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A low-cost portable cotton-based aluminum-air battery with high specific energy

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Abstract

In this study, a novel cotton-based aluminum-air battery is demonstrated. The battery is designed to be reusable so that a sheet of aluminum foil with 0.5 mm thickness can be used for tens of times by simply replacing the cotton substrate. In addition, an inexpensive industrial-grade aluminum alloy or waste aluminum foil can be fed to the battery to reduce its operation cost. Moreover, unlike the conventional aluminum-air battery which requires complicated flow management system, the present battery only needs a small reservoir to passively supply water for the electrode reaction, leading to a greatly simplified battery structure and improved systematic energy density. With NaOH as electrolyte, the optimized battery system exhibits a peak power density of 73 mW cm^{-2}, a specific capacity of 940 mA h g^{-1} and a specific energy of 930 mW h g^{-1}. This low-cost novel battery system is expected to be applied in various portable devices, such as cell phone, electric fans and point-of-care devices.

Keywords: Cotton-based; High energy density; Mechanically resuable battery; Aluminum-air battery

1. Introduction

There is a wide interest in the aluminum-air battery technology in recent years, which is one of the most promising power sources for the near future. It has the advantages of high theoretical voltage (2.7 V), high energy density (8100 Wh kg^{-1}) and capacity (2980 mA h g^{-1}), and its theoretical capacity is only next to that of lithium (3860 mA h g^{-1}) [1]. Since aluminum is the most abundant metal on earth with a low market cost, the aluminum-air battery is very cost-effective and highly feasible. An aluminum-air battery requires the use of an electrolyte solution of which,

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a strong alkaline, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), is frequently used. The electrode reactions under an alkaline environment are as follows:

$$\text{Anode:} Al+4OH^- \rightarrow Al(OH)_4^- + 3e^-$$

$$\text{Cathode:} O_2+2H_2O+4e^- \rightarrow 4OH^-$$

$$\text{Overall:} Al+3O_2+6H_2O \rightarrow 4Al(OH)_3$$

With decades of development, many studies have been conducted to optimize the performance of the aluminum-air battery system by many researchers, including the study on the effect of anode aluminum alloy[2, 3], cathode oxygen reduction reaction (ORR) catalyst[4, 5], and electrolyte composition[6-8]. On the basis of these research works, large battery systems with significant power output and delicate control system have been achieved[9], which are mostly applied in the transportation sector such as electric vehicles (EV). Nevertheless, traditional aluminum-air battery system is generally too bulky and too complicated to be applied in portable devices.

To achieve successful miniaturization and simplification of the conventional Al-air battery, developing a paper-based Al-air battery is one of the potential solutions, as cellulose paper is not only a low-cost material but also a good electrolyte substrate. In fact, paper-based power sources have already been investigated by different research groups [10, 11], proving them a suitable choice for powering portable devices such as point-of-care clinical devices. Paper-based power sources have many advantages, such as high flexibility, lightweight and low cost. Avoundjian et.al [12] reported an inexpensive paper-based aluminum-air battery in 2017, but the maximum power density was only 0.33 mW cm^{-2}, and the battery structure made it difficult for practical applications. Compared with traditional aluminum-air cells which can deliver a power density as high as 204 mW cm^{-2} [13], the present paper-based fuel cells and batteries are generally low in power output, which makes them impractical for application in our daily life. To improve the power output and operation lifetime, we have developed a cotton-based Al-air battery using low-cost industrial-grade Al plate. Compared with other paper-based batteries and fuel cells in the literature, the present battery system has achieved much longer discharge time and higher power density. Moreover, it is designed to be reusable, only by replacing the cellulose substrate.

2. Experimental

2.1. Materials

2.1.1. Al anode preparation

Both aluminum alloy 1060 with a purity of 99.6% and 4N pure aluminum (Guanfeng Metal Company, China) were studied in this paper, with the latter one as benchmark case. A 0.5mm-thick aluminum plate was cut into rectangular pieces of 1.5 cm x 4 cm with an effective reaction area of 1.5 cm x 1.5 cm, while the remaining part of Al was protected by tape serving as anode current collector. The reaction surface was grounded by silicon carbide paper, degreased in absolute ethanol and air dried before assembling into the battery.

