



A plug flow reactor model of a vanadium redox flow battery considering the conductive current collectors



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HIGHLIGHTS

- The copper current collector is included into a plug flow reactor model.
- A compromise between spatial resolution and computational efficiency is derived.
- Internal current distribution is studied in dependence of current and flow rate.
- The current collector prevents high over-potentials at the end of the single-cell.
- High over-potentials at the end of the cell are also prevented in a 40-cell stack.

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ABSTRACT

A lumped-parameter model for vanadium redox flow batteries, which use metallic current collectors, is extended into a one-dimensional model using the plug flow reactor principle. Thus, the commonly used simplification of a perfectly mixed cell is no longer required.

The resistances of the cell components are derived in the in-plane and through-plane directions. The copper current collector is the only component with a significant in-plane conductance, which allows for a simplified electrical network. The division of a full-scale flow cell into 10 layers in the direction of fluid flow represents a reasonable compromise between computational effort and accuracy.

Due to the variations in the state of charge and thus the open circuit voltage of the electrolyte, the currents in the individual layers vary considerably. Hence, there are situations, in which the first layer, directly at the electrolyte input, carries a multiple of the last layer's current. The conventional model overestimates the cell performance. In the worst-case scenario, the more accurate 20-layer model yields a discharge capacity 9.4% smaller than that computed with the conventional model. The conductive current collector effectively eliminates the high over-potentials in the last layers of the plug flow reactor models that have been reported previously.

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1. Introduction

One of the measures to fight climate change and to reduce the dependence of humanity on fossil fuels is the intensified use of renewable energy resources. However, the fluctuating nature of these energy sources contradicts the need for a non-intermittent energy supply. Electricity storage systems (ESS) such as batteries can help to overcome this hurdle. Introduced by Maria Skyllas-Kazacos and her fellow researchers at the University of New

South Wales [1–3], the all-vanadium redox flow battery (VRFB) has developed into one of the most suitable technologies for grid-scale ESS [4–6]. This is mainly because the working principle of a flow battery allows for an independent scaling of storage capacity and charging/discharging power.

However, one of the drawbacks of the VRFB is its low power density. To maintain a reasonable energy efficiency, the applicable current density is very limited. A large number of cells and stacks is therefore required for large-scale systems; thus, power-related costs for cell materials (graphite felt, bipolar plates, membranes, gaskets, etc.) are very high [7]. Optimization of flow cell design allows for a more effective utilization of the deployed materials. Modeling and simulation studies deliver insights into the loss

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mechanisms within the cell and thus lead to optimized cell designs.

1.1. Literature review and motivation

In general, flow battery modeling can be separated in terms of spatial resolution [8]. Very detailed models, which consider the variation of quantities in two or three dimensions deliver profound insights into the mechanisms within the cell. However, they are limited in the dimensions of the simulated cells. Three-dimensional models are presented in Ref. [9] (active cell area: 14 cm²) and [10] (4 cm²). Two-dimensional models are studied in Ref. [11] (100 cm²) [12], (10 cm²) and [13] (40 cm²). In Ref. [9], the distributions of velocity, concentration, over-potential and current density are studied. The electrolyte velocity is found to have a major effect on the distributions of the aforementioned quantities. The non-isothermal model presented in Ref. [10], focuses on heat generation mechanisms within the cell. In Ref. [11], the effect of hydrogen evolution on battery efficiency is studied. The model presented in Ref. [12] accurately predicts the capacity loss due to species crossover during at least 45 charging/discharging cycles. In Ref. [13], a two-dimensional model of a VRFB that is employed with an anion exchange membrane is presented.

Because of limited computational resources, it is still not possible to model a full-scale flow cell with a high spatial resolution in two or three dimensions. Therefore, full-scale cells and stacks are modeled using zero-dimensional or lumped-parameter approaches [14–17]. While it is possible to simulate large systems with up to six full-scale stacks with these models [16,17], they require an extensive set of simplifications. Therefore, efforts are necessary to improve the accuracy of lumped-parameter models, while preserving the advantage of a low demand for computational resources.

In Ref. [18], a zero-dimensional model is developed from a two-dimensional model by means of a scale analysis. It is observed that for most of the above-mentioned studies, the simplification is valid. In addition, the simplified model was validated against experiments with a 10-cm² cell [19]. However, the conditions, which are derived in Ref. [18], for the presented reduction in dimensionality are not fulfilled for a full-scale cell.

