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A comparative study of all-vanadium and iron-chromium redox flow batteries for large-scale energy storage

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HIGHLIGHTS

- Performance and cost of the VRFB and ICRFB are compared.
- Energy efficiencies of the VRFB and ICRFB are similar at high current densities.
- The ICRFB exhibits a higher capacity decay rate than does the VRFB.
- The ICRFB shows cost advantages at high power densities and large capacities.

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ABSTRACT

The promise of redox flow batteries (RFBs) utilizing soluble redox couples, such as all vanadium ions as well as iron and chromium ions, is becoming increasingly recognized for large-scale energy storage of renewables such as wind and solar, owing to their unique advantages including scalability, intrinsic safety, and long cycle life. An ongoing question associated with these two RFBs is determining whether the vanadium redox flow battery (VRFB) or iron-chromium redox flow battery (ICRFB) is more suitable and competitive for large-scale energy storage. To address this concern, a comparative study has been conducted for the two types of battery based on their charge–discharge performance, cycle performance, and capital cost. It is found that: i) the two batteries have similar energy efficiencies at high current densities; ii) the ICRFB exhibits a higher capacity decay rate than does the VRFB; and iii) the ICRFB is much less expensive in capital costs when operated at high power densities or at large capacities.

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1. Introduction

Renewable energy sources such as wind and solar energy have gained increasing attention due to growing environmental issues and sustainability over fossil fuel consumption. These renewables are intermittent and fluctuant in nature, requiring the need of large-scale energy storage systems for continuous and reliable power output. Redox flow batteries (RFBs) are electrochemical devices that utilize the electrochemical reactions between two redox couples to reversibly conduct the conversion between chemical energy and electrical energy. As shown in Fig. 1, an RFB consists of two flowing electrolyte solutions (positive and negative electrolytes) and two electrodes separated by an ion-exchange membrane (or a separator). The soluble reactants are contained within separate storage tanks and pumped through the porous electrodes where the electrochemical reactions (reduction and oxidation) take place. RFBs have several unique advantages including scalability, high energy efficiency, fast response, intrinsic safety, and long lifetime [1–3].

The iron chromium redox flow battery (ICRFB) is considered as the first true RFB and utilizes low-cost, abundant chromium and iron chlorides as redox-active materials, making it one of the most cost-effective energy storage systems [2,4]. The ICRFB typically employs carbon felt as the electrode material, and uses an ion-exchange membrane to separate the two electrodes. The ICRFB produces a standard voltage of 1.18 V through the following reactions:

Positive electrode:

$$Fe^{3+} + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Fe^{2+} \quad E^0 = +0.77\ \mathrm{V\ vs.\ SHE} \tag{1}$$

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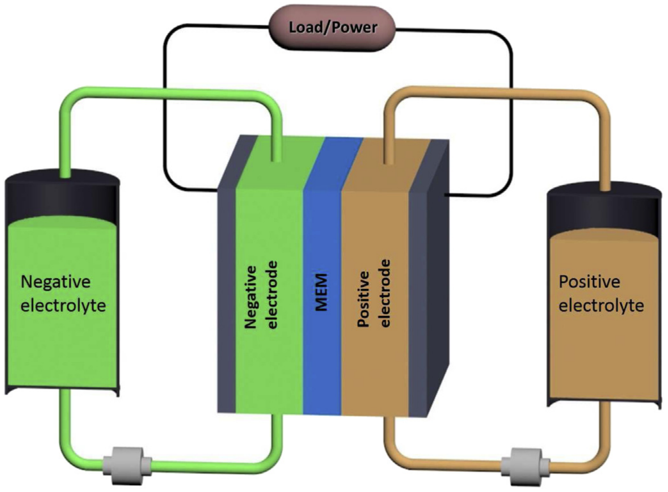

Fig. 1. Schematic of a redox flow battery.

Negative electrode:

$$Cr^{2+} \underset{charge}{\overset{discharge}{\rightleftarrows}} Cr^{3+} + e^- \quad E^0 = -0.41\text{ V vs. SHE} \tag{2}$$

Overall:

$$Fe^{3+} + Cr^{2+} \underset{charge}{\overset{discharge}{\rightleftarrows}} Fe^{2+} + Cr^{3+} \quad E^0 = 1.18\text{ V} \tag{3}$$

