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Review

Recent developments in materials for aluminum–air batteries: A review

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A B S T R A C T

The aluminum–air battery is an attractive candidate as a metal–air battery because of its high theoretical electrochemical equivalent value, 2.98 A h g^{-1}, which is higher than those of other active metals, such as magnesium (2.20 A h g^{-1}) and zinc (0.82 A h g^{-1}). This paper provides an overview of recently developed materials for aluminum–air batteries to be used in various elements, including the anode, air cathode and electrolyte. Aluminum can be alloyed with other active metal elements such as Tin (Sn), Indium (In), Gallium (Ga) and Zinc (Zn). Its binary and tertiary alloys demonstrate improved battery performance. Bifunctional air cathodes fabricated using oxygen reduction reaction (ORR) catalysts, CoO/N-CNT with oxygen evolution reaction (OER) catalysts, Ni–Fe-layered double hydroxide/CNT and MnO_2/N-CNT yield excellent results. With regard to electrolytes, several types have been considered: aqueous, non-aqueous, aprotic solvent and solid-state electrolytes. The addition of corrosion inhibitors to an aqueous electrolyte helps to enhance battery performance, whereas non-aqueous and aprotic solvent electrolytes can be used to prevent hydrogen evolution. Polymer electrolytes can overcome the battery leakage problem. As a conclusion, the future research trends related to this type of battery have also been indicated.

Contents

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Introduction

Because of the depletion of finite resources and the extensive growth in the demand for alternative energy worldwide, metal–air batteries have been proposed as alternative energy storage devices. Metal–air batteries have received particular attention because of their high energy density and capacity, the lack of dependence of their capacity on load and temperature, their flat discharge voltage and their low fabrication cost (depends on the metal used) [1–6]. Lithium–air (Li–air) batteries have been aggressively studied because of their broad potential for high-performance applications [7–10]. Such batteries can also operate as rechargeable batteries [11,12]. Unfortunately, however, during battery fabrication, the lithium must be handled under inert conditions because it is very sensitive to ambient conditions and poses an explosion hazard [13–15]. This is the greatest challenge for the Li–air battery. As alternatives, other active metal elements such as aluminum have been recommended.

Aluminum (Al) is an attractive candidate anode material for metal–air batteries because it has a high theoretical electrochemical equivalent value, 2.98 A h g^{-1}, which is the second highest after that of lithium (3.86 A h g^{-1}) and higher than those of other active metals, such as magnesium (2.20 A h g^{-1}) and zinc (0.82 A h g^{-1}) [16–18]. Aluminum is also an inexpensive metal, as it is the second most abundant metallic element after silicon, and is characterized by its environmental friendliness, non-toxicity and high recyclability [19]. The theoretical specific energy of an Al–air battery with an alkaline electrolyte can be as high as 200 W h kg^{-1}, and with a neutral salt solution, it is between 300 W h kg^{-1} and 500 W h kg^{-1} [18]. In this paper, we will provide an overview of recent material developments for various elements of aluminum–air batteries, including the anode, air cathode and electrolyte. Each component and material has its own strengths and challenges.

This type of battery comprises three main components: an anode, a cathode and an electrolyte. The discharging battery serves as a galvanic cell that drives the electrical current in an external circuit. The electrolyte plays an important role in such a battery because it is the conducting medium through which the two-way charge transfer proceeds between the electrodes [18]. The electrolyte also separates the anode and the cathode to avoid a short circuit and simultaneously provides hydroxide ions to maintain the electrochemical reactions [20].

The oxidation reaction at the anode depends on the type of electrolyte that participates in the reaction:

$$\text{Anode}: \quad Al \rightarrow Al^{3} + 3e \tag{1.1}$$

$$\text{Cathode}: \quad O_2 + 2H_2O + 4e \rightarrow 4OH^{-} \tag{1.2}$$

$$\text{Overall}: \quad 4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 \tag{1.3}$$

Another undesired (parasitic) reaction occurs at the anode because of the water reduction reaction. The parasitic hydrogen-generating reaction can be expressed as follows:

$$\text{Side reaction}: Al + 3H_2O \rightarrow Al(OH)3 + \frac{3}{2}H_2 \tag{1.4}$$

One major obstacle that hinders the deployment of the Al–air battery on a commercial scale is the self-corrosion rate of aluminum [21,22]. There are three main processes that occur on the surface of aluminum that hinder further oxidation at the anode in an aqueous-based cell: the formation of an oxide film of Al_2O_3 or $Al(OH)_3$; the formation of corrosion products, $Al(OH)_3$ and $Al(OH)_4{}^{-}$; and parasitic hydrogen evolution, which lowers the potential of the battery [23,24]. Because of this limitation, further development effort is needed to reduce the corrosion rate.

Anode material

Pure aluminum

Super-pure aluminum with a purity of 99.999% has been used in the past as an anodic material for the Al–air battery system because it has excellent electrochemical properties and operational potential at approximately −0.8 V vs. saturated calomel electrode (SCE) in an aqueous electrolyte [25]. Although it is, in most respects, a very suitable anode material, it suffers from a very high rate of corrosion, which makes it infeasible for application as an alternative power or energy source in place of fossil fuels. Other major difficulties that hinder the operation of Al–air cells are passive hydroxide layer formation and high corrosion currents with parasitic hydrogen evolution on the surface of the aluminum metal. Recently, the anode performance of 2N5 commercial grade aluminum with 99.5% purity has been studied to determine its potential for reducing self-corrosion and simultaneously improving battery performance [26].

Aluminum alloys

Modification of the aluminum anode material with low ratios of alloying components in aluminum alloy fabrication is needed to reduce the corrosion rate and increase the operation time for the Al–air battery system. Typical aluminum alloys that are commonly used in batteries at present are Al–Zn, Al–In, Al–Ga and Al–Sn [27–34]. Al alloys that combine multiple alloying components exhibit superior performance by virtue of the beneficial attributes of each individual alloying component.

Gallium (Ga) is an attractive alloying element that is known to activate the surface of aluminum in chloride solution. The activation of localized surface sites causes thinning of the passivated oxide film where the gallium is placed. A pure