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# Study on Durability and Stability of an Aqueous Electrolyte Solution for Zinc Bromide Hybrid Flow Batteries

# Study on Durability and Stability of an Aqueous Electrolyte Solution for Zinc Bromide Hybrid Flow Batteries

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**Abstract.** Zinc-bromine flow battery using aqueous electrolyte has advantages of cost effective and high energy density, but there still remains a problem improving stability and durability of electrolyte materials during long-time cell operation. This paper focuses on providing a homogeneous aqueous solution for durability and stability of zinc bromide electrolyte. For performance experiments of conventional and proposed electrolyte solutions, detailed cyclic voltammetry (CV) measurements (at a scan rate of 20 mV $s^{-1}$ in the range of -1.5 V~1.5 V) are carried out for 40 cycles and five kinds of electrolytes containing which has one of additives, such as (conventionally) zinc chloride, potassium chloride, (newly) lithium perchlorate, sodium perchlorate and zeolite-Y are compared with the 2.0 M $ZnBr_2$ electrolyte, respectively. Experimental results show that using the proposed three additives provides higher anodic and cathodic peak current density of electrolytes than using other two conventional additives, and can lead to improved chemical reversibility of zinc bromide electrolyte. Especially, the solution of which the zeolite-Y added, shows enhanced electrochemical stability of zinc bromide electrolyte. Consequently, proposed electrolytes have a significant advantage in comparison with conventional electrolytes on higher stability and durability.

## 1. Introduction

Recently, The flow battery technology has high interest of energy storage system for users who requires cost effective and eliminates the limitation of traditional battery systems that has a decoupling problem with the power and energy components of the system. The zinc bromine hybrid flow battery (ZBB) has characteristic of high power density and can be a useful rechargeable device for energy conversion [1]. The process of charging and discharging energy of ZBB is generally achieved through a reaction of redox couples like $Zn^{2+}$ / $Zn_{(s)}$ and $Br^-$ / $Br_2$ in zinc bromide electrolyte [2, 3]. The zinc-bromine electrolyte solution has the advantage of providing cost-effective high energy density for battery energy storage, but its distinctive-electrochemical property during cell charging causes a lot of problems, which leads to highly concentrated bromine in catholye and zinc metal deposition on the anode electrode surface. This is due to the fact that the activated bromine can corrode components of the cell and zinc metal can be formed a variety of dendritic morphology. This provides reason enough not only to decreasing the energy efficiency of ZBB but also to reduce the battery life cycle. Thus, zinc-bromine electrolyte solution has a significant influence on the electrochemical performance of ZBB for energy storage [4].

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Various additive materials such as quaternary ammonium salts and dendrite inhibitors has been deveopled which combine activated bromine and prevent indiscriminate formation of zinc dendrite, respectively[4]. Improving the electrolyte conductivity has also long been one of the major topics in the development of an electrolytic capacitor. In conventional electrolye solutions, zinc chloride or potassium chloride have generally been used for this purpose [5], but these additives can hinder stability and durability of zinc bromide electrolyte. Hence, there still remains a problem of improving stability and durability of electrolyte materials during long-time cell operation.

This paper focuses on providing additives such as lithium perchlorate, sodium perchlorate and zeolite-Y for durability and stability of the electrolyte. Depending on the kinds of conventional and new additives, electrochemical effects of these electrolytes are investigated by cyclic voltammetry measurement (CV) [6].

## 2. Experimental Method

### *2.1. Electrolyte Preparation*

Several kinds of additives such as $LiClO_4$, $NaClO_4$, zeolite-Y, $ZnCl_2$ and KCl are used to improve the stability and durability of electrolyte. These compounds have a stronger electronegativity than $ZnBr_2$. Zinc bromide electrolyte solution is prepared by electrolytic dissociation of zinc bromide powder which is supplied by Kanto Chemical Co., Japan. A certain amount of additives, $LiClO_4$, $NaClO_4$, zeolite-Y, $ZnCl_2$ and KCl are prepared into the electrolyte, respectively. The total content of zinc bromide in the electrolyte is determined as 2.0 mol $L^{-1}$, because minimum resistivity of the electrolyte and maximum solubility of bromine was observed at that concentration [7, 8].

### *2.2. Cyclic Voltammetry Measurement*

The CV is carried out on a potentiostat mode in a three-electrode cell kit which consists of electrolyte bridge and two reservoirs. To investigate the stability and electrochemical characteristic of the zinc bromide electrolyte, the current versus potential curves are recorded in the cell kit with platinum wire electrode as the counter electrode, saturated calomel electrode (SCE) as reference electrode, and a carbon felt electrode as 3D working electrodes, respectively. The potential range of cyclic voltammograms is -1.5 V to 1.5 V and the scan rate is 20 mV $s^{-1}$ [9]. To confirm the durability and electrochemical property of electrolytes, the tests are progressed for 40 cycles.

