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Experimental Research of Liquid Infiltration and Leakage in Zinc Air Battery

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Zinc-air batteries, despite their advantages of high energy density, operational safety, economic and technical viability, are limited by the problem of electrolyte leakage. This study presents a study on this problem and its effects on the performance of a zinc air battery. To elucidate the cause(s) of leakage, the following experiments were performed: determination of the surface properties of a film of PTFE (polytetrafluoroethylene) (main constituent of porous air electrode and porous diffusion layer), air-cooled discharge with two auxiliary tests porous air electrode voltage analysis and electroosmosis. The experimental results showed that: the hydrophobicity of a PTFE film is progressively reduced when it is soaked in a solution of KOH; liquid infiltration is most prominent when KOH solution is used as the conductive medium; in addition, temperature and voltage also affect the liquid infiltration phenomenon.

Keywords: Liquid Infiltration; Leakage; PTFE film; Zinc Air Battery

1. INTRODUCTION

The zinc air battery has received increased attention because of its unique advantages such as high specific energy, low toxicity, and cost-effectiveness[1-3]. These advantages render the zinc air battery as a promising propulsion device for cars, wherein a high energy density is desired. As a result, the market potential of zinc air battery is huge. However, the zinc air battery has problems that limit its applications and further progress[4-6]. The leakage phenomenon is one of the problems[7].

Leakage is generally observed on the surface of the porous air electrode after it has operated over a long period of time. If the leakage is severe, then there is a large accumulation of liquid (liquid infiltration), which seriously impedes the permeability of the porous air electrode and adversely affects the battery performance to the extent that the battery becomes inoperable. Moreover, if there is an excess loss of water then operating the battery can easily lead to a safety risk[8,9].

According to our knowledge, duo to zinc metal is oxidized to zinc ions, the zinc container becomes thinner as the cell is used. When the zinc case thins enough, zinc chloride begins to leak out of the battery. The old dry cell is not leak proof and becomes very sticky as the paste leaks through the holes in the zinc case. The zinc casing in the dry cell gets thinner even when the cell is not being used, as the ammonium chloride inside the battery reacts with the zinc. An "inside-out" form with a carbon cup and zinc vanes on the interior, while more study for leak resistant, has not been made since the 1960s[10].

In this study, the causes of leakage were investigated with the help of the following four self-designed experiments. To analyze corrosion, the surface properties of a PTFE film treated with the electrolyte were determined. In order to investigate the effect of temperature, the discharge of an air-cooled battery was performed along with two auxiliary tests. To examine the influence of voltage, the porous air electrode was subjected to different voltages. Finally, an electroosmosis test was performed similar to the work of Peŭc[11], to find its correlation with the electrolyte, voltage and the total charge on the battery.

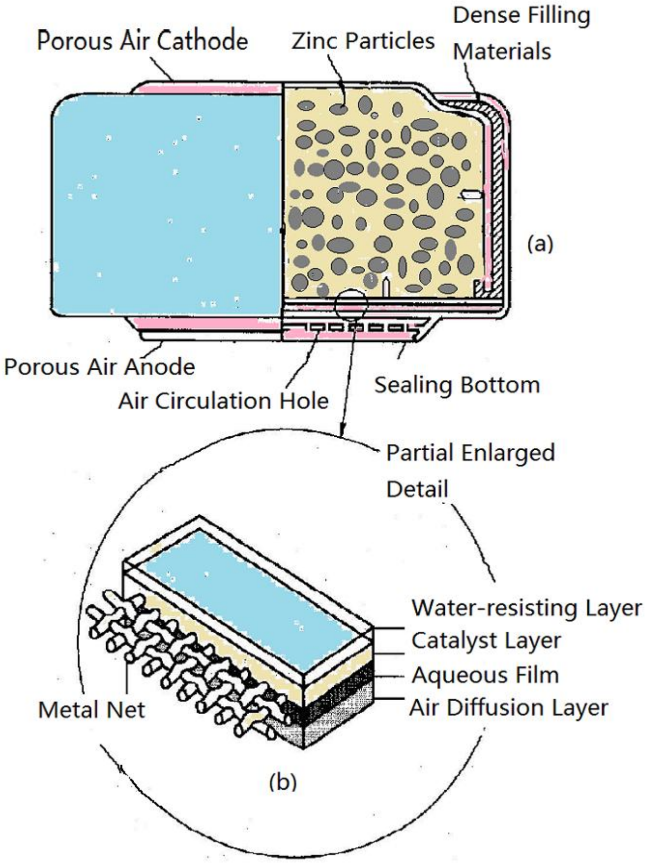

Figure. 1. A schematic of Zinc air battery, (a)constructional detail,(b)partial enlarged detail for porous air electrode.

