High-performance zinc bromine flow battery via improved design of electrolyte and electrode

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HIGHLIGHTS

- Chloride based salts were investigated to reduce the internal resistance in ZBFB.
- NH₄Cl was found to be more effective in enhancing electrolyte conductivity.
- The battery exhibits an energy efficiency of 74.3% at 40 mA cm⁻².
- Thermal treatment on electrode further increases the energy efficiency to 81.8%.
- The battery can be operated at a high current density of up to 80 mA cm⁻².

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ABSTRACT

The zinc bromine flow battery (ZBFB) is regarded as one of the most promising candidates for large-scale energy storage attributed to its high energy density and low cost. However, it suffers from low power density, primarily due to large internal resistances caused by the low conductivity of electrolyte and high polarization in the positive electrode. In this work, chloride based salts including KCl and NH₄Cl are investigated as supporting electrolyte to enhance electrolyte conductivity, while graphite-felt electrodes are thermally treated to improve electrocatalytic activity. It is found that the use of 4 M NH₄Cl as a supporting electrolyte enables the battery to be operated at a current density of 40 mA cm⁻² with an energy efficiency of 74.3%, whereas without the addition of a supporting electrolyte the battery only outputs an energy efficiency of 60.4%. In combination with a thermally treated graphite-felt electrode, efficiency further reaches up to 81.8% at the same current density. More impressively, we demonstrate that even at a high current density of up to 80 mA cm⁻², the battery is capable of delivering an energy efficiency of 70%, representing one of the highest performances of ZFBs in the open literature.

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1. Introduction

The increasing utilization of the renewable but intermittent energy sources such as solar and wind has raised great concerns on the reliability and stability of electrical grid infrastructure [1]. Large-scale electrochemical energy storage technologies are therefore regarded as a crucial solution to improve the grid reliability and power quality [2–5]. Among all electrochemical energy storage systems, redox flow batteries (RFBs) are widely regarded as one of the most promising candidates because of their excellent scalability, high energy efficiency, long cycle life and easy design [5–7]. Various redox couples have been developed for RFBs, including all vanadium flow battery (VFB) [8–11], iron-chromium flow battery (ICFB) [12–14], bromine/polysulphide flow battery (PSB) [15] and zinc bromine flow battery (ZBFB) [16,17]. Among them, the ZBFB has become more appealing as one of the promising candidates due to its high energy density, high cell voltage and use of abundant and low-cost materials [18–21].

In a ZBFB, the basic electrochemical reaction can be depicted as:

at negative electrode:

Zn ↔ Zn²⁺ + 2e⁻ (E° = −0.76 V vs. SHE) (1a)

at positive electrode:

Br₂ + 2e⁻ ↔ 2Br⁻ (E° = 1.08 V vs. SHE) (1b)

and overall:

Zn + Br₂ ↔ 2Zn²⁺ + 2Br⁻ (E° = 0.32 V vs. SHE) (1c)
Zn + Br₂ ↔ Zn²⁺ + 2Br⁻ \quad (E = 1.84 \text{ V})  

(1c)

During charging process, the metallic zinc deposits onto the negative electrode while elemental bromine forms at the positive electrode, which will further complex with the bromide ion and the addition of quaternary ammonium salt [22–24]. During discharging process, zinc and bromide ions are generated at the respective electrodes. Although very promising, the wide deployment of ZBFB has been hindered by its low operating current density (20 mA cm⁻²) or low power density, which is mainly caused by the relatively large polarization of the positive electrode and large internal resistance [18,25]. Since the low power density will lead to a larger materials consumption, larger stack size and higher cost, much work has been conducted to enhance the performance of ZBFB, but mainly on improving the electrocatalytic activity of the positive electrode [19,21,25–27]. For example, Munaiah et al. developed a carbon nanotubes based electrode for high performance ZBFB and demonstrated that CNT exhibits excellent electrocatalytic activity toward Br₂/Br⁻ redox reaction. The ZBFB fabricated with CNT electrode offered superior rate capability and reversibility during charge/discharge cycling [19,26]. Zhang et al. reported an activated carbon coated membrane for ZFB, aiming to reduce the internal resistance and positive electrode polarization. Their results showed that both the positive electrode overpotential and cell internal resistance decreased and thus an energy density of 75% was achieved at a current density of 40 mA cm⁻², which is attributed to the high electrochemical activity layer close to the membrane [18]. Although some progress has been made, it is clear that more work should be done to further improve the ZFB performance.

