



Short communication

All-solid-state Al–air batteries with polymer alkaline gel electrolyte



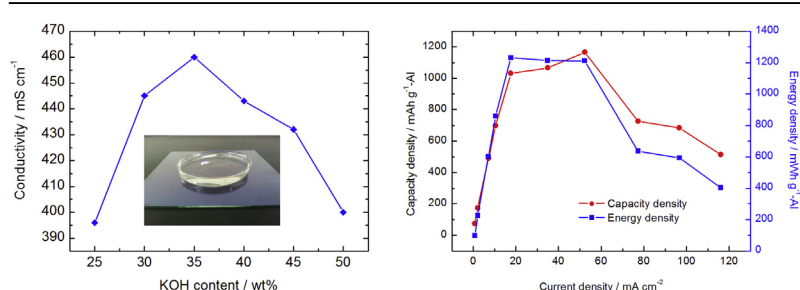
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HIGHLIGHTS

- PAA-based alkaline gel electrolyte with a high ionic conductivity of 460 mS cm^{-1} .
- Peak capacity and energy densities of $1166 \text{ mAh g}^{-1}\text{-Al}$ and $1230 \text{ mWh g}^{-1}\text{-Al}$.
- High area densities of 29.2 mAh cm^{-2} and 30.8 mWh cm^{-2} of the whole battery.
- High power density of 91.13 mW cm^{-2} .
- A novel separation design to inhibit anodic corrosion when not in use.

GRAPHICAL ABSTRACT



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ABSTRACT

Aluminum–air (Al–air) battery is one of the most promising candidates for next-generation energy storage systems because of its high capacity and energy density, and abundance. The polyacrylic acid (PAA)-based alkaline gel electrolyte is used in all-solid-state Al–air batteries instead of aqueous electrolytes to prevent leakage. The optimal gel electrolyte exhibits an ionic conductivity of 460 mS cm^{-1} , which is close to that of aqueous electrolytes. The Al–air battery peak capacity and energy density considering only Al can reach $1166 \text{ mAh g}^{-1}\text{-Al}$ and $1230 \text{ mWh g}^{-1}\text{-Al}$, respectively, during constant current discharge. The battery prototype also exhibits a high power density of 91.13 mW cm^{-2} . For the battery is a laminated structure, area densities of 29.2 mAh cm^{-2} and 30.8 mWh cm^{-2} are presented to appraise the performance of the whole cell. A novel design to inhibit anodic corrosion is proposed by separating the Al anode from the gel electrolyte when not in use, thereby effectively maintaining the available capacity of the battery.

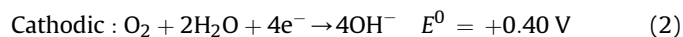
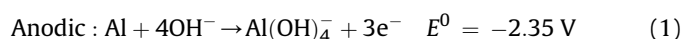
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1. Introduction

Metal–air batteries have a much higher capacity and energy density than other energy storage devices, such as Li-ion, Ni–Cd, and lead-acid batteries [1]. Active metals, including Li, Ca, Mg, Al, Fe, and Zn, can be employed as anode materials. Al is an ideal candidate because of its trivalence and atomic weight of 26.98. The theoretical specific capacity of Al is up to $2.98 \text{ Ah g}^{-1}\text{-Al}$, which is second only to that of Li ($3.86 \text{ Ah g}^{-1}\text{-Li}$). Al also exhibits a high

energy density of $8.10 \text{ Wh g}^{-1}\text{-Al}$ [2]. Furthermore, Al has attracted extended attention due to its abundance, low price, non-toxicity, and environmental friendliness.

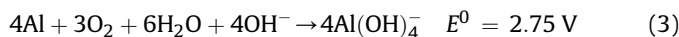
A typical Al–air battery is composed of an Al anode, an air cathode and an alkaline or brine electrolyte. The half-cell reactions on both electrodes are expressed as:



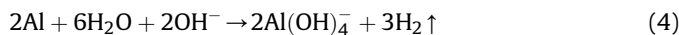
The overall Al–air battery reactions can be summarized as follows:

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There exists a parasitic hydrogen evolution effect at the Al anode as follows:



The electrolyte plays an important role in Al–air batteries. It separates the anode and the cathode to avoid short circuit and simultaneously provides OH^- to maintain the electrochemical reactions. Aqueous electrolytes are widely used in metal–air batteries because of their high ionic conductivities. However, the fluidity may lead to the penetrations and leakages through the capillaries in the porous air cathode. Hydrophobic polytetrafluoroethylene (PTFE) emulsion or powder can be adulterated into the air-diffusion layer of the air cathode to inhibit the leakage [3,4]. But the PTFE may obstruct the diffusion of both gas and reactants, so An et al. proposed an agar chemical hydrogel electrode binder to enhance mass transport [5]. Recently, combining the aqueous electrolyte and the polymer gel has become a promising method to solve these problems. Othman and Mohamad used hydroponic gel to store alkaline electrolyte for Zn–air cells [6,7]. The hydroponics gel absorbed aqueous potassium hydroxide solution and expanded into loosely bound jelly granules. However, the interface between gel granules and the anode was not smooth enough. Polymer-gelling agents, such as polyvinylalcohol (PVA) [8,9] or polyethylene oxide (PEO) [10], can turn the aqueous electrolyte into a gel membrane. This kind of polymer electrolyte has a low thickness (50–250 μm), as well as chemical and thermal stability. However, the ionic conductivity of PVA- or PEO-based gel is quite limited. In literature the PVA alkaline solid polymer electrolyte exhibited an ionic conductivity under of $1 \times 10^{-2} \text{ S cm}^{-1}$ [11,12]. Wu et al. added acrylic acid (AA) to enhance the conductivity of PVA-based electrolyte to 0.142–0.301 S cm^{-1} [13]. Gaikwad obtained a highly viscous and conductive alkaline gel electrolyte by applying polyacrylic acid (PAA) as an additive in KOH solution [14]. Nevertheless, the electrolyte remained mobile, and a mesh structure support was necessary to hold the electrolyte. Cross-linked PAA exhibits an excellent balance between ionic conductivity and mechanism strength. Free-standing polymer gel electrolyte (PGE) films could be synthesized with PAA and KOH solution, and used in alkaline batteries [15]. However, to the best of our knowledge, there are few studies on gel electrolytes for Al–air batteries available in literature. The current study presents an application of an all-solid-state Al–air battery employing PAA-based alkaline gel electrolyte, which is simply prepared to obtain a relatively high conductivity.

