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# A high-performance flow-field structured iron-chromium redox flow battery

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## HIGHLIGHTS

- A high-performance flow-field structured ICRFB is demonstrated.
- The ICRFB achieves an energy efficiency of 79.6% at 200 mA cm$^{-2}$ (65 °C).
- The capacity decay rate of the ICRFB is 0.6% per cycle during the cycle test.
- The ICRFB has a low capital cost of \$137.6 kWh$^{-1}$ for 8-h energy storage.

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## ABSTRACT

Unlike conventional iron-chromium redox flow batteries (ICRFBs) with a flow-through cell structure, in this work a high-performance ICRFB featuring a flow-field cell structure is developed. It is found that the present flow-field structured ICRFB reaches an energy efficiency of 76.3% with a current density of 120 mA cm$^{-2}$ at 25 °C. The energy efficiency can be as high as 79.6% with an elevated current density of 200 mA cm$^{-2}$ at 65 °C, a record performance of the ICRFB in the existing literature. In addition, it is demonstrated that the energy efficiency of the battery is stable during the cycle test, and that the capacity decay rate of the battery is 0.6% per cycle. More excitingly, the high performance of the flow-field structured battery significantly lowers the capital cost at \$137.6 kWh$^{-1}$, which is 28.2% lower than that of the conventional ICRFB for 8-h energy storage.

## 1. Introduction

The utilization of renewable energy resources such as wind and solar has been growing substantially, presenting an imperative need to develop large-scale energy storage devices to enable a continuous and reliable power output [1–4]. The redox flow battery (RFB) is regarded as one of the most promising large-scale energy storage technologies for intermittent renewables due to its unique advantages including ease of scalability, intrinsic safety and long cycle life [3,5].

Broad market penetration of the RFB requires it to be sufficiently inexpensive to compete with traditional back-up power generations such as natural gas turbines. The vanadium redox flow battery (VRFB), the most developed aqueous RFB [3,6–9], is estimated to have a vanadium material cost of \$189 kWh$^{-1}$ and a system cost of \$325 kWh$^{-1}$ [10], which are far higher than the cost target of \$100 kWh$^{-1}$ for the energy storage system set by US Department of Energy ARPA-E [11]. The low-cost redox-active material is critical in achieving an economically sound RFB to guarantee its successful commercialization. Thus, extensive efforts have been focused on developing alternative inexpensive redox-active materials [12–20]. The non-aqueous RFB has a potential to achieve high cell voltage and high energy density [2,21–26]. However, it is still in its early stage, and far from the field demonstration.

As the first RFB, the iron-chromium redox flow battery (ICRFB) capitalizes on the soluble redox couples of Fe(II)/Fe(III) and Cr(II)/Cr(III) in the acid supporting medium as the positive and negative electrolytes, respectively, which are separated by an ion exchange membrane or a separator [2,27]. The ICRFB stores and releases electric energy through the following electrochemical reactions:

Positive electrode:

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

Negative electrode:

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

Overall reaction:

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

The ICRFB utilizes cheap and plentiful chromium and iron elements as the redox-active materials with an estimated cost of \$17 $kWh^{-1}$, which provides a sufficient basis and possibility for enabling a cost-effective and competitive energy storage system [2,27,28]. An 1-MWh ICRFB energy storage system has achieved field demonstration in California, the US [29].

Conventionally, the ICRFB adopts a flow-through cell structure, as shown in Fig. 1a, in which the electrolyte is directly pumped through the porous electrode [30]. This type of cell structure is simple and straightforward to fabricate. However, an apparent disadvantage of this cell structure lies in the conflict between the flow resistance and ohmic resistance. A thinner electrode decreases the ohmic resistance, but significantly increases the flow resistance by reducing the cross-sectional area for electrolyte flow. For instance, it has been reported that the pump loss triples when the thickness of the electrode is reduced from 2.5 mm to 1.25 mm at the same flow rate [31]. To circumvent the high flow resistance and pump loss, traditional graphite felt electrodes have been designed to be relatively thick (typically 3.0–6.0 mm) [31–33], resulting in a high ohmic resistance of 3–5 Ω $cm^2$ [34,35]. Due to this reason, conventional ICRFBs are limited to a low operating current density of 40 mA $cm^{-2}$ with an energy efficiency of 70% at room temperature [34]. At an elevated operating temperature of 65 °C, the current density is still limited to 80 mA $cm^{-2}$ with an energy efficiency of approximately 80%, resulting in bulky and expensive cell stacks with an estimated cost of \$116 $kWh^{-1}$, which accounts for 60% of the ICRFB capital cost [28,36].

