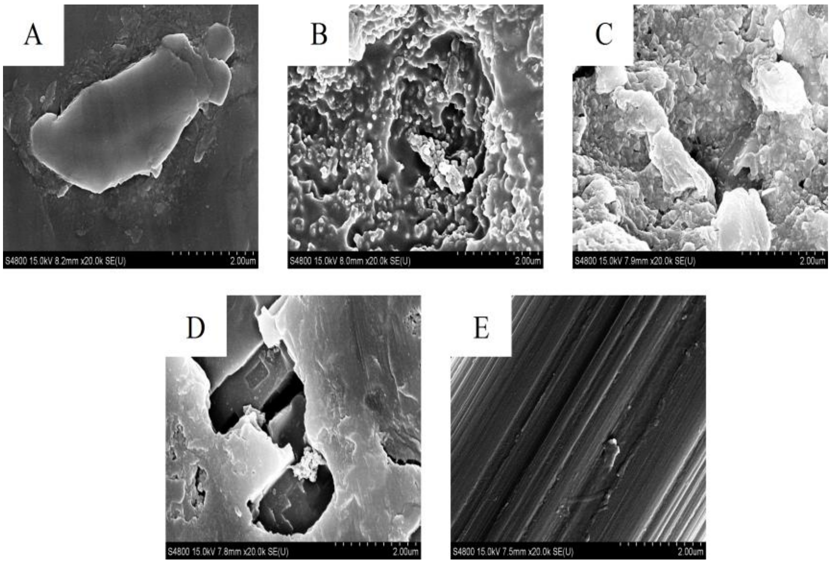

Figure 9. SEM photographs of current collectors after charge-discharge processes: (A): SS, (B): CP, (C): AF, (D): LF, (E): CF

SEM photographs of the five current collectors after charge-discharge processes are shown in figure 9. Compared to the morphology of the current collectors before charge-discharge processes in figure 3, the morphology of those current collectors after charge-discharge processes has changed a lot except CF. SS has swelled in figure 9 (A). The obvious corrosion has taken place in the surface of CP and AF. A big etch pit can be observed in figure 9 (D) (LF). SEM photograph of CF maintains almost the same as the original. In addition, the weight of CF keeps almost constant before and after charge-discharge processes while the weights of the other current collectors reduce to varying degrees. Thus it can be seen that CF keeps stable not only after immersion but also after charge-discharge processes, which is consistent with figure 3.

4. CONCLUSION

In conclusion, Stainless steel (SS) and carbon fiber (CF) exhibit higher stability than the others which are corroded by immersion. But the charge transfer resistance of SS loaded PANI is much higher than that of CF. The results of charge-discharge processes reveal Zn/polyaniline battery applying carbon fiber (CF) as a current collector has a stable output capacity of about 85.0 mAh g^{-1} with a columbic efficiency of above 98% at least 100 cycles between 0.70 and 1.50 V. CF seems to be the most suitable material as a current collector of the positive electrode of Zn/polyaniline battery. The study provides an academic foundation and application prospect for developing PANI secondary battery. Further experiment is being planned.

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