



Various Alcohols as Electrolysis Suppressants in Zn-air Secondary Batteries

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ABSTRACT

The gelling agent used in Zn-air cells plays a role in improving battery life. It prevents the evaporation of water and diffusion of Zn^{2+} ions away from the current collector. Additional functionality was incorporated by replacing some of the gelling agents with new materials. Alcohols with moderate viscosity, namely maltose, sucrose, poly ethylene glycol 600, and 2-hydroxyethyl cellulose, were used to replace some gelling agents in this work. Among these alcohols, poly ethylene glycol 600 and 2-hydroxyethyl cellulose improved the cycle life of full cells. This improved cycle life was attributed to the inhibition of water electrolysis and the improved cycle life of the anode.

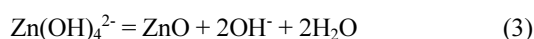
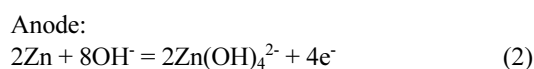
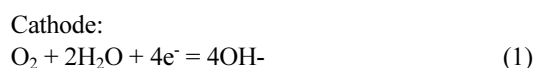
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1. Introduction

The high energy density of Zn makes Zn-air batteries an attractive form of energy storage. Zn-air batteries are more cost-effective when used as a secondary battery. Using an aqueous electrolyte for Zn-air batteries is very advantageous because it is inexpensive and nonflammable. However, the electrolyte suffers from evaporation and hydrogen evolution problems [1]. These issues need to be overcome when designing secondary batteries. Gelling agents in Zn-air batteries not only retard the rapid evaporation of water (solvent), but also keep Zn^{2+} ions near the current collector. Without the use of a gelling agent, the diffusion of Zn ions away from the electrode leads to a rapid decrease in capacity retention at the anode in every cycle. Polyacrylic acid (PAA)[2] is the typical gelling agent used in Zn-air batteries. It is chemically stable in concentrated base solutions, where it becomes the counter base, polyacrylates. A previous study [3] demonstrated that acetate ions, which have a simi-

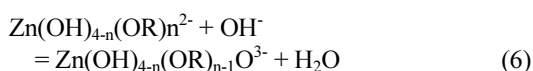
lar anionic structure to the acrylates, improved the capacity retention of anode cycles. Small alcohols, such as ethylene glycol, glycerol, and erythritol, also inhibited the reaction of the zincate ion to ZnO. These oxygen-bearing ligands delay the transformation of zincate ions to ZnO, which forms a resistive passive layer on Zn electrode. The irreversible formation of ZnO from Equations 1 through 4 [4-6] becomes slow due to the formation of modified zincate containing alkoxide ligands. Equations 5 and 6 express the bond breakage required for ZnO formation [3, 7-10] in neat KOH solution and in solution with alcohol additives. Because the covalent bond breakage shown in Equation 6 is slower than the acid-base reaction in Equation 5, alcoholic additives can enhance the cyclability of the overall reaction.



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Overall reaction:



In this study, larger alcohols were used to replace part of the gelling agent, providing a suitable level of viscosity for the solution. Polyethylene glycol (PEG) [5,11,12], sucrose, maltose, and 2-hydroxyethyl cellulose (HEC)[13] were selected. PEGs with high molecular weight are not miscible in the aqueous solution. Therefore, the effectiveness of PEG600 (MW 600) was evaluated in this study.

2. Experimental

Potassium hydroxide (KOH, 85%, Junsei Chemicals), poly(acrylic acid)(PAA, $M_v \sim 1,250,000$, Sigma-Aldrich Co.), polyethylene glycol 600 (PEG600, Alfa Aesar), sucrose (99.0%, Tokyo Chemical Industry Co., Ltd), maltose (99.0%, Sigma-Aldrich Co.), 2-hydroxyethyl cellulose (HEC, $M_v \sim 1,300,000$, Sigma-Aldrich Co.), zinc foil (99.994%, 0.1 mm, Alfa Aesar), zinc powder (99.9%, -100 mesh, Alfa Aesar), and carbon black (Super P black, Timcal Graphite & Carbon Inc.) were all used as received.

