



A review of vanadium electrolytes for vanadium redox flow batteries



Chanyong Choi^a, Soohyun Kim^a, Riyul Kim^a, Yunsuk Choi^a, Soowhan Kim^b, Ho-young Jung^c,
Jung Hoon Yang^d, Hee-Tak Kim^{a,*}

^a Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

^b OCI R & D center, OCI Company Ltd, 61 Sagimakgol-ro, 62 beon-gil, Jungwon-gu, Seongnam-si, Gyeonggi-do 462-807, Republic of Korea

^c Department of Environment & Energy Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 500-757, Republic of Korea

^d Energy Storage Department, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea

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ABSTRACT

There is increasing interest in vanadium redox flow batteries (VRFBs) for large scale-energy storage systems. Vanadium electrolytes which function as both the electrolyte and active material are highly important in terms of cost and performance. Although vanadium electrolyte technologies have notably evolved during the last few decades, they should be improved further towards higher vanadium solubility, stability and electrochemical performance for the design of energy-dense, reliable and cost-effective VRFBs. This timely review summarizes the vanadium electrolyte technologies including their synthesis, electrochemical performances, thermal stabilities, and spectroscopic characterizations and highlights the current issues in VRFB electrolyte development. The challenges that must be confronted to further develop vanadium electrolytes may stimulate more researchers to push them forward.

1. Introduction

Renewable energy is regarded as one of the important means of providing energy with sustainability. With increasing energy consumption and limited fossil fuels, it is considered by many an inevitable choice. However, for efficient implementation of renewable energies including solar and wind energy in electric grid applications, an energy storage system (ESS), which provides storage of the electric energy from renewable sources and its on-demand release, is required. An ESS should be energy-efficient, safe, reliable, and cost-effective. In this regard, redox flow batteries (RFBs) have gained increasing attention for ESS applications. RFBs are largely characterized by their spatial separation of energy storage and energy conversion function, which cannot be attained in other secondary batteries based on solid state active materials. Furthermore, this concept can be realized by using mobile active materials dissolved in electrolytes. The electrolytes, which deliver system energy, are stored in tanks, and are supplied to a stack for charging and discharging. Therefore, power and energy capabilities are independently tailored towards a more economical system.

Among the RFBs suggested to date, the vanadium redox flow battery (VRFB), which was first demonstrated by the Skyllas-Kazacos group [1], is the most advanced, the only commercially available, and

the most widely spread RFB. In contrast with other RFBs such as Zn-Br and Fe-Cr batteries, VRFBs exploit vanadium elements with different vanadium oxidation states as positive and negative active materials, and thus are free from cross-contamination problems [2,3]. They have evolved for three decades in the industry sector, but in academic circles are considered a new area that requires in-depth understanding and further developments. VRFBs can be characterized by their multi-scale and dynamic nature based on interdisciplinary technologies. In the material science and technology sector, the developments of highly efficient and durable electrodes, membranes, electrolytes, and bipolar plates are of interest. The charge, mass, and heat transport, and cell/stack design are the major issues in the battery design sector. Furthermore, system integration to combine stacks and balance of plants (BOPs) including tanks, pumps, sensors, electrical components, and control units is highly important in employing VRFBs for the electric grid. All the technologies collectively influence the performance of VRFBs in complex manners. The interdisciplinary nature of VRFBs has been well documented in recent reviews [4–6].

In this review, we describe the vanadium electrolyte technologies from the view point of VRFB design, and summarize recent issues and approaches regarding the electrolyte design for an advanced VRFB. The vanadium electrolytes, which usually include vanadium ions, counter anions, acids, and water, are the key component for VRFBs because

* Corresponding author.

E-mail address: heetak.kim@kaist.ac.kr (H.-T. Kim).

they are the highest cost factor [7] and dominantly influence VRFB performance. In particular, the electrochemical activity and the concentration and stability of vanadium ions determine the energy density and the reliability of VRFBs [8]. Owing to the pacesetting work from the pioneers of VRFBs [9], the vanadium electrolyte technology has been notably improved, and is under evolution towards a denser, more reliable, and more cost-effective system. Some reviews on vanadium redox flow batteries listed the recent issues on the vanadium electrolytes [10,11], however, these did not provide an intensive and diversified description regarding the vanadium electrolyte compositions, properties, influences on battery performances, and electrochemical/spectroscopic analysis. Very recently, an intensive review on the physical properties and characteristics of the vanadium battery electrolyte under different conditions was published [6]. Compared to the recently published reviews, the current contribution paid more attention to the interplay of the electrolyte properties and battery performances, and to the electrochemical and spectroscopic characterizations, which have not been collectively described yet but are highly important in the electrolyte design. Also we avoided simply listing various case studies of the electrolytes but tried to describe a linkage among the previous publications. The objective of this review is to provide a logical understanding on how the electrolyte design influences the battery performances, to deliver an organized information on the analysis platforms for an advanced electrolyte design, and to inform unresolved issues and unexplored area in this technology sector. In this regard, we will first briefly summarize the functions of the VRFB electrolyte, and after that, describe specific issues related to the synthesis, solubility and stability, electrochemical performance, and spectroscopic analysis.

