



Design of a setup for electrochemical measurements of aqueous Zn–air battery

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Abstract. Recently, metal–air batteries have become one of the prime competitors to the conventional lithium-based batteries. Battery setup design is extremely crucial in these batteries due to their partially open-cell configuration. This work is intended to provide a detailed information about the materials, strategy and idea to devise a simple and cost-effective setup to characterize a typical metal–air battery. In this regard, alkaline liquid zinc–air battery is assembled for the electrochemical measurements. The setup is compact, portable and easy to assemble–disassemble a metal–air battery. This design is simple and robust for laboratory scale characterization.

Keywords. Metal–air battery; design and development; electrochemical characterization.

1. Introduction

Metal–air batteries, with the advantages of low cost, ecological benefits, and high energy density, are promising technology for futuristic energy storage systems [1, 2]. Even though the field has been well-pursued in recent times, little attention is given to the battery configuration and design. Battery configuration is extremely crucial for metal–air batteries as they are prone to exhibit deteriorated electrochemical performance because of the electrolyte leakage due to their mandatory partially open-cell design to let in the atmospheric oxygen [3]. Researchers trying their first-time hands-on experiments on metal–air battery assembly may face difficulty in designing a setup for their research. In fact, there is no dedicated article that can provide a formal guidance to design and develop a setup for metal–air battery assembly at the amateur level.

Generally, a typical metal–air battery is assembled from a metal anode and an air-breathing cathode with a properly optimized electrolyte that can be classified as aqueous and non-aqueous batteries [4]. Among various metals, Ca, Al, Fe, Cd and Zn are appropriate for the aqueous system. On the other hand, due to the inherent property of lithium and few other elements, which usually tend to explosively react with atmospheric moisture and water, non-aqueous electrolyte is inevitably required (e.g., Li–air, Na–air and K–air batteries) [5]. Aqueous systems adopt potassium hydroxide (KOH) as electrolyte because of its high ionic conductivity,

good performance at wide range of temperature, high activity towards both anode and cathode [6–10]. There are good number of reports available on the battery performance with KOH concentration and zinc ion initial concentration [11–13]. It is found that corrosion of the Zn electrode increases when the concentration of KOH is increased. The corrosion is greater at higher KOH concentration (>7 M) because of the reversible potential difference between the Zn electrode reactions, and HER will also become negatively larger at higher KOH concentration. However, it is found that zinc redox kinetics is near its maximum at 6–7 M concentration, and the solubility of the ZnO discharge product increases with increase in concentration. Therefore, optimum molarity of KOH is achieved at about 6 M, as it provides maximum exchange current density of Zn dissolution [14]. Further, the introduction of 0.2 M Zn(Ac)₂ to the electrolyte could increase the reversibility of the redox reaction of Zn, which could enhance the cycling stability of the battery, and also the maximum ionic conductivity of $\sigma_{\text{ion}} = 0.626 \text{ S cm}^{-1}$ is achieved at this concentration [15, 16]. For this reason, majority of publications on Zn anode also use electrolytes composed of 6 M KOH with 0.1 – 0.2 M of a Zn-containing additive [2].

Aqueous aluminium and zinc batteries are actively pursued in recent times due to their remarkable theoretical energy densities (8076 and 1353 Wh kg⁻¹, respectively) [17]. Although Al–air cell has a much greater energy

density as compared to Zn–air, it is more easily corroded in alkaline media. Hence, Zn–air battery has practical advantage over Al–air battery. Moreover, metal–air battery as a whole is immensely broad area, so the present discussion is restricted to Zn–air battery. However, setup could also be used to fabricate other metal–air batteries. On the other hand, air electrode is the performance-decisive electrode in the Zn–air battery system because of the oxygen reduction/evolution reaction (ORR/OER) taking place at the triple phase boundary, where solid electrode is simultaneously interfaced with liquid electrolyte on one side and gaseous oxygen on the other side. Because of this, reaction kinetics is quite sluggish and complicated. Hence, most of the studies predominantly revolve around the development of bifunctional electrocatalyst for air cathode [18, 19], anode modification [20, 21] and electrolyte composition [22, 23]. However, in order to get reliable and reproducible results, researchers rely on their experimental setup because inappropriate setup designs may affect and falsify the measurement results leading to inaccurate conclusions.

