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Rapid detection of the positive side reactions in vanadium flow batteries

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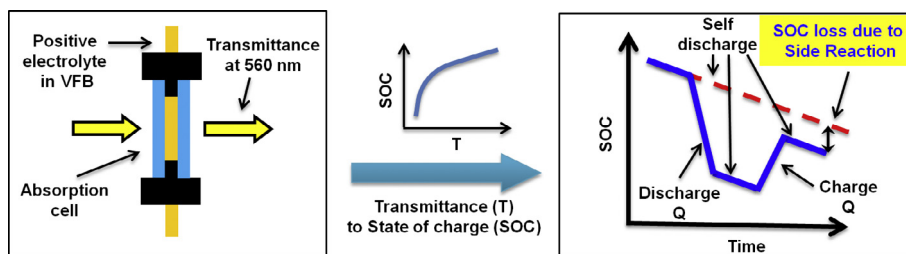
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HIGHLIGHTS

- A method for rapid measurement of the positive side reactions in VFB is presented.
- The SOC of positive electrolytes can be detected with resolution of 0.002%.
- Side reaction ratios at different charge currents, flow rates are obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

We present an optical detection method for rapid measurement of the positive side reactions in vanadium flow batteries (VFB). By measuring the transmittance of the positive electrolytes in VFB, the states of charge (SOC) of the positive electrolytes can be detected at very high resolution (better than 0.002% in the SOC range from 98% to 100%), due to the nonlinear transmittance spectra caused by the interactions between V(IV) and V(V) ions. The intensity of the positive side reactions of a VFB can be rapidly measured by a few steps, attributing to the fact that the positive side reactions occur only during the high voltage charging process. The ratios of the positive side reactions at different charge currents and different flow rates are obtained while causing no damage to the battery. This optical detection method can rapidly determine the optimal parameters of the VFB system, providing new means for studying the electrochemical reactions in the VFB system and rapid test in industrial production of VFBs.

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1. Introduction

In order to use renewable energies instead of fossil fuels, energy storage techniques have been developed in recent years [1–3]. Since been invented in the 1980s, the vanadium flow battery (VFB, also known as VRB or VRFB) has become one of the most promising energy storage techniques, due to its long cycle life, high efficiency, flexible design and reliability [4–10]. Recently, lots of researches have been dedicated to the fields of the VFB, including high stable electrolytes [11–15], high performance electrodes

[16–20], high selective membranes [21–25], online monitoring and so on [26–30].

In a VFB system, the positive and the negative electrolytes are stored in separate tanks and pumped into the battery stack, where the redox reactions take place. In the charge process, the tetravalent vanadium ions V(IV) in the positive electrolytes turn into pentavalent vanadium ions V(V), and the trivalent vanadium ions V(III) in the negative electrolytes turn into divalent vanadium ions V(II). In the discharge process, these reactions reverse.

Like other electrochemical systems, side reactions involving loss and gain of electrons may take places, such as the oxidation of V(II) by oxygen, the hydrogen evolution reaction on the negative electrode and the oxygen evolution reaction on the positive electrode, etc. [31,32]. These side reactions not only reduce the efficiency of the battery, but also lead to an imbalance between the

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positive and the negative ions, deteriorating the cycle life of the VFB system [28]. Moreover, the oxygen evolution reaction on the positive electrode may cause corrosion of the graphite electrodes and damage the battery [33,34]. Oxidation of V(II) can be prevented by better sealing of the negative electrolytes, but the the hydrogen evolution reaction on the negative electrode and the oxygen evolution reaction on the positive electrode cannot be easily handled. It has been demonstrated that the hydrogen evolution reaction is a more important limitation for the performances of VFB including power density and cycle life [35–37], as the oxygen evolution reaction can be avoid by applying a cut-off voltage while the hydrogen evolution reaction cannot [38,39]. However, in industrial VFB applications, an energy storage system is consists of many VFB stacks, and each stack is made of many series connected single cells. For complexity and cost considerations, it is impossible to monitor the voltage of every single cell in an energy storage system. Furthermore, as the single cells in one VFB stack are in a series connection while the positive and negative electrolytes are parallel supplied, the “Shunt current” effect may take place and leading to corrosion of the graphite electrode by oxygen evolution side reactions [40]. Therefore, it is possible to have the oxygen evolution side reaction in the industrial VFB system. Considering the serious damage with the oxygen evolution side reaction, it is important to minimize it by controlling various conditions of the VFB system, and to evaluate the resistant ability of a produced VFB.

