

#### MASTER

Exploring the role of the porous electrode microstructure in redox flow battery performance a pore network modeling approach for redox flow battery electrode optimization

van Gorp, R.

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### MASTER THESIS Exploring the role of the porous electrode microstructure in redox flow battery performance

A pore network modeling approach for redox flow battery electrode optimization

Student: Rik van Gorp 1396439 Supervisors: ir. M. van der Heijden Dr. A. Forner Cuenca Committee: Prof. Dr. Ir. D.C. Nijmeijer Dr. Ir. M.T. de Groot

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DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMISTRY





### Summary

Redox flow batteries are a promising technology for the long-term, large-scale storage of electrical energy. However, current elevated costs and suboptimal performance hinder widespread deployment. As a core component of the redox flow battery, the porous electrode largely determines the battery performance by providing both the active surface for electrochemical reactions and the flow geometry for mass and charge transport. Thus, optimizing the electrode offers a powerful strategy to increase the redox flow battery performance and decrease the costs.

The goal of this thesis is to expand the fundamental understanding of the role of the electrode three-dimensional microstructure within redox flow battery performance. To do so, a microstructure-informed pore network modeling framework was developed, based on the coupled mass and charge transport of a single-phase, reactive electrolyte. The presented model provides a computationally inexpensive route for electrode optimization, alleviating the need for empirical, time-consuming experimentation.

The response of the numerical framework was compared with experimental data for three distinct redox couples with different kinetics within a carbon fibrous commercial electrode (i.e. Freudenberg H23). The response of the numerical framework showed good agreement with experimental data for an organic electrolyte (TEMPO·/TEMPO<sup>+</sup>), but the agreement with two aqueous electrolytes (Fe<sup>2+</sup>/Fe<sup>3+</sup> and V<sup>4+</sup>/V<sup>5+</sup>) was limited, which was attributed to non-idealities induced by incomplete wetting during experimental flow cell operation.

The numerical framework has been used to conduct a case study, comparing the electrochemical performance of a recently developed non-fibrous electrode microstructure with a commercially available fibrous electrode. The theoretical analysis revealed an improved performance of the novel electrode. This was attributed to the coexistence of (1) macrovoids fractions consisting of larger pores (> 50  $\mu$ m), permitting high convective flow, with (2) an electrochemically active surface region consisting of smaller pores (~10  $\mu$ m), facilitating fast kinetics. The interplay of these microstructural characteristics was shown to limit the formation of ohmic and concentration overpotentials.

Finally, a novel genetic optimization approach was proposed for the bottom-up design of porous electrodes with optimal topology. The first results of the developed genetic optimization approach showed a promising increase of 5-15% in the electrochemical performance and a 46-47% decrease in the required pumping power of the generated networks, compared to completely random artificially generated cubic networks. The proposed genetic optimization methodology could serve as a base for future studies into the optimization of design characteristics for redox flow battery electrodes and other electrochemical technologies.

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## **Chapter 1. Introduction**

### 1.1 Motivation

The urgent need to reduce carbon emissions has motivated the development of low-carbon emitting renewable energy technologies, such as solar photovoltaics and wind power. Over the period of 2008-2018, the share of renewable energy utilization in the power generation sector has experienced an average yearly growth of 16% worldwide [1]. However, in contrast to conventional power plants, renewable energy sources are intermittent in nature, which compromises the stable operation of traditional energy grids [2]. Thus, widespread deployment of large-scale, stationary energy storage systems is required to compensate for the intermittent nature of renewable energy sources [3].

A promising technology for long-term electrical energy storage is the *redox flow battery* (RFB) [4], [5]. RFBs are electrochemical systems that interconvert chemical and electrical energy by leveraging redox couples, dissolved in liquid electrolytes, that are pumped through an electrochemical stack [6]. Their most appealing features, as compared to other sealed batteries (e.g. lithium-ion), are the ability to decouple power and energy capacity, high round-trip efficiency, extended durability, fast response times, low environmental impact and geographic independence [7].

Despite their promise, RFBs experience limited market penetration due to their current elevated costs and suboptimal performance. The current capital cost of the state-of-the-art (i.e. all-vanadium) RFB system is above \$400/kWh [8], which largely exceeds the \$150/kWh cost target set by the U.S. Department of Energy for the year 2020 [9]. Simultaneously, the deployment of RFBs for the integration of renewable energy storage within the electricity grid requires roundtrip efficiencies of 75-90%, system lifetimes of more than 10 years, and a storage capacity of 1-20 MW [9].

To meet these stringent targets, a substantial research effort is focused on the development of novel flow battery chemistries, advanced materials (e.g. electrodes and membranes), and electrochemical reactors, leveraging both experimental design as well as computational modeling approaches [10]–[15]. As a core component of the RFB, the *porous electrode* largely determines the battery performance by providing both the active surface for electrochemical reactions and the flow geometry for mass and charge transport. Thus, optimizing the electrode offers a powerful strategy to increase RFB performance and decrease the costs.

Traditionally, the RFB electrode design has been driven by empirical, trial-and-error experimentation which is time- and resource-consuming. Additionally, macroscopic, one-dimensional computer models have been employed, but these models fail to capture the complex effects of the *electrode three-dimensional microstructure* on the performance of the

RFB. And, while recent studies have shown that the electrode microstructure plays a critical role in the device performance [10], [12], [13], the characteristics of optimal electrode structures for RFBs remain to be discovered. Thus, there is a need to develop a novel computational methodology that can be used to accurately predict the influence of electrode microstructure properties on the performance of different types of RFBs. Ultimately, the methodology can be employed to perform bottom-up design of electrodes with optimal topology to lower pumping power requirements, increase power density, decrease overpotentials, and minimize material utilization.

### **1.2 Outline of the thesis**

This thesis investigates the role of the electrode three-dimensional microstructure within RFB performance. A sophisticated 3D numerical framework that successfully predicts local transport processes within ideally wetted porous electrodes was developed within the open-source software OpenPNM [16], and was tested for multiple RFB chemistries ( $Fe^{2+}/Fe^{3+}$ ,  $V^{4+}/V^{5+}$ , TEMPO·/TEMPO<sup>+</sup>). The model allows for systematic variations of critical parameters (e.g. microstructure, flow rate, concentration) to assess their respective impact, and has been used to discover microstructure-property-performance relationships for two physical porous electrodes. Moreover, the numerical framework was used to lay the foundation of a novel genetic optimization method for the bottom-up design of the topology of next-generation RFB electrodes.

A conceptual overview of the project is given in Figure 1.



**Figure 1** - Illustration of the project vision. Image extraction and artificial generation are used to analyze and optimize the microstructure-property-performance relationships within redox flow battery porous electrodes.

This thesis is divided into eight chapters. In Chapter 1, a brief motivation for the conducted work was given. Chapter 2 contains an overview on the RFB fundamentals and on the current state-of-the-art of numerical modeling of RFB electrodes. In Chapter 3, the generation of porous

electrode geometries either by the use of x-ray computed tomography (XTM) or by the use of artificial generation is examined. In Chapter 4, a computational model to analyze the flow behavior of specific redox couples within different electrode geometries is presented. Subsequently, an overview of the laboratory experiments that were conducted to validate the numerical model is presented in Chapter 5. In Chapter 6, the findings on the relation between the electrode microstructure and performance for two real electrode microstructures are reported. In Chapter 7, a novel genetic optimization approach is described that can be employed to perform bottom-up simulations to discover ideal electrode microstructural properties. Finally, the conclusions and an outlook for future work are presented in Chapter 8.

### Chapter 2. Redox flow batteries fundamentals

### 2.1 Redox flow batteries operating principles

RFBs are electrochemical systems that interconvert chemical and electrical energy by leveraging redox couples, dissolved in liquid electrolytes, that are pumped through an electrochemical cell [6]. An overview of the major components of a single cell RFB is shown in Figure 2.



**Figure 2** - Schematic overview of a single cell redox flow battery in discharge mode. Electrons are transported through the circuit and ions are transported in both electrolytes, and across the membrane.

The electrochemical core of the RFB consists of a membrane electrode assembly (MEA), which can be stacked to increase the power output of the system. Each MEA is composed of two electrodes, that are separated by a membrane.

In charge-mode, electricity is consumed within the electrochemical cell to drive the nonspontaneous redox reactions of the dissolved active species. In discharge-mode the reverse process takes places and spontaneous redox reactions are leveraged to generate electricity. During discharge, species A is oxidized in the negative half-cell, releasing electrons that can perform work on an external load. Simultaneously, species B is being reduced in the positive half-cell, by consuming electrons flowing from the external load. An ion-selective membrane prevents the mixing of the negative and positive half-cell electrolytes, while allowing specific ions to pass to the other half-cell to complete the electrochemical circuit. A general form of a single-electron redox reaction occurring in an RFB is given by [Eq. 2.1-2.2].

$$A^{(n-1)+} \stackrel{\text{discharge}}{\rightleftharpoons} A^{n+} + e^{-} \qquad \text{Negative electrode} \qquad \text{Equation 2.1}$$
$$B^{(m+1)+} + e^{-} \stackrel{\text{discharge}}{\rightleftharpoons} B^{m+} \qquad \text{Positive electrode} \qquad \text{Equation 2.2}$$

The classical flow pattern of an RFB, often used in academia, involves a flow-through setup, where the electrolyte is directly pumped through the porous electrode. Bipolar plates with flow channels can be added to divert from this setup, which results in decreased pressure drop over the system at the expense of shorter electrode-electrolyte contact time. Various flow channel designs with different performances have been proposed in the literature, such as the interdigitated and parallel flow field design [17-18].

One of the most appealing features of RFBs, as compared to other sealed batteries, is the ability to *decouple* power and energy capacity. The energy capacity of RFBs is dependent on the size of the electrolyte storage tanks and the concentration of the active species, whereas power capacity is dependent on performance factors such as pumping power, electrode structure and flow cell design [4]. Consequently, RFBs can operate at a wide range of operational power and discharge times, see Figure 3 [6]. Moreover, the deployment of RFBs is independent of geographical factors, such as the requirement for levitated water reservoirs for the application of pumped hydro storage. The combination of these factors make RFBs an attractive option for the long-term energy storage from a fluctuating electricity grid.



**Figure 3** - The application range of different energy storage technologies, based on energy stored and power output, reconstructed from Martín et al. [19]. The logarithmic scaled representation shows a relatively large energy operating window for flow batteries. CAES: Compressed air energy storage, SMES: superconducting magnetic energy storage.

#### 2.2 Redox flow battery types

A wide variety of RFB systems has been proposed in the past few decades, with industrial capacities up to 20 MW/80 MWh [3], [6-7], [20]–[22]. RFBs are classified based upon the *active species* that are used to chemically store energy and upon the *solvent* used to dissolve these active species.

Within each RFB two half-cell types are combined to obtain one electrochemical cell. The selection criteria for the combination of two half-cells are the thermodynamic potential, electrochemical reaction reversibility, cost and availability of the components, safety, and the solubility of the active species in the solvent. Moreover, half-cells operating with gaseous and solid redox couples can be combined with liquid half-cell redox couples to form hybrid flow batteries, such as the hydrogen-bromine RFB [23]. However, in this thesis, the focus will be on the characterization of porous electrodes within all-liquid RFB redox couples.

The expansion of RFBs started with the development of *aqueous* flow batteries, which utilize an aqueous solution of active species, combined with a strong acid supporting electrolyte (e.g. hydrochloric acid) to increase conductivity. Commonly studied aqueous systems include the iron/chromium (Fe/Cr) [24] and the all-vanadium RFB (VRFB) [25] systems. The Fe/Cr system [Eq. 2.3-2.4] is considered the first type of RFB and was developed in the 1970s at NASA.

$Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-}$	$E^0 = 0.77 V vs. RHE$	Equation 2.3	
$Cr^{2+} \rightleftharpoons Cr^{3+} + e^{-}$	$E^0 = -0.41$ V vs. RHE	Equation 2.4	

With  $E^0$  being the standard reduction potential [V] of the considered redox couple with respect to the reversible hydrogen electrode (RHE). The more positive the reduction potential of the species, the greater the affinity of the species for electrons and thus the higher the tendency to be reduced. The Fe/Cr system suffers from a relatively low open-circuit potential (i.e. the difference in reduction potential of both redox couples, 1.18V) and active species cross-over by transport through the membrane during operation.

Cross-over of species does not only lead to an efficiency loss, but also to a loss of capacity and therefore, a decrease in overall system performance over time. To mitigate this problem, RFB systems have been proposed that contain active species of the same element in various oxidation states. In these systems, cross-over only results in an efficiency loss, as the species will be reduced or oxidized after cross-over. The VRFB can be classified as one of these systems, as it employs the V(II)/V(III) redox couple at the negative electrode and the V(IV)/V(V) redox couple, commonly identified in the form of  $VO^{2+}$  and  $VO_{2^+}$ , at the positive electrode [Eq. 2.5-2.6].

$$V^{2+} \rightleftharpoons V^{3+} + e^ E^0 = -0.26 \text{ V vs. RHE}$$
 Equation 2.5  
 $VO^{2+} + H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^ E^0 = 1.00 \text{ V vs. RHE}$  Equation 2.6

Despite the convenient operating conditions, aqueous RFBs have some inherent disadvantages. Foremost, aqueous RFBs are concerned with the breakdown of water at higher voltages ( $E_{cell} > 1.23 \text{ V} \text{ vs}$ . RHE) due to water electrolysis, restricting their open-circuit potential window. For this reason, *non-aqueous* RFB systems have been proposed. Non-aqueous RFBs often use transition-metal complexes as active species, which are dissolved in organic solvents (e.g. acetonitrile), and combined with an organic supporting electrolyte (e.g. tetraethyl ammonium tetrafluoroborate) to increase conductivity [26]. Widely studied non-aqueous RFBs are the vanadium acetylacetonate (V(acac)<sub>3</sub>) RFB and the extremely fast all-organic 2,2,6,6,-teramethyl-1-piperidinylxy (TEMPO) RFB [27-28]. Although non-aqueous RFBs allow operation outside the potential window of water, their implementation is still limited due to the need for advancements in system cost, membrane performance and stability, and solubility of active species and supporting electrolytes [4].

#### 2.3 Porous electrode design

RFB electrode design comprises *a complex optimization problem*, since the design is subject to several contradictory requirements. First of all, the porous electrode has to provide both the active surface for the electrochemical reactions and the flow geometry for the transport of ions and electrons [29]. Moreover, fast kinetics and high selectivity towards the desired redox reaction have to be balanced with the mechanical, physical, and chemical stability of the electrode [30]. An ideal electrode should have a high electrochemical active area, a low electrical resistivity, an ability to operate at a wide range of current densities, a long cycling lifetime, a high stability, a resistance to oxidation, a reasonable cost and an optimized pathway for mass transport of ions and electrons [4].