Unlike VFB and ICBF employing strong acid (H₂SO₄ or HCl) as supporting electrolyte and therefore having a high electrolyte conductivity, ZnBr₂ solution is used as electrolyte for ZBFB and the electrolyte conductivity is low [18,19,28], which will undoubtedly lead to a high internal resistance. Thus, it is of great significance to enhance the electrolyte conductivity and reduce the cell internal resistance. Moreover, in conventional ZBFB, graphite felt (GF) or carbon felt (CF) are commonly used as electrodes. However, these carbon electrodes suffer from poor wettability and sluggish kinetics towards Br₂/Br⁻ redox reaction [29]. Though it is well accepted that surface modification of the carbon or graphite felt can enhance its wettability and electrochemical activities in VFBs [30–34], the effect of surface modification of graphite felt electrode in ZBFB has not been reported yet.

Herein, in this work, chloride based salts with a high ionic conductivity, i.e., potassium chloride (KCl) and ammonia chloride (NH₄Cl), are investigated as supporting electrolyte to enhance the electrolyte conductivity. Meanwhile, the graphite felts are subjected to thermal treatment to improve their electrochemical activities for Br₂/Br⁻ redox reaction. Results show that the cell resistance is greatly reduced by adding supporting electrolyte and the electrocatalytic activities of GF are significantly improved after thermal treatment. It is demonstrated that in a ZBFB with optimal electrolyte and electrode, high energy efficiencies of about 82% and 70% are achieved at current densities of 40 and 80 mA cm⁻² respectively, which is attributed to the reduced internal resistance and enhanced electrochemical activity of the thermally treated electrode.

2. Experimental

2.1. Electrolyte preparation

Zinc bromide (ZnBr₂, Aldrich, > 98%), potassium chloride (KCl, BDH Prolabo, > 99.95%) and ammonia chloride (NH₄Cl, Aldrich, >99.5%) were used commercially sourced and used without further purification. 2 M ZnBr₂ in DI water was used as electrolyte with and without supporting electrolyte. Certain amount of KCl or NH₄Cl was added into the solution to give a desired concentration.

2.2. Electrode preparation and ZFB setup

Graphite felts GFA5 (SG, SGL carbon group, Germany) were annealed at 500 °C for 2 and 4 h in air with a heating rate of 5 °C min⁻¹ in a muffle furnace to form thermally treated electrodes. The obtained electrodes are thereafter denoted as GF-2h and GF-4h. A lab-scale single flow battery is used to test the battery performance. For both sides, the flow cavities were machined on the graphite plates. At the negative side, one layer of GF with apparent areas of 2 cm × 2 cm was placed near the wall of the cavity, and served as the negative electrode. A 3.0-mm-thick non-conductive polyacrylonitrile porous felt contacted the GF, and served as the cavity filler. About 2 mm deep space between the anode surface and membrane was reserved for zinc deposition. The thickness was controlled by PTFE gaskets. At the positive side, a GF was placed into the cavity on the graphite plate. The compression ratio of the felts in this work was about 33%. 20 mL of the mixed solutions were used as both the negative and positive electrolytes. The electrolyte was circulated into the cell by a 2-channel peristaltic pump (Longer pump, WT600-2J) with a flow rate of 46 mL min⁻¹ (60 rpm).

2.3. Materials and electrochemical characterization

The morphologies of the electrodes were observed using a scanning electron microscope (SEM, JWOL-6700F) at accelerating voltage of 5.0 kV. X-ray photo electron spectroscopy (XPS) characterization was performed by using Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W.

Cyclic voltammetry tests were conducted using a typical three-electrode cell. Graphite felt with a geometric of 1 cm² was used as the working electrode and a saturated calomel electrode (SCE) and platinum mesh electrode served as the reference and counter electrodes, respectively. The EIS measurements were conducted by means of two-electrode connections controlled by PARSTAT 2273 impedance meter with sweeping frequencies over the range from 10 mHz to 10 kHz at the open circuit voltage when it was charged to 80 mA h at a current density of 20 mA cm⁻². The battery internal resistance was measured using AC impedance technique by a potentiostat (EG&G princeton, model M2273). The constant charge-discharge test of the ZBFB was measured busing a potentiostat/galvanostat (Arbin Instrument). The battery was charged for 30 min and then discharged to a cut-off voltage of 0.5 V at various current densities. The polarization curves were obtained by the following procedure. The battery was firstly charged 1 h at a current density of 20 mA cm⁻², and then was discharged for 30 s, rested for 20 s and charged for 30 s at the same current density ranging from 0 to 200 mA cm⁻². All the tests were conducted under ambient temperature (~23 °C), and repeated at least twice to guarantee reproducibility.

