Starting from the bottom: Coupling a genetic algorithm and pore network model for porous electrode design

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Graphical abstract:
Abstract

The microstructure of porous electrodes determines multiple performance-defining properties, such as the available reactive surface area, mass transfer rates, hydraulic resistance, and electronic conductivity. Thus, optimizing the electrode architecture is a powerful approach to enhance the performance and cost-competitiveness of electrochemical technologies. To this goal, the deployment of computational modeling has improved the fundamental understanding of reactive transport in porous electrodes; however, to date, it has mostly been used to simulate existing sets of materials. To expand our current arsenal of materials, we need to build computational frameworks that are predictive and can explore a large geometrical design space while being physically robust. Here, we present a novel approach for the optimization of porous electrode microstructure from the bottom-up that couples a genetic algorithm with a chemistry-agnostic electrochemical pore network model. In this first demonstration, we focus on optimizing redox flow battery electrodes. The genetic algorithm manipulates the pore and throat size distributions of an artificially generated microstructure with fixed pore positions by selecting the best-performing networks, based on the hydraulic and electrochemical performance computed by the model. For the studied VO$_2^+$/VO$_2$ electrolyte, we find an increase in the fitness of 75% compared to the initial configuration. The algorithm improves the fluid distribution by the formation of a bimodal pore size distribution containing preferential longitudinal flow pathways, resulting in a decrease of 73% for the required pumping power. Furthermore, the optimization yielded an increase in surface area resulting in an electrochemical performance improvement of 42%. Our results show the potential of using genetic algorithms combined with pore network models to optimize porous electrode microstructures for a wide range of electrolyte composition and operation conditions.

Keywords: genetic algorithm, pore network model, redox flow batteries, porous electrode microstructure, pore-scale modeling, electrochemical storage
1. Introduction

Porous electrodes are performance-defining components in next-generation electrochemical technologies, such as batteries, fuel cells, and electrolyzers, where they are responsible for multiple key functions affecting the thermodynamics, kinetics, and transport (1–7). In redox flow batteries (RFBs), which are the focus of this study, the porous electrode provides the surface area for electrochemical reactions, facilitates mass, charge, and heat transport, and dictates the hydraulic requirements of the reactor (8–11). Thus, the electrode microstructure determines the overall performance, durability, and operating cost of the system. However, the current arsenal of materials is limited to porous carbon fiber-based mats (e.g., papers, cloths, and felts) which have not been tailored to sustain liquid-phase electrochemistry. An effective means to improve the cost-competitiveness of RFBs is by designing tailored electrodes to satisfy the stringent cost and performance requirements of emerging electrochemical systems (12–14). However, the design of porous electrodes in convection-enhanced electrochemical systems is particularly challenging as multiple contradictory requirements (e.g., facile mass transport, high electrochemical surface area, and low pumping demands) must be satisfied simultaneously, motivating the development of advanced optimization strategies.

Porous electrode engineering has received notable attention in the past decade. Traditionally, the field was dominated by empirical design, where considerable research has been conducted on understanding the role of the electrode microstructure (5, 11, 15), increasing the active surface area and heteroatom content (16–18), and improving the flow distribution within porous electrodes (19–21). However, empirical design of electrodes is expensive, time- and labor-intensive, and limited to a narrow design space determined by existing manufacturing routes (12). To support experimental design, multiscale modeling of porous electrodes has been deployed in recent years in a variety of forms. For example, macrohomogenous models were used to understand the influence of cell-averaged properties on the overall stack performance (10, 22, 23). Alternatively, geometrically resolved models, such as the lattice Boltzmann method and computational fluid dynamic simulations, have been used to resolve reactive transport phenomena within porous electrode microstructures (24–26), which is needed to design advanced electrode architectures (26–31). And, while these computational efforts have improved our understanding of reactive transport phenomena in porous electrodes, most of these studies have focused on modeling existing sets of materials but have not yet been deployed to realize the bottom-up design of electrodes.
To make these computational tools truly predictive and accelerate materials discovery, the community will need to build frameworks that enable the self-driven exploration of a broad geometrical design space. A promising approach to fill this research gap is to couple pore-scale simulations with machine learning and heuristic algorithms (32–35). Facilitated by the rapid rise in computational power, the application of these methods has become an instrumental tool to optimize the topology of products for a wide-range of applications (e.g., aerospace, antennas, and heat exchangers), spurring interest to apply these methods for the optimization of porous electrode structures for electrochemical devices (32). The genetic algorithm (GA) is a widely used method that enables the heuristic optimization of a given design space and is based on the evolution of a population of candidate solutions, using operators based on diversity and selection (36). The objective of the GA is to discover, emphasize, and recombine good building blocks of solutions, which can be leveraged to generate increasingly better sets of candidate solutions for the given design case.