2.1.2. Air-breathing cathode preparation

Carbon paper (HCP135, Hesen Company, China) was selected as gas diffusion layer (GDL) for the air-breathing cathode, which has an extra carbon-based microporous layer (MPL) sprayed on its surface. MnO_2 was utilized as the oxygen reduction catalyst, which was dispersed in ethanol-water solution (1:1) with 1 wt.% Nafion binder. Next, the as-prepared catalyst ink was sonicated for 1h, and finally sprayed onto the carbon paper with an overall MnO_2 loading of 4 mg cm^{-2}.

2.1.3. Cotton-based alkaline electrolyte preparation

The electrolyte solution of 8 M NaOH was first prepared by using analytical-grade NaOH pellets (Aladdin Company, China) and 18.2 MΩ deionized water. As shown in Fig. 1a, a fixed volume of the NaOH solution was first dropped onto a cotton substrate (1.5 cm x 1.5 cm), which was next dried on a hotplate at 185 ℃. After drying, the as-prepared cotton-based alkaline electrolyte was stored in a vacuum environment to avoid NaOH deliquescing due to the water vapor in ambient air. A series of this type of solid electrolyte containing different amount of NaOH were fabricated, in order to study the effect of NaOH loading on the battery performance. During battery operation, only fresh water is needed so that it is convenience in application and its safety level is much improved compared with conventional Al-air battery with bulky alkaline electrolyte solution.

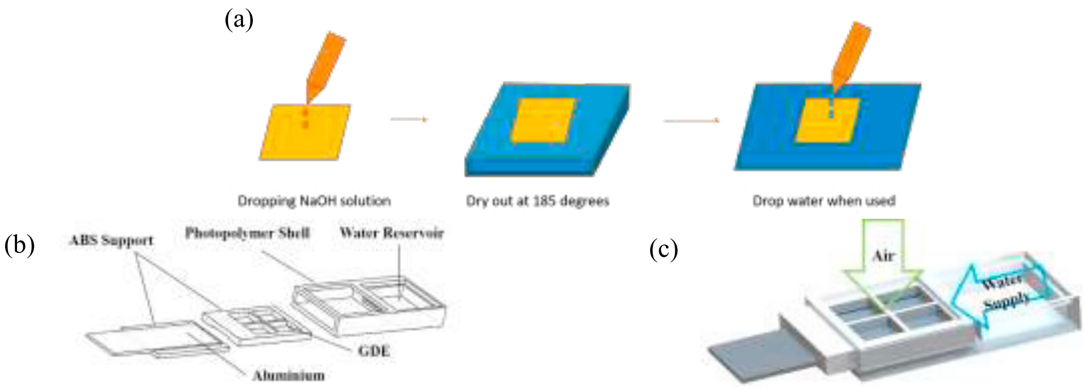

Fig. 1 Schematic diagram of (a) fabrication process of the cotton-based alkaline electrolyte; (b) exploded view of a single battery; (c) assembled battery.

2.2. Battery design and fabrication

As shown in Fig. 1b, a novel cotton-based aluminum-air battery system was designed, which contained two main parts, i.e. the battery part and the water reservoir part. The battery part was mainly composed of an anode support for fixing the aluminum plate and a cathode support for fixing the air-breathing electrode, both of which were made of Acrylonitrile Butadiene Styrene (ABS). On the cathode support, grooves were engraved to embed the electrode and to keep its catalyst surface as close as possible to the electrolyte substrate. It also has a space left for inserting the cotton-based alkaline electrolyte. Since it is convenient to insert the battery part into the shell part as shown in Fig. 1c, this battery design can be mechanically recharged simply by replacing the cotton-based electrolyte. In addition, a water reservoir was added in order to keep the cotton-based electrolyte wet throughout the battery operation time. The water transport rate could be tailored by adjusting the diameter of the water transport channels in the reservoir side wall. The water reservoir part was 3D printed using photopolymer.

2.3. Electrochemical testing

After adding 250 microliters of water into the water reservoir, the battery polarization curve was obtained by Linear Sweep Voltammetry from battery OCV to 0V, with a sweep rate of 25 mV s^{-1}. For comparison purpose, the control group was also tested by using untreated cotton substrate and 250 microliters of 8M NaOH solution as electrolyte.

All the electrochemical tests, including open circuit voltage (OCV), polarization curve and galvanostatic discharge curve, were carried out using an electrochemical work station (CHI660E, Chenhua Company, China) at a constant temperature of 298 K.

3. Results and Discussion

3.1. Effect of Aluminum purity

Although aluminum is the most abundant metal on earth, the performance and price of different aluminum alloys may differ. Several experiments were conducted to make the balance between their performance and cost. From the literature, low-grade aluminum may have some advantages due to its impurities. [2, 3] Thus, three types of aluminum were tested in this work: 4N pure aluminum (99.99% Al), 2N6 commercial aluminum alloy 1060 (99.6% Al), and waste aluminium from pill package. Their compositions are summarized in Table-1.

