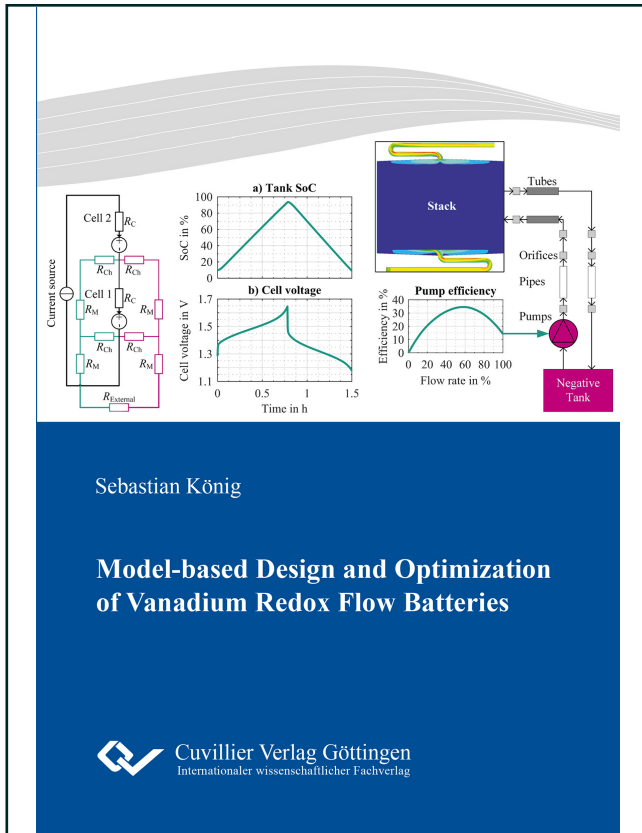




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Model-based Design and Optimization of Vanadium Redox Flow Batteries



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Internationaler wissenschaftlicher Fachverlag

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Chapter 1

Introduction and motivation

1.1 The need for electric energy storage

In 2015, every German grid-connected consumer had access to electricity with an average interruption (SAIDI – system average interruption index) of 12.7 min [2]. This corresponds to an outstanding supply security of 99.9998 %. The requirement of a secure electricity supply seems to contradict utilizing renewable energy sources (RES), such as photovoltaics (PV) and wind power plants because of their volatile nature. However, RES apparently had a positive effect on the supply security, as shown in Figure 1-1. Between 2006 and 2015, the share of RES in the German gross electricity consumption nearly tripled, while the SAIDI was cut in half.