The integration of optimization tools within electrochemical numerical frameworks has been recently deployed to support the numerical identification of fitting parameters and find optimal operational conditions (33, 37–39), as well as to support the design of cell components (40–43). Recently, Choi et al. utilized a GA in combination with a two-dimensional model of an all-vanadium flow battery to identify the fluid parameters using a fitness function involving the mean square error of the voltage between the experimental and simulated data. The simulated capacity-voltage curves showed good agreement with the experimentally obtained data, bringing the mean relative error between the model and experimental results down to ≤1.9% (e.g., from 6.7% to 0.62% for 80 mA cm⁻² and 60 mL min⁻¹) (37). Moreover, Tenny et al. leveraged a GA with a neural network to identify optimal electrode properties (e.g., thickness, porosity, kinetic rate constant), using a macrohomogenous model, to improve the power density in RFBs (33). Further, Roy et al. showed the potential of applying topology optimization to design porous electrodes for different electrochemical application, namely a flow battery and a supercapacitor. The authors optimized the current distribution which resulted in the formation of a porous material where the computed designs featured improved performance with respect to the baseline monolithic electrode (44). Finally, Wan et al. developed a coupled machine learning and GA data-driven approach to design porous electrodes for RFBs, which resulted in electrodes with larger specific surface area and high hydraulic permeability, but their design space was limited to fibrous structures (40). Inspired by these previous efforts, we aim to develop a computational framework that affords large
versatility of design, robust physical representativeness, and maintains a low computational cost.

To couple pore-scale simulations with genetic algorithms and optimize the electrode structure from the bottom-up, the modeling framework must resolve the relationship between the electrode microstructure and the battery performance in a computationally inexpensive manner. Geometrically-detailed modeling approaches (e.g., lattice Boltzmann method, computational fluid dynamics) are difficult to couple with heuristic algorithms because of their high computational demands. On the contrary, macrohomogenous models are computationally inexpensive, but are built on volume-averaged grids and thus fail to capture the electrode microstructure. Motivated by this challenge, here we explore the combination of pore network modeling (PNM), which is pore-scale but computationally light, with a GA for microstructural optimization. GAs utilizing PNMs have been used in other research fields, including the field of petroleum recovery. One example is the work of Jamshidi et al., who leveraged a genetic algorithm to extract a pore network with the static and hydraulic properties of a reservoir rock sample. However, to the best of our knowledge, the use of genetic optimization coupled with PNMs has not yet been explored in the context of electrode microstructure design and optimization.

Here, we couple for the first time a pore network model with a genetic algorithm to optimize the three-dimensional microstructure of flow battery electrodes from the bottom up. The model builds upon a previously developed PNM electrochemical framework, validated for different electrode microstructures and redox electrolytes. In this first demonstration, the GA is used to manipulate the pore and throat size distribution and thus optimize the electrode microstructure for a given set of RFB operating conditions and chemistry, assuming perfect wetting of the generated electrode structure. The model is driven by the evaluation of a fitness function that minimizes hydraulic power requirements and maximizes electrochemical power output. First, we describe the modeling framework, including the coupling of the iterative electrochemical PNM with the GA. Second, we demonstrate the methodology for a VO\(^{2+}/\text{VO}_2^+\) redox couple in a single electrolyte configuration building on artificially generated microstructures with fixed pore positions. Third, we evaluate the sensitivity of the microstructural evolutions towards variations in the electrolyte type and the flow cell operating conditions. Finally, we correlate the resulting performance with the microstructural evolutions originating from the optimization algorithm. Although the focus in this paper is on the optimization of porous electrodes for flow batteries, this computational platform can be tailored
to design porous materials for a wider variety of convection-enhanced electrochemical technologies such as hydrogen fuel cells, water electrolysis, and electrochemical CO$_2$ reduction electrolyzers.
2. Model development