3. Results and discussion

3.1. Effect of supporting electrolyte

The internal resistances of the ZBFBs with and without supporting electrolyte were measured and compared in Fig. 1a. It is shown that adding supporting electrolyte can greatly reduce the cell resistance and NH₄Cl is more effective. Specifically, the internal resistance without supporting electrolyte is 5.5 Ω cm⁻², which is
Reduced to 4.7 and 3.0 $\Omega \ \text{cm}^{-2}$ by adding 2 M KCl and NH$_4$Cl, respectively. This is due to the fact that the hydrated ion of NH$_4^+$ is smaller than K$^+$, thus leading to a higher mobility [35]. Since experimental conditions are kept the same except electrolyte composition, the reduction in internal resistance can be associated with conductivity change due to electrolyte addition. In order to confirm that the reduction of the cell resistance can lead to improvement in the battery performance, the charge-discharge performances of the flow batteries using these electrolytes were conducted at a current density of 40 mA cm$^{-2}$. It is found that the charge voltage plateau decreases and the discharge voltage plateau increases after adding supporting electrolyte (See Fig. S1a, supporting information). The reduction and enhancement of the charge voltage and discharge voltage are mainly due to the increase of electrolyte conductivity, as the reduced voltage value is almost the production of current density and reduced resistance. Fig. 1b summarizes the energy efficiency of these three flow batteries. An energy efficiency of 68.3% and 71.2% is achieved by adding 2 M KCl and 2 M NH$_4$Cl, respectively, compared to 60.4% if no supporting electrolyte is used, implying the effectiveness of improving ZBFB performance by adding supporting electrolyte. Consistently with the results in Fig. 1a, the highest energy efficiency is obtained by adding NH$_4$Cl as it exhibits the lowest internal resistance.

In order to investigate the effect of NH$_4$Cl concentration, the cell resistances with 2, 4 and 6 M of NH$_4$Cl were measured. From the results shown in Fig. 2a, it is shown that the cell resistance is firstly reduced from 3.0 to 2.0 $\Omega \ \text{cm}^{-2}$ as the concentration of NH$_4$Cl increases from 2 to 4 M, and then slightly increases to 2.1 $\Omega \ \text{cm}^{-2}$ when the NH$_4$Cl concentration is further increased to 6 M, indicating that the lowest resistance is obtained at a concentration of 4 M. This is because when the concentration is increased from 2 M to 4 M, more free ions are present which will contribute to the increase in the electrolyte conductivity with minor effect on the electrolyte viscosity. However, when the concentration of NH$_4$Cl is further increased to 6 M, the viscosity of the electrolyte will increase and therefore, lead to an increase of the resistance. The influence of the NH$_4$Cl concentration on the battery performance was evaluated by charge-discharge profiles. As shown in Fig. S2a, the charge voltage plateau firstly decreases from 2.02 V to 1.98 V and then rises to 2.00 V when the NH$_4$Cl concentration is 2, 4 and 6 M, respectively. While for the discharge process, the discharge voltage plateau increases from 1.46 to 1.53 V when the NH$_4$Cl concentration increases from 2 M to 4 M and then keep almost the same when the concentration of NH$_4$Cl is further increased to 6 M. The energy efficiency thus increases from 71.2% to 74.3% and then decreases to 74% as an increase of NH$_4$Cl concentration from 2 to 6 M, as depicted in Fig. 2b. These results suggest that an optimal concentration of 4 M NH$_4$Cl can significantly reduce the battery internal

![Figure 1](image1.png)  
Fig. 1. (a) Battery internal resistance and (b) energy efficiencies of the ZBFBs with 2 M ZnBr$_2$, 2 M ZnBr$_2$ + 2 M KCl, 2 M ZnBr$_2$ + 2 M NH$_4$Cl as electrolyte.