Table 1 Compositions of different types of aluminum (from MakeItFrom.com, waste aluminium was tested by EDX).

Composition (%)	Al	Si	Cu	Mg	Zn	Mn	Ti	V	Fe
AA 1060 type	99.60	0.25	0.05	0.03	0.05	0.03	0.03	0.05	0.350
High pure grade	99.99		No more than 0.01						
Waste aluminum	13.94		Polymer						

Fig. 2a indicates that the performance of AA 1060 type is superior than the other types of aluminum using the same amount of NaOH (0.5 millimoles). Impurities, such as Zn and Mg, may decrease the corrosion reaction in the form of galvanic effect, and hence improve the OCV. From Fig. 2b, AA 1060 type has a lower discharge voltage (c.a. 10%) than the high purity aluminum during galvanostatic discharge at 10 mA cm^{-2}, which also causes a shorter discharge time. It may be resulted from the higher alkaline consumption rate in the AA 1060. This difference is acceptable as the cost of AA 1060 (USD 2000 per ton from Alibaba) is much lower than that of the high purity 4N aluminum (USD 3000 per ton from Alibaba). In conclusion, the discharge performance of high purity aluminum is superior than commercial grade aluminium at low current densities. However, the commercial grade aluminum can deliver a higher power density output for instant discharge.

Besides commercial aluminum, the waste aluminium from tablet package also shows acceptable performance. Considering its negligible cost, the waste aluminium could still have a comparable output by simply increasing its reaction area, which makes it a promising method for utilizing waste Al in our daily life. And its power output is enough to drive a small electric fan (Fig. 2c). Considering both the cost and performance, the commercial aluminium alloy 1060 would be adopted in the following studies.

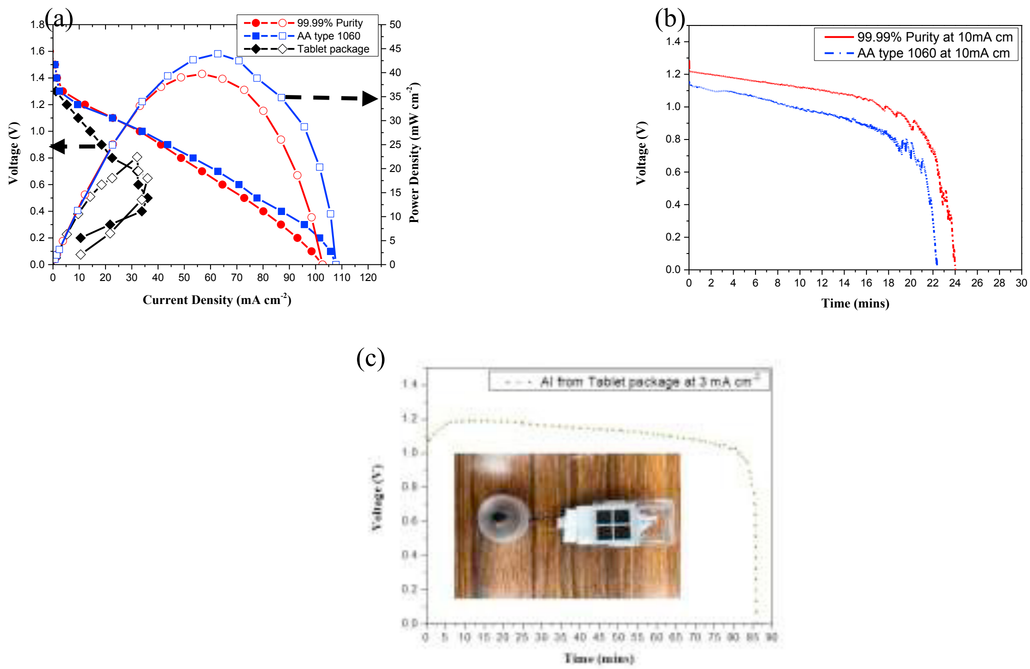

Fig. 2 Performance comparison between different kinds of aluminum: (a) Battery polarization curve; (b) Galvanostatic discharge test using commercial aluminum; (c) Galvanostatic discharge using waste aluminum.

