High Performance Redox Flow Batteries: An Analysis of the Upper Performance Limits of Flow Batteries Using Non-aqueous Solvents

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ABSTRACT

Redox Flow Batteries (RFBs) are a promising technology for grid-scale electrochemical energy storage. In this work, we use a recently achieved high-performance flow battery performance curve as a basis to assess the maximum achievable performance of a RFB employing non-aqueous solutions as active materials. First we show high performance in a vanadium redox flow battery (VRFB), specifically a limiting situation in which the cell losses are ohmic in nature and derive from electrolyte conductance. Based on that case, we analyze the analogous limiting behavior of non-aqueous (NA) systems using a series of calculations assuming similar ohmic losses, scaled by the relative electrolyte resistances, with a higher voltage redox couple assumed for the NA battery. The results indicate that the NA battery performance is limited by the low electrolyte conductivity to a fraction of the performance of the VRFB. Given the narrow window in which the NARFB offers advantages, even for the most generous limiting assumptions related to performance while ignoring the numerous other disadvantageous aspects of these systems, we conclude that this technology is unlikely under present circumstances to provide practical large-scale energy storage solutions.

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1. Introduction

Large-scale electrochemical energy storage is enjoying a surge of interest world-wide as an important component of systems for sustainably obtaining electricity with minimal environmental impact using renewable resources[1]. Solar and wind energy are renewable sources [2,3] that are, in general, readily available. However, an operational challenge arises because solar and wind sources are intermittent in nature [4]. Electrical energy storage devices can be applied as mediators between renewable energy farms and the electric grid, smoothing out the intermittency and enabling grid-level power generation for average, rather than peak, requirements.

Among the available energy storage technologies for large-scale applications, redox flow batteries (RFBs), as illustrated in Fig. 1, are promising candidates for this application [5]. Unlike conventional batteries, RFBs store redox active components separately from the electrochemical 'conversion' apparatus and therefore decouple the energy and the power, allowing relatively easy and inexpensive

scale-up as well as improved safety features, as discussed in the various reviews of the technology [such as 6,7,8,9]. In RFB systems, the volume and concentration of the solution determine the amount of energy that can be stored. On the other hand, the intrinsic performance of the cell controls the power density of the system and thus the size of the electrochemical converters. RFBs, in general, can be categorized in terms of the type of electrolyte used into aqueous systems [10–13], non-aqueous systems [14–16], and hybrid systems [17]. The latter include systems in which some of the redox states might be present in a solid state, such as a metal, in which case one electrode stores energy in the charged state. Several distinct characteristics among the proposed systems are the operating voltage window, the range of working temperature, cost, and safety.

Since the cell performance is strongly related to the cost of the entire system [18,19], significant efforts have been made to enhance performance of the aqueous systems [20–22]. In this work, we show representative data for a high performance all-vanadium redox flow battery (VRFB), with a peak power density of 1340 mW/cm^2. The polarization curve of this cell exhibits essentially a straight line, suggesting that only ohmic processes dominate the voltage loss during operation. This is a limiting, best-case scenario in that other sources of loss are minimized. We note
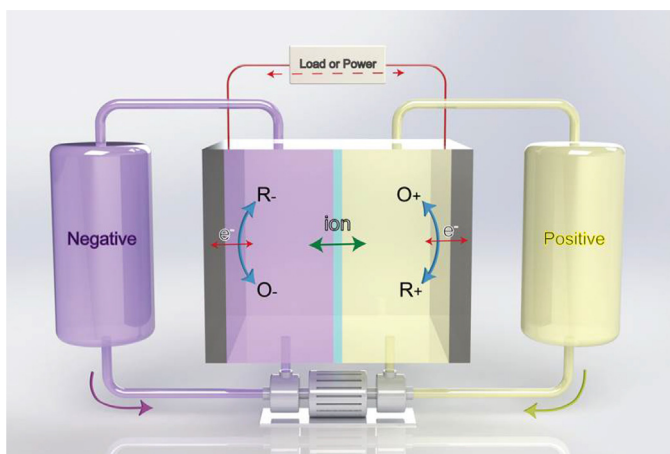
Fig. 1. Schematic illustration of the redox flow battery system.

that the operating conditions for this experiment included use of a small (5 cm^2) cell with a simple serpentine flow field and high flow rates. Testing in such a cell minimizes effects of flow or maldistribution of current, issues that are more effectively probed in larger-scale and more practical cells. However, with the elimination of those factors, such testing conditions provide a fine test bed for materials properties and their effects on cell performance. This is the primary emphasis in the analysis to come. By carrying out testing in this cell, we can also obtain meaningful results from polarization curve analysis. We can use conditions of very low utilization to avoid state-of-charge effects, as we have discussed elsewhere. When translated to a larger-scale system level, these results are subject to many other considerations, including balance of plant efficiency, notably the pumping power associated with high flow rate, and of course the cell does not operate in a short-length polarization mode in a real system.