![Figure 2](image2.png)  
Fig. 2. (a) Battery internal resistance and (b) energy efficiencies of the ZBFBs with 2 M ZnBr$_2$ and various concentration of NH$_4$Cl.
resistance and lead to an improvement in electrochemical performance. This high energy efficiency achieved in this work is even comparable to that employing an active carbon coated membrane electrode [18], implying the critical significance of the use of supporting electrolyte to reduce the cell internal resistance.

The performance of ZBFB with 4 M NH4Cl supporting electrolyte was further evaluated by polarization curve. As depicted in Fig. 3, all the I-V curves consist of a non-linear part (activation loss) at low current densities and a linear part (ohmic loss) at high current densities. When the ZBFB is operated at low current density, the I-V curves coincide for battery with and without supporting electrolyte, indicating that the addition of NH4Cl is of minor effect on reducing the activation loss, which may be caused by the high polarization of the positive electrode [19,21,25], and will be addressed in next section. When the operating current density is raised to a higher level, the potential drop of the ZBFB with NH4Cl supporting electrolyte is greatly reduced corresponding to the reduced internal resistance. For example, the discharge/charge voltage of the battery with 4 M NH4Cl is 1.07/2.39 V, which is much higher/lower than that with no supporting electrolyte (i.e., 0.70/2.72 V). These results, again, confirm the effectiveness of supporting electrolyte in reducing battery resistance and therefore, improving the battery performance.

3.2. Effect of electrode modification

As mentioned before, the electrochemical kinetics on the pristine GF electrode are quite sluggish, which may be caused by its poor wettability and electrochemical activity. In this regard, the GF electrodes are thermally treated at 500 °C for different duration to enhance its electrochemical performance. The morphological change of the carbon fiber surface introduced by thermal treatment were examined by SEM. It can be seen from Fig. 4 that the thermal oxidation can change the morphology of fiber surface by generating some cavities and the surface roughness is increased as the oxidation time increases. According to Fig. 4a, the fiber surface of pristine GF is smooth with some ravines on it. After thermally treated at 500 °C for 2 h, some pores are generated on the fiber surface, as shown in Fig. 4b. When the treatment duration increases to 4 h, much more pores are formed and some are clasped together to form larger pores (Fig. 4c). These generated pores will enhance the surface area of GF [29,30] and therefore, provide more reaction sites for the Br2/Br− redox reaction. The surface properties of the electrodes were analyzed by XPS, as shown in Fig. S3. It was found that with the increase of thermal treatment duration, the carbon to oxygen ratio decreases, implying that oxygen containing functional groups were generated on the carbon surface [32,33,36]. To analyze the formation of C-O groups, the O1s XPS spectra were fitted by three peaks, which is consistent with the results in literature [6,33]. It shows that thermal treatment benefits the formation of C-O groups, which can enhance the electrocatalytic activities towards Br2/Br− redox reaction [29].

In order to understand the electrocatalytic effect of the treated electrode on the Br2/Br− reaction, CV investigations were performed. Fig. 5a shows the comparison of the cyclic voltammograms of the different GF electrodes at a scan rate of 10 mV s−1. The oxidation and reduction current densities of the treated GFs are much larger than that of the pristine GF, implying that the kinetics of the Br2/Br− on the treated GF surface as well as the wettability are greatly improved. However, it is noted that the reduction peak of bromine on GF-4h is negatively shifted compared with GF-2h, which suggests that the excess oxidation of the GF surface may deteriorate the kinetic of the bromine reduction. Thus, mild oxidation of the GF at 500 °C for 2 h is enough to boost the electrocatalytic activity for Br2/Br− reaction. The stability of GF-2h in the electrolyte solution was further examined by cycling the CV at a scan rate of 50 mV s−1. As shown in Fig. 5b, negligible distinction can be observed after 50 cycles from the first cycle, indicating the good stability and high durability of GF-2h in the ZnBr2/NH4Cl electrolyte. The electrochemical performance was further studied by EIS. Fig. 6 depicts the Nyquist plots of the three different electrodes, all of which consist of a semicircle at high frequencies and a linear part at low frequencies. The diameter of the semicircle represents charge transfer resistance (Rct) while the linear part attributes to the mass diffusion process [21,37,38]. It is shown that the diameters of treated GFs are much smaller than that of the pristine one, confirming that the charge transfer resistance of Br2+/Br− on GF surface is dramatically reduced after thermal treatment. This may be attributed to the increase in oxygen containing functional groups and surface area which can enhance the electrochemical catalytic activity to the Br2/Br− redox reaction [29]. Consistently with the CV results, the charge transfer resistance is slightly increased when the thermal oxidation duration is extended to 4 h, which, again, confirms that thermal oxidation duration is a very important factor that influences the battery performance.