2. EXPERIMENTAL

To investigate the effect of temperature, two similar batteries were assembled and their performance was ensured to be the same. A schematic of Zinc air battery can be seen in Fig. 1, and we take two batteries as a group[12].

The effect of electrolyte infiltration on the corrosion of an porous air electrode was studied by determining the surface properties of a PTFE film representing the electrode, before and after its treatment with potassium hydroxide KOH, representing the electrolyte. For treatment, a PTFE film was soaked in 30% KOH (analytical grade level ≥ 99%) solution for several hours in a sealed container to prevent the influence of atmospheric carbon dioxide (CO_2) on the experimental result. Then, the film was removed and dried with a hair dryer. The untreated and treated PTFE films were both placed on a slender Plexiglass board, to observe and compare the experimental results. A few drops of 30% KOH solution were allowed to fall on both films and the droplets were observed and photographed. Using image analysis the contact angles of the drops on the films were compared.

AS we usually do, the two batteries were let to discharge at a current of 10A. One of them (named A1) was operated with cooling fans, and the other one (named A2) was operated in a sheltered environment. When leakage was detected on the surface of the porous air electrode, it was observed for 10 min and then the two batteries were swapped keeping other conditions unchanged. The experiment was conducted for 1.5h. For a comprehensive analysis of the result, two auxiliary experiments were performed. In the first auxiliary experiment, two batteries were assembled, weighing 400g and 390g, respectively. The two batteries were discharged at 10A for 6 h. The heavier 400g battery was discharged in the ambient without any air circulation, while the lighter 390g battery was discharged in the ventilated condition. After the discharge, the two batteries were weighed. In the second auxiliary experiment, the PTFE film was placed with KOH solution in a water bath at a constant temperature of 65^{o}C for 20 min (The maximum working temperature of the battery is about 65^{o}C). Then the PTFE film was taken out and the moisture on it was removed. Heated KOH solution was dropped on the PTFE film and the droplets were observed and photographed.

To examine the influence of voltage, the following experiment was performed. A copper box (representing a battery) was taken and 280 mL of 30% KOH solution was poured in it. The porous air electrode was vertically inserted in the solution in such a way that it did not touch the copper box. To facilitate observation, the air electrode was not stuck to a PTFE film. The positive terminal of the DC power supply was connected to the air electrode and the negative terminal was connected to ground. An insulation layer was placed between the copper box battery and the ground to prevent the box from grounding. For comparison, a reference battery was assembled in the same way as described above device but no power was supplied. The experiment was carried out for 8 h after which the results and electrodes of the two batteries were compared.

In 1809, the Russian scientist Peйc discovered the electroosmosis phenomenon[11]. In this study, a device similar to the one used by Peйc was employed to find a correlation of electroosmosis with the electrolyte, voltage and the total charge of a zinc air battery. Two polyethylene straws were inserted in wet clay, so that the level of liquid electrolyte in both straws was the same. The positive electrode of a 220 V direct current (DC) power supply was inserted in one of the straws and the negative electrode was inserted in the other. Once the power supply was turned on the height of the electrolyte connected to the negative terminal decreased while that of the other rose. The difference in height between the electrolytes in the straws was used to judge the strength of electroosmosis phenomenon.

To find a correlation between electroosmosis and electrolyte, the experiment described above was performed with different electrolytes. For the electrolytes 20% solutions of: potassium carbonate (K_2CO_3) (analytical grade, content ≥ 99.5%), sodium chloride (NaCl) (analytical grade, content ≥ 99.5%), barium chloride ($BaCl_2$) (analytical grade, content ≥ 98%) and KOH, were prepared respectively. In addition to these four kinds of electrolyte, tap water, which is also a kind of a conductive medium, was tested. For the electroosmosis experiment, the electrolytes were separately injected into the straws as a conductive medium. After the experiment, the clay, straw and conductive media were replaced. However, other conditions such as the 220 V DC power supply and the experimental duration of 45 min were maintained the same.

