

USE OF METAL ORGANIC FRAMEWORKS (MOFs) IN RECHARGEABLE ZINC-AIR BATTERIES

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ABSTRACT

Metal Organic Frameworks (MOFs) is a class of porous, crystalline materials, which consist of metal centers (metal complexes or metal ions) and organic linkers. Those structures demonstrate physicochemical properties, such as high surface area, open metal sites and large void space. Various morphologies can be obtained, by adjusting the synthesis conditions, while the applications include gas storage/separation, catalysis, dye/toxic substance removal and electrode materials, as well as other electrochemical applications. Electrically rechargeable zinc-air batteries are a very promising technology with an immense increase in worldwide research, due to high energy density, safety, low cost and abundance of crafting materials. Nevertheless, difficulties still emerge, which prevent mass production and everyday applications, as each main structural component faces its own challenges. In this work a prototype zinc-air battery was fabricated and the sonochemically synthesized Ni-MOF-74 is examined for its applicability to rechargeable zinc-air batteries, in particular air – electrode, in order to improve performance and cycling stability.

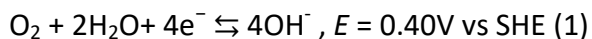
INTRODUCTION

Zinc - air batteries (ZABs) are seen as a promising candidate for next generation energy storage devices. The needed oxygen is not stored within the ZAB and can be supplied from the ambient air, therefore they offer a high theoretical energy density of 1353 Wh/kg. Zinc itself is a low-cost anode material and is also available in sufficient amounts in nature. Commonly, aqueous Zinc-Air Batteries consist of a zinc electrode, an air (oxygen) electrode, a porous separator and liquid electrolyte which is usually an aqueous potassium hydroxide (KOH) solution. All battery components are embedded into a housing. The separator is a porous membrane placed on top of the zinc electrode. The housing at the air electrode is usually equipped with holes so that oxygen can enter the cell and it is open to the surrounding air. A gas diffusion electrode (GDE) usually serves as air electrode. It consists of a gas diffusion layer (GDL) and a catalytically active layer (CL), which is applied on one side of the GDL and faces the separator. The CL usually contains an electrically conductive material, such as carbon powder, and a catalyst. The purpose of the GDL is to ensure a defined flux of oxygen to the reaction zone at the CL. Therefore, the GDL needs to demonstrate high porosity. The GDL pores are filled with gas and electrolyte during battery operation. In addition, air electrode might be supported by highly porous and hydrophobic polymer membranes. Those membranes are commonly made of Polytetrafluoroethylene (PTFE) and they are utilized to prevent electrolyte and water vapor flooding.

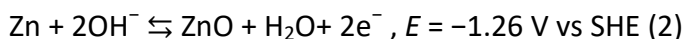
During discharge, the zinc-air battery functions as a power generator, while electrochemical coupling of the zinc metal to the air electrode is occurring in the presence of an alkaline media. Metal zinc is oxidized at the anode. The liberated electrons leave the zinc electrode and travel through an external load to the air electrode, producing zinc cations at the zinc electrode. At the same time, oxygen from the surrounding air diffuses into the porous air electrode and is ready to

be reduced to hydroxide ions via the oxygen reduction reaction (ORR) (forward Reaction (1)). ORR is occurring at a three-phase reaction site, which is the interface of gas oxygen, liquid electrolyte, and solid electrocatalysts. Generated OH⁻ then migrate from the reaction site to the zinc electrode, forming zincate ions (Zn(OH)₄²⁻), which at supersaturated concentrations, further decompose into insoluble zinc oxide (ZnO). Forward reaction (2) shows the zinc redox reaction^[1,2].

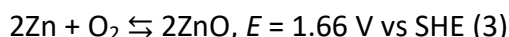
Air electrode reaction:



Zinc electrode reaction:



The overall reaction:



Upon recharging, above reactions may be reversed. The zinc–air battery is capable of storing electric energy through the oxygen-evolution reaction (OER) (backward Reaction (1)), occurring at the electrode–electrolyte interface. At the same time, zinc is deposited at the cathode surface (backward Reaction (2)). The overall reaction (Reaction (3)) can be simply shown as Zn combining with O₂ to form ZnO^[3]. Combining the aforementioned reactions, a theoretical voltage of 1.66 V is being obtained. However, the redox reactions of oxygen during the charging and discharging cycles are kinetically slow; thus, it is common to use catalysts to accelerate the process. Metal Organic Frameworks (MOFs) are also known as porous coordination polymers (PCPs). Over the past years, they have become very popular for their porosity and crystallinity^[4-7].

They consist of metal-based nodes-centers and organic ligands, assembled through strong coordination bonds and possess high surface area, open metal sites and large void space. Their chemical versatility can lead to various morphologies (cubes, spheres, rods, etc.). The controllable composition and accessibility of the adsorption sites gives the ability of capturing materials, as well as tuning them for specific applications. In terms of applications, MOFs have been well-known in the field of catalysis, gas storage/adsorption and gas separation, while recently they have also been very promising in biomedicine and electrochemistry. MOFs have been traditionally synthesized solvothermally at high temperatures for a prolonged time (hours or even days). In order to avoid these conditions, alternative methods have been used, such as microwaves, electrochemistry, mechanochemistry or sonochemistry^[8]. In this work a high intensity sonicator has been utilized for the synthesis of Ni-MOF-74, which is later examined as a potential candidate for CL.

