KTH Royal Institute of Technology

ZHAW Zurich University of Applied Sciences

Institute of Computational Physics

Master Thesis

A 1D Model of a Hydrogen-Bromine Redox Flow Battery

En 1D-modell för ett vätgas-brom-redoxflödesbatteri

Author: Jakub Włodarczyk
Supervisor ZHAW: Prof. Jürgen O. Schumacher
Supervisor KTH: Prof. Göran Lindbergh

Winterthur, Switzerland
October 18, 2018
Abstract

The strive for cutting out of a fossil-fuels dependence of countries’ economies has driven the global research into developing more sustainable power sources with the ultimate target to completely liberate from coal-fired and nuclear power plants. Shifting energy policies to renewable energy resources undoubtedly carries many beneficial features, but also poses a range of technical challenges, such as the necessity to overcome large fluctuations in the energy output from wind or photo-voltaic farms.

One solution to this problem proposed in the 1970’s is to integrate a large-scale energy storage device such as redox-flow batteries into the electrical grid. The thesis first presents a brief overview of flow battery technology and applications. Next, a one-dimensional, steady-state, macro-homogeneous mathematical model of a hydrogen-bromine flow battery is developed, described and solved. The results are in good agreement with existing experimental data. Moreover, a parametric study is performed to examine the impact of selected parameters on the overall performance of a single cell. A complete set of field variable plots is explicitly presented.

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acknowledgements</td>
<td>66</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>67</td>
</tr>
<tr>
<td>References</td>
<td>69</td>
</tr>
</tbody>
</table>
1 Introduction and Scope

The strive for cutting out of a fossil-fuels dependence on countries’ economies has driven the global research into developing more sustainable power sources with the ultimate target to completely liberate from coal-fired and nuclear power plants. Switching to renewable energy-based economy, although promising and environmentally-friendly, has proven to pose major problems with sustaining stable power delivery levels, mostly due to a fluctuating nature of wind, water, and solar energy resources. As of year 2017, energy storage comprised of 2% of the installed generation capacity in the U.S., 10% in Europe, and 15% in Japan [1].

On one sunny and windy Sunday, May 8th 2016, Germany achieved enough share of green energy converted so that keeping conventional power plants on was no longer necessary [2]. For safety reasons, however, they could not be completely switched off, resulting in energy surplus which drove the energy prices into negative figures. Given the power grid is a dynamic and inertial system, such spikes in electrical current overproduction can be perilous to the overall grid stability. A sample set of data collected from wind and solar power supplies is presented in Fig. 1 together with grid demand. It is evident that the problem of such variation in energy demand and supply calls for resolution, should the green energy shares become widely spread. In the light of projected substantial growth of the renewable energy sources shares, strict measures have to be taken to ensure a detachment of electricity generation and demand. In the European Union, 20% reliance on renewables is targeted by 2020 [3, 4] and 27% at minimum by 2030 [5], whereas the reported status for year 2016 amounted to 17% [5].

A natural remediation method for such a problem is to develop an energy storage device which would provide a reliable, cost-effective, long-life and minimum-service operation. For many years, energy storage has been realized by means of various batteries. However, the existing battery systems are not suitable to store the large amount of electric energy generated by fluctuating renewable energy produced by photo-voltaic power plants or wind turbines. Moreover, the materials used to produce such cells are expensive, and their capacity deteriorates rapidly if the charge-discharge cycles are intermittent. The aforementioned issues lead to a formulation of a set of requirements which an energy storage device shall fulfill in order to become a promising and competitive alternative to conventional solutions.
One such solution proposed in the 1970’s [7] is to utilize so-called redox-flow batteries (RFB), sometimes referred to as regenerative fuel cells. The present thesis highlights the most important aspects of RFBs with a special attention to one of the investigated chemistries, that is, Hydrogen-Bromine Redox Flow Batteries (HBRFB). Next, a one-dimensional mathematical model is developed, described and solved. The results are validated with the use of existing experimental data. Moreover, a parametric study is performed to examine the impact of selected parameters on the overall performance of a single cell.

Developing a robust modeling tool for HBRFB is a key to understanding the complex electrochemical and physical processes occurring in cells and stacks. To date, none of the existing papers have had explicit plots of all the balanced quantities included. The goal of the present work is to develop a 1D model of a HBRFB to simulate the driving potentials and fluxes of mass and charge in the through-plane direction of the cell assembly. A complete set of solution curves is shown in order to provide a better overview of the spatial evolution of field variables. This approach enables to track down possible errors and non-physical solutions in modeling, e.g. negative concentrations, as well as aids in the model validation process. The current thesis focuses on the underlying relationships governing the problem, with a detailed description of such topics as the importance of sign convention.
The thesis is one of the prerequisites for obtaining a Master of Science degree and is a part of the full-time Master’s program (120 ECTS) Chemical Engineering for Energy and Environment conducted at KTH Royal Institute of Technology Stockholm, Sweden. The work was done at the Institute of Computational Physics at ZHAW Zurich University of Applied Sciences, Winterthur, Switzerland between March and July 2018.
2 Overview of Redox Flow Batteries

2.1 Redox flow batteries as a promising technology

There are different possible ways to store energy available to date which can be classified with respect to the form of its storage. Energy can be stored mechanically as kinetic energy (flywheels) and as potential energy (pumped-storage hydroelectricity or compressed gas), electrically (directly in capacitors, supercapacitors) or chemically (indirectly in devices involving electrochemical reaction: secondary batteries or flow batteries). Some less common solutions involve electromagnetic energy from the Sun which can be converted to heat to melt salts which is in turn utilized to generate steam for electric power generators, satisfying intermittent energy demands. Good measures to compare different storage technologies are specific energy in Wh/kg and specific power in W/kg. These figures for different energy conversion devices are presented in Fig. 2.

Redox flow batteries provide an operating window with relatively large specific energy and small specific power. This characteristics make flow batteries applicable in large-scale energy storage, where the overall system weight is not a big concern. In recent years, redox flow batteries have gained increased attention as potential candidates for electrical energy storage due to its attractive features, not found in supercapacitors or secondary batteries [8].

Redox flow batteries usually involve simple electrode reactions and a deal of them have favorable electrode kinetics. In most cases, the reactions are highly reversible which translates to long battery lifespan and high round-trip efficiency. The batteries operate at low to moderate temperatures, decreasing device costs and the risks associated with explosion and flammability. Redox flow batteries constitute a promising solution for the regions of the world where pumped hydro and compressed gas energy storage availability is limited due to geographical reasons, as well as for smaller off-grid power loads.
What distinguishes RFBs from secondary batteries can be described in two categories [7]. Firstly, in a secondary battery, the electrochemically active material of anode and cathode is enclosed in a shell and the reactions occurring during charging and discharging change both chemical composition and physical properties of the electrodes. Secondary battery lifetime is thus dependent on the rate of all the irreversible transformations during the cycling process. In a RFB, the majority of the active material is stored outside of the actual cell assembly and the electrodes themselves are designed to be as inert as possible (graphite, precious metals) to reduce side reactions to minimum. Secondly, secondary batteries have very limited scaling-up possibilities since increasing the capacity implies using more active electrode materials which in turn require more non-active components such as current collectors, separators, and electrolyte. As a result, to achieve an effective enlarging of energy content or power output, the most reasonable solution is to stack, i.e. number-up, multiple smaller battery cells in a suited configuration (parallel, series, or mixed) rather than to manufacture larger cells themselves, which usually increases internal resistance. However, stacking cells requires addressing balancing the current and voltage out between each and every cell. Conversely, in RFB systems it is possible to separate the power- and energy-related scaling-up issues. To increase RFB capacity, more electrolyte is needed and because it is stored outside the cell, this goal is achieved by simply enlarging the electrolyte storage vessels. To obtain more power from the cell, more active surface area is required which usually means piling more cells onto one stack.
The introduction of RFBs on a large scale is definitely a challenging task. The primary reason why this technology is not too widespread nowadays, despite almost 40 years of development, is the system cost. The Nexight Group published a report in which the target capital cost for RFBs was estimated to 250 USD/kWh in 2015 decrementing to only 100 USD/kWh in 2030 [3]. In a recent study by Imperial College London in the UK, the competitive capital RFB cost to reach by 2019 is 650 USD/kWh provided that around 7 GWh or 4 billion USD of projects had been installed [9]. To reach the same capital cost for an equivalent lithium-ion batteries system, a minimum of 33 GWh of actual Li-ion running devices would be needed, which means that RFBs are at present a more viable solution. As denoted before, the target capital cost constitutes of roughly a half of the current cost estimations (provided sufficient investments made). The cost could be further reduced by introducing new, cheaper materials tailored exclusively for the RFBs, and developing more storage system facilities globally. Contrasting the secondary batteries with RFB cost-wise, it is estimated that RFBs become more cost-effective than conventional batteries when the storage time exceeds 3 days [4].

Depending on the application, several key performance targets for grid storage have been proposed [1]. The desired system lifetime should not be shorter than 10 years while maintaining the round-trip efficiency from 70 to 90%. The discharge duration should fall between 2 and 6 hours for long-duration applications, and the response time should be in the order of seconds or minutes for long-duration load following or electric energy time shift, respectively. When selecting the technology given the scale of an energy storage system, it is always desirable to weigh pros and cons of each of the solutions. Table 1 juxtaposes the advantages and disadvantages of RFBs.

Redox flow batteries are considered one of the most auspicious solutions for: (1) peak-shaving, (2) load-leveling (3), and frequency regulation. Peak-shaving is a technique used to reduce sharp maxima and minima in the load profile resulting from daily power usage fluctuations. Peak-shaving devices are usually installed at the power consumer’s site. Fast reaction times (within seconds) are normally desired in this application. Load-leveling works on a similar principle, except the storage device switches operation modes during longer intervals, charging on light grid loading periods and discharges upon higher power demand. Load-leveling devices thus require high-capacity solutions, being able to operate on hour-timescales. As a result, the load profile deviations from mean values can be significantly reduced. Frequency regulation addresses deviations from nominal grid frequency due to imbalance between power supply and demand. In order to maintain fairly steady frequency (typically 60 Hz in the Americas and 50 Hz in Europe and Asia), the energy storage devices must respond within fractions of a second. This is currently achievable with conventional resources like gas turbines, but only by maintaining
<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decoupling of energy and power scalability</td>
<td>Electrolyte leaking due to sealing problems; shunt currents due to high conductivity of the electrolytes</td>
</tr>
<tr>
<td>Separation of electrodes and electrochemical fuel</td>
<td>Ion-selective membrane durability</td>
</tr>
<tr>
<td>Electrodes are inert by design and do not undergo physiochemical changes</td>
<td>The high total mass and poor specific power of the system exclude RFBs from their mobile application</td>
</tr>
<tr>
<td>Promising total cost projections</td>
<td>Electrodes corrosion and side reactions (e.g. oxygen evolution and related carbon porous electrode oxidation)</td>
</tr>
<tr>
<td>Long lifetime and minimal maintenance costs</td>
<td>Species crossover though the membrane and catalyst poisoning</td>
</tr>
<tr>
<td>Safety of operation due to separation of active materials and electrodes</td>
<td>The use of aqueous solution limits the potential operating window</td>
</tr>
<tr>
<td>Ambient temperature operation</td>
<td>Vulnerability to temperatures below the freezing point; precipitation of salts may occur in low temperatures</td>
</tr>
<tr>
<td>Quick response time</td>
<td>Low solubility of some redox couples</td>
</tr>
<tr>
<td>High round-trip efficiency and very limited self-discharge</td>
<td>Immature technology, lack of materials tailored for RFB applications</td>
</tr>
<tr>
<td>Straightforward indication of the state of charge (e.g. color change of the active material ions solution during battery cycling)</td>
<td>Electrolyte degradation over time, fouling and pumping issues</td>
</tr>
<tr>
<td>Allowance for deep discharges and reduced risk of explosion or fire upon over-charge</td>
<td>High mass transfer limitations if the diffusive mass transport dominates</td>
</tr>
<tr>
<td>Broad operation window without sacrificing battery lifetime</td>
<td>Low energy density</td>
</tr>
</tbody>
</table>
them constantly in stand-by mode, which is costly and not too efficient. RFBs have the edge over other devices, being able to supply energy without long time lags.

### 2.2 Principles of operation

Redox flow batteries share characteristics of secondary batteries and fuel cells. Like every secondary battery, the idea is that a cell has the ability of charging and discharging in multiple cycles without too rapid degradation. In RFBs, the cycling process is also possible owing to high reversibility of used redox couples. However, the majority of the active material in the RFBs is stored externally in tanks, as shown in Fig. 3, and the electrolytes are continually pumped through the half-cells.

![Figure 3: Schematic of a typical RFB system. Figure adopted from [10].](image)

The construction of RFBs resembles much the solutions already known from the fuel cell industry. In fact, RFBs are sometimes referred to as “reversible fuel cells”. The main difference between RFBs and fuel cells is the fact that fuel cells are designed to operate in galvanic mode only, whereas RFBs work both in galvanic and electrolytic modes. On charging, RFBs behave similarly to electrolyzers. Reversing the electrochemical reactions in fuel cells (i.e. charging) is not easily attainable because of the nature of the redox reaction and cell design.

A typical setup of a RFB system consists of (1) two electrolyte storage vessels, one for the negative cell electrolyte and one for positive cell electrolyte, (2) two
electrolyte circulation pumps, and a cell stack, which consists of current collectors (4) bipolar plates, (5) flow distributors, (6) porous electrodes, (7) porous catalyst layers, and (8) an ion-selective membrane, as displayed in Fig. 3. The system also includes a number of auxiliary equipment, such as wiring, automatic control systems, temperature, pressure, and concentration sensors, piping, fittings and control valves, and heat exchangers.

