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State of charge monitoring of vanadium redox flow batteries using half cell potentials and electrolyte density

Simon Ressel^{a,b}, Florian Bill^a, Lucas Holtz^{a,c}, Niklas Janshen^a, Antonio Chica^b, Thomas Flower^a, Claudia Weidlich^c, Thorsten Struckmann^{a,*}

^a Hamburg University of Applied Sciences, Department of Mechanical Engineering and Production Management, Berliner Tor 21, 20099 Hamburg, Germany

^b Instituto de Tecnología Química, Universitat Politècnica de València—Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain

^c DEHEMA Forschungsinstitut, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany

HIGHLIGHTS

- Potential and Coulomb counting calibration doesn't need additional reference SOCs.
- SOC is estimated from in situ electrolyte density and potential measurements.
- Estimation errors for calibration and validation are below 0.04.
- In situ recalibrations during battery operation have been performed and validated.
- A state of health parameter is estimated in the potential calibration.

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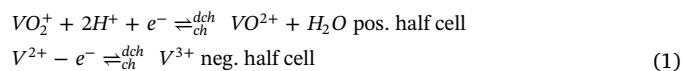
Redox flow battery
Vanadium redox flow battery
State of charge
State of health
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ABSTRACT

The operation of vanadium redox flow batteries requires reliable in situ state of charge (SOC) monitoring. In this study, two SOC estimation approaches for the negative half cell are investigated. First, in situ open circuit potential measurements are combined with Coulomb counting in a one-step calibration of SOC and Nernst potential which doesn't need additional reference SOCs. In-sample and out-of-sample SOCs are estimated and analyzed, estimation errors ≤ 0.04 are obtained. In the second approach, temperature corrected in situ electrolyte density measurements are used for the first time in vanadium redox flow batteries for SOC estimation. In-sample and out-of-sample SOC estimation errors ≤ 0.04 demonstrate the feasibility of this approach. Both methods allow recalibration during battery operation. The actual capacity obtained from SOC calibration can be used in a state of health model.

1. Introduction

In situ SOC estimation is a core element of battery management systems which are needed to enhance reliability, efficiency and life expectancy of batteries. This study analyzes SOC estimation methods for Vanadium redox flow batteries (VRFB). The VRFB technology with redox reactions



is a promising candidate for stationary electrical energy storage because of its independent scalability of power and energy capacity, potentially high cycle life, quick response times and direct current energy

efficiencies (e.g. Refs. [1,2]). Several demonstration projects from kW/kWh to MW/MWh have already been successfully installed and operated [2]. VRFB operation is accompanied by capacity losses and half cell imbalances caused by side reactions as well as ion and bulk crossover between the half cells. A unique advantage of VRFBs is the possibility to restore the capacity by electrolyte remixing and (electro) chemical rebalancing. The rebalancing process requires in situ detection of electrolyte imbalances which can be accomplished by SOC monitoring of the half cells [3].

The battery SOC is usually defined as $\text{SOC} = \frac{Q_{\text{act}}}{Q_{\text{max}}}$, with Q_{act} , the actual available electric charge and the battery capacity Q_{max} , the maximally available electric charge. It is estimated by different methods (see e.g. Refs. [4,5]):

* Corresponding author.

E-mail address: thorsten.struckmann@haw-hamburg.de (T. Struckmann).

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Coulomb counting relies on the transferred charge $\Delta Q = \int_{t_0}^{t_1} I(t) dt$ estimated as the time integral of the easily measurable external electric current $I(t)$ (taken as positive during charge)

$$SOC(\Delta Q) = m\Delta Q + SOC_0, \quad m = \frac{1}{Q_{max}} \quad (2)$$

starting from a known reference SOC_0 . Due to its simplicity it is widely used but suffers from inaccuracy of current measurements, error accumulation of the integration as well as from side reactions, crossover and total capacity loss. **Potentiometric titration** relies on the ex situ chemical analysis of the electrolyte components [3]. It suffers from the experimental effort and is time consuming, thus hardly suitable for online monitoring [6]. **Spectroscopic methods** like UV/vis spectroscopy rely on electrolyte absorbance for one or several wavelengths. While the method is established for the negative electrolyte it is difficult to apply for the positive electrolyte [3,7,8]. An online electrolyte spectroscopic monitoring system is described by Zhang et al. [6], which enables to monitor the transmittance spectra of the positive and negative electrolytes. The color changes of the positive and negative electrolytes in the vicinity of $SOC = 0$ and $SOC = 1$ are often qualitatively used as an indicator for 'completely' charged or discharged electrolytes [3,9]. **Electrolyte conductivity** is already used for SOC estimation [10] but needs calibration for varying electrolyte compositions. **Cell potential and terminal voltage measurements** use the Nernst equation, battery models or look-up tables for SOC estimation of the whole cell [4,11,12]. While the total cell voltage is current dependent and thus nonlinearly correlated to the Nernst equation, the total open circuit potential (OCP) doesn't reflect the half cell imbalances. **Half cell Nernst potential** measurements are applicable in situ with reference electrodes (REs) [8,10,13,14]. The Nernst equation is typically directly used for SOC estimation. Since REs can be implemented in both half cells, this methods enables the detection of imbalances. However estimation errors arise due to impurities in the RE and the instability of RE potential [15]. Because of this, recalibration during battery operation is needed. **Electrolyte density** is used for SOC estimation in lead-acid batteries [16]. The correlation of the Vanadium electrolyte density and SOC has been considered by Skyllas-Kazacos et al. [17] but without giving details on the measurement method and estimations. Density values of various vanadium(III) sulfate solutions at different acid concentrations and temperatures have been measured by Mousa [18]. **Battery models** typically rely on state models for the battery. They can combine different measurements with differential equations and/or Kalman filtering and are used in battery management systems for multi-parameter estimation(e.g. Ref. [19]). The methods proposed in this study though being stand-alone SOC estimation methods could be used as inputs for battery models.