Linear sweep voltammetry (LSV) was performed using a potentiostat (BioLogic Science Instruments, model SP-150) in order to observe the electrolysis of water on Zn. One side of the zinc foil (8 mm diameter) was exposed to electrolytes as the working electrode. A Hg/HgO electrode (1.0 M KOH solution, CHI102, CH Instruments, Inc.) and Pt wire were used as the reference and counter electrodes, respectively. The electrolyte used was 4.0 M KOH aqueous solution [14]. PAA was added to the electrolyte at a 0.5:25.5 (PAA: 4.0 M KOH solution) weight ratio to prepare a gel. One-fifth of the PAA was replaced with several alcohols to prepare the alcohol-added solutions. The scan started from an open circuit potential (OCP, -1.43 V) and moved in the negative direction at a scan rate of 5 mV s^{-1} . Current values at -1.9 V were compared to evaluate the intensity of electrolysis and H_2 production.

The anode for the half-cell tests was prepared with

a slurry mixture of Zn powder, Super P black, and PVA at a weight ratio of 93: 5: 2. The solvent for the slurry was deionized water. The slurry was spread on a Cu foil. The electrode was dried at 60°C for 24 h and pressed to the desired thickness of 150 μm . The prepared electrode was then exposed to electrolytes as the working electrode in a disc (8 mm diameter). An automatic battery cycler (model WBCS 3000, WonATech Co.) was used for the half-cell tests. Tests were performed in the potentiostatic mode, where a constant current (20 mA/cm^2) was applied during both the discharge and charge cycles. The cut-off potentials the charge and discharge cycles were -1.5 and -1.2 V (vs. Hg/HgO), respectively. Battery tests were performed with 2032 type coin cells. The air cathodes were purchased from MEET Co. The cathode for the cycle tests was composed of Co_3O_4 , carbon black, and polytetrafluoroethylene at a weight ratio of 10:50:40. [15,16] A separator (Celgard, 3501) was placed between the cathode and the anode gel. The anode gel contained zinc powder, carbon black, electrolyte, and PAA at a weight ratio of 73:1:25.5:0.5. The prepared gel electrolyte is mixed with zinc powder and carbon black by using a mechanical stirrer to form the Zn gel. The weight of the Zn gel in the cell was 1.5 g for all the tests. In order to observe the capacity improvement due to the additive, one-fifth of the PAA was replaced. Repeated tests were conducted for 1% depth discharge and recharge cycles. One discharge and recharge cycle took 23.7 min at 22.7 mA.

Conductivity measurements were performed using a conductivity meter (Mettler Toledo, Seven Go Pro SG7-FK2) at ambient temperature. A four-electrode conductivity probe (Mettler Toledo, Seven Go Pro Inlab 738) was calibrated with standards (Mettler Toledo) before the measurements were carried out. The viscosities of the electrolytes at room temperature were determined using capillary viscometers (SI Analytics GmbH, 525 40 and 525 43) and a viscosimeter (SI Analytics GmbH). The reported viscosity of each electrolyte was averaged from five measurements.

3. Results and Discussion

The gelation of the solution prevented the water from rapidly evaporating. Furthermore, the increased viscosity caused by the gelling agent makes the elec-

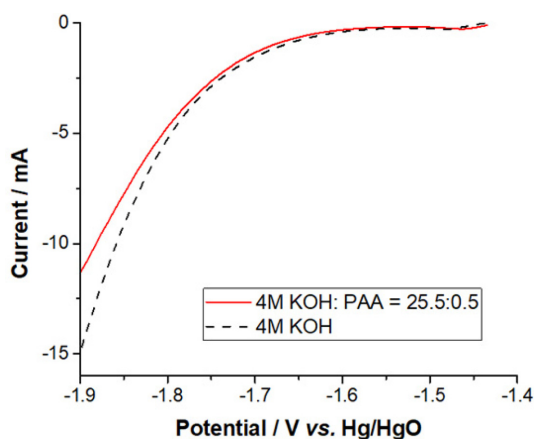


Fig. 1. LSV curves in 4.0 M KOH solution. Dotted line: 4.0 M KOH solution, solid line: 4.0 M KOH solution with PAA. All LSVs were measured on the Zn electrode.

