A hydrogen-ferric ion rebalance cell operating at low hydrogen concentrations for capacity restoration of iron-chromium redox flow batteries

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HIGHLIGHTS

- The performance of the hydrogen-ferric ion rebalance cell is investigated.
- Hydrogen utilization approaches 100% at low hydrogen percentages (<5%).
- A continuous rebalance is achieved at 60 mA cm\(^{-2}\) and 2.5% hydrogen percentage.
- The rebalance cell is estimated to be approximately 1% of system cost.

ABSTRACT

To eliminate the adverse impacts of hydrogen evolution on the capacity of iron-chromium redox flow batteries (ICRFBs) during the long-term operation and ensure the safe operation of the battery, a rebalance cell that reduces the excessive Fe(III) ions at the positive electrolyte by using the hydrogen evolved from the negative electrolyte is designed, fabricated and tested. The effects of the flow field, hydrogen concentration and H\(_2\)/N\(_2\) mixture gas flow rate on the performance of the hydrogen-ferric ion rebalance cell have been investigated. Results show that: i) an interdigitated flow field based rebalance cell delivers higher limiting current densities than serpentine flow field based one does; ii) the hydrogen utilization can approach 100% at low hydrogen concentrations (<5%); iii) the apparent exchange current density of hydrogen oxidation reaction in the rebalance cell is proportional to the square root of the hydrogen concentration at the hydrogen concentration from 1.3% to 50%; iv) a continuous rebalance process is demonstrated at the current density of 60 mA cm\(^{-2}\) and hydrogen concentration of 2.5%. Moreover, the cost analysis shows that the rebalance cell is just approximately 1% of an ICRFB system cost.

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1. Introduction

The massive utilization of intermittent renewables especially wind and solar energy urgently needs large-scale energy storage devices for grid stabilization [1–4]. The redox flow battery (RFB) offers great promise for grid-scale electricity storage because of the striking merits including easy scalability, intrinsic safety, fast response, high efficiency and long lifetime [5]. During the past decades, extensive efforts have been made to develop various RFB systems such as all-vanadium, all-copper, iron-cadmium, iron-chromium and quinone-based RFBs [6–19].

As shown in Fig. 1a, the iron-chromium redox flow battery (ICRFB) utilizes the affordable and benign Fe(II)/Fe(III) and Cr(II)/Cr(III) redox couples as the positive and negative active materials, respectively [20]. Since the ICRFB was invented by NASA in 1974, tremendous efforts have been made on the development and scale-up of ICRFBs [21–26]. The conventional flow-through structured ICRFB that uses thick electrodes (typically 3.0–6.0 mm) has high ohmic resistance, resulting in low operating current densities and costly cell stacks [5]. In the previous work, an interdigitated-flow-field structured ICRFB with carbon cloth electrodes demonstrates a dramatically increased operating current density of 480 mA cm\(^{-2}\) at the energy efficiency of 80.5% [27–29]. The peak power density of the ICRFB at 50% state-of-charge (SOC) was demonstrated to be...
The redox couple (the charge process due to the low redox potential of Cr(II)/Cr(III)) hydrogen evolution [24]. It occurs at the negative electrode during critical issue limiting the cycle performance of ICRFBs is the of ICRFBs is also important for practical applications. However, a [28].

Hydrogen evolution inhibitors such as Bi are typically deposited on electrolyte to be imbalanced, thus losing the battery capacity. The negative side, which causes the SOCs of positive and negative oxidized to Fe(III) ions compared to the reduced Cr(III) ions at the negative side, thus decreasing the triple phase boundary and deteriorating the performance of the rebalance cell. It is hard to achieve a stabilized triple phase boundary (hydrogen gas, ferric solution and solid catalyst) in chemical rebalance devices. The electrochemical rebalance device is advantageous due to the use of the membrane to separate the Fe(III) reduction (cathode, solution state) and hydrogen oxidation (anode, gas state) reactions. Thus, with the use of solid electrolyte such as perfluorosulfonic ionomer, it is easy to form the stabilized triple phase boundary (hydrogen gas, ionomer and solid catalyst) for hydrogen oxidation at the anode, and achieve a higher utilization of the catalyst compared to the chemical rebalance device.

Higher rebalance current densities indicate higher rebalance capacity of the devices and lower device cost. Another critical parameter is the operating hydrogen concentration. For the large-scale energy storage devices, the lower hydrogen concentrations in the headspace of the electrolyte tank signify lower explosion risk and higher safety of the system. It is highly desirable that the hydrogen concentration in the tank headspace is below the explosion limit of hydrogen in the air (4%) to avoid potential explosion risk. It is noted that the hydrogen concentration in the commercial all-V RFB systems may be higher than 8% after several months of operation due to the hydrogen evolution at the negative electrode [32]. The rebalance devices can be used to consume the evolved hydrogen and reduce the hydrogen concentration in the tank, thus ensuring system safety. However, operating the rebalance cell at low hydrogen concentrations significantly deteriorates the electrochemical kinetics and species transport, where the situation may be significantly different from the conventional hydrogen-iron fuel cells [34]. In addition, the flow rate of hydrogen is also an important factor influencing species transport and pump loss, which needs to be carefully designed.