The flow in the porous electrodes can be organized in different ways, depending on application. The three most common flow modes are presented in Fig. 4. In the flow-through mode, the electrolyte is forced through the porous electrode by a pressure differential. Better mass transfer conditions are achieved due to convective flow, sacrificing power loss on pumping due to substantial pressure drop. In the flow-by mode, the electrolyte flows in a flow channel and the electroactive species diffuse through the porous electrode. There is no convective flow in the porous electrode, therefore mass transfer limitations occur for high current densities due to reactant starvation. This flow design is characterized by much lower pressure drops across the stack. Interdigitated flow mode combines the features of both aforementioned modes, offering moderate pressure drops while maintaining reasonable mass transfer rates. However, precise manufacturing and sealing of such cells might render additional issues.

Half-cells represented in Fig. 4 are combined into membrane-electrode assemblies (MEAs) which form stacks, composed of 10 to 200 cell units [11]. A small-scale experimental set-up presented in Fig. 6 are used for preliminary measurements, cell cycling testing, parameter estimation, and aging studies. Successful candidates are scaled-up to a container- or plant-size devices, such as the one depicted in Fig. 5.

From the electrochemical point of view, two half-cell redox reactions are occurring in the cell. On discharge, species A in reduced form are being oxidized in the negative porous electrode, releasing electrons which travel through the external load. An ion-selective membrane allows the circuit-completing ion(s) to pass to the positive compartment while preventing intermixing of the two electrolytes. In the positive porous electrode, reduced species B are being oxidized and the electrons flowing from the external load are consumed. The two reactions can be generally written as follows. At the negative electrode:

\[
A^{(n-x)+} + xe^- \xrightarrow{\text{charge}} A^{n+} + xe^-, \quad n > x
\]  

(2.1)

At the positive electrode:

\[
B^{(m+y)+} + ye^- \xrightarrow{\text{charge}} B^{m+}
\]  

(2.2)
Figure 4: Schematic representation of three standard flow modes used in RFBs.

Figure 5: A plant-type, large-scale commercial all-vanadium RFB by Sumitomo Electric; Output power: 1MW, capacity: 5MWh. Figure adopted from [12].
For commercialized RFB cells, the typical charge-discharge current densities are in the range of 20–130 mA/cm$^2$ and the overall charge-discharge efficiency varies between 40 and 80% [14]. The open-circuit voltages for aqueous RFB electrolytes range from 1 to 1.6 V, and as high as 3.4 V for non-aqueous electrolytes [14]. For the most commercialized RFB chemistry, the all-vanadium RFB, the discharge time can vary from 3 to 10 h and the energy outputs from tens of kWh to 7 MWh [4].

A typical polarization curve of a flow battery is normally similar to those known from the field of low temperature fuel cells. However, for certain chemistries, there is a significant reduction of activation polarization losses due to vigorous kinetics in flow batteries, as compared to, for instance, rather sluggish oxygen reduction reaction employed in proton-exchange membrane fuel cells. A set of typical electrochemical performance curves is presented in Fig. 7. The aforementioned small activation loss in Fig. 7 (b) is manifested by almost linear curve for near open-circuit conditions. Moreover, an excellent coulombic efficiency 98% is observed which does not decrease over the cycles. Both energy and voltage efficiencies reach as high as 80% and are also stable over the cycles. The energy density of the RFB system is stable over operation time, but its value is rather low compared to other electrochemical systems. Nevertheless, this becomes less of an issue when stationary solutions are considered. Large dimensions of storage tanks are acceptable for most big-scale energy storage cases.
2.3 Classification of Redox Flow Batteries

The number of different flow battery systems is not facile to estimate, since different half-cell redox couples can be assembled together to produce new systems. In principle, gaseous, liquid, and solid phases of matter can be utilized in the electrode reactions. In the case of solid (for example deposition of metals or insoluble salts) or gaseous electrodes, flow batteries are referred to as “hybrid flow batteries”. What limits the freedom of redox couples choice for a RFB system is the redox potential (thermodynamically, the open-circuit potential cannot be too low nor too high), electrochemical reaction reversibility, solubility of active species, cost and availability of resources, and safety.

Several great reviews of existing state-of-the-art RFB systems have been written
to date [1, 3, 4, 7, 8, 11, 14–16] which list and categorize many different RFB chemistries. Soloveichik [4] divided the flow battery chemistries into 7 types, based on the state of matter used.

All-liquid aqueous flow batteries are systems which utilize two aqueous solutions of ions in each electrode compartment. Perhaps the most studied redox pair is the all-vanadium RFB, invented in 1986 by the research group of Skyllas-Kazacos. It involves vanadium salts having the oxidation states of $V^{II}/V^{III}$ and $V^{IV}/V^{V}$. One of the main energy density limiting factors in this type of RFBs is the solubility of the species, which in the case of vanadium chemistry is low when supporting electrolyte (sulfuric acid) is added. Other common all-liquid aqueous systems are: iron-chromium ($Fe^{II}/Fe^{III}$ and $Cr^{II}/Cr^{III}$) in hydrochloric acid solution, soluble metal-bromine, and polysulfide-bromine [4].

In hybrid RFBs with metal negative electrode, a metal is electroplated during charging. The positive electrode is a solution of either the same metal ions, or another redox couple in the liquid phase. Among others, the investigated RFB systems include zinc-halogen, zinc-cerium, all iron, all-copper or all-lead. In the cells involving electrodeposition, the problem of dendrite formation and salt precipitation are known to be the main obstacles for cell design.

In hybrid RFBs with a gas electrode, the gas-phase half-cell resembles those employed in the $H_2/O_2$ fuel cell industry. Hydrogen electrodes are most commonly chosen because of facile redox kinetics. Among these systems, a few worth attention are the hydrogen-halogen RFBs, whose round-trip efficiency is higher than that of comparable $H_2/O_2$ systems (~70% and 30–40%, respectively) due to faster cathodic reaction involving halogens instead of oxygen. Hydrogen-chlorine and hydrogen-bromine RFBs systems have been proposed in this field. Halogens, due to their corrosive nature, are usually stored in a liquid form, for example pressurized liquid chlorine tanks (10 bar) [4] or bromine aqueous solutions with complexing agents. Metal-air systems have also been investigated (for example zinc-air or vanadium-air) whose main advantage is decreased system size due to the fact that the air (oxygen) electrode does not require a storage tank.

Non-aqueous RFBs systems have the edge over aqueous electrolytes, because the cell voltage may reach far beyond the water decomposition reactions – oxygen and hydrogen evolution potentials, increasing the energy content, which is the product of voltage and charge. A common challenging task in non-aqueous systems is low electrolyte conductivity which leads to increased ohmic losses. Typical cells contain metal ions (Ru, V, Np, U, Co, Fe, Cu) in the form of complexes in non-aqueous solvents. High energy efficiencies have been reported (80–99%) [4] due to favorable kinetics.

Organic flow batteries attract more and more research attention owing to low-cost materials, bio-compatibility, and ability to tune various properties by in-
Introducing miscellaneous organic substituent groups to the carbon chain. The examples of organic compounds used are: quinones, furfural, o-xylene, or N-ethylidodecahydrocarbazole. Some of the systems require reaction-specific catalyst (e.g. Raney Nickel, Pt/Ru alloys) to achieve practically significant performance, whereas others, for instance 9,10-anthraquinone-2,7-disulfonic acid, do not need catalyst whatsoever [4].

The last major group of RFBs are the semisolid flow batteries. The idea is to use a conductive slurry electrolyte containing insoluble species (for example LiFePO$_4$/LiPF$_6$ salts suspended in ethylene carbonate–dimethyl carbonate). The electrochemical reaction occurs in the bulk of the electrolyte rather than on the surface of a porous electrode. This approach resolves the problem of limited species solubility. Slurries, however, have much greater viscosity than pure liquids which may lead to pumping issues and fouling.

### 2.4 The Hydrogen-Bromine Redox Flow Battery

#### 2.4.1 General Information

Historically, the first hydrogen-bromine flow battery was studied by Yeo and Chin in 1980 [17]. The paper outlined features such as high power density, low cost, high energy efficiency that make this particular chemistry a promising solution for energy storage.

A HBRFB cell can be operated in each of the three flow modes depicted in Fig. 4. Experimental analyses show that the flow-through mode in the bromine-bromide electrode allows to achieve less losses due to concentration polarization effects [18–20]. However, this work deals with a simple one-dimensional model which represents a flow-by mode to avoid solving the Navier-Stokes equations in 2 or 3 dimensions. A schematic of such system together with an indication of modeled domains is depicted in Fig. 8. The negative compartment consist of a current collector with flow channels (bipolar plate or end plate, depending on the position in the stack), a hydrogen gas diffusion layer (most commonly used is the flow-by mode due to high hydrogen gas diffusivity), and a catalyst layer. A proton-exchange membrane divides the cell and prevents from reactants intermixing. On the positive electrode side, a bromine/bromide liquid diffusion layer is contiguous to the membrane on one side, to a bipolar/end plate. Optionally, in the flow-by and interdigitated flow modes, the bipolar/end plates are equipped with flow channels.

The electrochemical reactions occurring in the HBRFB are described later in Section 2.5.1. In the excess of bromide anions, aqueous bromine is known to form complex compounds, for example tri-bromide ions, Br$_3^−$ [21]. Complexing agents such as polyethylene glycol can be added to further decrease the volatil-
Figure 8: Exploded view of a typical HBRFB cell components in flow-by mode in both electrodes with indicated modeled domains.
ity of bromine and mitigate crossover problems [22]. The cell operates at modest temperatures ranging from 25 to 50°C. The hydrogen side is usually pressurized up to tenths of bars, however experimental setups utilize pressures close to atmospheric [21]. Hydrogen can be pressurized using an external compressor or electrochemically. The latter method takes advantage of smaller parasitic power consumption [22]. The bromine side is normally kept at atmospheric pressure.

The reported peak power of a HBRFB is 1.4 W/cm². At smaller power loads of 0.4 W/cm² the voltaic efficiency is as high as 91%. The open-circuit voltage is a function of temperature, hydrogen pressure, and bromine/bromide species concentration, but a standard figure for reference purposes can be estimated to 1.09 V. On charging, the voltage usually reaches 1.4 to 1.6 V [18]. Concentration of bromine and bromide vary substantially in the reported studies. In fact, these parameters can be perceived as optimization variables due to their great impact on membrane performance, cost, and power characteristics. Exemplary values found in literature are, for instance, 0.9 M Br₂ and 1M HBr [18]. In a system cost sensitivity study [22], a bromine:bromide molar concentration ratio of 1:1 was suggested as a trade-off between good discharge performance and harmful effects of high free bromine content.

2.4.2 Materials

The materials used in experimental studies were: aluminum for end plates, stainless steel for current collectors, graphite for flow fields and layers of porous carbon for both porous electrodes [19]. Platinum is deposited on the hydrogen side, coated with PTFE to enhance two-phase mass transport. The membranes used are usually sulfonated tetrafluoroethylene-based polymers.

Despite HBRFB having a different characteristics than PEM fuel cells, still the most abundant materials for membranes are Nafion-based polymers. Modification of Nafion membranes have been studied including electrospun composites, for example 55 vol. % Nafion perfluorosulfonic acid and 45 vol. % inert (uncharged) polyphenylsulfone (PPSU) polymer [23]. The inert phase helps dealing with membrane swelling, decreases water uptake and prevents bromine crossover. Gas diffusion layers can be made of bi-layer carbon gas diffusion medium coated with Pt/C or RhₓSᵧ/C [21]. A typical Pt loading on the hydrogen side is low, for example 0.5 mg/cm². Pre-treated carbon felts of different kinds [24] having thicknesses of hundreds of µm are commonly used in the bromine compartment. No catalyst is needed owing to fast enough redox kinetics [18]. Among the sealant materials, Teflon found use in some experimental cells and proved good compatibility with bromine [18].
2.4.3 Performance

Working HBRFB cells achieved high energy efficiency (70-90%), and promising lifetime of 10,000 h [4, 25]. Typical polarization curves on discharge of both flow-by and flow-through from the experimental study by Cho are presented in Fig. 9. Flow-through mode usage yielded better performance overall. Another study by Kreuzer et al. [19], Fig. 10, shows the variation of discharge and charge polarization curves at different bromine concentrations (States of Charge). It shows that doubling the bromine concentration yields better performance on discharge by almost 0.5 W/cm², but not necessarily facilitates the charging process when bromide ions are consumed.

Cost market entry system capital of a HBRFB system was estimated to 220 USD/kWh, and levelized cost of delivered electricity 0.40 USD/kWh in a study by Singh and McFarland [22].

![Figure 9: Typical performance curves of a HBRFB cell in (a) flow-by mode, (b) flow-through mode. Figure adopted from [18].](image)
2.4.4 State of the Art

Practical stacks
The HBRFB concept has been known for several decades. Relatively high power density makes these batteries an attractive topic to perform more studies on. Little data is available about commercial systems involving hydrogen-bromide chemistry. A grid installation of a 50 kW/100 kWh stacks has been reported [4]. The current mainstream efforts towards broad commercialization of HBRFB include development of new, cheaper bromine poisoning-resistant catalyst, novel membranes tailored for this particular chemical composition, cheaper and reliable sealants and resilient cell housing materials.

HBRFB modeling
The very first RFB modeling attempts date back to 1973 and describe the electrochemical behavior of ferrous chloride–ferric redox couples [8]. The RFB chemistry which attracted the majority of attention in terms of simulation is the all-vanadium system due to a dynamic research towards broader commercialization. The literature on HBRFB systems simulation is rather scarce.

To date, only a few multiphysics HBRFB models have been developed, with the complexity ranging from already relatively complicated 1–dimensional models [26, 27], through 2–D simulations [28, 29] and a 3–D study [25]. Another model by Huskinson and Aziz [30] was solved without setting up a system of partial
differential equations, utilizing a fairly detailed description of different parameters variation (diffusivities, open-circuit potential, solution density).