3.2. Effect of electrolyte substrate

Different from other paper-based batteries, cotton-based battery structure is proposed in this work. In order to find the most suitable substrate, battery performances with either paper or cotton were compared with carefully controlled amount of NaOH and H_2O. As shown in Fig. 3a, the cotton-based battery could achieve higher peak power density than the paper-based battery, indicating the advantage of cotton-based structure. In addition, the cotton substrate containing dry NaOH provides higher concentration of NaOH solution when water is added, making its performance even superior than the untreated cotton substrate with 250 microliters of 8M NaOH solution. And a peak power density of 73 mW cm^{-2} was obtained by the 4 mmoles NaOH substrate. Fig. 3b also illustrates that the cotton-based battery has a better performance than the paper based one for long-term discharge, showing that the cotton substrate has the ability to support longer discharge time (130 minutes) than cellulose paper.

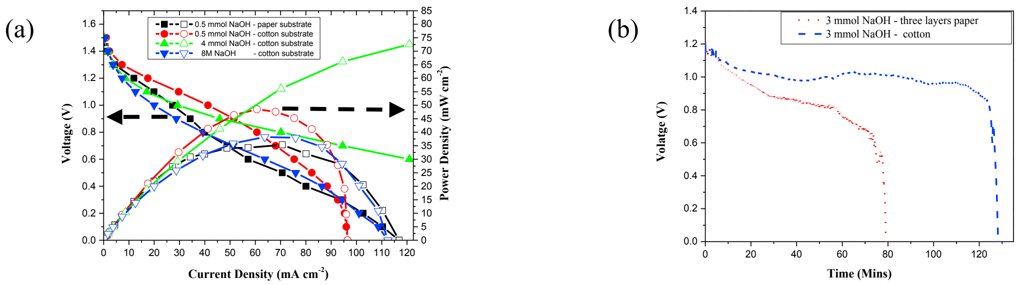

Fig. 3 Performance comparison between different kinds of electrolyte substrate: (a) Battery polarization curve; (b) Galvanostatic discharge at 10 mA cm^{-2}.

The above findings can be illustrated by the different structure observed. As shown in Fig. 4a, the pores between the 3-D structure fibres is filled with NaOH dry particles, while the NaOH particles only attached to the cellulose fibres in the paper substrate (Fig. 4b). Therefore, cotton substrate could contain more NaOH than the paper substrate. Moreover, dense NaOH particles between the cotton fibres provides larger reaction area and alkaline concentration, promoting the reaction efficiency. Thus, the cotton substrate is more advantageous for the proposed portable Al-air battery.

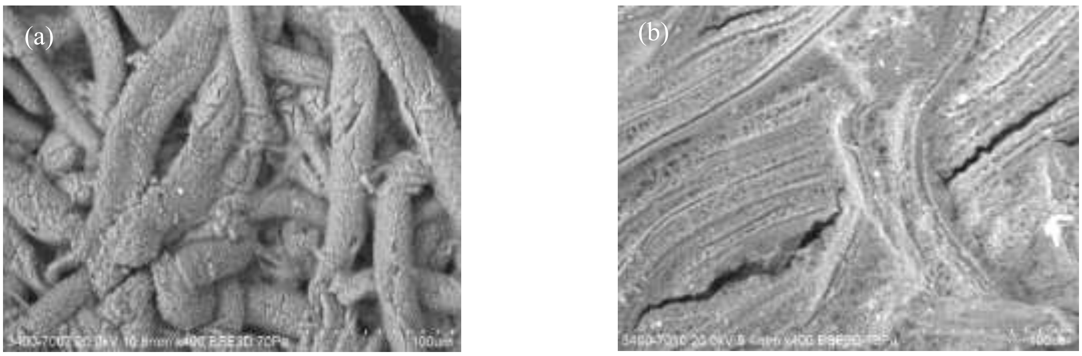

Fig. 4 SEM image of substrate with dry NaOH particles: (a) Cellulose paper substrate; (b) Cotton substrate.