To find a correlation between electroosmosis and voltage, different voltages were applied to the setup via the DC power supply, keeping the other conditions unchanged. The differences in height of the liquid levels corresponding to different voltages were compared. The power-up duration was 45 min, and the conductive medium was 20% KOH solution. To find a correlation between electroosmosis and the total charge of the battery, a combined electroosmosis and charging test was performed. In current literature, it is believed that the transport (leakage) of electrolytes/water is caused by the drag created by electrons or ions. In order to (in)validate this viewpoint, an experimental setup similar to the one of Peйc was constructed. Two tubes were injected with tap water to the same height and connected in series to a 300 mA ammeter and a DC power supply.

The supply was turned on for a period of 45 min. During the experiment, the current was recorded and after the experiment the height difference between the water columns in the two tubes was measured. The total charge quantity was calculated from the experimental data. Using the geometry of the straw and the fluid column height difference, the volume difference was calculated, and eventually converted into number of water molecules[13]. Finally, the total amount of charge and the total number of water molecules were compared. The voltage applied was changed and the whole experiment was repeated.

3. RESULTS AND DISCUSSIONS

To study the influence (corrosion) of electrolyte infiltration on the surface of an porous air electrode, the contact angle of droplets of KOH on PTFE films were determined. As shown in Figure. 2, the contact angle decreased with the duration of soaking in KOH solution. The film treated for 60 h had a lower contact angle than the untreated film. The film treated for 136 h had a contact with KOH, which was significantly smaller than those on the other samples. This implies that with the extent of soaking the hydrophobic character of the PTFE film deteriorates progressively. Since current zinc air batteries have a layer of PTFE film stuck on the surface of the air electrode, they will all inevitably be subject to corrosion by KOH solution (electrolyte) making the PTFE film gradually less hydrophobic. As a result, the leakage increased progressively.

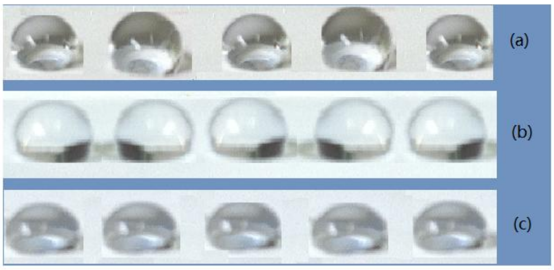

Figure 2. Results of surface property experiment of PTFE film, (a) unhandled PTFE film, (b) Soak for 72 hours' PTFE film, (c)Soak for 148 hours' PTFE film.

The results of the experiments on the effect of temperature showed that after 1.5 h, leakage was detected earlier in the battery that was being cooled (A1). No liquid infiltration was observed in the cooled battery (A1) when leakage appeared in A2. After the positions were exchanged, and the batteries were observed for 1.5 h, the leakage in battery A2 was significantly reduced, while liquid infiltration was observed in the battery A1. The results of the first auxiliary experiment showed that after being discharged, the weight of the heavier battery that was not ventilated increased in weight slightly from 400 g to 401 g, while the weight of the lighter battery that was ventilated, reduced from 390 g to 387 g.

Figure 3. Results of Temperature on PTFE film contact angle influence, (a) PTFE film contact angle at room temperature,(b) PTFE film contact angle after boiling water immersion.

On calculation, both these batteries had gained 30g by absorbing oxygen during the process of being discharged. Therefore, the loss of water by the heavier non-ventilated battery was 29g, while that of the lighter ventilated battery was 33g. The higher release of water by the lighter battery was not easily observable and could have been caused by the ventilation, which might have increased the speed of evaporation. The results of the second auxiliary experiment as shown in Figure 3, revealed that on heating the contact angle on the PTFE film decreased significantly. In other words, with the increase in temperature, the hydrophobic nature of the PTFE film becomes poor. Therefore, temperature will affect liquid infiltration in a battery. In summary, both ventilation and cooling can reduce the influence of high temperature on the hydrophobic nature of a PTFE film, and consequently, liquid infiltration can be reduced.