2.4.5 Challenges

Flow battery technology is a very promising perspective for energy storage of the future. However, several technical issues must first be resolved in order to make this technology practical. All flow batteries share similar challenges and issues [11]. For certain chemistries additional complications arise due to sealing problems, the nature of the electrolytes and active species, or operating conditions.

In general, flow batteries suffer from issues regarding flow distribution. The best possible scenario would be to force the liquid through the cell in a plug flow regime so that the majority of the electrode surface is exposed to uniform species concentration. In reality, however, the fluid experiences local stagnation phenomena which cause depletion of the reactants and reduces the fraction of utilized surface. One possibility to rectify the performance is to use porous electrodes and higher flow rates which can help maintaining a sub-plug flow regime in the cells.

When the cells are connected in series between which a difference in electric potential exists, the so called shunt currents occur which lead to self-discharge, because part of the current is being by-passed by means of ionic migration from one cell to another. A way to mitigate this problem is to use longer flow channels within single cell. On the other hand, too long channels generate large pumping losses, so an optimum is usually sought.

Depleted electrolyte after passing through the stack is usually returned to the storage tank in a closed loop. This causes the concentration of active species to drop due to a constant dilution. This process is transient in nature, so the concentration of the species being currently consumed in the electrochemical reaction entering the cell is decreasing at every instant. Using two tanks for fresh and spent electrolyte can help, but adds substantial cost, complexity, and space occupied by the system.

Another issue known in the flow battery cells is the intermixing of species due to ionic migration in the electric field. The most common unwanted phenomenon is the crossover of water from one compartment to another, which dilutes one of the electrolytes and concentrates the other. In the charging process, the flux may be reversed, but it is never symmetrical, hence over time, the composition of the electrolytes will change permanently and will require additional treatment (regeneration), for example, using reverse osmosis processes.

For the hydrogen-bromine chemistry in particular, additional issues arise due to plethora of reasons. First, the dissolved bromine is a very corrosive substance. Bromine ions in water solution form strong hydrobromic acid which attacks many metals and polymers. Therefore, material issues are of the main priority when it
comes to the requirements for a safe and robust design.

Perhaps the most detrimental issue for HBRFB operation is the phenomenon of bromide and bromine species crossover through the PEM membrane. Bromide present in the hydrogen compartment corrodes and poisons the Pt catalyst, significantly reducing its lifetime \[31\]. The membrane thickness is one of the most critical parameters in the MEA. Since the kinetics of both redox reactions are facile, the main source of losses is the ohmic resistance of the membrane. Thicker membranes limit the migration of bromine and bromide species to the hydrogen half-cell, at the cost of decreased proton conductivity. Membrane water content is another key parameter and has long been known from the PEM fuel cell systems. In the case of HBRFB, not only does the water content impact the protonic conductivity, but also bromine and bromide transport. Water channels in the PEM create diffusion and migration paths for both unwanted intruding species \[20\].

The final remark about the challenges with HBFBs concerns safety. Bromine solutions have the normal boiling point around 60°C \[18\]. Working stacks thus require a reliable heat management system to prevent bromine releases to the environment. One way to lower the bromine vapor pressures is to dissolve complexing agents in the positive electrolyte. However, this solution may generate new issues such as forming a viscous, layer on the PEM membrane which impedes ionic transport. Hydrogen gas itself also contributes to increased care about the safety measures. Sealing technology is a very important component in the cell assembly. It provides a gas and liquid tightness at elevated pressures, temperatures, and mechanical stresses inside the cell while being inert to any of the species present in the cell.

2.5 Theoretical Background

2.5.1 Electrochemical Reactions

In the HBRFB, the two half-cell reactions are described below. The reactions represent the overall stoichiometry only and not the actual mechanisms occurring in the battery.

At the negative electrode dissolved hydrogen gas diffuses to the catalyst surface and is oxidized to protons on discharge. In the reverse process of charging, protons are reduced to hydrogen gas which dissolves in liquid water and diffuses away. Finally, the concentration of hydrogen gas reaches the saturation point and hydrogen gas evolution takes place. The half-cell reaction can be written as:

\[
\text{H}_2 \xrightarrow{\text{discharge}} 2\text{H}^+ + 2e^- \quad (2.3)
\]

At the positive electrode dissolved bromine gas diffuses to the catalyst surface and is reduced to bromide anions on discharge. In the reverse process of charg-
ing, bromide species are oxidized to bromine which dissolves in liquid water or is complexed by the excess of bromine anions. The half-cell reaction can be written as:

\[
\text{Br}_2 + 2e^- \xrightarrow{\text{charge}} 2\text{Br}^- \quad (2.4)
\]

The total reaction in the electrochemical cell is formally considered as formation or decomposition of hydrobromic acid:

\[
\text{H}_2 + \text{Br}_2 \xrightarrow{\text{charge}} 2\text{HBr} \quad (2.5)
\]

**2.5.2 Equilibrium Potential**

The equilibrium potential for the negative redox couple is described by the Nernst Equation:

\[
E_{\text{eq},-} = E^\circ_- + \frac{RT}{2F} \ln \left( \frac{c^{\circ+}_H}{c^{\circ}_H} \right) \quad (2.6)
\]

where \(E_{\text{eq},-}\) is the equilibrium potential of reaction (2.3), \(E^\circ_-\) is the standard potential of reaction (2.3), \(R\) is the universal gas constant, \(T\) is the temperature, \(F\) is the Faraday constant, \(c^{\circ+}_H\) is the bulk concentration of protons in the porous catalyst layer, \(c^{\circ}\) is the standard concentration (1 mol/L), \(p^\circ_{\text{H}_2}\) is the hydrogen gas partial pressure in the bulk gas phase, and \(p^*_\text{H}_2\) is the standard gas pressure (1 bar). The concentrations in the Nernst equation are normalized by a standard concentration of 1 mol/L to achieve non-dimensionality in the logarithms’ arguments. Since the mass transport effects are assumed negligible for hydrogen diffusion in the positive half-cell, the concentrations in the Nernst equation are taken as the concentrations in the bulk.

The equilibrium potential for the positive redox couple is also described by the Nernst Equation:

\[
E_{\text{eq},+} = E^\circ_+ + \frac{RT}{2F} \ln \left( \frac{c^{\circ}_{\text{Br}_2}/c^{\circ}_{\text{Br}}}{c^{\circ}_{\text{Br}_2}/c^{\circ}_{\text{Br}}^2} \right) \quad (2.7)
\]

where \(E_{\text{eq},+}\) is the equilibrium potential of reaction (2.4), \(E^\circ_+\) is the standard potential of reaction (2.4), \(c^\circ_{\text{Br}_2}\) and \(c^\circ_{\text{Br}}\) are the concentrations of bromine and bromide, respectively, at the surface of the carbon porous electrode. The concentrations in the Nernst equation are normalized by a standard concentration of 1 mol/L to achieve non-dimensionality in the logarithms’ arguments.

The solutions used in the HBRFB are assumed not very concentrated as the first approximation, therefore concentrations instead of activities are employed in the Nernst equations. Nevertheless, hydrogen bromide may reach the concentrations as high as 7 mol/L [32]. Moreover, the standard potentials derived from the state
functions (enthalpy and entropy of formation) are in principle weak functions of temperature. Again, for simplification purposes, these values are taken as constant parameters defined later in the model description.

2.5.3 Electrode Kinetics

Electrode kinetics is often described by means of the classical Butler-Volmer equation which applies for the specific redox couple (half-cell reaction) for given electrode material, and only at the very surface of the electrochemically active layer [33]:

$$j = j_0 \left[ \exp \left( \frac{\alpha_a F}{RT} (E - E_{eq}) \right) - \exp \left( -\frac{\alpha_c F}{RT} (E - E_{eq}) \right) \right]$$  \hspace{1cm} (2.8)

where $j_0$ is the exchange current density, $\alpha_a$ and $\alpha_c$ is the anodic and cathodic transfer coefficient, respectively, and $(E - E_{eq})$ is the surface overpotential. For a one-electron single-step, first order electrochemical reaction, the exchange current density derived from the electrode kinetics theory depends on the reduced and oxidized species [33]:

$$j_0 = F k^o (c_{\text{red}}^o)^{\alpha} (c_{\text{ox}}^o)^{1-\alpha}$$  \hspace{1cm} (2.9)

where $k^o$ is the standard reaction rate constant, $c_{\text{red}}^o$ and $c_{\text{ox}}^o$ are the surface concentrations of reduced and oxidized species, respectively. In addition, $\alpha \equiv \alpha_a$ and $\alpha_c = 1 - \alpha_a = 1 - \alpha$.

2.5.4 General Conservation Laws

The model is based on a macro-homogeneous approach where the variables within the subdomains are volume-averaged. The notion of representative elementary volumes is used, where the exact pore structure in the electrodes is not resolved.

A generic scalar conservation equation is used to represent the conservation principle in physics:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \Gamma = S$$  \hspace{1cm} (2.10)

where $\rho$ is the density of the balanced quantity (electrical charge in coulombs or matter in moles) having the units of $[\text{C m}^{-3}]$ or $[\text{mol m}^{-3}]$, respectively, $\Gamma$ is the flux of the balanced quantity, $[\text{C m}^{-2} \text{s}^{-1}]$ or $[\text{mol m}^{-2} \text{s}^{-1}]$, and $S$ is the source term in $[\text{C m}^{-3} \text{s}^{-1}]$ or $[\text{mol m}^{-3} \text{s}^{-1}]$, respectively. The first term on the left hand side is the accumulation of the quantity in the control volume, the second is the net transport of the balanced quantity from/to the control volume and the third term is the production or consumption of the balanced quantity within the control volume.
The expressions used to describe the flux of the balanced quantities depend on the quantity itself. For the transport of charged chemical species, the flux is governed by the Nernst-Planck equation:

\[ N_i = -[D_i \nabla c_i - c_i \mathbf{v} + u_i z_i c_i \nabla \phi_l] \]  

(2.11)

where \( N_i \) is the molar flux of species \( i \), \( D_i \) is the molecular diffusion coefficient of species \( i \), \( c_i \) is the concentration of species \( i \), \( \mathbf{v} \) is the velocity vector field of the fluid, \( u_i \) is the ionic mobility of species \( i \), \( z_i \) is the valence (charge) of species \( i \), and \( \phi_l \) is the ionic potential in the liquid phase. The mobility of species in diluted solution can be approximated with the use of the Einstein relation: \( u_i = D_i/(RT) \). The first term on the right hand side accounts for the transport of the species due to diffusion, the second – due to convection, and the third – by means of migration of charged species in the electrical field.

For the electronic conduction in a solid matrix (for example in a graphite felt), the flux of electrons \( j_s \) is governed by Ohm’s law which in differential form reads:

\[ j_s = -\sigma_s \nabla \phi_s \]  

(2.12)

where \( \sigma_s \) is the electronic conductivity of the matrix phase (e.g. graphite) and \( \phi_s \) is the electrostatic potential in the solid phase.

The ionic current density \( j_l \) is related to the transport of charged species (net molar fluxes of dissolved ions). It can be expressed as the sum of the molar fluxes multiplied by \( F \) and the respective valence \( z \), because positively charged species migrate in the opposite direction than the negatively charged species:

\[ j_l = F \sum_i z_i N_i. \]  

(2.13)
3 Model Derivation

3.1 Model Assumptions

A profound understanding of the phenomena occurring in the through-plane direction builds a strong basis for model development in two and three dimensions, where the inclusion of advanced Computational Fluid Dynamics or flow through porous media is possible.

The model presented in the current work is developed in three spatial dimensions, but implemented in a one-dimensional domain to obtain a base case solution of the most important flux contributions that determine the cell performance. A simple 1D model can be tested and troubleshot in a short time due to its computational efficiency.

The computational domain consists of 3 distinguished subdomains (counting from the left hand side): the Negative Gas Catalyst Layer (NGCL), the Proton-Exchange Membrane (PEM), and the Positive Liquid Diffusion Layer (PLDL). The subdomains are presented schematically in Fig. 11.

The purpose of developing the model is to set up and solve a system of partial differential equations describing charge and mass conservation principles in order to obtain the values of important quantities such as fluxes, electric potentials, concentrations, and source terms within the computational domain. The model input data are quantities having a defined physical meaning, such as porosity or exchange current density, which can be taken from the experimental data. By comparing the simulation curves with experimental results, the model can be validated. The model aims at giving an insight on the internal processes occurring in the cell. Once validated, it also provides a good basis for cell optimization without the need for repetitive empirical testing (factorial design, etc.).

