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INFLUENCE OF DIFFERENT AIR ELECTRODE STRUCTURES TO DISCHARGE CHARACTERISTICS IN RECHARGEABLE ZN-AIR BATTERY

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ABSTRACT

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Keywords: energy storage, sustainability, air electrode, discharge

1. INTRODUCTION

According to a study published in 2020 [1]: humanity's primary energy consumption (PEC) increased by nearly 31 times (173,340 TWh) by 2019 compared to the energy use trends from the thermal transformation of by-products and waste from agricultural production sectors in the base year 1800. The last 200 years, the roles of fossil fuels (2019: 136,761 TWh; 78.9%), nuclear energy (2019: 6,923 TWh; 3.99%) and renewable sources (2019: 17,402 TWh; 10.0%) have also constantly increased in electricity generation. The European Green Deal (EGD) established the objective of becoming climate neutral in 2050 which requires a greenhouse as emissions reduction of 55% by 2030 and turn significantly higher shares of renewable energy sources (from 20% to 40% on average) in the so-called power energy grids [2] which is self-evident to electrochemical energy storage devices are essential in the future energy network to compensate the unpredictable energy generation and supply. The rechargeable metal-air (MAB) batteries are regarded as an "eco-friendly" energy storage technology for their operational safety and high theoretical energy density (e.g. Li-air: 5928 Wh/kg; Al-air: 5779 Wh/kg; Na-air: 1680 Wh/kg; Zn-air: 1218 Wh/kg) is approximately five times higher than that of the most advanced lithium-ion batteries and they are also considered by many studies as a hybrid design of secondary batteries and fuel cells [3]. Metal-air rechargeable systems are featured with open cell air-electrode structure which admit the generate electricity through a redox reaction between active metallic material and oxygen gas accessed from the air [4]. The special advantage of metal-air batteries that only this active metallic has to be stored in the battery system. Typically, MAB are divided into two types pursuant to their non-flammable electrolytes: the aqueous ones are not sensitive to moisture as long as the so-called aprotic (organic) solvents are more degradable by moisture [5]. MAB are generally composed of a pure metal (such as Li, Zn etc.) anode, a separator, a multilayer porous air electrode (as a cathode) and electrolyte (usually an alkaline solution of KOH or NaOH with the concentration of 6–8 M). The separator/ polymeric membrane is a crucial part of a Zn-air battery (ZAB) as greatly influencing its performance and stability through suppress the dendrite growth [6]. The cathode in a ZAB is consist of three parts: the gas diffusion layer (GDL), current collector and the catalyst layer, have play a vital role in catalyse of oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) ensured the co-conversion of electrical and chemical energy [10]. The architecture of ZABs are split into two groups: mechanical and electrical [7]. The main difference between them is the charge process in mechanical type takes place with removing and replacing the discharged anode and chemical products (such as zinc oxides, zincates) as long as in the other ones the electrical energy converted to chemical energy within rechargeable battery system. The working principles of a ZAB are made of the following elementary physical and chemical processes: the discharge, dissolution of the Zn-metal anode, dissolution of the discharge products in alkaline electrolyte

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with the formation of $ZnO_{(s)}$ and finally the charging process, which means the reduction of $ZnO_{(s)}$ to Zn metal [8]. The equilibrium potential of zinc-air cell is 1,65 V, which can be lower at discharge due to the internal- activation, ohmic and concentration loss of the cell, and higher at charge under real operating conditions. The reasons of more interests in Zn are the two order of magnitude lower global market price per tonne compared to lithium and the multiple theoretical and practical specific energy density of rechargeable ZAB compared to the worldwide Li-ion designs [9] By optimising of the oxygen reduction- and evolution reactions, the overpotential of between discharge – charge can be reduced which contributes to improve the cycling-performance [11]. Wang et al. [12] investigated two cathode (air electrode I-II.) designs with different thickness of catalyst- (rGO: reduced graphene oxide), current collector (Ni-foam)- and GDL layers (PTFE). In terms of the microstructure and electrochemical properties, Ni foam as a bifunctional: current collector and gas diffusion layer can intensify the charge performance in rechargeable ZAB. In another study [13] the high-temperature thermal decomposition (pyrolysis) mentioned as a well-known method for the synthesis of carbon nanoparticles that can be deposited with mixture of polymer binder and conductive additive as a catalyst layer on the surface of bifunctional Ni-foam. Zhang et al. [14] fabricated carbon nanofiber-based precious-metal-free catalysts as air-cathode by electrospinning method. Despite the ORR and OER processes are improved in rechargeable ZAB the authors highlight the special laboratory needs and expensive equipment of electrospinning technology which limit the large-scale production of these catalyst. The aim of this study is to assemble a prototype of rechargeable Zn-air battery that can be represented the influence on each basic air electrodes to electrochemical characteristics in discharge process.

