



Perspective

A horizontal zinc-air battery with physically decoupled oxygen evolution/reduction reaction electrodes



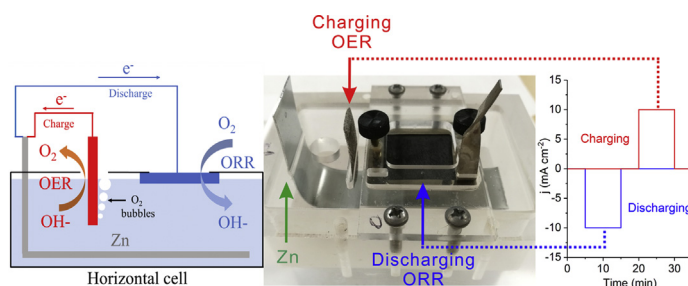
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HIGHLIGHTS

- A horizontal Zn-air cell with physically decoupled OER/ORR electrodes is designed.
- The design allows for effective management of O_2 transport and pressure.
- ORR active MnOx is electrodeposited on C paper without binding agents.
- OER active Co-Fe alloy, with an oxidized surface, is electrodeposited on Ni foam.
- The fabricated catalysts have comparable cycling efficiency with Pt-Ru (58%).

GRAPHICAL ABSTRACT



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ABSTRACT

A horizontal Zn-air battery has been designed to enable the use of physically decoupled and catalytically efficient ORR and OER electrodes for discharge and charge, respectively. The horizontal design features a horizontally positioned ORR electrode and a vertically positioned OER electrode, allowing effective management of oxygen transport and pressure. The ORR catalyst (MnOx) and OER catalyst (Co-Fe alloy) are fabricated via one-step electrodeposition on carbon paper and Ni foam, respectively. MnOx is identified as a combination of Mn_3O_4 nanorods and α - Mn_2O_3 spheres. Co-Fe is deposited as a solid solution film with an oxidized surface. Electrochemical tests show that both catalysts have comparable or even better activity than their commercial Pt-Ru catalyst counterpart. The catalysts are cycled at 20 mA cm^{-2} to examine their durability. Cycling potential affects catalyst durability, with improved lifetime under separate ORR and OER conditions compared with the full ORR-OER voltage range. The fabricated catalysts are assembled into a Zn-air battery for discharge-charge cycling tests and show the same average efficiency (58%) as commercial Pt-Ru catalysts.

1. Introduction

Electrically rechargeable Zn-air batteries have gained renewed interest among the various technologies available because of their high theoretical energy density and low cost [1,2]. As an open system, Zn-air batteries need to work in an environment where the air quality can be monitored and controlled. Humid air can cause air electrode flooding while dry air can cause rapid electrolyte evaporation [3]. A Zn-air

battery cannot last very long in ambient air due to the presence of CO_2 in the atmosphere. CO_2 can react with KOH and precipitate as K_2CO_3 that gradually blocks the pores in the gas diffusion layer [4]. Therefore, the most suitable application for a Zn-air battery is stationary energy storage. Several start-up Zn-air companies in stationary energy storage have entered the market in recent years, such as EOS Energy, Fluidic Energy, WatTech Power and ZincNyx Energy Solutions. All these companies emphasize the advantages of Zn-air batteries, such as safety,

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affordability and scalability from kW to MW systems. The most important consideration then is to extend the lifetime as much as possible.

The large-scale industrial deployment of zinc-air batteries has been hampered by several problems, i.e., low round-trip energy efficiency and poor cycling stability. A rechargeable Zn-air battery requires active catalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) to improve discharge-charge efficiency. The catalysts for ORR and OER can be integrated into one electrode or can work separately [5–7]. An electrode integrated with both ORR and OER catalysts or bifunctional catalysts has several problems. Firstly, synthesis of bifunctional catalysts with high catalytic activity toward both ORR and OER is difficult, requiring complex fabrication procedures. However, catalysts that are active for either ORR or OER can be synthesized by relatively simple methods. Some are made from non-precious metals, like carbon-based materials (e.g., N-doped carbon), transition metal oxides (e.g., Co_3O_4) or perovskites [8–10], with higher activity and/or durability than some noble metal-based catalysts (e.g., Pt, Ru, IrO_2). Secondly, the support materials also have a significant influence on the performance of catalysts [11]. Carbon-based substrates, which are often used for ORR catalyst loading, are vulnerable during the high-voltage charge process [12]. An electrode with a carbon substrate will gradually lose its function during the charging process due to corrosion of the carbon. Finally, the charging and discharging processes for Zn-air batteries have different requirements for the electrodes. The discharge process is driven by ORR and requires an air electrode that is not flooded by the electrolyte. The charging process during which OER happens, on the other hand, is more favored when the electrode is submerged in the electrolyte. As such, it is beneficial from a cycling efficiency point of view if the ORR and OER catalysts are synthesized and loaded on separate substrates. The high voltage during charging is detrimental to many materials due to their high solubility in alkaline solutions, according to Pourbaix diagrams [13]. These materials include carbonaceous materials that are used as the support material for ORR catalysts and conductive agents (carbon black, graphite, etc.), several transition metal oxide catalysts like MnOx and noble metals such as Pt. All these materials are damaged by high charge potentials and would be more durable if they were only subjected to reducing discharge potentials. Other metal oxides like Ni-Fe or Co-Fe (oxy)hydroxide are stable and OER active under high charge potentials, making them good candidates as an independent electrode for charging [14,15]. Therefore, a design that incorporates physically decoupled electrodes for discharging and charging is able to provide more flexibility to optimize ORR and OER electrocatalytic behavior [16].