In this work, the performance of the hydrogen/ferric ion rebalance cell and its dependence on the flow field, hydrogen concentration and gas flow rate have been investigated. The capital cost of the rebalance cell has been analyzed based on the experimental data.

Fig. 1. (a) Schematic of an iron-chromium redox flow battery; and (b) schematic of a complete iron-chromium redox flow battery stack incorporating a hydrogen-ferric ion rebalance cell.

As high as 1077 and 694 mW cm$^{-2}$ at 65 and 25 °C, respectively [28].

In addition to the output power density, the cycle performance of ICRFBs is also important for practical applications. However, a critical issue limiting the cycle performance of ICRFBs is the hydrogen evolution [24]. It occurs at the negative electrode during the charge process due to the low redox potential of Cr(II)/Cr(III) redox couple (−0.41 V vs. SHE) as follows:

At the negative electrode:

$$2H^+ + 2e^{charge} \rightarrow H_2 \quad E^0 = 0 \text{ V vs. SHE} \quad (1a)$$

At the positive electrode:

$$Fe^{3+} + e^{charge} \rightarrow Fe^{2+} \quad E^0 = 0.77 \text{ V vs. SHE} \quad (1b)$$

When the hydrogen evolution occurs, the extra Fe(II) ions are oxidized to Fe(III) ions compared to the reduced Cr(III) ions at the negative side, which causes the SOCs of positive and negative electrolyte to be imbalanced, thus losing the battery capacity. The hydrogen evolution inhibitors such as Bi are typically deposited on the electrode surface to alleviate hydrogen evolution [30], but it is hard to completely eliminate hydrogen evolution. To eliminate the adverse impacts of hydrogen evolution on the battery capacity and achieve stable long-term operation, a rebalance device that reduces the accumulated Fe(III) ions in the positive electrolyte using the evolved hydrogen is required to restore the battery capacity as shown in Fig. 1b [24]. In fact, all the RFBs in which the negative redox couple has a lower redox potential than hydrogen electrode, including Zn-Br, all-V, Fe-Cr and all-Fe redox systems, will also encounter hydrogen evolution issue and need the rebalance devices to manage the evolved gas. The NASA group developed an electrochemical rebalance device named as hydrogen-ferric ion rebalance cell, which intrinsically was a fuel cell using hydrogen as the fuel (anode) and ferric chloride solution as the oxidant (cathode) [31]. Recently, A.H. Whitehead et al. have developed an in-tank chemical rebalance device, and achieved a rebalance current density of 19.1 mA cm$^{-2}$ at hydrogen concentration of 90% [32]. S. Selverston et al. modified the chemical rebalance method and demonstrated a rebalance current density of 60 mA cm$^{-2}$ at hydrogen pressure of 4.5 psig (hydrogen concentration of 27.6%) [33]. For the chemical rebalance devices, the ferric solution directly contacts the reactor. The liquid solution may cover the surface of the catalyst during the rebalance operation, and block hydrogen gas from the catalyst, thus decreasing the triple phase boundary and deteriorating the performance of the rebalance device.
2. Methodologies

2.1. Rebalance cell setup and test

Two layers of carbon cloth (ELAT-H, 2.0 × 2.0 cm²) were thermally pretreated in ambient air at 500 °C for 5 h, and served as the cathode for Fe(III) reduction. Nafion 117 was used as the membrane. A commercial electrode with Pt/C catalyst layer (Johnson Matthey, Pt loading of 2 mg cm⁻²) was used as the anode. The polytetrafluoroethylene sheet served as the gaskets. The interdigitated and serpentine flow field (IFF and SFF) with the channel depth 1.5 mm, the channel width 1.0 mm and rib width 1.0 mm were machined on the graphite block. The interdigitated flow field was used at the cathode, and both interdigitated and serpentine flow fields were used at the anode. The gold-coated copper current collectors were connected to the graphite block and clamped by the aluminum endplates. For the polarization tests, 50 mL solution with the SOC of 50% (0.5 M FeCl₂ + 0.5 M FeCl₃ + 2.5 M HCl) was used as the catholyte. For the continuous rebalance tests, 25 mL solution with the SOC of 100% (1.0 M FeCl₃ + 3.0 M HCl) was used as the catholyte. The catholyte was circulated in the Norprene® #16 Chemical Tubing by a peristaltic pump (Longer pump, BT100-2J). The hydrogen and nitrogen mixture gas is used at the anode with back pressure of an atmospheric pressure (1 atm). The hydrogen concentrations is represented by the hydrogen mole percentage in the H₂/N₂ mixture gas. The cell tests were conducted on a potentiostat/galvanostat (Arbin Instrument) at the room temperature. The catholyte flow rate was 20 mL min⁻¹. The anode gas flow rate was controlled at 100 standard-state cubic centimeter per minute (scm) by a flow gauge (D08-4F, Sevenstar). The internal resistance and electrochemical impedance spectroscopy (EIS) of the cell were determined by conducting AC impedance analysis (100 kHz–0.1 Hz, 5 mV) on a potentiostat (EG&G Princeton, model M2273).

