Short communication

A novel dry bipolar rechargeable battery based on polyaniline

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Abstract

Polyaniline powder of high conductivity is prepared by chemical polymerization of aniline in solutions containing 0.10 M aniline, 2 M perchloric acid and 0.15 M ammonium persulfate at 5 °C. The powder is mixed with graphite and acetylene black for obtaining high conductivity. The chemically-synthesized polyaniline doped with perchloric acid is then used as a cathode in the construction of a bipolar rechargeable battery which employs anti-acid stainless steel as a conductive substrate for a bipolar electrode. The proposed battery contains electrochemically-synthesized zinc powder as an anode material and a solution which contains 1 M $Zn(ClO_4)_2$ and 0.5 M $NClO_4$ and 1.0×10^{-4} M Triton-X100 at pH of 3.2 as a battery electrolyte. To prevent hydrogen reduction, 1 wt.% of electrochemically-synthesized optalloy is mixed with zinc powder which contains 2 wt.% MgO, 4 wt.% ZnO and 1 wt.% sodium carboxymethyl cellulose. To investigate the effect of separator thickness on battery efficiency, three batteries are constructed with one, two and three layers of separators. Each sub-cell from the battery has an open-circuit voltage of 1.6 V. Two bipolar batteries with open-circuit voltages of 3.2 and 6.4 V are constructed and tested successfully for 100 charge–discharge cycles. The batteries have a capacity of 110 mA h g^{-1} and Coulombic efficiency of >90%.
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1. Introduction

In recent years, considerable interest has been shown in the use of polyaniline as a conducting organic polymer [1,2]. It has been found that polyaniline film or powder exhibits several redox couples in aqueous solutions. The quasi-reversible nature of polyaniline can be utilized in aqueous secondary batteries [3–5]. The majorities of the reported rechargeable batteries based on polyaniline are typically wet batteries, in which hydrochloric acid is used as dopant acid and the corresponding electrolyte contains $ZnCl_2$ and NH_4Cl at a pH of 4 or above [6–10].

In previous studies, we employed polyaniline in a chemical sensor [11] and a wet rechargeable battery [12], and also showed that polyaniline doped with perchlorate acts as a more suitable cathode material than the chloride-doped polyaniline for use in dry rechargeable batteries [13].

In recent years, much research has been conducted on bipolar systems for application in batteries [14–16]. An important approach to achieving high-energy batteries is to decrease the thickness of the electrodes. Bipolar flat plate electrodes allow the use of the thin plates.

A battery with a bipolar configuration is known to be superior to conventional batteries in terms of power output. In a conventional monopolar battery, the current generated by the active materials travels to a current-collector and through an outer circuit to reach the next cell. In a bipolar battery, the negative active material is placed on one side of a conductive substrate and the positive active material on the other side, and electrons can flow through the substrate to the next cell. Accordingly, because of a much shorter electrical path, the power loss due to Ohmic drop in the circuit is minimized. The volume of the battery is also reduced through elimination of the outer circuit materials, such as straps, posts and tabs [15]. The application of a bipolar cell design offers several advantages and therefore methods are sought to introduce the design into modern batteries. The design principle is strongly influenced by the choice of the electrochemical couple of the storage system [14]. Another advantage of the bipolar design is that the cross-section for the electric current-collectors is the size all over the bipolar stack. The connecting bipolar plate can be made from metal foil or other electronically conducting materials. The bipolar plate has to prevent any electrolytic bridges between adjacent sub-cells [17].

Although various substrates, e.g. stainless steel, lead, silver and carbon–polymer composite foils, have been used in

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the construction of bipolar electrodes for different batteries, such as lead–acid and nickel–metal hydride [15,18–21], to the best of our knowledge, there is no previous report on the use of bipolar electrodes in polyaniline batteries.

In this work, a novel dry rechargeable battery based on the use of polyaniline doped with perchlorate ions, an electrolyte of $Zn(ClO_4)_2$, NH_4ClO_4 and Triton-X100 at pH 3.2 and the anti-acid stainless steel bipolar flat electrodes are reported. Optalloy is used in the anode mixture in order to increase the overvoltage for the reduction of H^+ ions and, consequently, to prevent the formation of Zn–hydrogen local cells. Triton-X100 is included in the battery electrolyte to prevent the formation of zinc dendrites [22]. To increase the conductivity of polyaniline, graphite powder and acetylene black are also added to the polyaniline powder [13]. Electrochemically-synthesized zinc powder is mixed with magnesium oxide and zinc oxide to increase zinc reversibility and sodium carboxymethyl cellulose is added to form suitable links between the zinc particles. The proposed battery shows good behavior during 100 cycles of charge and discharge. In the battery, each sub-cell had an open-circuit voltage (OCV) of 1.6 V.

