

A new insight into electrode processes of vanadium redox flow battery by thermo-electro-chemistry method



Minghua Jing^a, Ye Qin^{a,*}, Quan Shi^b, Jianguo Liu^{a,*}, Chuanwei Yan^a

^a Liaoning Engineering Research Center for Advanced Battery Materials, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

^b Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

ARTICLE INFO

Article history:

Received 12 September 2017

Received in revised form 12 October 2017

Accepted 16 October 2017

Available online 5 November 2017

Keywords:

Thermo-electro-chemistry

Vanadium redox couples

Electrode process

Oxygen evolution

VRFB

ABSTRACT

In this study, the electrochemical reactions along with the corresponding temperature change in the vanadium acid solutions have been investigated by the thermo-electro-chemistry method for the first time. It turned out that the electrochemical oxidation of V(II) and reduction of V(V) are both exothermic, so substantial heat could be created by the electrochemical reaction during the discharging process, which may adversely affect the stability and efficiency of the VRFB. The temperature change characters of different electrochemical redox reactions imply that lower temperature may be advantageous for the discharge process, while higher temperature is helpful to the charge process. Besides, oxygen evolution as a main side reaction along with the oxidation of V(IV) is seen to occur at a relatively lower potential and highly depends on the vanadium ion concentration in the electrolyte. Moreover, it is found that the V(III)/V(IV) solution is more likely to suffer from oxygen evolution in oxidation processes and hydrogen evolution in reduction processes than pure V(IV) and V(III) solutions. These results demonstrate that the thermo-electro-chemistry method shows great significance and application prospect in investigating the electrode kinetics and will be helpful to optimize the work conditions and related components in a VRFB.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Vanadium redox flow battery (VRFB) as a promising large-scale energy storage system has aroused increasing attention. Investigations on its electrode processes are particularly important for better understanding the kinetics and further improving the battery performance [1–3]. At present, electrochemical measurements have been widely used to analyze the electrochemical processes of vanadium redox couples [4–9]. However, the thermal response during the electrochemical reactions have not been investigated although it will supply more comprehensive information related to the electrode processes, and the generating heat from electrochemical reactions is non-negligible in a large-scale VRFB energy storage system.

Thermo-electro-chemistry method is an effective technique to monitor the thermal response on the electrode surface during the certain electrode processes, and it has been applied to a variety of practical applications [10,11], particularly for reflecting the certain

electrode processes. Yasuhis [12] clarified the electrochemical Peltier heat in a polypyrrole- NaClO_4 aqueous solution system by the thermo-electro-chemistry method and evaluated the entropy change in the dedoping process of ClO_4^- ions, suggesting the significance of the thermo-electro-chemistry technique for obtaining useful knowledge on the electrochemical process of conducting polymers from the viewpoint of entropy change. Xiao [13] studied the thermal-electrochemical behaviors of various lithium ion batteries with different cathode materials by electrochemical-calorimetric technique and concluded that improving the charge-discharge rate would increase heat production and enthalpy change and decrease discharge capacity. Moreover, greater entropy value would arouse greater confusion degree and worse reversibility. These results provided a theoretical basis for optimizing battery design and choosing suitable charge-discharge rate for more effective thermal management. As we all know, electrode processes and temperature are both of great significance and need to be considered seriously in the vanadium redox flow battery (VRFB) design and control for an efficient and safe operation. However, so far there are no research reports with respect to VRFB applications on monitoring of electrochemical reaction heat using such a sensing approach.

* Corresponding authors.

E-mail addresses: yqin@imr.ac.cn (Y. Qin), jgliu@imr.ac.cn (J. Liu).

In this study we are the first to investigate the use of this novel analytical approach for effective investigating the electrode processes in a VRFB. We know that the generating heat in a VRFB is mainly come from ohmic resistance, pump power and electrochemical reactions. At present, researchers have put forward the ideas of reducing the released heat through decreasing the internal resistance and optimizing the pump revolution speed for better battery stability and higher system efficiency. However, the thermal response during the electrochemical reactions have not been investigated in a VRFB, although this part of heat should not be ignored in the large-scale energy storage batteries. Herein, thermo-electro-chemistry method has been applied firstly in investigating the thermal response during the electrochemical redox reactions of different vanadium ions for further optimizing the operating conditions of VRFB.

Besides, it is generally believed that the overpotential of oxygen evolution side reaction (OER) is higher enough than the oxidation of V(IV), and the adverse effects from OER towards the charging processes is negligible. In this work, the lower onset potential of OER on the graphite electrode has been observed by the thermo-electro-chemistry method for the first time and it highly depends on the concentration and species of vanadium ions in the electrolyte, which suggesting that the OER is another critical factor affecting the battery performance and system efficiency.

Moreover, we firstly found the effect of the valence state of vanadium ions on the extent of oxygen and hydrogen evolution side reactions.

All these results will be of help in optimizing the key components and specific operating conditions for a VRFB. The thermo-electro-chemistry method will have broad application prospects in investigation the electrode processes in a VRFB.

