



## Short communication

## A new hybrid redox flow battery with multiple redox couples

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## HIGHLIGHTS

- ▶ Two redox couples were employed in an aqueous redox flow battery system.
- ▶ Stable cycling of over 100 cycles was demonstrated with negligible capacity fading.
- ▶ Fe/V hybrid redox flow battery represents the most efficient use of the expensive vanadium source.

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## ABSTRACT

A redox flow battery using  $V^{4+}/V^{5+}$  vs.  $V^{2+}/V^{3+}$  and  $Fe^{2+}/Fe^{3+}$  vs.  $V^{2+}/V^{3+}$  redox couples in chloric/sulfuric mixed acid supporting electrolyte was investigated for potential stationary energy storage applications. The Fe/V hybrid redox flow cell using mixed reactant solutions and operated within a voltage window of 0.5–1.7 V demonstrated stable cycling over 100 cycles with energy efficiency ~80% and negligible capacity fading at room temperature. A 66% improvement in the energy density of the Fe/V hybrid cell was achieved compared with the previously reported Fe/V cell using only  $Fe^{2+}/Fe^{3+}$  vs.  $V^{2+}/V^{3+}$  redox couples.

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## 1. Introduction

The burgeoning rise of green and renewable energy technologies, such as solar and wind, has attracted much scientific and social interest in recent years. They are increasingly being recognized as essential components of future global energy production as awareness of environmental deterioration, resource depletion, and energy security continuously increases around the world. However, to seamlessly integrate a renewable power source with the current aging grid, an effective electrical energy storage system is needed to overcome the variable and stochastic nature of renewable sources [1]. Redox flow batteries (RFBs) have, therefore, attracted much research interest lately, mainly because of their capability to store large amounts of power or energy (up to multi-MW and -MWh, respectively). In contrast with the traditional batteries, in an RFB

the conversion between electrical energy and chemical (or electrochemical) potential occurs as the electrolytes containing active redox species flow through two electrodes separated by an ionic conducting membrane or separator. This unique mechanism gives the RFBs unparalleled advantages over other secondary battery systems, such as the separation of power and energy, long service life, easy thermal management, quick response, and capability to withstand power supply fluctuation.

Since the invention of the Fe/Cr redox flow battery in 1975 at the National Aeronautics and Space Administration (NASA) [2], the redox flow battery has undergone continuous development. A number of other redox chemistries were reported, including  $V^{2+}/V^{3+}$  vs.  $Br^-/ClBr_2$  [3–5],  $Br_2/Br^-$  vs.  $S/S^{2-}$  [6,7],  $Br^-/Br_2$  vs.  $Zn^{2+}/Zn$  [8,9],  $Ce^{4+}/Ce^{3+}$  vs.  $V^{2+}/V^{3+}$  [10],  $Fe^{3+}/Fe^{2+}$  vs.  $Br_2/Br^-$  [11],  $Mn^{2+}/Mn^{3+}$  vs.  $V^{2+}/V^{3+}$  [12],  $Fe^{3+}/Fe^{2+}$  vs.  $Ti^{2+}/Ti^{4+}$  [13], and others [14]. Among them, GEN 2Fe/Cr RFB [15] and all vanadium flow batteries (VRBs) [16–19] are probably the most researched and promising systems; both were invented and developed in the 1980s in efforts

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to alleviate the severe cross-contamination encountered in the original Fe/Cr system.

While significant progress was made in advancing RFBs with the demonstration of multi-MWh VRB systems [20] and the market-available Fe/Cr RFB system [21], the current technologies cannot meet all of the performance and cost-requirement matrices for broad market penetration. One of the main challenges facing RFBs is the intrinsically low energy density compared with other secondary energy storage systems such as lithium-ion batteries. With the voltage limitation of aqueous systems, this issue is tackled mainly by increasing the concentration of active species used in the electrolyte in previous research [22], which was often hindered by the solubility and stability issues of the active redox ions in the electrolyte solutions. In the field of solid state energy storage systems, the need for high energy and high power density has spurred research and development of multi-electron reaction materials as electrodes [23]. The rationale behind the design of the multi-electron electrode lies in Equation (1) for energy density ( $E_d$ ), in which  $M$  is the unit weight (or volume),  $F$  is the Faraday constant,  $E_i^0$  is the electromotive force of each redox reaction, and  $n_i$  is the number of electrons transferred per mole of reactants in each redox reaction. Clearly, more electron transfer results in a higher energy density [23].

$$E_d = \frac{\sum n_i F E_i^0}{\sum M_i} \quad (1)$$

In an aqueous RFB system, multiple electron transfer from a single element is probably difficult to realize due to the narrow voltage window limited by water electrolysis. However, it is possible to employ multiple electrons from different elements. The energy density (based on electrolyte only) of an RFB utilizing multiple electrons thus can be expressed as in Equation (2), which is similar to Equation (1).

$$E_d = \frac{\sum C_i V_{\text{tank}} F E_i^0}{V} \quad (2)$$

In Equation (2), energy density  $E_d$  is expressed in unit volume  $V$  (including both catholyte and anolyte), where  $C_i$  is the minimal concentration of all active species participating in the oxidation or reduction reaction  $i$ ,  $E_i^0$  is the voltage of each redox reaction, and  $V_{\text{tank}}$  is the half-cell electrolyte volume containing active specie  $C_i$ . From Equation (2), introducing multiple redox reactions with suitable voltage ranges therefore will improve the energy density of the RFB systems. Herein we report the electrochemical performance of a hybrid Fe/V RFB system utilizing both  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{V}^{4+}/\text{V}^{5+}$  redox couples in catholyte and a  $\text{V}^{2+}/\text{V}^{3+}$  redox couple in anolyte.