2.2. Cost analysis

The cost of rebalance cell depends on the component cost, the evolved hydrogen rate and rebalance current density. The costs of components listed in Table 1 are referenced from the literature [35,36]. The equivalent current density of hydrogen evolution can be calculated based on the assumption that all the capacity loss is caused by hydrogen evolution:

\[ i_{HE} = \frac{\Delta Q}{A t} \]  

(2)

where \( i_{HE} \) is the equivalent current density of hydrogen evolution calculated based on the cycle performance of the previous work [29]; \( \Delta Q \) is the decayed capacity during the cycle test; \( A \) and \( t \) are active area of the ICRFB and operation duration, respectively. When equilibrium, the capability of rebalance devices should match the evolved hydrogen rate. For one kilowatt ICRFB, the active area of the rebalance cell can be calculated as follows:

\[ A_{re} = \frac{1 kW \cdot i_{HE}}{P_{RFB} \cdot i_{re}} = \frac{1000i_{HE}}{i_{re} V_{re}} \]  

(3)

where \( A_{re} \) and \( i_{re} \) are the active area of the rebalance cell and rebalance current density; \( P_{RFB}, i \) and \( V \) are the power density, operating current density and average output voltage of the ICRFB, respectively. The cost of rebalance cell for 1 kW ICRFB is:

\[ C = A_{re} \sum Q_i \]  

(4)

where \( C \) and \( Q \) are the rebalance cell cost per kilowatt of the ICRFB and unit cost of the component, respectively.

3. Results and discussion

3.1. The effects of flow field design

Since the rebalance cell is expected to operate at the extremely low hydrogen concentrations to ensure system safety, the flow field design should have a significant influence on the mass transport loss and performance of the rebalance cell. As shown in Fig. 2a, the rebalance cell with the IFF-based anode exhibits better performance than one with the SFF-based anode at the high current densities. It is because that the IFF has non-continuous flow channels, and forces the species to flow through the electrode, thus providing higher mass transport rate than the SFF.

3.2. The effects of hydrogen concentration

The effects of hydrogen concentration on the performance of rebalance cell is investigated using the rebalance cell with the IFF-based anode. Since the flow resistance of the setup is relatively small and the back pressure is 1 atm (absolute pressure), the total pressure of H₂/N₂ mixture gas is approximately 1 atm. The hydrogen partial pressure can be calculated as the product of hydrogen mole percentage and total pressure. The hydrogen concentrations of 1.3%, 2.5%, 5%, 15% and 30% indicate the hydrogen mole percentage in the H₂/N₂ mixture gas is approximately 1 atm. The hydrogen partial pressure can be calculated as the product of hydrogen mole percentage and total pressure. The hydrogen concentrations of 1.3%, 2.5%, 5%, 15% and 30% indicates the hydrogen partial pressures of 1317, 2533, 5066, 15199 and 30398 Pa, respectively. As shown in Fig. 2b, with the hydrogen concentration increasing from 1.3% to 15%, the output voltage and limiting current density increase dramatically. When the hydrogen concentration increases further increases to 30%, the increase of the limiting current density is limited by mass transport of Fe(III) species at the cathode. The theoretical limiting current densities based on the fed hydrogen of 1.3%, 2.5%, 5%, 15% and 30% are 47, 90, 180, 539 and 1077 mA cm⁻², respectively, while the observed limiting current densities that the rebalance cell delivers are 45, 85, 175, 250 and 271 mA cm⁻², respectively. It is shown that the hydrogen utilization of the IFF-based rebalance cell can approach 100% at low hydrogen concentrations (<5%).

As shown in Fig. 3a, the charge transfer resistance of hydrogen oxidation reaction (HOR) increases with the hydrogen concentration decreasing. The apparent exchange current density of the anode can be calculated as follows [37]:

\[ J_0 = \frac{RT}{R_{cat} nF A} \]  

(5)

where \( J_0 \) is the apparent exchange current density; \( R_{cat} \) is the anode charge transfer resistance that can be fitted using the equivalent circuit model in reference [37]; \( n \) is the number of electrons involved in HOR. It is found that apparent exchange current density is proportional to the square root of hydrogen concentration at the hydrogen concentrations ranging from 1.3% to 50% as exhibited in

Table 1

Component costs of the rebalance cell.

