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Chemical kinetics analysis of a zinc-air fuel cell

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Abstract

Zinc-air batteries and zinc-air fuel cells (ZAFC) are types of metal-air batteries that use zinc and oxygen from the air to generate power. They have high energy densities and are cost-effective to manufacture. During discharge, zinc particles form a porous anode saturated with electrolyte, while oxygen reacts at the cathode to form hydroxyl ions that migrate into the zinc paste and release electrons to travel to the cathode. In this study, a ZAFC was designed and produced with polyvinyl chloride (PVC) thermoplastic without any separator. The performance of the prepared air cathode in various temperatures and concentrations of the KOH electrolyte was evaluated. The results showed high current density and low Tafel slope at a high and low current density at a temperature of 318 K and a concentration of 4M. The prepared ZAFC has an open-circuit potential (OCP) of 1.346 V. The current density of $166.5\,\mathrm{mA \cdot cm^2}$ was obtained at the onset potential of 0.73 V. The power density and discharge capacity of the cell were 205.5 mW, and 283 mAh, respectively. These results show a high-performance single cell.

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1 Introduction

In recent years, many researchers studied ZAFCs because they have many diverse advantages such as high specific energy, non-toxic, low-cost fuels of metallic zinc and air, good environmental compatibility, low pollution output, and good reversibility [1–4]. Diverse types of ZAFC and zinc-air batteries have been developed such as mechanically and electrically rechargeable zinc-air batteries and primary ZAFCs [5,6].

In general, Metal-air fuel cells (e.g., Zn, Mg) convert chemical energy into electrical energy [7]. The properties of zinc including shape and size of zinc particles, high-energy density, low cost, and regeneration of zinc caused it to become a suitable candidate as an anode for metal-air fuel cells; however, redistribution of zinc particles decreases active surface area and cell performance [5,8,9].

Wang et.al. [5] proposed that zinc morphology depends on the rates of ion transfer, charge transfer, and atom attachment at different depositing conditions. The cathode in the ZAFC is called air-cathode which uses atmospheric oxygen as the oxidant. An air-cathode is formed by three important constituents including an active layer, a gas diffusion layer, and a current collecting layer. The active layer is a catalytic layer where the oxygen reduction reaction (ORR) happens. The gas diffusion layer, which oxygen can be moved through, contains carbon black and hydrophobic organic polymer particles like polytetrafluoroethylene (PTFE). The gas diffusion layer facilitates the permeation of the reactant from alkaline media to the catalytic sites. Gas diffusion layers are indispensable for the good performance of the ZAFC [10].

The ratio of PTFE for gas diffusion layers has been offered at 30-70 wt% [11]. Moreover, the properties of the carbon are so crucial to producing air cathodes with high performance [12]. The current collecting layer is simply created from a metal mesh such as Ni and Ag [11–13]. The ORR is one of the most important reactions in the ZAFC that occurs in the cathode. Because of the sluggish kinetics of the ORR, many catalysts have been studied to facilitate this reaction. Platinum has high activity as the catalyst and is extensively investigated. Although for a long time, Pt has been the best catalyst for the ORR, it has a high cost and is not commodious [5,14]. For these reasons, other catalysts are examined for the ORR such as manganese oxides, cobalt oxides, silver, Pt-alloy, spinel, and organometallic compounds [9,15,16]. Morphology, size, and ratio of metals are important features for performance and catalytic activity in Pt-alloy [17]. In general, the ZAFC consists of an air cathode, a zinc anode, a separator, and an alkaline electrolyte. Oxygen diffuses into the cathode from the atmosphere and reduces to hydroxyl ions. Then, hydroxyl ions move into the anode and react with Zn, and finally zincate ions form. Aqueous alkaline electrolytes such as potassium hydroxide are suitable electrolytes for the ZAFC because it has many properties such as high activity, high conductivity, and low corrosion gassing [18].