Traditionally, commercial electrodes consist of *carbon fibers*, that are synthesized by carbonization of a polymer precursor and manufactured into a coherent structure, based on the design of the carbon backing of polymer electrolyte fuel cell gas diffusion layers (GDLs) [10]. Carbon fibers offer high porosity, high electrical conductivity, low cost, and good stability, which makes them suitable as electrodes for RFBs [31]. The manufacturing processes of the carbon fibers vary per manufacturer and these processing differences give each type of carbon fiber its distinct property set. Despite similar bulk porosities (80-95%) [32] and fiber diameters (5-10  $\mu$ m) [33], a distinct microstructure is present for each type of carbon fiber electrode, see Figure 4. The differences in microstructure can be characterized based on various electrode properties, such as the pore size distribution (PSD), pore connectivity, and specific surface area [10].



**Figure 4** - X-ray tomography images of different carbon fibers: (a) a Freudenberg paper sample, (b) a SGL 29AA paper sample and (c) a Toray paper sample, visualized in ParaView [34].

While the fibrous carbon materials used in GDLs of fuel cells are functional for RFBs due to the overlap in property sets, specific property requirements for RFBs are not integrated into their design. In contrast to the multiphase transport in fuel cell technology, full utilization of an RFB electrode is based on the facilitation of liquid transport and wetting throughout the entire electrode. Considerable effort is put in the production of carbon electrodes that facilitate high active surface area, have high electrolyte-philicity, and contain catalytically-active surface functional groups to improve the electrode performance. Various treatments have been successfully applied to carbon paper, such as etching [35], nanoparticle deposition [36], and thermal treatment [11]. However, all these methods are based on empirical models. Ultimately, to design optimal porous electrodes, a more fundamental understanding of the role of the electrode microstructure on flow cell performance is required.

### 2.4 Numerical Modeling of Porous Electrodes

Numerical modeling of porous media is a valuable tool for analyzing and quantifying the effect of electrode properties on flow cell performance. Traditionally, the focus of numerical modeling of porous media has been on the extraction of oil in petroleum reservoirs [37]. However, the last years have seen a renewed importance in porous modeling for the field of fuel cells and flow battery systems.

The current numerical understanding of flow batteries is primarily based on macroscopic continuum models [38]–[41]. These cell-level models include kinetics, ohmic and mass transfer losses, where the electrolytic cell is divided into a volume-averaged computational grid. Macroscopic models have aided in investigations of the effect of membrane properties, electrolyte types, flow field design and flow rate effects on cell performance [17], [42]–[44]. Although useful for predictions of cell performance, the volume averaging of the computational grid omits the effect of the electrode microstructure on RFB performance. Moreover, the accuracy and sensitivity of macroscopic continuum models are heavily dependent on the

empirical relationships that describe the transport properties within the structure, such as permeability coefficients or effective diffusivity coefficients [16], [45].

On the other hand, highly detailed methods, such as finite element methods (FEM) and lattice Boltzmann methods (LBM) have been employed to gain insight into the transport within porous materials [32], [46-47]. These models directly solve the flow field of the electrolyte and can therefore deal with highly complex geometries, but require large computation power to solve the defined set of equations. The large number of nodes required to model even a few pores and the complexity of multiphysics problems limit the application of these models to a small subdomain of the electrode.

*Pore network modeling* (PNM) represents an alternative modeling approach that is able to capture microstructural effects on the mesoscale at a reasonable computational cost [12-13]. In PNM, the complexity of the model equations is reduced, while the underlying physics is retained, see Figure 5.



**Figure 5** - Representation of the level of complexity and detail for the various modeling techniques used to model porous media. The right image was adapted from Zhang et al. [32].

Instead of directly solving the momentum equations within the porous electrode, the porous space is approximated by a network of spheres and cylinders. The structural properties of the porous material can be obtained from imaging techniques or from artificial generation techniques [48]–[51]. Transport of mass and charge within the porous material is based on finite difference schemes, in which 1D analytical solutions are leveraged to reduce the computational costs (see Chapter 4.3). Agnaou *et al.* demonstrated that this simplification of the model equations results into a computational time reduction up to 10<sup>4</sup> times compared to FEM simulations within the same geometry, with a limited loss in computational accuracy [52]. Therefore, PNMs can be leveraged to study complex flow problems in relatively large domains, and are suitable for optimization studies for the RFB electrode microstructure.

To date, few studies have been published on PNMs for electrochemical devices. Moreover, most of the published work considers the physics for multiphase flow seen in fuel cell technology [53]–[55]. Arguably, the biggest contribution to the field of PNM was delivered by the group of prof. Gostick, University of Waterloo, that developed the open-source PNM toolkit OpenPNM in Python [16]. The OpenPNM environment contains a large set of equations that can be used to construct pore networks and to perform flow simulations in these networks. [12]. Recently, a hydrogen-bromine RFB model, built with OpenPNM, was published by Sadeghi et al. [13]. Additionally, Lombardo et al. presented a framework for transient PNM to simulate the coupled flow, species and charge transport within porous electrodes and applied it to a VRFB [12]. This initial work in the field focused primarily on the development of the modeling equations. However, the implementation of all the relevant physics in PNMs is still open-ended. Unfortunately, the model of Lombardo et al. neglects the model equations to compute the voltage drop over the membrane and the thickness of the electrode. The model of Sadeghi et al. on the other hand is only valid for the specific case of the hydrogen-bromine RFB, where the hydrogen compartment can be considered as an ideal half-cell. Moreover, mass transfer towards the electrode within the porous electrode is not considered in both presented models.

In this thesis, a novel PNM framework is presented that improves on the existing models. The framework's versatility is tested by the validation of three distinct RFB electrolytes: an aqueous, kinetically facile electrolyte using the  $Fe^{2+}/Fe^{3+}$  redox couple, an aqueous, kinetically sluggish electrolyte using the  $V^{4+}/V^{5+}$  redox couple and an organic, kinetically facile electrolyte using the TEMPO-/TEMPO<sup>+</sup> redox couple. This novel PNM model opens up a wide range of possibilities for the characterization and optimization of porous electrode microstructures for flow battery applications.

## Chapter 3. Imaging and generation of porous electrodes

Due to the large improvements made on computational power in the last decade, analytical techniques to visualize the microstructure of porous media have become an established field [56]. Within this work, two distinct approaches have been used to obtain microporous electrodes geometries for PNM. The first approach consists of the extraction of physical electrode structures, using *x*-*ray tomography* (XTM) in combination with a network extraction algorithm, which is explained in Chapter 3.1. The second approach consists of the artificial generation of porous networks that represent desired structures or approximate real structures with a specialized set of network generation rules, using the geometry module presented in OpenPNM, which is elucidated in Chapter 3.2 [16].

### 3.1 X-ray computed tomography of real electrode structures

XTM is a non-invasive technique that can be used to obtain quantitative morphological information in the micrometer range. XTM produces grayscale images, which reflect the range of x-ray attenuation values (i.e. the reduction of the x-ray beam intensity) for the scanned material at various 2-dimensional cross-sections. The different cross-sections of the material are combined to recreate a virtual representation of the 3-dimensional scanned structure. The desired porous network is obtained from this virtual model by a series of image processing steps, consisting of smoothing, segmenting, and network extraction [56].

### 3.1.1 X-Ray scanning

Electrode materials were scanned in an uncompressed state using laboratory micro-CT at an isotropic resolution of  $3.3 \mu m$ . The scans were carried out using a peak potential of 45 kVp and a current of  $88 \mu A$  to acquire 312 image projections over the length of the electrode.

#### 3.1.2 Smoothing and segmentation methods

Gray-scale images produced using XTM contain a certain degree of noise that has to be reduced. Care has to be taken to preserve phase edges while applying noise reduction filters to limit losses of features in the virtual model. In this work, a *median filter* with a radius of 2.0 pixels was used to reduce the noise in the gray-scaled image. Median filters use the median value of a specified neighborhood surrounding the voxel in consideration and replace that voxel value with the median value of this neighborhood, thereby smoothening the image [56]. A voxel represents a 3D volume within the virtual model (congruent with a pixel in 2D). Subsequently, each voxel in the grey-scale image has been assigned to either the solid or void phase using *a K-means cluster segmentation filter* [56]. In K-means clustering, the image is segmented in two clusters: the solid phase and the void phase. These clusters are iteratively updated until all voxels are assigned to one of the clusters [56]. The reported median filter and K-means cluster

segmentation filter had been imported as plug-ins in the image processing software ImageJ [57], [58].

To prevent boundary effects from sample cutting, a 1.0 mm high and wide sample selection was obtained from the center of the processed image, where the thickness of the electrode was reduced by removal of the first and last few image layers in this dimension. The obtained binarized electrode sample is displayed in Figure 6a.



**Figure 6** - Visualization of (a) a processed x-ray tomography image of a Freudenberg paper electrode, (b) the resulting extracted pore network and (c) an overlay of the x-ray tomography image with the extracted pore network  $(1000x1000x151 \ \mu m)$ .

### 3.1.3 Network extraction

The open-source *SNOW network extraction* algorithm was used to extract the pore network (PN) from the obtained binarized image, see Figure 6b [49-50]. The SNOW algorithm has been developed for the extraction of porous networks from tomographic images and was previously validated for porous media with a wide range of porosity (20-85%) by Gostick [49]. The network extraction operation was run on a desktop computer with 32 GB of RAM memory. For the extracted networks, a standard deviation value of the applied convolution mask ( $\sigma$ ) of 0.4 and a value for the radius (R) of the spherical structure element of 4 voxels was used. A more detailed explanation of these parameters and the procedure of the SNOW algorithm can be found in Appendix I.

### 3.2. Artificial Generation of Microporous Networks

Previous work in the field of PNM has utilized artificial generation as an alternative tool to generate PNs. These artificially generated structures are based on the geometry formulas of various shapes, such as spheres, cylinders, and polygons. Systematic studies on the geometry of the artificially generated structures have subsequently been performed in order to investigate the effect of various pore-scale characteristics, such as porosity and wettability, on the overall performance of the generated porous electrode [13], [53], [59].

In this work, *cubic lattices* were generated utilizing the OpenPNM Network class. This class takes a network shape, spacing, and connectivity as input and produces a network with the pore and throat coordinates as an output. The shape of the cubic lattices describes the number of generated pores in each dimension, the spacing describes the distance between the different pore centers in the cubic lattice, and the connectivity displays the total number of throat connections that a single pore within the cubic lattice embodies.

Topological properties were subsequently attributed to the network's pores and throats by the use of the OpenPNM Geometry class. In this operation, geometrical formulas of spheres and cylinders are leveraged together with a random seed value, in order to create pseudo-randomly distributed topologies. In the following subchapters, the most important topological properties, displayed in Figure 7, are briefly explained.



Figure 7 – Schematic diagram of the most important topological properties in a pore-throat-pore conduit.

#### 3.2.1 Pore diameter

The pore diameter was assigned by a pseudo-random process. First, a random value between the two boundaries, called the seed  $(S_p)$ , was generated for each pore. In this research, the boundary points 0.2 and 0.7 were taken, which is identical to the standard option in the OpenPNM StickAndBall geometry class. Subsequently, the maximum pore size  $(d_{p,max})$  was determined by finding the maximum pore diameter that can be placed in each location without overlapping any neighboring pore. The randomly generated seed value of each pore was multiplied with the maximum pore size to find the pore diameter [Eq 3.1].

$$d_p = S_p \cdot d_{p,max}$$
 [m] Equation 3.1

#### 3.2.2 Throat diameter

Each throat diameter was determined from the minimum pore size of the two pores that the throat is connecting. This minimum pore size was subsequently multiplied by a throat sizing factor,  $f_T$ , of 0.5 to obtain the diameter,  $d_T$ , of the connecting throat [Eq. 3.2]. The throat sizing factor was kept identical to the standard option in the OpenPNM StickAndBall geometry class.

$$d_T = f_T \cdot \min(d_{p,1}, d_{p,2}) \qquad [m] \qquad \text{Equation 3.2}$$

#### 3.2.3 Throat cross-sectional area

The throat cross-sectional area  $(S_T)$  was determined from the throat diameter, assuming that each throat is a perfect cylinder [Eq. 3.3].

$$S_T = \frac{\pi}{4} \cdot d_T^2 \qquad [m^2] \qquad \text{Equation 3.3}$$

#### 3.2.4 Pore surface area

The pore internal surface area  $(A_p)$  was calculated by subtracting the throat cross-sectional area of all neighboring throats of the pore  $(N_T)$  from the surface area of a perfect sphere with diameter  $d_p$  [Eq. 3.4]. Note that the pore internal surface area  $(A_p)$  is different from the pore cross-sectional area  $(S_p)$ .

$$A_p = \pi \cdot d_p^2 - \sum_{j=1}^{N_T} S_T \qquad [m^2] \qquad \text{Equation 3.3}$$

#### 3.2.5 Throat conduit lengths

The throat conduit length  $(L_T)$  is defined as the summed length of two half-pores and the connected throat, and is used for calculating the hydraulic transport through a network. In cubic networks, the summed conduit length is equal to the applied network spacing.

#### 3.3 Cubic network

Random cubic networks can be generated using the presented geometrical formulas. The input properties used to generate a cubic network of 1296 pores are given in Table 1. A visual representation of the cubic network is presented in Figure 8. Boundary pores and throats, required for the implementation of transport algorithms, were generated at each surface.

 Table 1 - Overview of the input properties used to develop the model network visualized in Figure 8.

	Value	Units
Network shape	[18, 18, 4]	[x, y, z]
Spacing	50	μm
Connectivity	6	_
Pore seed	$0.2 \le S_{p} < 0.7$	_
Throat sizing factor	0.5	—



**Figure 8** - Visualization of an artificially generated random cubic lattice with [18, 18, 4] pores in the x, y and z direction. The colors indicate the relative size of the generated pores and throats. Boundary pores and throats are present on the edges of the network.

## Chapter 4. Multiphysics pore network model

The extracted and artificially generated networks can be subjected to a variety of pore-scale physics models. In this chapter, the assumptions, computational domain, physics, and numerical implementation of the developed multiphysics PNM are discussed. The developed model aims to give insight into the reactive transport occurring within an RFB electrode. The presented model provides a novel, computationally inexpensive route for electrode optimization for different redox couples, alleviating the need for empirical, time-consuming experimentation.

### 4.1 Model assumptions and adopted sign convention

### 4.1.1 Model assumptions

PNMs are an idealization of real porous structures. In PNMs, it is assumed that the void space within the porous structure can be approximated by spherical pores and cylindrical throats, see Figure 9. Each pore is assumed to be a well-mixed body and transport in the pore network occurs within the throats. The validity of this assumption was verified among others by Yang *et al.*, by comparison of two direct numerical simulations using FEM and LBM with experimental data [60]. The idealization of the void space allows for the reduction of complexity of the considered model equations, while still retaining information about the microporous structure of the porous electrode.