The concept of a 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. Recombination of good building blocks are leveraged to generate increasingly better sets of candidate solutions for the given design case. In this study, we utilized the geometrical functions available within OpenPNM, an open-source framework for pore network simulations (50), to generate cubic networks with a random distribution of pore sizes and fixed pore positions. The hydraulic and electrochemical performances of the generated cubic network structures were simulated by a model that solves for coupled electrochemical kinetics, mass transport, and momentum transport, described in detail in our previous work (27). Subsequently, a GA is applied to evaluate the performance of each individual network based on a fitness function to combine the best-performing solutions and ultimately find optimal microstructural design characteristics (e.g., the pore size distribution) for a specific system and operating conditions. For reference, the required computational time on a single Intel® Core™ i7-8700K CPU was ~48 hours for the evolution of 1000 generations for the reference system, using 50 individuals per generation and 10 parent networks (~3 seconds per network). It should be noted that the performance and fitness of all networks in a single generation could be computed concurrently if multiple computational cores were used.

2.1 Network generation

Cubic lattices were generated with the Cubic class algorithm in the OpenPNM Network module. This algorithm takes a network shape, spacing, and connectivity as inputs and produces a network with the pore and throat coordinates as an output. The shape of the cubic lattices determines the number of generated pores in each dimension, the spacing captures the center-to-center distance of adjacent pores in the cubic lattice, and the connectivity displays the total number of throat connections that a single pore within the cubic lattice embodies. The topological properties were subsequently attributed to the network’s pores and throats using the OpenPNM Geometry module. Geometrical formulas of spheres and cylinders were employed together with a random seed value to create randomly distributed topologies. The most important topological properties are displayed in Figure 1.
Figure 1: (a) Schematic overview of a single electrolyte vanadium redox flow battery. (b) A magnification of the porous electrode microstructure and the pore-throat conduit listing the most important topological properties, namely the pore diameter \(d_p\), throat diameter \(d_t\), throat cross-sectional area \(S_t\), throat length \(L_t\), and pore internal surface area \(A_p\).

The pore diameter was assigned by a random process that depends on the maximum pore diameter and a modification factor, called the seed \(S_p\). This seed value is randomly generated for each pore and is confined between two boundary points, where in this work the boundary point values were arbitrarily chosen as 0.2 and 0.7 for the pore diameter, based on the standard option in the OpenPNM StickAndBall geometry class. 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, according to

\[ d_p = S_p \cdot d_{p,max} \] (1)

To prevent the formation of connecting throats with a diameter larger than that of the smallest neighboring pore, each throat diameter was based on the smallest pore size of the two pores that the throat is connected to. This minimum pore size was subsequently multiplied by a throat factor of 0.8 to obtain the diameter of the throat \(d_T\). The throat factor is based on the ratio of the pore and throat diameters used by Sadeghi et al. to reasonably represent the porous structure of a commercial SGL 25AA electrode, which is a representative carbon fiber-based electrode used in flow batteries (29).

\[ d_T = 0.8 \cdot \min (d_{p,1}, d_{p,2}) \] (2)

The throat cross-sectional area \(S_T\) was determined from the throat diameter assuming that each throat is a perfect cylinder (equation (3)), whereas the throat internal surface area \(A_T\) was calculated as the area of a cylinder mantel (equation (4)).

\[ S_T = \frac{\pi}{4} \cdot d_T^2 \] (3)

\[ A_T = \pi \cdot d_T \cdot L_T \] (4)
where $L_T$ is the throat length, calculated as the length between two throat end points. The throat conduit length on the other hand is defined as the summed length of two half-pores and the connected throat, and was used for calculating the hydraulic transport through the network. In cubic networks, the summed conduit length is equal to the network spacing.

The pore internal surface area ($A_p$) was calculated by subtracting the throat cross-sectional area of all neighboring throats of the pore, with $N_T$ being the number of neighboring throats, from the surface area of a perfect sphere with diameter $d_p$.

\[
A_p = \pi \cdot d_p^2 - \sum_{j=1}^{N_T} S_T
\]

Equation (5) is an approximation of the pore internal surface area as the actual curvature of the intersection between the pore and throat was not taken into account. Note that the pore internal surface area is different from the pore cross-sectional area and that the pore and throat volumes were calculated using geometrical formulas of spheres and cylinders.