3.3. Effect of NaOH loading

Fig. 5a illustrates the effect of different NaOH loadings on discharge time, from which it is obvious that a higher loading of NaOH could obtain longer discharge time due to increased amount of reactant. The maximum specific capacity reached 940 mA h g^{-1} and the maximum specific energy 930 mW h g^{-1} for the 3 mmoles discharge. The relationship between the NaOH loading and its discharge time is shown in Fig. 5b. It is found that the relationship between the discharge time and NaOH loading is almost linear from 0.5 mmoles to 4 mmoles (R^2=99.2%). A correlation equation can be obtained. Theoretically the discharge time T_{theory} should be equal to the time calculated by consuming all the OH^-. However, a correction factor, C, should be added due to corrosion and systematic error induced by battery design, which could describe the efficiency of the discharge process. The formula could be applied in commercial products, by which users could determine the amount of NaOH for the discharge time they wanted.

$$T_{pratical} = C * T_{theory} = C * \frac{\text{Number of Electrons}}{\text{Discharge Current}} = C * \frac{3/4 * F}{J * S} * n(OH^{-})$$

where the constant C is determined to be 0.75 from the curve, F is Faraday constant, J is current density, S is reaction area and n is the amount of NaOH.

Comparative specific energies were illustrated in Fig. 5c, the Al-air battery proposed in this paper has the largest practical specific energy compared with the specific energy of Zn-air and Fe-air batteries[14].

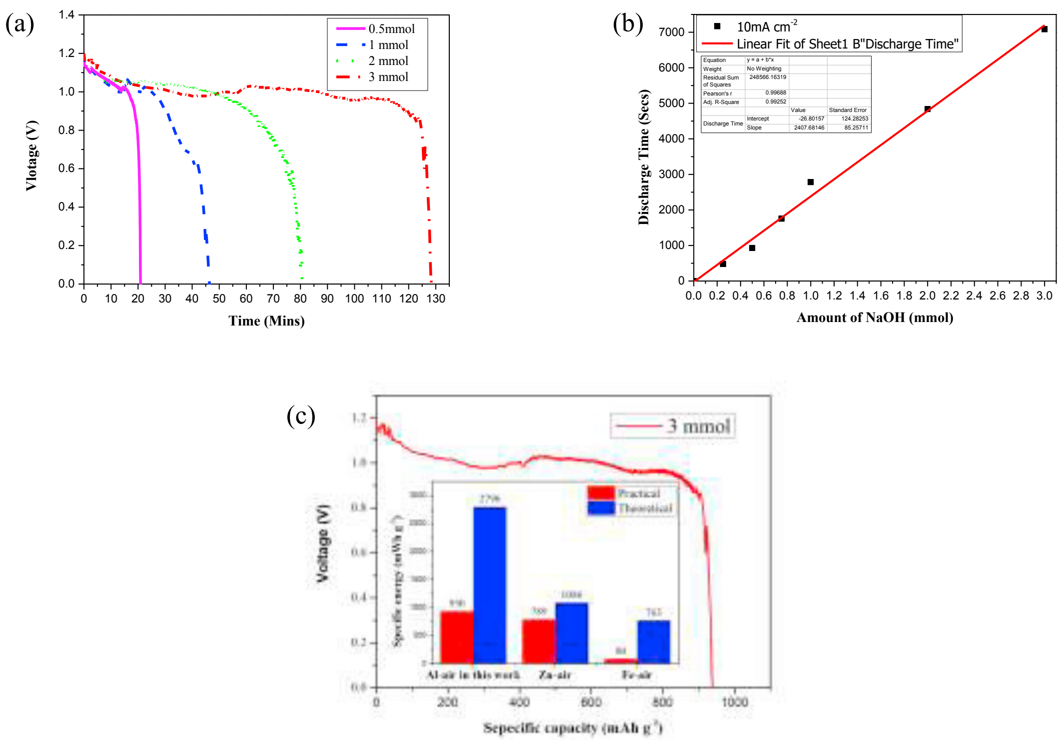

Fig. 5 Parametric study on discharge time for different amounts of NaOH inside the cotton substrate: (a) Galvanostatic discharge at 10mA cm^{-2}; (b) Linear fitting for the discharge time; (c) Galvanostatic discharge (vs capacity) and comparative specific energies.

4. Conclusions

In this paper, a low-cost portable cotton-based aluminum-air battery was successfully developed, which has a high potential for commercialization due to its high performance, portability and simplicity in operation. To simplify the battery system, cotton-based alkaline electrolyte was utilized, together with a water reservoir for continuous water supply. In this manner, the complicated electrolyte management system in conventional Al-air batteries can be eliminated, together with the potential risk of electrolyte leakage. The peak power density is as high as 73 mW cm^{-2}, which is almost 100 times higher than other paper-based power devices in the literature[12]. A high specific capacity of 940 mA h g^{-1} and specific energy of 930 mW h g^{-1} were also achieved, indicating a high energy efficiency of this battery design. This low-cost battery technology is especially suitable for powering various small electronic applications, such as cell phone charging, electric fans and point-of-care devices.

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