Several attempts have been made to use physically decoupled electrodes in Li-air and Zn-air batteries [17–19]. Most of these use a traditional setup with vertically deployed electrodes [20]. This configuration allows for easy assembly of the electrodes but does not tailor the environment for the needs of each electrode. A vertical Zn anode will have the reaction product (Zn dendrites) deposited mostly at the bottom of the cell due to gravity effects, leading to a higher risk of short-circuiting. A vertical ORR electrode will have the same liquid pressure on its surface as that on an OER electrode. Such a high pressure could easily cause flooding of the ORR electrode by the electrolyte and reduce the amount of three-phase boundaries, even if hydrophobic carbon paper is used as the substrate [21]. In practical terms, the high pressure induced by a large quantity of electrolyte could lead to physical destruction of the fragile carbon paper.

Zn-air batteries with all the electrodes in a horizontal configuration have been reported to improve cycle life and performance durability [22–24]. In this study we have developed a Zn-air battery hybrid design with a horizontally arranged ORR electrode and Zn electrode, but with a vertical OER electrode (Fig. 1a and b). The ORR electrode is placed on top of the cell to reduce the electrolyte pressure on it. The OER electrode is vertically immersed in the electrolyte to enable full contact with the electrolyte and ensure easy exhaust of generated oxygen during OER [25]. Internal short-circuiting caused by Zn dendrite

formation during repeated cycling is the primary failure mode of rechargeable Zn-air batteries [26]. Zinc dendrites can grow progressively on repeated cycling and cause an internal short circuit [27,28]. Sufficient space was left between the electrodes to prevent this from happening. In order to avoid manual switching between the ORR and OER electrodes, two channels of a potentiostat are synchronized to perform discharge and charge alternately (Fig. 1b).

MnOx is anodically electrodeposited on carbon paper as the ORR catalyst and Co-Fe is cathodically electrodeposited on Ni foam as the OER catalyst. The MnOx layer has been identified as a combination of Mn_3O_4 (hausmannite) and $\alpha\text{-Mn}_2\text{O}_3$ (bixbyite), both of which have been reported as highly active ORR catalysts [29,30]. Mn_3O_4 has been synthesized as an ORR catalyst in several studies [31,32]. However, most of the studies use a solution based method such as solvothermal or thermal decomposition [33,34]. The synthesized catalyst particles are then mixed with a binding agent (PTFE or Nafion) and a conductive agent (carbon black, carbon nanotube, graphene, etc.) and then sprayed on the air electrode. Other methods include sputtering of MnOx followed by thermal oxidation [29]. In our work, all the above steps are simplified into one-step electrodeposition. The active material is grown directly on the gas diffusion layer without any additives. The direct growth results in lower contact resistance and shorter oxygen diffusion paths between the current collector and the active material. Therefore, fabrication is simpler and lower cost than other reported methods. This is important for large-scale applications such as stationary batteries. In addition, annealed Mn_3O_4 is more active than as-deposited Mn_3O_4 , showing comparable ORR activity to noble metal catalysts.

The electrodeposited Co-Fe catalyst is, in fact, a solid solution of Fe and Co with the surface oxidized. It has been shown to be an active and durable OER catalyst according to our previous research [35]. Electrodeposited Co-Fe based catalysts have been reported in the literature, but most of these are deposited as Co-Fe oxyhydroxide [36]. In this study, Co-Fe is electrodeposited on Ni foam (instead of the carbon paper used in [35]) to take advantage of nickel's high conductivity and stability in alkaline solutions. Electrochemical tests show that both catalysts have comparable or even better activity than their commercial Pt-Ru catalyst counterpart. The durability of the MnOx catalyst is significantly enhanced by using it exclusively for ORR instead of as an ORR-OER bifunctional catalyst. Finally, MnOx and Co-Fe are assembled into a Zn-air battery as decoupled electrodes for discharge and charge tests.

2. Experimental

2.1. Electrodeposition of MnOx and Co-Fe catalysts

Electrodeposition of MnOx was performed in a two-electrode configuration, where Teflon-coated porous carbon paper (SGL 39BC gas diffusion layer or GDL) and Pt mesh were used as the working electrode and the counter electrode, respectively. The substrate area for anodic MnOx electrodeposition was 5.1 cm^2 ($1.7\text{ cm} \times 3\text{ cm}$). Pulse electrodeposition at a current of 6 mA was applied with a 0.25 s ON-time and a 0.5 s OFF-time for each cycle with 2400 cycles in total (Fig. S1a). The solution for MnOx deposition contained 0.02 M manganese acetate, 0.02 M sodium acetate and 100 mg L^{-1} sodium dodecyl sulfate. The Co-Fe OER catalysts were cathodically electrodeposited on Ni foam with an area of 4.2 cm^2 ($1.6\text{ cm} \times 2.6\text{ cm}$) at a constant current of 300 mA for 4 min. The Ni foam was cleaned prior to electrodeposition with acetone, followed by 1 M HCl and then isopropanol with sonication. The Ni foam was finally rinsed several times with de-ionized water. The electrolyte was the same as the one used in our previous work [37], containing CoSO_4 (0.1 M), FeSO_4 (0.1 M), sodium citrate (0.2 M), boric acid (0.2 M), L-ascorbic acid (0.05 M) and sodium dodecyl sulfate (400 mg L^{-1}). Co-Fe was electrodeposited on both sides of the nickel foam by placing the Ni foam between two counter electrodes of Pt mesh (Fig. S1b). The mass loading of MnOx on GDL was

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