Short communication

A Novel Flexible Aluminum//Polyaniline Air Battery

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The electrochemical behavior of pure aluminum (Al) foil in the NH_4Cl electrolyte was investigated, and it was found that the additives sodium nitrate and triethanolamine (TEA) play a synergistic role in the activation of the Al electrode. Using the Fe(III)-anthraquinone-2,6-disulfonate(AQDS)-doped polyaniline electrode (PANI/Fe) as the air electrode, Al as counter electrode, a gel electrolyte of NH_4Cl, TEA and $NaNO_3$, a flexible and ultrathin air battery was prepared. The resulting Al//PANI/Fe air battery exhibits excellent electrochemical performance, and it has a thickness of approximately 0.5 mm, a discharge plateau of 1.2 V, and a discharge capacity of 50 mAh·cm^{-2}. The battery is inexpensive, environmentally friendly, and feasible to use as a disposable battery.

1. INTRODUCTION

With the recent rapid development of electronic equipment and technology, the size of electronic equipment and devices has decreased in various fields. Recently, the study of miniature energy storage systems with high energy density has received increasing attention in, for example, ionic transdermal drug delivery in medicine[1], active radio－frequency identification (RFID) tags[2,3] and wearable electronic devices[4-7]. In addition to research, an increasing number of companies have begun offering ultrathin flexible power source solutions. These developments mean that, with the development of electronic equipment and technology, flexible battery technology exhibits huge potential.

Al is the most abundant metal in the Earth's crust and one of the most easily recycled metals. Al is inexpensive, causes no pollution and has a high specific energy. Because of its high ductility and lightweight, it has been used widely as a cheap, flexible material in production and life. However, as a

battery anode material, Al has certain shortcomings. Although Al has a very negative standard potential of −1.67 V, a 1–3 nm thick alumina film can easily form on its surface. This alumina film can regrow once damaged, and its properties and structure are very stable. This dense oxide film makes Al an excellent lightweight anticorrosive material. However, as a battery electrode, this oxide film is detrimental to the ion exchange between the Al base and the solution, which increases electrode resistance and leads to a much lower working potential of the Al electrode than its standard potential[8]. In studies on the use of Al as electrode material, the activation of the Al electrode is mostly achieved by alloying Al. The alloying elements are doped on the surface of Al, thus preventing the formation of alumina film and decreasing the thickness and resistance of the oxide film. Additionally, when the electrode runs in strong alkali solutions[9], the alloy elements accelerate the oxide film dissolution, thus increasing the electrode potential. In Al alloy research, Ga, In, Sn, Pb, Bi, Hg, Cd, Mg and Mn are the commonly used alloying elements for the activation of the Al electrode[10-17]. For example, the solution treatment of an alloy of Al-Ga-Bi-Pb at 500°C for 8 h can effectively decrease the polarization of the alloy material and improve the discharge voltage[18]. Z.G. Sun, H.M. Lu, L. Fan, Q.S. Hong, J. Leng, C.B. Chen showed that the amount of Ga can impact the extent of the potential negative shift of the Al electrode, while the addition of Sn can inhibit the high self-corrosion rate of the activated Al anode[19]. M.G. Liang, J.B. Wen, J.G. He, D.D. Chen showed that adding In and Mg in an Al-Ga-Mn alloy can further decrease the potential of the Al alloy and inhibit the self-corrosion rate; the open-circuit potential and discharge voltage of the prepared Al-Ga-Mn-Mg-In alloy reached −1.797 V and −1.485 V, respectively[20]. All studies of Al alloys show that alloying by Ga, In and other rare metals is beneficial to the destruction of the passive film on the Al surface. Thus, these rare metals are the main alloying elements for Al alloys. Mg, Mn, Zn and other metals can improve the anticorrosion performance of Al alloys[21,22]. As research progresses, an increasing number of elements are added to Al alloys (from 3 components to 5 or 6 components). The addition of rare metal elements, combined with the complex preparation processes, has resulted in the very high cost of these alloys. In addition, the addition of environmentally toxic metal elements such as Cd and Pb in Al alloys makes the originally environmentally friendly Al a threat to the environment[23,24]. Therefore, although multicomponent Al alloys have achieved excellent effects, such as the negative shift of the potential of the Al anode and the decrease in the self-corrosion rate, they are not suitable for disposable electrode materials.