## 2. Experimental

The electrolyte was prepared by dissolving  $\text{VOSO}_4$  (Sigma–Aldrich, 99%) and  $\text{FeCl}_2$  (Sigma–Aldrich, 98%) in concentrated HCl (Sigma–Aldrich, 37%) at room temperature for the Fe/V redox flow battery test, which yielded active iron and vanadium concentrations of 1.5 M respectively with 1.5 M sulfate and 6.8 M chloride ions in the final electrolyte, hereafter denoted as the 1.5Fe/V/S–6.8Cl. Cyclic voltammetry (CV) was carried out in 1.5Fe/V/S–6.8Cl electrolyte to identify redox couples and electrochemical reversibility using a Solartron 1287 potentiostat (Solartron Analytical, USA). A glassy carbon electrode (CH Instruments, USA) and Ag/AgCl electrode (CH Instruments, USA) were used as the working and reference electrode respectively, while a platinum flag served as the counter electrode. Various scan rates were used during the test.

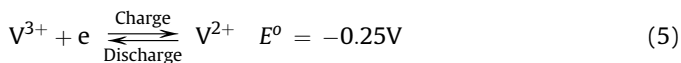
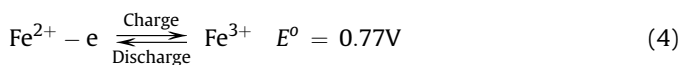
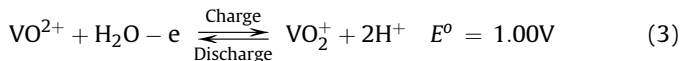
The cell performance was tested using an in-house designed flow cell system, which consists of a single cell connected with two

Pyrex<sup>®</sup> glass beaker reservoirs through a peristaltic pump (Cole-Parmer, USA) and Viton<sup>®</sup> tubing [24]. In each half cell, graphite felt (SGL Carbon Group, Germany) served as a porous electrode which was settled in a groove on a non-porous graphite current collector plate with one inlet and one outlet connections. The depth of the groove in the graphite plates was designed to maintain a 10% compression on the encapsulated graphite felt. The apparent area (i.e., the area in contact with the membrane) of the graphite felt was  $10 \text{ cm}^2$  ( $2 \times 5 \text{ cm}$ ); it was oxidized in air at  $400^\circ\text{C}$  for 6 h prior to the test to improve the electrochemical activity and hydrophilicity. Before the cell assembly, the Nafion<sup>®</sup> NR-212 membrane was soaked in deionized water for more than 24 h at ambient temperature.

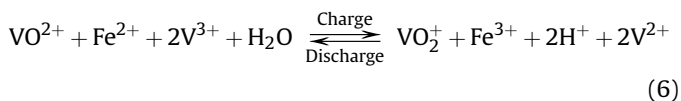
The electrochemical performance of the Fe/V flow battery was evaluated with a constant current method using a potentiostat/galvanostat (Arbin Instruments, USA). Each half-cell reservoir consisted of 1.5Fe/V/S–6.8Cl mixed acid solution as both positive and negative electrolyte, which was circulating through the graphite felt electrode at a flow rate of  $20 \text{ mL min}^{-1}$ . Each half-cell reservoir was purged with nitrogen gas and then sealed preceding the electrochemical test to minimize the oxidation of the active species. The flow cell was cycled in the voltage window between 0.5 V and 1.7 V at a constant current density of  $50 \text{ mA cm}^{-2}$ .

## 3. Results and discussion

As shown in Fig. 1(a), a cyclic voltammogram (CV) was first performed on the 1.5Fe/V/S–6.8Cl electrolyte to investigate the available redox reactions and their reversibility and kinetics. The CV tests were carried out using glassy carbon electrodes at ambient temperature with a scan rate of  $10 \text{ mV s}^{-1}$ . The current density was normalized to the geometrical area of the working electrode. As in our previous work on the V/V mixed acid and Fe/V system [22,24,25], a combination of three redox couples ( $\text{V}^{2+}/\text{V}^{3+}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , and  $\text{V}^{4+}/\text{V}^{5+}$ ) were identified in Fig. 1(a), which correspond to the following redox reactions in Equations (3)–(5).



Due to lack of an additional redox couple on the negative side, a double volume is used for the negative electrolyte (reaction (5)). The overall cell reaction can be written as Equation (6)



Based on the CV results of the  $\text{V}^{4+}/\text{V}^{5+}$  vs.  $\text{V}^{2+}/\text{V}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  vs.  $\text{V}^{2+}/\text{V}^{3+}$  redox couples in the sulfate–chloride mixed acid electrolyte, a hybrid RFB system can be constructed with two similar equilibrium cell potentials to that of the V/V and Fe/V redox flow batteries.

The electrochemical cycling performance of the RFB system based on the  $\text{V}^{4+}/\text{V}^{5+}$  vs.  $\text{V}^{2+}/\text{V}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  vs.  $\text{V}^{2+}/\text{V}^{3+}$  redox couples in the sulfate–chloride mixed acid electrolyte was then tested with a lab-made flow cell within the voltage window of 0.5–1.7 V at  $50 \text{ mA cm}^{-2}$  current density with an NR-212 membrane as described in the Experimental section.

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