**Figure 9** - Schematic representation of the performed idealization of the pore network in PNM. (Left) schematic overview of a cross-section of a real porous structure and (right) its approximated pore network structure, adopted from Koplik et al. [61].

Within the presented PNM, the following model assumptions have been made:

- 1. The electrochemical cell operates at steady-state conditions.
- 2. The electrochemical cell operates at isothermal conditions.
- 3. The crossover of active species through the membrane is neglected.

- 4. The considered electrolyte solution is modeled as a single-phase, diluted, incompressible, Newtonian fluid that has a uniform viscosity throughout the porous electrodes.
- 5. Due to the small flow dimensions, the flow within the porous structure is classified as a creeping flow.
- 6. Due to the high electric conductance in the solid phase in comparison to the liquid phase, the electric potential of the solid electrode phase is assumed to be constant throughout the electrode. The solid phase potential is assumed to equal the applied cell voltage in the cathodic compartment and to equal zero in the anodic compartment.
- 7. The charge flux within the liquid phase is approximated using the bulk conductivity of the electrolyte. Migration effects are therefore neglected.
- 8. The half-cell reaction is described as a single-step reaction mechanism and neglects the formation of intermediates that are adsorbed on the electrode surface.
- 9. The electrochemically active surface area of a pore is equal to its geometrical internal surface area.
- 10. The electrochemical reaction is only occurring in the pores and not throughout the connecting throats.

### 4.1.2 Sign convention

The governing equations presented in the following subchapters are based on the convention of describing the flux of *positive charges*. During discharge, a positive current travels from the negative half-cell towards the positive half-cell, while in charge mode the opposite process occurs and the signs of the current density (*j*) and overpotential ( $\eta$ ) are reversed. According to the common electrochemical convention, current and overpotentials are positive in the case of an anodic reaction (oxidation) and negative in the case of a cathodic reaction (reduction). An overview of the implications of this sign convention on the sign of the source term (production of species) for the oxidized ( $S_{ox}$ ) and reduced species ( $S_{red}$ ) can be found in Table 2.

Discharge		Charge				
Half-cell	Negative	Positive	Negative	Positive		
Туре	Anode	Cathode	Cathode	Anode		
	Physics					
j(η)	+	_	_	+		
η	+	—	—	+		
	Source terms					
Sox	+	_	_	+		
<b>S</b> <sub>red</sub>	_	+	+	—		

 Table 2 - Sign convention table for the negative and positive half-cell in an redox flow battery.

#### 4.2 Computational domain

The presented numerical framework efficiently predicts local transport within the porous electrode and offers a flexible platform on which different RFB chemistries can be implemented. In this thesis, *symmetric RFB simulations* were performed for three distinct redox couples,  $VO_2^+/VO_2^+$ , Fe<sup>2+</sup>/Fe<sup>3+</sup> and TEMPO<sup>+</sup>/TEMPO<sup>+</sup>, in order to validate the predicted the electrochemical behavior within a porous carbon fiber electrode (see Chapter 5).

The symmetric cell simulations were performed using the co-current operation of the anodic and cathodic half-cell (i.e. the inlet for both half-cells is located at their bottom faces). In the symmetric cell set-up, the oxidation reaction of the redox couple occurs in the anodic half-cell, whereas the reduction reaction of the *same* redox couple takes place in the cathodic half-cell. The membrane that separates the two half-cells is treated as a macro continuum entity, and therefore only the overall macroscopic ionic resistance of the membrane is considered. A 2D representation of the computed domain for the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple is presented in Figure 10.



**Figure 10** - Schematic overview of (a) the modelled domain for the  $Fe^{2+}$  and  $Fe^{3+}$  redox couple in blue showing the electrolyte flow inlet and outlet boundaries and in red the electrolyte potential boundaries and (b) a magnification of a pore-throat-pore conduit with relevant fluid transport quantities.

#### 4.3 Model physics

The considered physics within the three-dimensional porous electrode are described by the equations of fluid transport, species mass transport, and charge transport. Moreover, the coupling of the flow field, both half-cells, and the membrane is controlled by the applied boundary conditions. The following subchapter describes the governing equations and the formulated boundary conditions within the electrochemical cell for the case of *cell discharge*.

#### **4.3.1 Fluid transport**

The fluid transport within the porous electrode is described by the steady state Navier-Stokes equations through cylindrical pipes (*Stokes flow*). The mass balance for the electrolyte phase around each pore in the network is described by [Eq. 4.1].

$$-\sum_{j=1}^{N_T} \rho u_{ij} S_{ij} = 0 \qquad [kg s^{-1}] \qquad Equation 4.1$$

With,  $\rho$  the electrolyte density [kg m<sup>-3</sup>],  $u_{ij}$  the fluid velocity from pore i to pore j [m s<sup>-1</sup>] and  $S_{ij}$  the cross-sectional area of the throat connecting pore i and j [m<sup>2</sup>].

The Hagen-Poiseuille equation can be used to express the velocity field based on the pore pressures [Eq. 4.2].

$$u_{ij} = \alpha_{ij} (p_i - p_j) \qquad [m s^{-1}] \qquad Equation 4.2$$

With  $a_{ij}$  the hydraulic conductance of the throat connecting pore i and j [m Pa<sup>-1</sup> s<sup>-1</sup>] and p the pressure in pore i or j [Pa]. The hydraulic conductance is described by [Eq. 4.3].

$$\alpha_{ij} = \frac{S_{ij}}{8\pi\mu L_{ij}} \qquad \qquad [\text{m Pa}^{-1} \text{ s}^{-1}] \qquad \qquad \text{Equation 4.3}$$

With  $\mu$  the dynamic viscosity of the electrolyte [Pa s] and  $L_{ij}$  the conduit length of the connecting throat [m].

The boundary conditions for fluid transport consist of a Dirichlet (constant) inlet pressure boundary condition at the boundary pores at the bottom of the electrode, and a discharge pressure boundary condition at the top of the electrode sample. The inlet pressure boundary condition is determined by setting a target inlet velocity. From the target inlet velocity the target flow rate ( $Q_{in}$ ) is calculated, using [Eq. 4.4].

$$Q_{in} = u_{in}A_{in} \qquad [m^3 s^{-1}] \qquad Equation 4.4$$

With  $u_{in}$  the inlet velocity of the electrolyte [m s<sup>-1</sup>] and  $A_{in}$  the geometrical inlet area of the electrode [m<sup>2</sup>]. Subsequently, the inlet pressure at the bottom boundary pores is iteratively updated until the total flow rate entering the network matches the target flow rate. A discharge pressure of 0 Pa was set at the outlet boundary pores.

Neumann (gradient) no-flux boundary conditions were set to the boundary pores at the boundaries of the width and thickness of the electrode (i.e. dv/dx = 0).

#### 4.3.2 Species Transport

Mass transport of chemical species in the porous electrodes is described by the advectiondiffusion-reaction equation. The conservation equation around each pore for the active species that is consumed is described by [Eq 4.5].

$$-\sum_{j=1}^{N_T} m_{ij} S_{ij} = \frac{I_i}{nF}$$
 [mol s<sup>-1</sup>] Equation 4.5

With  $m_{ij}$  the mole flux of the active species between pore i and pore j [mol m<sup>-2</sup> s<sup>-1</sup>],  $I_i$  the applied current in pore i [A], *n* the number of electrons participating in the half-reaction and *F* the Faradaic constant [C mol<sup>-1</sup>].

The mole flux  $m_{ij}$  is derived from the exact solution for the one-dimensional advectiondiffusion equation [Eq 4.6], based on the approach of Sadeghi *et al.* [62].

$$m_{ij} = u_{ij}(c_i + \frac{c_i - c_j}{\exp(Pe) - 1})$$
 [mol m<sup>-2</sup> s<sup>-1</sup>] Equation 4.6

With  $c_i$  the concentration the reacting species in pore i [mol m<sup>-3</sup>] and *Pe* the local Peclet number at the considered throat [Eq. 4.7].

$$Pe = \frac{u_{ij}l_{ij}}{D}$$
 [-] Equation 4.7

With *D* the diffusion coefficient of the active species in the electrolyte  $[m^2 s^{-1}]$ .

The applied current  $I_i$  is defined by the Butler-Volmer equation in [Eq. 4.8] for the anodic compartment and in [Eq. 4.9] for the cathodic compartment.

$$I_{i,a} = j_0^a A_i \left(\frac{C_{i,s}^{red}}{C_{ref}^{red}}\right) \left[ \exp(-\frac{\alpha_a F \eta_a}{RT}) - \exp\left(\frac{\alpha_c F \eta_a}{RT}\right) \right]$$
[A] Equation 4.8

$$I_{i,c} = j_0^c A_i \left(\frac{C_{i,s}^{ox}}{C_{ref}^{ox}}\right) \left[ \exp(\frac{\alpha_a F \eta_c}{RT}) - \exp\left(-\frac{\alpha_c F \eta_c}{RT}\right) \right]$$
[A] Equation 4.9

With  $j_0$  the exchange current density  $[A m^{-2}]$ ,  $A_i$  the electrochemically active internal surface area of pore i  $[m^2]$ ,  $C_{i,s}$  the concentration of the reduced form or the oxidized form at the electrode surface  $[mol m^{-3}]$ ,  $C_{ref}$  the reference concentration of the reduced form or the oxidized form at which the exchange current density was measured  $[mol m^{-3}]$ ,  $\alpha_a$  and  $\alpha_c$  the anodic and cathodic reaction transfer coefficients [-],  $\eta_c$  and  $\eta_a$  the overpotentials in the cathodic and anodic compartment [V], R the ideal gas constant  $[J K^{-1} mol^{-1}]$  and T the operating temperature [K]. The exponents  $\alpha_a$  and  $\alpha_c$  can typically be related to each other by [Eq. 4.10].

$$\alpha_a + \alpha_c = n$$
 [-] Equation 4.10

The electrode overpotential in the cathodic half-cell is calculated from the difference between the solid phase potential ( $\varphi_s$ ), the electrolyte potential ( $\varphi_e$ ) and the equilibrium potential of the electrode ( $E_{oc}$ ) defined against the same reference electrode [Eq. 4.11]. This overpotential term does include the activation and concentration overpotential terms, but not include the ohmic overpotential originating from the electrolytic and membrane resistances.

$$\eta_c = \varphi_s - \varphi_e - E_{oc}$$
 [V] Equation 4.11

The electrode overpotential in the anodic half-cell is calculated by [Eq. 4.12]

$$\eta_a = \varphi_s - \varphi_e$$
 [V] Equation 4.12

In this work, the general Butler-Volmer equations [Eq 4.7-4.8] were modified to include mass transfer of the active species towards the *electrode surface*. The mass transfer of species is described by [Eq. 4.13-4.14].

$$I = Fk_m^{red}A_i \left(C_{i,b}^{red} - C_{i,s}^{red}\right)$$
 [A] Equation 4.13

$$I = -Fk_m^{ox}A_i(C_{i,b}^{ox} - C_{i,s}^{ox})$$
 [A] Equation 4.14

With  $k_m$  the mass transfer coefficient of the considered species  $[m \cdot s^{-1}]$  and  $C_{i,b/s}$  the bulk or surface concentration of the active species  $[mol m^{-3}]$ . By substitution of [Eq. 4.13-4.14] into [Eq. 4.8-4.9] the Butler-Volmer equations for a one-electron electrochemical reaction, including mass transfer limitations are obtained [Eq. 4.15-4.16].

$$I_{a} = \frac{j_{0}^{a}A_{i}\left(\frac{C_{i}^{red}}{C_{ref}^{red}}\right)\left[\exp\left(-\frac{\alpha_{a}F\eta_{a}}{RT}\right) - \exp\left(\frac{\alpha_{c}F\eta_{a}}{RT}\right)\right]}{1 + \frac{j_{0}^{a}}{Fk_{m}^{red}C_{ref}^{red}}\exp\left(-\frac{\alpha_{a}F\eta_{a}}{RT}\right) + \frac{j_{0}^{a}}{Fk_{m}^{ox}C_{ref}^{ox}}\exp\left(\frac{\alpha_{c}F\eta_{a}}{RT}\right)}$$

$$I_{c} = \frac{j_{0}^{c}A_{i}\left(\frac{C_{i}^{ox}}{C_{ref}^{ox}}\right)\left[\exp\left(\frac{\alpha_{a}F\eta_{c}}{RT}\right) - \exp\left(-\frac{\alpha_{c}F\eta_{c}}{RT}\right)\right]}{1 + \frac{j_{0}^{c}}{Fk_{m}^{red}C_{ref}^{red}}\exp\left(\frac{\alpha_{a}F\eta_{a}}{RT}\right) + \frac{j_{0}^{c}}{Fk_{m}^{ox}C_{ref}^{ox}}\exp\left(-\frac{\alpha_{c}F\eta_{a}}{RT}\right)}$$
[A] Equation 4.15

It may be verified that [Eq. 4.15-4.16] reduce to the case without mass transfer limitations [Eq. 4.13-4.14] when the mass transfer terms approaches infinity  $(k_m \rightarrow \infty)$ .

An estimation of the mass transfer coefficient towards the porous electrode was obtained by neglecting inertia effects and applying the film theory, assuming that the film layer is equal to the pore radius of every pore [Eq 4.17].

$$k_m = 2\frac{D}{d_p} \qquad [\text{m s}^{-1}] \qquad \text{Equation 4.17}$$

The boundary conditions for species transport are a Dirichlet boundary condition for the concentration at the inlet of the porous electrode  $C_{in}$  and Neumann boundary conditions for all other boundaries (i.e. dC/dx = 0).

#### 4.3.2 Charge Transport

The conservation of charge around each pore is coupled with the species transport in the electrochemical cell by the current and the potential field, and is described by [Eq 4.18].

$$-\sum_{j=1}^{N_T} I_{ij} S_{ij} = I_{BV}$$
 [V] Equation 4.18

With  $I_{ij}$  the charge flux from pore i to j [A m<sup>-2</sup>], which is proportional to the potential field in the liquid phase [Eq. 4.19].

$$I_{ij} = \beta_{ij}(\varphi_i - \varphi_j)$$
 [A m<sup>-2</sup>] Equation 4.19

Where  $\beta_{ij} = \sigma_l / l_{ij}$  is the electrical conductance of the connecting throat [S m<sup>-2</sup>],  $\sigma_l$  the bulk electrolyte conductivity [S m<sup>-1</sup>] and  $\varphi_i$  and  $\varphi_j$  are the liquid potential in pore i and j [V].