2. MATERIALS AND METHODS

The rechargeable ZAB prototype (Fig. 1) assembled by four square of 10 mm thick and 60 mm side lengths poly(methyl methacrylate) is so-called "plexiglass" sheets was placed vertically as the following layer-order: the Zn anode is above the bottom so-called first plexiglass, the electrolyte above it and the surface of electrolyte is in contact with the pores of Ni foam.

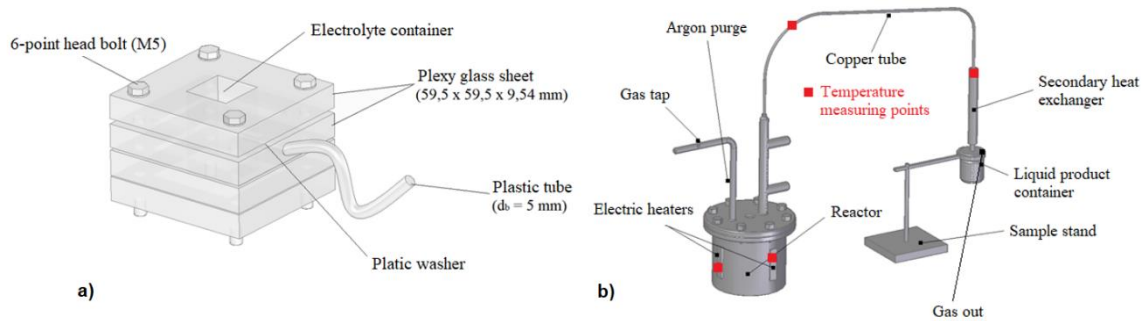

Figure 1. a) ZAB's schematic illustration b) Laboratory pyrolysis system's model (Solid Edge)

The electrolyte was injected into the electrolyte container by a syringe via a plastic tube as shown in Figure 1.a. The electrolyte was prepared by 30 w/w% potassium hydroxide and 2 n/n% $ZnCl_2$ or 0,05 wt% MnO_2 (one time) dissolved in deionized water, to investigate the effects of electrolyte additives on the voltage-current correlation of the discharge in ZAB prototype. Each architecture of air electrodes were applied can be listed as follows Table 1.

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Table 1. Air-electrodes with different number of layers

Cathodes	Abbreviations
Ni-foam (1)	fNi
Ni-foam + graphite layer (2)	fNi+s
Ni-foam + graphite layer + carbon nanoparticles (3)	fNi+s+C_p

The dendrite layers deposed while discharge on the 18.45x18.45x4 mm Zn anode surface were removed with 60 grit sandpaper before each measure. As an air electrode was utilized a 25x25x1.7 mm Ni-foam of 95-97% porosity with >99.8% purity. It was coated in (2) – (3) cathodes with a thin conductive graphite layer (Kontakt Chemie GRAPHIT 33) as a binder and also with carbon nanoparticles in (3) cathode was obtained from the pyrolysis of peanut shell as a catalyst layer.

The synthesis of carbon nanoparticles from peanut shell was carried out two steps: an initial so-called pre-carbonization pyrolysis process in a batch reactor at 500 °C for 2 h argon environment and a carbonization when the activated sample was carbonized under Ar atmosphere as well in a batch reactor at 730-780 °C for about 2 h. The oxygen atoms were slightly emerged from the matrix lattice structure similarly the low melting point Na-compounds with the formation of carbon-monoxide and carbon-dioxide in a closed high-temperature system under inert atmosphere (Fig. 2).