To proceed with model development, the following model assumptions are made:

1. The cell operates at isothermal and isobaric conditions;

2. Convective mass transport is neglected in all domains. The model focuses on diffusional processes inside the 3-layer sandwich electrode assembly and does not take into account the bulk flow of reactants. The model reflects the conditions encountered in a flow-by mode cell;

3. The cell operates in a steady-state;

4. The crossover of bromine and bromide species through the membrane is neglected;

5. The electrolyte solution in the positive electrode is modeled as diluted;
6. The current collectors are assumed having a very high electrical conductivity implying no ohmic potential drop;

7. The platinum catalyst activity is constant;

8. The feed flowing to the negative and positive electrodes has uniform and constant concentration;

9. Water in the system is considered as a solvent only, water transport or phase transitions *per se* are not modeled;

10. The half-cell reactions are assumed to follow a single-step reaction mechanism without the formation of adsorbed intermediates;

11. The electrochemical reactions are occurring in the liquid phase for both dissolved H₂/protons and bromine/bromide;

12. The solvent constitutes of liquid water.

![Figure 11: Schematic of the model domain. The numbers correspond to the respective interfaces.](image)

### 3.2 The Nernstian Losses

The mass transport by molecular diffusion in the liquid phase usually occurs slowly enough to give rise to concentration gradients near the electrode surface. The local concentration variations influence the equilibrium potential predicted by the Nernst equation, thus the surface concentrations are introduced in Eq. (2.7). However, in practical experimental setups it is an arduous or infeasible task to measure the surface concentrations with high accuracy, therefore the surface concentration-dependent equilibrium potential is quantified with the use of a reference electrode
positioned in the bulk of the solution, whose concentration $c_i,\text{ref}$ may be conveniently chosen. Hence, the functional form of Eq. (2.7) reads now as:

$$E_{eq,\text{+}} = E^\circ_\text{+} + \frac{RT}{2F} \ln \left( \frac{c^{s}_{\text{Br}_2}/c^\circ}{(c^\circ_{\text{Br}^-}/c^\circ)^2} \right) + \frac{RT}{2F} \ln \left( \frac{c^{s}_{\text{Br}_2,\text{ref}}/c^\circ}{(c^\circ_{\text{Br}^-\text{ref}}/c^\circ)^2} \right) - \frac{RT}{2F} \ln \left( \frac{c^{s}_{\text{Br}_2,\text{ref}}/c^\circ}{(c^\circ_{\text{Br}^-\text{ref}}/c^\circ)^2} \right). \quad (3.1)$$

It is common to use the known or pre-defined bulk concentrations as the reference concentrations, therefore Eq. (3.1) can be rewritten as:

$$E_{eq,\text{+}} = E^\circ_\text{+} + \frac{RT}{2F} \left[ \ln \left( \frac{c^{s}_{\text{Br}_2}/c^\circ}{(c^\circ_{\text{Br}^-}/c^\circ)^2} \right) + \ln \left( \frac{c^{s}_{\text{Br}_2}/c^\circ}{(c^\circ_{\text{Br}^-}/c^\circ)^2} \right) - \ln \left( \frac{c^{s}_{\text{Br}_2}/c^\circ}{(c^\circ_{\text{Br}^-}/c^\circ)^2} \right) \right]. \quad (3.2)$$

or, upon rearrangement:

$$E_{eq,\text{+}} = E^\circ_\text{+} + \frac{RT}{2F} \left[ \ln \left( \frac{c^{s}_{\text{Br}_2}}{c^\circ_{\text{Br}_2}} \right) + \ln \left( \frac{c^{s}_{\text{Br}_2}/c^\circ}{(c^\circ_{\text{Br}^-}/c^\circ)^2} \right) - \ln \left( \frac{c^{s}_{\text{Br}_2}/c^\circ}{(c^\circ_{\text{Br}^-}/c^\circ)^2} \right) \right]. \quad (3.3)$$

It is also convenient to define the equilibrium potential evaluated at reference (bulk) concentrations denoted with asterisks (*):

$$E^*_{eq,\text{+}} = E^\circ_\text{+} + \frac{RT}{2F} \ln \left( \frac{c^{s}_{\text{Br}_2}/c^\circ}{(c^\circ_{\text{Br}^-}/c^\circ)^2} \right). \quad (3.4)$$

For the negative electrode, the dissolved hydrogen gas is assumed to diffuse to the platinum catalyst active surface at a rate sufficiently high to neglect the concentration polarization in the Butler-Volmer equation which thus reads:

$$j_- = j_{0,-} \left[ \exp \left( \frac{\alpha_{a,-} F}{RT} \eta_- \right) - \exp \left( - \frac{\alpha_{c,-} F}{RT} \eta_- \right) \right]. \quad (3.5)$$

where $j_{0,-}$ is the exchange current density for the negative electrode defined in section 3.8. The negative cell overpotential is defined as:

$$\eta_- = \phi_s - \phi_l - E_{eq,-} \quad (3.6)$$

The adopted sign convention is such that anodic overpotential and current density are positive.

For the positive electrode, the kinetic expression relating current density and overpotential is more complex due to mass transport effects. Starting from the general form of the Butler-Volmer equation (Eq. (2.8)) and incorporating Eq. (3.3)
together with the concentration-dependent definition of the exchange current density (Eq. (3.76) defined later in Section 3.8), the final form of the electrochemical kinetic equation can be expressed as:

$$\dot{j}_+ = j_{\text{ref},+} \left[ \left( \frac{c_{\text{Br}^-}}{c_{\text{Br}^*}} \right)^{p_{\text{Br}^-}} \left( \frac{c_{\text{Br}^2}}{c_{\text{Br}^*}} \right)^{q_{\text{Br}^2}} \exp \left( \frac{\alpha_a,+F}{RT} \eta_+ \right) - \left( \frac{c_{\text{Br}^-}}{c_{\text{Br}^*}} \right)^{p_{\text{Br}^-}} \left( \frac{c_{\text{Br}^2}}{c_{\text{Br}^*}} \right)^{q_{\text{Br}^2}} \exp \left( -\frac{\alpha_c,+F}{RT} \eta_+ \right) \right].$$

(3.7)

where $p_i$ and $q_i$ are the anodic and cathodic electrochemical reaction orders and are expressed as [34]:

$$p_i = \gamma_i + \frac{\alpha_{a,+} \nu_i}{n_i},$$

$$q_i = \gamma_i - \frac{\alpha_{c,+} \nu_i}{n_i}.$$  

(3.8)

and $j_{\text{ref},+}$ is the reference exchange current density for the positive electrode. The stoichiometric coefficients are defined as positive for anodic reactants and negative for cathodic reactants, thus $\nu_{\text{Br}^-} = +2$ and $\nu_{\text{Br}^2} = -1$. For simplicity, the reaction (2.4) is assumed to be an elementary step (even though it involves the transfer of two electrons and the occurrence of a simultaneous transfer is highly improbable [33, 35, 36]). With this assumption, the reaction orders correspond to the stoichiometric coefficients in the reaction 2.4. Moreover, the cathodic reaction rates are set to zero for the reaction in the anodic direction, and the anodic reaction rates are set to zero for the reaction in the cathodic direction. This is implied by the fact that the rate of the elementary reaction in the anodic direction does not depend on the concentrations of the oxidized species and the rate of the elementary reaction in the cathodic direction does not depend on the concentrations of the reduced species. At equilibrium, comparison of Eq. (3.7) to the Nernst equation suggests that [33]:

$$p_i - q_i = \nu_i$$

(3.9)

This conclusion is drawn assuming that $\alpha_{a,+} + \alpha_{c,+} = n$ and $\alpha_{a,+} = 1.0$, $\alpha_{c,+} = 1.0$. The theoretical justification of the selection of these parameters is not completely rigorous [33], and the adopted values commonly appear in experimental studies [36, 37]. Stated explicitly, the reaction rates are taken as follows (using Eq. (3.9)):

$$p_i = \begin{cases} 2 & \text{for } i = \text{Br}^- \\ 0 & \text{for } i = \text{Br}^2 \end{cases} \quad q_i = \begin{cases} 0 & \text{for } i = \text{Br}^- \\ 1 & \text{for } i = \text{Br}^2 \end{cases}$$

(3.10)

The overpotential in the positive cell is defined relative to the bulk concentrations via $E_{\text{eq},+}^*$ as:

$$\eta_+ = \phi_s - \phi_l - E_{\text{eq},+}^*$$

(3.11)

By convention, the cathodic overpotential and current density are negative.
3.3 Estimating surface concentrations

The model does not solve the governing equation in the pore-size scale. Rather than that, it gives the volume-averaged values at a certain point in the space, therefore an approach allowing for determination of surface concentrations has to be proposed in order to compute the surface concentrations of bromine/bromide species. It is also assumed that the steepest concentration gradients are present mostly in the very surrounding region adjacent to the pores surface, so utilizing the volume-averaged approach yields the bulk concentration at the particular point in the void pore structure (including the concentration variations near the surface in the global concentration average does not affect much its value). Having this assumption at hand, a steady-state mass balance can be performed on the bromine and bromide species at the liquid-pore interface to approximate the surface concentrations and eliminate them from the kinetic expressions:

\[
\frac{D_{\text{Br}^-}}{r_p} (c_{\text{Br}^-} - c_{\text{Br}^-}^s) = \frac{j_+}{F} \tag{3.12}
\]

\[
\frac{D_{\text{Br}_2}}{r_p} (c_{\text{Br}_2} - c_{\text{Br}_2}^s) = -\frac{j_+}{2F} \tag{3.13}
\]

where \(D_{\text{Br}^-}\) is the diffusion coefficient of bromide anions in water, and \(D_{\text{Br}_2}\) is the diffusion coefficient of bromine in water. The left-hand sides of Eq. (3.12) and Eq. (3.13) are derived from the film theory of mass transport (Nernst diffusion layer model), where the thickness of the diffusion layer is estimated to have average size comparable to that of the mean pore radius, \(r_p\). This approach has been proposed in several papers treating flow batteries of miscellaneous chemistries, including the HBRFB [25, 26, 29, 37, 38].

Equations (3.12) and (3.13) present a system of Domain Algebraic Equations which has to be solved simultaneously with the system of partial differential equations. Despite the fact that the system (3.12) and (3.13) admits an analytical solution for preselected \(p_i\) and \(q_i\), for the sake of a less constrained parametrization, the system of algebraic equation is solved numerically. This allows for making \(p_i\) and \(q_i\) changeable later (enabling, for example, parameter fitting to experimental data).

3.4 Sign Conventions

Adopting a uniform sign convention is crucial to every electrochemical problem, especially in the field of reversible systems that are flow batteries. It is therefore a good idea to present a recapitulation of the significance of the employed sign conventions.
First of all, the governing equations describing the electronic current are based on the standard definition of electrostatic potential and the current arises due to the movement of positive charges. Following this description, the vector of current density due to the movement of electrons ("physical current") will have the opposite sign to the current density vector due to the movement of positive charges ("technical current"). The source terms in the electronic current conservation equations signify the production or consumption of positive charges due to electrochemical reactions. On charging, the electrons generated in the hydrogen half-cell are traveling in the negative direction with respect to the X-axis orientation. This means that the positive charge-based current densities which are being solved for in the model will have a positive direction (and sign). On discharging, the reverse process takes place and the signs are reversed.

Following the well-known convention in electrochemistry, currents and overpotentials resulting from the reaction in the anodic direction are positive, whereas currents and overpotentials resulting from the reaction in the cathodic direction are negative. The current densities resulting from the Butler-Volmer or Tafel equations are formally vectors, per the definition of the current density. However, in the macro-homogeneous approach, the direction of the electrochemical transfer current density across the electrode’s phase boundary on the nano-scale is ignored, since the electrodes are porous and thus the phase boundary is distributed in a complex manner throughout the electrode volume. The sign of this current does not tell anything about the actual direction of this current in space. The current density resulting from the Butler-Volmer or Tafel equations is related to the source or sink terms in the continuity equations via the surface to volume factor (specific surface area) \( a \). Therefore, the signs of the sources or sinks only imply whether the charge, heat, momentum or mass is produced or consumed at the specific point in space.

The stoichiometric coefficients used in both electrochemical reactions are defined as positive for anodic reactants and negative for cathodic reactants. For example, during the discharge process, in the following expression for the source term of hydrogen in the negative compartment:

\[
S_{\text{H}_2,\text{aq}} = \frac{\nu_{\text{H}_2,\text{aq}} a}{nF} \cdot j_-
\]  

(3.14)

\( S_{\text{H}_2,\text{aq}} \) has to be negative (consumption of hydrogen occurs). \( j_- \) is positive by convention (anodic currents) and \( \nu_{\text{H}_2,\text{aq}} \) is equal to -1, making the whole right hand side of the equation negative, and so is \( S_{\text{H}_2,\text{aq}} \). On charging, \( j_- \) becomes negative (cathodic currents) and the whole source term becomes positive (production of hydrogen due to HER). Table 2 provides a summary of the adopted sign convention. The stoichiometric coefficients are listed in Table 6.
Table 2: Sign table for the quantities used in the model. “+” signifies $>0$, “−” signifies $<0$.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Discharge</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j(\eta)$</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>$\eta$</td>
<td>+</td>
<td>−</td>
</tr>
</tbody>
</table>

Required by the physics of the problem

<table>
<thead>
<tr>
<th>Quantity</th>
<th>NLDL</th>
<th>PLDL</th>
<th>NLDL</th>
<th>PLDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_s$</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>$S_l$</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>$S_{H^+}$</td>
<td>+</td>
<td>0</td>
<td>−</td>
<td>0</td>
</tr>
<tr>
<td>$S_{Br^-}$</td>
<td>N/A</td>
<td>+</td>
<td>N/A</td>
<td>−</td>
</tr>
<tr>
<td>$S_{H_2,eq}$</td>
<td>−</td>
<td>N/A</td>
<td>+</td>
<td>N/A</td>
</tr>
<tr>
<td>$S_{Br_2}$</td>
<td>N/A</td>
<td>−</td>
<td>N/A</td>
<td>+</td>
</tr>
</tbody>
</table>

3.5 Governing Equations

The general form of the governing equations applies in all considered domains. However, care must be taken when plugging in miscellaneous parameters to the equations such as diffusivities or porosities, as these vary depending on the material in the subdomains. One of the model assumptions is steady state operation, therefore the time derivative term in Eq. (2.10) is set to zero. The dependent variables in the model are listed in Table 3. The source terms used in each of the subdomains are collected in Table 4 and briefly described in the following paragraphs. The model parameters have been collected in Table 6, Table 7 and Table 8 with the distinction of subdomains.