A few reports have added Zn–air battery configuration in their studies with different structural designs based on the intended practical applications. For instance, Hopkins *et al* [24] mention a setup design to study the electrochemical performance of Zn–air battery. Hao *et al* [25] used a delicate, beaker-like setup wherein the distance between the electrodes is relatively larger, as a result reproducibility and comparison of battery-to-battery measurements become difficult and series resistance also increases. Further, for long-term usage, when the concentration of electroactive species declines, ions may experience higher resistance through the electrolyte to reach the host electrode which will negatively impact the battery performance. Moreover, setup details are assumed to be understood by the readers where several of these things remain unclear to budding researchers, such as how the electrodes remain intact to the walls of setup, dimensions and materials of setup, volume of electrolyte chamber, etc. All these aspects are made clear in the present work by a simple design of setup with ordinarily available materials. Finally, unlike a broad hole, a fine (<1 mm diameter) electrolyte injection channel is created in the setup that does not need any extra stopper to prevent spilling out of electrolyte. It is a convenient inlet to maintain the electrolyte level. Apart from these, most of the studies on metal–air batteries commonly utilize a setup with elementary description. Therefore, in this study, complete emphasis is given to battery setup design and it is demonstrated to efficiently carry out electrochemical measurements. Galvanostatic discharge curves, long-term cycle stability, open-circuit potential were measured to realize the effective working of the setup. This study empowers early researchers to learn the conceptual, technical and practical aspects of a metal–air battery setup design by leveraging effective and easily available resources for laboratory electrochemical characterization. The

setup is simple and convenient for multiple time assembly and disassembly of these batteries.

2. Experimental

2.1 Materials

Materials used in this study are of low cost and easily available. Acrylic sheet constitutes the major part of the present setup. A high quality (1 × 1 ft) acrylic sheet of thickness 10 mm and 3 mm is purchased from BIGMALL India Pvt. Ltd. Stainless steel nut and bolts for tightening purpose are taken from Fasteners and Allied Products Pvt. Ltd, India. Electrodes are situated at the electrolyte interface by air-tight silicone ‘O’ rings (RS Components India). To seal the battery, air-permeable thin silicone membrane (thickness: 200 microns) is purchased from OJOS Pvt. Ltd, India. Zinc plate of 99.9% purity is purchased from the EXPE Technologies, India. Similarly 99.9% pure nickel foam (pore size 110 ppi and thickness 1.6 mm) is purchased from GRS Corporation, India. Further, zinc electrode is polished with emery paper (first by extra-fine grit P600 and later by super-fine P1000 grit) prior to the battery assembly.

2.2 Electrode preparation and battery assembly

To evaluate the potentiality of the present setup, electrodes for Zn–air battery are prepared by the following procedure. A facile and easier synthetic method for cathode preparation is adopted. Recently Co_3O_4 is increasingly explored because of its good catalytic behaviour [26–28]. The air cathode used in this study comprises nickel foam current collector (10 × 10 mm) coated with cobalt oxide (Co_3O_4) as an active catalyst. The catalyst is prepared by spray pyrolysis technique to obtain Co_3O_4 nanorods, whose details are published in our previous work [29]. Planar Zn plate (10 × 10 mm) is used as anode. Potassium hydroxide (6 M KOH) and 0.2 M zinc acetate is used as electrolyte. Electrolyte chamber of the setup holds about 0.5 ml of electrolyte.

3. Results and discussion

3.1 Leak-proof structural design of the setup

Building an adequate design model is a starting point for any battery assembly setup and its optimization. The schematic of home-made setup for electrochemical measurement of Zn–air battery is shown in figure 1a. It consists of a solid transparent acrylic as a central skeleton whose thickness, length and breadth are 10, 50 and 35 mm, respectively. A hole of 8 mm diameter is drilled along its thickness by careful machining with the four corner holes of