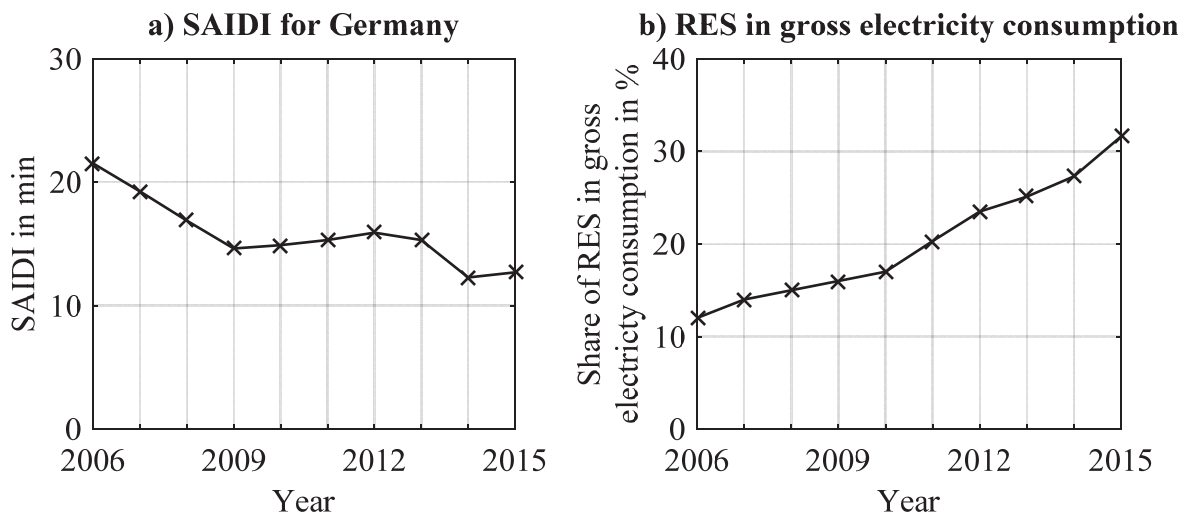


Figure 1-1: SAIDI and share of RES in the gross electricity consumption in Germany

It is beyond dispute that the de-carbonization of an energy system requires additional flexibility options, to balance generation and demand. Besides energy storage systems (EES), wide-area grid expansion and demand side management (DSM) will also contribute to these flexibilities.

Among all energy storage technologies, batteries are the most flexible but also the most expensive one. In March 2017, the global energy storage database of the U.S. Department of Energy listed 323 grid-scale battery storage projects with an individual nominal power of 1 MW or more. This number includes all contracted projects, projects under construction and projects in operation. In total, the database lists battery energy storage systems (BESS) with a total power of 2,804 MW and a total capacity of 4,176 MWh. For comparison, pumped-storage power plants with a total power of 6,850 MW are installed in Germany only [3]. Hence today, batteries play a minor role in grid-scale energy storage.



However, in 2016, several major BESS projects were published. Three of them, with a total power of 341 MW, are given here as a sample. National Grid, the transport system operator (TSO) of England and Wales, procured 201 MW of so-called enhanced frequency response (EFR) contracts after a tendering exercise [4]. All accepted bids went to providers that plan to install BESS.

In Southern California, we can find another recent example for the large-scale penetration of the electric power grid by batteries. In 2015, a massive leak in the Aliso Canyon storage facility, a natural gas storage plant, caused an ongoing natural gas shortage [5]. As this fuel is in particular used by the so-called ‘peaker plants’ – gas-driven power plants that deliver energy in times of peaking demand, the region currently faces a significant lack of fast responding generation units [6]. Therefore, the utilities Southern California Edison and San Diego Gas & Electric procured more than 50 MW of lithium-ion batteries to manage this shortage. The largest project within this tender is a 20 MW/80 MWh battery system.

Also, between mid-2016 and the beginning of 2017, the German energy company steag GmbH installed six 15 MW/22 MWh batteries in their power plants in Germany [7]. The company markets these systems to deliver primary frequency reserve power, but they add flexibility to steag’s power plant portfolio also.

Because of versatile marketing options, short installation times and falling prices, the market for grid-scale BESS is growing dynamically. While today, batteries first and foremost represent high-power ESS, there will also be a need of high-energy ESS in the future, e.g., to replace fossil-fueled peaker plants and to store PV energy for the nighttime.

1.2 Fundamentals

1.2.1 Setup and characteristics of a flow battery

A flow battery comprises the same elements as a conventional battery. It consists of two electrodes, in conventional batteries often denoted as anode (negative electrode) and cathode (positive electrode), a separator to isolate both electrodes, plus an electrolyte, which enables an ionic charge transfer between the electrodes. However, in flow batteries, the tasks of these elements are different. First and foremost, the electrodes in a flow battery do not partake in the redox reactions. They just offer the surface area for the electrochemical reaction to take place, and the electric conductivity to distribute and to collect the electrons. Thus, the electrodes of a flow battery do not store any energy. Instead, the energy storage is an additional task of the electrolyte. Therefore, we have to separate the electrolyte into the negative electrolyte (anolyte) and the positive electrolyte (catholyte). An ion-exchange membrane prevents the two electrolytes in the flow cell from mixing.

