Degradation mechanisms in the non-aqueous vanadium acetylacetonate redox flow battery ☆

Aaron A. Shinkle [a], Alice E.S. Sleightholme [a], Lucas D. Griffith [a],
Levi T. Thompson [a,b], Charles W. Monroe [a,*]

[a] Department of Chemical Engineering, University of Michigan, Ann Arbor 48109-2136, USA
[b] Department of Mechanical Engineering, University of Michigan, Ann Arbor 48109-2136, USA

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ABSTRACT

Electrochemical and physical measurements elucidate several thermodynamic properties and chemical factors that affect the performance of a non-aqueous all-vanadium flow battery. An H-type test cell was constructed that demonstrates stable coulombic efficiencies of 70% without flow after several weeks of slow cycling, with a steady plateau voltage near 1.7 V during most of the discharge step. Environmental oxygen and water are associated with side reactions that affect long-term charge/discharge response of the battery. Oxygen passivates the electrode and may react with the solvent or supporting electrolyte, while water can cause the formation of oxovanadium complexes. Reversible cycling of the vanadyl acetylacetonate complex appears possible.

1. Introduction

Grid penetration of intermittent renewable energy sources, which is presently increasing at rates of up to 50% per annum [1], cannot continue without a parallel development of methods to store massive quantities of energy. Redox flow battery (RFB) systems promise efficient, scalable energy storage well suited for such large-scale applications [2,3]. Interest in flow batteries began more than 30 years ago and several system chemistries have been demonstrated in the intervening decades [2,3]. The most commonly implemented systems sustain little capacity fade over time, are minimally susceptible to self-discharge, and have relatively high energy and power efficiencies. Existing RFB technologies are used to manage excess capacity on the utility grid [4] and level or shave the intermittent power delivered by distributed wind or solar energy systems [5,6].

Fundamental performance characteristics of an RFB cell are determined primarily by the redox-active species, solvent, supporting electrolyte, and separator material. The choice of redox-active species determines the RFB cell voltage. In combination with the solvent, the active species also dictate the electrochemical stability and charge capacity of the fluids. Separator materials inhibit RFB self-discharge. Because ions from the supporting electrolyte move across the separator to maintain an overall charge balance during cell operation, the separator and support also affect the power and energy efficiency of the battery [7]. State-of-the-art RFB systems offer saturated active-species concentrations of 2–3 M [8]. When tested in H-cell configurations they yield coulombic efficiencies of 75–85% and discharge at potentials near 1.5 V with energy efficiencies of 60–70% [9,10]; more refined reactor designs demonstrate coulombic efficiencies of up to 97% with 86% energy efficiency [11]. Most RFBs use water as a solvent, an acid support, and a microporous [7] or ion-exchange membrane [12] separator.
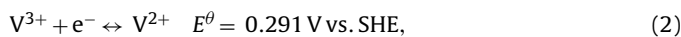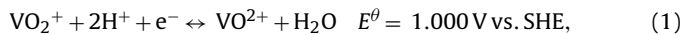
The original RFB configurations used different redox-active species in the anolyte (which contains the negative electrode, an anode during discharge) and catholyte (positive, a cathode during discharge). Examples of dual-active-species RFB chemistries include the iron/chromium, iron/titanium, and sodium-polysulfide/bromine hybrid systems, as well as the recently commercialized zinc/bromine hybrid system [13–17]. Like polymer-electrolyte fuel cells, all RFB implementations suffer from active-species crossover, and most require periodic electrolyte reactivation following long-term operation [7,18,19]. Dual active-species chemistries may be problematic because they can degrade irreversibly when constituents of the anolyte and catholyte mix.

Single active-metal RFBs, which include the popular aqueous all-vanadium system suggested by Pelligri and Spaziante [20] and later realized by Skyllas-Kazacos [21–23], mitigate the crossover problem by employing redox-active species that contain a single active-metal center. In single-metal RFBs, crossover only causes self-discharge, a reversible process that can occur without degrading the electrolyte materials.

Although it relies on a single active metal, the aqueous all-vanadium system employs four distinct redox-active species to maintain a sufficiently high cell voltage. During discharge, V^V reduces to V^{IV} on the positive electrode and V^{II} oxidizes to V^{III} at the negative electrode. The catholyte contains vanadyl and pervanadyl ions, whereas the anolyte contains vanadium ions. In sulfuric acid at pH near zero, the all-vanadium RFB half-reactions are [22–26]

$$VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O \quad E^\theta = 1.000\,V\ \text{vs. SHE}, \tag{1}$$

$$V^{3+} + e^- \leftrightarrow V^{2+} \quad E^\theta = 0.291\,V\ \text{vs. SHE}, \tag{2}$$

Thus the overall cell reaction is

$$V^{2+} + VO_2^+ + 2H^+ \leftrightarrow V^{3+} + VO^{2+} + H_2O \quad \Delta E^\theta = -1.291\,V. \tag{3}$$
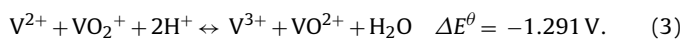
The support acid provides protons, making the equilibrium cell potential pH-dependent. Crossover in single-metal RFBs has been observed to cause as much as 10% self-discharge over 72 h [27]. Since this self-discharge involves the mixing of various oxovanadium ions with vanadium ions, the anolyte and catholyte in the aqueous all-vanadium RFB may still require periodic regeneration during the lifetime of the battery. Also, half-reaction (1) is kinetically sluggish due to the high reorganization energy of the oxovanadium species.

