Electrochimica Acta 191 (2016) 695–704

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Broad temperature adaptability of vanadium redox flow battery—Part 2: Cell research

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

[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

ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form 13 January 2016
Accepted 20 January 2016
Available online 22 January 2016

Keywords:
Vanadium redox flow battery
Temperature adaptability
Efficiency
Cycling stability
Capacity fading

ABSTRACT

The operating temperature of vanadium redox flow battery (VRFB) will change with seasons and places. Hence, the broad temperature adaptability of VRFB is one of the key issues which affect its large-scale practical application. In our previous work, we have reported the impact of temperature (−35 °C–50 °C) on the static stability, physicochemical and electrochemical properties of five typical vanadium electrolytes (Electrochim. Acta, 2016, 187, 525). As a follow-up study, VRFB single cells are evaluated in this paper at a broad temperature range under current density of 40–200 mA cm^{-2}. The results show that VRFB can operate from −20 °C to 50 °C with acceptable energy efficiency under appropriate current densities (e.g. 65%–78% at 100 mA cm^{-2}). Ohmic and polarization resistances of VRFB decrease with temperature while the voltage efficiency and electrolyte utilization present the opposite tendency. The fast crossover of the vanadium ions at high temperatures aggravates the capacity fading of the cell. Notably, VRFB suffers much more damage during alternate temperatures operation between moderate temperature and high temperature, which should be given special attention.

1. Introduction

With the non-renewable resources exhausted rapidly and continuously, the renewable energy resources have been developed quickly to meet the increasing energy demand and to reduce the carbon emission [1,2]. Energy storage system is indispensable to the renewable energy resources owing to its intermittency property. The all-vanadium redox flow battery (VRFB), as one of the most promising large-scale energy storage batteries, has got much attention and acquired great progress for the sustaining investigation [3–10].

Much effort has been contributed to improve the performance and decrease the cost of VRFB, for example seeking high concentration electrolyte [11–19], high power density electrodes [20–24], low-cost and high ion selective membranes [25–31]. However, specialized studies in terms of temperature-related performance of VRFB are few up to our knowledge [32–35]. Teng et al. studied the effect of temperature (25 °C–45 °C) on the charge-discharge and self-discharge process of VRFB (1 M vanadium electrolyte, 25 cm^2 electrode) under the current density of 40 mA cm^{-2} [32]. Mohamed et al. reported the effect of temperature (15 °C–35 °C) on the efficiencies of VRFB (1.6 M vanadium electrolyte, 25 cm^2 electrode) under the current density of 60 mA cm^{-2} [34]. Zhao et al. carried out a preliminary study by using fuel cell method to test the polarization curves of VRFB (1 M vanadium electrolyte, 5 cm^2 electrode) in the temperature range of 15 °C–55 °C [35]. It can be seen that relatively narrow temperature ranges, especially at low temperatures, have been studied in previous works.

The broad temperature adaptability of VRFB is one of the key issues which affect the large-scale and safety application of VRFB. Unfortunately, the suitable operating temperature of VRFB is limited within the range of 10 °C–40 °C due to the instability of vanadium electrolyte [4,36]. 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 concentration [19]. Skyllas-Kazacos and co-workers have done a great deal of work to improve the concentration and stability of vanadium electrolytes by optimizing the electrolyte composition and adding some additives [11–16]. Researchers at the Pacific Northwest National Laboratory (PNNL) have proposed another strategy employing chloride [37] or a

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

http://dx.doi.org/10.1016/j.electacta.2016.01.165

sulfate-chloride mixed acid system [38–40] as the supporting electrolytes instead of the pure sulfuric acid solutions, which shows better thermal stability and solubility.

Practical application of VRFB at extended temperature range is more important than that of static stability test of independent materials such as vanadium electrolytes, membranes and electrodes. Recently, a few researches focusing on the VRFB evaluation of high concentration electrolytes and novel membranes at broad temperature ranges have been reported [41–44]. Skyllas-Kazacos and co-workers have studied the effect of a wide range of additives (e.g. inorganic acids and salts, low-molecular-weight organic compounds, polymeric organic compounds and polyphosphate-based additives) on the low temperature (1 °C and 5 °C) stability of $V_{(II)}$ and $V_{(III)}$ electrolytes and tested the VRFB performance at 5 °C under the current density of 40 mA cm^{-2} [41]. Skyllas-Kazacos and co-workers have also studied the effect of inorganic additives (phosphate and sulphate salts et al.) on the high temperature (50 °C) stability of $V_{(V)}$ electrolyte and tested the VRFB performance at 45 °C under the current density of 40 mA cm^{-2} [42]. Li and Zhang et al. have reported the successful application of low-cost porous nanofiltration membranes in VRFB at −5 °C–50 °C under the current density of 80 mA cm^{-2} [43,44].