The boundary condition for the electrolyte potential at the membrane  $(\varphi_m)$  in a specific halfcell is iteratively calculated from the electrolyte potential at the membrane in the other halfcell, using Ohm's law to include the average voltage loss across the membrane interphase  $\Delta \varphi_m$ [Eq. 4.20].

$$\Delta \varphi_m = R_m I_m \qquad [V] \qquad Equation 4.20$$

With  $R_m$  the resistance of the membrane [ $\Omega$ ] and  $I_m$  the current passing the membrane [A].

Neumann boundary conditions for the voltage were applied at the inlet and outlet of the porous electrode and at the current collector (i.e. dV/dx = 0).

#### 4.4 Numerical implementation and data extraction

#### 4.4.1 Numerical implementation

The backbone of the constructed numerical algorithm consists of the coupled mass and charge transport within the porous electrode. In the developed algorithm, the individual transport equations within the anodic and the cathodic compartment are updated sequentially within an *iterative algorithm*. The main steps involved in the computation of the cell performance are explained in this section. A detailed flowchart of the constructed algorithm is displayed at the bottom of this chapter in Figure 11 and the corresponding Python code can be found in the supplementary information S.1.

Due to the assumption of a dilute electrolyte, fluid transport within the porous electrode is considered to be independent from the other transport processes and can therefore be directly solved to obtain the velocity and pressure field [Eq. 4.1-4.2]. The velocity field of the liquid electrolyte is passed onto the iterative algorithm for species and charge transport. The species and charge transport equations consists of two nonlinear systems of equations [Eq. 4.5, Eq. 4.18] that are coupled by the Butler-Volmer equation [Eq. 4.15-4.16]. The iterative scheme

consecutively solves the advection-diffusion reaction equation [Eq. 4.5] and the potential field [Eq. 4.18]. Both half cells are coupled, using the found solution for the electrolyte potential at the membrane in one half cell to calculate the electrolyte potential at the other side of the membrane in the other half cell. In this step, Ohm's law was used to account for the membrane resistance [Eq. 4.20]. The calculated electrolyte potential is subsequently used as a (constant) boundary condition for the charge transport equation in the second half cell.

In order to obtain the polarization curve, the numerical model solves the coupled transport equations over a given voltage range. Since the iterative algorithm starts at the open-circuit voltage, the initial guess for the overpotential in the first iteration was set to 0 V. The initial concentration within all pores,  $c_{0,i}$ , was set to the inlet concentration  $c_{in}$ . While progressing to higher cell potentials, the initial guesses for the concentration, potential field and overpotential are based on the solution of the previous cell potential.

Numerical convergence is achieved when the specified relative and absolute tolerances are met. These specified tolerances are based on the total current ( $I_{total}$ ) generated or consumed in a half-cell [Eq. 4.21].

$$I_{total} = \sum_{j=1}^{N_p} I_{local,j}$$
 [A] Equation 4.21

The relative error in the total current estimation ( $\epsilon_{rel}$ ) can be calculated for both compartments by [Eq. 4.22].

$$\epsilon_{rel} = \frac{I_{total}^n - I_{total}^{n-1}}{I_{total}^{n-1}}$$
[-] Equation 4.22

With n being the iteration number.

The absolute error ( $\epsilon_{abs}$ ) consists of the difference in total current between both half-cells, and is defined by [Eq 4.23].

$$\epsilon_{abs} = I^a_{total} - I^c_{total}$$
 [A] Equation 4.23

The tolerance for the relative error  $(\tau_{rel})$  was set to  $5.0 \cdot 10^{-5}$  and the absolute error  $(\tau_{abs})$  to  $6.0 \cdot 10^{-4} \text{ A cm}^{-2}$ .

In order to counteract divergence of the solution due to the highly nonlinear nature of both the system, two numerical strategies were employed. The first strategy consists of underrelaxtion during the updating of the concentration and potential field, which is a well-known technique to keep iterative computation stable [13]. In underrelaxation, a relaxation factor  $\omega$  is used to dampen the obtained solution [Eq. 4.24].

$$c_i^{n+1} \leftarrow c_i^{n+1}\omega + c_i^n(1-\omega)$$
 [mol m<sup>-3</sup>] Equation 4.24

The second strategy consists of linearization of the charge transport source term. In the case that the considered active species has facile kinetics (i.e. a large exchange current density), the

mass transport and charge transport equations become strongly coupled. In this case, linearization of the current generation term can mitigate divergence. The derivation of the charge transfer source term is further elaborated on in Appendix II.

#### 4.4.1 Data extraction

From the converged solution, the pressure field, concentration field, potential field and current distribution within the porous electrode can be calculated. Additionally, the obtained electrode overpotential can be divided in three separate terms: the activation overpotential  $\eta_{act}$ , the concentration overpotential  $\eta_c$ , and the ohmic overpotential  $\eta_{ohm}$ .

The *activation overpotential* is defined as the potential difference above the equilibrium potential that is required to produce the achieved current, neglecting the effect of the surface concentration in the Butler-Volmer equation. The activation overpotential term in found for every pore by minimizing the difference between the ideal current,  $I_{ideal}$ , obtained from [Eq. 4.25-4.26] and the obtained current *I* from [Eq. 4.15-4.16].

$$I_{a,ideal} = j_0^a A_i \left(\frac{C_{in}^{red}}{C_{ref}^{red}}\right) \left[\exp(-\frac{\alpha_a F \boldsymbol{\eta}_{a,act}}{RT}) - \exp\left(\frac{\alpha_c F \boldsymbol{\eta}_{a,act}}{RT}\right)\right] \quad [A] \quad \text{Equation 4.25}$$

$$I_{c,ideal} = j_0^c A_i \left(\frac{C_{in}^{ox}}{C_{ref}^{ox}}\right) \left[ \exp(\frac{\alpha_a F \boldsymbol{\eta}_{c,act}}{RT}) - \exp\left(-\frac{\alpha_c F \boldsymbol{\eta}_{c,act}}{RT}\right) \right]$$
[A] Equation 4.26

With  $c_{in}$  the inlet concentration of the active species [mol m<sup>-3</sup>].

The *concentration overpotential* is defined as the summation of mass transfer and depletion effects on the overpotential. The concentration overpotential can be obtained by substracting the overpotential found using [Eq. 4.11-4.12] with the activation overpotential found using [Eq. 4.25-4.26].

The *ohmic overpotential* takes the electrolytic and membrane resistivity into account. The ohmic overpotential within an electrode can be obtained from the potential field [Eq. 4.27].

$$\eta_{ohm,el} = \varphi_i - \varphi_{mem}$$
 [V] Equation 4.27

With  $\varphi_i$  the electrolyte potential in pore i [V], and  $\varphi_{mem}$  the average potential in the pores closest to the membrane in the considered electrode [V]. The contribution of the membrane can be obtained directly from [Eq. 4.20].

In the analyzed symmetric flow battery set-up, the (absolute) overpotential contributions sum up to the applied cell potential ( $E_{cell}$ ) [Eq. 4.28].

$$E_{cell} = \eta_{act} + \eta_c + \eta_{ohm} \qquad [V] \qquad Equation 4.28$$



Figure 11 - Algorithmic flowchart, line (1) and (2) depict the coupling of the potential field between the anodic and cathodic half-cell.

## **Chapter 5. Experimental methods**

Symmetrical flow cell experiments were conducted in order to validate the theoretical model. In this chapter, the procedure of the validation experiments is explained. First, the preparation of the electrolyte stock solutions is presented. Afterwards, an overview of the performed electrolyte characterization experiments is given. Finally, the symmetric flow battery set-up is explained.

### 5.1 Electrolyte preparation

### 5.1.1 Vanadium(IV)/(V) stock solution

Vanadium(IV) sulfate oxide hydrate (99.9%, Alfa Aesar) and sulfuric acid (95.0-98.0%, Sigma-Aldrich) were dissolved into deionized water to obtain a 0.2 M V(IV) and 1.0 M sulfuric acid solution.

The obtained stock solution was electrochemically converted in order to produce vanadium(V) sulfate. In this electrochemical oxidation step, 50 mL of the prepared electrolyte was placed into two glass reservoirs and was subsequently pumped through the positive and negative sides of a VRFB at 10 mL min<sup>-1</sup>, see Figure 12.



Figure 12 - Schematic overview of the vanadium conversion cell.

Graphite current collectors with milled in flow-through flow fields were used. Two pieces of the untreated Freudenberg H23 paper electrodes with an external area of 2.5 cm<sup>2</sup> were placed on top of each current collector, using compressible gaskets. A Nafion 212 membrane was used to separate the two half-cells [63]. Subsequently, the cell was tightened to 2.2 Nm using a torque-controlled screwdriver. Afterwards, the electrolyte was pumped through the battery for 50 min to ensure optimal wetting, using a Masterflex L/S® Easy-Load® II pump and LS-14 tubing. Finally, a BioLogic VMP-300 potentiostat was used in potentiostatic mode convert the V(IV) electrolyte to V(III) on the negative side and to V(V) on the positive side, by holding a potential of 2.0 V until a steady current of ~10 mA was measure. Humidified nitrogen was bubbled through both electrolyte tanks during the entire duration of the experiments to prevent

oxidation of the redox couples from exposure to oxygen. A 50% SOC V(IV)/V(V) solution was obtained by mixing the retrieved V(V) solution with the initial V(IV) solution in a 1:1 volumetric ratio.

### 5.1.2 Iron(II)/Iron(III) stock solution

An electrolyte stock solution of 0.1 M ferrous chloride (FeCl<sub>2</sub>) hydrate (98%, Sigma-Aldrich), 0.1 M ferric chloride (FeCl<sub>3</sub>) hydrate (97%, Sigma-Aldrich) and 1.0 M sodium chloride (NaCl) ( $\geq$  99.0%, AkzoNobel), dissolved in deionized water was prepared.

### 5.1.3 TEMPO·/TEMPO<sup>+</sup>(+) stock solution

The numerical model was validated for the organic (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO<sup>-</sup>) and the 2,2,6,6-Tetramethyl-1-piperidinyloxy-oxo tetrafluoroborate (TEMPO<sup>+</sup>) redox couple using the data presented in Forner-Cuenca *et al.* [10]. In order to estimate the density and conductivity of the electrolyte used in this set-up, a stock solution of 1.0 M tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) (99%, Sigma-Aldrich), dissolved in acetonitrile (99.8%, Sigma-Aldrich) was prepared.

### 5.2 Electrolyte characterization

### 5.2.1 Density and conductivity measurements

Electrolyte density measurements were performed *in triplo* for the three synthesized electrolytes using a Sartorius ED224S analytical balance and an electrolyte volume of 10 mL.

Conductivity measurements were performed using a two-electrode Swagelok conductivity cell, see Figure 13, similar to the setup used in Milshtein *et al.* [64]. The compartment of the conductivity cell was flooded with electrolyte and sealed shut. Electrochemical impedance spectroscopy (EIS) was conducted using the VMP-300 potentiostat at the open circuit voltage and at room temperature (23 °C) with an amplitude of 10 mV and a frequency range of 1 MHz - 100 Hz. The high frequency intercept was identified as the value of the resistance. EIS measurements were performed *in triplo*. Furthermore, the measurement for all three samples was repeated five times. A calibration curve of the conductivity cell was obtained using aqueous conductivity standards (0.01M, 0.1M and 1.0M aqueous KCl solutions), and was used together with the cell resistances to gain insight into the conductivity of the different electrolytes.


**Figure 13** - (a) schematic overview of a Swagelok conductivity cell, reproduced from Milshtein et al. [64], (b) Photograph of the (disconnected) Swagelok conductivity cell used for the conductivity measurements.

## 5.3 Symmetric flow battery set-up

Symmetric flow cell experiments were conducted in an RFB cell for the synthesized vanadium and iron electrolytes using a two-electrode set-up, see Figure 14. Graphite current collectors were used, resulting in a flow-through flow field. Two pieces of the untreated Freudenberg H23 electrodes with a thickness of 210  $\mu$ m and an external area of 2.55 cm<sup>2</sup> were placed on top of each current collector using an incompressible gasket with a thickness of 200  $\mu$ m, ensuring minimal compression. A porous separator was used to separate the two half-cells (Daramic 175 SLI Flatsheet Membrane) [65]. Electrochemical experiments were performed at inlet velocities of 1.5, 5.0 and 20.0 cm/s. Humidified nitrogen was bubbled through both electrolyte tank during the entire duration of the experiments to prevent oxidation of the redox couples from exposure to oxygen. Polarization curves were obtained by employing a constant voltage step of 0.025 V and measuring the steady state current in a voltage range of 0.0 to 1.0 V.



**Figure 14** - (a) Schematic overview of a symmetric flow battery configuration, (b) photograph of the vanadium (IV)/(V) symmetric flow cell setup with (1) the N<sub>2</sub> humidifier trap, (2) backup bulk electrolyte stock solution, (3) electrolyte reservoir solution and (4) the symmetric flow cell.

# Chapter 6. Model validation and real electrode comparison

In this chapter, the results from the developed numerical framework are displayed. First, the network extraction and algorithm are validated with experimental data (Chapter 6.1). Secondly, the power of the numerical framework is demonstrated by analysis and comparison of the electrochemical performance in a case study of two distinct electrode microstructures (Chapter 6.2).

### **6.1 Model validation**

In this subchapter, the modeling results are compared with the results obtained from symmetric flow cell experiments for the three distinct chemistries. Additionally, the accuracy of the network extraction for the used Freudenberg H23 paper is evaluated [49]. First, a comparison of the PSD of the obtained PN with mercury intrusion porosimetry (MIP) data found in literature was performed. Secondly, permeability simulations were performed and the effective permeability was compared with values from literature. Afterwards, the obtained electrochemically active surface area (ECSA) is compared with literature data. Finally, the electrochemical performance predicted by the numerical model is compared with the experimental data obtained for the Fe<sup>2+</sup>/Fe<sup>3+</sup>, the V<sup>4+</sup>/V<sup>5+</sup> and the TEMPO<sup>+</sup>/TEMPO<sup>+</sup> redox couples.

#### 6.1.1. Network extraction

The PSD from the extracted Freudenberg H23 PN was compared with the PSD from MIP measurements, presented in Forner-Cuenca *et al.* [10]. In MIP, an external pressure is applied in order to force the intrusion of mercury within a porous substrate. The applied external pressure *P* can be related to the pore diameter  $d_p$  by the Washburn Equation [Eq. 6.1].

$$d_p = -\frac{4\gamma\cos\theta}{P}$$
 [m] Equation 6.1

With  $\gamma$  the surface tension [N m<sup>-1</sup>] of mercury and  $\theta$  the contact angle between mercury and the wall [°]. Forner-Cuenca *et al.* assumed a constant contact angle of 130° in their measurements to derive the PSD [10]. A comparison of the PSD of the extracted Freudenberg PN with MIP data is presented in Figure 15. In this figure, the normalized volume is defined as the fraction of the total pore volume that is occupied by all pores within a 2 µm pore size range.