Chemistries that exploit one- or two-electron disproportionation of chargeable metal complexes [28–31] further refine the single-metal RFB concept because they minimize the need for regeneration steps. Recently Liu et al. [32] reported that vanadium acetylacetonate, $V(acac)_3$, could be used as the active material for a single-metal RFB involving only three redox-active species. It was proposed that the dominant electrochemical half-reactions in the non-aqueous vanadium acetylacetonate RFB are

$$V(acac)_3^+ + e^- \leftrightarrow V(acac)_3, \tag{4}$$

and

$$V(acac)_3 + e^- \leftrightarrow V(acac)_3^-. \tag{5}$$

During discharge, V^{IV} reduces to V^{III} according to reaction (4) on the positive electrode and V^{II} oxidizes to V^{III} on the negative electrode. The overall reaction is

$$V(acac)_3^+ + V(acac)_3^- \leftrightarrow 2V(acac)_3. \tag{6}$$
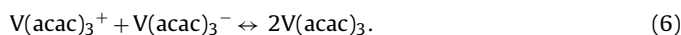
If crossover of either charged complex occurs, the negatively and positively charged species will combine in the solution phase, causing self-discharge by formation of the neutral intermediate. No regeneration is required. Since support ions are not involved in reaction (6), the concentration of supporting electrolyte should not affect the equilibrium voltage.

Only three adjacent oxidation states of vanadium appear in reaction (6), as opposed to the four states in reaction (3). Yet the energetics of half-reactions (4) and (5) lead to a standard cell potential near 2.2 V for the $V(acac)_3$ RFB reaction (6) – ~0.8 V higher than reaction (3) in 2 M H_2SO_4. Using non-aqueous supporting electrolytes, the $V(acac)_3$ RFB system has been operated for many cycles without significant deterioration [32].

This paper presents a further study of the non-aqueous vanadium acetylacetonate RFB chemistry. The discussion emphasizes how the use of non-aqueous RFB chemistries requires consideration of several new engineering aspects. For instance, the exposure of system materials to environmental oxygen and water before and during battery assembly can significantly affect performance. The charge/discharge response over long-term cycling is discussed in light of these environmental effects.

2. Experimental

2.1. Solution preparation

Non-aqueous electrolytic solutions consisted of anhydrous acetonitrile (CH_3CN, 99.8%, Aldrich, U.S.) solvent with tetraethylammonium tetrafluoroborate (TEABF$_4$, 99%, Fluka, U.S.) supporting electrolyte. Vanadium(III) acetylacetonate ($V(acac)_3$, 97%, Aldrich, U.S.) or vanadyl(II) acetylacetonate ($VO(acac)_2$, 98%, Aldrich, U.S.) active metal species were used for non-aqueous voltammetry. For solubility studies, binary solutions of $V(acac)_3$ in anhydrous CH_3CN were prepared. Charge/discharge experiments were performed with anolyte and catholyte comprised of $V(acac)_3$ and TEABF$_4$ in CH_3CN. Aqueous electrolytic solutions were prepared by dissolving vanadium(IV) oxide sulfate hydrate ($VOSO_4 \cdot xH_2O$, 99.99%, Alfa Aesar, U.S.) and sulfuric acid (99.999%, Aldrich, U.S.) in deionized water (18 MΩ, Millipore Milli-Q Advantage).

2.2. Cyclic voltammetry

Cyclic voltammetry was performed in an airtight three-compartment cell using an Autolab PGSTAT302N Potentiostat/Galvanostat (Ecochemie, Netherlands). In all voltammetry experiments, the working electrodes were 3 mm diameter (0.07 cm^2 area) glassy-carbon disk electrodes (Basi, U.S.), which were polished with 15, 6, and 0.1 μm silicon carbide polishing paper, washed, and dried for 8 h prior to each experiment. The counterelectrode was a 5 cm^2 graphite plate (Graphite Store, U.S.), which was cleaned with 15 μm silicon carbide polishing paper, sonicated for 15 min, and dried for 8 h prior to each experiment.

Reference electrodes were connected to the working-electrode compartment of the electrochemical cell via a Luggin capillary. A saturated mercury/mercurous sulfate (Radiometer Analytical, France) reference electrode was used for measurements with the aqueous electrolytic solution. Voltammetry of the non-aqueous solutions was performed using an Ag/Ag$^+$ (Basi, U.S.) reference electrode, which consisted of a silver-metal electrode immersed in a solution of 0.01 M silver nitrate (Basi, U.S., 99%) and 0.1 M tetraethylammonium perchlorate (Alfa Aesar, U.S., 98%). A bridging solution of 0.05 M tetraethylammonium nitrate (Fluka, U.S., 98%) was used to establish a thermodynamically meaningful potential for working electrodes immersed in the TEABF$_4$ support.

All the solutions were deoxygenated with pre-purified nitrogen (99.998%) prior to experiments, which were performed under a blanket of flowing nitrogen unless stated otherwise. For experiments involving oxygen, solutions were subsequently oxygenated with oxygen gas (99.993%). All the presented results were obtained after performing several cycles at 500 mV s^{-1} (until the voltammogram stabilized – typically 15 cycles) to remove any residual electrochemically active contaminants.

2.3. Battery cycling

Charge/discharge tests in a glass H-type cell were performed using an experimental design essentially similar to the test reported by Liu et al. [32]. The H-cell used for the present study was smaller, however, with an interelectrode distance of approximately 9 cm, a membrane area of 2 cm^2, and anolyte and catholyte solutions with 10 mL volumes. A Neosepta AHA anion-exchange membrane (ASTOM, Japan) was used to separate the anolyte and catholyte. Prior to cell assembly, the membrane was soaked in