

A NEW IRON/VANADIUM (FE/V) REDOX FLOW BATTERY

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ABSTRACT

A novel redox flow battery using $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{V}^{2+}/\text{V}^{3+}$ redox couples in chloride supporting electrolyte and in chloric/sulfuric mixed-acid supporting electrolyte was investigated for potential stationary energy storage applications. The iron/vanadium (Fe/V) redox flow cell using mixed reactant solutions operated within a voltage window of 0.5~1.35 volts with a nearly 100% utilization ratio and demonstrated stable cycling over 100 cycles with energy efficiency > 80% and almost no capacity fading. Stable performance was achieved in the temperature range between 0 °C and 50 °C. Unlike the iron/chromium (Fe/Cr) redox flow battery that operates at an elevated temperature of 65 °C, the necessity of external heat management is eliminated. The improved electrochemical performance makes the Fe/V redox flow battery a promising option as a stationary energy storage device to enable renewable integration and stabilization of the electric grid.

Keywords: redox flow battery, hydrochloric acid, sulfuric acid, Fe/V, mixed acid, energy storage

INTRODUCTION

Redox flow batteries (RFBs) are electrochemical devices that store electrical energy in liquid electrolytes [1]. The energy conversion between chemical energy and electricity energy is carried out as liquid electrolytes flow through cell stacks. This advantage, along with their capability to safely store large quantities of electricity in a simple design and release it according to demands, makes it an ideal technology for the grid and micro-grid applications. Among the known redox flow batteries, the iron/chromium (Fe/Cr) and all-vanadium RFBs, or VRBs, are the two most widely developed. The Fe/Cr RFBs may be appealing for their potential low materials cost, but the low potential (-0.41 volts [V]) of the $\text{Cr}^{2+}/\text{Cr}^{3+}$ redox couple can lead to hydrogen evolution during operation, complicating the system, raising the cost, and inviting safety concerns. VRBs demonstrate excellent electrochemical activity. However, the instability and high oxidation reactivity of the V^{5+} species in positive electrolyte require the use of high-cost Nafion membrane and limit operational temperatures to 10~40 °C [2]. This narrow operational temperature window and, in particular, the up limit (40 °C), often necessitate electrolyte temperature control in practical systems. Such heat management causes as much as 20% additional

energy loss and significantly increases the overall operating cost [3].

In our work, we proposed and investigated the electrochemical performance of a new RFB that employs a $\text{V}^{2+}/\text{V}^{3+}$ solution anolyte and a $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution catholyte or a mixed solution as both the catholyte and anolyte. A standard voltage of 1.02 V can be obtained. The iron/vanadium (Fe/V) system was intended to make use of benefits from both Fe/Cr and all-vanadium systems while circumventing their intrinsic issues. Compared with the $\text{Cr}^{2+}/\text{Cr}^{3+}$ redox reaction, the $\text{V}^{2+}/\text{V}^{3+}$ pair possesses a much better electrochemical activity, which would free the system from using the expensive catalysts and the high-temperature management system. Moreover, the evolution of hydrogen (H_2) gas during charging can be curtailed since the working potential of $\text{V}^{2+}/\text{V}^{3+}$ (-0.25 V) is considerably higher than that of $\text{Cr}^{2+}/\text{Cr}^{3+}$ (-0.41 V). On the positive side, the $\text{V}^{4+}/\text{V}^{5+}$ is replaced with the less oxidative and electrochemically reversible $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. Thus, the Fe/V system was expected to demonstrate an improved stability at elevated temperatures and also enable the system to use low-cost membranes other than Nafion. To demonstrate the capabilities of the proposed flow battery, the Fe/V redox couples in chloride-supporting electrolytes and in chloride/sulfuric acid

mixed electrolytes were investigated for electrochemical properties, temperature stability, and performance. This paper reports the details of the work.