trollysis of water sluggish. Fig. 1 shows that PAA slows the rate of electrolysis, the H_2 evolution reaction on the Zn electrode. The H_2 evolution rate was compared with the currents at -1.9 V. More negative voltages than -1.9 V resulted in larger current sizes; however, it was difficult to compare current values because hydrogen generation becomes more severe and the current is accompanied by higher noise. Immediately after filling the solutions in the cell, LSV curves were obtained in order to avoid corrosion as much as possible. Otherwise, Zn^{2+} ions would be produced through corrosion, which would significantly influence current values. The current intensity at -1.9 V decreased by 30% due to PAA addition. It was observed that the addition of a gelling agent suppressed hydrogen evolution. PAA has numerous acrylate groups on its backbone. It has not yet been ascertained whether the increased viscosity of the solution or the acrylate functional group plays the

primary role in this suppression. Functional groups and their role in the battery will be investigated in future studies. The electrolyte containing PAA (4.0 M KOH: PAA = 25.5:0.5) will be referred to as the baseline electrolyte in the remainder of this work. The influences of electrolytes on the cell performance were assessed by modification of the baseline solution. Replacement of the gelling agent with alcoholic additives reduced the viscosity of the solutions, which led to higher electrolyte conductivities compared to the baseline electrolyte. The increased conductivity of the solution is a favorable condition for electrochemical reactions.

The viscosity and conductivity changes caused by replacing 20% of PAA with alcohol are listed in Table 1. The content of alcohol was only 0.4% in the entire electrolyte, which has little influence on the KOH concentration. Electrolytes with different alcohols are compared to the baseline electrolyte. The conductivity changes due to the additives were small, but the viscosity changes were large.

The LSV curves in Fig. 2 were obtained for all solutions listed in Table 1. Although the conductivities and viscosities of the solutions were improved by alcohol additions compared to the baseline electrolyte, the electrolysis rates were decreased. This means that alcohols suppress electrolysis. Alcohols with higher molecular weights, like HEC and PEG600, are better suppressants than those with low molecular weights, such as sucrose and maltose. There was no correlation with either the viscosity or conductivity and the H_2 evolution reaction, according to Table 1.

Deceleration of the reaction rate of H_2 evolution was also observed with small-size alcohols such as methanol, ethanol, isopropyl alcohol, and n-butyl alcohol. These light alcohols were not used in this work because their viscosities are very different

Table 1. Viscosity and conductivity of the baseline electrolyte and electrolytes with 0.4% alcohols. Viscosity and conductivity were obtained at 25°C.

Electrolyte (weight ratio)	Additive	Viscosity (cP)	Conductivity (mS/cm)
Baseline electrolyte 4M KOH : PAA (25.5:0.5)		55425.8	529
4M KOH : PAA: alcohol (25.5:0.4:0.1)	Maltose	10935.9	543
	Sucrose	11466.3	543
	PEG 600	3616.8	550
	HEC	25217.3	541

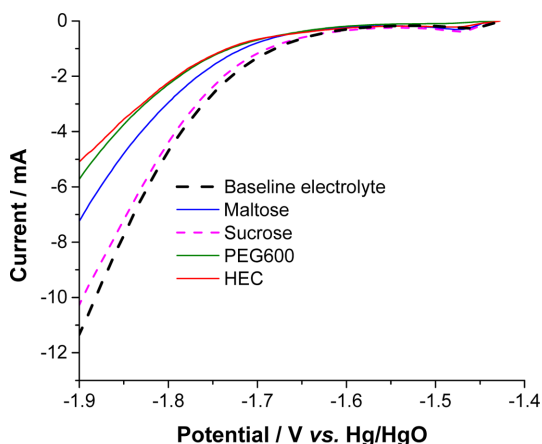


Fig. 2. LSV curves in 4.0 M KOH solutions with additives compared to the baseline electrolyte. The electrolytes were composed of 4.0 M KOH, PAA, and additive at a ratio of 25.5: 0.4: 0.1.

