



Validating and improving a zero-dimensional stack voltage model of the Vanadium Redox Flow Battery

S. König*, M.R. Suriyah, T. Leibfried

Karlsruhe Institute of Technology (KIT), Institute of Electric Energy Systems and High-Voltage Technology (IEH), Engesserstrasse 11, 76131 Karlsruhe, Germany



HIGHLIGHTS

- Experimental data from a mature industrial-scale stack is used for validation.
- Measures are presented to protect manufacturer's IP during publication.
- Straightforward approach for quantifying the model error is presented.
- Mass transfer coefficients for both half-cells are derived separately.
- Apparent active electrode surface is introduced for zero-dimensional model.

ARTICLE INFO

Keywords:

Vanadium Redox Flow Battery
Validation
Modeling
Simulation
Concentration overpotential
Mass transfer

ABSTRACT

Simple, computationally efficient battery models can contribute significantly to the development of flow batteries. However, validation studies for these models on an industrial-scale stack level are rarely published.

We first extensively present a simple stack voltage model for the Vanadium Redox Flow Battery. For modeling the concentration overpotential, we derive mass transfer coefficients from experimental results presented in the 1990s. The calculated mass transfer coefficient of the positive half-cell is 63% larger than of the negative half-cell, which is not considered in models published to date.

Further, we advance the concentration overpotential model by introducing an apparent electrochemically active electrode surface which differs from the geometric electrode area. We use the apparent surface as fitting parameter for adapting the model to experimental results of a flow battery manufacturer. For adapting the model, we propose a method for determining the agreement between model and reality quantitatively. To protect the manufacturer's intellectual property, we introduce a normalization method for presenting the results.

For the studied stack, the apparent electrochemically active surface of the electrode is 41% larger than its geometrical area. Hence, the current density in the diffusion layer is 29% smaller than previously reported for a zero-dimensional model.

1. Introduction

1.1. General introduction

One way of dealing with the fluctuating nature of renewable energy sources is the installation of large-scale batteries. Because of their decoupled power and energy rating as well as because of their low energy related costs, flow batteries are a very promising technology to fulfill the task of balancing demand and renewable generation [1]. In the Vanadium Redox Flow Battery (VRFB), patented in 1988 by Maria Skyllas-Kazacos and coworkers, deploying the same substances in both half-cells prevents the common problem of cross-contaminating the two

electrolytes through the membrane which separates the two half-cells. Today, the VRFB is the most mature flow battery technology.

Compared to conventional batteries, the VRFB still faces some challenges. Two major issues are the high power related costs and the comparatively low efficiency [1,2]. Both issues need to be addressed on all levels, from lab-scale to system level, both with experimental and model-based approaches.

Regarding model-based approaches, detailed two- or three-dimensional models contribute to understanding the fundamental processes within the flow battery but are too complex to conduct system-level studies. For this purpose, we need simple, computationally efficient but yet accurate zero-dimensional models [3].

* Corresponding author.

E-mail address: sebastian.koenig@kit.edu (S. König).

1.2. Concentration overpotential modeling

One promising task for system level VRFB models is the flow rate optimization [4–9]. For this task, it is of utmost importance to accurately model how the VRFB reacts on changing the flow rate. The flow rate most strongly affects mass transfer in flow cells and thus the concentration overpotential. Hence, for conducting flow rate optimization studies, accurately modeling the concentration overpotential is highly important.

All flow rate optimization studies using zero-dimensional models presented to date face two drawbacks [4–7,10]. First, they use the mass transfer coefficient of the negative half-cell for the positive half-cell as well. For the negative half-cell of a VRFB, the mass transfer coefficient is introduced in Ref. [11]. In this work, we derive the mass transfer coefficient of the positive half-cell from experimental results for the first time in literature [12,13].

Secondly, even if they consider concentration overpotential at all, they apply the macroscopic current density to the diffusion layer which in operation evolves around the fibers of the porous graphite electrodes. As the electrochemically active surface area of the electrode is much larger than its geometrical area, this is not adequate. However, in a zero-dimensional model it is also not adequate to use the total physically available electrode surface area. Hence, we introduce an apparent electrochemical active electrode area which we derive from experimental data during a validation process.