The electrochemical reactions of ZAFC in the alkaline electrolyte can be explained as follows [19,20]:

- At the positive (cathode) electrode:

$$\begin{cases} O_2 + 2H_2O + 4e^- \longrightarrow 4\,OH^-\,, \\ E_0 = 0.40\,V\,. \end{cases} \tag{1}$$

- At the negative (anode) electrode:

$$2\,Zn \longrightarrow 2\,Zn^{2+} + 4\,e^-\,, \tag{2}$$

$$\begin{cases} 2\,Zn^{2+} + 4\,OH \longrightarrow 2\,Zn(OH)_2\,, \\ E_0 = -1.25\,V\,, \end{cases} \tag{3}$$

$$2\,Zn(OH)_2 \longrightarrow 2\,ZnO + 2\,H_2O\,. \tag{4}$$

- Overall cell reaction:

$$2\,Zn + O_2 \longrightarrow 2\,ZnO\,, \quad E_0 = 1.65\,V\,. \tag{5}$$

The ZAFC is an appropriate candidate for an alternative energy generator [18, 21]. Therefore, many studies have been done on various aspects of these cells such as the study of zinc morphology in the anode, the type of catalyst used in the cathode, and the separator [22–24]. In this study, for the first time, we developed a simple and inexpensive zinc-air single cell without a separator and investigated its electrochemical properties. A zinc-air cell without a separator shows high power and current density.

2 Experimental

2.1 Materials

The metallic zinc in the form of zinc sheet and Pt/C 20% were purchased from Sigma-Aldrich, Carbon Vulcan XC-72R from Cabot, Isopropyl Alcohol, KOH, and PTFE from Merck, Nafion from DuPont. All of the materials were used without purification.

2.2 Design of single cell

A ZAFC was designed simply. The cell was produced with corrosion-resistant polyvinyl chloride (PVC) thermoplastic in an alkaline solution. A zinc sheet was used as an anode. Air-electrode was fabricated in three layers; a diffusion layer on the air side, an active layer on the electrolyte side [25], and a current collecting layer. The first layer is the gas diffusion layer which was made of carbon Vulcan XC-72R and PTFE.

The PTFE solution: carbon Vulcan ratio was 30:70; Millipore water/2-propanol 1 : 1 and 3 drops of glycerin as a solvent were added to the mixture and sonicated for 20 min until a homogeneous paste was obtained. Then, it was put in an oven at 353 K for 3 h. The obtained paste was pressed on the silver mesh. The active layer was produced from 31.5 mg 20% Pt/C and 10 μL Nafion as the hydrophobic catalyst binder; 10 mL millipore water/2-propanol 1 : 1 was added to the mixture. Catalyst ink was sonicated for 20 min to prepare a homogeneous mixture, then the active layer was cast onto the gas diffusion layer. Finally, the fabricated electrode was put into the oven for 15 min at 573 K and 15 min at 613 K for stabilizing, respectively.

The prepared air-electrode was used as a ZAFC's cathode. By changing the temperature and concentration of the electrolyte, variables like activation energy (E_a), current density, and Tafel slope of the air-cathode were investigated. A standard three-electrode system attached to the EG&G potentiostat/galvanostat (PARSTAT 2273) instrument was used to investigate the air-cathode's properties. The working electrode was the prepared air cathode. The counter and reference electrodes were Pt sheet and Hg/HgO, respectively. The linear sweep voltammetry (LSV) was carried out in the potential range of 0.05 V to 0.35 V vs. Hg/HgO. Besides, the output power density and current density of a single ZAFC were evaluated.

3 Results and discussion

A single cell of ZAFC was designed and investigated based on the simple structure. The zinc sheet is permanently put in the vicinity of the electrolyte in the cell. The air was supplied as an oxidant for the air cathode. Moreover, the efficiency of the constructed catalyst at different temperatures and concentrations on glassy carbon electrodes (GCE) was investigated.

