Vanadium Redox-Flow-Battery (VRFB) System Electrolyte Preparation with Reducing Agents

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To meet the increasing energy demand, research effort has been devoted to the development of new and renewable energy resources. A Redox-Flow-Battery (RFB) is attractive due to its applications in large-scale energy storage [1]. RFB is a type of rechargeable battery consisting of two tanks of soluble redox reactants, which determine the system energy storage capacity, and the battery stack, which determines the system power capacity. Since the Iron/Chromium (Fe/Cr) RFB was initiated by NASA in 1970s, various redox chemistries have been developed and evaluated, such as polysulphide/bromine RFB, all-vanadium RFB, and others [2]. Among these RFB systems, vanadium redox flow batteries (VRFB) are considered especially attractive, since the electrochemically active reactants are vanadium species in four different oxidation states in both electrolyte solutions. As such, the undesired cross-contamination of anolyte and catholyte through the cell separator is eliminated, although reactant crossover still results in coulombic-efficiency losses.

VRFB employs the redox couples of V^{2+}/V^{3+} as anolyte and VO^{2+}/VO_2^+ (*i.e.*, V^{4+}/V^{5+}) as catholyte, both dissolved in aqueous acid solutions, which are stored in two external tanks. During charge and discharge, the two electrolyte solutions are pumped from the storage tanks to cells in one or more cell stacks, where the conversion between chemical energy and electrical energy takes place. The reversible potentials of the V^{2+}/V^{3+} couple and V^{4+}/V^{5+} couple are -0.26 V (RHE) and 1.0 V (RHE), respectively.

The electrolyte solutions are a key component of a VRFB system. Therefore, research has been devoted to the development of VRFB electrolyte production, including on a large scale [3]. However, many of the reported preparations have various disadvantages, which limit scalability and/or have negative cost implications. For example, very low solubility of V_2O_3 and V_2O_5 prevent the direct production of solutions with high vanadium concentrations. Low stability of some initial compounds, such as VCl_3, introduces handling difficulties. Currently, a common route to make VRFB electrolytes, especially on a lab-scale, is to dissolve vanadyl sulfate (V^{4+}) in sulfuric-acid solution, which is subsequently charged to V^{2+} and V^{5+} in anolyte and catholyte, respectively. However, in order to accommodate a change of two oxidation states in the anolyte (*i.e.*, convert V^{4+} to V^{2+}), the initial catholyte volume is twice that required, and the excess catholyte must be disposed of as waste. This is obviously not environmentally or financially desirable.

This presentation will discuss approaches to produce VRFB electrolyte solutions with high energy densities without generating waste, which is accomplished by utilizing reducing agents at relatively benign conditions. This approach enables starting a VFRB with equal volumes of vanadyl sulfate (V^{4+}) in aqueous acid for the anolyte and catholyte solutions. After an initial charge of the VFRB to V^{3+} in the anolyte and V^{5+} in the catholyte, a reducing agent is introduced into the catholyte side to reduce the produced V^{5+} solution back to V^{4+}, which

provides discharged VRFB electrolytes of V^{3+} on anolyte and V^{4+} in the catholyte. The overall process is depicted in Figure 1.

The reducing agents tested in this work include oxalic acid, formic acid, and ethanol alcohol. Oxalic acid demonstrates 100% conversion in 2-hour reaction at 60 ^{O}C and 85% conversion at room temperature, which allows for simple electrolyte production, even at a large scale. The use of reducing agents has been discussed by others (*e.g.,* [4]), and a thermodynamic model predicts 100% conversion of the reaction between V^{5+} and oxalic acid. However, the reaction kinetics observed here are significantly better than what one might expect with the two-phase reaction as reported before. It will also be shown that the electrochemical performance of a high power density VFRB cell is not affected by the electrolyte-production method described herein, relative to the results obtained with the more conventional, waste-generating method.
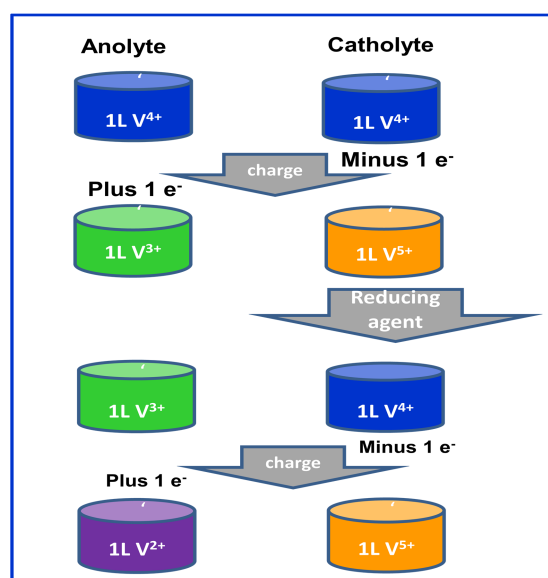

Figure 1. Simple VRFB electrolyte preparation method with no waste stream.

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