1.3. Model validation

Validating stack- and system-level models is an elaborate task and published works are rare. In Ref. [14], the authors set up an equivalent electric circuit model which is subsequently validated using measurement data of a 5 kW/20 kWh VRFB. Shunt current and pump losses are modeled as parasitic current source. In Ref. [15], a similar model is proposed but with an extended network using RC-elements to describe the dynamic behavior of the VRFB. The authors use a three-stack system with a power rating of around 15 kW to gather experimental data for validating the model. Another similar model can be found in Ref. [16]. This model has an extended mechanical part for calculating the pump power demand and is validated using a 19-cell stack with a power rating of 2.5 kW. A stack comprising 14 cells, each with an electrode area of 875 cm², is used for validation in Ref. [9], but model and reality are not in a very good agreement. Finally, a 2 kW/10 kWh VRFB is used in Ref. [17], to validate a comprehensive multi-physical model. The authors adapt the concentration overpotential model and introduce a plug-flow-reactor principle to improve the agreement of model and reality. However, the adaptations in the concentration overpotential model are not motivated by electrochemical processes.

The aforementioned validation studies face two drawbacks. First, the agreement of model and reality is only shown qualitatively and is not evaluated quantitatively. Hence, in this work, we present a well structured method for quantitatively rating the agreement of a stack-level VRFB model with a real system.

Secondly, most of the presented studies comprise simple equivalent circuit models. We can use such models to predict the behavior of an existing system, but not for further developing its design and operational strategy. Hence, we use a stack voltage model, which we can flexibly parametrize with key design and operational parameters.

For validating the model, we use experimental data from a German flow battery manufacturer. Manufacturers are a very good source for experimental data because they gather a lot of this data in their test rigs. Further, their systems are usually more mature than prototypes made by research institutes. However, publishing data from manufacturers requires measures to protect its intellectual property (IP). Hence, we present a method for normalizing voltage curves. This allows for comparing simulation and measurement, but prevents the reader from drawing unjustified conclusions regarding stack performance.

Table 1
Nomenclature.

Abbreviation	Expression
EMF	Electromotive force
EOC	End-of-charge
EOD	End-of-discharge
OCV	Open-circuit-voltage
RMS	Root-mean-square
RMSE	Root-mean-square-error
SoC	State-of-charge
VRFB	Vanadium Redox Flow Battery
Sub-/Superscripts	Expression
C	Cell
COP	Concentration over-potential
DL	Diffusion layer
E	Electrode
El	Electrolyte
V	Vanadium
T	Tank
2	V ²⁺
3	V ³⁺
4	VO ²⁺
5	VO ₂ ⁺
+	Positive half-cell
–	Negative half-cell
in	Input
out	Output

2. Methodology

2.1. Nomenclature

The nomenclature which we use in this work is shown in Table 1.

2.2. Experiments

For generating reference measurements to validate the model, we conduct consecutive charging and discharging cycles in a test rig of a German flow battery manufacturer. The deployed stack is newly manufactured, comprises 40 individual cells and has a power rating of 5 kW. All cycles are conducted between SoC limits of 15% and 85%. In total, we carry out six experiments using different combinations of constant flow rate and charging/discharging current. Each experiment consists of at least three consecutive cycles. Before each experiment, we completely mix the positive and negative electrolyte and carry out a re-conditioning to ensure, that a well-balanced non-degraded electrolyte is used. The electrolyte is the standard vanadium electrolyte with a vanadium concentration of 1.6 mol L⁻¹. For protecting the IP of the manufacturer, we cannot disclose the detailed parameters of the stack, such as electrode dimensions and deployed materials.

2.3. Simplifications and assumptions for the modeling

The presented model is isothermal. The measured tank SoC is used as input parameter, which allows for neglecting vanadium crossover through the membrane and shunt currents. Activation overpotential is neglected due to reasons extensively laid out in Ref. [18]. The cell is assumed to be perfectly mixed and all cells are assumed to be equally well supplied with electrolyte.

2.4. Modeling the stack voltage

With the aforementioned simplifications, all cells of the stack behave exactly identically. Consequently, we only model a single cell and

Download English Version:

<https://daneshyari.com/en/article/7725918>

Download Persian Version:

<https://daneshyari.com/article/7725918>

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