Journal of Power Sources 390 (2018) 261–269

Contents lists available at ScienceDirect

Journal of Power Sources

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

Real-time monitoring of capacity loss for vanadium redox flow battery

Zhongbao Wei[a], Arjun Bhattarai[a], Changfu Zou[b], Shujuan Meng[c,*], Tuti Mariana Lim[d,**], Maria Skyllas-Kazacos[e]

[a] Energy Research Institute @ NTU, Nanyang Technological University, Singapore 637141, Singapore
[b] Department of Electric Engineering, Chalmers University of Technology, Gothenburg, Sweden
[c] School of Space and Environment, Beihang University, Beijing 100081, China
[d] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore
[e] School of Chemical Engineering, The University of New South Wales, UNSW, Sydney, NSW 2052, Australia

HIGHLIGHTS

- A method for online capacity loss monitoring is proposed for VRB.
- A circuit model with RLS-based online model adaption is proposed for VRB.
- Extended Kalman filter is used for online SOC and capacity loss co-estimation.
- The proposed method is verified with lab-scale experiments.

ARTICLE INFO

Keywords:
Battery modeling
Parameter identification
Capacity loss
State of charge
Vanadium redox flow battery

ABSTRACT

The long-term operation of the vanadium redox flow battery is accompanied by ion diffusion across the separator and side reactions, which can lead to electrolyte imbalance and capacity loss. The accurate online monitoring of capacity loss is therefore valuable for the reliable and efficient operation of vanadium redox flow battery system. In this paper, a model-based online monitoring method is proposed to detect capacity loss in the vanadium redox flow battery in real time. A first-order equivalent circuit model is built to capture the dynamics of the vanadium redox flow battery. The model parameters are online identified from the onboard measureable signals with the recursive least squares, in seeking to keep a high modeling accuracy and robustness under a wide range of working scenarios. Based on the online adapted model, an observer is designed with the extended Kalman Filter to keep tracking both the capacity and state of charge of the battery in real time. Experiments are conducted on a lab-scale battery system. Results suggest that the online adapted model is able to simulate the battery behavior with high accuracy. The capacity loss as well as the state of charge can be estimated accurately in a real-time manner.

1. Introduction

Energy storage systems have been playing a key role in diversifying energy sources and adding more renewable alternatives into the existing energy market [1–4]. Specifically, battery storage systems have been widely used in various applications like wind and solar energy storage, emergency back-up power, peak shaving, load-levelling and transportation electrification [5–7]. Amongst the multiple battery technologies available, the all-vanadium redox flow battery (VRB) proposed by Skyllas-Kazacos [8,9] and co-workers has shown outstanding potential due to its unique attributes of cross contamination elimination, independent capacity and power rating, tolerance to deep discharge, high energy efficiency, and long cycle [10]. While intensive studies have been performed on the cell design, testing, and performance enhancement [11–16], the system-level techniques are still under development from the perspective of real applications. A reliable battery management system (BMS) which monitors the essential battery states is pivotal to enhancing the overall reliability and efficiency, and to extending the calendar life of the VRB [1,11].

The capacity is a critical indicator in BMS. It is known that as with all types of batteries, a substantial capacity decay can occur during the long-term operation. The capacity loss of VRB majorly comes from two processes. Firstly, the different diffusion rates of vanadium species across the separator will lead to capacity loss due to a build up of

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: mengsj@buaa.edu.cn (S. Meng), TMLim@ntu.edu.sg (T.M. Lim).

https://doi.org/10.1016/j.jpowsour.2018.04.063
Received 20 February 2018; Received in revised form 13 April 2018; Accepted 17 April 2018

vanadium ions in one half-cell and a corresponding decrease in the other. This further causes an imbalance of both the volume and total vanadium species concentrations in two half-cells as water and volumetric transfer of electrolyte can also take place during charging and discharging [17,18]. Secondly, gassing side reactions at both half-cells during charging can further affect the imbalance in the vanadium species oxidation states and therefore the SOC of each half-cell, as can air oxidation of the negative half-cell electrolyte. Unlike most other battery systems however, almost all of the capacity loss in practical VRB systems can be restored by periodically partially remixing the two half-cell electrolytes. Large-scale VRB systems have been successfully operated over tens of thousands of cycles with negligible capacity loss, simply by partially remixing the two half-cell electrolytes, operating within optimal SOC limits and sealing the negative half-cell reservoir to prevent air oxidation of the V(II) ions in solution. Poor design and operation that leads to hydrogen evolution during charging at high SOCs and air oxidation of the negative half-cell electrolyte can however lead to capacity loss that cannot be restored by simple remixing. Such capacity loss requires electrochemical or chemical rebalancing, but this can be readily minimized by voltage control during charging and by sealing the negative half-cell electrolyte tank. In spite of this, the long-term operation of the VRB still relies on an advanced control system that can monitor capacity loss and make decisions on when to initiate the re-balance processes. The mathematical models used to simulate capacity loss in VRB have been investigated in recent years [19–24]. Skyllas Kazacos and Goh [22] reported models focusing particularly on the vanadium ion diffusion across separator. Concentration profiles of vanadium ions at different states were simulated as a function of time to predict the expected capacity loss over extended charge–discharge cycling. Models focusing on the hydrogen evolution [23] and oxygen evolution [24] were also built based on the mass, charge, energy and momentum conservation. The effects of different operating parameters such as flow rate, current density and temperature were systematically discussed. Tang et al. [19] further proposed a comprehensive model by incorporating the ion diffusion and side reactions together. All these studies give deep insights into the mechanism of capacity loss and are instructive to the battery design and long-term operation analysis. However, these models depend largely on the parameters which are closely tied to the system properties like the electrolyte composition and membrane material and are more suitable for system analysis and optimization. The real-time monitoring of the capacity loss in real applications needs to be further elaborated.