<table>
<thead>
<tr>
<th>Component</th>
<th>Cost</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane, $ m⁻²</td>
<td>500</td>
<td>[36]</td>
</tr>
<tr>
<td>Bipolar plate, $ m⁻²</td>
<td>55</td>
<td>[36]</td>
</tr>
<tr>
<td>Cathode, $ m⁻²</td>
<td>70</td>
<td>[36]</td>
</tr>
<tr>
<td>Gasket, $ m⁻²</td>
<td>10</td>
<td>Estimated</td>
</tr>
<tr>
<td>PVC frame, $ m⁻²</td>
<td>17</td>
<td>[36]</td>
</tr>
<tr>
<td>Anode GDL, $ m⁻²</td>
<td>70</td>
<td>[36]</td>
</tr>
<tr>
<td>Anode Pt catalyst, $ g⁻¹</td>
<td>63.5</td>
<td>[35]</td>
</tr>
<tr>
<td>Cell manufactory</td>
<td>10% of material cost</td>
<td>Estimated</td>
</tr>
</tbody>
</table>

3.3. Effects of gas flow rate

As shown in Fig. 2c, the limiting current densities of the rebalance cell increases linearly with the flow rate of H₂/N₂ mixture gas increasing. The theoretical limiting current densities are 44, 79, 115 and 180 mA cm⁻² at the gas flow rate of 24, 44, 64 and 100 sccm, respectively, while the observed limiting current densities are 42, 74, 110, 175 mA cm⁻², respectively. The utilization of hydrogen approaches 100% at the hydrogen concentration of 5% within the flow rate of 100 sccm. It is shown that the IFF-based rebalance cell can effectively oxidize the low-hydrogen-concentration H₂/N₂ mixture gas.

3.4. Continuous rebalance process

As shown in Fig. 4a and b, the IFF-based rebalance cell operates at different current densities and hydrogen concentrations. It is found that even at a low hydrogen concentration of 2.5%, the
rebalance cell can operate stably at a rebalance current density up to 60 mA cm$^{-2}$. With such a low hydrogen concentration in the tank headspace of RFBs, the energy storage system can passively avoid the potential explosion risk even if mixed with the intruded air, and achieve high safety. The theoretical capacity of 25 mL ferric solution (1.0 M FeCl$_3$ + 3.0 M HCl) is 670 mAh, while the practical discharge capacities are around 630 mAh. The change of the solution color indicates that the Fe(III) species can be effectively reduced to Fe(II) species as shown in the insert image of Fig. 4a.

3.5. Cost of rebalance cell

The cost of the rebalance cell has been analyzed based on the output power density of the ICRFB. According to our previous results, the equivalent current density of hydrogen evolution is calculated to be no more than 1.06 mA cm$^{-2}$ when the battery operates at 320 mA cm$^{-2}$ [29]. As shown in the insert image of Fig. 5, the most expensive component is the noble metal catalyst. With the lower catalyst loading, the cost of rebalance cell can be reduced remarkably. The second most costly component is the perfluorosulfonic membrane, which may be substituted by the low-cost porous membranes in the future. The cost of the rebalance cell is estimated to be $13.4 \text{kW}_{\text{th}}$ with the Pt catalyst loading of 2 mg cm$^{-2}$ and rebalance operating current density of 60 mA cm$^{-2}$, while the cost of the ICRFB is estimated to be $1100.9 \text{kW}_{\text{th}}$ according to the previous work [27]. The results show that the rebalance cell accounts for around 1% of system cost, and does not significantly increase the total cost of ICRFB system. It is also found that the cost of the rebalance cell can be reduced dramatically with the increased rebalance current density.

4. Conclusions

In summary, this work investigates the performance of hydrogen-ferric ion rebalance cells that operate at low hydrogen concentrations. The effects of the flow field, hydrogen concentration and gas flow rate on the rebalance performance have been studied, and the cost of the rebalance cell is estimated. It is shown that: i) the IFF based rebalance cell delivers higher current densities compared with the SFF based one; ii) the hydrogen utilization of the rebalance cell approaches 100% at the low hydrogen concentrations (<5%); iii) the apparent exchange current density of hydrogen oxidation is proportional to the square root of the hydrogen concentration at the hydrogen concentration from 1.3% to 50%; and iv) a continuous and stable rebalance process is demonstrated at a current density of 60 mA cm$^{-2}$ and a hydrogen concentration of 2.5%. Furthermore, the rebalance cell is estimated to be approximately 1% of ICRFB system cost.

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References