In addition to leakages, the anodic corrosion is another obstacle to further commercialization of Al–air batteries [16,17]. Anode materials dissolve in alkaline electrolytes severely, thereby leading to the self-discharge. Meanwhile, parasitic hydrogen evolution may cause potential safety hazards. Thus, early Al–air batteries normally used low-concentration alkaline or neutral brine solutions as electrolytes to retard the corrosion rate, but the capacity and power densities of the battery were concurrently limited [18–20]. The Al anode can be discharged to 105.0 mAh g^{-1} and 5.5 mW cm^{-2} with 0.6 M KOH solution. Al alloy mixed with small amounts of Sn, In, or Zn can suppress corrosion [21,22]. The contact of In and Sn lead to micro-galvanic cells. The In ions dissolved into the solution and redeposit on the cathodic surface to decrease the hydrogen evolution. On the other hand, several corrosion inhibitors in the electrolyte, such as organic acids and ionic liquids, also exhibit good performance [23,24]. PAA, which is mentioned above as a polymer gel agent, is indicated to be a corrosion inhibitor for Al in electrolyte solutions [25,26]. Arthur and Umoren indicated that the polymer adsorbed on the surface of Al to suppress the corrosion in both alkaline and acid environment [27,28]. Amin et al. found that

polymers with larger molecular weight had a better performance due to the stronger adsorption [29].

In this work a novel all-solid-state Al–air battery with PAA-based alkaline gel electrolyte is demonstrated as a substitute for aqueous energy storage devices. The following section presents a detailed process of electrolyte preparation and Al–air battery fabrication for reproducibility. In addition, the electrochemical characteristics of the electrolyte is measured and discussed. Furthermore, the discharge tests of the all-solid-state Al–air battery are carried out. Finally, a separation design is proposed to inhibit the Al corrosion when the battery is not in use.

2. Experimental

2.1. Materials

All materials used in this work were of analytical grade, and used without further treatment. Reagents for the electrolyte synthesis, including KOH, acrylic acid (AA), ZnO, $\text{K}_2\text{S}_2\text{O}_8$, and *N,N'*-methylene-bisacrylamide (MBA), were purchased from Sinopharm Chemical Reagent (Co., Ltd). The anode was made of a 0.2 mm thick, pure Al mesh with a real area ratio of 37.3%. For the air cathode, the activated carbon, ether black, Ni foam, and poly(vinylidene fluoride) (PVDF) were purchased from Shenyang Kejing. Catalysts including La_2O_3 , SrO, and MnO_2 were from Tianjin Fuchen. And the organic solvent *N*-methyl-2-pyrrolidone (NMP) was provided by Sinopharm.

2.2. Synthesis of alkaline gel electrolyte

The alkaline gel electrolyte was obtained by casting a mixture of i) an alkaline solution, ii) a gel agent, and iii) a polymerization initiator onto a glass substrate and then polymerized. i) KOH (12 g) was dissolved in double distilled water (19 g), and then added with ZnO (0.4 g) to form an alkaline solution with pH 14.7. The ZnO additive in alkaline solutions was used as a corrosion inhibitor [30–33]. The solution was treated with ultrasonication bath until completely homogeneous. ii) The gel agent was composed of AA (2 g) with cross-linker MBA (0.3 g). iii) In addition, a 16 wt% $\text{K}_2\text{S}_2\text{O}_8$ solution (2 g) was used as the polymerization initiator. Firstly, the alkaline solution was added into the gel agent to obtain a slightly viscous liquid with white granular precipitates. The precipitates were then removed through percolation to obtain a clear and light yellow filtrate. Afterward, the polymerization initiator was dropped into the filtrate with continuously rapid stirring to colorless and clarity. The final solution was immediately poured into a petri dish (70 mm diameter) to form a liquid film of 3 mm thickness. After about 5 min polymerization at room temperature, the electrolyte was solidified to be transparent, elastic and freestanding. The thickness was almost the same as the liquid film before polymerization, which had been verified by Zhu et al. [34]. Gel electrolytes with different composites were synthesized in the same way for characterization comparison.

2.3. Fabrication methods

2.3.1. Al anode

The Al mesh was abraded with emery papers (400–800 grit) and then immersed in a 0.5 M KOH solution for 1 min to remove the oxide layer. The surface-treated specimen was rinsed with double distilled water and then dried using a filter paper. Finally the Al mesh was cut into a rectangle plate (40 × 30 mm) and soldered to a Ni current collector. Holes on the mesh were considered as escape channels for hydrogen generated during corrosion. Otherwise, the obstructed gas might form bubbles in the gel film to separate the

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