According to the technical definition, the denotation anode and cathode, as well as anolyte and catholyte, refer to the discharging process. During the discharging process, the cathode is the positive pole, and thus absorbs electrons; the anode is the negative

pole and thus releases electrons. During the charging process, the polarity of the battery cell does not change, but the roles of the electrodes do. The negative electrode now has to absorb electrons and thus it becomes the cathode; the positive electrode becomes the anode. Hence, in a battery, the denotations anode and cathode are conflicting. Consequentially, the terms positive and negative electrode, as well as positive and negative electrolyte are exclusively used in this work.

The deployment of liquid electrolytes for storing the energy, offers a key advantage. By replacing the electrolyte via a pair of inlets and outlets, the redox flow cell can be used to charge and discharge an arbitrary amount of electrolyte. Hence, in a flow battery, the charging and discharging power is defined by the power and the number of the individual cells, which are usually assembled to stacks. The deployed amount of electrolyte defines the energy storage capacity. Thus, the two most important characteristics of any battery, its nominal power and discharge capacity can be chosen independently from each other. This is the unique feature of a flow battery.

1.2.2 Advantages and disadvantages

The arbitrary ratio between power and storage capacity allows for an excellent adaptability of a flow battery to the intended use case. It is possible to change the ratio during the lifetime of the battery system by adding more cells or more electrolyte.

Also, the energy-related costs are low. For a large discharge capacity, the marginal costs of the Vanadium Redox Flow Battery (VRFB) tend to the expenses of the energy storage medium. According to [8], the material costs for the electrolyte of a VRFB is 2.47 €L^{-1} . Referred to the theoretical energy density of the standard vanadium electrolyte, which is 30 WhL^{-1} , this corresponds to specific energy-related costs of only 52 €(kWh)^{-1} . Today, the costs are indeed higher, mainly because significant production costs come on top of the electrolyte's material cost. Also, the usable specific energy density for a reasonable power density is substantially lower than the theoretical value. Hence, today, the costs for the vanadium electrolyte are in the range of 270 €(kWh)^{-1} referred to the useable capacity [8]. To compare this cost on a system level, we also need to take the costs of the tanks into account. However, compared to the cost differences of lithium-based batteries on cell and system level, a flow battery has significant less overhead costs. In particular, it does not require cell balancing, single-cell monitoring, and cell packaging.

For mid-term to long-term storage, it is noteworthy that electrolyte, stored in the tanks, will not suffer from any self-discharge. Note, that this is not valid for the energy stored in the stacks themselves. However, in a reasonably dimensioned flow battery, this is only a small fraction of the totally stored energy.

Today, the high power related costs can be considered to be the biggest disadvantage of a VRFB. Due to the small number of units, assembling of stacks is manual labor.