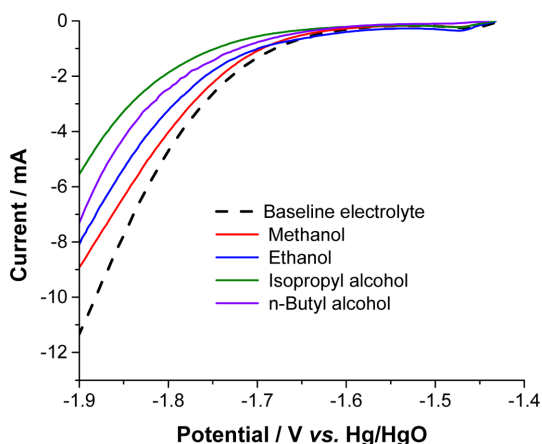


Fig. 3. LSV curves in 4.0 M KOH solutions with light-weight alcohols in comparison with baseline electrolyte. The electrolytes were composed of 4.0 M KOH, PAA, and alcohol at a ratio of 25.5: 0.4: 0.1.

from that of PAA. However, these light alcohols can explain the inhibition of electrolysis due to alcohols. Fig. 3 shows the H_2 evolution currents on the Zn electrodes in electrolytes containing 0.4% alcohols. When compared to the light alcohols, heavier alcohols led to a greater decrease in the electrolysis rate, which is similar to that observed for the larger alcohols shown in Fig. 2. Because the alcohol content of the solution is low, the current resulting from the breakdown of alcohol is also

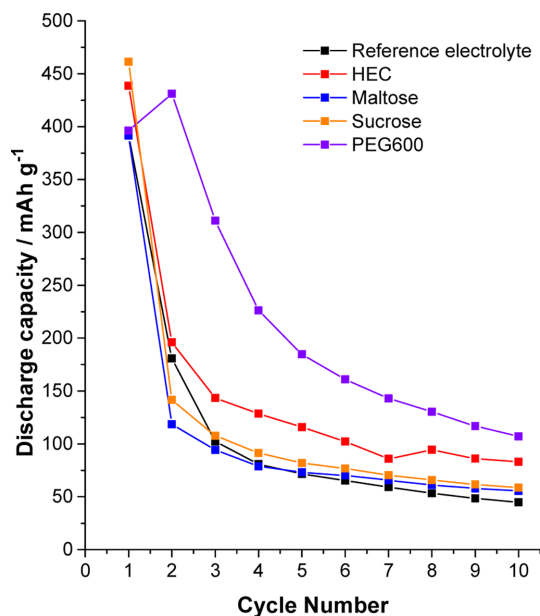


Fig. 4. Half-cell cycle tests with electrolytes in Table 1. The discharge values are averaged values from three measurements.

small. If the additive inhibits electrolysis, it can also inhibit the consumption of water during the cell cycle. Suppression of water consumption is one of the important factors that can increase battery life.

Alcohol improves the cyclability of the anode by forming a complex with Zn^{2+} to inhibit the formation of ZnO . All the tested solutions improved capacity retention at the 10th cycle compared to the baseline electrolyte, as shown in Fig. 4. Among them, larger alcohols (such as PEG600 and HEC) were better at capacity retention than smaller ones (like sucrose and maltose). The capacity value for the PEG600 solution (107 mAh g^{-1}) was 2.4 times higher than that of the baseline electrolyte at the 10th cycle (44 mAh g^{-1}). The capacity value from the HEC solution (81 mAh g^{-1}) was 1.8 times higher than that of the baseline electrolyte at 10th cycle.

The inhibition of electrolysis and improvement of half-cell cycles were observed by the addition of alcohols. It is necessary to confirm that these two improvements are still maintained in full-cell tests. Fig. 5 shows the full-cell cycle tests with a repetition of 1% discharge and recharge cycles. If the water is depleted or a large amount of ZnO accumulates,