Among the many conductive polymers[25,26], irons doped polyaniline (PANI) has become one of the most attractive because of the low cost of the monomer, its simple synthesis process, and its excellent stability and conductivity. irons doped PANI has shown huge potential in electrochemical energy materials because of these characteristics.

In the present study, Al was used as an anode material and activated by additives to the weak acidic electrolyte. The air electrode is the PANI/Fe composite film deposited on graphite paper using the galvanostatic method. Using filter paper as the material to separate the anode and the cathode of the battery and as the supporting substrate for the gel electrolyte, a low-cost and environmentally friendly disposable flexible air battery was prepared. The electrodes performance and battery discharge performance of the resulting battery were investigated.

2. EXPERIMENTAL SECTION

2.1 Equipment and materials

Equipment: CHI660D electrochemical analyzer/workstation (CH Instruments Ins.), 101-OAB-type electric heating air-blowing drier (Tianjin Taisite Instrument Co., LTD), and 5V/10II A-type high-accuracy battery testing equipment (Neware Inc., Shenzhen).

Materials: Flexible graphite paper, carboxymethyl cellulose, pure Al foil (thickness of 0.01 mm), concentrated H_2SO_4, NH_4Cl, $FeCl_3$, aniline, and $FeCl_2$; all are analytic grade. The water used was doubly deionized water.

2.2 Preparation of PANI/Fe air electrode

The treated graphite paper was used as the cathode, and inert graphite flake was used as the anode. The double-sided PANI/Fe air electrode was prepared via deposition at a constant current density of 5.0 $mA \cdot cm^{-2}$ for 2 h in a solution containing 0.25 $mol \cdot L^{-1}$ aniline, 1 $mol \cdot L^{-1}$ H_2SO_4, 10 $mmol \cdot L^{-1}$ $FeCl_3$, 8 $mmol \cdot L^{-1}$ $FeCl_2$ and 0.01$mol \cdot L^{-1}$ AQDS.

2.3 Preparation of the gel electrolyte and assembly of the battery

A solution containing 2 $mol \cdot L^{-1}$ NH_4Cl, 0.1 $mol \cdot L^{-1}$ triethanolamine (TEA) and 0.05 $mol \cdot L^{-1}$ $NaNO_3$ was prepared. After adjusting the pH of the solution to 3 using HCl, 3 wt% carboxymethyl cellulose was added to the solution. The resulting mixture was stirred for 30 min by a magnetic stirrer and then remained stationary for 4 h so that the electrolyte could undergo sufficient gelation to obtain the gel electrolyte.

After soaking the filter paper in the gel electrolyte for 2 min, the Al foil electrode, filter paper and air electrode were assembled in sequence. The battery was covered with polytetrafluoroethylene film which made the diffusion layer permeable only to air and prevented the permeation of water.

2.4 Al electrode and battery performance tests

A three-electrode system was used to attain the Tafel polarization curves, as well as the open-circuit potential of the Al electrode and the PANI/Fe air electrode. In the system, the counter electrode was the Pt electrode and the reference electrode was the saturated calomel electrode (SCE). The scanning rate for the polarization curve was 1 mV/s, and the scanning time for the open-circuit potential was 15 min. Using battery test equipment, the battery was discharged to 0 V at a constant current of 0.5 mA to test the charge-discharge performance of the prepared battery.