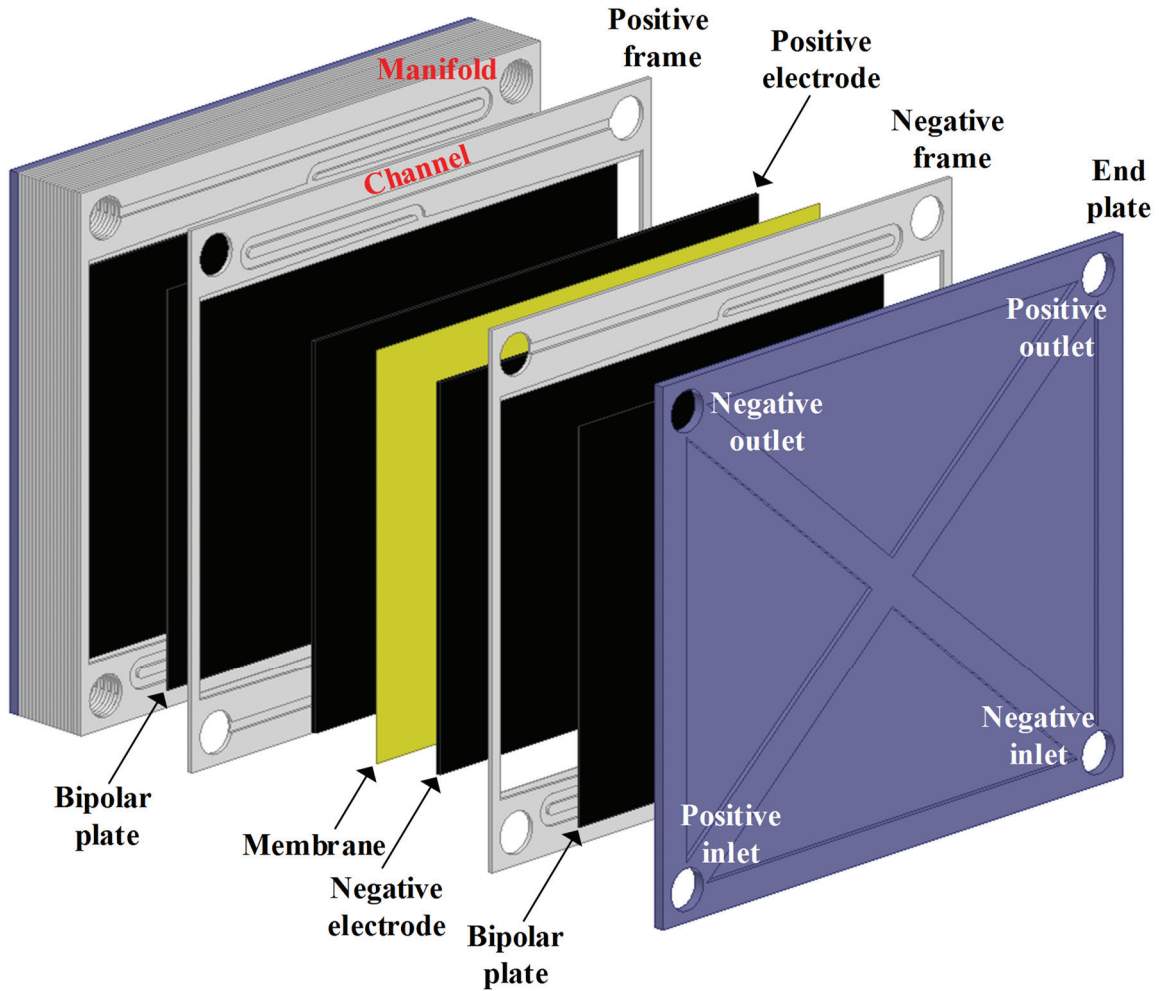


Figure 1-2: Structure and elements of generic flow battery cells, assembled to a stack