3.1 The effect of temperature of the electrolyte on the ORR

The experiment aimed to investigate the impact of temperature on cell performance, and the findings were presented in Figure 1 in various temperatures (303, 308, 313, and 318 K). The results indicated that cell performance improved as the temperature increased until it reached 318 K. The cause of this change in performance was attributed to the electrolyte's low activity at lower temperatures, which reduced its ion diffusivity, leading to increased cell polarization and faster termination voltage [26]. Increasing the temperature leads to an increase in the molecular motions and the molecular collisions of oxygen per unit of time. It enhanced the rate of the ORR. As the temperature of the electrolyte increased, its activity also increased, resulting in more molecules with high kinetic energy that could overcome activation energy more easily. This led to a higher reaction rate and an increase in cell voltage.

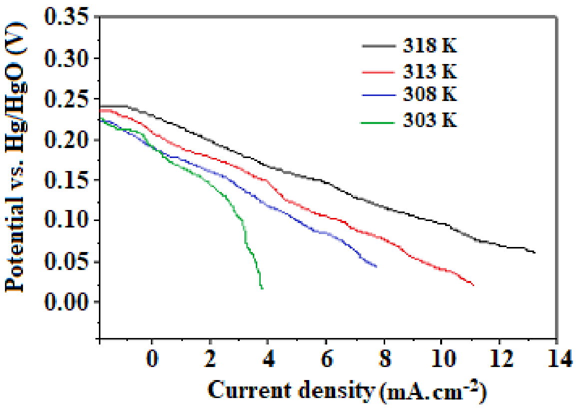

Fig. 1. Polarization curve of the constructed catalyst on GCE at various temperatures (303 K, 308 K, 313 K and 318 K) in O_2-saturated 4M KOH.

The kinetic parameters of the electrode such as Tafel slope, exchange current density, and open-circuit potential (OCP) at low current density (LCD) and high current density (HCD) in different temperatures and O_2-saturated 4M KOH are summarized in Table 1. We obtained the highest exchange current density, highest OCP, and lowest Tafel slope at 318 K.

When temperature is low, electrolyte activity decreases and ion diffusivity is lower, leading to faster cell polarization and termination voltage. On the other hand, high cell temperatures can cause electrolyte dehydration and drying, resulting in water permeation and loss due to evaporation. This can lead to ZAFC failure when the KOH solution evaporates. Additionally, electro-osmotic force should not be disregarded during high-power discharge as it can increase water permeation and loss [26].

3.2 The effect of concentration electrolyte on the ORR

Changes in the electrolyte concentrations (0.5, 1, 2, 3, and 4M) of O_2-saturated KOH at 318 K are shown in Figure 2. Increasing the electrolyte concentration results in incrementing the number of ions as well as the electrical conductivity of the electrolyte. It led to increase in the current density and improved cell performance.

Table 1. The kinetic parameters of the constructed catalyst on GCE at various temperatures and O_2-saturated 4M KOH.

Tem	LCD $b(\mathrm{mV\cdot dec^{-1}})$ HCD		LCD $i_0(\mathrm{mA\cdot cm^{-2}})$ HCD		OCP (V)
303 K	20.4	108	1.0056	1.039	0.2918
308 K	18.9	68.5	1.0105	1.049	0.329
313 K	14.5	66.1	1.0112	1.069	0.3423
318 K	11.6	58.5	1.0137	1.112	0.3652

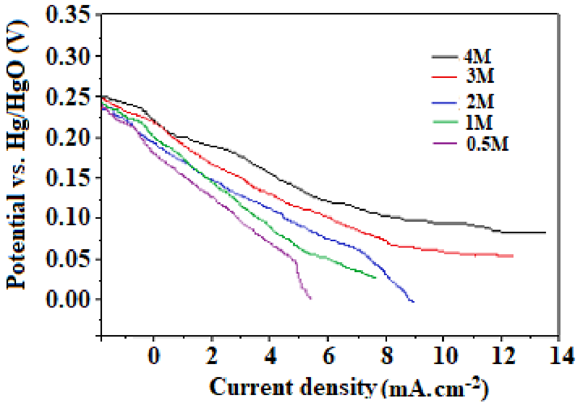

Fig. 2. Polarization curve of the constructed catalyst on GCE at various concentrations (0.5M, 1M, 2M, 3M, 4M) and 318 K.