With the aim of extending the operating temperature limit of the VRFB, our strategy is to carry out a series of fundamental research around the theme of broad temperature adaptability of VRFB. 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 is selected in this series of study. In the first part of this work [45], we have reported the broad temperature adaptability of five types of vanadium electrolytes, namely $V_{(II)}$, $V_{(III)}$, $V^{3.5+}$ (V^{3+}:VO^{2+} = 1:1), $V_{(IV)}$ (VO^{2+}) and $V_{(V)}$ (VO_2^+). The static stability, viscosity, conductivity, cyclic voltammetry and electrochemical impedance spectroscopy of the electrolytes have been investigated and compared in the temperature range of −35 °C–50 °C. These results enable us to 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.

In this study, the electrochemical characterization, battery performance and long-term cycling stability of VRFB in the temperature range of −20 °C–50 °C are presented comprehensively. The capacity fading mechanism under both constant temperatures and alternate temperatures is discussed in details.

2. Experimental

2.1. Construction of broad temperature research platform

The broad temperature research platform consists of VRFB single cell, peristaltic pumps (BT100M, Baoding ChuangRui), thermostat (GDH-2005B, Shanghai JingHong), electrochemical workstation (PARSTAT 2273, Ametek) and battery testing system (CT-3008W-5V6A, Neware), as shown in Fig. 1. The temperature deviation of the thermostat was ±0.5 °C. The detailed parameters and structure of the VRFB single cell were described previously [46–48]. Two 50 mL solutions of 1.5 M $V^{3.5+}$ (V^{3+}:VO^{2+} = 1:1) with 2.0 M free sulfuric acid were used as positive and negative electrolytes, respectively. The electrolytes were cyclically pumped into VRFB with a flow rate of 60 mL min^{-1}. A Nafion 117 membrane (7 cm × 7 cm) pretreated according to the standard procedure [28] was used as the separator. Two graphite felts (5 cm × 5 cm × 0.5 cm, Gansu Haosi) thermal activated in air at 420 °C for 10 h were used as the electrodes. The VRFB single cell and the electrolyte tanks were put in the thermostat while the peristaltic pump was put outside the thermostat, as shown in Fig. 1. All the electrolyte pipelines were covered with heat preservation cotton to maintain the setting temperature. The electrolyte temperature would be slightly different in each part of the flow loop such as in the tank, pipe and cell. So, the temperature mentioned in this paper is corresponding to the electrolyte tank and single cell.

2.2. Characterization

Electrochemical impedance spectroscopy (EIS) of the VRFB single cell was performed on electrochemical workstation after the temperature maintained at the set point for an hour. The test frequencies were controlled between 10^{-3} and 10^{6} Hz and the amplitude voltage was 5 mV. The EIS was record at both the initial state ($V^{3.5+}$ in the positive and negative electrolyte) and after pre-charge state (pure $V_{(III)}$ in the negative electrolyte and pure $V_{(IV)}$ in the positive electrolyte) of the cell [45].

A scanning electron microscope (SEM, Supra® 55, Zeiss) was used to study the surface morphology of the graphite felt electrodes before and after test. The used graphite felt electrodes

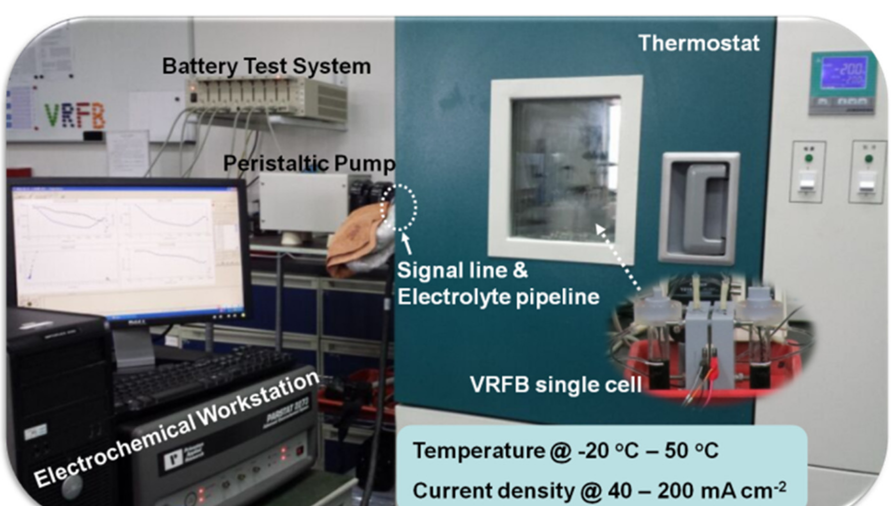

Fig. 1. Photograph of the research platform used to study the broad temperature adaptability of VRFB.