EXPERIMENTAL

The electrolyte for the Fe/V redox flow battery test was prepared by dissolving vanadyl sulfate (VOSO_4), vanadium trichloride (VCl_3), and iron chloride (FeCl_2) in hydrogen chloride (HCl) and sulfuric acid (H_2SO_4). Cyclic voltammetry (CV) was carried out using Solartron 1287 potentiostat (Solartron Analytical, USA). A platinum (Pt) wire and silver/silver chloride (Ag/AgCl) electrode were used as the counter and reference electrode, respectively. A custom-made graphite felt ($\phi = 5.5$ mm) electrode was used as the working electrode. The scan rate was 0.5 mV/s. The identical graphite felts without catalysts were used in both CV and flow cell testing.

The cell performance was measured under a constant current using an in-house-designed flow cell system that was connected with a potentiostat/galvanostat (Arbin Institute, College Station, TX). The apparent area (i.e., the area in contact with the membrane) of the graphite felt was 10 cm^2 ($2 \text{ cm} \times 5 \text{ cm}$). Nafion membrane and Daramic hydrocarbon separator were used in the tests. An electrolyte volume of 50 milliliters (mL) and a flow rate of 20 mL/min were used during the tests. The flow cell was charged to 1.3 V and then discharged to 0.5 V at a current density of $50 \text{ mA}/\text{cm}^2$. The composition of the electrolytes after cycling was determined by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) after appropriate dilution.

During the stability tests, the samples were kept static without any agitation and monitored daily by the naked eye for any change of color indicating the oxidation of the membrane.

RESULTS AND DISCUSSION

Figure 1(a) shows the CV results of 1.5Fe/V-3.8HCl electrolyte. Two pairs of redox couples ($\text{V}^{2+}/\text{V}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$) were observed in the sulfate-chloride mixed-acid solution, suggesting that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples have adequate reversibility to be used as the positive and negative electrolytes for the proposed RFB system.

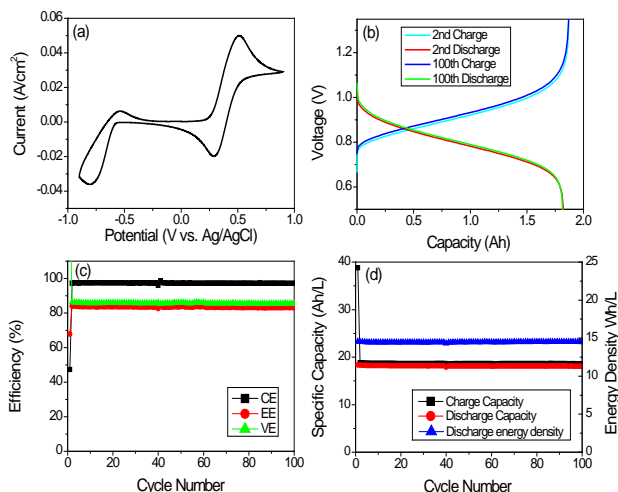


Fig. 1. A cyclic voltammetry (CV) spectrum (a) on glassy carbon electrode in the 1.5Fe/V-3.8HCl electrolyte at 10 mV/s scan rate and the electrochemical performance of a Fe/V mixed acid redox flow cell with 1.5Fe/V-3.8HCl electrolyte in each half-cell and NR 212 as the membrane; (b) cell-voltage profile with respect to cell capacity during the 2nd and 100th cycles of the charge/discharge process; (c) cyclic coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) as a function of cycle number; (d) variation of specific volumetric capacity and discharge energy density with cycle number in a Fe/V mixed-acid redox flow cell using 1.5Fe/V-3.8HCl electrolyte in each half-cell with charge/discharge current density of $50 \text{ mA}/\text{cm}^2$.

The electrochemical cycling performance of the RFB system based on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ vs. $\text{V}^{2+}/\text{V}^{3+}$ redox couples was tested in the laboratory-made flow cell within the voltage window of 0.5~1.35 V at $50 \text{ mA}/\text{cm}^2$ current density with a NR212 membrane. As indicated by the CV scan results, no gas evolution issues were observed over a wide potential range of 1.8 V, which renders the Fe/V RFB with the sulfate-chloride mixed-acid supporting electrolyte considerable freedom with cell operational voltage control in maximizing the electrolyte utilization ratio while preventing the gassing problem. As shown in a typical plot of cell voltage profile with respect to the cell capacity (Figure 1(b)), the RFB cell performance corroborates the CV study, in which a state of charge in the range of 0~100% is demonstrated

during the charge/discharge cycling, resulting in a utilization ratio close to 100%. Moreover, as shown in Figure 1(b), the voltage profile of the 100th cycle overlaps with that of the 2nd cycle, suggesting not only stable electrochemical cycling, but also a successful mitigation of the gassing issue over a long run (more than 30 days).

