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Broad temperature adaptability of vanadium redox flow battery—Part 1: Electrolyte research

Shuibo Xiao[a], Lihong Yu[b], Lantao Wu[a], Le Liu[a], Xinping Qiu[a,c], Jingyu Xi[a,*]

[a] Institute of Green Chemistry and Energy, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China
[b] School of Applied Chemistry and Biological Technology, Shenzhen Polytechnic, Shenzhen 518055, China
[c] Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China

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ABSTRACT

The broad temperature adaptability of vanadium redox flow battery (VRFB) is one of the key issues which affects the large-scale and safety application of VRFB. Typically, five types of vanadium electrolytes, namely V^{2+}, V^{3+}, $V^{3.5+}$ (V^{3+}:VO^{2+} = 1:1), V^{4+} (VO^{2+}) and V^{5+} (VO_2^{+}), are the most common electrolytes' status existing in VRFB system. In this work, the physicochemical and electrochemical properties of these vanadium electrolytes are studied in detail at a broad temperature range (-35 °C–50 °C). The results show that all types of vanadium electrolytes are stable between -25 °C–30 °C. The temperature fluctuation will largely influence the conductivity and viscosity of the electrolytes. Besides, the electrochemical properties of the positive (VO^{2+}) and negative (V^{3+}) electrolytes are greatly affected by the temperature; and the charge transfer process fluctuates more greatly with the temperature variation than the charge diffusion process does. These results enable us to better and more comprehensively evaluate the performance of the electrolyte changing with the temperature, which will be beneficial for the rational choice of electrolyte for VRFB operation under various conditions.

1. Introduction

As the environment continuously deteriorates, it's more urgent to develop renewable energy to replace traditional energy resources. However, the random and intermittent nature of renewable energy resources like solar energy and wind energy induces instability to the grid, which vastly limits their development [1–3]. In order to smooth out the intermittency of renewable energy production, electrical energy storage (EES) has become an indispensable part to integrate the grid and renewable energy [4]. Among different kind of energy storage technologies, redox flow batteries (RFB) have been proposed as a promising large-scale EES, owing to its low cost, flexible design, high safety and long cycle-life [5,6].

A redox flow battery is an electrochemical system which stores electric energy in two separated electrolyte tanks containing different redox couples. Among various RFBs, the all-vanadium redox flow battery (VRFB) is one of the most developed RFBs due to its high energy efficiency, elimination of electrolyte cross-contamination, and low capital cost for large-scale energy storage [7–10]. The standard open circuit potential of VRFB is 1.26 V, and it uses $V_{(IV)/V(V)}$ and $V_{(II)/V(III)}$ dissolved in sulphuric acid as the positive and negative electrolytes respectively, carbon fabric materials as the electrodes, and ion exchange membranes (IEMs) as the separators [11–13]. Until now, much effort has been devoted to fully study and promotes the technique of the VRFB, such as low cost and high ion selectivity membranes [14–18], high activity and power density electrodes [19–21], and high concentration and stability electrolytes [22,23].

The current VRFB technology is still not ready for broad market penetration due to the low energy density (< 25 Wh kg^{-1}), which is mostly caused by the low solubility and stability of the electrolyte solutions [24]. There are many factors affecting the VRFB performance such as the concentration of vanadium ions and sulfuric acid, the operating temperature, the state of charge (SOC) and the electrochemical activity of electrodes [25], among which the operating temperature influence should be especially noticed. Usually, $V_{(II)}$, $V_{(III)}$, and $V_{(IV)}$ are inclined to form precipitation under a relatively low temperature, while the $V_{(V)}$ solution presents poor stability at high temperatures and high vanadium concentrations

* Corresponding author.
E-mail address: xijy@tsinghua.edu.cn (J. Xi).

