Development of a 3D Zinc-Entrained Activated Charcoal Anode for Air-Breathing Battery

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Abstract- A 3D zinc-entrained activated charcoal anode was developed to address the problem of low output current density in conventional planar-anode air-breathing batteries. The anode was a compacted and sintered mix of activated charcoal (AC), polyethylene (PE) and ammonium bicarbonate (ABC). These serve as matrix, binder and pore-former respectively. Samples were compacted at varying ratios of (AC/PE). ABC and evaluated for suitability as anode structure using Water absorption, Hydrophobicity and Electrical conductivity tests. They were infused under vacuum with ZnSO₄ solutions of 0.1, 0.2, 0.3, 0.4, and 0.5 M. It was followed by in-situ galvanostatic electroreduction of Zn⁺⁺ ion to elemental zinc to achieve zinc entrainment inside the matrix. This was carried out at varying time intervals. The anode was characterized using Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and X-Ray Fluorescence (XRF). The 3D zinc-entrained anode and a planar zinc anode were evaluated and compared in air-breathing battery configuration using polarisation experiments. Optimal composition of the anode was determined to be 25% (AC/PE) and 10% ABC while optimal conditions for zinc entrainment was 0.4 M ZnSO₄ and 150 mins electroreduction time. The microstructures reveal that zinc is being preferentially deposited around the rim of the AC matrix.

Keywords- Air-cathode, battery, electrodeposition, zinc

1 INTRODUCTION

The rising profile of “green” and alternative power sources has accelerated the pace of battery research globally. Popular portable-oxidant power systems such as the Lithium ion battery could experience multiple folds increases in energy density if the oxidant is dispensed with and the space saved used for more lithium storage (Rahman et al., 2013). Air-breathing batteries use a metal as an anode, just like a Li-ion battery, but crucially oxygen from the environment is used as the cathode. Air-breathing batteries are composed of three main parts: metal anode, electrolyte and air cathode (Vincenzo and Benedetto, 2014). In the discharge process, oxidation reactions occur at the metal anode and oxygen reduction reaction (ORR) is induced in the air cathode. Several metal-air batteries have been studied, such as lithium-air, sodium-air, zinc-air, magnesium-air, aluminum-air and air-air batteries (Li and Dai, 2014). All have very high theoretical energy densities, about 2-10 fold higher than that of lithium-air batteries. This enables a much lighter cell, potentially making metal-air cells promising candidates for next-generation power of Electric vehicles (Linden, 2002).

Zinc-air batteries represents a safe, environment-friendly and potentially cheap way to store and deliver electrical energy and have found commercial usage in many applications such as hearing aids, watches, mobile phones, digital camera, pagers etc. These are however low-power consuming applications because cell performance is hampered by the characteristic low output current and rapid power loss of conventional anode zinc – air battery (Lee et al., 2011). This renders the zinc-air cell unsuitable for high current applications in distributed generation and stationary power. These limitations are traceable to the two-dimensional reaction surfaces of conventional planar zinc anode which constrains the surface area for cell reactions.

In this work, a 3D zinc-entrained anode was developed to increase the available surface areas for anodic oxidation reaction per unit cell without a drastic increase in cell dimensions. This 3D anode and conventional planar anode were respectively combined with an air-breathing cathode and characterized using polarisation studies.

2 MATERIALS AND METHODS

2.1 MATERIALS

A strategy for improving the current output of zinc-air batteries is by increasing the surface area of the zinc anode (Tian et al., 2012). In this work, zinc was sequestered inside a microporous, inert 3D framework to increase its surface area. Inertness is needed to avoid framework corrosion and mixed potentials at the anode while microporosity aids electrolyte permeation.

2.1.1 Activated Charcoal (AC)

The AC (Sigma Aldrich, Germany) served as the matrix for the 3D-anode inside which electroformed zinc was deposited. AC was also used for fabricating both the gas diffusion layer and the reactive layer of the air cathode.

2.1.2 Zinc Sulphate (ZnSO₄)

ZnSO₄ (BDH Chemicals, Poole England) served as the precursor for the in-situ electrodeposition of zinc inside the AC matrix.