There are many factors which determine the level of the hydrogen and oxygen evolution side reactions (also called gassing reactions). Theoretically, lower electrolyte concentration, higher chemical activity, larger flow rate and lower charge current density will lead to lower level of gassing reactions. But in an actual VFB system, higher electrolyte concentration and higher charge current density are demanded to improve the energy and power density, smaller flow rate is required to reduce the energy consumption and the pressure of the pumps. These demands are contrary to the requirements for reducing side reactions. Therefore, methods that can detect the ratio of the side reactions are needed to determine the optimal parameters such as flow rate and current density. However, there is no such method at present. The level of the side reactions with one set of parameters can only be estimated by measuring the pressure and composition changes of the gas in the electrolyte tanks or the titration results of the electrolytes after a several charge–discharge cycles [41–43]. Such long and complicated steps are not suitable for determine the optimal parameters of a new VFB system. Also the battery may be damaged by the oxygen evolution side reactions after several charge–discharge cycles.

As the side reaction only happens during the charge process but not the discharge process, if one can precisely detect the state of charge (SOC) variation of the electrolyte of VFB in the charge process, then he can determine the ratio of the side reaction of VFB by comparing the actual SOC variation with the theoretical SOC variation brought by the charging capacity. To achieve this measurement, on-line detection of SOC with high detection resolution is required. However, traditional detection methods cannot meet this requirement. Potentiometric titration and mass spectrometry have complex steps [41–43], and therefore are not suitable for on-line detection. The traditional open-circuit voltage (OCV) method is difficult to detect the SOC of imbalanced VFBs and the sensitivity is relatively low [44]. The conductivity method [28] has low detection resolution and is vulnerable to many factors including temperature, concentration of sulfuric acid, etc. Traditional UV–vis spectrum method encounters challenges when detecting the SOC of electrolytes in VFB, as the absorbance of the positive electrolyte does not obey the Beer’s law and is not the linear combination of the absorbance of its components, due to the interactions between V(IV) and V(V) ions at such high concentration [28]. Our group

proposed an on-line spectroscopic method to monitor the electrolytes, as a solution to this challenge. Transmission spectrum rather than absorption spectrum is used for better signal noise ratio (SNR) and the entire spectrum is utilized instead of the data at one wavelength [45,46]. By comparing the transmittance spectrum of the electrolyte with the spectra in a pre-prepared database using the algorithm we proposed, SOC of the electrolyte can be on-line monitored at a SOC resolution of better than 0.5% [47]. More groups have focused on the spectroscopic study of the VRB electrolytes [26,27,48–50], with the detection resolution in the range of 0.5–1%. However, these SOC resolutions are not enough for detection of side reactions, therefore until now no on-line detection of side reactions has been reported.

In our previous work, we found that the transmittance of the positive electrolyte varies rapidly near the regions of SOC 0% (pure V(IV)) and 100% (pure V(V)), due to the interactions between V(IV) and V(V) ions in the positive electrolyte, shown in Fig. 1 (experimental results of averaged transmittance spectra at different SOC [46,47]). Such drastic change of the transmittance with SOC provides us a novel way to monitor the SOC of the VFB electrolyte at a very high resolution. In this paper, based on this nonlinear transmittance spectra and the fact that the positive side reactions occur only during the high voltage charge process [33,34], we develop a new optical detection method, which can quantitatively measure the ratio of the positive side reaction with different sets of battery parameters in a relatively short period of time. This optical detection method can rapidly determine the optimal parameters of the VFB system while causing no damage to the battery, providing new means for studying the electrochemical reactions of the VFB system and rapid test in industrial production of VFBs.

2. Experimental section

2.1. Sytem setup

Fig. 2a and b show the schematic and the photograph of the experimental setup, respectively. The experimental setup consists of two systems: the VFB system (VFB in Fig. 2) and the analyzing system (AS in Fig. 2).

In the VFB system, the positive and the negative electrolytes are stored in two tanks (T1 and T2 in Fig. 2). A magnetic stirrer (MS in Fig. 2, IKA Topolino) is placed under tank T1 to ensure that the

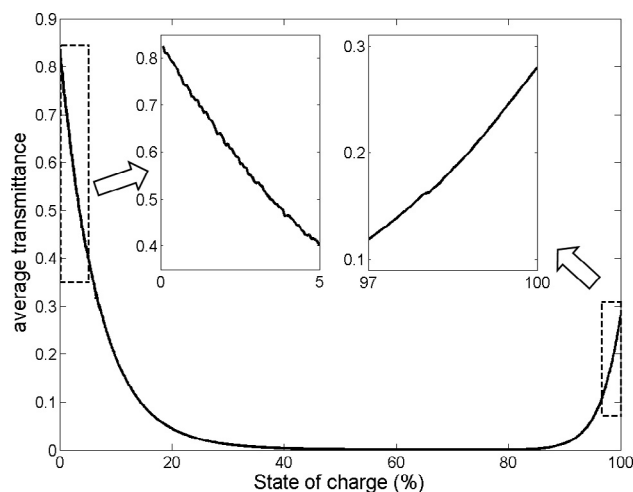


Fig. 1. The dependence of the average transmittance spectra on the state of charge (SOC) of the positive electrolyte in VFB. The averaged spectral range is 420–690 nm; the absorption length is 0.5 mm; the electrolyte has 2.0 mol L⁻¹ vanadium ions and 4.5 mol L⁻¹ sulfate ions.

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