2. Experimental

2.1. Reagents and materials

Aniline, ammonium persulfate and zinc chloride were obtained from Aldrich. Triton-X100 and all other reagents, such as hydrochloric acid, sodium hydroxide and other compounds were of analytical reagent grade (prepared from Fluka or Merck). Argon (purity of 99.999%) was obtained from the Roham Gas Co. The water used in all experiments was double-distilled.

2.2. Apparatus

All electrosynthesis experiments were carried out with a BHP 2061-C electrochemical analyzer (Behpajoh Co., Isfahan, Iran). Potential measurements were performed with a digital multimeter (model 8503, Sa-Iran Co., Iran) and pH measurements with a Metrohm pH-meter model 691. All charge and discharge experiments on batteries were conducted with a battery test unit (BPT Co., Tehran, Iran).

2.3. Methods

Polyaniline was synthesized by chemical polymerization from a solution of 0.10 M aniline, 2 M perchloric acid and 0.15 M ammonium persulfate at 5 °C. Argon gas was passed through the polymerization solution to remove dissolved oxygen and, during polymerization, argon was passed across the surface of the solution to prevent oxygen diffusion. After 24 h, the mixture was filtered, washed with water and 2 M $HClO_4$ solution, and poured into tetrahydrofuran to separate

the polyaniline small chains, which are soluble in tetrahydrofuran. It should be noted that the presence of small chains decreases the conductivity of polyaniline. The mixture was then filtered and washed three times with a 2 M $HClO_4$ solution and double-distilled water, respectively. The resulting polyaniline was dried under vacuum at 80 °C and powdered to particles of diameter of 54–73 μm by using of two sieves of 200 and 270 mesh. Then, 80 g of the powder was mixed with 18 g of graphite and 2 g of acetylene black to prepare the cathode of the battery. Zinc powder (92 g) was mixed with optalloy powder (1 g), magnesium oxide (2 g), zinc oxide (4 g) and sodium carboxymethyl cellulose (1 g) to prepare the anode of the battery. A solution containing 1 M $Zn(ClO_4)_2$, 0.5 M NH_4ClO_4 and 1×10^{-4} M Triton-X100 at a pH of 3.2 served as the battery electrolyte. The separator was made from cellulose acetate separator.

3. Results and discussion

Due to the dependence of battery efficiency on the conductivity of the cathode, the anode and the bipolar substrate, all these components should have high conductivity. The conductivity of polyaniline depends on various parameters, such as aniline concentration, ammonium persulfate (oxidant) and dopant acid (perchloric acid) concentrations in the synthesis solution, and the temperature of polymerization. Thus, polyaniline was synthesized under the optimum conditions [13] summarized in Table 1.

Because of the dependence of bipolar battery efficiency on the adhesion of active material to the substrate, the design and construction of battery assembly is very important [14,18]. Thus, in assembling the battery, the different components should be completely connected to each other. To achieve this, after overlaying of the battery components, three bolts and nuts were used to press them together efficiently. The configuration of the proposed bipolar battery is shown in Fig. 1. Anti-acid stainless steel was used as a suitable substrate for construction of the bipolar electrodes and the cathode current-collector, brass alloy for the anode current-collector, and polyethylene as the battery cover.

To investigate battery efficiency, the performance was investigated during 100 charge and discharge cycles at constant current. The effect of current density on battery capacity was examined; the results are shown in Fig. 2. Maximum capacity is displayed at a current density of 250 mA g^{-1} of

Table 1
Optimum conditions for synthesis of high-conductive polyaniline doped with perchlorate