2.1.3 Ammonium Bicarbonate (ABC)

ABC (Qualikem, India) served as “pore former” to impart porosity and facilitate permeation ZnSO₄ in the AC matrix.

2.1.4 Polyethylene (PE)

The PE used was locally procured and converted into powder form by grinding. It served as the binder for the AC matrix.
2.1.5 Carbon-supported Platinum Catalyst
1 wt. % carbon-supported platinum catalyst (Sigma-Aldrich, Germany) was used to catalyse cathode reactions.

2.1.6 Nickel-plated Steel Mesh
Steel mesh plated with nickel was locally produced. This served as the current collector at the triple phase boundary region.

2.1.7 Aqueous PTFE Dispersion
Aqueous dispersion of 60% PTFE (Sigma-Aldrich, Germany) was utilized to impart hydrophobicity on the AC in the gas diffusion layer.

2.1.8 Conventional Planar Zinc Anode
This was salvaged from 1.5 V Zinc - Manganese (IV) oxide dry cell.

2.2 METHODS

2.2.1 Production of Reduction Cup & Deposition Bath
The reduction cup contains the AC matrix and other constituents mixed with it to form the 3D-zinc entrained anode. The reduction cup was fabricated using lathe machine and power hack saw while the deposition bath was produced using a 3D printer (Ultimaker Model). The basic setup of the deposition bath is presented in the block diagram in figure 1.

[Image: 3D block diagram of the assembled deposition bath]

2.2.2 Optimization of Materials Composition and Processing Parameters
Key characteristics of the PE-bound AC matrix are: hydrophobicity, porosity, and electrical conductivity. These were evaluated at different formulations of PE, AC and ABC using standard tests. All these constituents were used in powdered form to enable dry mixing and facilitate homogeneity in the mixed compound.

2.2.3 Performance Assessment of Various Compositions of AC, PE and ABC
AC and PE were compounded at 20, 25, 30, 35 and 40 wt. % PE. Afterwards, ABC was introduced into the PE/AC matrix at various ratios and compounded (See Table 1). The mixtures were compressed and subjected to Water absorption test (ASTM D570–98), Hydrophobicity test (ASTM D7334–08) and Electrical conductivity test (ASTM D257 – 07).

Table 1. Composition of (AC/PE) : ABC

| Samples | Composition          |
|---------|----------------------|
| 1       | 20% (AC/PE) : 10% ABC|
| 2       | 20% (AC/PE) : 15% ABC|
| 3       | 20% (AC/PE) : 20% ABC|
| 4       | 25% (AC/PE) : 10% ABC|
| 5       | 25% (AC/PE) : 15% ABC|
| 6       | 25% (AC/PE) : 20% ABC|
| 7       | 30% (AC/PE) : 10% ABC|
| 8       | 30% (AC/PE) : 15% ABC|
| 9       | 30% (AC/PE) : 20% ABC|
| 10      | 35% (AC/PE) : 10% ABC|
| 11      | 35% (AC/PE) : 15% ABC|
| 12      | 35% (AC/PE) : 20% ABC|
| 13      | 40% (AC/PE) : 10% ABC|
| 14      | 40% (AC/PE) : 15% ABC|
| 15      | 40% (AC/PE) : 20% ABC|

2.2.4 Effect of ZnSO₄ Concentration on Zinc Entrainment
ZnSO₄ concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 M was infused under vacuum into compacted samples. In-situ electro-reduction of zinc ions was galvanostatically carried out at a current density of 0.02 Acm⁻² in accordance with Alias and Mohamad (2015). Weights of samples were taken before and after the electroreduction and the samples were also split open to expose interior surfaces for microstructural analysis.

2.2.5 Effect of Electroreduction Time
Electroreduction time was varied for 30, 60, 90, 120 and 150 min. using 0.4 M ZnSO₄ electrolyte. The samples were then weighed to know the amount of zinc deposited.

