A novel high-energy-density positive electrolyte with multiple redox couples for redox flow batteries

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A high-energy-density positive electrolyte with multiple redox couples is proposed. The presence of Br− improves the reversibility of the Fe3+/Fe2+ couple. The anodic oxidation of Br− and Fe2+ follows first-order reaction on graphite. The electrode kinetics and mass transfer improve with temperature.

Low energy density resulting from the limited solubility of conventional electroactive species in electrolyte solutions has been one of the most critical barriers in the viability of redox flow batteries. Here we report a novel positive electrolyte that consists of two redox couples, viz. Fe3+/Fe2+ and Br2/Br−. It is shown that both the capacity and energy density of this positive electrolyte are, respectively, as high as 804 Ah L−1 and 827 Wh L−1. Salient findings from the electrochemical characterizations of the electrolyte are as follows: (i) the two redox couples are reversible on the graphite electrode, in particular the presence of Br− further improves the reversibility of Fe3+/Fe2+; (ii) the anodic peak current in the cyclic voltammetry increases linearly with the concentration of Fe2+ and Br−, indicating that the oxidation of these ions follows a first-order reaction; (iii) the diffusion coefficients of Br− and Fe2+ are 14.16 × 10−6 and 3.11 × 10−6 cm2 s−1, respectively; and (iv) the reversibility and mass transfer of the reactive species improves with an increase in temperature.

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1. Introduction

The fast development of wind and solar energy increases demands for new and large-scale energy storage systems to dispatch and integrate renewable power. Storage technologies have been rapidly developed to address these growing demands and among these, redox flow batteries (RFB), such as iron/chromium [1], polysulfide/bromide [2], zinc/cerium [3] and all-vanadium [4,5], are considered to be a promising technology.

In the past decades, the all-vanadium redox flow battery (VRB) has perhaps received the most attention, and extensive studies have been carried out to optimize the electrolyte and cell configuration [6–9]. Steps toward commercialization have been taken, but certain issues still need to be addressed before VRB can be used for broader applications. For example, VRB suffers from low charge and energy density, which is due to poor solubility and stability of the electrolyte, especially at the anode [10]. It is reported that V5+ ions suffer from thermal precipitation at elevated temperatures, whereas V2+, V3+ and V4+ ions precipitate at a temperature below 10 °C, restricting the applicable temperature range from 10 to 40 °C and an energy density of 25–30 Wh L−1 [11–13].

Recently, enormous work has been done to increase the solubility and stability of the electrolyte. One method is to increase the concentration of sulfuric acid, which is understandable by considering the V5+ thermal precipitation reaction [13]:

\[ \text{VO}_{2}^{+}(\text{H}_{2}\text{O})_{3}^{+} \rightleftharpoons \text{H}_{3}\text{VO}_{4}^{+} + \text{H}^{+} \] (1)

An increase in the concentration of H+ facilitates the reverse reaction and thus stabilizes the positive electrolyte. However, the case cannot be applied to other vanadium species; that is to say, more concentrated sulfuric acid deteriorates the stability of V2+.
V$^{3+}$ and V$^{4+}$ ions. Hence, a compromise must be made to optimize the vanadium concentration when sulfuric acid is used as the supporting electrolyte.

Alternatively, additives are employed to improve the stability of the electrolyte, which is based on their complexation effect with the V ions. Organic additives such as l-glutamic acid [14], trihydroxyethyl aminomethane [15], coulter dispersant [16] and inorganic stabilizers such as K$_2$SO$_4$ [17] have been extensively investigated. Notably, chloride ion has been identified as an effective additive which prevents the precipitation of the V ions [18]. Kim et al. [19] used chloride acid as supporting electrolyte, and the concentration of vanadium ions was able to be increased up to 3.0 M. Similar supporting electrolytes can also be applicable to the Fe-based positive electrolyte [20–23]. They further employed mixed redox couples, viz. Fe$^{3+}$/Fe$^{2+}$ and V$^{5+}$/V$^{4+}$, as the catholyte to increase the energy density [24]. In 2002, Skyllas-Kazacos et al. [25] proposed a new type of flow battery called G2 VRB, which employs Br$_2$/Br$^-$ or Br$_2$Cl$^-$/Br$^-$ couples as the catholyte and V$^{5+}$/V$^{4+}$ as the anolyte. The energy density of the flow battery was reported to be 30–50 Wh L$^{-1}$.

In this work, we report a novel high-energy-density positive electrolyte consisting of two redox couples, viz. Fe$^{3+}$/Fe$^{2+}$ and Br$_2$/Br$^-$. Both ferrous halide and hydrogen bromide are highly soluble and possess favorable electrochemical performance in aqueous solutions. Thus, the capacity and energy density can be dramatically increased by mixing the two redox couples. The effect of the ion concentration and temperature is on the electrochemical behavior is investigated.