Table 3: Dependent variables used in the model.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_s$</td>
<td>V</td>
<td>Electrostatic potential (in the solid phase)</td>
</tr>
<tr>
<td>$\phi_l$</td>
<td>V</td>
<td>Ionic potential (in the liquid phase)</td>
</tr>
<tr>
<td>$c_{Br_2,eq}$</td>
<td>mol m$^{-3}$</td>
<td>Concentration of dissolved bromine gas</td>
</tr>
<tr>
<td>$c_{H_2,eq}$</td>
<td>mol m$^{-3}$</td>
<td>Concentration of dissolved hydrogen gas</td>
</tr>
<tr>
<td>$c_{Br^-}$</td>
<td>mol m$^{-3}$</td>
<td>Concentration of bromide anions</td>
</tr>
<tr>
<td>$c_{H^+}$</td>
<td>mol m$^{-3}$</td>
<td>Concentration of protons</td>
</tr>
</tbody>
</table>
I. Equations in the Negative Gas Catalyst Layer

(a) Conservation of the electronic current – charge balance in the solid phase

The conservation equation for electrons in the negative gas catalyst layer reads:

\[ \nabla \cdot \mathbf{j}_s = S_s \]  

(3.15)

where \( S_s \) is the source term of electrons. The flux of electrons (i.e. the electric current) has already been expressed in its basic form of a differential Ohm’s law in Eq. (2.12) which is also applicable in the current model:

\[ \mathbf{j}_s = -\sigma_{\text{eff}}^s \nabla \phi_s \]  

(3.16)

where \( \sigma_{\text{eff}}^s \) is the effective electronic conductivity of the solid phase (negative electrode). The source term for electrons in the NGCL is equal to the electric current generation due to the electrochemical reaction (as described by the Butler-Volmer equation) per volume of the catalyst layer:

\[ S_s = -R_{\text{el,}}^- = -a_\text{ } \cdot \mathbf{j}_- \]  

(3.17)

where \( -R_{\text{el,}}^- \) is the electrochemical reaction rate and \( a^- \) is the specific surface area of the electrochemically active material in the negative gas catalyst layer (here Pt metal) in \( \text{m}^2/\text{Pt}/\text{m}^3\text{electrode volume} \).

(b) Conservation of mass – dissolved H\(_2\) balance

The conservation equation for the dissolved hydrogen gas in the negative electrode reads:

\[ \nabla \cdot \mathbf{N}_{\text{H}_2,\text{aq}} = S_{\text{H}_2,\text{aq}} \]  

(3.18)

where \( S_{\text{H}_2,\text{aq}} \) is the source term for hydrogen gas in the liquid phase. The flux of dissolved hydrogen is governed by Fick’s law:

\[ \mathbf{N}_{\text{H}_2,\text{aq}} = -D_{\text{H}_2,\text{aq}}^{\text{eff}} \nabla c_{\text{H}_2,\text{aq}} \]  

(3.19)

where \( D_{\text{H}_2,\text{aq}}^{\text{eff}} \) is the effective diffusion coefficient of dissolved hydrogen in water. The source term of dissolved hydrogen is defined with the use of Faraday’s law:

\[ S_{\text{H}_2,\text{aq}} = \frac{\nu_{\text{H}_2,\text{aq}} a^-}{nF} \cdot \mathbf{j}_- \]  

(3.20)

where \( \nu_{\text{H}_2,\text{aq}} \) is the stoichiometric coefficient for hydrogen gas which follows the sign convention explained earlier (positive for anodic reactants and negative for cathodic reactants).
(c) Conservation of the ionic current in the liquid phase

The conservation law for the ionic current in the liquid phase reads:

\[ \nabla \cdot \mathbf{j}_l = S_l \]  \hspace{1cm} (3.21)

Flux of bromine anions is zero in the negative compartment (no crossover assumption), therefore the flow of ionic current is only due to the transport of protons:

\[ \mathbf{j}_l = Fz_{\text{H}^+} \mathbf{N}_{\text{H}^+} \]  \hspace{1cm} (3.22)

The source of ionic current arises due to electrochemical reaction and can be written as:

\[ S_l = +R_{\text{el}} = a_- \cdot j_- \]  \hspace{1cm} (3.23)

Equation (3.22) can then be rewritten plugging in Eq. (3.29):

\[ j_l = -z_{\text{H}^+}^2 \frac{D_{\text{eff}}^{\text{H}^+} F^2 c_l}{RT} \nabla \phi_l. \]  \hspace{1cm} (3.24)

where \( c_l \) is the fixed negative charge concentration in the membrane. The term \( z_{\text{H}^+}^2 D_{\text{eff}}^{\text{H}^+} F^2 c_l/(RT) \) is a constant which can be lumped into a material parameter, by the analogy to Ohm’s law:

\[ j_l = -\sigma_{l \text{eff}}^\text{eff} \nabla \phi_l. \]  \hspace{1cm} (3.25)

where \( \sigma_{l \text{eff}}^\text{eff} \) is the effective proton conductivity in the ionomer.

(d) Conservation of mass – \( \text{H}^+ \) balance

Formally, the conservation of mass for protons can be expressed as:

\[ \nabla \cdot \mathbf{N}_{\text{H}^+} = S_{\text{H}^+} \]  \hspace{1cm} (3.26)

And the flux of protons is given by:

\[ \mathbf{N}_{\text{H}^+} = - \left[ D_{\text{H}^+}^{\text{eff}} \nabla c_{\text{H}^+} + \frac{z_{\text{H}^+} D_{\text{H}^+}^{\text{eff}} F}{RT} c_{\text{H}^+} \nabla \phi_l \right] \]  \hspace{1cm} (3.27)

The source term for protons can be related to the electrochemical reaction rate by Faraday’s law:

\[ S_{\text{H}^+} = \frac{\nu_{\text{H}^+} a_-}{nF} \cdot j_- \]  \hspace{1cm} (3.28)
The concentration of protonic species is assumed constant within the whole volume of the ionomer deposited in the catalyst layer due to the fact that the negative charges (sulfonic acid groups -SO$_3$H) are fixed and the principle of electroneutrality holds. Thus, $c_{H^+} = \text{const} = c_I$ and $\nabla c_{H^+} = 0$, so Eq. (3.27) reduces to:

$$N_{H^+} = -\frac{z_{H^+}D_{H^+}^{\text{eff}}Fc_I}{RT} \nabla \phi_l.$$  \hfill (3.29)

As signalized before in Eq. (3.22), the flux of protons in the NGDL is a scaled (equivalent) version of the ionic flux, thus solving a separate governing equation for proton transport may lead to convergence issues due to over-specification of the problem. As a consequence, the proton balance is not solved in the NGDL. The concentration of protons is unambiguously given by $c_I$ and the flux of protons can be calculated explicitly as $N_{H^+} = j_l/(Fz_{H^+})$.

II. Equations in the PEM Layer

(a) Conservation of the ionic current in the humidified membrane phase

The governing equation for the ionic current in the PEM reads:

$$\nabla \cdot j_l = S_l$$  \hfill (3.30)

Using Eq. (3.34) and similarly introducing the protonic conductivity of the ionomer one arrives at the equivalent of Ohm’s law for the ionic current:

$$j_l = -\sigma_l \nabla \phi_l.$$  \hfill (3.31)

There is no electrochemical reaction occurring in the membrane, therefore:

$$S_l = 0$$  \hfill (3.32)

(b) Conservation of mass – H$^+$ balance

The conservation law for protons in the PEM is expressed as:

$$\nabla \cdot N_{H^+} = S_{H^+}$$  \hfill (3.33)

The flux of protons in the membrane reads:

$$N_{H^+} = -\left[ D_{H^+} \nabla c_{H^+} + \frac{z_{H^+}D_{H^+}F}{RT} c_{H^+} \nabla \phi_l \right]$$  \hfill (3.34)
The concentration of protonic species is assumed constant within the whole volume of PEM due to the fact that the positive charges (sulfonic acid groups -SO$_3$H) are fixed. Thus $c_{H^+} = \text{const} = c_t$ and $\nabla c_{H^+} = 0$ and Eq. (3.34) reduces to:

$$N_{H^+} = -\frac{z_{H^+} D_{H^+} F c_t}{RT} \nabla \phi_l.$$  \hspace{1cm} (3.35)

It follows that the flux of protons is caused by migration in the solution electric field, and not due to concentration gradient. A similarity of Eq. (3.35) to Eq. (3.24) allows for rewriting Eq. (3.35) as:

$$N_{H^+} = -\frac{\sigma_l}{z_{H^+} F} \nabla \phi_l = j_l/(F z_{H^+}).$$  \hspace{1cm} (3.36)

For the reasons already mentioned, it is redundant to solve an additional differential equation for the protons as all the necessary quantities can be derived from the ionic current balance, since the protons are the only charged species considered in PEM domain. There is no electrochemical reaction in the PEM, so the production of protons in the membrane is zero:

$$S_{H^+} = 0$$  \hspace{1cm} (3.37)

### III. Equations in the Positive Liquid Diffusion Layer

(a) Conservation of the electronic current – charge balance in the solid phase

The conservation of electronic current in the positive carbon electrode reads:

$$\nabla \cdot j_s = S_s$$  \hspace{1cm} (3.38)

The flux of electrons is governed by Ohm’s law:

$$j_s = -\sigma_{s}^{\text{eff}} \nabla \phi_s$$  \hspace{1cm} (3.39)

and the electron source is due to the electrochemical reaction:

$$S_s = -R_{el,+} = -a_+ \cdot j_+$$  \hspace{1cm} (3.40)

where $a_+$ is the carbon material specific surface area in $\text{m}^2_{\text{carbon}}/\text{m}^3_{\text{electrode}}$.

(b) Conservation of mass – Br$^-$ balance
The bromide anions conservation equation in the positive electrode compartment reads:

$$\nabla \cdot N_{Br^-} = S_{Br^-}$$  \hspace{1cm} (3.41)

The bromide species flux is governed by the Nernst-Planck Equation:

$$N_{Br^-} = - \left[ D_{Br^-}^{\text{eff}} \nabla c_{Br^-} + \frac{z_{Br^-} D_{Br^-}^{\text{eff}} F}{RT} c_{Br^-} \nabla \phi_l \right]$$  \hspace{1cm} (3.42)

where $D_{Br^-}^{\text{eff}}$ is the effective bromide anion diffusion coefficient and $c_{Br^-}$ is the bromide species concentration in the bulk liquid in the volume of the pores. The source term of bromide species is expressed as:

$$S_{Br^-} = \frac{\nu_{Br^-} a_+}{nF} \cdot -j_+$$  \hspace{1cm} (3.43)

(c) Conservation of mass – dissolved Br$_2$ balance

The governing equation for dissolved bromine in the positive electrode compartment reads:

$$\nabla \cdot N_{Br_2} = S_{Br_2}$$  \hspace{1cm} (3.44)

And the flux of bromine is expressed as Fick’s law owing to the fact that bromine species are electrically neutral.

$$N_{Br_2} = -D_{Br_2}^{\text{eff}} \nabla c_{Br_2}$$  \hspace{1cm} (3.45)

The source term of bromine is written with the use of Faraday’s law:

$$S_{Br_2} = \frac{\nu_{Br_2} a_+}{nF} \cdot -j_+$$  \hspace{1cm} (3.46)

(d) Conservation of the ionic current in the liquid phase

The conservation of ionic current in the positive electrode compartment is expressed as:

$$\nabla \cdot j_l = S_l$$  \hspace{1cm} (3.47)

and the ionic flux is written as:

$$j_l = F \left( z_{Br^-} N_{Br^-} + z_{H^+} N_{H^+} \right)$$  \hspace{1cm} (3.48)

The source of ionic current is due to electrochemical reaction, as specified below:

$$S_l = +R_{cl} = a_+ \cdot j_+$$  \hspace{1cm} (3.49)
Formally, the governing equation for proton transport in the PLDL reads:
\[
\nabla \cdot \mathbf{N}_{H^+} = S_{H^+} 
\]
And the proton flux is defined as:
\[
\mathbf{N}_{H^+} = - \left[ D_{eff}^{H^+} \nabla c_{H^+} + \frac{z_{H^+} D_{eff}^{H^+} F}{RT} c_{H^+} \nabla \phi_l \right] 
\]
Protons do not participate in the electrochemical reaction in the positive electrode, thus:
\[
S_{H^+} = 0 
\]
Due to the fact that the solution (posolyte) must remain electroneutral, the concentration of protons and bromide anions has to be the same at every point in the liquid phase (except for the small volume of liquid which exists close to the electrode surface and is subject to the charge distribution due to the electric double layer formation). In reality, the condition is fulfilled naturally, which may not be the case in numerical studies [39] which always involve certain degree of approximation. Writing 6 differential equations for 6 dependent variables should satisfy the definiteness of the problem. However, imposing an additional equation:
\[
c_{H^+} = c_{Br^-} 
\]
which stems from the electroneutrality constraint causes that the problem becomes over-specified. The simplest remedy to this issue is to replace one of the governing equations for charged species with the electroneutrality condition Eq. (3.53). In this work, the equation for protons transport (Eq. (3.50)) as the replaced equation is selected.

3.6 Boundary Conditions

In the following section an overview of boundary conditions employed in the model is presented. The boundaries are numbered according to Fig. 11.

I. Boundary conditions for electronic charge conservation equation
The reference potential of electrons is arbitrarily set to zero at boundary 1 (Dirichlet boundary condition):
\[
\phi_s|_1 = 0.00 \text{ V} 
\]
No electron flux from the membrane is assumed (Neumann boundary condition), because the membrane is not an electronic conductor:

\[ \mathbf{j}_s \cdot \hat{n}|_2 = 0 \]  
where \( \hat{n} \) is a unit vector normal to the electrode surface. At the positive battery terminal the total cell voltage is imposed (Dirichlet boundary condition), which simulates the potentiostatic cell operation:

\[ \phi_s|_4 = E_{cell} \]  

II. Boundary conditions for dissolved hydrogen gas conservation equation

Constant concentration of dissolved hydrogen gas at the boundary Gas Diffusion Layer – NGCL (Dirichlet boundary condition) is employed. The additional assumption of gas-liquid equilibrium from Henry’s law and no mass transfer resistance on the gas-liquid interface yields the following boundary value of hydrogen gas concentration:

\[ c_{\text{H}_2,\text{aq}}|_1 = \frac{p_{\text{H}_2}}{H_{\text{H}_2/\text{Nafion}}} \]  
where \( H_{\text{H}_2/\text{Nafion}} \) is Henry’s constant for hydrogen in humidified Nafion given in Section 3.8.