2.2.6 Production of 3D Zinc-Entrained Anode
The optimal formulation of the anode constituents was determined to be 25% AC/PE and 10% ABC. This was compacted into a reduction cup and infused under vacuum with 0.4 M ZnSO₄. In-situ galvanostatic electroreduction of Zn²⁺ ion to elemental zinc was done for 150 min. for zinc entrainment inside the 3D matrix.

2.2.7 Production of Air-Breathing Cathode
Materials for air-breathing cathode were selected based on the suggestions of Dobley et al. (2006). The air-breathing cathode was fabricated based on materials and processing conditions described by Gharebi et al. (2005). It involves a ring-mounted current collector sandwiched in-between a hydrophobic AC – ammonium bicarbonate mix (gas-diffusion layer), and a catalyst-enriched AC reactive layer.

2.2.8 Microstructural Studies
The microstructural morphology was characterized with the aid of an optical microscope (OM), scanning electron microscope (SEM) and X-Ray Fluorescence (XRF).
2.2.9 Polarisation Studies in Air-Breathing Configuration
Polarisation studies were carried out to determine the current-voltage characteristics at varying levels of imposed load for the air-breathing battery using both conventional and 3D zinc-entrained anodes. The study was carried out using a KOH electrolyte prepared at the optimised concentration of 4 M (Aremo et al., 2015) and a plot of the Open Circuit Voltage (OCV) Vs. current at different imposed load was obtained.

3 RESULTS AND DISCUSSION

3.1 MATERIALS COMPOSITION AND PROCESSING CONDITIONS OPTIMIZATION FOR AC/PE
Results for water absorption, hydrophobicity and electrical conductivity tests for AC/PE are presented in figures 2 – 4. In the water absorption test, increase in the wt. % of PE in the matrix led to decrease in the water absorption. Similarly, the influence of the PE is noticeable in the hydrophobicity and electrical conductivity test curves. Increases in the wt. % of PE cause increase in the contact angle of water on the sample surface. Increase in contact angle implies high hydrophobicity of the sample surface. However, a key requirement of the 3D anode matrix is a high electrolyte absorption rate; that is high hydrophilicity. 20 wt. % PE exhibits low hydrophobicity, however the weak bond in the matrix due to this low PE % renders it weak and prone to easily disintegrate on handling. This prompted the choice of 25 wt. % PE as the mixture of interest.

Fig. 2: Water Absorption Test Curve for AC/PE.
Fig. 3: Hydrophobicity Test Curve for AC/PE

3.2 MATERIALS COMPOSITION AND PROCESSING CONDITIONS OPTIMIZATION FOR (AC/PE): ABC
The ABC pore former decomposes at 60 °C into NH₃(g), CO₂(g) and H₂O(g) leaving behind pores (Resnik et al., 2004). Results for water absorption, hydrophobicity and electrical conductivity tests for (AC/PE): ABC are presented in figures 5 – 7. From the plots, porosity increases the water absorption rate of the matrix, reduces its contact angle (hydrophobicity) and reduces electrical conductivity. The 25% (AC/PE): 10% ABC mix has the highest water absorption rate and highest electric conductivity.

Fig. 4: Electrical Conductivity Curve for AC/PE
Fig. 5: Water Absorption Curve for (AC/PE): ABC
Fig. 6: Hydrophobicity Curve for (AC/PE):ABC
3.3 Effect of Electrolyte Concentration on the Entrainment of Zinc

The micrographs in figures 8 – 12 confirm the entrainment of the zinc in the activated charcoal. The dark portion of the micrographs represents the activated charcoal matrix while the shiny portions represent the entrained zinc. The results obtained from image analysis of the micrographs aided in quantifying the extent of zinc deposition coverage in the matrix. This is presented in the curve in figure 13. The figure indicates a dip in amount of entrained zinc at 0.2 M and a peak at 0.4 M electrolyte concentrations. The dip at 0.2 M can be attributed to the aspect ratio of the structure of the compacted activated charcoal in the reduction cup. Nilson et al. (2003) reported that during electrodeposition, natural stir by convention that occurs in cavities due to density differences have little or no effect when the cavity is less than 100 µm. In other words, the concentration within the cavities of high aspect ratio structures is independent of the bulk concentration. Thus, the effectiveness of the electrolyte depends on its initial volume that permeates into the cavity.