2. Capacity and energy density analysis

Eqs. (2) [24,26] and (3) [27] could be employed to respectively calculate the energy and capacity density:

\[ E_d = \frac{\sum C_i n F_i \Delta E_i}{3600} \]  
\[ C_d = \frac{\sum C_i n F_i}{3600} \]

where $E_d$ is the energy density (Wh L$^{-1}$), $C_i$ is the concentration of electroactive species (mol L$^{-1}$), $C_d$ is the capacity density expressed in unit volume (Ah L$^{-1}$), $n$ is the mole of electron transfer per mole of species, $F$ is the Faraday constant (C mol$^{-1}$) and $\Delta E_i$ is the standard potential of each redox reaction (V).

The capacity and energy density of several typical redox couples are calculated and listed in Table 1. It is seen that the saturated concentration of Fe$^{3+}$/Fe$^{2+}$ and Br$_2$/Br$^-$ is much higher than that of VO$^{2+}$/VO$^{2+}$, which yields a higher volumetric capacity and energy density. By mixing the Fe$^{3+}$/Fe$^{2+}$ and Br$_2$/Br$^-$ couples, the capacity and energy density of this positive electrolyte are, respectively, as high as 804 Ah L$^{-1}$ and 827 Wh L$^{-1}$. The performance of this mixed electrolyte is promising for the application in redox flow batteries.

3. Experimental procedure

The positive electrolyte was prepared by dissolving FeCl$_2$ (A.R., Guangzhou Chemical Reagent Factory) in HBr aqueous solution.

The electrochemical test was carried out by the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in a three-electrode system (the graphite a radius of 3.0 mm as the working electrode, saturated calomel electrode (SCE) with a salt bridge as reference electrode and platinum wire as counter electrode). For EIS, the electrode potential was set to be 0.40 V for Fe$^{3+}$/Fe$^{2+}$ and 0.85 V for Br$_2$/Br$^-$, respectively, with applying a magnitude of 10 mV and varying the frequency of the alternating voltage from $1 \times 10^2$ to $1 \times 10^2$ Hz.

A lab-made cell was assembled with the Toray carbon paper (coated with 5.0 mg cm$^{-2}$ Vulcan XC-72) as the positive electrode, the commercial ETEK anode (with Pt loading of 0.20 mg cm$^{-2}$) as the negative electrode, and Nafion 115 membrane as the separator. The positive chamber was pumped with the mixed electrolyte (containing 1.0 M FeCl$_2$, 1.0 M HBr and 2.0 M HCl) and the negative side pumped hydrogen. The battery was then cycled between 0.2 and 1.4 V at a constant current density of 20 mA cm$^{-2}$ to collect the charge/discharge performance at room temperature.

4. Results and discussion

4.1. Effect of FeCl$_2$ concentration

Fig. 1 shows the color of the FeCl$_2$ solution in two supporting electrolytes, viz. HCl and HBr. It can be seen that the color of the solution becomes darker as the FeCl$_2$ concentration increases in the two supporting electrolytes. The solution appears to be more yellow in HBr than in HCl at the same FeCl$_2$ concentration, indicating a stronger complexation between Fe$^{3+}$ and Br$^-$. Fig. 2a presents the CV result of the FeCl$_2$ solution in 1.0 M HBr. Two anodic peaks at 0.5 and 1.0 V and two cathodic peaks at 0.4 and 0.65 V are present in the curves. The anodic and cathodic peaks at 0.5 and 0.4 V correspond to the Fe$^{3+}$/Fe$^{2+}$ couple, and those at

![Fig. 1. Color of the solution containing FeCl$_2$ with various concentrations (from left to right 1.0, 1.5, 2.0, 2.5 M) in (a) 1.0 M HCl, and (b) 1.0 M HBr. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](Image 338x81 to 536x359)
First, it can be seen that the diffusion coefficient of both Br\(^-\) and Fe\(^{2+}\) decreases when the FeCl\(_2\) concentration is increased, which results from the enhanced interaction among the ions and the increased viscosity of the solution. The significant drop in the Br\(^-\) diffusion coefficient explains the noticeable decrease in the anodic peak current of Br\(^-\), as shown in Fig. 2a. Furthermore, Eq. (4) indicates that the increase in the FeCl\(_2\) concentration causes an increase in the anodic peak current of Fe\(^{2+}\).

To gain a better understanding of the Fe\(^{2+}\) oxidation reaction, the anodic current at 0.45 V is plotted against the FeCl\(_2\) concentration, as shown in Fig. 3. The figure shows that the oxidation current (i.e., reaction rate) plots a straight line against the concentration, indicating that the oxidation of Fe\(^{2+}\) on the graphite electrode is a first-order reaction.