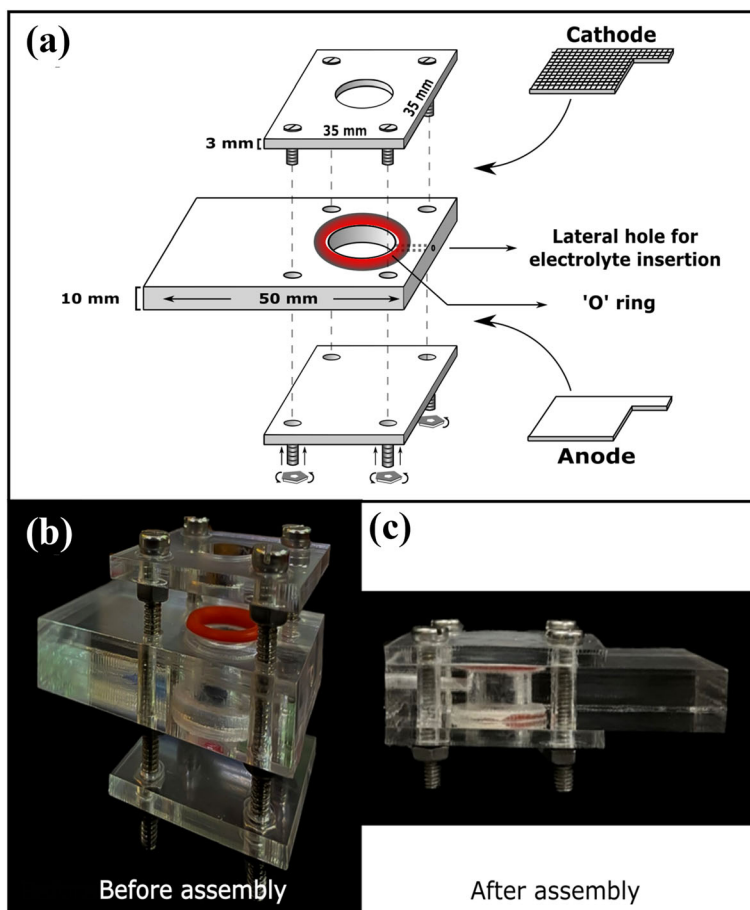


Figure 1. (a) A digital drawing depicting setup details. Real photos of the setup (b) before and (c) after assembly.

diameter 4 mm each. This central hole acts as a chamber for liquid electrolyte. Further, a thin groove of 1 mm thickness is extended from the circumference of central hole on both the sides so that the 'O' ring easily rests on it. Further, two more acrylic sheets (thickness: 3 mm) to cover the electrodes are cut into 35×35 mm square pieces along with coaxial corner holes matching with central acrylic sheet, as shown in figure 1b. One of these sheets is also drilled with 8 mm diameter central hole to cover the cathode side to let in the atmospheric oxygen, which is one of the requisites of Zn–air battery. To fill the air gaps at anode and to avoid the electrolyte leakage from the cathode pores, these electrodes are covered with thin silicone membrane to seal the setup completely. Silicone is one of the most gas permeable and hydrophobic elastomers, which is universally regarded as the best-in-class elastomer for gas diffusion and gas separation [30–32]. Silicone rubber is a polymerized silicone (polysiloxane) and is based on an inorganic oxygen-silicon molecular chain with organic side groups attached to the (tetravalent) silicon. It has an excellent barrier against liquids, but many gas molecules can pass through it as if there is no barrier. Silicone polymer matrix provides the passage for O_2 molecules (diameter: 0.346 nm), which migrate

between free volumes (holes) in the rubber matrix. This notable property of silicone being able to permit oxygen molecules through it and at the same time preventing the leakage of liquid electrolyte, makes it a great material to seal the Zn–air batteries. Other gas molecules such as H_2 , NO , CO_2 , N_2 , etc. can also diffuse through the silicone membrane, as they have comparable atomic radii. Since the metal–air batteries in general operate efficiently in open air, it is believed that there would not be considerable inhibitory effect on the battery performance by the diffusion of other gas molecules. However, under extreme conditions, CO_2 contamination can increase the overpotential for surface reaction by forming carbonate by-products, thereby hampering the battery performance (extremely high CO_2 contamination). Hence, the device naturally performs better if operated in pure oxygen atmosphere. But, it takes away the practicability of the battery, therefore metal–air batteries are preferred to be tested in open conditions. Moreover, the purpose of using silicone membrane in present case is to prevent liquid leakage without stopping the gaseous oxygen into the battery system from surrounding.

All the setup components are arranged along with Zn anode and air cathode by using mechanical fasteners.