3. RESULT AND DISCUSSION

3.1 Effect of electrolyte additives on the electrochemical performance of the Al electrode

Figure 1 shows the scheme of the Al/PANI air battery. The main body of the battery was covered by a breathable preservation film that prevented the rapid loss of water. In a pH range of 4.5–8.5, the oxide film on the Al surface is very stable. In other Al air battery studies, a high concentration of KOH solution is normally used as the electrolyte solution to maximize the conductivity of the solution and the corrosion rate of the passive film. However, strong alkali electrolytes exhibit high corrosion. Once the leakage of electrolyte solution can cause serious hazards. In addition, PANI can lose its intrinsic conductivity and electrochemical activity in high-pH solutions because of dedoping of protonic acid[27,28]. In contrast, the weak acidic electrolyte can decrease the environmental hazard by the electrolyte solution and improve the conductivity and electrochemical property of the PANI air electrode. Al mainly undergoes pit corrosion at a pH under 4.5[29,30]. Pit corrosion easily occurs for halide ions (Cl^- in particular). Cl^- has a strong penetration capability for oxide films on Al surfaces[31-33]; it is transported through oxygen vacancies, defects and local dissolution. Because the radii of Cl^- and O^{2-} are very close (the radius of Cl^- is 0.181 nm, while that of O^{2-} is 0.140 nm), Cl^- transport through oxygen vacancies in the passive film is possible. On the contrary, F^- reacts with Al^{3+} to form insoluble AlF_3 and is therefore detrimental to the corrosion of the oxide film on the Al surface.
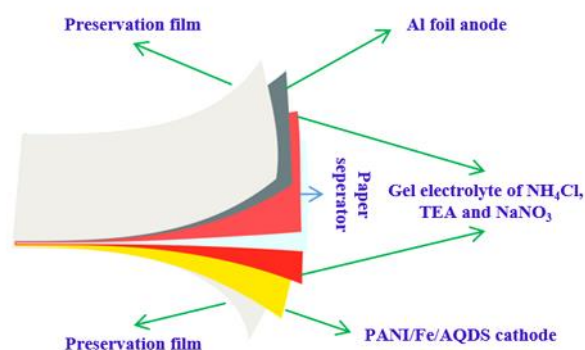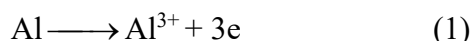

Figure 1. Scheme of the Al/PANI air battery

Therefore, in the electrolyte solution, Cl^- exhibits the best effect on the pit corrosion of the oxide film on the Al surface. The anodic dissolution reaction of Al in acidic solutions is shown in Equation (1):

$$Al \longrightarrow Al^{3+} + 3e \qquad (1)$$

Using 2 mol·L⁻¹ NH_4Cl solution as the blank control, the effect of the additives TEA and $NaNO_3$ in the electrolyte solution on the Al electrode was explored; the Tafel polarization curve is shown in Figure 2.
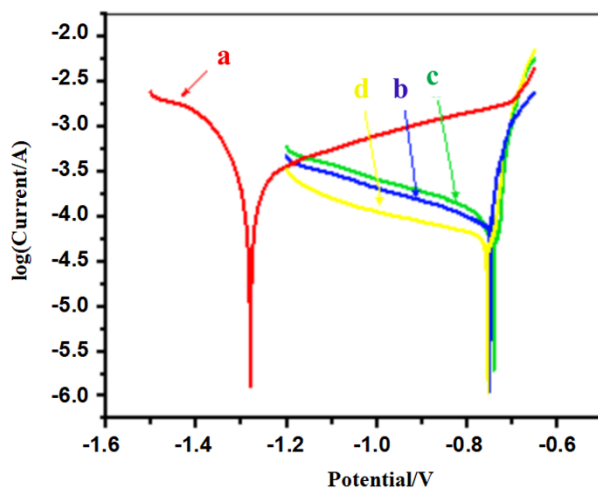
Figure 2. Polarization curves in the Tafel region of Al electrodes in a electrolyte solution (pH = 3) with various additives (The scanning rate: 1 mV/s): a, 0.1 mol·L^{-1} NaNO$_3$ and 0.05 mol·L^{-1} TEA; b, 0.1 mol·L^{-1} TEA; c, 2 mol·L^{-1} NH$_4$Cl solution as control; d, 0.05 mol·L^{-1} NaNO$_3$.

It can be seen from Figure 2 that the addition of either TEA or NaNO$_3$ to the electrolyte solution does not result in a large effect on the corrosion potential of the Al electrode, but the addition of both TEA and NaNO$_3$ causes a significant negative shift of the corrosion potential of the Al electrode. Zaid, Saidi, Benzaid, Hadji[34] found that pit corrosion of the oxide film on the Al surface via Cl$^-$ requires a certain incubation period. Moreover, the thicker the oxide film is, the slower the corrosion rate of the oxide film by Cl$^-$. In a neutral solution that contains only Cl$^-$, the corrosion of the oxide film on the Al surface is a rather slow process. Under acidic conditions, because NO$_3^-$ is a strong oxidant, it can be used as the cathode for the corrosion of Al; its reaction is shown in Equation (2):