2. Experimental

A three-electrode system with spectroscopically pure graphite (0.385 cm^2) as the working electrode, a piece of platinum (4 cm^2) as the auxiliary electrode and saturated calomel with a salt bridge full of saturated KCl solution as the reference electrode are placed in a U-type compartment [14]. Specially, a thermistor is embedded into the working electrode and sealed with epoxy resin. The SRC-100 Solution-Reaction Calorimeter [14] (Wuhan University, China) with a precision resistor inside is used to measure temperature change on the working electrode surface and output potential signals when electric current passed through. The corresponding electric current and electrode potential signals are simultaneously collected by a Gramy reference 600 electrochemical workstation. In this experiment, all chemicals are analytical reagent and all solutions are prepared with de-ionized water.

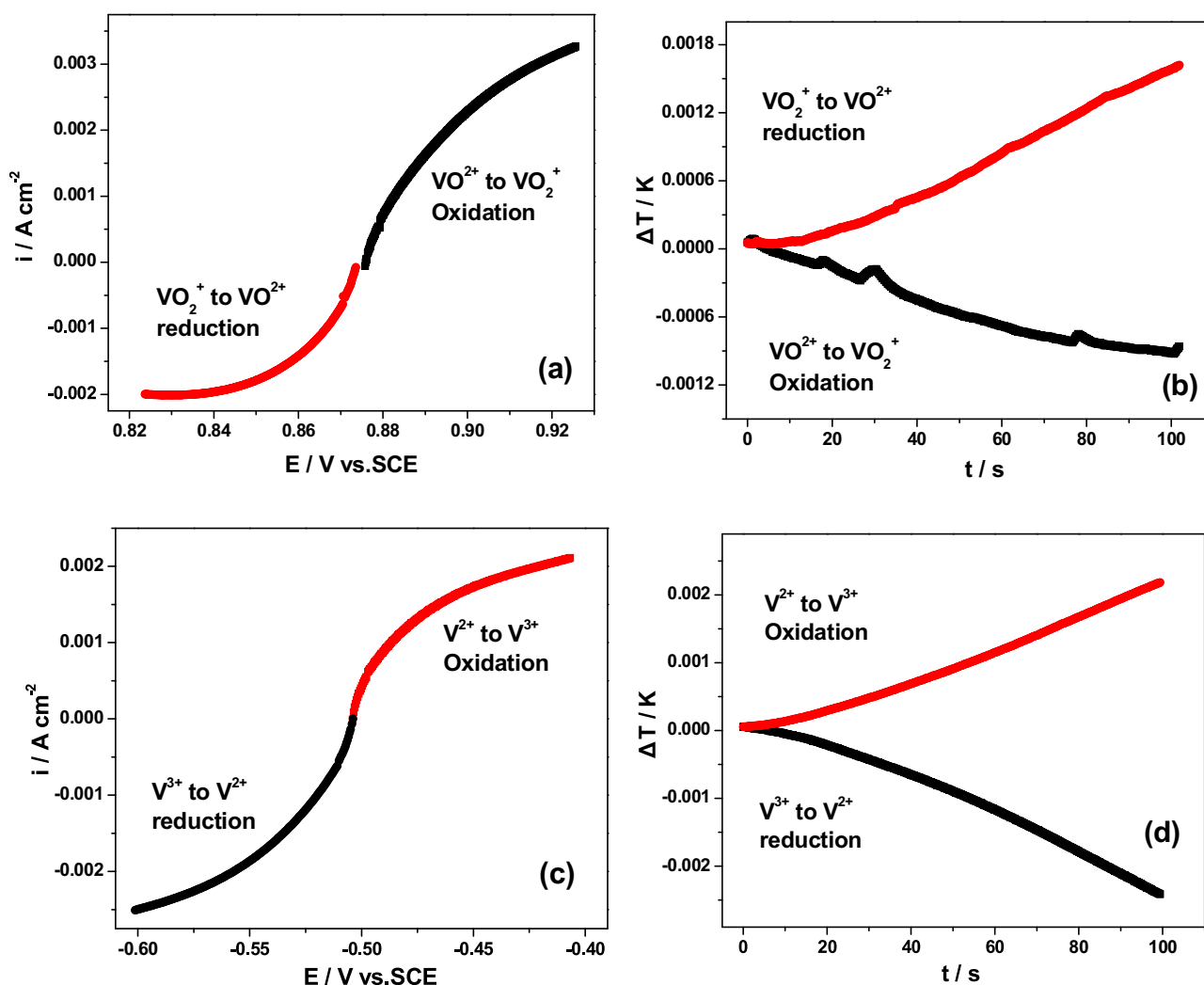


Fig. 1. Linear sweep voltammograms on the spectroscopically pure graphite electrode in $0.1 \text{ M (IV)}/0.1 \text{ M (V)} + 2.0 \text{ M H}_2\text{SO}_4$ (a) and $0.1 \text{ M (II)}/0.1 \text{ M (III)} + 2.0 \text{ M H}_2\text{SO}_4$ (c) and the corresponding temperature variation curves (b) (d).

Download English Version:

<https://daneshyari.com/en/article/7540274>

Download Persian Version:

<https://daneshyari.com/article/7540274>

[Daneshyari.com](https://daneshyari.com)