Further, these electrodes are sandwiched between the covering acrylic sheets with the help of nuts and bolts, and electrolyte is filled through the lateral hole by using a syringe. Covering plates generate pressing force on the electrodes which tightly reside over silicone 'O' rings on either side. A real image of the complete setup filled with electrolyte after mechanical fastening is shown in figure 1c. It is observed that the setup accommodates Zn–air battery electrodes quite comfortably with no electrolyte leakage. Moreover, chemical resistance of used Perspex (acrylic) for concentrated potassium hydroxide at room temperature is quite good. It can tolerate continuous exposure to KOH for several months. And its transparent nature is advantageous to observe electrolyte level in the electrolyte chamber. These properties of acrylic make it suitable to be used as a battery assembly setup material. Additionally, synthetic 'O' rings used are also immune to the harsh KOH medium. Present setup is limited to its application for assembling the air-battery components for electrochemical measurements. It can be modified further based on the targeted applications. If required, even the acrylic could be replaced by a more-lighter and chemically inert material. There is still a room for improvisation for a permanent solution to make the setup air-tight and leak-proof rather than manually covering the electrodes every time with silicone membrane while assembling the battery.

3.2 Basic electrochemical performance test of assembled Zn–Air battery

To demonstrate the efficiency of the setup, basic electrochemical characterizations have been carried out after constituting a Zn–air battery. The open-circuit potential (OCP) is the difference between the electrochemical potentials of the negative electrode (μ_N) and the positive electrode (μ_P), which lies within the electrolyte stability

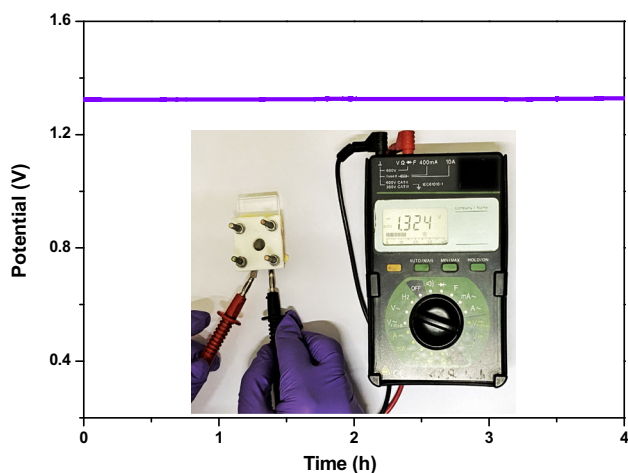


Figure 2. Open-circuit potential of the Zn–air battery tested for 4 h.

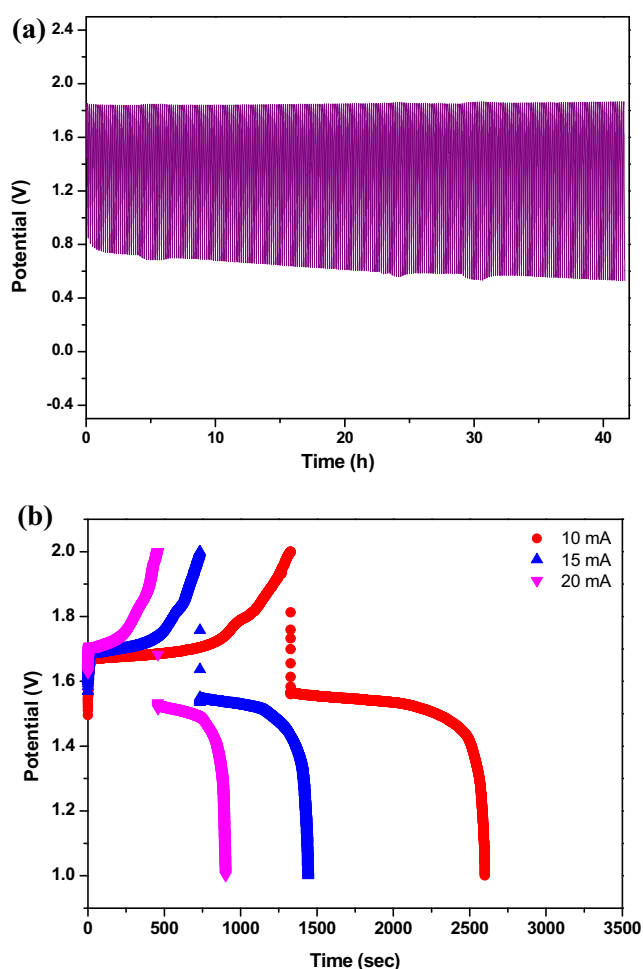


Figure 3. (a) Charge–discharge polarization curves of an assembled Zn–air battery at 5 mA cm^{-2} with time period of 10 min per cycle. (b) Discharge performance at different current densities.