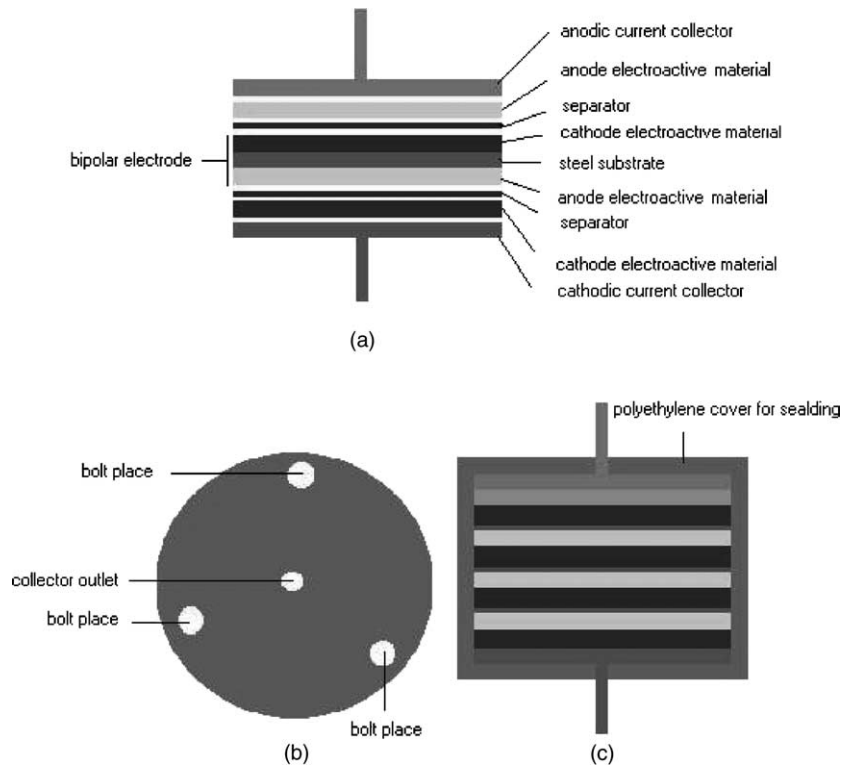| Optimized parameter	Optimum amount
Aniline concentration (M)	0.1
Ammonium persulfate (M)	0.15
Perchloric acid (M)	2
Synthesis temperature (°C)	5

Fig. 1. Structure of proposed bipolar battery, stainless steel used as cathode current-collector and conductive substrate for bipolar electrode, and brass alloy used as anode current-collector: (a) presentation of different parts of bipolar battery; (b) orthograph of battery; (c) 6.4 V sealed bipolar battery containing three bipolar electrodes.

polyaniline. At higher current densities, however, only the outer layer of the electroactive material can contribute to the charge and discharge processes and, consequently, the battery capacity is decreased. Current densities greater than $250 \, \text{mA g}^{-1}$ can also cause a decrease in the Coulombic efficiency of the battery (Fig. 3). Therefore, a current density of $250 \, \text{mA g}^{-1}$ was selected for the charge and discharge of batteries.

The voltage–time behavior of the proposed battery during various charge and discharge cycles at a constant current of $250 \, \text{mA g}^{-1}$ is shown in Fig. 4. The variation of capacity and Coulombic efficiency of the battery was calculated from Eqs. (1) and (2):

$$C = \frac{it}{w} \tag{1}$$

where C is the capacity (mA h g^{-1}), i the current (mA), t the time (h), and w the polyaniline weight (g).

$$\text{Coulombic efficiency} = \frac{t_2}{t_1} \times 100\% \tag{2}$$

where t_1 and t_2 are the times of charge and discharge at constant current, respectively.

The variation of capacity and Coulombic efficiency during charge and discharge processes is presented in Figs. 5 and 6, respectively. The battery capacity decreases significantly with increasing number of cycles. This can probably be related to the degradation of polyaniline and/or increasing
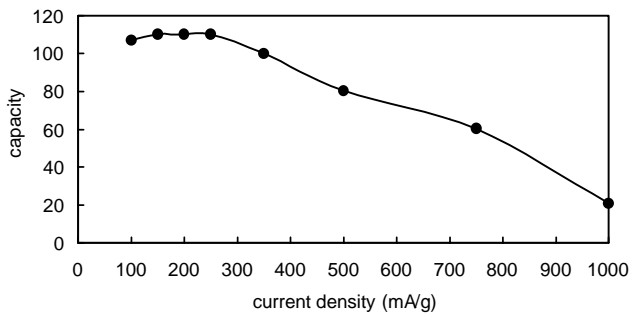

Fig. 2. Effect of current density on battery capacity. Capacity is in mA h g^{-1} with respect to polyaniline weight.
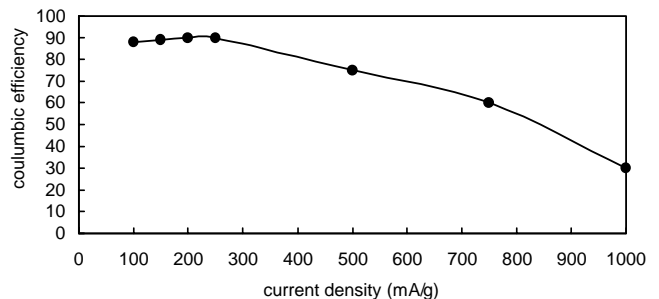