3.4 Effect of Deposition Time on Electrodeposited Zinc

Electrodeposition was carried out at 30, 60, 90, 120 and 150 mins. Weights were taken before and after each deposition and the difference is plotted Vs. time in Figure 14. From the plot, increase in electrodeposition time led to increase in the weight of entrained zinc. The optimal time for the entrainment of the zinc was determined to be 150 min due to the peak in the curve.
3.5 Entrained Zinc Anode

The composition for the matrix is 25% (AC/PE): 10% ABC and the electro-reduction was carried out at the optimized deposition time of 150 mins. The zinc was entrained into the pores of the activated charcoal matrix that were created by ammonium bicarbonate. The entrained-zinc interlinks each other through the electrical conductivity of the activated charcoal matrix to form a 3D structure across its volume, increasing the effective surface area of the zinc anode.

3.6 X-ray Fluorescence

The XRF result for analysis carried out on entrained-zinc Anode (25% (AC/PE): 10% ABC) is presented in Table 2. It indicates the extent of entrainment of zinc to be 32.12 wt. % of the matrix. This shows that the zinc was successfully entrained deep and in an appreciable quantity in the AC matrix.

Table 2. X-Ray Fluorescence Analysis of the Entrained-zinc Anode Result

| Elements | Conc. Value | Conc. Error | Unit |
|----------|-------------|-------------|------|
| P        | 0.9737      | ±0.2895     | wt.% |
| Cl       | 4.4864      | ±0.1891     | wt.% |
| K        | 1.3856      | ±0.0516     | wt.% |
| Ca       | 0.3160      | ±0.0183     | wt.% |
| Ti       | 0.0439      | ±0.0041     | wt.% |
| Mn       | 0.0454      | ±0.0024     | wt.% |
| Fe       | 1.8639      | ±0.0138     | wt.% |
| Zn       | 32.1186     | ±0.0624     | wt.% |
| As       | 0.0125      | ±0.0016     | wt.% |
| Rb       | 0.0220      | ±0.0024     | wt.% |
| Zr       | 0.0151      | ±0.0025     | wt.% |
| Ni       | 0.1367      | ±0.0032     | wt.% |
| Mo       | 0.0803      | ±0.0073     | wt.% |
| Others   | 58.4999     |             | wt.% |

3.7 Scanning Electron Microscopy Micrograph

SEM micrographs are presented in figures 15 – 17. The grey regions of the micrograph marked A, R and X show the PE-bonded AC matrix, while the dark regions marked B, S and Y indicates the pores. The white regions marked C, T and Z show the entrained-zinc. The micrograph indicates that a fairly large area is occupied by the entrained-zinc and the zinc was preferentially electrodeposited around the rim of the pores as can be shown in the whitish regions (region C) in figure 15. Figure 16 shows that these deposits (region T and R) preferentially occur around the pores (region S). The pores, deposited zinc and the grey areas (represented by Y,X,Z respectively) are shown in greater detail in figure 17.

3.8 Polarisation Studies

Polarisation is the deviation of actual measured cell potential from theoretical cell potential. The polarisation curves of Figure 18 show the performance of the entrained-zinc and the conventional zinc. The OCV of the entrained-zinc was 1.44 V. This is an improvement over an earlier attempt by Abbassi et al. (2013) which yielded an OCV of 1.25 V when increase in the surface area of the zinc was achieved by using zinc powder. Also, the current density/mm² output of the 3D zinc-entrained air battery is about 2.5 times higher than that of the conventional zinc-air battery. The 3D entrained Zinc-air battery was used to power 3V headlamp by connecting it in series with a standard 1.5 V dry cell as shown in Figure 19.
of about 2.5 times higher than the conventional 2D planar zinc-air battery, making it potentially well suited for higher-power applications.

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