Dissolved hydrogen gas is not transported through the PEM (Neumann boundary condition):

\[ \mathbf{N}_{\text{H}_2,\text{aq}} \cdot \hat{n}|_2 = 0 \]  

III. Boundary conditions for protons conservation equation

The protons are not transported outside the NGCL (Neumann boundary condition):

\[ \mathbf{N}_{\text{H}^+,} \cdot \hat{n}|_1 = 0 \]  

Concentration continuity at the catalyst/PEM interface is assumed (Dirichlet boundary condition):

\[ c_{\text{H}^+,}|_{2,\text{NGCL}} = c_{\text{H}^+,}|_{2,\text{PEM}} = c_f \]  

The governing equation for protons in the PEM is not solved for, because the flux of protons is directly proportional to the flux of the ionic current (protons are the only current-conducting species in the PEM). The flux of protons through the PEM-PLDL interface has to be continuous (no surface sinks or side reactions) and a way to express this fact is to link the ionic flux in the PEM with the actual proton flux in the PLDL as follows:

\[ \hat{n} \cdot \mathbf{j}|_{3,\text{PEM}} = F \hat{n} \cdot \mathbf{N}_{\text{H}^+,}|_{3,\text{PLDL}} \]
The electroneutrality condition at the end of the PLDL (Dirichlet boundary condition) requires that the concentration of protons is equal to the concentration of bromide anions:

\[ c_{H^+}|_4 = c_{Br^-}^* \]  

(3.62)

**IV. Boundary conditions for bromine species conservation equation**

No bromine crossover to the membrane is assumed (Neumann boundary condition):

\[ \mathbf{N}_{Br_2} \cdot \hat{n}|_3 = 0 \]  

(3.63)

The bromine concentration at the inlet to the PLDL is set as one of the model parameters (Dirichlet boundary condition):

\[ c_{Br_2}|_4 = c_{Br_2}^* \]  

(3.64)

**V. Boundary conditions for bromide species conservation equation**

No bromide species crossover to the membrane is assumed (Neumann boundary condition):

\[ \mathbf{N}_{Br^-} \cdot \hat{n}|_3 = 0 \]  

(3.65)

The bromide concentration at the inlet to the PLDL is set as one of the model parameters (Dirichlet boundary conditions):

\[ c_{Br^-}|_4 = c_{Br^-}^* \]  

(3.66)

**VI. Boundary conditions for ionic charge conservation equation**

There is no ionic flux outside the NGCL (Neumann boundary condition):

\[ \mathbf{j}_i \cdot \hat{n}|_1 = 0 \]  

(3.67)

No contact resistance between NGCL and PEM is assumed (the same ionomer material):

\[ \phi_i|_{2,NGCL} = \phi_i|_{2,PEM} \]  

(3.68)

Continuity of ionic current at the PEM-PLDL interface yields:

\[ \mathbf{j}_i \cdot \hat{n}|_{3,PEM} = \mathbf{j}_i \cdot \hat{n}|_{3,PLDL} \]  

(3.69)

A Gibbs-Donnan potential jump at the PEM-PLDL interface is taken into account due to different concentrations of protons in each of the phases:

\[ \phi_i|_{3,PLDL} = \phi_i|_{3,PEM} + \frac{RT}{F} \ln \left( \frac{c_{H^+}|_{3,PLDL}}{c_{H^+}|_{3,PEM}} \right) \]  

(3.70)
In order to simulate the Gibbs-Donnan potential jump without solving additional potential-related equations such as Planck-Boltzmann equations [40], a simplified approach is adopted based on the idea of thin-layer or contact resistance. To achieve the continuity of ionic flux across the membrane-solution interface, two expressions for ionic current density are utilized on each of its side:

\[
j_l|_{3,\text{PLDL}} = \frac{\phi_l|_{3,\text{PLDL}} - \phi_l|_{3,\text{PEM}}}{\delta_{EDL}} \cdot \sigma_{H^+}
\]  

(3.71)
on the PLDL side and

\[
j_l|_{3,\text{PEM}} = j_l|_{3,\text{PLDL}}
\]  

(3.72)
on the PEM side. Additional parameters \(\delta_{EDL}\) and \(\sigma_{H^+}\) are explained and calculated in Section 3.8.

Outside of the porous layer (in the bulk liquid, modeling of which is out of the present work’s scope) the only mechanisms of mass transport are convection and diffusion, therefore the solution must remain electroneutral (ionic currents stemming from protons and bromide anions cancel each other out):

\[
F(z_{\text{Br}^-} \cdot N_{\text{Br}^-}|_4 + z_{\text{H}^+} \cdot N_{\text{H}^+}|_4) = 0
\]  

(3.73)
Comparison of Eq. (3.73) to Eq. (2.13) shows that this boundary condition can be written equivalently as:

\[
j_1 \cdot \hat{n}|_4 = 0
\]  

(3.74)
3.7 Summary of Formulae

In this section, a tabular summary of formulae is presented.

**Table 4:** Source terms used in the model.

<table>
<thead>
<tr>
<th>Source</th>
<th>NGDL</th>
<th>PEM</th>
<th>PLDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_s$</td>
<td>$-R_{el,-}$</td>
<td>N/A</td>
<td>$-R_{el,-}$</td>
</tr>
<tr>
<td>$S_1$</td>
<td>$+R_{el,+}$</td>
<td>0</td>
<td>$+R_{el,+}$</td>
</tr>
<tr>
<td>$S_{Br_2}$</td>
<td>N/A</td>
<td>N/A</td>
<td>$\frac{\nu_{Br_2^{aq}}}{nF} \cdot j_-$</td>
</tr>
<tr>
<td>$S_{H_2,aq}$</td>
<td>$\frac{\nu_{H_2,aq}}{nF} \cdot j_-$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$S_{Br^-}$</td>
<td>N/A</td>
<td>N/A</td>
<td>$\frac{\nu_{Br^-}}{nF} \cdot j_+$</td>
</tr>
<tr>
<td>$S_{H^+}$</td>
<td>$\frac{\nu_{H^+}}{nF} \cdot j_+$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 5:** Boundary conditions. Numbers 1-4 represent interfaces according to Fig. 11.

<table>
<thead>
<tr>
<th>Interface</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\phi_s$</td>
<td>$\phi_{s,1}=0.00 \text{ V}$</td>
<td>$j_1 \cdot \hat{n}_2=0$</td>
<td>$j_2 \cdot \hat{n}_3=0$</td>
<td>$\phi_{s,4}=E_{cell}$</td>
</tr>
<tr>
<td>$\phi_l$</td>
<td>$j_1 \cdot \hat{n}_1=0$</td>
<td>$\phi_{l,2,PEM} = \phi_{l,1}$</td>
<td>$j_3 \cdot \hat{n}_{3,PLDL}$</td>
<td>$j_4 \cdot \hat{n}_4=0$</td>
</tr>
<tr>
<td>$c_{Br_2,aq}$</td>
<td>N/A</td>
<td>N/A</td>
<td>$N_{Br_2} \cdot \hat{n}_3=0$</td>
<td>$c_{Br_2} \cdot \hat{n}<em>4=c</em>{Br_2}^{*}$</td>
</tr>
<tr>
<td>$c_{H_2,aq}$</td>
<td>$c_{H_2,aq,1} = \frac{p_{H_2}}{T}$</td>
<td>$N_{H_2,aq} \cdot \hat{n}_2=0$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$c_{Br^-}$</td>
<td>N/A</td>
<td>N/A</td>
<td>$N_{Br^-} \cdot \hat{n}_3=0$</td>
<td>$c_{Br^-} \cdot \hat{n}<em>4=c</em>{Br^-}^{*}$</td>
</tr>
<tr>
<td>$c_{H^+}$</td>
<td>$N_{H^+} \cdot \hat{n}_1=0$</td>
<td>$c_{H^+} \cdot \hat{n}<em>{2,PEM}=c</em>{H^+}$</td>
<td>$\hat{n}<em>{3,PEM} \cdot F=\hat{n} \cdot N</em>{H^+}$</td>
<td>$c_{H^+} \cdot \hat{n}<em>4=c</em>{H^+}^{*}$</td>
</tr>
</tbody>
</table>

*Additionally, the Gibbs-Donnan potential is imposed according to Eq. (3.70).*

3.8 Estimation of Model Parameters

Exchange current density is given for the specific redox couple and the electrode material. It is also dependent on species concentration and on temperature. The exchange current density for the hydrogen reduction/oxidation reactions (HRR/HOR) on a platinum-ionomer substrate was estimated in an experimental
HBRFB study [19] to 1.00 mA/cm²Pt (at 22 °C and 3 psig, humidified hydrogen) and this value is taken as the reference exchange current density for the negative electrode. For the HRR/HOR reactions, different values of ($\alpha_{a,-} + \alpha_{c,-}$) may be assumed and the literature most often reports this sum to fall between 1.0 and 2.0 [41]. To remain coherent with the experimental study [41], the values of $\alpha_{a,-}$ and $\alpha_{c,-}$ were both assumed to be equal to 0.5.

The exchange current density is a kinetic parameter and thus is a function of temperature. According to [42], the temperature dependence of $j_0$ was found to follow the Arrhenius law with the activation energy equal to 16 kJ/mol. Moreover, $j_0$ depends on hydrogen partial pressure raised to the power of 0.5 [29, 35, 37]. The proposed corrected form of the exchange current density for the negative electrode is expressed as:

$$j_{0,-} = j_{0,ref,-} \left( \frac{p_{H_2}}{p_{H_2,ref}} \right)^{0.5} \cdot \exp \left[ \frac{16000 \text{ J/mol}}{R} \left( \frac{1}{(80 + 273.15)[K]} - \frac{1}{T} \right) \right] \quad (3.75)$$

For the positive electrode, the exchange current density is assumed to follow an empirical power-law concentration dependence [33, 34], expressed as:

$$j_{0,+} = j_{0,ref,+} \left( \frac{c_{Br}^8}{c_{Br}^0} \right)^{\gamma_{Br^-}} \left( \frac{c_{Br_2}^8}{c_{Br_2}^0} \right)^{\gamma_{Br_2}} \quad (3.76)$$

The $\gamma_i$ coefficients depend on the order of the chemical reaction with respect to $i$-th species, as specified in Eq. (3.8). Due to lack of experimental data involving temperature dependence of the positive electrode exchange current density, it is assumed constant.

Henry’s constant for hydrogen in humidified Nafion is expressed as follows [44]:

$$H_{H_2/Nafion} = 0.255 \times 10^5 \cdot \exp(170[K]/T) \quad (3.77)$$

The diffusion coefficients of ionic species in liquid and electrode porosities are assumed constant and listed in Table 6. The diffusion coefficients are in principle lower in the porous media than in the bulk solution. To reflect this fact, the following expression is used (Bruggemann correction):

$$D_{i}^{\text{eff}} = \varepsilon^{1.5}D_{i} \quad (3.78)$$

where $\varepsilon$ is the porosity of the porous layer (different values for NGCL and PLDL) and $D_{i}$ is the diffusion coefficient of species $i$ in water. The ionic conductivity of the ionomer is assumed constant. However, due to the fact that the NGCL is a porous medium, a correction factor is assumed to take into account non-uniformity of the ionomer layer:

$$\sigma_{i}^{\text{eff}} = \varepsilon^{1.5}\sigma_{i} \quad (3.79)$$
### Table 6: Constant parameters used in the model.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j_{0\text{ref},-})</td>
<td>Exchange current density of the electrochemical reaction in the negative cell compartment&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.0</td>
<td>A m&lt;sup&gt;−2&lt;/sup&gt;</td>
<td>[19]</td>
</tr>
<tr>
<td>(j_{0\text{ref},+})</td>
<td>Reference exchange current density in the positive half-cell&lt;sup&gt;5&lt;/sup&gt;</td>
<td>5.5</td>
<td>A m&lt;sup&gt;−2&lt;/sup&gt;</td>
<td>[18]</td>
</tr>
<tr>
<td>(\alpha_{c,-})</td>
<td>Symmetry factor for the cathodic reaction in the negative cell compartment</td>
<td>0.5</td>
<td>–</td>
<td>[19]</td>
</tr>
<tr>
<td>(\alpha_{a,-})</td>
<td>Symmetry factor for the anodic reaction in the negative cell compartment</td>
<td>0.5</td>
<td>–</td>
<td>[19]</td>
</tr>
<tr>
<td>(\alpha_{a,+})</td>
<td>Symmetry factor for the anodic reaction in the positive cell compartment</td>
<td>1.0</td>
<td>–</td>
<td>[36, 37]</td>
</tr>
<tr>
<td>(\alpha_{c,+})</td>
<td>Symmetry factor for the cathodic reaction in the positive cell compartment</td>
<td>1.0</td>
<td>–</td>
<td>[36, 37]</td>
</tr>
<tr>
<td>(p_{\text{H}_2,\text{ref}})</td>
<td>Hydrogen reference partial pressure</td>
<td>101 325.00</td>
<td>Pa</td>
<td></td>
</tr>
<tr>
<td>(T_{\text{op}})</td>
<td>Cell operating temperature</td>
<td>298.15</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>(c_{\text{Br}^-}^*)</td>
<td>Reference (bulk) concentration of bromide anions</td>
<td>1</td>
<td>mol L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>[19]</td>
</tr>
<tr>
<td>(c_{\text{Br}_2}^*)</td>
<td>Reference (bulk) concentration of bromine</td>
<td>0.24</td>
<td>mol L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>(D_{\text{Br}^-})</td>
<td>Diffusion coefficient of the bromide anions in water&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.08 × 10&lt;sup&gt;−9&lt;/sup&gt;</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;s&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>[19]</td>
</tr>
<tr>
<td>(D_{\text{Br}_2})</td>
<td>Diffusion coefficient of bromine in water&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.2 × 10&lt;sup&gt;−9&lt;/sup&gt;</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;s&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>[29]</td>
</tr>
<tr>
<td>(D_{\text{H}^+})</td>
<td>Diffusion coefficient protons in water&lt;sup&gt;c&lt;/sup&gt;</td>
<td>9.31 × 10&lt;sup&gt;−9&lt;/sup&gt;</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;s&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>[29]</td>
</tr>
<tr>
<td>(D_{\text{H}_2,\text{aq}})</td>
<td>Diffusion coefficient of dissolved hydrogen in water&lt;sup&gt;c&lt;/sup&gt;</td>
<td>9.15 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;s&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>[29]</td>
</tr>
<tr>
<td>(E^\circ_{\text{Br}_2/\text{Br}^-})</td>
<td>Standard equilibrium potential for Br&lt;sub&gt;2&lt;/sub&gt;/Br&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1.09</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>(E^\circ_{\text{H}_2/\text{H}^+})</td>
<td>Standard equilibrium potential for H&lt;sub&gt;2&lt;/sub&gt;/H&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.00</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>(n)</td>
<td>Number of electrons transferred</td>
<td>2</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(z_{\text{Br}^-})</td>
<td>Valence of bromide anions</td>
<td>−1</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(z_{\text{H}^+})</td>
<td>Valence of protons</td>
<td>+1</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(\nu_{\text{Br}^-})</td>
<td>Stoichiometric coefficient of bromide ions</td>
<td>+2</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(\nu_{\text{Br}_2})</td>
<td>Stoichiometric coefficient of bromine</td>
<td>−1</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(\nu_{\text{H}^+})</td>
<td>Stoichiometric coefficient of protons</td>
<td>+2</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(\nu_{\text{H}_2,\text{aq}})</td>
<td>Stoichiometric coefficient of hydrogen</td>
<td>−1</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(\epsilon_w)</td>
<td>Dielectric constant of liquid water&lt;sup&gt;d&lt;/sup&gt;</td>
<td>78.304</td>
<td>–</td>
<td>[43]</td>
</tr>
</tbody>
</table>

<sup>a</sup>Evaluated at 298 K and \(P_{\text{H}_2,\text{ref}}=1\) atm.