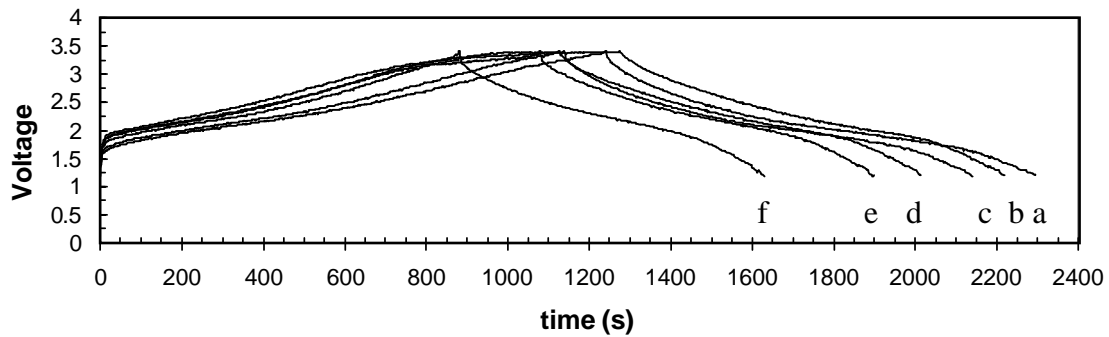Fig. 3. Effect of current density on Coulombic efficiency (%).

Fig. 4. Voltage–time behavior of 3.2 V bipolar battery during various cycles of charge and discharge under constant current (250 mA g^{-1}): (a) cycle 1; (b) cycle 10; (c) cycle 20; (d) cycle 30; (e) cycle 40; (f) cycle 60.
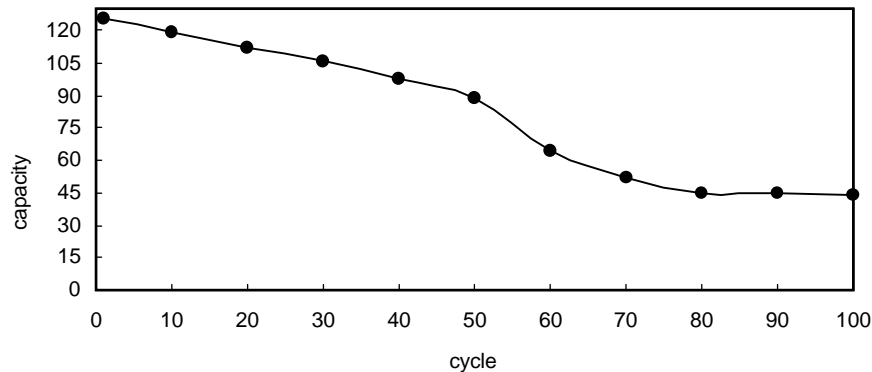

Fig. 5. Effect of cycle life on battery capacity. Capacity is in mA h g^{-1} with respect to polyaniline weight.

internal resistance of the battery. On the other hand, Fig. 6 shows that the Coulombic efficiency of the battery not only has not decreased with cycle life, but also has increased after cycle 60. The observed increase can be attributed to suitable reorientation of polyaniline chains and, consequently, to increased electronic and ionic conductivity of polyaniline.

A comparison between the voltage–time behavior of 3.2 and 6.4 V bipolar batteries (Fig. 7) shows that increasing the sub-cells in the battery stack has no major influence on battery efficiency.

Increasing the internal resistance (*r*) of the battery causes an Ohmic drop (*ir*) in battery voltage during its operation. It

is well known that the internal resistance depends on various parameters, such as the conductivity of the electroactive material, the conductivity of the bipolar substrate, electrolyte conductivity and nature, and the thickness and number of the separator layers. To investigate the effect of separator thickness on battery efficiency, three batteries were constructed with one, two and three layers of separators. The resulting voltage–time behavior is shown in Fig. 8. Curves (a) and (b) are for batteries with one and two layers of separator, respectively, during the 100th cycle of charge and discharge. It can be seen that an increase in the number of separator layers causes a greater Ohmic drop in battery voltage. This
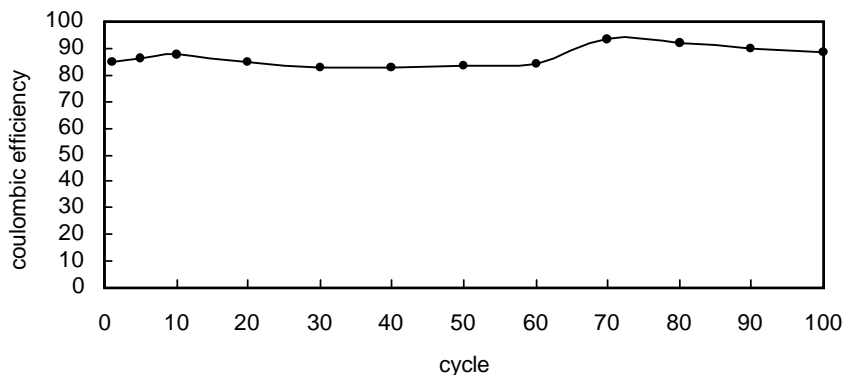