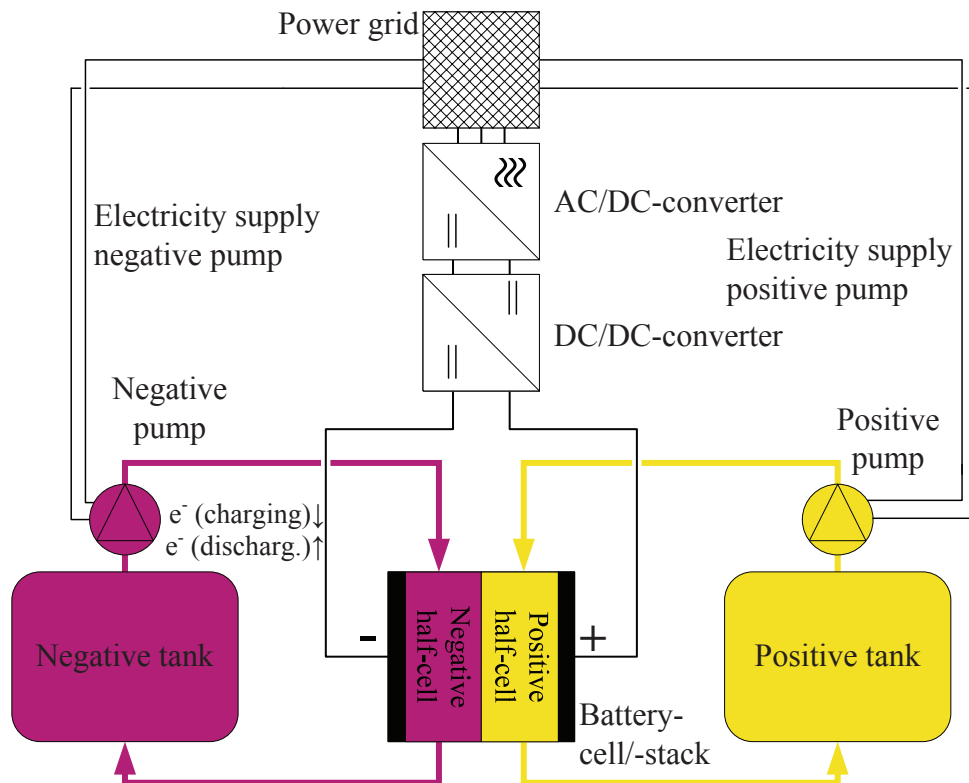


Figure 1-3: Composition of a flow battery system

Also, most companies only buy small quantities of the required materials from their suppliers. Hence, the stack-related costs are rather high. In [8], stack specific costs of more than $8,000 \text{ €(kW)}^{-1}$ are calculated. The costs for the pumps, the piping and the power conditioning system (PCS) further increase the power-related costs.

The PCS for a flow battery is usually more complex than for other types of batteries. Reasons are the low cell voltage, the limitation in the series connection of the cells and large voltage variations with state-of-charge (SoC) and charging/discharging currents. Finally, flow batteries suffer from a lower efficiency than lithium-based batteries. A comparatively high internal resistance, which also limits the power density, and additional loss mechanisms, such as the pump power demand, the crossover of vanadium ions across the membrane, as well as the shunt currents, reduce the VRFB efficiency.

1.2.3 Composition of a flow cell

In a flow cell, the electrode should provide a large contact area with the electrolyte. Therefore, porous graphite felts are predominantly used as electrodes. Between both electrodes, the ion exchange membrane is placed. As a single flow cell usually provides a low voltage of less than 2 V, a larger number of cells is connected in series electrically, as shown in Figure 1-2. This is efficiently realized by using so-called bipolar plates, made of a composite graphite material. These plates provide the planar electric connection of the electrode and simultaneously seal each positive half-cell from the successive negative half-cell. On top of the first and last bipolar plates, current collectors made from copper are placed. In the conventional stack design, massive aluminum endplates are used combination with threaded bolts, nuts and strong springs to clamp the stack. This is to obtain a high compact pressure all over the flow cells. The compact pressure reduces the contact resistances and improves the sealing. Finally, to electrically isolate the endplates from the stack, a plastic layer is placed between the current collector and the endplate. Note that the current collectors, the isolating plastic layer, as well as gaskets and bolts, used for the clamping, are not displayed in Figure 1-2.

The so-called frame, usually made from plastics using injection molding, provides the outer support. The frame also includes the inlet and outlet channels, which are required to partly decouple the electrolyte supply paths of the flow cells from each other.

Internally, the positive and the negative electrolytes are supplied and re-collected via four manifolds, commonly used by all flow cells of the stack.

1.2.4 Components of a flow battery system

A flow battery comprises two main units. The electrochemical active energy conversion unit, which is an arbitrary number of flow cells, and at least one pair of tanks, as shown in Figure 1-3. Figure 1-4 shows a universal flow battery design, in which six 30-cell stacks are connected to one pair of tanks with a volume of 8,000 L each. The system, rated 54 kW/216 kWh, is used in a model-based study [9].