$$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O \qquad (2)$$
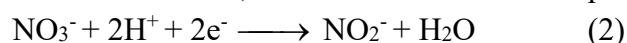
A small amount of NO$_3^-$ can corrode the oxide film on the Al surface, thus decreasing the thickness of the oxide film[35,36]. In the meantime, uneven corrosion results in defects and pit corrosion on the surface of the oxide film, providing anchoring points for Cl$^-$ on the oxide film. Al^{3+} in the solution close to the oxide film could undergo hydrolysis. In Cl$^-$-containing weak acidic solutions, Al^{3+} hydrolyzes to form a Al(OH)$_2$Cl salt film. The pore wall that adsorbs Al(OH)$_2$Cl is in a passivated state. The high concentration of Cl$^-$ and low pH in the pits can prevent the formation of a passive film. However, at the apex of pits without a salt film, Al undergoes active dissolution, thus resulting in further growth of pits. When the apex of pits is covered by the salt film, the pit is completely passivated and stops growing. Some studies[19-20] have shown that TEA can specifically adsorb on metal surfaces, thus altering the structure of the interfacial electric double layer on the surface of the metal[37-39]. Because of the presence of an empty orbital in the outer orbit of Al, TEA can coordinate with Al^{3+} by providing a lone pair of electrons from an N atom. Because TEA is terminated with a hydrophilic group (-OH), it is beneficial to the dispersion of coordination ions in a solution. The coordination of TEA with Al^{3+} in the Al oxide film pits likely results in the dissolution of the salt film, thus preventing the formation of a salt film. In addition, it is also beneficial to the dispersion of Al^{3+} to the solution, thus decreasing the interfacial resistance of the Al surface. Therefore, the Al electrode is prominently activated in the

NH$_4$Cl electrolyte with NaNO$_3$ and TEA as actives, of which corrosion potential was illustrated by the Tafel curve Figure 2a.

3.2 Performance of the flexible air battery

Using either 2 mol·L^{-1} NH$_4$Cl as the gel electrolyte and PANI as the cathode (battery b) or 2 mol·L^{-1} NH$_4$Cl, 0.1 mol·L^{-1} TEA, 0.05 mol·L^{-1} NaNO$_3$ as the gel electrolyte and PANI/Fe air electrode as the cathode (battery a), the battery with Al foil as the anode was connected to the battery tester. The battery was discharged at a constant current density of 0.5 mA·cm^{-2} until the potential decreased to 0 V; the results are shown in Figure 3.
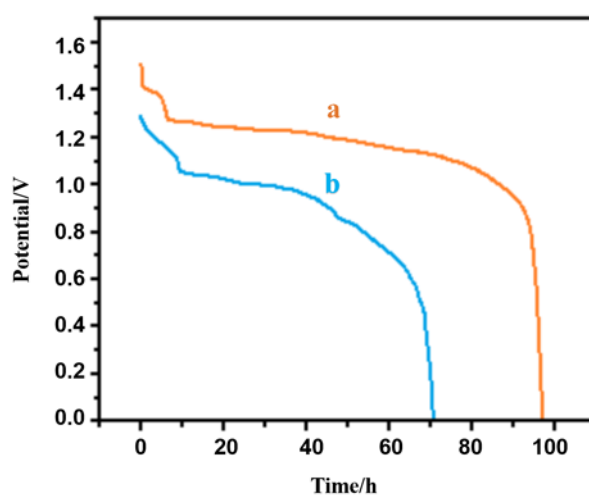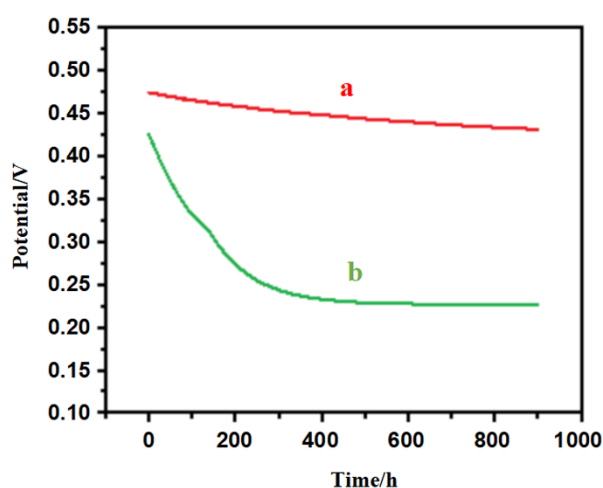

Figure 3. Galvanostatic discharge of the battery under various electrolyte conditions at 0.5 mA·cm^{-2}: a, 2 mol·L^{-1} NH$_4$Cl, 0.1 mol·L^{-1} TEA, 0.05 mol·L^{-1} NaNO$_3$ as the gel electrolyte and PANI/Fe air electrode as the cathode; b, 2 mol·L^{-1} NH$_4$Cl as the gel electrolyte and PANI as the cathode.