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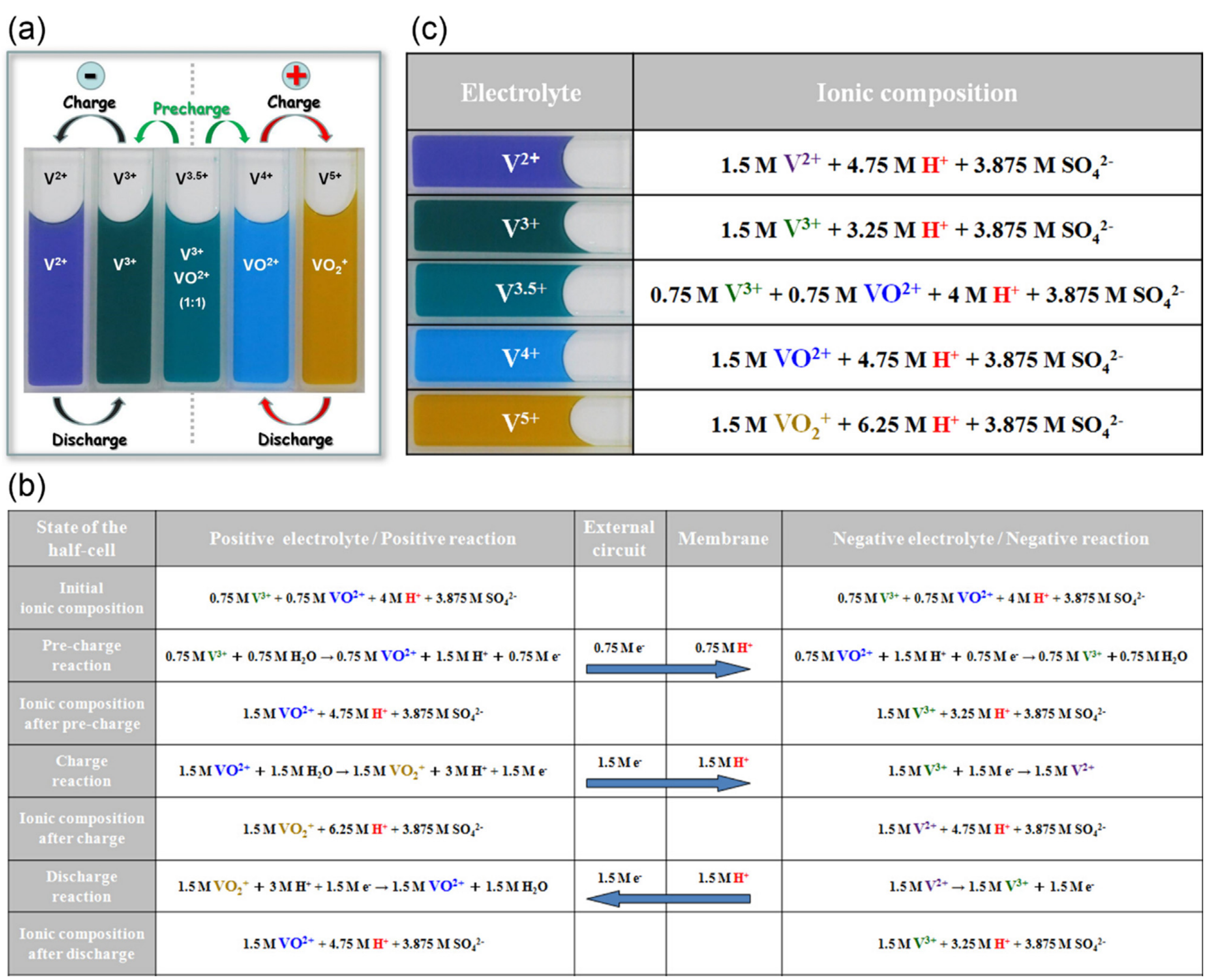
[26]. Detailed studies have been conducted on the solubility of vanadyl sulfate in concentrated sulfuric acid solutions based on the solubility [27,28]. Great efforts have been directed to prevent or delay the precipitation in the electrolyte of the VRFB. It is found that high sulfuric acid concentration can dramatically enhance the stability of $V_{(V)}$ solution. But it also takes negative impact on the solubility of the $V_{(II)}$, $V_{(III)}$, and $V_{(IV)}$ ions [22]. Some organic or inorganic chemicals can be used as additives to stabilize the vanadium ions [29–34]. These additives could improve the stability of the electrolyte in a relatively wide range of temperatures (-5 °C–40 °C). Yang et al. proposed another strategy employing chloride [35] or a sulfate-chloride mixed acid system [24] as the supporting electrolytes instead of the pure sulfuric acid solutions, which shows better thermal stability and solubility.