**Figure 15** - Pore size distribution of the Freudenberg network obtained with mercurily intrusion porosimetry (MIP) and the SNOW pore network extraction algorithm (PN).

The PSD obtained from the extracted PN and the MIP dataset are in good agreement. However, the MIP distribution is shifted towards smaller pore sizes. Additionally, in contrast to the MIP dataset, pores larger than 56  $\mu$ m are not present within the PN. Both findings appear to be well explained by inaccuracies introduced by the used measurement techniques.

Firstly, the shift towards smaller pore sizes for the MIP dataset can be attributed to the inkbottle effect. In MIP measurements, it is assumed that every pore is either directly connected to the surface of the medium or through connections with larger pores. When this assumption is not met, smaller pores will form an obstruction to flow from and towards the larger internal pores. This leads to the misattribution of the pore volume of the larger internal pores to the smaller pore sizes and thus shifts the PSD to smaller pore sizes [66].

Secondly, the discrepancy at larger pore sizes can possibly be explained by the segmentation of individual pores within the SNOW extraction algorithm. Due to the presence of inhomogeneities within the electrode image, it can be difficult to distinguish the exact boundaries of pores and throats, which can lead to the fragmentation of a single pore [49]. Additionally, since the surface regions of conventional fibrous electrodes are generally of higher porosity than the bulk electrode [49], the trimming of the surface regions of the XTM image prior to PN extraction, as explained in Chapter 3.1.2, is another possible reason for the absence of larger pores within the PN.

Because of the quadratic interrelationship between throat size and hydraulic conductance, see [Eq. 4.2-4.3], the absence of large pores (which are generally interconnected by larger throats) can have a significant effect on the transport of electrolyte through the PN. In order to investigate the transport of fluid through the porous electrode, in-plane and through-plane

permeability coefficients for the extracted network were estimated from the pressure field within the network.

In this work, the in-plane permeability is defined as the average permeability in the direction in line with the carbon fibers (the width and length of the electrode). The through-plane permeability is defined as the permeability perpendicular to the carbon fibers (the thickness of the electrode). The *anisotropy ratio* is the ratio between the in-plane permeability and the through-plane permeability. The anisotropy ratio is important, because it provides information about the alignment of pores and therefore the distribution of electrolyte within the network. When most pores are oriented in the flow direction (i.e. high anisotropy ratio), the flow in the other directions will become more tortuous. On the one hand, a high anisotropic ratio can have favorable effects, because it reduces the pressure drop over the length of the electrode. This results in lower pumping power requirements. On the other hand, a high anisotropic ratio can introduce a concentration gradient over the thickness of the electrode, which in turn can lead to the evolution of concentration overpotentials, and thus limited performance.

The through-plane permeability of Freudenberg H23 has not been experimentally determined, but was estimated by multiplying the ratio of through-plane air permeability (in L m<sup>-2</sup> s<sup>-1</sup>) of Freudenberg H23 and H2312 found in the Freudenberg technical datasheet [67], with the through-plane air permeability of Freudenberg H2315 I6 (the former name of H23I2) presented in Hasanpour *et al.* (in um<sup>2</sup>) [68].

The extracted in-plane and through-plane permeability coefficients are compared with the experimental in-plane and estimated through-plane permeability coefficients in Table 3.

	Pore network	Experimental data	Ref	Units
In-plane permeability	3.8	4.2	[67]	$\mu m^2$
Through-plane permeability	1.1	1.2*	[67-68]	$\mu m^2$
Anisotropy ratio	3.5	3.4	_	_

**Table 3** - In-plane and through permeability coefficients, and the anisotropy ratio of the pore network and experimental data, \* estimated from data found in [67] and [68].

The results presented in Table 3 show that there is a reasonable agreement between the experimental and simulated permeability coefficients. However, the values obtained from the PN are still 9.5% and 8.3% lower than the experimentally obtained in-plane and through-plane permeability coefficients, respectively. The found underestimation of the permeability coefficients matches with previous findings on the SNOW network extraction. Gostick attributed a similar error for the SNOW extraction of Toray paper to the trimming steps taken in image processing [49]. Due to the absence of part of the high porosity surface regions, the final permeability value for the simulated network is reduced. This result is in line with the absence of pores larger than 56  $\mu$ m found in the PN (Figure 15). The obtained mismatch in

permeability tensors indicates that the model will slightly overpredict the pressure drop induced by electrolyte transport through the Freudenberg PN. Importantly, the anisotropy ratio obtained from the extracted network does show close resemblance with the ratio obtained from experimental data, which is an indicator that alignment of pores within the extracted network concurs well with the alignment of the real fibrous electrode.

Another critical parameter for the extraction of the PN is the ECSA. The extracted PN has a total geometrical internal surface area of  $0.34 \text{ m}^2 \text{ g}^{-1}$ , whereas Forner-Cuenca *et al.* reported an experimentally determined active surface area of  $0.15 \pm 0.01 \text{ m}^2 \text{ g}^{-1}$  for the Freudenberg H23 electrode through analysis of the electrochemical double layer capacitance [10]. There are several possible explanation for the observed mismatch in the ECSA. First of all, the ECSA of the PN is estimated based on an approximated pore space within a simplified geometry, and can therefore lead to an over- or underestimation of the real ECSA. Secondly, assumptions made in the experimental determination of the Variation observed between both values [11], [69]. A correction factor of 0.44 can be utilized to scale the ECSA within the PN to the experimentally determined ECSA, however given the uncertainties introduced by the experimental setup, the obtained geometrical internal surface area can already be considered a reasonable approximation of the true ECSA.



**Figure 16 -** Current density versus voltage plots for three distinct RFB chemistries: (a) a  $V^{4+}/V^{5+}$ , (b) an Fe<sup>2+</sup>/Fe<sup>3+</sup> and (c) a TEMPO<sup>+</sup>/TEMPO<sup>+</sup> electrolyte at inlet velocities of 1.5, 5.0 and 20.0 cm s<sup>-1</sup>.

The response of the numerical model was compared with the electrochemical performance observed in the symmetric RFB experiments for the  $Fe^{2+}/Fe^{3+}$ .  $V^{4+}/V^{5+}$  and  $TEMPO^+/TEMPO^+$ redox couples, see Figure 16. To account for species depletion over the length of the electrode in the validation experiments, the numerical framework was modified to model the entire length of the laboratory electrode using a network-in-series approach. An explanation of this adjustment made in the model is presented together with a list of the chemistry specific model parameters in Appendix II. The developed model proved to be numerically robust, where the only fitting parameter used within the validation study was the electrical conductivity, to account for induced cell resistances (e.g. cable and contact resistances) within the symmetric flow cell experiments.

The tests reveal a substantial disagreement between the experimental data and the model prediction for the aqueous electrolytes, displayed in Figure 16a ( $V^{4+}/V^{5+}$ ) and Figure 16b (Fe<sup>2+</sup>/Fe<sup>3+</sup>), at lower electrolyte velocities (1.5 and 5.0 cm s<sup>-1</sup>). In both cases, a decreased laboratory performance is observed, which suggests that the model overidealizes the masstransfer limitations for aqueous electrolytes. Furthermore, the performance of the Fe<sup>2+</sup>/Fe<sup>3+</sup> electrolyte seems to agree well with the model prediction at a higher electrolyte velocity of 20 cm s<sup>-1</sup>, whereas the V<sup>4+</sup>/V<sup>5+</sup> electrolyte shows an additional discrepancy around 0.01-0.02 A cm<sup>-2</sup>.

Finally, the experimental results of the organic TEMPO $^+$  electrolyte, displayed in Figure 16c, agree well with the simulated performance, with a maximum deviation of 13% of the model in the mass-transfer limiting regime.

The observed overprediction of the electrochemical performance for the modeled aqueous electrolytes can be explained by the neglected effect of electrode wetting. The developed PNM holds the assumption that the considered electrode is fully wetted, which means that all the ECSA is equally accessible and that the fluid transport in the open space of the porous structure can be characterized as single-phase flow. However, it has been shown that in the real operation of RFBs unfavorable interactions between aqueous electrolytes and untreated carbon paper electrodes can result in gas holdup within the porous electrode [11], [70]. Especially at lower velocities, this may lead to *liquid channeling*, which in turn leads to incomplete electrode utilization and hence decreased cell performance. Due to their lower surface tension, organic electrolytes (i.e. acetonitrile based electrolytes) have been demonstrated to fully wetting untreated carbon electrodes [10], and it is hypothesized that for this reason the results of the TEMPO·/TEMPO<sup>+</sup> electrolyte aligns quite well with the simulated results, in contrast to the aqueous electrolytes.

Moreover, the sudden increments in voltage observed around 0.01-0.02 A cm<sup>-2</sup> within the  $V^{4+}/V^{5+}$  laboratory electrolyte seems to indicate that the description of a single-step reaction mechanism, described by the Butler-Volmer equation, is inadequate for the used  $V^{4+}/V^{5+}$  electrolyte. Previous research has demonstrated that the  $V^{4+}/V^{5+}$  reaction kinetics is highly sensitive to the atomic ratio of oxygen and carbon on the surface of the electrode [11], [71]. The sudden increments can indicate that the surface chemistry of the untreated Freudenberg H23 electrode inhibits facile charge transfer and thus causes a deviation from the ideal single-step reaction mechanism enforced within the developed algorithm.

The observed limitations suggest that a more detailed, multiphase model is required to study the mass and charge transfer within non-ideal porous electrodes; however, this is beyond the scope of the current study. It is hypothesized that the model is able to generate the correct response for the  $Fe^{2+}/Fe^{3+}$  and  $V^{4+}/V^{5+}$  redox couples at lower inlet velocities, if thermal or electrochemical electrode pretreatment steps are leveraged to improve the hydrophilicity of the electrode [11], [71], but further research is required.

The performed validation study stresses the importance of electrode surface chemistry control, which turns out to be imperative to obtain well-wetted electrodes. The findings of this study suggest that when full wettability and facile kinetics are realized, the presented model can be leveraged to predict electrode microstructure-performance relationships for optimized RFB operation.

### 6.2 Analysis of real electrode performance

The developed numerical model can be used to analyze the microstructural performance of existing RFB electrodes. Extracted performance indicators can be related to the unique property set obtained from the PNs and XTM images of the RFB electrodes. Key performance indicators

obtained from the numerical model include the pressure field, the (over)potential fields and the current field. Key property metrics that can be extracted from the PNs include the electrode dimensions, the PSD, the permeability coefficient, the anisotropic ratio, the porosity profile, the internal surface area, and the network connectivity. Additionally, macroscopic quantities can be extracted, such as the average ohmic, kinetic and activation overpotential within the electrode.

In this subsection, a case study is conducted to investigate the enhanced performance of a recently synthesized phase separated electrode (PSE), which presents a very distinct microstructure compared to traditional, fibrous electrodes. The results of these sections are presented as a comparison of the performance indicators and the property set of the novel PSE and the validated Freudenberg H23 electrode.

## 6.2.1 Phase separated electrode extraction

A network extraction of a binarized image of the PSE was performed, following the procedure given in Chapter 3.1.3. The used XTM image was provided by Mr. Charles Tai-Chieh Wan (MIT, Chemical Engineering), and was obtained with a scanning resolution of 0.386  $\mu$ m. In order to allow the extraction of a larger network, the computation cost was reduced by compression of the image resolution to 0.736  $\mu$ m prior to the network extraction procedure. The extracted pore network is presented in Figure 17.



**Figure 17** - Visualization of (a) a processed x-ray tomography image of the phase separated electrode, (b) the resulting extracted pore network and (c) an overlay of the x-ray tomography image with the extracted pore network ( $500x500x453 \ \mu m$ ).

The PSE contained a set of relatively small pores compared to the Freudenberg electrode, which required the use of a higher resolution XTM image. In order to run the SNOW algorithm on the available desktop computer with 32GB RAM memory, the electrode sample had to be reduced

to 0.5 mm wide, 0.5 mm long and 0.45 mm thick. A validation of the electrochemical performance of the extracted PSE with experimental data is given in Appendix III.

## 6.2.2 Comparison of electrode properties

The permeability, anisotropy ratio, internal surface area, porosity, the coordination number and the number average pore size are important electrode properties that influence the electrochemical performance. These quantities are shown in Table 4 for the Freudenberg H23 electrode and the PSE. As explained in Chapter 3.2, the coordination number is defined as the number of pores that a single pore is connected to within the network. Furthermore, because of the limited data on the true ECSAs of both electrodes (see Chapter 6.1.1), the intrinsic geometrical surface area, assigned by the SNOW algorithm, was used as the ECSA in this comparison (i.e. no correction factor was applied).

	Freudenberg H23	PSE	Units
In-plane permeability	3.8	0.85	μm²
Through-plane permeability	1.1	0.74	$\mu m^2$
Anisotropy ratio	3.5	1.1	_
Internal surface area	1622.0	1784.5	$\rm cm^2 \ cm^{-3}$
Porosity	74.3	80.1	%
Average coordination number	9.1	6.9	_
Number average pore size	14.1	6.3	μm

 Table 4 - Macroscopic properties of the Freudenberg H23 electrode and the phase separated electrode (PSE).

The macroscopic analysis listed in Table 4 reveals that the novel PSE has a 44% smaller average pore size than Freudenberg H23. Additionally, Table 4 reveals that the in-plane and throughplane permeability in the PSE are decreased by a factor 4.5 and 1.5, respectively, compared to the Freudenberg H23 electrode. This causes a decrease in the anisotropy ratio of PSE to 1.1. These results highlight that the pressure drop per unit of distance, predicted by the Hagen-Poiseuille equation [Eq. 4.2], will be larger for the PSE than for the Freudenberg H23 electrode. On the other hand, the observed lower anisotropy ratio in the PSE indicates that the electrolyte will have a less hindered flow path throughout the thickness of the PSE. Therefore, the flow can distribute more uniformly in all directions within the PSE than within the Freudenberg H23 electrode H23 electrode. Additionally, Table 4 shows that the extracted PSE has a higher porosity, a 10% increase in geometrical internal surface area and a 24% decrease in average connectivity compared to the Freudenberg H23 PN.

Although the macroscopic classification of the electrode structures is useful to outline the overall design of both electrodes, it does not describe the complete relationship between

network structure and electrochemical performance. Apart from the 10.0% increase in geometrical surface area, the increased performance of the PSE cannot be explained, and a characterization of the microstructure is required to gain a more detailed insight into the properties of both networks. Using the PNM framework, the PSD, the connectivity distribution, and the porosity gradient of both networks are obtained, see Figure 18-20.



**Figure 18 -** Pore size distribution of (a) the extracted Freudenberg H23 electrode and (b) the extracted PSE. The extracted Freudenberg H23 electrode PSD resembles a Gaussian distribution, with pores sizes varying between 6 and 48  $\mu m$ . The extracted PSE PSD shows a more random distribution, with pore sizes varying between 2-124  $\mu m$ .