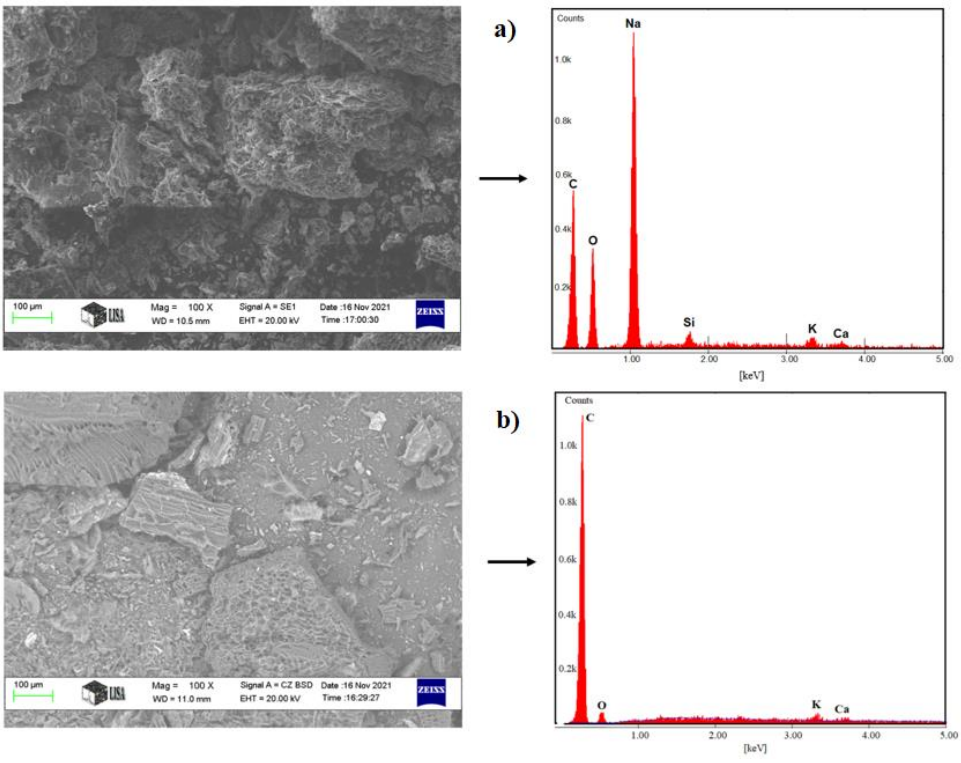

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Figure 2. SEM and XRF images before (a) and after (b) the synthesis of peanut shell

The chemical activation with NaOH solution changes the microstructure of the material: the pore content increases, with the release of gases (e.g. CO_2, CO) formed during the reaction. The microstructure of peanut shell samples are strongly influenced by the chemical activation with NaOH solution: with the releasing of gas products (such as CO_2, CO) simultaneously the pore numbers can be increased. Generally, the acid exfoliation is a process in which layered materials are expanded by chemical forces to modifying the chemical structure of the 2D nanomaterial precursor via appropriate reaction routes into single-or few-layer sheets [15]. The carbon nanoparticles as a catalyst monolayer on nickel foam improve its surface conductivity. All the steps for the production of carbon nano particles (1-100 nm) are listed in Figure 3.

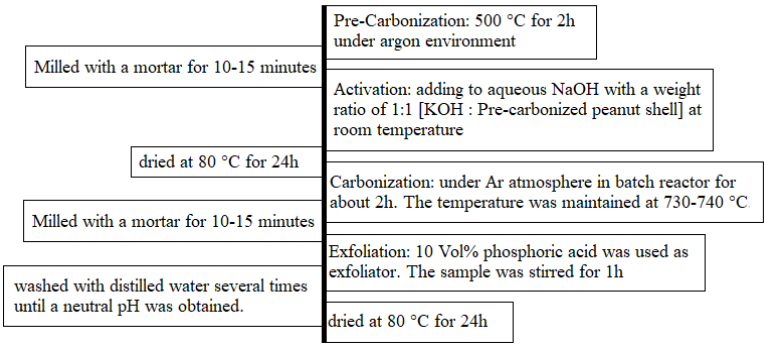

Figure 3. Synthesis steps for producing carbon nanoparticles

As for the working principle of ZAB cells in alkaline electrolyte solution (Fig. 4), on discharge the Zn is oxidized at the anode, forming $Zn(OH)_4^{2-}$ (Equation 1.). The supersaturation of $Zn(OH)_4^{2-}$ generates white-coloured ZnO, which is presented as an insulating powder in the system (Equation 2.). At the cathode (air electrode), the O_2 molecules are diffused through the bifunctional Ni foam as gas diffusion layer (GDL) between the outside and inside of the cell due to the pressure difference and when they reach the conductive electrocatalyst graphite layer will be reduced (Equation 3.). The key process of a ZAB air-electrode is a three-phase (gas-liquid-solid) reaction: on discharge, the solid catalyst intensify the reduction of oxygen gas to hydroxide ions in the electrolyte. On charge, oxygen is evolved at the positive electrode and Zn is electroplated at the negative electrode upon completion of the cycle.