The performance of the ZBFB with the GF electrodes was further evaluated in a flow battery using the optimized electrolyte. Charge-discharge profiles recorded at a current density of 40 mA cm−2 are compared and shown in Fig. 7a. All the batteries are charged for 30 min and the average charge voltage plateau is 1.98, 1.92 and 1.94 V for pristine GF, GF-2h and GF-4h, respectively; while the average discharge voltage plateau is about 1.52, 1.62 and 1.60 V. The decrease of the charging voltage and the increase of the discharging voltage is mainly attributed to the reduced positive electrode overpotential as all other components are the same. Thus the voltage efficiency of the battery can be enhanced to about 83% when using GF-2h as a positive electrode. Fig. 7b compares the energy efficiencies of the battery employing these three electrodes. It can be observed that the battery with a GF-2h electrode exhibits a highest energy efficiency up to 81.8%, which is much higher than those reported values [18,19,21,26,27,39]. This good performance may be attributed to the enhanced electrocatalytic activities of thermally treated GF as well as the increased electrolyte conductivity. In addition, the absence of the bromine sequestration agent (BSA) and the use of the Naion membrane may also have some contribution to this improved performance. To further reveal the variation of the performance with rate, the flows battery with GF-

![Fig. 3. Polarization curves of the ZBFB with 4 M NH4Cl and without supporting electrolyte.](image-url)
2h electrode was subjected to charge-discharge with different current densities. As shown in Fig. 7c, the average charge voltage plateau increases as the current density increases, while the discharge voltage plateau decreases, which is ascribed to the increase in polarization induced by the increased current density [17]. Fig. 7d summarizes the energy efficiencies of the battery operated under various current densities. It can be seen that the battery with GF-2h electrode presents higher energy efficiencies than those with pristine and GF-4h electrodes. In particular, the battery with the GF-2h electrode can be operated at a high current density of 80 mA cm$^{-2}$ with an energy efficiency of around 70%. This achieved efficiency is among the highest performances, suggesting the excellent electrocatalytic activity of the thermally treated graphite fiber. In addition, the polarization curves further reveal that the activation loss is eliminated (See Fig. S4).

The cycling performance was also conducted to test the stability of the treated GF electrode and the electrolyte. From the voltage versus time plot in Fig. 8a, we can see that the charge voltage remains quite stable while the discharge voltage increases slightly over cycling, resulting in an overall improvement in VE (See Fig. 8b). Meanwhile, relatively stable CE and EE were achieved though there is some fluctuation, which may be attributed to the zinc dendrite formation or hydrogen evolution. These results successfully demonstrate its descent stability and durability in zinc bromine flow battery systems.

4. Conclusion

In summary, highly ionic conductive supporting electrolytes (i.e., KCl and NH$_4$Cl) were investigated to reduce the electrolyte resistance and graphite-felt electrodes were thermally treated to enhance the electrochemical activity in ZBFB. It is found that with 4 M NH$_4$Cl as supporting electrolyte, the ZBFB exhibits an energy efficiency of 74.3% at a current density of 40 mA cm$^{-2}$, compared with an energy efficiency of 60.4% without supporting electrolyte. Meanwhile, substituting the pristine graphite-felt electrode into a thermally treated one further increases the energy efficiency to
81.8% at the same current density. Furthermore, it is demonstrated that the ZBFB can be operated at a high current density up to 80 mA cm\(^{-2}\), with an energy efficiency of about 70%. In addition to the excellent rate capability, the presented ZBFB also exhibits a good stability during cycling test, suggesting that adding supporting electrolyte and thermal treatment on positive electrode is a facile yet effective approach to enhance the performance of ZBFB.

Fig. 7. (a) Charge–discharge curves and (b) energy efficiency at a current density of 40 mA cm\(^{-2}\); (c) Charge–discharge curves and (d) energy efficiency at various current densities.

Fig. 8. Cycling performance of a ZBFB with GF-2h electrode. (a) voltage versus time plot; (b) columbic, voltage and energy efficiencies during the 50 charge–discharge cycles.
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.04.058.

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