Non-aqueous redox flow batteries (NARFB) have been proposed by several researchers as a means to improve the energy density of such systems, with the extended voltage window of the potential redox couples as a major advantage [14,15,23]. Nevertheless, the voltage loss due to ohmic effects is likely to be more significant in NARFBs, given that the conductivity of non-aqueous *organic solvent-based* electrolyte is usually at least two orders of magnitude lower than that of the aqueous acidic media. We note that the term non-aqueous refers to a very broad class of electrolytes and the conductivity of such systems as ionic liquids and similar solvents can be higher. In most ILs to date, however, the transference of the electro-active species is not necessarily high. This motivates us to compare the best-case performance limit for the aqueous and the non-aqueous RFBs by estimating the ohmic loss of the systems.

In general, the losses in the cell stem from thermodynamic, kinetic and mass transport limitations in addition to ohmic losses related to electrolyte and membrane conductivity. Thermodynamic losses show up primarily in concentration polarization effects in the cell; kinetic losses stem from any sluggish kinetics at the positive or negative electrodes; mass transport losses occur within the active porous electrode. In our previously published work, we have analyzed kinetics of electrode processes and indicated that these indeed can be sluggish. However, we also have shown that in a cell employing a suitable electrode with high internal surface areas, there is little to no loss incurred from electrode kinetics even with a carbon electrode material. Mass transport limitations will be discussed in more detail below. Considering the high-performance VRFB data to represent a proof-of concept that we

can indeed achieve pure ohmic limitation in such a device, we calculate best-case performance of non-aqueous systems using a simple ohmic model. Note that several additional factors which can be unfavorable for the NARFBs are not considered in the calculation. These are discussed at the end of this communication. This motivates a discussion of design-limiting aspects for favorable applications of the NARFB.

Recently, Darling et al. [24] presented an analysis that compared various options, including aqueous and non-aqueous redox flow battery options. However, the level of detail presented regarding performance was limited. Here we present a more detailed analysis of the latter. The point of this paper is a focus on the materials limitations incurred by some different classes of chemistry used. The losses referred to above from systems and from state of charge are likely to be similar for the aqueous and NARFB cases (though we suggest that Darling's analysis is slightly too favorable to NARFBs in terms of cost, at least.) We believe our analysis will stimulate consideration of what cell components limit performance and why, perhaps leading to improvement in NARFBs that we do not take into account in the analysis grounded in present-day reality.

2. Experimental

2.1. Vanadium solution

Vanadium solutions were prepared by dissolving vanadium(IV) sulfate oxide hydrate (99.9%, Alfa Aesar) into diluted sulfuric acid. 1.7 M VO_2^+ and 1.7 M V^{2+} in 5 M total sulfate solution were prepared by electrochemically charging the initial solution at 1.8 V until the charging current density fell to < 10 mA/cm^2 in a nitrogen environment. The resultant volume of each solution was 400 mL.

2.2. Cell configuration

Battery testing was conducted using a zero-gap cell configuration.[17] As described previously, the 5 cm^2 single cell (Fuel Cell Technologies) hardware consisted of aluminum end plates, gold-plated current collectors, and graphite blocks with a single serpentine flow field for electrolyte distribution. Multiple sheets of experimental grade carbon paper, referred as CP-ESA, were stacked at each side and served as the electrode of the battery. A single piece of Nafion 211 (Ion Power) was used as the membrane for the battery.

2.3. Polarization curve testing

Prior to the polarization measurement, the cell was conditioned by sequentially charging and discharging at 200 mA/cm^2 for several 10 min steps. The discharge polarization curve measurement[20] was performed using a Bio-Logic potentiostat coupled with a 20A booster. An applied voltage was held for 10 seconds to develop a steady state current followed by impedance spectroscopy over the frequency range from 5 kHz to 1 kHz for measuring high frequency resistance (HFR). The solution in each compartment of the individual electrodes was not recirculated. Instead, the outlet from each electrode was directed to a separate outlet bottle. This operation mode is referred to as "single pass" and allows us to maintain a controlled state of charge at each operating current. A constant flow rate of 90 mL/min was maintained with a 2 channel peristaltic pump. The battery and the solution bottles were installed in an environmental chamber set at 30 °C. Each electrolyte storage bottle was blanketed with flow of ultra-high purity nitrogen.