<sup>b</sup>Evaluated at \(c_{\text{Br}^-}^*\) and \(c_{\text{Br}_2}^*\).

<sup>c</sup>at “room temperature” which is not indicated in [29], therefore \(T_{\text{ref}}=25^\circ\)C is assumed.

<sup>d</sup>Evaluated at 25°C.
The electronic conductivity of the solid matrix is assumed constant. Both electrodes are a porous medium, therefore a correction factor is assumed to take into account non-uniformity of the conductive solid layers:

$$\sigma_s^{\text{eff}} = (1 - \varepsilon)^{1.5} \sigma_s$$  \hfill (3.80)

The potential jump between liquid phase and the membrane due to the Gibbs-Donnan effect does not occur abruptly. Potential changes continuously at the solution-membrane interface and within the membrane itself, as indicated in [40]. However, in the current model, in order to avoid solving Poisson-Boltzmann equations, the potential is assumed to change linearly within the Electric Double Layer, whose thickness is estimated using the Debye length, $\delta_{\text{EDL}}$ [33]:

$$\delta_{\text{EDL}} = \sqrt{\frac{\varepsilon_w \varepsilon_0 k_B T}{2 e_{H^+} N_A \varepsilon_{elm}^2}}$$  \hfill (3.81)

where $\varepsilon_w$ is the dielectric constant of water, $\varepsilon_0$ is the permittivity of free space, $e_{elm}$ is the elementary charge, $k_B$ is the Boltzmann constant and $N_A$ is the Avogadro constant. Note that number 2 in the denominator is employed in order to quantify the bulk concentration of bromide anions in the bulk, which are assumed the same as the concentration of protons due to electroneutrality condition.

The conductivity of protons in water close to the membrane surface is estimated using the following expression:

$$\sigma_{H^+} = \frac{Z_{H^+}^2 D_{H^+} F^2 c_{H^+}}{RT}$$  \hfill (3.82)

which results from Eq. (3.24). The order of magnitude of the Debye lengths obtained in the simulations was $10^{-9}$ m.

**Table 7:** Properties of the positive electrode [29].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_+$</td>
<td>Electrode thickness</td>
<td>150</td>
<td>$\text{µm}$</td>
</tr>
<tr>
<td>$s_+$</td>
<td>Specific surface area (carbon fibers)</td>
<td>$5.07 \times 10^4$</td>
<td>$\text{m}^{-1}$</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Mean pore radius size in the positive electrode</td>
<td>50.3</td>
<td>$\text{µm}$</td>
</tr>
<tr>
<td>$\varepsilon_+$</td>
<td>Electrode porosity</td>
<td>0.873</td>
<td>–</td>
</tr>
<tr>
<td>$\sigma_{s,+}$</td>
<td>Electronic conductivity</td>
<td>200</td>
<td>$\text{S} \cdot \text{m}^{-1}$</td>
</tr>
</tbody>
</table>
Table 8: Properties of the negative electrode and PEM from [29], unless stated otherwise.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_c$</td>
<td>Catalyst layer thickness</td>
<td>8</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>$a_-$</td>
<td>Specific surface area (active Pt surface)</td>
<td>$5.77 \times 10^7$</td>
<td>$m^2_{Pt}/m^3$</td>
</tr>
<tr>
<td>$\varepsilon_-$</td>
<td>Electrode porosity</td>
<td>0.2</td>
<td>–</td>
</tr>
<tr>
<td>$\sigma_{s, -}$</td>
<td>Electronic conductivity</td>
<td>200</td>
<td>$S/m$</td>
</tr>
<tr>
<td>$L_{PEM}$</td>
<td>Membrane thickness</td>
<td>50</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>$\sigma_l$</td>
<td>Ionic conductivity</td>
<td>$7.8 \times 10^{-2}$</td>
<td>$S/cm$</td>
</tr>
<tr>
<td>$c_f$</td>
<td>Fixed acid group concentration in the ionomer</td>
<td>1000</td>
<td>mol$^{-3}$</td>
</tr>
</tbody>
</table>

*Estimated for Nafion 117, at 100% RH and ambient temperature [45].

3.9 Mesh and Numerical Implementation

The problem was solved using COMSOL Multiphysics v. 5.3a with General Form PDE module. 1-dimensional mesh was composed of 360 equally spaced elements, with the maximum element size of $0.58 \times 10^{-6}$ m, maximum element growth rate (a factor limiting the size difference of two adjacent mesh elements) of 1.1 and resolution of narrow regions of 1. No mesh refinement was used.

A stationary, nonlinear MUMPS solver with the relative tolerance of $10^{-6}$ was used. The solution method was Newton method with initial damping factor of 1 and minimum damping factor of $10^{-4}$. Termination technique was based on tolerance with maximum number of iterations of 250. The solver achieved errors in the magnitude of $10^{-15}$ for each potential step. The solver used an auxiliary sweep of potentials set at the outermost boundary of the PLDL. The voltage sweep step size was 10 mV. The Lagrange shape functions were used for all governing equations with quadratic element order. Solution obtained from the previous step were used as the initial guess in the next step for faster convergence and better stability.

At high current densities, the cell suffers from reactant starvation (bromine on discharge, bromide on charge) on the PLDL side which is caused by rather high mass transport limitations as compared to hydrogen on the NGCL side. Due to the characteristics of numerical solution, when the concentration of reactants reaches values close to 0 mol/dm$^3$, the solver produces non-physical solution such as negative concentrations. A remedy to this issue was employed in order to be able to simulate the cell performance at stress conditions. A popular approach in the numerical methods is to modify source terms, in this case, the electrochemical reaction rate $R_{el,+}$ to

$$R_{el,+} = \begin{cases} 
0 & \text{if } |R_{el,+}| \leq 10^{-6} \text{A m}^{-3} \\
R_{el,+} & \text{otherwise} 
\end{cases}$$ (3.83)
so that the reactants are not further consumed when the source term is sufficiently small, for example less than or equal to $10^{-6}$ A/m$^3$. Nonetheless, in the present model, this approach generated instabilities and solver would crash after reaching high starvation, since toggling the reaction rate in that manner is itself a source of discontinuity. A second, successful approach was to transform the governing equations for bromine and bromide to the logarithmic space using a substitution:

$$u_1 = \log \left( \frac{c_{Br_2}}{1 \text{ mol L}^{-1}} \right)$$

(3.84)

and

$$u_2 = \log \left( \frac{c_{Br^-}}{1 \text{ mol L}^{-1}} \right).$$

(3.85)

The governing equations (3.13) and (3.12) were solved for the new variables $u_1$ and $u_2$. For other equations (e.g. solving for surface concentrations), the exponents of these two variables were employed to transform the logarithms back to the physical concentration.
4 Results and Discussion

The following section includes three main parts. First, the model is solved using the base case parameters presented in Section 3.8. The complete set of plots on charging and discharging modes is presented together with a discussion. Next, parameters from a study by Yarlagadda and Nguyen [27] are used in order to compare the simulation results to published cell performance curves. Lastly, a few key parameters are varied to see their impact on the overall cell performance.

4.1 Modeling Results – Base Case

The cell was simulated in the potentiostatic mode and the color legends in the following figures are used to represent the potential sweeps of $E_{cell}$.

4.1.1 Potentials and Concentrations

Figures 12 and 13 show the distribution of electrostatic and ionic potentials, respectively. The discontinuity in liquid potential due to Donnan effect is clearly visible especially for high currents, due to increased local concentration gradients of protonic species (starvation on discharge, build-up on charge). Fig. 14 shows the surface overpotentials in the cell. It can be seen that the bromine/bromide half-cell contributes to the majority of the activation polarization losses as compared to small polarization of the hydrogen electrode.

![Electrostatic potential distribution in the solid phase on (a) discharge, (b) charge.](image)

**Figure 12:** Electrostatic potential distribution in the solid phase on (a) discharge, (b) charge.
Figure 13: Ionic potential distribution on (a) discharge, (b) charge.

Figure 14: Surface overpotential distribution on (a) discharge, (b) charge.

Figures 15 and 16 show the variation of dissolved bromine concentration in the bulk and on the carbon electrode surface of the PLDL. The simulation reveals how the increased current density impacts the concentration profiles. On discharge, when bromine is consumed, the concentration drops drastically due to diffusion mass transport limitations. On charge, bromine is produced and diffuses back to the flow channel at limited speed which generates concentration buildup.
Figure 15: Dissolved bromine concentration distribution in the PLDL on (a) discharge, (b) charge.

Figure 16: Dissolved bromine surface concentration distribution in the PLDL on (a) discharge, (b) charge.

Figures 17 and 18 show the variation of bromide concentration in the bulk and on the carbon electrode surface of the PLDL. The behavior shows certain similarities to the bromine concentration plots. High nonlinearities in Fig. 16 are due to a complex migration-diffusion coupling.
Figure 17: Bromide concentration distribution in the PLDL on (a) discharge, (b) charge.

Figure 18: Bromide surface concentration distribution in the PLDL on (a) discharge, (b) charge.

Figures 19 and 20 show the normalized surface concentrations with respect to bulk concentration of bromine and bromide species, respectively. High starvation of bromine on discharge and moderate starvation of bromide on charge is clearly visible.
Figure 19: Bromine surface concentration to bromine bulk concentration ratio distribution in the PLDL on (a) discharge, (b) charge.

Figure 20: Bromide surface concentration to bromide bulk concentration ratio distribution in the PLDL on (a) discharge, (b) charge.

Fig. 21 and Fig. 22 show the concentration profiles of protons in the PLDL and dissolved hydrogen in the NGCL. Very insignificant hydrogen concentration gradients are formed during discharge due to good mass transport conditions in the NGCL. It should be noted, however, that the concentration of dissolved hydrogen on charge exceed the values predicted by equilibrium (Henry’s Law). This is due to the fact that in the current model no phase transitions are taken into account,
where normally the created hydrogen would evolve from the liquid water, maintaining constant saturation concentration. This phenomenon does not influence any of the modeled parameters and thus is believed to introduce very small error to the results.

Figure 21: Protons concentration distribution in the PLDL on (a) discharge, (b) charge.

Figure 22: Dissolved hydrogen gas concentration distribution in the NGCL on (a) discharge, (b) charge.
4.1.2 Fluxes

Figures 23 through 28 show the fluxes of all the six dependent variables. The fluxes follow the adopted sign convention. The flux of protons in the PLDL is constant which agrees with expectations - the source term of protons in this domain is equal to zero.

Figure 23: Flux of the electronic current in the solid phase on (a) discharge, (b) charge.

Figure 24: Flux of the ionic current in the liquid phase on (a) discharge, (b) charge.
Figure 25: Flux of bromine in PLDL on (a) discharge, (b) charge.

Figure 26: Flux of bromide in PLDL on (a) discharge, (b) charge.
4.1.3 Source Terms

Figures 29 through 33 show the source terms which follow the adopted sign convention.
Figure 29: Source term of electronic current on (a) discharge, (b) charge.

Figure 30: Source term of ionic current on (a) discharge, (b) charge.
Figure 31: Source term of aqueous bromine on (a) discharge, (b) charge.

Figure 32: Source term of bromide on (a) discharge, (b) charge.
4.1.4 Redox Flow Cell Performance

Fig. 34 shows the polarization and power density curves on cell discharge and charge. Small activation polarization on discharge is one of the advantages of flow batteries. The main losses are caused by ohmic resistance of the cell, predominantly the membrane. Starvation effects on discharge are clearly distinguishable from ca. 0.88 V. On charge, activation polarization is much more profound because of a different nature of the bromide anions oxidation reaction. At high potentials (more than 1.35 V), starvation of bromine anions sets in and the limiting charging current is approached, further increasing the potential may lead to side reaction or detrimental electric breakthrough.
4.2 Model Validation

There is little experimental data on flow-by mode-operated HBRFB. In a paper by Yarlagadda and Nguyen [27], a 1D model investigating both flow-by and flow-through modes compared well with experimental data from the flow-through cell. Therefore, it is believed, that comparing the current model with the verified flow-by 1D model by Yarlagadda will give a reasonable insight on validity.