Fig. 4 shows the EIS results conducted at two electrode potentials, viz. 0.40 and 0.85 V. Fig. 4a shows that the increasing FeCl\(_2\) concentration may reduce the charge transfer resistance of Fe\(^{2+}\) oxidation. In comparison, Fig. 4b demonstrates that the effect on the electrochemical performance of the Br\(_2\)/Br\(^-\) couple is negligible with a more concentrated solution. Additionally, the charge transfer resistance of Br\(_2\)/Br\(^-\) couple is generally found to be larger than that of the Fe\(^{3+}\)/Fe\(^{2+}\) couple. A likely explanation for this may be due to the fact the Fe\(^{3+}\)/Fe\(^{2+}\) reaction is a single-electron-transfer outer-sphere reaction, whereas the Br\(_2\)/Br\(^-\) is a multi-step reaction with at least one chemical step, viz. breaking/making the Br–Br bond [28].

### 4.2 Effect of the HBr concentration

Fig. 5 illustrates the CV results of the electrolytes containing 2.0 M FeCl\(_2\) and HBr of various concentrations. First, it can be seen that the peak potential separation of Fe\(^{3+}\)/Fe\(^{2+}\) shows a slight...
decrease by increasing the HBr concentration. This decrease signifies an enhanced reversibility of the Fe$^{3+}$/Fe$^{2+}$ couple, which confirms the aforementioned strong complexation between Fe$^{2+}$ and Br$^-$.

Second, the Br$^-$ oxidation current increases with the HBr concentration. As previously mentioned, the peak is controlled by the mass transfer of Br$^-$, which is why it is understandable that the peak current increases in response to an increase of the concentration of HBr. Furthermore, another redox couple appears at higher potentials when the HBr concentration is raised to 2.0 M, which becomes more pronounced at 2.5 M. This can be attributed to the presence of polyhalide ions at high Br$^-$ concentration, which experience the following redox reactions in the electrolyte [29]:

\[
\text{BrCl}_2 + 2e^- \rightleftharpoons \text{Br}^- + 2\text{Cl}^- \tag{5}
\]

or

\[
\text{ClBr}_2 + 2e^- \rightleftharpoons 2\text{Br}^- + \text{Cl}^- \tag{6}
\]

The standard potential is around 0.80 V vs. SHE [30] for Reaction (5) and 1.09 V vs. SHE [31] for Reaction (6). Reaction (5) may dominate at lower HBr concentrations, which shows a single redox couple in CV curves. Increasing the concentration favors Reaction (6) and another redox is found to be present.

To obtain the reaction order, the current density at 0.85 V is plotted against the HBr concentration, as shown in Fig. 6. A linear relationship can be observed between the Br$^-$ reaction rate and the concentration, which indicates that the oxidation of Br$^-$ on the graphite electrode also follows a first-order reaction.

Fig. 7 depicts the EIS results of the above-mentioned solutions. Fig. 7a–b explicitly shows that the charge transfer of both the Fe$^{2+}$...
and Br\textsuperscript{-} oxidation decreases as the HBr concentration increases. This confirms that the presence of HBr can improve the reversibility of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} couple.

4.3. Effect of temperature

Fig. 8 illustrates the effect of temperature on the electrochemical performance of the mixture electrolyte. It is seen that as the temperature rises, the peak current density of both Fe\textsuperscript{2+} and Br\textsuperscript{2}/Br\textsuperscript{0} oxidation increase and the onset potential shows a negative shift. Such an improvement in performance can be primarily attributed to the favorable electrochemical kinetics of the redox couples at elevated temperatures. The temperature raise also yields a favorable effect on the mass transfer of the reactive species in the electrolyte, which additionally contributes to the increase in the anodic current.

4.4. Flow cell test

A lab-made cell was assembled and tested with a positive electrolyte made of 1.0 M FeCl\textsubscript{2}, 1.0 M HBr and 2.0 M HCl. The charge/discharge curves are shown in Fig. 9. Two plateaus in the voltage are observed in both the charge and discharge curves. The charge voltage plateau at ~0.75 V and discharge plateau at ~0.40 V correspond to the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} couple, and the charge plateau at ~1.20 V and discharge plateau at ~0.55 V to the Br\textsuperscript{2}/Br\textsuperscript{0} couple. It is noted that this result is still preliminary, and future work is needed to optimize the electrode material and operating conditions of the flow battery.

5. Conclusions

A novel multi-redox-couple positive electrolyte containing Fe\textsuperscript{3+}/Fe\textsuperscript{2+} and Br\textsuperscript{2}/Br\textsuperscript{0} couples is developed to increase the capacity and energy density of redox flow batteries. The capacity and energy density of this positive electrolyte are as high as 804 Ah L\textsuperscript{-1} and 827 Wh L\textsuperscript{-1}, respectively. The electrochemical test reveals that the anodic oxidation of Fe\textsuperscript{2+} and Br\textsuperscript{-} follows a first-order reaction, and the two redox couples are reversible on the graphite electrode. Furthermore, an increase in temperature improves the reversibility and mass transfer of the reactive species. The battery test shows a decent charge/discharge performance with this positive electrolyte, indicating its applicability in redox flow batteries.

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