The model-based methods have been used in the BMS of different battery chemistries, especially for the lithium-ion battery [25–28]. The model-based observers connect the onboard measureable signals to the immeasurable battery internal states through a battery model which is mostly in the form of state-space equations [29–32]. This type of method appeals to real-time applications and has great potential to be used to monitor the capacity loss of the VRB. However, it has to be noted that an accurate model is a prerequisite for the reliable monitoring of VRB states. Till now, a variety of VRB models has been studied for either design optimization or control-oriented implementation. The electrochemical models [23,24] are characterized by complicated partial differential equations (PDEs) and are not realistic for the real-time application. To solve this problem, Tang et al. [19,33] proposed several mathematical models which simplified the electrochemical models by considering the key physical and chemical processes. One potential challenge is that the model parameters which determine the modeling accuracy are empirical and depend largely on the knowledge of battery chemistries. In contrast, the equivalent circuit models (ECMs) [34–38] demand much less physicochemical knowledge and exhibit an excellent adaptability. They can also achieve a good trade-off between the model complexity and accuracy thus has been favorable for real-time applications.

The ECM-based methods have been used for battery management applications in the VRB, albeit quite limited. Mohamed et al. [39] proposed the use of the second-order RC model for the VRB and adopted the extended Kalman filter (EKF) to identify the model parameters. A thermal-dependent ECM was developed to model the VRB dynamics while the EKF was used to online observe the state of charge (SOC) in Ref. [40]. The capacity fading factor was further incorporated and the sliding mode observer (SMO) was used to estimate the SOC of the VRB in Ref. [41]. The aforementioned methods prescribe the model parameters offline and assume them to be constant for the entire working cycles. However, the model parameters are affected by many factors such as temperature, flow rate, current magnitude and direction, SOC, and battery aging or state of health. In this regard, the estimation accuracy and robustness can easily decline if the model parameters are left without adaption. Moreover, the potential of using the model-based observers for the online monitoring of VRB capacity loss has not been investigated.

In this paper, we propose to use a first-order RC model to capture the dynamics of the VRB. The time-variant model parameters are online identified with the recursive least squares (RLS) method to keep the model accurate and robust under a wide range of operating conditions. With the online adapted battery model, an EKF-based joint estimator is formulated to observe the capacity loss of the VRB in real time. Another technical merit is that the proposed method can estimate the SOC of the VRB along with the capacity loss detection without the use of additional open-circuit cells. Lab-scale experiments are carried out to verify the performance of the proposed method. The proposed method is also compared with its offline model based counterpart to highlight its superiority in terms of the accuracy, convergence and robustness.

The rest of paper is organized as follows. Section 2 introduces the first-order RC model for VRB and the associated online model parameterization method. Section 3 discusses the EKF-based capacity loss detection and SOC estimation. Section 4 describes the experimental details. Section 5 presents the algorithm verification, comparison and discussion, while Section 6 draws the key conclusions.

2. Battery model

2.1. Battery modeling

The proposed state monitoring method depends largely on a high-fidelity battery model. The battery models with higher order are generally more accurate in capturing the nonlinear battery dynamics in multiple time scales, but the higher complexity and lower numerical stability will be the byproducts that constrain their implementation in real applications [42]. In light of this, the first-order RC model shown in Fig. 1 is used in this paper to manage the trade-off between the model complexity and precision.

The left part of Fig. 1 describes the dynamics of SOC which is defined as the percentage of remaining capacity with respect to the maximum capacity. The dynamics of SOC is expressed as:

$$z_{k+1} = z_k - \eta I_{L,k} t_s / Q_k \tag{1}$$

where z_k denotes the SOC of VRB, Q_k denotes the cell capacity with the unit of ampere-seconds, η is the coulombic efficiency which can be calibrated with characteristic tests, t_s is the onboard sampling time

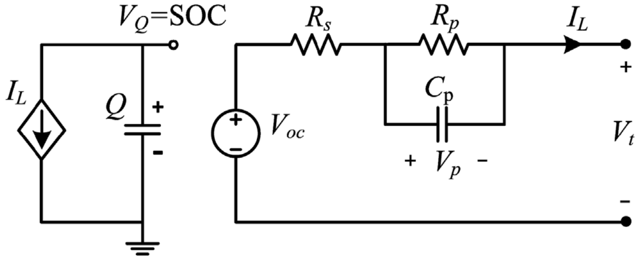

Fig. 1. Schematic diagram of the first-order RC model.