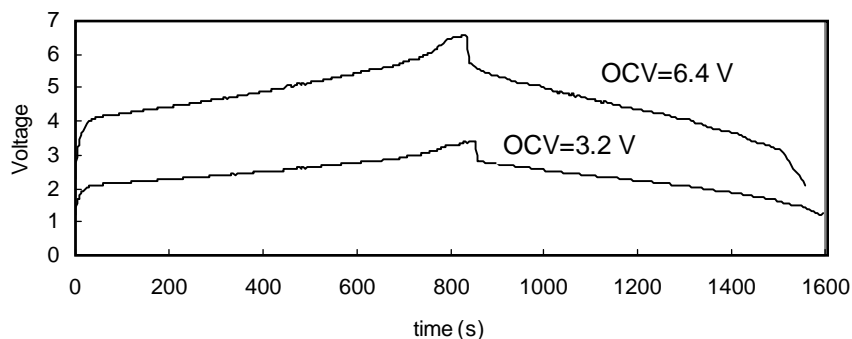Fig. 6. Effect of cycle life on battery Coulombic efficiency (%).

Fig. 7. Comparison of voltage–time behavior of bipolar batteries with open-circuit voltages of 3.2 and 6.4 V, respectively.
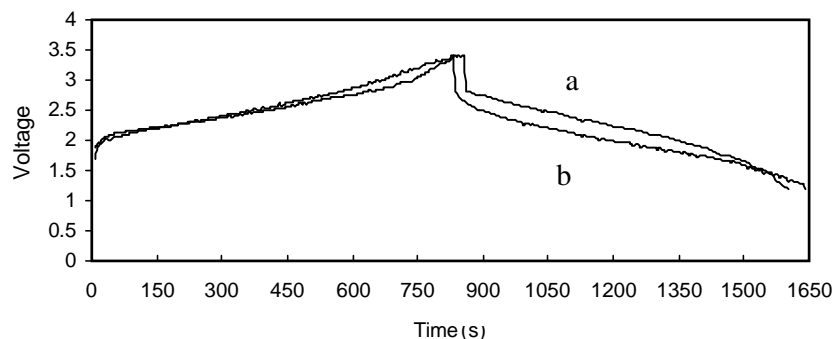

Fig. 8. Effect of separator thickness on battery behavior: (a) one layer of separator; (b) two layers of separator.

Table 2
Effect of number of separator layers on battery characteristics at 100th cycle of charge and discharge

Parameter	One layer	Two layers
Charge time (s)	428.4	415.1
Discharge time (s)	373.2	406.3
Ohmic drop (ir, V)	0.25	0.36
Discharge capacity (mA h g^{-1})	44.20	49.20
Coulombic efficiency (%)	88.0	97.9

is due to an increase in the internal resistance of the battery. The battery with two layers of separator has a higher capacity and Coulombic efficiency than that with one layer. This is obviously due to the increased separating efficiency of the separator. The results from these experiments are summarized in Table 2. The battery with three layers of separator has no suitable efficiency.

4. Conclusions

The application of the bipolar design in polyaniline batteries is quite novel and useful. Anti-acid stainless steel is used as a suitable conductive substrate in the construction of zinc–polyaniline bipolar electrodes. By using the proposed structure in bipolar batteries, the following limitations are removed or reduced:

(i) losses of power due to contact resistance;
(ii) electrolytic bridges between sub-cells;
(iii) problems with the sealing of adjacent sub-cells.

The proposed dry bipolar battery is inexpensive, simple, and possesses high capacity and Coulombic efficiency. Electrochemical studies of the use of optalloy in the anode mixture show that it increased the overvoltage of hydrogen release and thus prevents corrosion of the anode (zinc) and bipolar plate in acidic media.

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