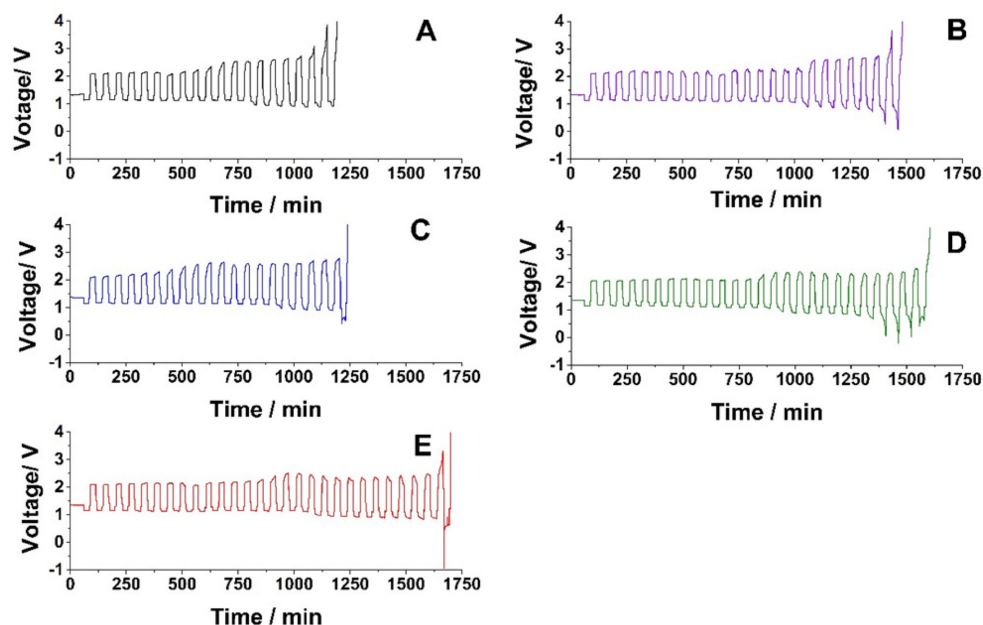


Fig. 5. Full cell test cycles with the electrolytes listed in Table 1. A: baseline, B: maltose, C: sucrose, D: PEG600, E: HEC. There was a 30 s rest time at every cycle.

resistance increases, which leads to an inoperable battery. The point at which the rapid increase of the operation voltage occurs was considered to be the end of the life of the battery. The life tests in Fig. 5 show that all alcohol additives helped improve the cycle life. In particular, PEG600 and HEC with higher molecular weights were observed to be better among the alcohol additives studied. The diminution of electrolyte depletion by alcohol additives and the improvement of the anode lifetime were therefore shown to be effective at improving the lifetime of the full cell. This suggests that the alcohol additives provide two improvements to full cell operation without interfering with the operation of the cathode. We found that the higher-molecular-weight alcohols used in this study were most effective in improving performance.

There are many other alcohols to consider when selecting additives. However, alcohols with very high molecular weights were not suitable for this work because they have a low degree of solubility in a high-concentration KOH solutions. Insoluble materials, such as polymers [17,18], are another type of electrolyte for Zn-air cells where aqueous basic solutions are limited. Alcohols with low solubility can be

further investigated as polymer electrolytes or gels. Alcohols with low molecular weights, such as ethanol, propanol, and butanol, can perform similar work to that we observed in alcohols studied in this work. However, these light alcohols are more volatile than water, resulting in the rapid loss of alcohol during cell operation.

In this work, some mid-size alcohols that were chemically stable in KOH solutions were evaluated as additives for Zn-air batteries. These were not volatile and were furthermore well-miscible in concentrated KOH solutions. There are many other alcohols with moderate molecular weights that can compete with these alcohols. Concentration variations of these alcohols could provide better performance at various KOH concentrations. The addition of alcohols could adjust the viscosity, conductivity, and inhibition of reactions in the cells.

4. Conclusions

Maintaining a proper viscosity during the operation of a Zn-air battery helps to maintain the lifetime of the anode. The gelling agent, PAA, prevents rapid evaporation of water and prevents Zn^{2+} ions from dif-

fusing too far away from the electrode. Replacing some of the gelling agent with other additives provides additional functions which can improve the life of the battery. In this study, electrolysis of water was suppressed by the addition of alcohols. Light-weight alcohols worked well as gas suppressants. However, these were not suitable because they are volatile during battery operation. Moderate-weight alcohols are not volatile and have moderate viscosity, allowing the replacement of some of the gelling agent. PEG600 and HEC were advantageous at simultaneously reducing the electrolysis of water and improving the lifetime of the anode. These additives improved the lifetime of the full cell as well, indicating that they do not interfere with the operation of the cathode.

Acknowledgement

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