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The effects of design parameters on the charge-discharge performance of iron-chromium redox flow batteries

Y.K. Zeng, T.S. Zhao *, X.L. Zhou, L. Zeng, L. Wei

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

HIGHLIGHTS

- The effects of design parameters on the ICRFB performance are investigated.
- The energy efficiency of the present ICRFB reaches 80.5% at 480 mA cm^{-2}.
- The power density reaches 1077 and 694 mW cm^{-2} at 65 and 25 °C, respectively.
- The dominant loss of ICRFBs operating at 25 and 65 °C is the ohmic loss.

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ABSTRACT

The objective of this work is to understand and identify key design parameters that influence the battery performance of iron-chromium redox flow batteries (ICRFBs). The investigated parameters include the membrane thickness, electrode compression ratio, electrode pretreatment and catalyst loading. Results show that: (i) with a thin NR-211 membrane and a high electrode compression ratio of 62.5%, the operating current density of the ICRFB can reach as high as 480 mA cm^{-2} at an energy efficiency of higher than 80%; (ii) the bismuth catalyst loading has insignificant effect on the battery performance in the range of 0.52–10.45 mg cm^{-2}; (iii) the moderately oxidative thermal pretreatment of the electrode improves the energy efficiency compared to the as-received electrode while the electrode prepared with a harsh pretreatment deteriorates the battery performance; and (iv) for the present ICRFBs operating at both 25 °C and 65 °C, the dominant loss is identified to be ohmic loss rather than kinetics loss.

1. Introduction

The unprecedented development of electricity generation from renewables especially wind energy raises an urgent need to develop grid-scale energy storage devices for the renewable integration and reliable electricity supply [1–3]. The redox flow battery (RFB) is one of the most promising large-scale energy storage technologies due to its unique features such as easy scalability, intrinsic safety, long service life, fast response and high efficiency [3,4]. Various RFB systems including all-vanadium, all-copper, all-iron, iron-chromium and anthraquinone-based RFBs have been developed over the past decades [5–19]. However, the current RFB technologies are still far away from the stringent performance and cost requirement for the successful commercialization in energy storage market.

The iron-chromium redox flow battery (ICRFB) utilizes the inexpensive Fe(II)/Fe(III) and Cr(II)/Cr(III) redox couples as the positive and negative active materials, respectively [20]. The cost of iron and chromium materials is as low as \$17 kW h^{-1}, which renders the ICRFB a great promise to be a cost-effective energy storage system [4]. At the cathode, the Fe(II)/Fe(III) redox couple has an excellent electrochemical kinetics with a kinetic constant of 8.6×10^{-2} cm s^{-1} on the thermally pretreated electrode [21], while at the anode, the kinetic constant of the Cr(II)/Cr(III) redox couple on the bismuth catalyst is as high as 1.35×10^{-3} cm s^{-1} [22], which is comparable to that of the V(II)/V(III) redox couple reported in the literature [23]. During the past decades, tremendous efforts have been made on the development and scale-up of ICRFBs [24–27]. For instance, a MWh-level ICRFB in California has finished field demonstration recently [28].

The conventional flow-through structured ICRFB directly forces the electrolyte to flow through the porous electrode [29]. However, the conventional ICRFBs have to use thick electrodes (typically 3.0–6.0 mm) to avoid prohibitively high pump loss [30,31], which

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* Corresponding author.
E-mail address: metzhao@ust.hk (T.S. Zhao).

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inevitably leads to a high ohmic resistance [32]. Consequently, the conventional ICRFB has a low operating current density of 80 mA cm^{-2}, resulting in cumbersome and costly stacks [4]. The fuel-electrolyte-fed fuel cell also has liquid electrolyte, and typically has a low-resistance cell structure, which can be borrowed to the flow battery technology [33–36]. Recently, a flow-field structured ICRFB with thin carbon paper electrodes demonstrates a significantly increased operating current density of 200 mA cm^{-2} at the energy efficiency of 79.6% mainly due to the reduced ohmic resistance [17]. Further enhancement of ICRFB performance is achieved by adopting the interdigitated flow fields, which enhances the active species transport at the porous electrode and enables a more uniform catalyst distribution [18].

In addition to the electrode structure and flow field design, other design parameters including membrane thickness, electrode compression ratio, catalyst loading and electrode pretreatment are also expected to affect the battery performance [21,37–41], but these parameters have not been systematically investigated in the ICRFB system. The previous study shows that the compression ratio of 20% of the conventional carbon felt electrode delivers the highest energy efficiency in a vanadium redox flow battery (VRFB) [38], but the compression of the advanced carbon cloth electrode with high specific surface area has not been investigated in RFBs. It is found that the carbon cloth gas diffusion layer with the compression ratio of 50% has lower ohmic resistance than that with the compression ratio of 30%, but worsens the fuel cell performance due to the poor transport property [42]. The effect of membrane thickness has been investigated in VRFB systems, but shows contradictory results [39,40]. Moreover, the temperature adaptability of the ICRFB is of great significance for practical applications such as the emergency startup at room temperature, as the ICRFB is generally designed to operate at the elevated temperature with the thermal management to avoid the issue of chromium aging [43].