As an energy storage device, VRFB is usually used in different climates areas. The environmental temperature can affect the properties of electrolyte and electrode kinetics pronouncedly, which thereby influences the battery performance. Unfortunately, there have been few specific reports dealing with the temperature influences on the electrolyte properties. In this paper, we focused on temperature effect on the physicochemical and electrochemical properties of the different vanadium ion solutions ($V_{(II)}$, $V_{(III)}$, $V^{3.5+}$, $V_{(IV)}$ and $V_{(V)}$) from -35 °C to 50 °C. In order to establish a scientific and reasonable research method, the electrolyte with a moderate composition of 1.5 M vanadium in 3.875 M total sulphate was selected in this series of study. The static stability, viscosity, conductivity, cyclic voltammetry and electrochemical impedance spectroscopy of the electrolytes were investigated and compared. These features are used to evaluate and predict battery performance varying with the temperature, and then can further be used to determine the electrolyte composition referring to the environment.

2. Experimental

2.1. Preparation of electrolyte

The initial $V^{3.5+}$ electrolyte ($V_{(III)}/V_{(IV)}$ = 1:1) was prepared by electrolytic dissolution of the suitable weight of V_2O_5 in the H_2SO_4 supporting electrolyte. Then, the $V^{3.5+}$ electrolyte was injected into a vanadium redox flow battery (VRFB) and charged at a constant current density of 80 mA cm^{-2}. The detail parameters of the VRFB single-cell was described previously [36,37]. By precisely controlling the charged electric quantity, four kinds of pure vanadium electrolyte with single valence could be obtained, namely the violet electrolyte of $V_{(II)}$, the green electrolyte of $V_{(III)}$, the blue electrolyte of $V_{(IV)}$ and the yellow electrolyte of $V_{(V)}$. In this paper, $V_{(II)}$, $V_{(III)}$, $V^{3.5+}$, $V_{(IV)}$ and $V_{(V)}$ are used to denote V^{2+}, V^{3+}, $V^{3.5+}$, V^{4+}



(c)

Electrolyte	Ionic composition
V^{2+}	1.5 M V^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}
V^{3+}	1.5 M V^{3+} + 3.25 M H^+ + 3.875 M SO_4^{2-}
$V^{3.5+}$	0.75 M V^{3+} + 0.75 M VO^{2+} + 4 M H^+ + 3.875 M SO_4^{2-}
V^{4+}	1.5 M VO^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}
V^{5+}	1.5 M VO_2^+ + 6.25 M H^+ + 3.875 M SO_4^{2-}

(b)

State of the half-cell	Positive electrolyte / Positive reaction	External circuit	Membrane	Negative electrolyte / Negative reaction
Initial ionic composition	0.75 M V^{3+} + 0.75 M VO^{2+} + 4 M H^+ + 3.875 M SO_4^{2-}			0.75 M V^{3+} + 0.75 M VO^{2+} + 4 M H^+ + 3.875 M SO_4^{2-}
Pre-charge reaction	0.75 M V^{3+} + 0.75 M H_2O → 0.75 M VO^{2+} + 1.5 M H^+ + 0.75 M e^-	0.75 M e^- →	0.75 M H^+ →	0.75 M VO^{2+} + 1.5 M H^+ + 0.75 M e^- → 0.75 M V^{3+} + 0.75 M H_2O
Ionic composition after pre-charge	1.5 M VO^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}			1.5 M V^{3+} + 3.25 M H^+ + 3.875 M SO_4^{2-}
Charge reaction	1.5 M VO^{2+} + 1.5 M H_2O → 1.5 M VO_2^+ + 3 M H^+ + 1.5 M e^-	1.5 M e^- →	1.5 M H^+ →	1.5 M V^{3+} + 1.5 M e^- → 1.5 M V^{2+}
Ionic composition after charge	1.5 M VO_2^+ + 6.25 M H^+ + 3.875 M SO_4^{2-}			1.5 M V^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}
Discharge reaction	1.5 M VO_2^+ + 3 M H^+ + 1.5 M e^- → 1.5 M VO^{2+} + 1.5 M H_2O	← 1.5 M e^-	← 1.5 M H^+	1.5 M V^{2+} → 1.5 M V^{3+} + 1.5 M e^-
Ionic composition after discharge	1.5 M VO^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}			1.5 M V^{3+} + 3.25 M H^+ + 3.875 M SO_4^{2-}

Fig. 1. (a) Photographs of five types of vanadium electrolytes. The corresponding vanadium species changes during precharge and charge-discharge process is also shown in the figure; (b) Reaction equations of the vanadium electrolytes in positive and negative half-cell during different status of the VRFB; (c) Ionic compositions of the five types of vanadium electrolytes.