The concentration of KOH in the electrolyte can impact the internal resistance of ion exchange between electrodes. Research has shown that a 2M concentration of KOH resulted in better performance for a metal alkaline fuel cell with an aluminum anode [27]. However, simply increasing the concentration of electrolytes does not necessarily improve cell performance. It is important to maintain a suitable electrolyte flow to facilitate effective ion exchange. If the concentration of ions is too low, it can cause a delayed supply of ions for electrochemical reactions [28]. A low concentration of KOH can also lead to high resistance of the electrolyte and concentration polarization at the Zn electrode. On the other hand, increasing the KOH concentration can result in an increase in oxidation potential at the Zn electrode and a decrease in reduction potential at the air electrode. While the open circuit potential remains relatively stable, a potential gap may be observed during current output.

The Tafel slope, exchange current density, and OCP at LCD and HCD are summarized in Table 2. We can see the highest exchange current density, the highest OCP, and the lowest Tafel slope in 4M as well as 318 K.

Table 2. The kinetic parameters of the constructed catalyst on GCE at various concentrations of O_2-saturated KOH and 318 K.

Conc. (M)	LCD $b(\mathrm{mV\cdot dec^{-1}})$ HCD		LCD $i_0(\mathrm{mA\cdot cm^{-2}})$ HCD		OCP (V)
0.5	17.5	119	1.0066	1.038	0.267
1	11.6	103.4	1.0085	1.069	0.298
2	6	87	1.0087	1.107	0.286
3	3.8	55.1	1.0146	1.184	0.365
4	3.2	50.4	1.0396	1.227	0.371

The E_a required to perform the ORR at concentrations of 0.5 to 4M and temperatures of 303 to 318 K were investigated using the Arrhenius relationship, equation (6):

$$\ln i_0 = \ln A - \frac{E_a}{RT} \tag{6}$$

The E_a can be achieved from the slope of plotting $1/T$ versus i_0 (Figure 3).

The results are shown in Table 3. At high temperatures and concentrations, the molecules of the reactants have higher collisions due to their higher kinetic energy. As a result, they can more easily provide E_a and become active complexes. Thus, the lowest E_a is calculated at 4M KOH which indicates the best kinetic reaction.

Table 3. Activation energy changes at various temperatures and concentrations.

Conc. (M)	E_a $(\mathrm{J\cdot mol^{-1}})$
0.5	31.23
1	25.7
2	20.54
3	16.62
4	10.04

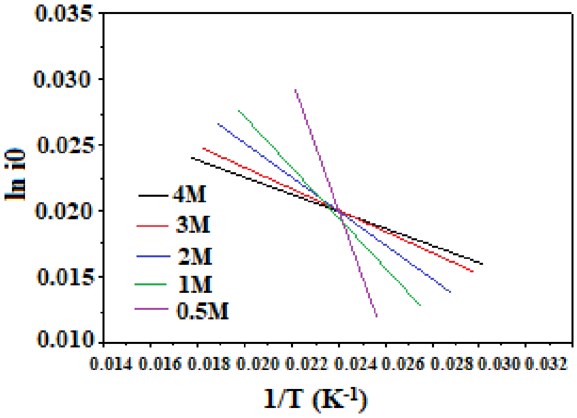

Fig. 3. Activation energy changes at various temperatures and concentrations.

3.3 The performance of the single cell

In the single ZAFC, the cathode and anode are in direct contact together an electrolyte. As shown in Figure 4, the OCP of the single cell is equal to 1.346 V, and the current density of the single cell is achieved at 166.5 mA $\cdot$ cm^{-2} to 0.73 V.