In principle, the model parameters were taken from [27] with a few exceptions owing to a different modeling approach. First, the kinetic parameters $p$ and $q$ for both bromine and bromide were adopted without change from Table 6, assuming the reactions in the positive electrode as elementary ones (from the theory of the active complex). Second, the Donnan potential is not modeled in [27], and has also been removed in this modeling case (replaced with continuity condition for the ionic potential) for comparison purposes. The result is presented in the Fig. 35. The compared results from both models correspond to each other and manifest a very decent agreement with a maximum relative error of ca. $-0.38\%$. The error in percent relative to the model by Yarlagadda and Nguyen is growing for increasing current densities which seem to be caused by differences in ohmic resistance model formulation. Unfortunately, a full analysis and comparison of the whole polarization curve was not possible due to a very limited amount of experimental and modeling data in this field.

Figure 34: Polarization and power density curves of a single HBRFB cell on (a) discharge, (b) charge.
Figure 35: Comparison of the current 1D model polarization curve with the results obtained in [27].

4.3 Parametric Study

PLDL thickness

A parametric study on variation of the PLDL thickness ($L_{PLDL}$) is presented in Fig. 36. It is visible how the smaller thicknesses affect the activation polarization region, because the same current is passed through smaller surface area, generating more activation overpotential. The effect on limiting current density (i.e. starvation) is not large for discharge mode, but becomes substantial for the charge mode. Thinner PLDL layers allow for achieving larger charging current densities (and thus faster charging).
Figure 36: Discharge and charge polarization curves for different values of PLDL thickness. The sign of the current density on charging was taken as the absolute value for the sake of a better graphical appearance.

PEM thickness
A parametric study on variation of the PEM thickness ($L_{PEM}$) is presented in Fig. 37. Increasing the membrane thickness increase the ohmic loss associated with protonic conductivity. Graphically, the effect manifests itself as the variation of polarization curve slope in the ohmic losses region. As expected, the membrane thickness does not influence the activation polarization and mass transport regions. It is imperative to note that the model does not predict the crossover of bromine species through the PEM, so thinner membranes apparently yield less ohmic losses, but may also cause augmented bromine transport to the negative compartment. This may cause Pt catalyst poisoning and an immediate performance deterioration.
Figure 37: Discharge and charge polarization curves for different values of PEM thickness. The sign of the current density on charging was taken as the absolute value for the sake of a better graphical appearance.

Bromine concentration

The impact on battery performance of various bulk bromine concentrations is shown in Fig. 38. Clearly, the bromine, which is consumed during the discharge, has a dramatic influence on the discharge limiting current densities. For high bromine concentration (e.g. 5 mol/L), little concentration polarization is seen and all the losses in high current regions are attributed to ohmic resistance. The concentration of bromine has little impact on the charging performance, and the slight shift of the curves is due to variation of the open circuit potential resulting from the Nernst equation.
Figure 38: Discharge and charge polarization curves for different values of bromine concentration, keeping bromide concentration constant (1 mol/L). The sign of the current density on charging was taken as the absolute value for the sake of a better graphical appearance.

Bromide concentration
The impact on battery performance of various bulk bromide anions concentrations is shown in Fig. 39. Bromide species, which constitute the reactants on charging, have a large impact on the charging curves shape. Larger concentration of bromide allow to obtain higher charging currents without abrupt drop due to limiting charging current densities. At the same time, the bromine concentration shows much larger influence on the discharge curve than the bromine species. The discharge polarization curves are translated downwards for increasing bromide concentration due to open-circuit potential diminution which results from the Nernst equation.
Figure 39: Discharge and charge polarization curves for different values of bromide concentration, keeping bromine concentration constant (0.24 mol/L). The sign of the current density on charging was taken as the absolute value for the sake of a better graphical appearance.
5 Summary and Future Development

The presented model is a simple, yet robust tool for predicting the performance of a flow-by hydrogen-bromine redox flow battery. It proves useful for analyzing the cell behavior as a function of key process parameters such as electrode and membrane thicknesses or species concentration. Modeling results agree with the scarce experimental and modeling data available.

The 1D model may be perceived as a first step for understanding the processes occurring in hydrogen-bromine flow cells as well as constitutes a basis for modeling techniques development in the future. The current work emphasizes the significance of adopting a consistent sign convention. The cell is operated in both galvanic (discharging) and electrolytic (charging) modes, which means that a high level of equations generality is highly desired to facilitate the simulation of both modes without the need for an error-prone sign adjustment task.

This 1D model opens up the possibilities for development in many directions. The topic can be further extended in the following categories:

- Addition of heat generation and transport effects;
- Accurate simulation of Open Circuit Voltage at different States of Charge;
- Including of bromine and bromide species crossover modeling (crucial for HBRFB operation);
- Advanced formulation of membrane transport processes (e.g. membrane conductivity in different environments);
- Model extension of cell water management;
- Battery cycling simulations, battery aging and catalyst poisoning considerations;
- Modeling of (electro)chemical phenomena occurring in the HBRFB during operation, for example: complexation, salt precipitation, side reactions, fouling, electrode degradation;
- Modeling of flow phenomena in cell channels, modeling flow-through and interdigitated modes, investigation of channel design on the overall battery performance;
- Pore-scale electrode modeling;
- Up-scaling issues of the whole HBRFB system;
• Transient response and stability of the whole HBRFB system;
• Modeling of RFB stacks in large scale.
Acknowledgements

I would like to express a deep gratitude to Professor Jürgen Schumacher for accepting my application and allowing me to write this Master Thesis at the Institute of Computational Physics, ZHAW, Switzerland. My stay in Switzerland would not be possible if it were not for funding, which was obtained from the FlowCamp project budget, sponsored by the European Union as a part of Maria Skłodowska-Curie actions in the Horizon 2020 program. I am grateful to Professor Göran Lindbergh from KTH Royal Institute of Technology for allowing me to pursue the Master Thesis Project abroad and revising the thesis.

I greatly acknowledge a favorable decision of the FlowCamp project organizers, Dr. Peter Fischer and Carolyn Fisher who, as initiated by Prof. Schumacher, agreed to incorporate my Master Thesis project into the program.

I highly appreciate all the support from my Colleague Dr. Roman Vetter, who helped me to overcome numerical issues while solving the problem and provided me with a deal of precious advice in the field of simulations. He, together with a fellow PhD Student Gaël Mourouga, took part in very seminal discussions by the whiteboard, which led to a better understanding of the problem and provided a constructive criticism to the results. For all of that, thank you.

Finally, I would like to thank my Parents for supporting me during my Master’s degree studies abroad, never denying to give honest advice, and treating all my choices very seriously.

More detailed investigation on the Hydrogen-Bromine Redox Flow Battery modeling will be performed and published during the PhD studies of the Author at the Institute of Computational Physics under the FlowCamp project.

Jakub Włodarczyk
October 18, 2018
Winterthur, Switzerland
Nomenclature

Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBRFB</td>
<td>Hydrogen–Bromine Redox Flow Battery</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen Oxidation Reaction</td>
</tr>
<tr>
<td>HRR</td>
<td>Hydrogen Reduction Reaction</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane-Electrode Assembly</td>
</tr>
<tr>
<td>NGCL</td>
<td>Negative Gas Catalyst Layer</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton-Exchange Membrane</td>
</tr>
<tr>
<td>PLDL</td>
<td>Positive Liquid Diffusion Layer</td>
</tr>
<tr>
<td>RFB</td>
<td>Redox Flow Battery</td>
</tr>
<tr>
<td>SOC</td>
<td>State of Charge</td>
</tr>
<tr>
<td>USD</td>
<td>United States Dollar</td>
</tr>
</tbody>
</table>

Latin Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hat{n} )</td>
<td>Interfacial normal unit vector</td>
<td>–</td>
</tr>
<tr>
<td>( j_i )</td>
<td>Ionic current density</td>
<td>A m(^{-2})</td>
</tr>
<tr>
<td>( j_e )</td>
<td>Electronic current density</td>
<td>A m(^{-2})</td>
</tr>
<tr>
<td>( N_i )</td>
<td>Molar flux</td>
<td>mol m(^{-2}) s(^{-1})</td>
</tr>
<tr>
<td>( v )</td>
<td>Velocity</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>( a )</td>
<td>Electrochemically active specific surface (Pt or C) area</td>
<td>m(^2) m(^{-3})</td>
</tr>
<tr>
<td>( c_i )</td>
<td>Concentration</td>
<td>mol m(^{-3})</td>
</tr>
<tr>
<td>( D_i )</td>
<td>Diffusion coefficient in the bulk</td>
<td>m s(^{-2})</td>
</tr>
<tr>
<td>( E )</td>
<td>Electric potential</td>
<td>V</td>
</tr>
<tr>
<td>( E_{cell} )</td>
<td>Imposed cell voltage</td>
<td>V</td>
</tr>
<tr>
<td>( H )</td>
<td>Henry’s constant</td>
<td>atm cm(^3)/mol</td>
</tr>
<tr>
<td>( j_0 )</td>
<td>Exchange current density</td>
<td>A m(^{-2})</td>
</tr>
<tr>
<td>( k )</td>
<td>Rate constant of electrochemical reaction (1(^{st}) order)</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>( n )</td>
<td>Number of electrons transferred</td>
<td>–</td>
</tr>
<tr>
<td>( p )</td>
<td>Partial pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>( p_i )</td>
<td>Anodic electrochemical reaction order</td>
<td>–</td>
</tr>
<tr>
<td>( q_i )</td>
<td>Cathodic electrochemical reaction order</td>
<td>–</td>
</tr>
<tr>
<td>( R_{el} )</td>
<td>Volumetric current generation rate</td>
<td>A m(^{-3})</td>
</tr>
<tr>
<td>( r_p )</td>
<td>Mean pore radius size in the positive electrode</td>
<td>m</td>
</tr>
<tr>
<td>( S_i )</td>
<td>Species mass source</td>
<td>mol m(^{-3}) s(^{-1})</td>
</tr>
<tr>
<td>( S_i' )</td>
<td>Ionic current source</td>
<td>C m(^{-3}) s(^{-1})</td>
</tr>
<tr>
<td>( S_e )</td>
<td>Electronic current source</td>
<td>C m(^{-3}) s(^{-1})</td>
</tr>
<tr>
<td>( T )</td>
<td>Absolute temperature</td>
<td>K</td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>( u_1, u_2 )</td>
<td>Concentration transformation variables for bromine and bromide, respectively</td>
<td>–</td>
</tr>
<tr>
<td>( u_i )</td>
<td>Mobility</td>
<td>m(^2) V(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( z_i )</td>
<td>Valence</td>
<td>–</td>
</tr>
</tbody>
</table>

Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>Transfer coefficient</td>
<td>–</td>
</tr>
<tr>
<td>( \delta_{EDL} )</td>
<td>Thickness of the Electric Double Layer</td>
<td>m</td>
</tr>
<tr>
<td>( \epsilon_{w} )</td>
<td>Dielectric constant of water</td>
<td>–</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Overpotential</td>
<td>V</td>
</tr>
<tr>
<td>( \gamma_i )</td>
<td>Empirical exponent in the dependence of ( j_0 ) on the surface concentration of ( i )-th species</td>
<td>–</td>
</tr>
<tr>
<td>( \nu_i )</td>
<td>Stoichiometric coefficient</td>
<td>–</td>
</tr>
<tr>
<td>( \phi_l )</td>
<td>Electrostatic potential in the liquid phase</td>
<td>V</td>
</tr>
</tbody>
</table>

67
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ</td>
<td>Electrostatic potential in the solid phase</td>
<td>V</td>
</tr>
<tr>
<td>σ</td>
<td>Electronic or ionic conductivity</td>
<td>S m$^{-1}$</td>
</tr>
<tr>
<td>ε</td>
<td>Porosity of the electrode material</td>
<td>–</td>
</tr>
</tbody>
</table>

### Physical Constants

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_0$</td>
<td>Dielectric constant of free space</td>
<td>8.854 · 10$^{-12}$ F m$^{-1}$</td>
</tr>
<tr>
<td>$\epsilon_{elm}$</td>
<td>Elementary charge</td>
<td>1.602 · 10$^{-19}$ C</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
<td>96485 C mol$^{-1}$</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>1.381 · 10$^{-23}$ JK$^{-1}$</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro constant</td>
<td>6.022 · 10$^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>8.31446 J mol$^{-1}$ K$^{-1}$</td>
</tr>
</tbody>
</table>

### Superscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>in the bulk</td>
</tr>
<tr>
<td>o</td>
<td>standard</td>
</tr>
<tr>
<td>eff</td>
<td>effective</td>
</tr>
<tr>
<td>s</td>
<td>at the surface of the electrode</td>
</tr>
</tbody>
</table>

### Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>in the positive cell compartment</td>
</tr>
<tr>
<td>–</td>
<td>in the negative cell compartment</td>
</tr>
<tr>
<td>i</td>
<td>of species i; i $\in$ {Br$_2$,aq, H$_2$,aq, Br$^-$, H$^+$}</td>
</tr>
<tr>
<td>l</td>
<td>in the liquid phase</td>
</tr>
<tr>
<td>s</td>
<td>in the solid phase</td>
</tr>
<tr>
<td>a</td>
<td>anodic</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous (dissolved)</td>
</tr>
<tr>
<td>c</td>
<td>cathodic</td>
</tr>
<tr>
<td>eq</td>
<td>equilibrium</td>
</tr>
<tr>
<td>op</td>
<td>cell operating temperature</td>
</tr>
<tr>
<td>ox</td>
<td>oxidized species</td>
</tr>
<tr>
<td>red</td>
<td>reduced species</td>
</tr>
<tr>
<td>ref</td>
<td>reference</td>
</tr>
</tbody>
</table>
References