In the recent literature, a flow-field cell structure with a thin electrode has been applied to all-V, $H_2$/Fe and $H_2/Br_2$ RFB systems. The novel cell configuration dramatically improves battery performance, primarily owing to a reduced ohmic resistance [18,37–40]. Radically different from the flow-through cell structure in which the electrolyte is distributed through random pores of the electrode, the flow-field cell structure is designed with well-defined flow channels adjacent to the electrode to distribute the electrolyte across the entire electrode area. With the assistance of the flow field, the electrolyte transport in the in-plane direction is independent of the porous electrode. Thus, the pump loss would be less sensitive to the electrode thickness than that of the flow-through cell structure. As a result, the flow-field structured cell structure enables the installation of a thinner electrode [33,38]. It is reported that the pump loss for the flow-field cell structure with an 1.0 mm-thickness electrode is only 47% of that for the flow-through cell structure with a 3.0 mm-thickness electrode at the same flow rate of 72 mL $min^{-1}$ [40]. Moreover, carbon paper, typically used as the gas diffusion layer in fuel cells, is another type of carbon material, which has higher stiffness, lower contact resistance and reduced thickness compared to the graphite felt, making it a good electrode candidate for the flow-field cell structure [33].

In this work, it is found that the high ohmic resistance of the conventional ICRFB critically limits the battery performance. To enhance the battery performance, a flow-field structured ICRFB is developed. The energy efficiency of the present ICRFB remains at 76.3% with a current density of 120 mA $cm^{-2}$ at room temperature (25 °C), while the energy efficiency reaches 79.6% with a current density of 200 mA $cm^{-2}$ at 65 °C. The extended cycle test has been conducted. Furthermore, the cost reduction induced by the present ICRFB is quantified through the capital cost analysis.

## 2. Experimental

### 2.1. ICRFB setup

A lab-scale flow-field structured ICRFB setup was designed and fabricated. As shown in Fig. 1b, both negative and positive electrodes were made of two layers of carbon paper (SGL, 10AA, 0.4 mm thickness) with active area of 2.0 cm × 2.0 cm, which were separated by the Nafion® 212 membrane and sealed by PTFE gaskets. The electrodes were pretreated in concentrated sulfuric and nitric acids with volume ratio of 3:1 at 50 °C for 5 h [12]. Then the electrodes were rinsed in deionized water until the pH of the rinsed water approached 7, and dried in air at 120 °C for 2 h. The serpentine flow fields with channel width 1.0 mm, channel depth 1.0 mm and rib width 1.0 mm were machined on the pyrolytic graphite plates, and served to distribute the electrolyte across the active area of the electrodes. The gold-coated copper current collectors were placed adjacent to the graphite plates, and were clamped by the aluminum end plates. 20 mL mixed-reactant solutions of 1.0 M $FeCl_2$ (Aladdin) + 1.0 M $CrCl_3$ (Aladdin) + 3.0 M HCl (VWR) + 0.005 M $Bi^{3+}$ ($Bi_2O_3$: Aladdin) were used as both the positive and negative electrolytes. The electrolytes were circulated in the Norprene® #16 Chemical Tubing by a 2-channel peristaltic pump (Longer pump, WT-600-2J). As a comparison, the conventional flow-through structured ICRFB setup with the graphite felt electrode of 2.0 cm × 2.0 cm active area (SGL, GFA 6, 6.0 mm thickness) was used. The flow-through structured ICRFB had the same electrode pretreatment process and electrolyte composition as the flow-field structured one. All the electrodes of the ICRFBs have a compression ratio of approximately 20%.

### 2.2. ICRFB performance characterization

The charge-discharge tests were conducted on Arbin BT2000 (Arbin® Instrument). The internal resistance of the battery was measured by the built-in function of Arbin BT2000 using a current interrupt method [40–42]. The cell and the electrolyte reservoirs were kept in a temperature chamber at a designated temperature. The cut-off voltages for the charge-discharge tests at room temperature (25 °C) were 0.8 V and 1.25 V, while the cut-off voltages were 0.8 V and 1.2 V for the tests at 65 °C to mitigate hydrogen evolution, which could occur at the negative electrode during the charge process. The flow rate of the electrolyte was 50 mL $min^{-1}$. The cycle test was conducted at 160 mA $cm^{-2}$ and 65 °C. The electrode was characterized by a scanning electron microscope (JEOL-6300 SEM) and energy dispersive X-ray spectrum (EDX).

## 3. Results and discussion

### 3.1. Effect of the electrode surface modification

The carbon paper electrodes are proposed to be used in the flow-field structured ICRFB. The effect of the electrode surface modification on the battery performance has been studied. The battery is tested at 40 mA $cm^{-2}$ and 25 °C. Initially, the electrolyte is 1.0 M $FeCl_2$ + 1.0 M $CrCl_3$ + 3.0 M HCl without $Bi^{3+}$ ions. As shown in Fig. 2, the ICRFB with pristine carbon paper shows a low voltage efficiency of 72.4% due to the slow kinetics of Cr(II)/Cr(III) redox