From an examination of the influence of voltage on the leakage phenomenon, it was observed that the level of liquid electrolyte in an air electrode rose when a voltage was applied. This shows that voltage is also one of the factors that affect leakage.

Table 1. Electroosmotic effect of different conducting media

Conductive medium	Voltage	Experimental time	Liquid level difference
Tap water	220V	45 min	3.1mm
$BaCl_2$	220V	45min	4.3mm
K_2CO_3	220V	45min	31mm
NaCl	220V	45min	5.2mm
KOH	220V	45min	34mm

The results of the experiments on finding a correlation between electroosmosis and electrolyte are shown in Table 1. The liquid level differences were large, at 31 mm and 34 mm, when the conductive medium (electrolyte) was K_2CO_3 and KOH, respectively. On the contrary, when the conductive medium were NaCl, $BaCl_2$ and tap water, the liquid level differences were small at 5.2 mm, 4.3 mm and 3.1 mm, respectively. This might be because KOH and K_2CO_3 are alkalis and the surface tension of their solutions is sensitive to electricity, leading to the electroosmosis phenomenon. Since zinc air batteries predominantly use KOH as the electrolyte, leakage due to electroosmosis will occur during their operation.

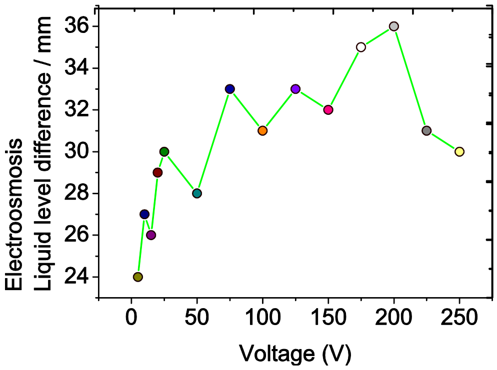

Figure 4. Electroosmotic effect of different voltages.

The results of the experiments on finding a correlation between electroosmosis and voltage are shown in Figure 4. It appears that a change in voltage does not influence the liquid level difference significantly. The average height difference was 30.6 mm, the maximum was 36 mm and the minimum was 24 mm. Electroosmosis seems to be triggered by the application of voltage, though it does not seem to be controlled by it. Therefore, we can surmise that the magnitude of voltage does not influence electroosmosis.