Reference SOC₀ for SOC calibration are typically obtained from mixtures of $SOC \approx 0$ and $SOC \approx 1$ electrolytes and/or Coulomb counting [3]. The completely charged or discharged states are indicated by color changes and low current densities for high discharge or charge overpotentials. Apart from systematic errors due to the imprecisely known electrolyte composition, these reference SOC₀ are difficult to apply for recalibration during battery operation. Thus, in addition to in situ SOC estimation, self consistent reference SOC₀ are needed for in situ recalibration.

In the following sections we propose and examine two SOC monitoring methods for the negative VRFB half cell. The first method combines Coulomb counting with in situ measurements of the half cell potential using REs. By this way reference SOC₀ and the reference potential for the SOC estimation are calibrated in one step, and due to the self consistency of the calibration, no additional reference SOC₀ are needed. For the second method density modules are implemented in the electrolyte cycle of a VRFB to measure the in situ densities during operation. After correcting the temperature dependence of the density the reference SOC₀ obtained by the first method are correlated to the measured density values. Experimental VRFB data from a 'complete

discharge-charge' calibration cycle (within $SOC \approx 1$ and $SOC \approx 0$) and validation cycling (6 constant current cycles) are used to calibrate, recalibrate and validate the proposed methods. Auxiliary measurements have been carried out to determine the temperature dependence of the density. Results of the calibration process with estimation errors and validation results considering the parameter stability as well as estimation errors for cycling data are analyzed. In total, more than 100 h of battery operation are covered. This study extends work on SOC estimation done by Weidlich et al. [8,20].

2. Experimental

2.1. In situ measurement of half cell potential and electrolyte density

The overall test setup is implemented in the test rig described in Ref. [21]. In situ electrolyte density and potential measurements are conducted by use of a flow through density module and custom made flow armatures. To avoid high pressure load on the density module and reference electrodes (REs), sensors are implemented behind the half cell outlets of the VRFB cell. This setup might show discharge-charge time lag effects since the electrolyte composition in the measuring cells differs from the reservoir electrolyte. However, the effects are expected to be small as the VRFB is operated with a high electrolyte excess $\lambda = |I_{stoi}/I_{cell}|$ in the test runs.

Electrolyte density is measured using DMA 35n Liquid Density Modules of Anton Paar. The module determines the density of liquids up to 2 g ml^{-1} using the oscillating U-tube principle. Validation with distilled water has been performed and confirmed the quoted systematic errors below 0.0005 g ml^{-1} . The corresponding sample temperature is measured directly by a built-in temperature sensor.

Half cell potential is measured using a Hg/Hg_2SO_4 reference electrode (HgE) in $2M H_2SO_4$ (Sensortechnik Meinsberg) against a heat treated flow-by graphite felt electrode (SIGRACET GDL #2614 Pyron, SGL Carbon). The reference electrode with an inner electrolyte containing sulfuric acid has been chosen to fit the solvent composition of the vanadium electrolyte. To avoid pressure driven influx of the measured electrolyte into the inner electrolyte of the reference electrode, a pressure compensation pipe is installed between the electrolyte cycle and the RE. The calibration of the reference electrode by repeated measurements against a saturated calomel gauge electrode (Sensortechnik Meinsberg) resulted in a potential shift of 654 mV with respect to the standard hydrogen potential and an estimated systematic measurement error of $\approx 1 \text{ mV}$. Thus the standard potential of the negative half cell against the reference electrode is expected to be in the range of $E_{nhc}^0 = -0.255V - 0.654V = -0.909V$ vs. HgE. The half cell potential differences have shown no significant deviations from the open circuit voltage of the battery cell which confirms the validity of the half cell potential measurements.

2.2. Calibration and validation data

Calibration and validation measurements of the electrolyte density and potential were done with a planar VRFB test cell (Micro Flow Cell, ElectroCell) with 10 cm^2 active membrane area and $(3.15 \times 3.15) \text{ cm}^2$ flow-through graphite felt (SIGRACELL KFD 4.6 EA, SGL Carbon) electrodes. Heat treatment of the electrodes was done by SGL Carbon and electrode compression ratio was set to 24%. The cation exchange membrane (fumasep F10100, FUMATECH BWT GmbH) with a thickness $t = 100 \mu\text{m}$ was employed as separator material. The test cell was integrated in the test rig and operated in 4-tank and 2-tank mode during calibration and validation cycling, respectively. Prior to all measurements the test setup was purged with Ar gas. 100 ml of $0.8M VOSO_4$, $0.4M V_2(SO_4)_3$, $0.05M H_3PO_4$ and $2M H_2SO_4$ (GfE-Metalle) often denoted as '1.6M $V^{3.5+}$ electrolyte' was filled in each tank at the beginning of every measurement run. To prevent oxidation of electrolyte the

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