(a) With 0.05 mol·L^{-1} NaNO$_3$、 0.1 mol·L^{-1} TEA   (b) Without NaNO$_3$、 TEA

Figure 4. Effect of additives on the potential of the PANI electrode

It can be seen from the figure that the working voltage of battery a is approximately 0.3 V higher than that of battery b. In addition, battery a has an obvious discharge plateau while discharging. The synergistic effect of $NaNO_3$ and TEA has produced a certain effect on the activation of Al electrode potential. However, the working voltage of the battery is still far below the expected value. This is likely because NO_3^- and TEA can also be adsorbed on the cathode, forming a layer on the surface of the PANI electrode that is detrimental to ion diffusion [40]. Figure 4 shows the open-circuit potential of the PANI electrode in the solution containing additives. It can be seen from the figure that, with the addition of $NaNO_3$ and TEA to the solution, a decrease in the open-circuit potential of the PANI electrode appeared; this agrees with the above hypothesis.

The PANI electrode doped with Fe(III)-AQDS exhibited excellent air catalytic performance, shown in Figure 5. There is a steady discharge plateau between 1.0 V and 1.2 V; the capacity increased by almost 40%, seen from the Figure 5a. Because the ion diffusion in a gel electrolyte is slower than that in a liquid electrolyte, the accumulation of precipitates on electrodes results in an increase in battery resistance, which leads to a decrease in battery potential until the battery stops working.

After the battery stopped working, the Al foil electrode was replaced, and the battery was coated with new gel electrolyte. After sitting stationary for 10 h, the battery was tested for discharge; the results are shown in Figure 5b. It can be seen from the figure that after the battery sits stationary for a certain period under natural conditions, the potential of the battery rebounds significantly, which is due to that the cathode material has excellent air catalytic performance. However the discharge capacity approaches 70% of the initial discharge capacity, and the discharge voltage is also slightly lower than the initial discharge voltage. The accumulative discharge capacity is much more than that of the system of Al-0.5In as anode for Al–air battery in inhibited alkaline solutions[41]. This is probably attributed to the irreversibility of the de-doping of Fe ions and the accumulation of insoluble materials on the cathode.
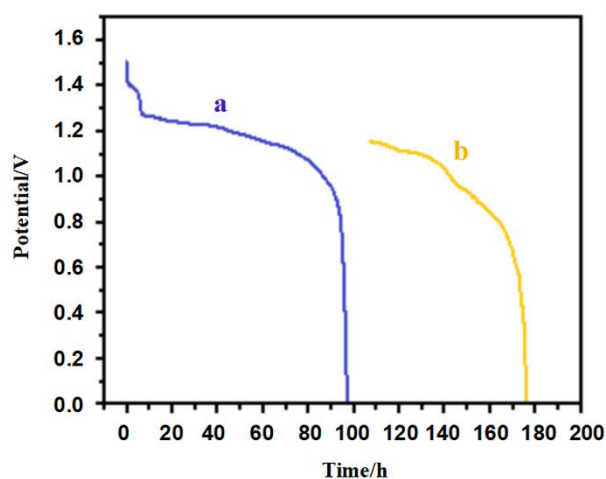

Figure 5. Rebounding of the battery potential when the battery sits stationary under natural conditions at 0.5 mA·cm^{-2} ：a, first discharge; b, second discharge

4. CONCLUSION

Because the preparation and materials are inexpensive and the other materials used do not cause environmental pollution, the prepared Al//PANI air battery shows feasibility as a disposable battery. The synergistic corrosion effect of the additives TEA and NaNO$_3$ on the oxide film on the Al surface results in a large negative shift of the corrosion potential of Al. In consequence, the working voltage of the battery in such an electrolyte is improved by approximately 0.3 V. The PANI/Fe air electrode exhibits excellent air catalytic performance and a stable discharge plateau while discharging at a constant current density of 0.5 mA·cm^{-2}. The discharge capacity reaches almost 50 mAh·cm^{-2}. The potential and capacity of the battery can rebound a large extent after sitting stationary under natural conditions. Therefore, the Al//PANI/Fe air flexible battery shows feasibility as a disposable battery.

CONFLICTS OF INTEREST
There are no conflicts to declare.

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