## 3. Results and discussion

To investigate influence of additives on the electrochemical properties, anodic peak current ($I_{PA}$), cathodic peak current ($I_{PC}$) and peak current density ratio ($I_{PA}/I_{PC}$) are obtained from the CV experiments. Figure 1 shows the electrochemical property of these electrolytes, and measurement results to compare durability and stability of these electrolytes for 40 cycles. Also, Table 1 indicates the related $I_{PA}$ and $I_{PC}$ data where these values measured on $2^{nd}$, $10^{th}$ and $40^{th}$ cycle, respectively. It can be seen that the $I_{PA}$ of the electrolytes with each of $LiClO_4$, $NaClO_4$ and zeolite–Y has higher anodic peak current and the $I_{PC}$ of the aqueous solutions with $LiClO_4$ and zeolite-Y slightly decrease. And also the peak current density ratios of these solutions with additives show value close to 1.0, excepting the KCl.

Table 1 also demonstrates that the $I_{PA}$ of the electrolyte can be enhanced by additives as $LiClO_4$, $NaClO_4$ and zeolite–Y, respectively. The $I_{PC}$ of the solution with each of KCl, $LiClO_4$ and zeolite–Y slightly decrease. It is found from these results that $I_{PA}$ of all electrolytes (in comparison to $I_{PC}$) is continuously decreased in progress up to 40 cycles. In the case of ideal electrolyte can be seen that peak currents have to be undiversified during long time operation. But when additives are added into the electrolytes, anodic and cathodic peak current decrease. Thus, this result indicates that all kinds of additives can hinder durability of electrolyte for a long time. But anodic peak current decreasing rate of solution with additives as zeolite-Y or $LiClO_4$ slightly decline and the cathodic peak current decreasing rate can be improved by additives as KCl or zeolite-Y. The peak current density ratios of zinc bromide electrolyte with $LiClO_4$, $NaClO_4$ or zeolite-Y are closer to 1.0 than that of without additive, and also peak current density decreasing rates of electrolytes with $LiClO_4$ or zeolite-Y can be enhanced.