EXPERIMENTAL SECTION

All chemicals (Ni(NO₃)₂·6H₂O (≥97%), 2,5 dihydroxy-terephthalic acid (dhtp) (98%), zinc powder <65micron (≥98%), N-N-Dimethylformamide (DMF) (≥99.8), ethanol (≥98%) were used as received without further purification. Celgard 3401 separator membrane and Sigracet Gas Diffusion Layer (GDL-10AA)(Carbon paper) were also used for the battery fabrication.

Synthesis of Ni-MOF-74

The solution was prepared by dissolving a mixture of the metal nitrate (3.14 mmol) and dhtp (0.949 mmol) in a 15:1:1 (v/v/v) mixture of DMF (65 mL), ethanol (5 mL) and deionized water (5 mL), while stirring. The mixture was transferred to a 3-neck round-bottom flask and synthesis was

carried out in a nitrogen environment via a continuous flow under ultrasound irradiation for 1 hour. The sonicator used was a Vibra Cell VCX 750 W (20 KHz) at a power output of 65 %. After letting the vessel cool down to room temperature, the solid was recovered by centrifugation and washed once with DMF, and then with methanol. The solid was kept immersed in methanol for 4 days; the solvent was refreshed once a day. Finally the MOF was activated in vacuo for 12 hours at 100 °C.

Preparation of MOF@GDL

10 mg of Ni-MOF-74 was mixed with 150 μ L Nafion (5%) and 750 μ L isopropanol under ultrasound irradiation for 10 min. The GDL (diameter of 2 cm) was coated with the above mixture and dried overnight at room temperature.

Preparation of Battery prototype

Battery testing was performed in a home-made liquid Zinc-air battery cell with (6cm x 6cm) (Figure1). A Gas Diffusion Layer made of carbon paper was used as air electrode with a surface area of 3.14 cm² exposed to the electrolyte. That electrode was later coated with Metal Organic Framework Ni-MOF-74. A zinc pellet with the exact same surface area acted as anode electrode and stainless steel was used as current collector for both positive and negative electrodes. Zinc pellet has been shaped after pressing 5 grams of Zn powder (< 65 μ m) under 10 tons. Also, a celgard 3401 PP membrane (thickness 3x25 μ m) has been utilized as separator between the two electrodes.



Figure 1. Photograph of zinc-air battery.

RESULTS AND DISCUSSION

Battery testing

Battery performance have been evaluated through electrochemical measurements. A potentiostat (Bio-Logic SP-150) has been used for this purpose. Figure 2a shows the charge and discharge polarization curves before and after galvanostatic charge-discharge cycling performance with Ni-MOF-74 serving as both an OER and ORR catalyst.

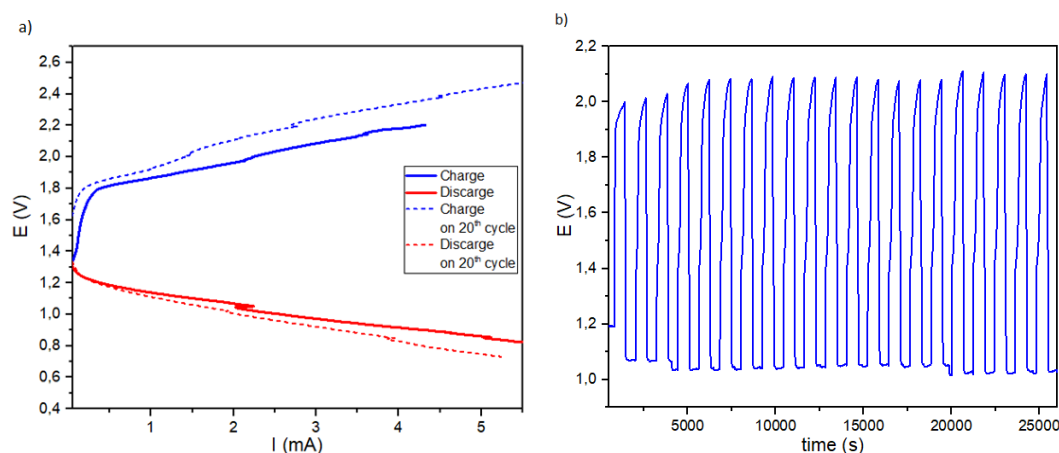


Figure 2. a) Charge and discharge polarization curves. b) Galvanostatic discharge-charge cycling at 2mA

Charge - discharge voltage gap was observed to be wider after charge - discharge cycling, due to slight deterioration of the battery. When cycled at the constant current of 2 mA, the zinc - air battery produced an initial charge potential of 2.02 V and discharge potential of 1.07 V, with a voltage gap of 0.95 V (figure 2b). After 20 cycles of 10min charge/10min discharge per cycle, the battery showed a slight performance loss with a small increase in the voltage gap by 0.13 V. The observed performance loss is probably due to exposure of the catalyst to positive potential during oxygen evolution reaction causing catalyst oxidization. However, a constant open circuit voltage (OCV) of 1.39 V (84% of the theoretical voltage) has been observed, even after the electrochemical experiments, indicating high stability during battery cell performance.

CONCLUSIONS

In this work, a prototype battery has been constructed and a Metal Organic Framework was applied to construction, showing great electrochemical performance. In particular Ni-MOF-74 has been utilized as a bifunctional catalyst coated on cathode electrode. Battery has been electrochemically tested with a potentiostat in order to be evaluated, showing promising results for MOFs utilization in rechargeable battery construction. Furthermore, other MOFs could be investigated for battery cell applications by means of electrochemical experiments and/or microstructural examination.

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