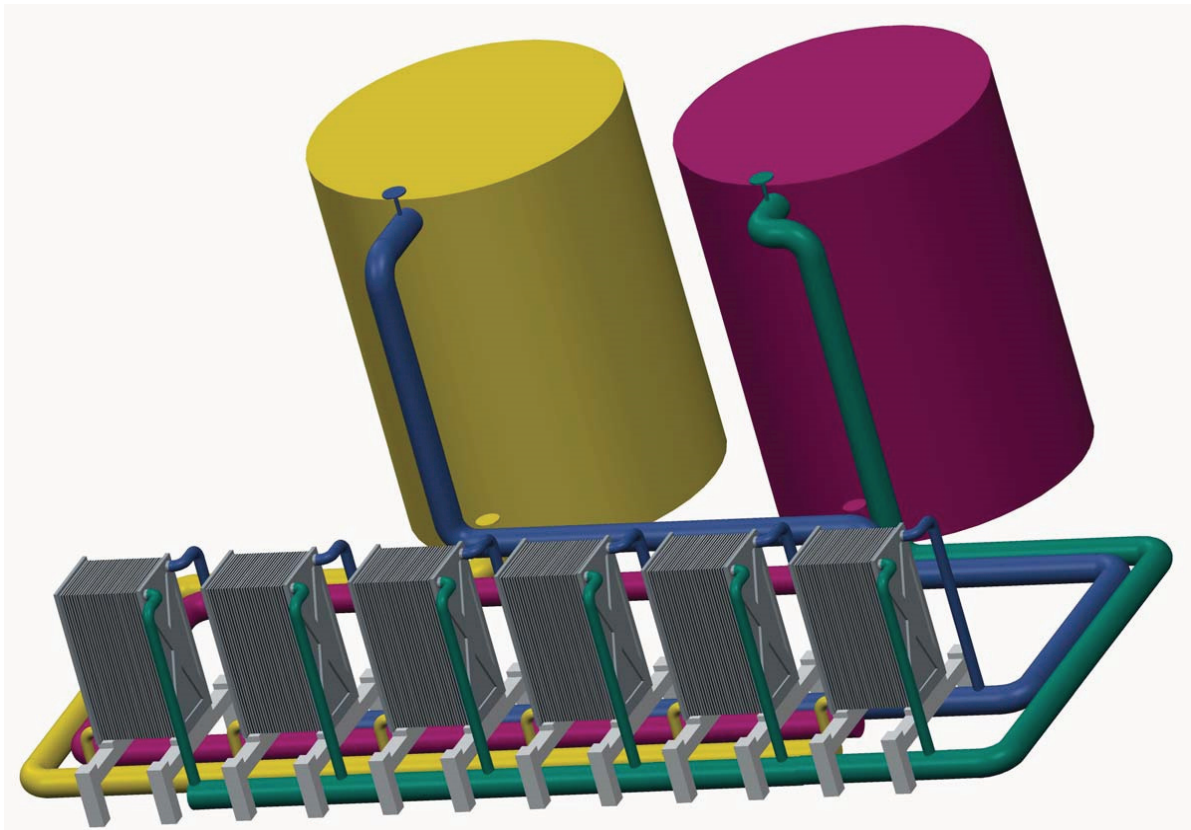


Figure 1-4: CAD scheme of a generic flow battery system with six stacks and two tanks



Figure 1-5: 2-kW/10-kWh VRFB prototype by SCHMID Energy Systems GmbH, Freudenstadt, Germany [10]



Figure 1-6: Gildemeister CellCube stacks;
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Figure 1-7: Interior view of a Gildemeister CellCube container;
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If the use case requires a more compact system, the stack is often placed on top of the tanks, as shown in Figure 1-5. Large systems consist of a large number of stacks and are often placed into containers, as shown in Figure 1-6 and Figure 1-7.

Additional components are usually two pumps, electric and hydraulic networks, as well as a PCS. A PCS normally consists of a DC/DC-converter (DC – direct current) and an AC/DC-converter (AC – alternating current). The DC/DC-converter adapts the low, load- and SoC-depending battery DC voltage to the high and constant DC voltage of the AC/DC-converter. The latter provides the conversion of the DC voltage into the AC voltage, existing in the power grid. The pumps can be supplied directly from the battery or from the power grid. Note, that the former is difficult if the battery is not used for a longer period and the energy stored in the stack is lost due to self-discharge.