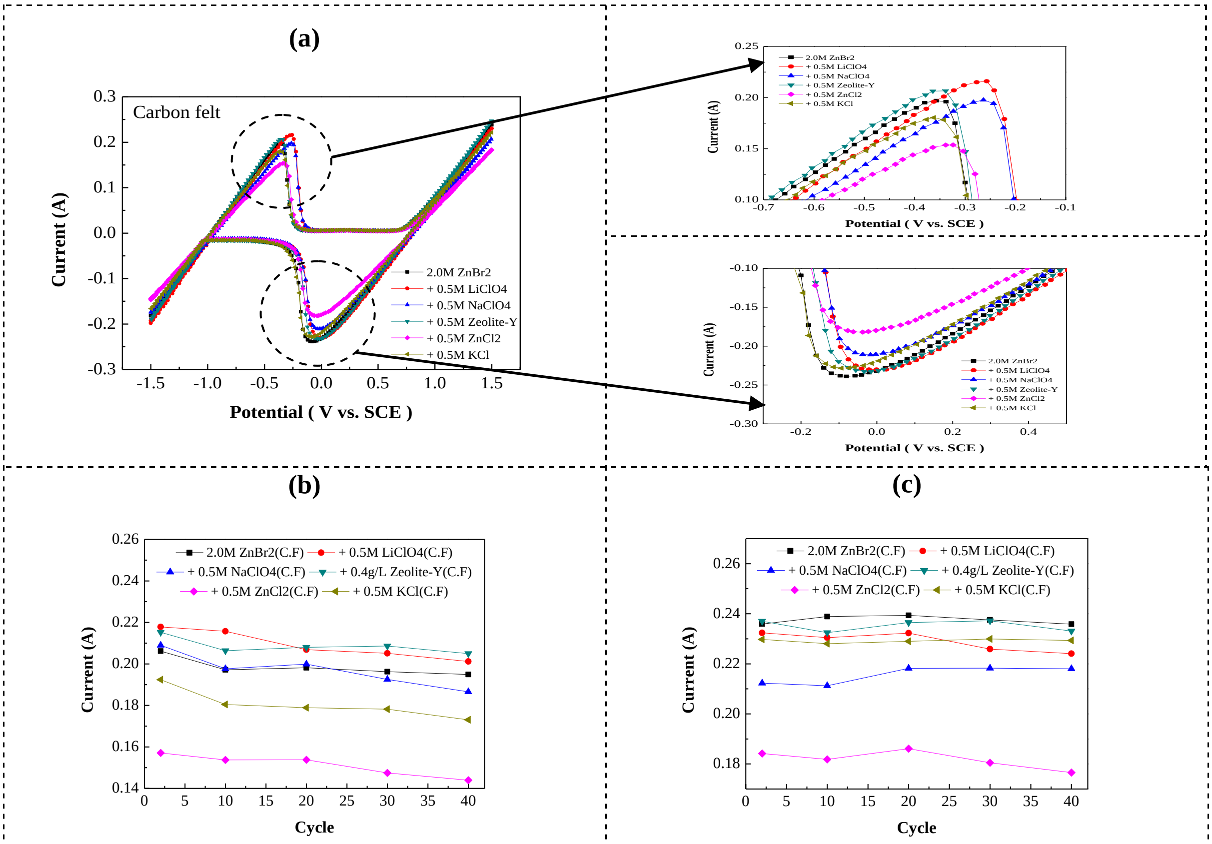


**Figure 1.** (a) Cyclic voltammograms at 10th cycle for the electrochemical property of electrolytes, (b) the anodic peak currents, and (c) the cathodic peak currents of the zinc bromide electrolyte with various additives such as $LiClO_4$, $NaClO_4$, zeolite-Y, $ZnCl_2$ and KCl.

**Table 1.** The related data of Figure 1

| Sample | 2nd cycle | | | 10th cycle | | | 40th cycle | | |
|---|---|---|---|---|---|---|---|---|---|
| | $I_{PA}$ (A) | $I_{PC}$ (A) | $I_{PA}$ / $I_{PC}$ | $I_{PA}$ (A) | $I_{PC}$ (A) | $I_{PA}$ / $I_{PC}$ | $I_{PA}$ (A) | $I_{PC}$ (A) | $I_{PA}$ / $I_{PC}$ |
| **2.0 M $ZnBr_2$** | 0.20613 | 0.23592 | 0.874 | 0.19713 | 0.23810 | 0.828 | 0.19492 | 0.23585 | 0.826 |
| **2.0 M $ZnBr_2$ + 0.5 M $ZnCl_2$** | 0.15705 | 0.18417 | 0.853 | 0.15371 | 0.18153 | 0.847 | 0.14391 | 0.17654 | 0.815 |
| **2.0 M $ZnBr_2$ + 0.5 M KCl** | 0.19239 | 0.22977 | 0.837 | 0.18041 | 0.22805 | 0.791 | 0.17307 | 0.22932 | 0.755 |
| **2.0 M $ZnBr_2$ + 0.5 M $LiClO_4$** | 0.21783 | 0.23237 | 0.937 | 0.21572 | 0.23044 | 0.936 | 0.20114 | 0.22408 | 0.898 |
| **2.0 M $ZnBr_2$ + 0.5 M $NaClO_4$** | 0.20897 | 0.21228 | 0.984 | 0.19766 | 0.21076 | 0.938 | 0.18656 | 0.21804 | 0.856 |
| **2.0 M $ZnBr_2$ + 0.4 g/L Zeolite-Y** | 0.21519 | 0.23701 | 0.908 | 0.20662 | 0.23244 | 0.889 | 0.20497 | 0.23307 | 0.879 |

## 4. Conclusions

To improve the stability and durability of zinc bromide electrolyte, the effects of the electrochemical behavior in these additives as $ZnCl_2$, KCl, $LiClO_4$, $NaClO_4$ and zeolite-Y are studied and in order to investigate the electrochemical characteristics of the electrolyte, the carbon felt electrode as 3D working electrode is used. As a result, the carbon felt electrode can be appropriate at the reduction oxidation reaction of bromine and zinc for ZBB. But the creation of zinc dendrite is accelerated by the carbon felt electrode, so the anodic peak current decreasing rate has a higher ratio than the cathodic peak current decreasing rate. The anodic current of electrolyte for ZBB can be improved by additives as $LiClO_4$ and zeolite-Y, and also the cathodic current is slightly diminished by KCl and zeolite-Y. Moreover, the decreasing rates of the electrolyte with experimented additives can show almost considerable changes in comparison with the electrolyte without additive. Also, the experiment results can show that $LiClO_4$ and zeolite-Y are proper additional materials at the anodic peak current decreasing rate, as well as KCl and zeolite-Y appertain to the cathodic peak current decreasing rate. Thus, the electrolyte with zeolite-you can indicate that the peak current decreasing rate of anodic and cathodic slightly decreased, and also anodic and cathodic currents enhanced in comparison with conventional electrolytes. It will be used as a promising additive for the electrolyte of ZBB.

## 5. Acknowledgments

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