Extensive studies on ICRFBs have been carried out over the past few decades [5–8]. Due to the fast kinetics of the Fe(II)/Fe(III) redox reaction, bare carbon felt is typically adopted as the electrode material at the positive side, while at the negative side, the catalyst is generally necessary to enhance the electrochemical kinetics of the Cr(II)/Cr(III) redox reaction. Meanwhile, the catalyst must have a high overpotential towards the hydrogen evolution reaction because thermodynamically, hydrogen ions are more easily reduced than Cr(III) ions. Hydrogen evolution not only reduces the coulombic efficiency, but also causes the state of charge (SOC) of positive and negative electrolytes to be imbalanced over prolonged cycles, eventually causing capacity decay. To counter these issues, catalysts, such as Bi and Au–Tl, are deposited on the electrode surface to enhance the electrochemical kinetics of the Cr(II)/Cr(III) redox reaction, and alleviate hydrogen evolution [5,8]. In addition, a rebalance cell that manages produced hydrogen and rebalances the SOC of electrolytes can be installed to avoid the negative effects of hydrogen evolution on the battery capacity [9].

Another problem is that membranes in ICRFBs are permeable not only to charge-carrier ions (H^+/Cl^-), but also to active species (Fe and Cr ions). On the other hand, the use of Fe and Cr ions on the positive and negative electrodes, respectively, creates a large concentration difference through the membrane for the respective ions, resulting in a high crossover rate and serious capacity decay even after short-term operation. To tackle this issue, the mixed-reactant solutions consisting of premixed Fe and Cr salts were proposed for both positive and negative electrolytes, which significantly reduced the net crossover rates, thereby enabling lengthier operation [10]. Although the incorporation of mixed-reactants shows promise, long-term operation of ICFB still leads to some redox-ion crossover caused by electro-migration, diffusion and convection. The capacity decay in during long-term operation can be somewhat recovered by simply remixing the positive and negative electrolytes, which is typically executed in redox flow batteries [9,11,12]. In addition to the fundamental research, extensive efforts have been made to scale-up the ICRFB for the purpose of large-scale energy storage [9,13–16]. For instance, a 250 kW/1 MWh ICRFB energy storage system has been demonstrated in California, the US [16].

Radically different from the ICRFB, the vanadium redox flow battery (VRFB) that utilizes V(II)/V(III) and V(IV)/V(V) redox couples eliminates cross-contamination between negative and positive compartments [17]. In addition, the VRFB has particular advantages, such as excellent electrochemical kinetics and negligible side reaction [18–20]. In VRFBs, the electrochemical reactions are as follows:

Positive electrode:

$$VO_2^+ + 2H^+ + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} VO^{2+} + H_2O \quad E^0 = +1.01\text{ V vs. SHE} \tag{5}$$

Negative electrode:

$$V^{2+} \underset{charge}{\overset{discharge}{\rightleftarrows}} V^{3+} + e^- \quad E^0 = -0.25\text{ V vs. SHE} \tag{6}$$

Overall:

$$VO_2^+ + V^{2+} + 2H^+ \underset{charge}{\overset{discharge}{\rightleftarrows}} VO^{2+} + V^{3+} + H_2O \quad E^0 = 1.26\text{ V} \tag{7}$$

The VRFB was invented and pioneered by Skyllas-Kazacos and co-workers at the University of New South Wales in the 1980s [17,21]. In the past few decades, much effort has been focused on further improving the battery performance, such as fabricating powerful catalysts, optimizing electrodes and membranes, and developing numerical tools [22–29]. However, market penetration of the VRFB for large-scale energy storage is limited by the high capital cost, which results from the use of expensive vanadium redox couples [11,19] and Nafion membranes. It is shown that a VRFB system with a 4-h discharge duration has an estimated capital cost of \$447 kWh^{-1}, in which the electrolyte and membrane account for 43% and 27%, respectively [30]. However, the targeted capital cost for a large-scale energy storage system is estimated to be at \$100 kWh^{-1} [31]. Reducing the capital cost remains a major challenge for the commercialization of VRFBs.

In summary, the ICRFB uses low-cost redox-active materials, but suffers from system complexity due to the need for SOC rebalancing. While the VRFB exhibits excellent kinetics, it is off-set by its high capital cost. The above discussion between VRFBs and ICRFBs raises an open-ended question: which technology is more competitive for large-scale energy storage systems? The objective of this work is to attempt to answer this question via conducting a comparative study in terms of the charge–discharge performance, cycle performance, and capital cost. The energy efficiency and capacity decay rate of the VRFB and ICRFB are examined from the experiments. An analysis of the capital cost was conducted based on these obtained figures.

2. Experimental

A typical flow-through cell structure was adopted for the battery tests. Both negative and positive electrodes were composed of 2.0 cm × 2.5 cm active area (SGL, GFA 6) graphite felt. The electrodes were treated at 400 °C for 6 h in ambient air to enhance the electrochemical activity and hydrophilicity [32]. Silica gaskets were selected to give a compression ratio of 20% for both the negative and positive electrodes. Nafion 212 is used for the membrane.

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