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Review

A review of electrolyte additives and impurities in vanadium redox flow batteries

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ABSTRACT

As one of the most important components of the vanadium redox flow battery (VRFB), the electrolyte can impose a significant impact on cell properties, performance and capital cost. In particular, the electrolyte composition will influence energy density, operating temperature range and the practical applications of the VRFB. Various approaches to increase the energy density and operating temperature range have been proposed. The presence of electrolyte impurities, or the addition of a small amount of other chemical species into the vanadium solution can alter the stability of the electrolyte and influence cell performance, operating temperature range, energy density, electrochemical kinetics and cost effectiveness. This review provides a detailed overview of research on electrolyte additives including stabilizing agents, immobilizing agents, kinetic enhancers, as well as electrolyte impurities and chemical reductants that can be used for different purposes in the VRFBs.

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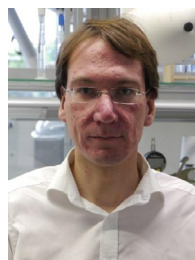
Liuyue Cao received her Bachelor's degree (2011) and Master's degree (2014) in Materials Science and Engineering from Hunan University, China. She is currently a Ph.D. candidate at the University of New South Wales, Sydney where she is working on vanadium redox flow batteries, with a focus on membrane and electrode materials.



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1. Introduction

The vanadium redox flow battery (VRFBs) pioneered at the University of New South Wales, Sydney (UNSW) in 1980s [1,2] is presently attracting increasing attention and commercial interest in both on- and off-grid energy storage applications including wind and solar energy storage, load-leveiling, peak shaving, back-up power supply and power arbitrage. By utilization of the V(V)/V(IV) and V(III)/V(II) redox couples reactions in the catholyte and anolyte respectively, the VRFB can successfully avoid cross contamination issues observed in other RFB chemistries that employ different elements in each half-cell.

Fig. 1 depicts the typical structure of a VRFB. Two pumps are used to circulate the vanadium electrolytes from the tanks to the surface of the electrodes in the cell stack where the electron transfer reactions take place. During the charging process, VO_2^+ ions in the positive half-cell are oxidized to VO_2^{+} while V^{3+} ions in the negative half-cell are reduced to V^{2+} ions. During the discharge process, reactions occur in the reverse direction. Differing from solid-state batteries, the electrolytes are not only ionic conductors, but also the cell reactants and products. Therefore, the concentration of vanadium in the electrolyte determines the energy density of the system. Though a high energy density is not the main priority for stationary energy storage systems, it is desirable in terms of reducing footprint and tank manufacturing costs.

Early UNSW studies showed that V^{2+} concentrations up to 4 M could be obtained in HCl [3,4], however, the risk of HCl vapour emissions during operation or at elevated temperatures hindered its further development at UNSW. Sulphuric acid, instead, can provide reasonable reactant concentration (2 M) and open circuit voltage (1.4 V) without hazardous gas emissions. However, the solubility of V(V) ions in sulphuric acid solution increases with total sulphate concentration and decreases with temperature while that of V(IV), V(III) and V(II) show exactly the opposite trends. Therefore, a composition of 1.5–2 M vanadium in 3–5 M sulphuric acid solution is normally recommended to achieve adequate energy density and thermal stability for vanadium ions of all valence states. Several companies including Sumitomo, Rongke Power, Imery (previously named Deeya), Glex (previously named Gildemeister), RedT etc, are using the vanadium sulphuric electrolyte with such compositions.

One critical factor for the VRFB is that efficient cell performance is dependent on the reaction kinetics of the V(V)/V(IV) and V(III)/V(II) couples. Several reviews have summarized the methods used to improve the reaction kinetics with most focussing on electrode modifications, however, only limited enhancement has been achieved so far [5–9].

Another key point is the capital cost associated with the electrolyte, especially when the VRFB system needs to meet high energy capacity requirements. Typically, for energy to power ratios greater than 4 (or energy storage capacities greater than 4 h), the electrolyte contributes a high percentage of the per kWh capital

cost, thus becoming critical to the economics of the VRFB. Vanadium pentoxide, V_2O_5 , a comparatively cheaper vanadium compound, is a typical raw material used to prepare the vanadium electrolyte. It is commercially available in a range of grades and purity levels. Although no standard for electrolyte specifications has been set in the market, an electrolyte of high purity is always favoured by customers to avoid possible negative effects on performance, and this may result in a higher cost for the electrolyte solution. In addition, facile and economic reduction methods are required to reduce the V(V) solution to lower valence states in both preparation and rebalancing processes in order to realize the indefinite cyclic life of the electrolyte. The choice of chemical reductants used could potentially introduce impurities that could impact on the long-term properties of the electrolyte.

As discussed above, the current state-of-the-art electrolyte composition for the VRFB has many benefits, but has a relatively low energy density and operating temperature range compared with other battery technologies. The use of high purity vanadium raw materials in electrolyte production can also increase the cost of the VRFB. One economically efficient approach to address these problems is to employ lower purity vanadium as raw material for electrolyte production and to incorporate additives in the electrolyte to modify the characteristics while keeping the bulk properties the same. This topic has been receiving considerable attention in recent years, however no review article has been previously published on the specific subject of vanadium electrolyte additives. This review starts with a brief introduction to the vanadium electrolyte chemistry and vanadium salt solubilities, and then categorizes and discusses the various electrolyte additives studied for the VRFB, on the basis of their function including precipitation inhibitors, immobilizing agents, kinetic enhancers, electrolyte impurities and chemical reductants. A brief description of electrolyte additives used in other vanadium-related RFB systems is also included. Finally, we probe into the future directions and perspectives of vanadium electrolyte research.

2. Understanding vanadium chemistry and stability

In the early research studies of the VRFB by Skyllas-Kazacos and co-workers at UNSW Sydney, the vanadium electrolytes were reported to have excellent stability in the temperature range of -5 to 20 °C for up to a year. Moreover, neither decomposition nor precipitation was observed during continual charge–discharge testing even at temperatures up to 60 °C, although the solution compositions and state-of-charge range used at each temperature were not disclosed. Further studies did however show that the fully charged positive electrolyte of 2 M V(V) in 2–3 M H_2SO_4 was inclined to gradually precipitate when stored at high temperatures without charge–discharge cycling [10]. Precipitation problems and possible consequences of flow restrictions or blockages in the operation of the cell thus became the focus of further detailed investigation. Al-

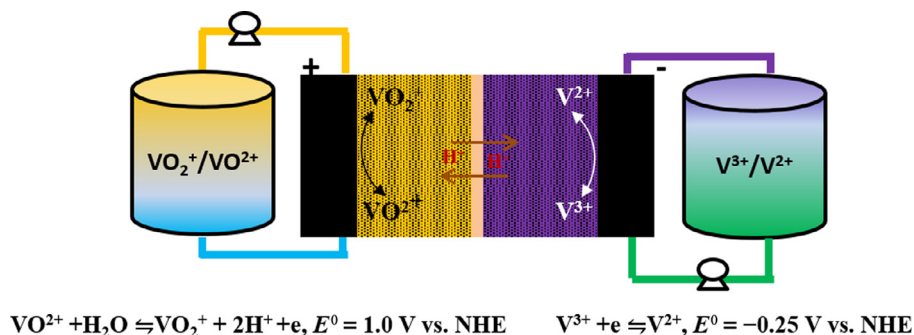


Fig. 1. Schematic of vanadium redox flow cell.

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