**Figure 19** - Connectivity distribution (logarithmic) of (a) the extracted Freudenberg H23 electrode and (b) the extracted PSE. The extracted Freudenberg H23 electrode shows less dispersion in the obtained connectivity values than the PSE.



**Figure 20** - Porosity profiles of (a) the extracted Freudenberg H23 electrode and (b) the extracted PSE. The extracted Freudenberg H23 electrode shows a relatively uniform porosity profile in the length and width dimension, but an 11.1% variation in porosity over its thickness, with the more porous regions at the surface of the electrode. The extracted PSE shows larger variations in its porosity profile in the length and width dimension, and a 17.3% variation in porosity over its thickness, with the less porous regions at the surface of the electrode.

The microscopic characteristics of both networks highlight two key differences between the networks. First of all, although the average pore size and connectivity of the PSE is smaller than that of the Freudenberg H23 electrode, the distribution of both quantities is more dispersed within the PSE. Further analysis indicates that a set of the larger pores observed in the PSE PN are the same set of pores that show an extremely high connectivity within the network. It is hypthesized that these *macrovoids* play a central role in the distribution of fluid throughout the electrode. Secondly, whereas the porosity profile of the extracted Freudenberg H23 electrode shows high porous regions at both surfaces of the electrode, the porosity profile of the PSE shows a  $\pm$  30 µm region that is 17.3% lower in porosity at the top surface of the electrode. It is speculated that if this low porosity region translates to a region with higher ECSA, the ohmic losses due to electrolyte transport can be reduced by positioning this low porosity region on the membrane-side during flow cell operation, similar to the design principle behind zero-gap electrode cells [72].

#### 6.2.3 Comparison of electrode performance

The performance of the Freudenberg H23 electrode and the PSE was evaluated by performing simulations with the iron electrolyte at non-rate limiting conditions ( $v_{in}$ = 20 cm s<sup>-1</sup>) presented in Appendix II, which showed good agreement with experimental results (see Chapter 6.1.2).

The macroscopic electrochemical performance of electrodes can be analyzed using the polarization curve. The predicted polarization curves, divided in the different contributing overpotential terms, for both networks at non-rate limiting conditions are given in Figure 21.



**Figure 21 -** Symmetric flow cell polarization curves of (a) the Freudenberg H23 electrode and (b) the phase separated electrode with an inlet velocity of 20  $cm s^{-1}$  for the 0.1M Fe<sup>2+</sup> 0.1M Fe<sup>3+</sup> electrolyte.

The most striking result from the polarization curves is the significant difference in ohmic overpotential between both electrodes at a constant current density. Although the Freudenberg H23 electrode is thinner, the total ohmic overpotential within the anode and cathode is significantly higher than in the PSE. For instance, at a current density of 400 mA cm<sup>-2</sup>, the summation of the anodic and cathodic ohmic overpotential for the Freudenberg H23 electrode is 0.61V and for the PSE 0.34V. It should be noted that the absolute values for the ohmic overpotentials should be handled with care, as these values are heavily dependent on the (low) conductivity of the chosen 0.1M Fe<sup>2+</sup> and 0.1M Fe<sup>3+</sup> model electrolyte. However, the proportional difference in ohmic overpotential between both electrodes is remarkable, and can be used to explain differences in the performance of both electrodes.

In order to assess the electrochemical performance on the pore-scale level, the distribution of the pressure, current and overpotential terms within both electrodes are presented in the following subsections. Although the developed algorithm models the mass and charge transport in 3D (see Figure 6 and Figure 17), the distributions are presented as a set of 2D fields over the thickness and length of the electrode to improve the clarity of the results. The values within the pores in the width-direction were averaged in the case of the pressure and overpotential fields and summed in the case of the current field. All field graphs presented are obtained at a constant current density of 400 mA cm<sup>-2</sup> at an inlet velocity of 20 cm s<sup>-1</sup> within a 500  $\mu$ m long and wide section for both electrodes.

#### 6.2.3.1 Pressure drop

Pressure drop must be minimized to ensure energy efficient RFB performance. The PNM gives access to the pressure fields within both electrodes, see Figure 22.



**Figure 22** - Pressure field within a 500  $\mu m$  section in (a) the Freudenberg H23 electrode, and (b) the phase separated electrode, at an inlet flow velocity of 20 cm s<sup>-1</sup>. The cathodic compartment is displayed on the left side and the anodic compartment on the right side.

The pressure distribution in both electrodes is a direct result of the difference in the in-plane permeability of both electrodes. The computed pressure drop of 26.6 MPa m<sup>-1</sup> within the Freudenberg H23 electrode is significantly lower than the computed pressure drop of 84.3 MPa m<sup>-1</sup> within the PSE. It should be noted that the higher computed pressure drop for the PSE is not solely the result of the lower permeability of the PSE electrode, but is also partly explained by the choice to compare the electrodes at a constant inlet velocity, which is a measurement standard often seen in flow battery literature [10], [73]. As the PSE is thicker (453 µm) than the Freudenberg H23 electrode (184 µm), the total electrolyte flow rate entering the PSE is larger than that entering the Freudenberg H23 electrode. This increase in thickness will therefore contribute to the higher pressure drop requirement.

#### 6.2.3.2 Current generation

The current distribution within the PN gives insight into the formation of highly electrochemically active regions (hotspots) and less electrochemically active regions (coldspots). The current fields of both electrodes are presented in Figure 23.



**Figure 23** - Current field within a 500  $\mu m$  section in (a) the Freudenberg H23 electrode and (b) the phase separated electrode, at an inlet flow velocity of 20 cm s<sup>-1</sup> and a current density of 400 mA cm<sup>-2</sup>. The cathodic compartment is placed on the left side and the anodic compartment on the right side.

Figure 23 shows an intriguing difference between the current distribution of the two electrodes. The electrochemical activity is shown to be more dispersed throughout the Freudenberg H23 electrode than throughout the PSE. Remarkably, most of the electrochemical activity within the PSE seems to take place close to the membrane interface, affirming its similarity with zero-gap electrodes. It is hypothesized that the highly connected macrovoids in the phase separated electrode play a crucial role in sustaining the higher ionic flues near the membrane, by facilitating high (through-plane) conductive transport of active species.

In order to quantitively assess the current distribution within both electrodes, the current per unit of volume, the *internal current density*, is compared at a constant voltage of 0.5 V. Applying this metric allows for true comparison of both electrode performances for a given operating potential, irrespective of the electrode thickness. The internal current density as a function of the electrode thickness is given in Figure 24.



**Figure 24** - Current density as a function of the electrode thickness from the current collector  $(0 \ \mu m)$  to the membrane in (a) the Freudenberg H23 electrode and (b) the phase separated electrode, at an inlet flow velocity of 20 cm s<sup>-1</sup> and a current density of 400 mA cm<sup>-2</sup>.

Figure 24 reveals that in both electrodes 50% of the electrochemical work is originating from the 40-60 µm top layer closest to the membrane interface. However, the figure also highlights the absence of a high internal current density close to the membrane within the Freudenberg H23 electrode, but the presence of this high internal current density region within the PSE. This trend provides more evidence for the claim that the low porosity region at the surface of the PSE is extremely important for its electrochemical performance. In fact, the data indicates that the higher porosity region at the surface of conventional fibrous electrodes plays a detrimental role in the performance of current flow battery electrodes. This finding is compelling, because it concurs well with the intended application of the fibrous electrodes within fuel cells. In fuel cells, the fibrous electrodes serve as current collectors that promote transport of fluids from and towards a thin catalytic surface close to the membrane [74]. However, in a flow battery, the electrode has a dual function, as it provides both the active surface for the electrochemical reactions and the flow geometry for the transport of electrolyte. The obtained results points to the idea that adjustment of the electrode thickness and surface porosity will play an important role in future flow battery electrode design, which is further discussed in Chapter 6.2.4.

#### 6.2.3.3 Overpotential fields

The overpotential fields within both electrodes at a constant current density of 400 mA  $\rm cm^{-2}$  are shown in Figure 25. Figure 25a shows higher activation overpotentials within the Freudenberg H23 electrode to obtain the same current output. This is in line with the lower internal current densities within the Freudenberg electrode. Additionally, part of the higher activation overpotentials can be explained by the difference in thickness between the electrodes. As the Freudenberg electrode is thinner, the required internal current density for the same power output per external surface area unit is higher. Furthermore, the higher porosity region at the surface of Freudenberg H23 electrode leads to decreased performance close to the membrane and thus increased ionic transport pathways. Figure 25b highlights that the ohmic overpotential of the Freudenberg H23 electrode is significantly higher than in the PSE, as a result of the increased ionic pathways. Finally, Figure 25c reveals that the concentration overpotential is significant in the most electrochemically active regions for both electrodes, even at a flow rate of 20 cm s<sup>-1</sup>. Specifically, the concentration overpotential is more confined within the Freudenberg H23 electrode, which can be partly explained by the higher current per volume requirements and partly by the higher anisotropic ratio of the Freudenberg H23 electrode, which describes a higher obstruction to flow in the thickness direction.



**Figure 25** - Overpotential fields within a 500  $\mu m$  section in (a) the Freudenberg H23 electrode and (b) the phase separated electrode, at a inlet flow velocity of 20 cm s<sup>-1</sup> and a current density of 400  $mA \ cm^{-2}$ . The cathodic compartment is placed on the left side and the anodic compartment on the right side.

### 6.2.4 Conclusions of the case study

The conducted case study has given an account of the differences observed in performance between the Freudenberg H23 electrode and the novel PSE. The findings of this study suggest that the increased electrochemical performance of the PSE can be attributed to three distinct characteristics. First of all, the PSE is simply thicker than the Freudenberg H23 electrode and can therefore generate more current per external surface area unit. However, this increased performance comes at the expense of a higher pressure drop. More interestingly, the PSE contains a set of macrovoids that enable distribution of electrolyte throughout the entire thickness of the electrode, limiting the formation of concentration overpotentials within the most electrochemically active regions. Moreover, the PSE possesses a highly electrochemically active region at the surface of the electrode which is placed close to the membrane, whereas this region is more dispersed throughout the thickness of the electrode within the Freudenberg H23 electrode. This highly active surface region plays an important role in the increased performance of the PSE, by limiting the impact of ohmic overpotentials.

The findings of this theoretical case study point towards the idea of the adjustment of the electrode thickness and surface porosity for future flow battery electrode design. It is proposed to investigate electrodes with lower porosity surfaces facing the membrane, as they will potentially show increased performance over conventional flow battery electrodes. Additionally, it is proposed to investigate the performance of thinner (phase separated) electrodes of 30-60  $\mu$ m. Although these thin electrodes are expected to show lower external current and power densities, the reduced ohmic overpotentials within these electrodes can result in highly efficient electrodes. These type of electrodes can be especially useful in the field of organic flow batteries, where electrolyte conductivity is still significantly limiting the performance of the overall system [26], [75].

It should be noted that the current research is limited to the non-mass transfer limited case. The simulations are presented for a small section of the electrode and it is hypothesized that concentration polarization might form a bottleneck at larger electrode lengths or at lower flow velocities. It is anticipated that an optimization study can be carried out that can give more insight into the delicate balance of pressure drop and electrochemical performance for optimal industrial use of next-generation flow battery electrodes.

# Chapter 7 Artificial optimization of electrode structures

A challenging area in the field of artificial generation is the implementation of *machine learning* to obtain valuable design criteria for porous electrode structures. In this chapter, the OpenPNM geometry functions are integrated into a novel *genetic optimization* approach. The proposed optimization approach is envisioned to form the foundation of a novel method for the bottom-up design of the topology of next-generation RFB electrodes.

In this study, the application of a genetic algorithm (GA) for the optimization of the pore and throat size distribution within cubic PNMs is explained. The procedure of the proposed GA is explained in Chapter 7.1. The results of the study are presented in Chapter 7.2. Throughout the study, the total number of pores, pore positions, network connectivity and total ECSA are kept constant.

# 7.1 Genetic algorithm implementation

The GA is a mathematical optimization heuristic inspired by Charles Darwin's theory of evolution, and is the most prominent example of evolutionary computation [76]. The concept of the GA is based on the evolution of a population of candidate solutions to a given design case, using operators based on natural diversity and selection. The objective of the GA is to discover, emphasize and recombine good *building blocks* of solutions. The recombination of good building blocks can be leveraged to generate increasingly better sets of candidate solutions for the given design case.

Some preliminary work in the field of genetic optimization for PNM was carried out in 2009 by Jamshidi *et al.* [77]. In their work, Jamshidi *et al.* used a genetic optimization algorithm to generate a PN that approaches the static and hydraulic properties of a reservoir rock sample [77]. As far as known, the use of genetic optimization has never been considered within the field of battery electrode design and optimization.

Genetic optimization comprises of five operations: initialization, selection, crossover, mutation and termination. During initialization, a random set of candidate solutions, called the population, is generated. The population evolves in successive generations. In each generation, a fitness function is used to assess the adequacy of each candidate solution. Subsequently, the selection operator selects the most fit individuals in the population, called the parents, for reproduction. These selected parents produce new individuals, called offspring, through a crossover and mutation operation. In the crossover operation, the offspring networks inherit their structure by mixing the information from both parent networks, and in the mutation operation, stochastic changes are made in the offspring's structure to broaden the search domain [76]. The genetic optimization is stopped when a specified termination criterium is reached, which can be based either on the desired fitness or on the total number of generations. A schematic overview of the developed genetic algorithm for cubic networks is presented in Figure 26.



**Figure 26** – Schematic flowchart of the operations in the proposed genetic algorithm for cubic networks. Where  $A_{tot}$  represents the total internal surface area of the generated pores,  $Q_{in}$  the inlet flow rate,  $c_{in}$  the inlet concentration,  $\Delta P$  the pressure drop, I the obtained (total) current, and  $\xi$  the fitness.

# 7.1.1 Initialization

A population of cubic networks was initialized by the OpenPNM network generation functions. The topologies of the generated cubic networks were randomly generated, based on the geometric models of OpenPNM, as explained in Chapter 3.2. To allow for fair comparison between different PN geometry distributions, a network scaling step was taken. After initialization of each network, the total internal surface area was controlled by uniform scaling of the pore diameters, matching the total internal surface area to that of a reference network.

# 7.1.2 Selection

The selection procedure of the GA follows the principle of *survival of the fittest*. The fitness of the PNs was assessed by the developed electrochemical model (see Chapter 4). The model was

used to obtain the pressure drop, total current and cell voltage for each individual microstructure. The electrochemical power (P) was subsequently determined by [Eq. 7.1]

$$P = I \cdot E_{cell}$$
 [W] Equation 7.1

With *I* the generated total current [A] and  $E_{cell}$  the applied cell potential [V]. Additionally, the pumping power loss,  $\Xi$ , was determined by [Eq. 7.2]

$$\Xi = \frac{Q \cdot \Delta p}{\eta_p} \qquad [W] \qquad Equation 7.2$$

With Q the electrolyte flow rate  $[m^3 s^{-1}]$ ,  $\Delta P$  the pressure drop [Pa], and  $\eta_p$  the pumping energy efficiency.