2.2 Iterative electrochemical algorithm

In this work, we elected to use symmetric flow cells with a single electrolyte configuration to ensure a constant state-of-charge of 50%. This configuration enables studying electrode performance and overpotentials in isolation without competitive phenomena such as species crossover through the membrane or distinct redox kinetics in each half-cell (10, 12). Thus, the modeled domain consists of two symmetric, mirrored porous electrodes in co-flow operation mode (Figure 1). Therefore, the open circuit voltage is 0 V, and the opposite redox reactions take place in each of the half cells (i.e., the oxidation reaction in the anodic compartment and the reduction reaction in the cathodic compartment). In addition, a flow-through flow field design was employed since it provides near-unidirectional velocity distribution at the inlet channel, thereby simplifying the boundary conditions (51).

The electrochemical PNM framework described in our previous work solves the fluid transport and successively the coupled mass and charge transport within the anodic and cathodic compartments using an iterative algorithm (27). The model equations and boundary conditions can be found in Section A1 in the Appendix. The iterative algorithm was integrated in the GA as visualized in Figure 2. First, the fluid transport was solved to obtain the pressure field described by the Navier-Stokes equation, from which the velocity is back-calculated using the Hagen-Poiseuille equation. Because of the assumption of dilute electrolyte, the fluid transport can be solved independently from the mass and charge transport of individual species (29). The
pressure field was subsequently fed in the iterative algorithm to solve the coupled mass and charge transport within the electrode using two nonlinear systems of equations: the advection-diffusion-reaction and the conservation of charge. The two nonlinear systems of equations are coupled by the Butler-Volmer equation to obtain the species concentration and potential field. The coupling of both half cells was done by treating the membrane as a macro continuum entity, allowing the protons to be transported between both half cells. Thus, only the overall macroscopic ionic resistance of the membrane (Ohm’s law) was considered, which coupled the charge transport within one half cell with the electrolyte potential at the membrane boundary in the other half cell (29).

The electrochemical model was solved for an arbitrarily applied potential with an initial guess for the overpotential and concentration. The initial guess of the overpotential was set to zero for the first network in the first generation, while the overpotential guess for the next networks was based on the previously modeled network results to speed up the iterative algorithm. The initial guess of the concentration was set to the inlet concentration for all modeled networks (100 mol m\(^{-3}\) for both vanadyl ion, VO\(^{2+}\), and pervanadyl ion, VO\(_2^+\), species).

The numerical convergence was achieved when the specified relative and absolute tolerances were met, defined by the total current generated or consumed, and bound by a maximum number of iterations. To counteract the divergence of the solution caused by the highly nonlinear nature of the system, under-relaxation was used for the concentration and potential fields using a constant relaxation factor (Table 1). In addition, a linearization of the charge transport source term was considered as explained in detail in our previous work (27).

### 2.3 Genetic operations

Genetic optimization comprises five operations: initialization, selection, crossover, mutation, and termination. During initialization, a random set of candidate solutions is generated, called the population. This population evolves in successive generations where in each generation a fitness function is used to assess the adequacy of each candidate solution. Subsequently, the selection operator selects the fittest individuals in the population (i.e., the parents) for reproduction. These selected parents produce new individuals (i.e., the 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 (52). The genetic optimization is stopped when a specified termination criterion is reached,
which can be based either on the desired fitness or the total number of generations. A schematic overview of the developed framework is presented in Figure 2, followed by a detailed description of each operation in the algorithm.

Figure 2: Schematic flowchart of the operations in the proposed genetic algorithm together with illustrations showing the changes in the network structure after each operation, where different colored squares represent different building blocks.

2.3.1 Initialization
The topologies of 50 cubic networks were randomly generated using the OpenPNM geometry functions. In this work, the optimization of a relatively small, cubic three-dimensional electrode structure (676 pores) was considered, see Table 1. Drawing inspiration from commercially available electrodes (e.g., Freudenberg H23 and SGL 25AA), we chose an electrode thickness of 220 μm and a pore size range of 2-38 μm (11). The electrode area was set to 580 x 580 μm². The boundary pores and throats required for the implementation of the transport algorithms were generated at each surface.

To allow for a meaningful comparison between the pore networks generated in different generations, a network scaling step was taken after initialization. In this step, the total pore volume of each generated network was matched to the pore volume of a reference network by
uniformly scaling of all pore diameters. Thus, maintaining a constant network porosity during the evolution and simultaneously providing evolutionary freedom to optimize for the total pore surface area. The reference network consists of pores with a diameter of 20 μm and throats with a diameter of 15.6 μm. The pore-to-throat diameter ratio was chosen to represent commercial porous electrodes using the data reported by Sadeghi et al. (29).