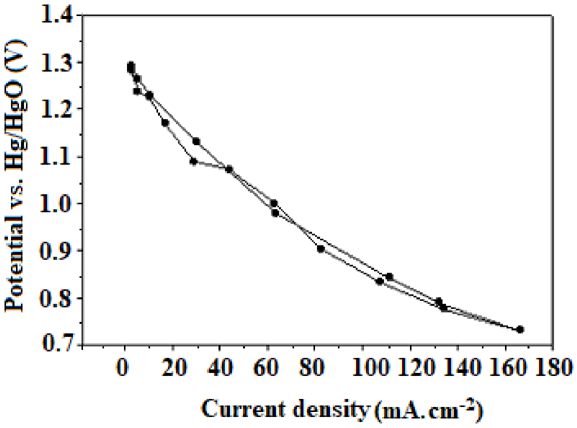

Fig. 4. Polarization curve of single cell ZAFC in O_2**-saturated KOH and** 273 K.

The power density-current density plot of the cell at 4M KOH and 273 K is shown in Figure 5.

The corresponding output power density of the cell is equal to 205.5 mW. According to the fuel cell discharge curve shown in Figure 6, the discharge capacity of the cell is equal to 283 mAh at 0.73 V. These results demonstrate that manufactured ZAFC has a very good performance.

A high concentration of KOH at the Zn electrode is beneficial as it leads to a higher electric potential, while an excessively high concentration at the air electrode during high electrical loads can intensify polarization and lower cell voltage.

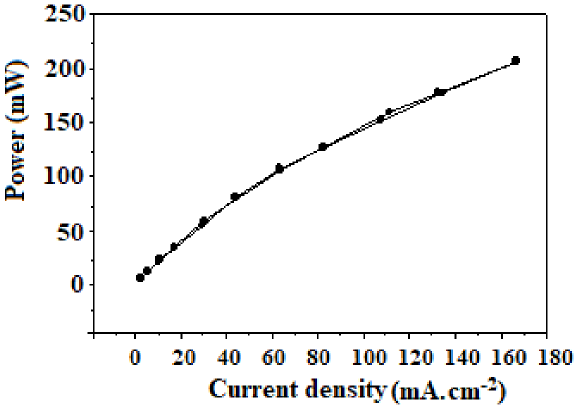

Fig. 5. The curve of power of single-cell versus current density in O_2**-saturated KOH and,** 273 K.

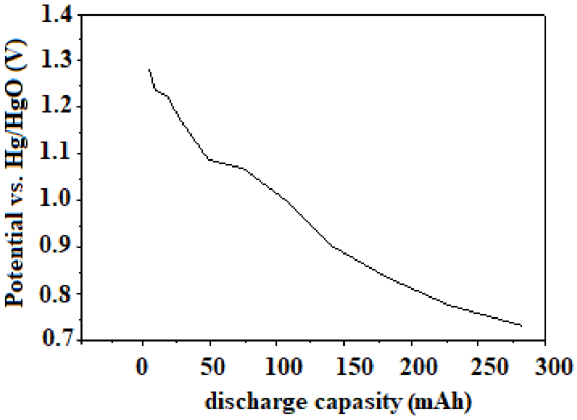

Fig. 6. The curve of the discharge capacity of single cell versus potential in O_2**-saturated KOH and,** 273 K.

4 Conclusions

The ZAFCs are promising applications for the future. For the first time, a ZAFC of simple structure was designed and constructed with PVC thermoplastic which is stable to the alkaline solution, without the use of any separator. Three-layer air-cathode was prepared and the effects of various temperatures and concentrations of the KOH electrolyte were investigated on it. Increasing in temperature and concentration of the electrolyte led to an increase in the current density and a decrease in the Tafel slope. The lowest E_a was obtained at a concentration of 4M by increasing temperature. This result demonstrates that the ORR has better energy to occur at 4M and 318 K in comparison to other temperatures and concentrations.

However, over time, the viscosity of the electrolyte increases which harms the efficiency of the cell at high current densities. To prevent this process, the electrolyte must be replaced with a fresh electrolyte.

Finally, the ZAFC performance was investigated, and the results show the high power density and high current density of the cell in 4M KOH and 273 K.

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