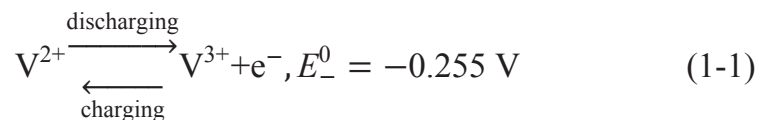
1.2.5 A short history of flow batteries

In 1949, Dr. Walter Kangro patented a process for storing electric energy using a conversion cell and a reservoir [11]. In [12], he evaluates titanium and iron chloride as well as titanium and iron sulfate as two possible redox couples for the utilization in a flow battery.

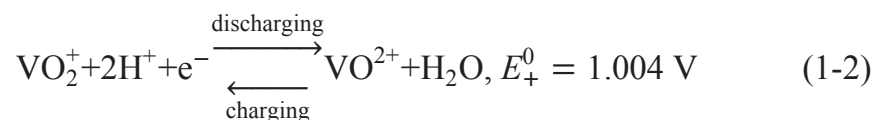
In the early 1970s, the National Aeronautics and Space Administration (NASA) became interested in redox flow batteries [1]. They focused on the iron and chromium redox couple, covering many system-related topics, such as shunt currents and optimized flow rate control strategies (FRCS).

In the 1980s, Maria Skyllas-Kazacos pioneered the all-vanadium redox flow battery at the University of New South Wales (UNSW) in Australia. The corresponding patent was granted in 1988 [13]. One key finding was that up to 2 mol of pentavalent vanadium ions are dissolvable in 2 mol of sulfuric acid. This permits utilizing the transition metal vanadium, having four oxidation states, as a redox couple in both half-cells. In a VRFB, the fundamental redox reactions are as follows [14]. The fundamental processes are shown in Figure 1-8.

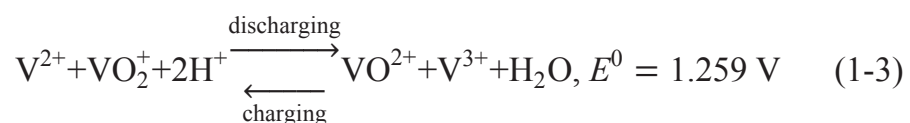
- Negative half-cell:



- Positive half-cell:



- Total-cell reaction:

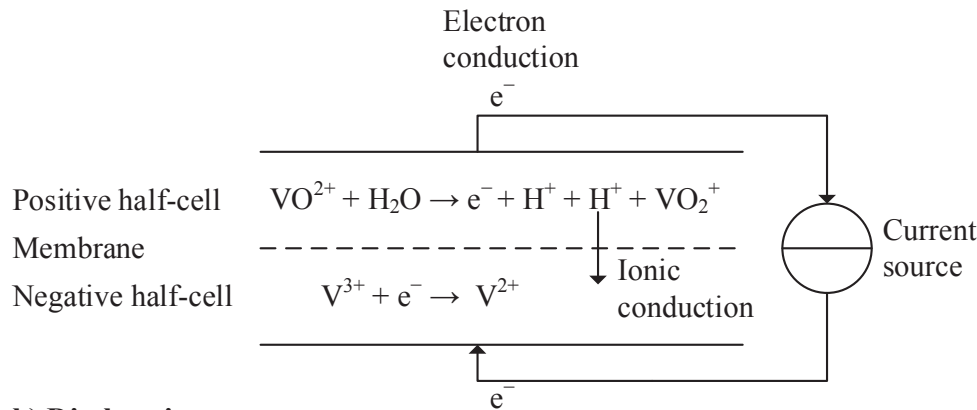


Using vanadium in both half-cells solved one key problem of previously studied redox couples, which was the crossover of ions over the membrane into the respective opposite