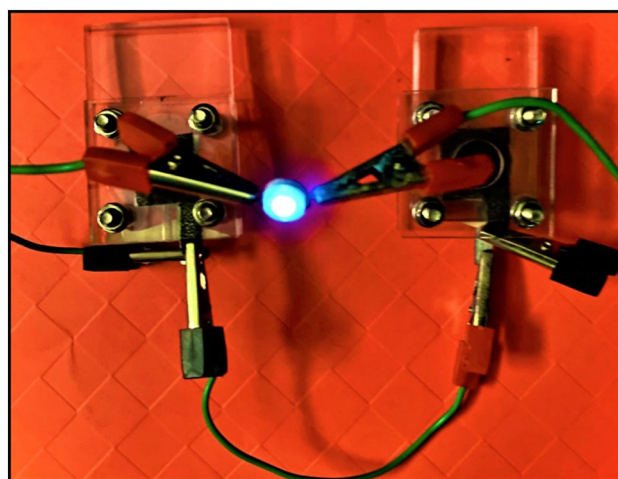


Figure 4. Optical image of the setup incorporated to glow 3 V commercial LED by connecting two Zn–air batteries in series.

window. Before sealing the battery with silicone membrane, it is observed that electrolyte starts leaking through the gaps created because of the differential pressure at the interface of central acrylic sheet and the electrodes. Due to this, gradual decrease in the nominal voltage is observed when the battery's OCP is measured. This was overcome by introducing silicone membranes at the covering ends of the setup, this modification prevents the electrolyte leakage that is demonstrated by the flat curve in the later measured OCP, as shown in figure 2. In fact, the OCP can also be examined for much longer time (typically few days), but we restricted our measurements for 4 h since no leakage was found for the stipulated time.

Cycle life is usually defined as the number of charge–discharge cycles a battery can perform before its nominal capacity falls below 80% of its initial rated capacity. As far as electroactive species are concerned, both Zn^{2+} and OH^- are equally important because Zn^{2+} contributes to anode reversibility and OH^- ions contribute to oxygen reduction/evolution reaction at the cathode side. These ions collectively participate in the battery performance. However, particularly in electrolyte, Zn^{2+} ions are crucial because of their migratory role between the electrodes. During battery operation, a large amount of zinc is expected to dissolve, migrate and re-deposit under non-uniform conditions. Cycling stability of battery is tested at 5 mA cm^{-2} with 10 min per cycle time. Battery showed decent stability of about 90 charge–discharge cycles, which run non-stop for about 15 h, as shown in figure 3a. Generally, for solid-state metal–air batteries, cell cycling will be done at a current density in the range of $0.1\text{--}2\text{ mA cm}^{-2}$ [33, 34], and for liquid alkaline batteries, it is done at current densities typically ranging from 2 to 20 mA cm^{-2} [7, 35, 36]. In some cases, cycling stabilities at 50 mA cm^{-2} are also demonstrated to prove the effective working of electrocatalysts [37]. It is to be noted here that higher current density leads to quick battery discharge, and synthesized materials cannot withstand such high current densities. Therefore, current density of 5 mA cm^{-2} is the most adequate and common that is optimum for wide range of materials in liquid alkaline batteries. Therefore, the discharge performance of battery at different current densities (10, 15 and 20 mA cm^{-2}) is measured, which is represented in figure 3b, and it proved the inverse dependence of discharge time on the applied current density. Additionally, the galvanostatic charge–discharge plots at different current densities are converted to specific capacity scale based on active catalyst weight in the air cathode (supplementary figure S1). These tests verify the setup reliability. Moreover, the setup can be used to assemble/disassemble any metal–air battery of choice due to their almost identical configuration. In order to test setup's practicability, battery is incorporated to glow 3 V commercial LED by connecting two Zn–air batteries in series, which were assembled in the setup as shown in figure 4. Considering this, battery structure can be further developed into more advanced design with improved

materials and advanced sophistication. Of course, the setup is well utilized to assemble metal–air batteries in many studies in past. However, for first timers, it is fruitful to have detailed formal guidance to design a setup for their laboratory experiments.

4. Conclusions

In summary, detailed information about the materials, strategy and idea to devise a simple, low-cost and effective 'conventional' home-made setup to accommodate battery components of a Zn–air battery has been discussed. This is the widely accepted design for the metal–air battery to make a simple setup with easily available raw materials. A Zn–air battery has been successfully assembled in the present setup, its reliability and leak-proof design is demonstrated by basic electrochemical testing.

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