2. Basic principles of VRFB electrolytes

2.1. Electrochemical reactions and composition

The VRFB consists of a stack and two electrolyte tanks, as shown in

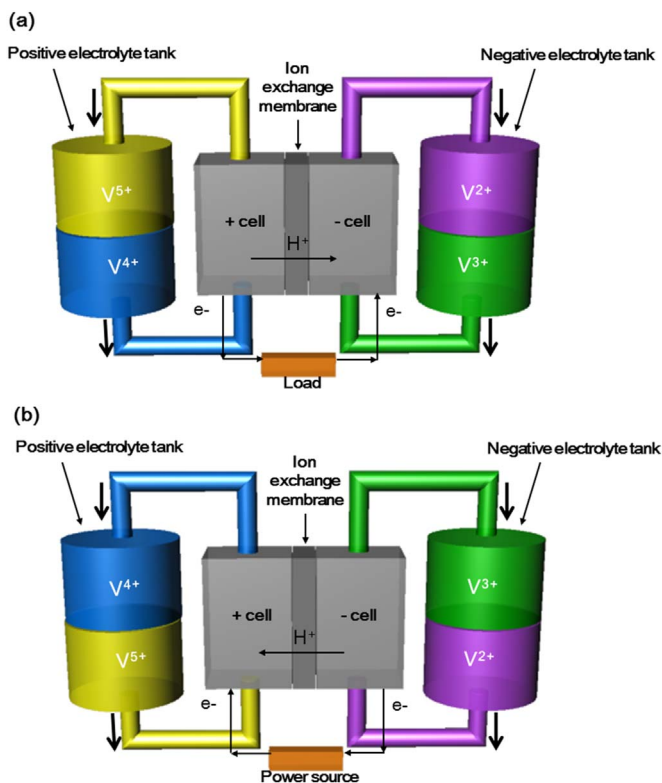
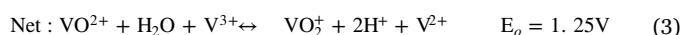
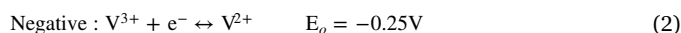
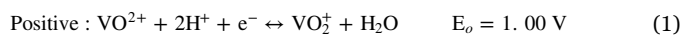


Fig. 1. Schematic of vanadium redox flow batteries. (a) Charging, (b) discharging.

Fig. 1. Positive and negative vanadium electrolytes are separately stored in the tanks, and individually circulated through the stack and the corresponding tanks. In the stack, the two electrolytes are separated by a proton exchange membrane. The carbon-felt based electrodes placed on the both sides of the membrane provide reaction sites for the electrochemical reactions of the electrolytes. However, the electrodes themselves do not participate in the redox reactions. Therefore, the durability of the electrodes is quite high when operation conditions are properly controlled [12].

At the positive electrode, the electrochemical reaction between VO_2^+ (vanadium oxidation state of +4) and VO_2^+ (+5) is as given in Eq. (1). At the negative electrode, the electrochemical reaction between V^{3+} (+3) and V^{2+} (+2) occurs as expressed in Eq. (2). In this review, VO_2^+ , VO_2^+ , V^{3+} , and V^{2+} are denoted as V(V), V(IV), V(III), and V(II), respectively, to show their oxidation states. The net reaction having a standard cell voltage of 1.25 V can be described in Eq. (3).



If V(III) is included in the positive electrolyte, V(III) is oxidized to V(IV) prior to the oxidation of V(IV) to V(V) during charging. Similarly, V(IV) in the negative electrolyte is reduced to V(III) during charging prior to the reduction of V(III) to V(II). These reactions are described in Eq. (4)



In its most common configuration, the positive VRFB electrolyte consists of V(IV) and V(V) ions in a H_2SO_4 aqueous solution, and the negative VRFB electrolyte consists of V(II) and V(III) ions in a H_2SO_4 aqueous solution [13]. During cycling, protons are transferred between the negative and positive electrode surfaces across the positive and negative electrolyte phases and proton-conducting membrane for charge balance.

2.2. Solvation structure of vanadium ions

The solvation structures and dynamics of V^{2+} , V^{3+} , VO_2^+ and VO_2^+ cations have been investigated by various techniques to understand the chemistry of the vanadium electrolyte, and they are summarized in Table 1. Both V^{2+} and V^{3+} cations are hydrated with 6 water molecules, which can be written as $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ [14–16] and $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ [14–17], forming an octahedral structure. Because of the higher charge density of V^{3+} than V^{2+} , the trivalent vanadium complex has shorter vanadium-ligand bond length and a distorted hydration structure compared to the divalent vanadium complex [15,16]. The VO_2^+ cation has 5 water molecules in the first hydration shell, and has an octahedral structure composed of 5 water molecules and a vanadyl oxygen [16,18–20]. As a result of geometry optimization, the octahedral structure of $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ is distorted by repulsion of oxy-oxygen [16,18], and the axial V-O bond length is longer than the average equatorial V-O bond length. For the VO_2^+ cation, two different hydration structures were suggested, octahedral $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ [16,21,22] and bipyramidal $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ [16,21,23]. However, a bipyramidal structure is favored over an octahedral structure as a result of geometry optimization and thermodynamic calculations [16,21,23], and therefore the bipyramidal structure is the most stable and dominant for the hydrated VO_2^+ complex.

2.3. Influence of the electrolytes on VRFB performances

From the system design perspective of the VRFB electrolytes, the energy density of the VRFB is significantly influenced by their electrochemical activities and vanadium ion concentrations. The size of the

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