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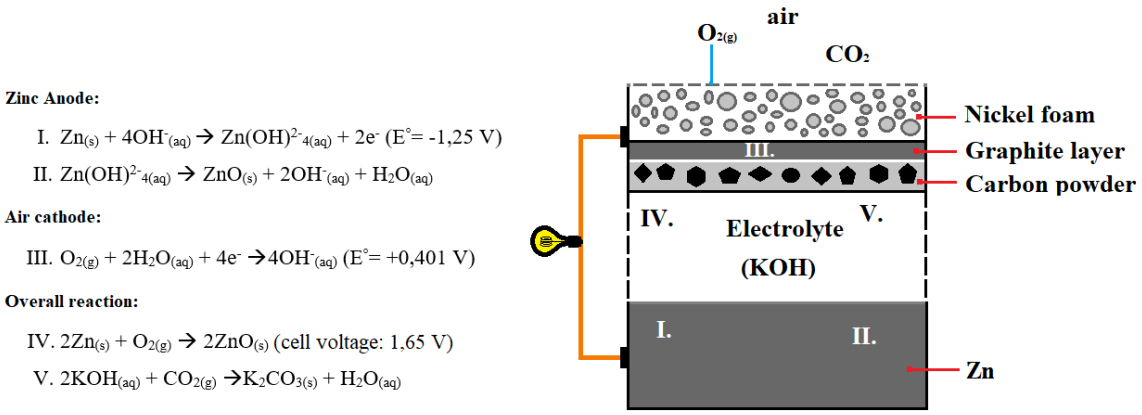

Figure 4. Schematic illustration of working principle on discharge process in ZAB [15].

The significant Zn dendrite-growth can be explained by the irreversible deposition of zincate ions during the discharge/charge which is one of the major challenges today in the development of rechargeable ZAB architectures. Since 2014, with the first application of pH neutral or quasi-neutral electrolytes (e.g. NH4Cl, ZnCl2) the dendrite formation can be minimized at the anode-side reactions in contrast to alkaline electrolytes [16]. Another problem in discharge-charge processes is the sensitivity of highly alkaline electrolytes to the carbon-dioxide of ambient air. As described in Equation 5., CO_2 from ambient air can react with the KOH content of electrolyte, forming carbonates which may clog the pores of the air electrode and thus block the oxygen pathway is necessary for ORR. This problem can also be avoided using non-toxic and non-corrosive pH- neutral electrolytes.

3. RESULTS AND DISCUSSION

The aim of the first measurings in initial ZAB prototype was to represent the elementary chemical phenomena (potential difference between the two electrodes, voltage-current signal output through the cathode) on discharge, therefore the sandwich-structured ZAB did not yet include a separator (PP membrane). Based on the results of presented so far drawing general trends need further experiences. Figures 5. and 6. show the influence of $ZnCl_2$ and MnO_2 additives to the voltage-current values was investigated on discharge.

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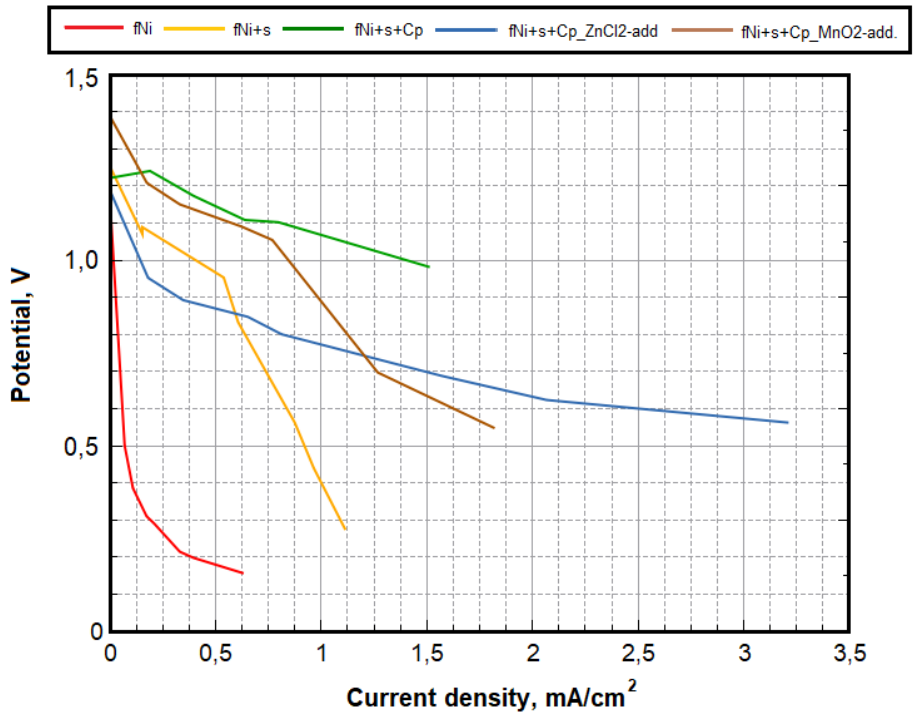

Figure 5. Correlation of potential and current density in each ZAB measurements.