The fitness,  $\xi$ , of the PN was assessed by combining the electrochemical performance with the hydraulic performance by [Eq. 7.3].

$$\xi = \frac{P - \Xi}{P}$$
 [-] Equation 7.3

The networks with the highest fitness value  $(\xi \rightarrow 1)$  were selected as parents for the mating pool.

#### 7.1.3 Crossover

The crossover operator randomly selects two parent networks from the mating pool to produce an offspring network. The pore size and throat size information of the produced offspring network was inherited from both parents via a two-step procedure. First, a locus  $(c_p)$  was randomly selected between the first index (0) and the final index  $(n_p)$  of the pore diameter array. The geometry information before the locus was obtained from the first parent, and the geometry information after the locus from the second parent.

#### 7.1.4 Mutation

The mutation operator allows for random changes to occur in the generated offspring networks, which is a critical operation for the exploration of the entire search domain. The degree of mutation was controlled by a mutation chance and a mutation range. The mutation chance describes the probability that a mutation occurs within each pore, whereas the mutation range  $(\sigma_M)$  describes the severity of the mutation. If a pore was selected for mutation, a random mutation value,  $c_M$ , was stochastically chosen between  $(1 - \sigma_M) \leq c_M \leq (1 + \sigma_M)$ . The mutated pore diameter  $(d_p^M)$  was subsequently determined from the old pore diameter  $(d_p^0)$  by [Eq 7.4].

$$d_p^M = c_M \cdot d_p^o \qquad [m] \qquad Equation 7.4$$

In order to maintain a fair comparison between the network geometries, the pore diameters of each newly generated offspring network were again uniformly scaled up or down, until the total internal surface area matches that of the specified reference network.

# 7.1.5 Termination

The genetic optimization was terminated when the maximum number of generations is reached.

# 7.1.6 Model parameters

An overview of the parameters used within the genetic optimization study is presented in Table 5. The network shape and spacing were selected to mimic the shape of a ~175  $\mu$ m thin and ~900  $\mu$ m long porous electrode. Additionally, the total internal surface area of the reference network was selected, based on the average internal surface area of 100 randomly generated porous networks. The pumping efficiency was assumed to be 0.9 [78]. Moreover, the population size, mutation factor, number of generations and the mutation chance have been arbitrarily chosen, and should be the subject of future research.

The potential of the genetic optimization algorithm was explored for the optimization of a kinetically sluggish ( $j_0 = 1.0 \text{ A cm}^{-2}$ ) and kinetically facile ( $j_0 = 100 \text{ A cm}^{-2}$ ) aqueous electrolyte.

The remaining properties of the simulated aqueous electrolyte and the cell operating conditions can be found in Appendix V. The python code can be found in the supplementary information S.2.

Parameter	Value	Units
Spacing	50	μm
Total surface area	142	$\rm cm^2 \ cm^{-3}$
Network shape	[18, 18, 4]	_
Connectivity	6	_
Population size	50	_
<b>Pumping efficiency</b>	0.9	_
Amount of offspring	50	_
Mutation factor	0.10	_
Mutation chance	0.05	_
<b>Crossover point</b>	$0 < c_p < n_p$	_

 Table 5 – Parameters used within the genetic optimization study.

#### **Amount of generations**

#### 300

#### 7.2 Genetic algorithm results

In this section, the GA's results for the kinetically sluggish ( $j_0 = 1.0 \text{ A cm}^{-2}$ ) and kinetically facile ( $j_0 = 100 \text{ A cm}^{-2}$ ) systems are presented. The analysis of the presented results is two-fold. First, because of the novelty of the GA approach, the suitability of the GA within the field of battery electrode design and optimization is established. Secondly, it is speculated that the modification in the kinetics will lead to variations in the balance of reactive surface area and electrolyte transport properties within the PN. Therefore, the effect of the modification in exchange current density on the pore and throat size distributions of the optimized networks is investigated.

In order to determine the viability of the GA, the progression of the fitness values of each generation's most fit individual was followed, see Figure 27. The required computational time was ~12.5 minutes per generation (~15 seconds per PN) using a single Intel® Core(TM) i7-8700K CPU.



**Figure 27** – Progression of network fitness value of each generation's most fit individual for (a) a kinetically sluggish ( $j_0 = 1.0 \ A \ cm^{-2}$ ) and (b) a kinetically facile ( $j_0 = 100 \ A \ cm^{-2}$ ) aqueous electrolyte.

The progression of the candidate solutions reveals that the performance of the most fit PNs improves with every generation. The most fit PN after 300 generations showed a 5% and 15% increase in the electrochemically output and a 46% and 47% decrease in the required pumping power compared to a completely random cubic network for the kinetically sluggish and kinetically facile system, respectively. This observation indicates that genetic optimization could indeed be a viable route for battery electrode optimization.

Although progression in the fitness is made with each generation cycle, the absolute performance of the generated cubic PNs is underwhelming. In all cases the electrochemical work is smaller than the required pumping power ( $\xi < 0$ ), which means that the amount of

pumping work required to pump the electrolyte through the PN is higher than the electrochemical work that can be retrieved from the system. However, the absolute performance is highly dependent on the chosen test case, and can readily be increased by variations in the electrolyte composition (active species concentration, density and viscosity), variations in the operating conditions (inlet velocity and cell voltage), and variations in the electrode properties (length, connectivity and total surface area). Finding the optimum balance of electrode properties and operating conditions for a specific industrial electrolyte has not been investigated, but is encouraged to be the subject for future research.

To investigate the increase in performance of the produced offspring networks, 2D snapshots of the network throats closest to the membrane in the cathodic compartment were obtained from the most fit individuals at three selected generations, see Figure 28.



**Figure 28** – 2D snapshots of the network throats in the plane closest to the membrane for the most fit individuals at generation 1, 150 and 300. Boundary pores have been excluded from the image.

The single most striking observation that emerges from Figure 28 is the alignment of larger throats in the 2D plane, interwoven with clusters of smaller throats. The alignment of throats is observed for both tested exchange current densities, and highlights the importance of pore positioning, as the contiguous placement of larger pores facilitates the formation of low resistance transport pathways within the PN. The formation of these low-resistance transport pathways shows similarities to the macrovoids present in the analyzed PSE (See Chapter 6).

Chapter 6.2 revealed that variations in the network properties over the thickness of the electrode play a critical role in the increased performance of the analyzed PSE. Therefore, aside from investigating the PSD of the most fit network structure after 300 generation, the PSDs for the four 2D pore planes that build up the thickness of this network were analyzed, see Figure 29.



**Figure 29** – (a) Pore size distributions of the most fit 3D networks and the individual pore layers that make up the thickness of the porous electrode, ordered from the layer closest to the membrane to the pore layer closest to the current collector. (b) Visual representation of the pore sizes within the most fit 3D networks, with electrolyte transport occurring from front to the back of the electrode.

Figure 29 shows that the overall PSD of the optimized network is relatively similar in the case of the kinetically sluggish and kinetically facile electrolyte, with an average pore size, of 27-29  $\mu$ m. However, differences are observed for the individual pore layers. In both cases, the PSD of pores closer to the current collector is shifter towards smaller pore sizes compared to the PSD of the pores closer to the membrane.

At first view, the presence of larger pores closer to the membrane seems to contradict the earlier findings of a highly active microporous layer presented in Chapter 6.2. However, care has to be taken when analyzing the results of the GA. In fact, the observed relocation of larger pores to the membrane side is a direct result of one of the limitations of the GA's methodology. The microporous layer presented in Chapter 6.2 is highly active, because the cluster of smaller pores significantly increases the ECSA close to the membrane surface. Since the number of pores and the pore position is set constant in the GA, the ECSA close to the membrane can only be increased by relocating larger pores closer to the membrane.

Figure 29 also reveals that the difference in the average pore size of the current collector pores and the membrane pores is less pronounced in the case of the kinetically sluggish system (25-27 µm and 27-29 µm) than in the case of the kinetically facile system (23-25 µm and 29-31 µm). A possible reason for this variation is the increased electrochemical performance of the kinetically facile system (j = 184 mA cm<sup>-2</sup>) compared to the kinetically sluggish system (j = 172 mA cm<sup>-2</sup>). Because of the increased electrochemical performance, the effect of ohmic resistance in the electrode becomes more pronounced, catalyzing the shift of ECSA towards the membrane surface. However, caution must be taken when this shift of ECSA is considered. The progression of the optimization (Figure 27) shows that the most fit individual after 300 generations has not yet yielded a stable fitness value over multiple generations for both analyzed current densities. It is possible that longer computation might shift the PSD even further for both analyzed cases, which will lead to similar shifts of the ECSA for both optimized network after more generations.

The presented result give rise to three key features of the presented GA in need of further development. Most importantly, the GA code should be extended to allow autonomous placement of pores within the PN. The mutation operator can be leveraged to stochastically place, migrate and delete pores within the considered design space. In this case, it might be more suitable to keep the total pore volume constant, instead of the total reactive surface area. This feature will allow the algorithm to decides between the placement of a cluster of smaller pores, favoring the total reactive surface area, or larger pores, favoring the electrolyte transport through the PN. Simultaneously, parallel computational techniques should be explored in order to curb the computational costs of the GA. In theory, the fitness of all PNs in a generation can be computed concurrently if multiple computational cores are leveraged. It is envisioned that the Dutch supercomputer, Cartesius, can be exploited to run a modified, parallelized GA code to drastically reduce the computational costs (to ~12.5 seconds). Finally, the chosen GA parameters in this study should be the subject over further investigation. It is hypothesized that modifications in the chosen population size, mutation chance and mutation factor can have a significant impact on both the exploration of the entire design domain, and on the progression of the fitness value with each generation cycle.

If all these features are considered, the developed GA has the potential to become a powerful new optimization technique for the bottom-up design of porous battery electrodes.

# **Chapter 8. Conclusions and outlook**

This thesis has expanded the fundamental understanding of the role of the electrode microstructure within redox flow battery performance, utilizing a novel numerical pore network modeling framework. The conclusions from the study and suggestions for future work are presented below.

- **Constructed a three-dimensional electrochemical model** A pore network modeling framework was developed based on a simplified microstructural geometry. The physics of mass transport, charge conservation, and electrochemical kinetics were implemented to simulate single-phase electrolyte flow through porous electrodes in redox flow batteries. The model is chemistry-agnostic and can be adapted to different chemistries of interested, provided that the electrolyte completely wets the electrode surface. In the future, I suggest implementation of the migration of active species within the mass transport equation, utilizing the full Nernst-Planck formulation.
- Validated the pore network extraction of a commercial fibrous electrode The SNOW algorithm was used to extract a pore network for the commercially available fibrous Freudenberg H23 electrode. The pore size distribution, permeability coefficients, and internal surface area of the extracted network showed good agreement with experimental data. Differences found in the microstructural properties were attributed to restrictions imposed by image processing and experimental limitations. The most important suggestion for future work is to focus on systematic correlation of the electrochemically active surface area within simplified geometries using roughness correlations.
- Compared the electrochemical response of the numerical model with symmetric flow cell experiments The response of the developed algorithm was compared with experimental data for three distinct redox couples with different kinetics  $(Fe^{2+}/Fe^{3+}, V^{4+}/V^{5+} \text{ and TEMPO} \cdot /TEMPO^+)$  within an untreated Freudenberg H23 PN. The computed performance of the TEMPO ·/TEMPO<sup>+</sup> redox couple aligned well with the experimental performance reported in Forner-Cuenca *et al.* [10]. Additionally, the  $Fe^{2+}/Fe^{3+}$  redox couple showed a matching response in the non-rate limiting regime  $(v_{in} = 20 \text{ cm s}^{-1})$ . Agreement of the model's results was lacking with the  $Fe^{2+}/Fe^{3+}$  experiments at rate limiting conditions and with all  $V^{4+}/V^{5+}$  experiments. Future studies should focus on repetition of the symmetric flow cell experiments for the two aqueous electrolytes, using thermally or electrochemically pre-treated electrodes to ensure full wettability of the electrode surface. Furthermore, rigorous calibration of the pump flow rate should be conducted, to ensure high accuracy of the used pumping flow rate.
- Analyzed the electrochemical performance of existing porous electrodes The electrochemical performance of a recently discovered non-fibrous phase separated electrode was compared with the performance of a fibrous Freudenberg H23 electrode. The increased performance of the phase separated electrode was attributed to the coexistence of (1) highly interconnected macrovoids fractions consisting of larger pores (> 50  $\mu$ m), permitting high convective flow, with (2) an electrochemically active surface regions consisting of smaller pores (~10  $\mu$ m), facilitating fast kinetics. The interplay of these microstructural characteristics was shown to limit the formation of

ohmic and concentration overpotentials. Future numerical research can aid the design of phase separated electrodes by analyzing the macrovoids to micropores ratio, and by exploring the ideal thickness of phase separated electrodes. Future experimental research should focus on the development of anisotropic electrodes, with enhanced electrochemical surface area at the membrane-side surface, and should investigate the performance and mechanical stability of thinner (30-60  $\mu$ m) porous electrodes to decrease ohmic overpotentials.

• Constructed a novel genetic optimization approach for the bottom-up design of battery electrodes – The first results of the developed genetic algorithm showed a promising increase in the overall performance of the optimized network, and the proposed methodology could serve as a base for future studies into optimized topologies for battery electrodes. Future studies should focus on expansion of the GA methodology by allowing autonomous pore placement within the design domain. Furthermore, parallel computational techniques should be explored, together with optimized genetic algorithm parameters, in order to curb the computational costs and maximize the efficiency of the optimization method.

More broadly, the developed numerical framework opens up the possibility for advanced numerical investigations into the interdependence of flow field, membrane and electrode designs to improve cell performance. Furthermore, to broaden the knowledge on the interplay between pore-scale characteristics and the solid structural design of the electrode, the numerical framework can be leveraged to analyze pore networks extracted from artificially generated electrodes, developed in material simulation software, such as GeoDict [79].

All in all, the developed methodology can play an important role in the bottom-up design of electrodes with optimal topology. Improved electrode designs will lead to lower pumping power requirements, increase power density, decrease overpotentials, and minimize material utilization within redox flow battery operation. Thus, it is hoped that the conducted research can contribute to the widespread deployment of large-scale, stationary energy storage systems and aid the transition towards a low-carbon energy infrastructure.