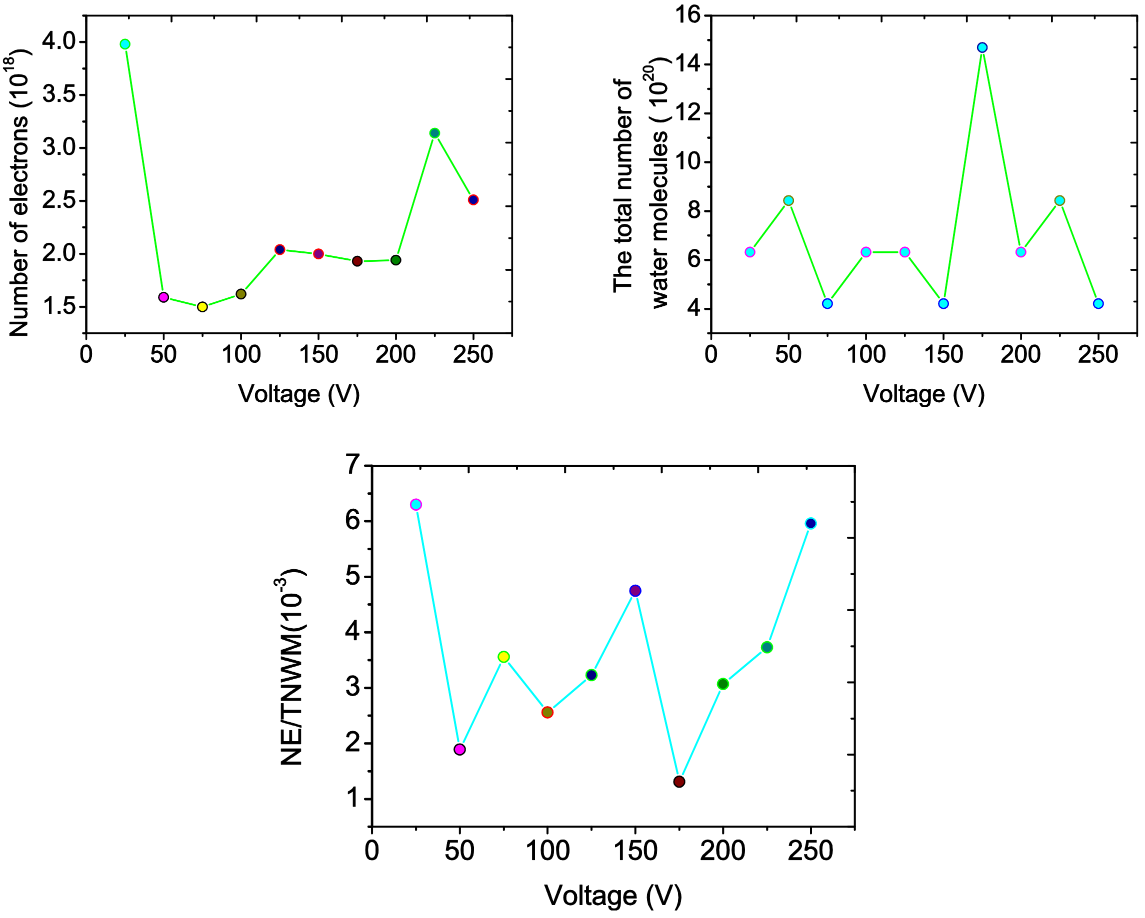

Figure 5. Electroosmotic effect of the amount of charge, (a) The relationship between number of electrons and amount of charge. (b) The relationship between total number of water molecule and amount of charge.(c) The relationship between number of electrons / The total number of water molecules and amount of charge

The results of the experiments on finding a correlation between electroosmosis and the amount of charge are shown in Figure 5. Based on electron/ion assisted transport theory, the ratio between the number of electrons or ions and the total number of water molecule appears to be about 9-4 in magnitude. This implies that each electron or ion was dragging several thousand water molecules with it. As far as we know, an electron or an ion can only drag less than ten water molecules. Therefore, from our experimental results, it appears that the electron/ion assisted transport theory is not true. So the influence of the amount of charge on leakage can be essentially ignored.

4. CONCLUSION

This study indicates that the long time store of Zinc Air Battery results in a surface seepage phenomenon in gas diffusion porous electrode. Figure 2 and Table 1 shows that the PTFE wetting angle changed by immersion with KOH. and at the same time, an electric potential difference also makes the electrolyte infiltration in porous electrode easily, and leakage happens. Moreover, leakage phenomenon is particularly implicated in large current working, a big reason is the reduction of the surface tension of electrolyte which caused by the increment of temperature at large current.

In conclusion, we can make the following statements:

1. The hydrophobicity of a PTFE film is progressively reduced when it is soaked in a solution of KOH. This implies that in a zinc air battery, liquid infiltration into the PTFE containing air electrode will also progressively increase culminating in the leakage of the electrolyte.

2. Electroosmosis is most prominent when KOH solution is used as the electrolyte. Therefore, in zinc air batteries that use KOH, the problem of liquid infiltration and leakage will be most severe. This may be because of the sensitivity of the surface tension of a KOH solution to electricity.

3. Change in voltage does not affect the amount of liquid infiltration, as hinted by Peŭc earlier. However, the application of voltage triggers infiltration leading to electrolyte leakage.

4. With temperature, the viscosity and surface tension of an electrolyte are reduced, which make liquid infiltration and leakage easy. A zinc air battery generates heat during its operation, which further aggravates the battery liquid infiltration. With the help of ventilation and cooling, the temperature of a zinc air battery can be significantly decreased, reducing the risk of liquid infiltration.

In summary, liquid infiltration phenomenon is influenced by many factors, such as PTFE film property, voltage, electrolyte and temperature. To overcome this problem, all its contributing factors must be addressed comprehensively and collectively, and then corresponding control measures should be taken.

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