Figure 1(c) demonstrated the efficiencies of the Fe/V cell with the sulfate-chloride mixed-acid electrolyte up to 100 cycles, in which a CE of > 97% and a VE of ~85% were achieved, leading to an overall EE of ~82% at 50 mA·cm⁻². The Fe/V cell also exhibited excellent capability retention as shown in Figure 1(d) with no obvious capacity loss throughout the 100 cycles. The discharge energy density representing the ultimate capability of the cell to deliver the useful energy is also plotted in Figure 1(d), in which close to 15 Wh·L⁻¹ of specific volumetric energy density was obtained over 100 cycles of electrochemical cycling.

The cycling tests were then carried out at 25, 50, and 0 °C, with the flow battery cycled at each temperature over ~20 cycles (roughly 10 days). The electrolyte reservoirs were periodically examined, and no precipitation was found. At higher temperature (50 °C), a higher voltage efficiency of ~86% was obtained owing to the enhanced electrode reactions and reduced polarization at the elevated temperature. However, the cell performance was compromised with a lower CE of ~92% due to the increased crossover, leading to similar overall EE as for the cycling at 25 °C (~80%). At 0 °C, the system demonstrated a lower VE (~70%) and EE (~67%) caused by the more sluggish reaction and the increased electrolyte impedance at low temperature.

The cycling performance of the Fe/V cell at different temperatures affirms that the Fe/V flow battery with sulfate-chloride mixed-acid electrolyte can be operated in the temperature window of 0~50 °C. Given adequate insulation combined with generation of waste heat and subsequent system heating during operation, most areas around the world should thus be able to accommodate the Fe/V flow battery without the need for active heat management.

CONCLUSION

A novel RFB system based on Fe²⁺/Fe³⁺ vs. V²⁺/V³⁺ redox couples in sulfate-chloride mixed-acid electrolytes was successfully demonstrated in a laboratory-scale flow cell. With 1.5-M Fe and 1.5-M V in 1.5-M sulfate and 3.8-M total chloride solution, the redox flow cell achieved an EE of > 80% and no capacity fading over 100 cycles when employing NR212 as the membrane. The electrochemical cycling that was performed at different temperatures suggested that the Fe/V flow battery with sulfate-chloride mixed-acid electrolytes can be operated in the temperature window between 0 °C and 50 °C. The Fe/V flow battery with sulfate-chloride mixed-acid electrolyte using a polyethylene microporous separator as membrane delivers satisfactory cell efficiencies over 50 cycles, rendering great potential for developing a low-cost and long-life Fe/V RFB for large-scale energy storage.

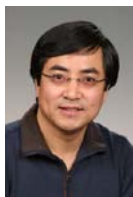
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BIOGRAPHICAL NOTE



Conference presenter: Dr. Liyu Li has broad experience in the fields of clean coal and biomass utilization, carbon dioxide capture, and redox flow batteries for grid-level electricity storage. He also has broad experience in developing inorganic absorbents, hydrogen storage materials, heterogeneous catalysts, inorganic ion exchangers, and glass and ceramic nuclear waste forms. He has published 60

peer-reviewed scientific papers and has given more than 100 presentations at national and international scientific conferences in these areas. He also holds five U.S. patents, three foreign patents, and has eight U.S. patent applications on file. Dr. Li is a project manager and lead principal investigator at Pacific Northwest National Laboratory. At this position, he has both research management and technical supervisory responsibilities for the execution of governmental and industrial projects. Dr. Li joined Pacific Northwest National Laboratory in 1998.