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Symbol	Description	Units
E <sup>0</sup>	Standard reduction potential	V
$S_p$	Random seed value	_
d	Diameter	m
$f_T$	Throat sizing factor	_
Α	Internal surface area	m <sup>2</sup>
S	Cross-sectional area	m <sup>2</sup>
L	Conduit length	m
j	Current density	$A m^{-2}$
η	Overpotential	V
S <sub>ox</sub>	Source term oxidized species	mol s <sup>-1</sup>
S <sub>red</sub>	Source term reduced species	mol s <sup>-1</sup>
$N_T$	Number of throats	_
ρ	Density	$kg m^{-3}$
u	Fluid velocity	$m s^{-1}$
$lpha_{ij}$	Hydraulic conductance	m Pa <sup>-1</sup> s <sup>-1</sup>
p	Pressure	Ра
$\mu$	Dynamic viscosity	Pa s
Q	Flow rate	$m^3 s^{-1}$
m	Mole flux	$mol m^{-2} s^{-1}$
Ι	Current	А
n	Number of electrons	_
F	Faradaic constant	C mol <sup>-1</sup>
С	Concentration	$mol m^{-3}$
Pe	Peclet number	_
D	Diffusion coefficient	$m^2 s^{-1}$
j <sub>0</sub>	Exchange current density	$A m^{-2}$
α	Transfer coefficient	-
R	Universal gas constant	$J K^{-1} mol^{-1}$
Т	Operating temperature	К
arphi	Potential	V
$k_m$	Mass transfer coefficient	m s <sup>-1</sup>
$I_{ij}$	Charge flux	$A m^{-2} s^{-1}$
$\sigma_l$	Electrical bulk conductivity	$\mathrm{S}\mathrm{m}^{-1}$
β	Electrical conductance	S m <sup>-2</sup>
R	Resistance	Ω
$\epsilon$	Error value	_
τ	Tolerance	—

ω	Damping factor	_
γ	Surface tension	$N m^{-1}$
heta	Contact angle	o
Р	Electrochemical power	W
Ξ	Pumping power	W
ξ	Fitness value	_
$c_p$	Cutting locus	_
$n_p$	Number of pores	_
$\sigma_M$	Mutation range	_
$C_M$	Mutation value	_

Sub- and superscripts	Description	
i	Within pore i	
ij	Transport from pore i to pore j	
in	Inlet	
out	Outlet	
m	Membrane or mutation	
OX	Oxidized form	
red	Reduced form	
BV	Butler-Volmer	
ref	Reference	
S	Solid	
e	Electrolyte	
a	Anode	
c	Cathode or concentration	
act	Activation	
ohm	Ohmic	
0	Initial	
Abbreviation	Description	
RFB	Redox flow battery	
MEA	Membrane electrode assembly	
VRFB	Vanadium redox flow battery	

2,2,6,6,-teramethyl-1-piperidinylxy Gas diffusion layer

X-Ray tomography

Pore network

Pore network modeling

Phase separated electrode

Pore size distribution

Electrochemically active surface area

TEMPO

GDL

XTM

PN PNM

PSE

PSD

ECSA

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# Appendix

# I. Explanation of the SNOW algorithm

The base of the SNOW algorithm is watershed segmentation. Watershed segmentation converts an image into a topographic map, where the brightness of each point represents its height [80]. Subsequently, the different peaks in the tomographic map are used to segment the image in different regions (pores and throats). In order to increase the accuracy and computational memory requirement of this algorithm, the SNOW algorithm pre-processes the image in four main steps.

In the first step, the distance transform of the pore space is obtained, which labels each voxel of the image with the distance to the nearest obstacle voxel (solid electrode fiber). A gaussian filter is applied in this step, in order to limit the amount of peaks that are unfairly labeled as local maxima, by smoothing the artificial rectangularity of the solid wall. The impact of the gaussian filter can be altered by changing the standard deviation of the applied convolution mask ( $\sigma$ ). The larger the standard deviation, the flatter the mask around each voxel. This results in a more pronounced blurring effect of the filter, where a sigma value between  $0.2 \le \sigma \le 0.4$  often yields a proper compromise between reducing the amount of spurious peaks and over smoothing the image [49].

Secondly, a maximum filter with a spherical structuring element of radius R is applied. This filter replaces the value of each voxel with the maximum value found within radius R. The appropriate value of the radius is dependent on the porosity of the network and the XTM resolution. When the radius is chosen too small, many artificial pores will be found. When the radius is too large, some small pores might be missed. A value of R = 5 voxels was proposed by Gostick *et al.*, however the effect of R and  $\sigma$  was not explored extensively for a variety of networks and the optimal value can change based on the network characteristics and scan rate [49]

As a third step, a dilating peak method is used to see if there are adjacent peaks with larger tomographic values. When these peaks are found, the corresponding point is deemed a saddle points and removed from the tomographic map.

Finally, nearby peaks that overlap each other are merged into one peak. The sets of markers created in these four steps are passed on to a marker-based watershed algorithm. This algorithm produces an image with integer values indicating which pore regions each voxel belongs to. From this value map, the pore connectivity can be extracted by region isolation, dilation and comparison of overlapping labels. Finally, pore and throat geometric properties (pore size, throat diameter and length and pore connectivity) are extracted by analyzing the voxel information in the distance map of each isolated pore [49]. It should be noted that quantities

such as internal surface area, in contrast to artificial generation of pore networks, are calculated based on the voxel information in the distance map. Therefore, the obtained surface area for each pore can be significantly larger than expected from the geometrical surface area obtained using the geometrical formula's for spheres and cylinders (see Chapter 3.2).

### **II.** Numerical implementation

#### II.(a) Linearization of the source term in the ohmic conduction algorithm

The charge transport equation is highly nonlinear, since the current generation term is exponentially dependent on the overpotential term. In the case that the considered active species has facile kinetics (i.e. a large exchange current density), the mass transport and charge transport equations are strongly coupled. In order to mitigate divergence, the charge transport source term was linearized around the current solution for the voltage field. The derivation of the charge transfer source term in the case of the cathodic compartment is shown in this appendix. A similar derivation was conducted for the anodic compartment.

The governing cathodic Butler-Volmer equation can be rewritten in the form presented in [Eq. A. 2.1].

$$I_{c} = \frac{c_{1}[\exp(m_{1}\eta_{c}) - \exp(-m_{2}\eta_{c})]}{1 + c_{2}\exp(m_{1}\eta_{c}) + c_{3}\exp(-m_{2}\eta_{c})}$$
[A] Equation A.2.1

With 
$$c_1 = j_0^c A_i \left(\frac{C_i^{ox}}{C_{ref}^{ox}}\right), c_2 = \frac{j_0^c}{Fk_m^{red}C_{ref}^{red}}, c_3 = \frac{j_0^c}{Fk_m^{ox}C_{ref}^{ox}}, m_1 = \frac{\alpha_a F}{RT} \text{ and } m_2 = \frac{\alpha_c F}{RT}.$$

The overpotential term can be rewritten into the electrolyte potential term using [Eq A. 2.2.]

$$\varphi_e = \varphi_s - \eta_c - E_{oc}$$
 [V] Equation A.2.2

Taking the derivative with respect to  $\varphi_e$  gives [Eq. A.2.3]

$$\frac{dI_c}{d\varphi_e} = \frac{\begin{pmatrix} c_1 \begin{pmatrix} -c_3 m_2 \exp(m1\eta_c - m_2\eta_c) - c_2 m_2 \exp(m1\eta_c - m_2\eta_c) \\ -c_2 m_1 \exp(m1\eta_c - m_2\eta_c) - c_3 m_1 \exp(m1\eta_c - m_2\eta_c) \\ -m_2 \exp((-m_2\eta_c) - m1 \exp(m_1\eta_c) \end{pmatrix} \end{pmatrix}}{(1 + c_2 \exp(m_1\eta_c) + c_3 \exp(-m_2\eta_c))^2}$$
[A V<sup>-1</sup>] Equation A.2.3

The source term,  $S_{red}$ , can subsequently be linearized by [Eq. A.2.4]

$$S_{red} = \frac{dI_c}{d\varphi_e} \cdot \varphi_e^n + I_c^{ad-dif} - \frac{dI_c}{d\varphi_e} \varphi_e^{n-1}$$
 [A] Equation A.2.4

With  $\varphi_e^n$  the new potential field to be solved for [V],  $I_c^{ad-dif}$  the current field obtained from the mass transport equation [A] and  $\varphi_e^{n-1}$  the previous estimation of the potential field [V].
## II.(b) Network-in-series model

To account for species depletion over the length of the electrode in the validation experiments, the numerical framework was modified to match the entire length of the laboratory electrode (1.7 cm) using a network-in-series approach. In this approach, multiple PNs are placed behind one another, and the concentration at the end of the first PN is considered as the inlet concentration of the next PN. In order to map the concentration between the boundary pores of the two networks, each network was manipulated to become a mirrored copy (mirrored in the flow dimension) of the previous network, see Figure II. 1. The mass and charge transport algorithms are solved independently for each anode-cathode couple in the series.

The code implementation of the network-in-series model can be found in the Supplementary Information.



**Figure II. 1** - Schematic visualization of a network-in-series model with 3 pore networks, separated by dashed lines. Convective transport takes place from left to right. Species consumption is depicted by the color in the network. Concentration overpotentials are larger at the end of the porous electrode.

## II.(c) Chemistry specific model parameters

Chemistry specific model parameters are listed in Table II. 1. The inlet velocity was varied between 1.5, 5.0 and 20.0 cm s<sup>-1</sup>, and the cell potential was varied from 0.0 to 1.0 V for the  $V^{4+}/V^{5+}$  and  $Fe^{2+}/Fe^{3+}$  electrolytes and from 0.0 to 0.6 V for the TEMPO<sup>+</sup>/TEMPO<sup>+</sup> electrolyte. The exchange current density of the  $V^{4+}/V^{5+}$  and the TEMPO<sup>+</sup>/TEMPO<sup>+</sup> electrolytes was fitted within the range of exchange current densities reported. Additionally, a calibration was applied by tuning the electrical conductivity of the electrolytes in order to account for non-idealities occurring within the experiments, such as contact resistances, that are not captured within the numerical model.

	$V^{4+}/V^{5+}$	Ref	$Fe^{2+}/Fe^{3+}$	Ref	TEMPO ·/TEMPO+	Ref	Units	Description
Туре	Aqueous	[-]	Aqueous	[-]	Organic	[-]	_	_
Electrolyte	$1.0 \text{ M} \text{H}_2\text{SO}_4$	[-]	1.0 M NaCl	[-]	1.0 M TEABF4	[-]	_	Used supporting electrolyte
ρι	992	Exp	1015	Exp	852	Exp	${\rm kg}{\rm m}^{-3}$	Electrolyte density
ρ <sub>s</sub>	480	Exp	480	Exp	480	Exp	${\rm kg}{\rm m}^{-3}$	Electrode density
R <sub>m</sub>	0.16	[81]	0.16	[81]	0.04	[81]	$\Omega \ cm^2$	Membrane areal resistance
μ	0.89	[-]	0.89	[-]	0.34	[-]	mPa s	Solvent viscosity
$\sigma_{l}$	4.5	Fit	34	Fit	72	Fit	mS cm <sup>-1</sup>	Bulk electrolyte conductivity
$\alpha_{c}$	0.42	[82]	0.5	[-]	0.5	[-]	_	Cathodic transfer coefficient
$\alpha_{a}$	0.42	[82]	0.5	[-]	0.5	[-]	_	Anodic transfer coefficient
D	$V^{4+} 2.11 \cdot 10^{-10}$	[83]	Fe <sup>2+</sup> 5.7 · 10 <sup>-10</sup>	[84]	TEMPO 1.3 · 10 <sup>-9</sup>	[85]	$m^2 s^{-1}$	Red/Ox diffusion coefficients in the
	$V^{5+} 2.11 \cdot 10^{-10}$		Fe <sup>3+</sup> 4.8 · 10 <sup>-10</sup>		TEMPO <sup>+</sup> 1.3 · 10 <sup>-9</sup>			electrolyte
jo	0.39	[11]	23.0	[84]	375	[85]	$\mathrm{A}\mathrm{m}^{-2}$	Exchange current density
<b>c</b> <sub>ref</sub>	100	[-]	100	[84]	250	[-]	$ m mol~m^{-3}$	Reference concentrations of active species
c <sub>in</sub>	100	[-]	100	[-]	250	[-]	mol m <sup>-3</sup>	Inlet concentrations of active species

**Table II. 1 -** List of chemistry specific model parameters used within this study. Exp: experimental measurement, Fit: fitted value

## III. Validation of the electrochemical performance of the phase separated electrode

Limited experimental data was available for the recently discovered phase separated electrode. The phase separated electrode was validated for a voltage range of 0.0 to 0.1 V at an inlet velocity of 20 cm s<sup>-1</sup>, see Figure III. 1.



**Figure III.** 1 – Polarization curve of the phase separated electrode using an iron electrolyte specified in Table III.1 at an inlet velocity of 20 cm s<sup>-1</sup>. The experimental datapoints correspond well with the simulated results. The simulated results are separated in the different contribution overpotentials in the right figure.

Figure III. 1 reveals a good agreement between the model response and the experimental data of the phase separated electrode at non-rate limiting conditions ( $v_{in} = 20 \text{ cm s}^{-1}$ ) Because of the improved wetting of the Because of the non-limiting conditions, it is hypothesized that the observed linear trend can be extrapolated for operation at voltages up to 1.0 V.

	Fe <sup>2+</sup> /Fe <sup>3+</sup>	Ref
Electrolyte	2.0M HCl	[-]
σ <sub>l</sub>	23.0	Fit
jo	23.0	[11]
<b>c</b> <sub>ref</sub>	100	[-]
c <sub>in</sub>	250	[-]

Table III. 1 – Properties of the iron electrolyte used in the symmetric flow battery experiments for the phase separatedelectrode. The unreported properties are assumed similar to the iron electrolyte displayed in Table II.1.

## IV. Genetic optimization parameters

The properties of the aqueous electrolyte, and the cell operating conditions that were used in the genetic optimization study are listed in Table V. 1.

Table V. 1 -	- Properties	of the aqueous	electrolyte a	and the cell	operating	conditions	used in	the g	enetic
optimization	study.								

Parameter	Value	Unit
E <sub>cell</sub>	0.5	V
v <sub>in</sub>	20	cm s <sup>-1</sup>
c <sub>in</sub>	250	$mol m^{-3}$
Cref	250	mol m <sup>-3</sup>
$\alpha_{c}$	0.5	_
α <sub>a</sub>	0.5	_
D	1.3.10-9	$m^2 s^{-1}$
R <sub>m</sub>	0.16	$\Omega \ cm^{-2}$
$\rho_l$	1000	$kg m^{-3}$
μ	8.9 ·10 <sup>-4</sup>	Pa s
$\sigma_l$	10	$S m^{-1}$

PO Box 513 5600 MB Eindhoven The Netherlands tue.nl

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