In this work, the effects of design parameters including electrode compression ratio, electrode pretreatment, membrane thickness and catalyst loading on the ICRFB charge-discharge performance are investigated. It is demonstrated that the ICRFB with the thinner NR-211 membrane and higher electrode compression ratio of 62.5% achieves a high current density of 480 mA cm^{-2} without sacrificing the energy efficiency.

2. Experimental

2.1. Cyclic voltammetry

Cyclic voltammetry (CV) experiments were conducted using a three-electrode system on a workstation (Autolab, PGSTAT30). A glassy carbon electrode (GCE), platinum mesh electrode and saturated calomel electrode (SCE) served as the working electrode, counter electrode and reference electrode, respectively. The solution of 1.0 M $FeCl_2$ + 1.0 M $CrCl_3$ + 3.0 M HCl + 5.0 mM Bi^{3+} (dissolving with Bi_2O_3) was used for Fe/Cr redox system, while the solution of 1.0 M $VOSO_4$ + 3 M HCl + 5.0 mM Bi^{3+} was used for all-V redox system as a reference. The measurement was performed at a scan rate of 50 mV s^{-1} at room temperature (25 °C).

2.2. Battery setup

The carbon cloth (ELAT-H, 0.4 mm) were thermally pretreated in ambient air at the designated temperature, and served as the electrode. Both the negative and positive electrodes were made of two layers of carbon cloth with an active area of 2.0 cm × 2.0 cm, which were separated by a Nafion® membrane. Both NR-211 and NR-212 were used without any pretreatment. The polytetrafluoroethylene gaskets (0.3 and 0.5 mm thickness) were used to give a specific electrode compression ratio. The interdigitated flow fields with the channel depth 1.5 mm, the channel width 1.0 mm and rib width 1.0 mm were grooved on the graphite plates. The gold-coated copper current collectors were connected to the graphite plates and clamped by the aluminum endplates. 20 mL of mixed-reactant solution (1.0 M $FeCl_2$ + 1.0 M $CrCl_3$ + 3.0 M HCl) was used as the initial anolyte and catholyte, respectively. The Bi^{3+} ions with the designated concentration were added in the anolyte and catholyte, respectively. The electrolytes were circulated in the Norprene® #16 Chemical Tubing by a 2-channel peristaltic pump (Longer pump, WT600-2 J).

2.3. Battery test

The battery tests were conducted on a potentiostat/galvanostat (Arbin Instrument). The cell and the electrolyte reservoirs were placed in a temperature chamber at the constant temperature (65 °C). For the polarization test, ICRFBs were charged to approximately 50% state-of-charge (SOC) before the tests. For each current density, the battery discharged for 20 s, rested for 10 s, and charged at the same current density for 20 s to keep the SOC constant during the polarization test. For the charge-discharge tests, the voltage window was 0.8–1.2 V with an electrolyte flow rate of 50 mL min^{-1}. The internal resistance of the flow cell and dry cell were was determined by conducting AC impedance analysis (100 kHz to 0.1 Hz, 5 mV) on a potentiostat (EG&G Princeton, model M2273). The Bi-deposited negative electrode was characterized by a scanning electron microscope (JEOL-6300 SEM).

3. Results and discussion

3.1. Fe/Cr redox system

Fig. 1 shows the CV curves of the Fe/Cr and all-V redox systems. For the positive side, the peak separation of the Fe(II)/Fe(III) redox couple is significantly smaller than that of the V(IV)/V(V) redox couple, indicating that the Fe(II)/Fe(III) redox couple has a superior electrochemical kinetics compared to the V(IV)/V(V) redox couple. For the negative side, the redox potential of the Cr(II)/Cr(III) couple is approximately 80 mV more negative than that of the V(II)/V(III) redox couple. There is no obvious hydrogen-evolution peak after the Cr(III)-reduction peak. The electrodeposited bismuth has been demonstrated to have an excellent catalytic effect for both the Cr(II)/Cr(III) and V(II)/V(III) redox couples [1,26,43]. The peak current

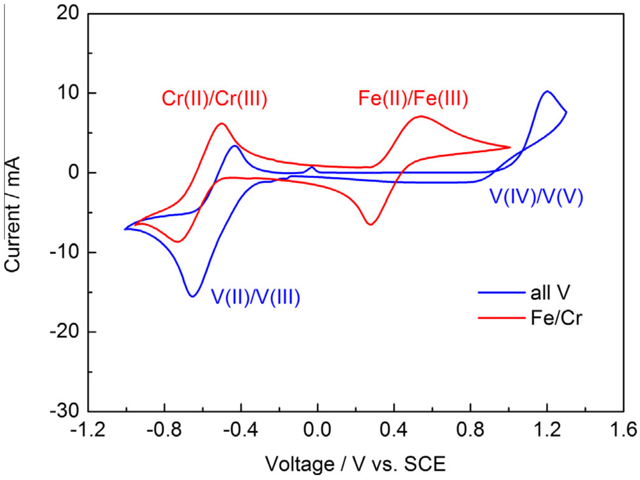

Fig. 1. Cyclic voltammetry of the Fe/Cr and all-V redox systems at a scan rate of 50 mV s^{-1}.