This suggests a clear correlation between the electrical conductivity enhancing effect of the additional layers (graphite coating + surface active carbon grains) on the Ni foam and the calculated power increase by discharging the Zn anode of the ZAB. The so-called no-load idle voltage for all three measurements (without dopant) and for the ZnCl2 doped measurement is approximately 1.2 V, which is equivalent to the voltage of a Ni-MH rechargeable pencil battery. In comparison, the MnO2 case showed a slight voltage increase (about 17%). In terms of the slope of the polynomial functions describing each series of measurements, the undoped triple-layered (green dashed line) and ZnCl2 doped (blue dashed line) cases show an increase of 13x and 12x, respectively, compared to the plain Ni foam.

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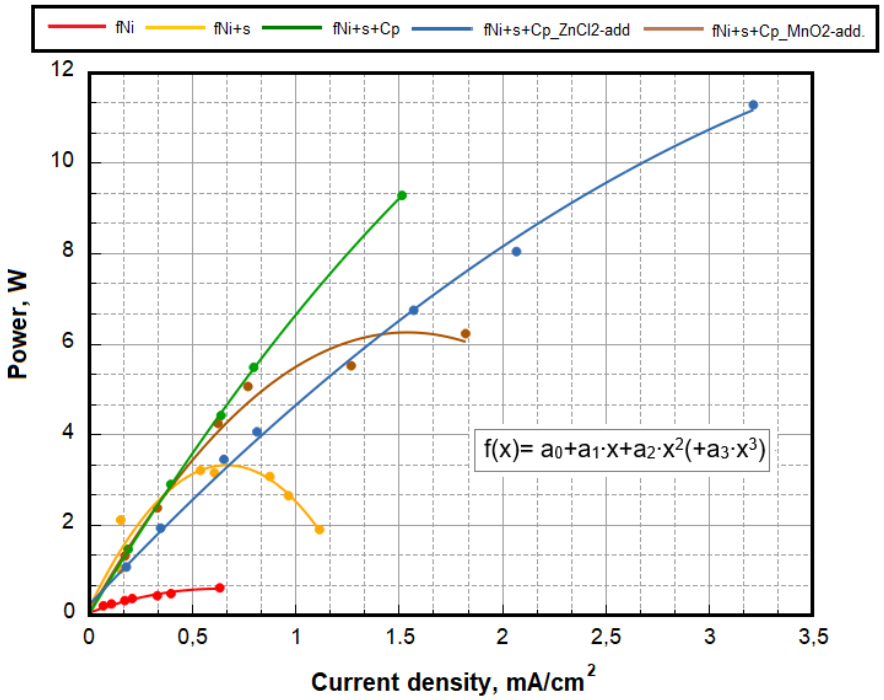

Figure 6. Performance of different air electrode architectures on discharge

Figure 6 again demonstrates the favourable electrochemical effect of the ZnCl2 electrolyte additive on the ZAB discharge process, where together with the additive-free triple layer case it produced the most favourable measurement results in terms of power density (Pd) - current density.

4. CONCLUSIONS

In my research, I investigated air electrodes with different layering schemes (Ni-foam, Ni-foam + graphite coating, Ni-foam + graphite coating + carbon powder including surface-active nano particles) to prototype a rechargeable Zn-air battery. During my initial measurements, I investigated the current-voltage relationship at discharge, from which the performance values for each design were determined. In 1-1 measurements, I also investigated the effect of different additives ZnCl2 (2 n/n%) and MnO2 (0.05 wt%) on the above parameters. This showed that the electrical conductivity of the graphite coating and the high specific surface area of the carbon powder increased the performance of the ZAB prototype compared to plain Ni-foam. Again, the most striking increases (13-fold and 12-fold, respectively) were recorded in my measurements of the additive-free trilayer and the ZnCl2 electrolyte-additive-enriched triple layer. All this will contribute to the next stage of my research to construct a more efficient air electrode ZAB design, which will be comparable in discharge-recharge characteristics with existing functional rechargeable ZAB systems in the literature.

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