Another attempt to reduce the model complexity was presented in Ref. [20]. While the computational time was reduced by a factor of 75, the simplified model showed significantly reduced accuracy compared to the initial two-dimensional model. One of the reasons for the lack of accuracy of lumped-parameter models is the assumption that the flow cell behaves like a continuously stirred reactor [14–17,20–22].

Full-scale flow cells have cell heights of several hundreds of millimeters [14–17,22]; thus, a significant variation in the state of charge (SoC) has to be taken into account within the cell. This cannot be considered in the conventional lumped-parameter approach. Subsequently, a dynamic plug flow reactor (PFR) model has been introduced [23]. The PFR approach extends the zero-dimensional model into a one-dimensional one. However, the number of elements required to realize the spatial resolution is very small compared to two- or three-dimensional models. In Ref. [23], a cell with a height of 300 mm is divided into 60 layers, each with a height of 5 mm. The study highlights the inhomogeneities in the concentration of vanadium ions as the electrolyte flows through the cell. In Ref. [23], these inhomogeneities result in voltage variations within different layers. This is because of the low conductivity of the cell elements (bipolar/end plate, felt electrode and membrane) in the fluid-flow direction (in-plane direction). Consequently, the last layers suffer from high over-potentials, especially at the end of the charging process, because of the depletion of the respective vanadium species in these layers. However, while the presented modeling approach shows good performance for the modeling of

redox flow cells, the study does not include highly conductive copper plates, which in practice are placed on the top of the first and last cells of a stack to realize the electric connection.

This study adapts the PFR approach presented in Ref. [23] and extends it by considering the highly conductive copper current collectors. The voltage difference, which is applied between the positive and the negative current collectors, is constant for all layers. Consequently, the high over-potentials in the last layers, as described in Ref. [23], cannot evolve.

In fact, the main difference between the presented PFR model and the previously published one, is the boundary condition. In Ref. [23], a galvanostatic boundary condition is applied to all layers. Hence, they all carry the same current. In our study, we apply a potentiostatic boundary to all layers. Thus, we apply the same voltage across every individual layer. Also, all our layers are macroscopically bounded by a galvanostatic boundary condition. The question about the interchangeability of the two boundary conditions has already been studied for fuel cells in Ref. [24]. For a fuel cell, the interchangeability mainly depends on the applied current density, the conductivity of the electrode and the geometry of the cell. However, if we apply the derived "interchangeability number" to a full-scale VRFB cell, we derive a value of around 40. Hence, according to [24], if we apply a stoichiometric or flow factor substantially larger than two, we are allowed to interchange the boundary conditions. In that case, both, our model, and the model from Ref. [23] would yield the same results. However, the question is if a flow factor between five and ten, which is applied to a VRFB in practice, is sufficiently larger than two. This question is addressed in this work.

1.2. Structure of the presented work

First, the equivalent electric network for a redox flow cell, which is subdivided into layers in the fluid-flow direction, is derived. Subsequently, the electro-chemical model for the resulting one-dimensional model is presented. Next, the impact of the layer number on the simulation results is evaluated. Finally, a model with 10 layers is used to obtain insights into the current distribution of the individual layers. At the same time, variations in the composition of the constant layer voltage from the electrolyte's open-circuit-voltage (OCV) and the different over-potentials for the different layers are also studied.

2. Equivalent electric circuit

Fig. 1 a) shows a simplified scheme of a redox flow cell, including the denotations for the dimensions (width, height and thickness) for the through-plane (\perp) and in-plane (\parallel) directions. Usually, the current collector is made of copper. The end-plates are made of a graphite composite material (Schunck Group, Grade FU 4369 [25]). Porous graphite felts (SGL Group, GFD4.6 EA [26]) are used as electrodes, and Nafion 115 is used as the membrane. The properties of the materials are given in Table 1. According to [26], the uncompressed height of the graphite felt is 4.6 mm. In the simulations, an electrode height of 4 mm is assumed, resulting in a compression rate of 13%; thus, the electrical resistance is decreased by 60% [26].

The cell dimensions are the same as those presented in Ref. [15]. From the conductivities given in Table 1, the in-plane and through-plane resistances for each element of the cell can be derived using Eq. (1). The denoted length, width and height are consistent with Fig. 1 a) for the through-plane resistances but not for the in-plane resistances. For the latter, the current-flow direction is the same as the electrolyte-flow direction. Therefore, the element thickness is the cell height and vice-versa. The resulting resistances of the

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