Section 1.3 – Objectives of the presented work

half-cell. Although this process still occurs in the VRFB, it only leads to a certain self-discharge but does not damage or harm the electrolytes. Today, the VRFB is the most mature flow battery technology [15]. Reference [15] provides a very comprehensive presentation about the history of flow batteries and possible redox couples.

a) Charging process



b) Discharging process

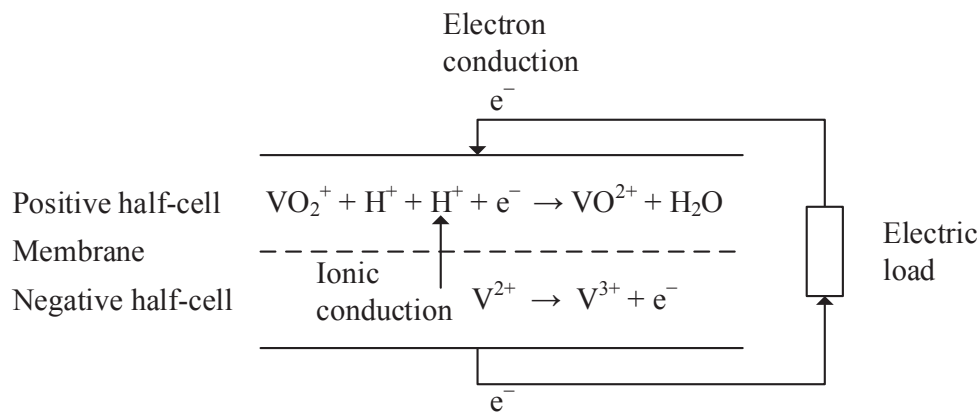


Figure 1-8: Fundamental redox reactions in a VRFB [14]

1.3 Objectives of the presented work

The presented work targets at increasing the VRFB system efficiency in both design and operation phase. Thereby, the reduction of losses caused by shunt currents, concentration overpotential and pump power demand is the overall goal. This goal is pursued using the following four steps:

- A multi-physical modeling approach for setting up a lumped-parameter model of a VRFB on a system level.
- A validation of the model with experimental data from VRFB manufacturers.
- An extensive holistic study on the impact of cell design on battery performance.
- An innovative flow rate control strategy.

1.4 Structure of the presented work

The presented work is organized as follows. In Chapter 2, a comprehensive multi-physical lumped-parameter model of the VRFB is presented. Each modeling aspect is illustrated with numerical examples to improve the understanding of the fundamental



Section 1.5 – The flow factor

internal processes in a VRFB. Relevant definitions for the system design and operation are introduced in Chapter 3. Subsequently, the developed cell voltage model is extensively validated in Chapter 4 using measurement data from three different VRFB manufacturers.

In Chapter 5, twenty-four different cell designs are created using finite element analysis (FEA) simulations. The validated model and the derived cell designs are then deployed in a single-stack system design study in Chapter 6. In Chapter 7, the same is done for a system using a three-stack string. For both systems, a flow rate optimization is carried out simultaneously.

In Chapter 8, the author's previously published innovative flow rate control strategy [16] is summarized and a stack voltage controller is introduced for overcoming the drawback of a reduced discharge capacity. The improved method is extensively compared against the established flow rate control strategies. Finally, the work is summarized in Chapter 9 and an outlook is given, providing future research topics. Additional figures and calculations are included in the Appendix.

1.5 The flow factor

One key parameter used in this work is the so-called flow factor. Hence, it is shortly introduced at the very beginning. For operating a flow battery, a minimal flow rate is required. This flow rate is given by Faraday's first law of electrolysis. As shown in Section 8.2 on page 120, the minimal flow rate depends on the SoC as well as on sign and magnitude of the applied current. The flow factor scales the minimally required flow rate. Hence for a flow factor of five, the actually applied flow rate is five times larger than electrochemically required. Consequently, only 20 % (one fifth) of the particular vanadium ions partaking in the respective reactions are converted as the electrolyte flows through the cells. Thus, there is a large surplus of reactants, which facilitates the reactions.