**Table 1**: Parameters used for the genetic optimization study.

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<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Spacing</td>
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<td>Porosity</td>
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<td>Network shape</td>
<td>[13, 13, 4]</td>
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<tr>
<td>Network dimensions</td>
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<td>Connectivity</td>
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<td>Number of generations</td>
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<td>Number of offspring</td>
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<td>Absolute tolerance</td>
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<td>Maximum iterations</td>
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</tr>
<tr>
<td>Relaxation factor</td>
<td>0.1</td>
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### 2.3.2 Parent selection

The selection procedure of the GA follows the principle of the survival of the fittest. The fitness of the networks was extracted from the developed electrochemical model which resolves the total generated current and pressure drop for each microstructure. The thermodynamic maximum electrochemical power ($P_{max}$) was determined by

$$P_{max} = I \cdot E_{cell}$$

where $I$ is the total current, and $E_{cell}$ the open circuit cell potential of a full-vanadium battery system, which is assumed to be to 1.26 V (53). As we are fixing the overpotential ($E_{losses}$), we aim to increase the maximum electrochemical power by reaching higher total currents at a fixed overpotential. The electrochemical power loss ($P_{el}$), capturing the overpotentials in the cell, was defined as

$$P_{el} = I \cdot E_{losses}$$

where $E_{losses}$ is the combined overpotential (activation, ohmic, mass transfer) present in the single electrolyte cell. For the reference system, the overpotential losses were arbitrarily set to 0.5 V, which corresponds to 40% of electrochemical losses as heat during cell discharge.
Additionally, the pumping power \( (P_{pump}) \) required to pump the electrolyte through the electrode was determined by

\[
P_{pump} = \frac{Q \cdot \Delta P}{\eta_p}
\]

where \( Q \) is the electrolyte flow rate (with an applied velocity of 1.5 cm\(^{-1}\) for the reference system), \( \Delta P \) the pressure drop, and \( \eta_p \) the pumping energy efficiency, which was assumed to be 0.9 (54). The fitness \( (\xi) \) of the pore network was subsequently calculated by comparing the electrochemically generated power to the summation of the maximum electrochemically generated power and pumping power

\[
\xi = \frac{P_{max} - P_{el}}{P_{max} + P_{pump}}
\]

It must be noted that, in this work, we are optimizing the electrode structure for one specific redox couple \( (\text{VO}^{2+}/\text{VO}^{2+}) \) in a symmetric cell system. Therefore, we assume for this theoretical exercise that the overpotential resulting from the other redox pair (the \( \text{V}^{2+}/\text{V}^{3+} \) redox pair in a full-vanadium battery) is identical to be able to subtract \( P_{el} \) from \( P_{max} \).

The maximum fitness is achieved when the pumping losses are zero, even though the overpotential losses are not (fully) optimized. The maximum fitness value is thus dependent on the fixed overpotential losses (0.5 V for the reference system). Finally, the ten networks with the highest fitness value \( (\xi \rightarrow 0.603 \) for the reference system) were selected as parents for the mating pool.

### 2.3.3 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 random pore number was selected between the first \( (0) \) and the final index \( (n_p) \) of the pore diameter array. Subsequently, the geometry information (e.g., pore and throat diameters) before this pore number was obtained from the first parent, and the geometry information after the locus was inherited from the second parent, resulting in the offspring network.
2.3.4 Mutation

The mutation operator allows for random pore diameter changes in the generated offspring networks, which is critical for the exploration of the entire search domain. The degree of mutation was controlled by the mutation chance and the mutation range. The mutation chance describes the probability that a mutation occurs within each pore and 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

$$d_p^M = c_M \cdot d_p^0$$  \hspace{1cm} (10)

To maintain a constant network porosity and thus a fair comparison between the network geometries in between different generations, the pore diameters of each newly generated offspring network were uniformly scaled up or down until the total pore volume matches that of the specified reference network.

2.3.5 Termination

The genetic optimization was terminated when the maximum number of generations (1000) was reached.

2.4 Operating parameters

In this study, we apply the numerical framework to optimize the electrode microstructure for the all-vanadium flow battery since this is the state-of-the-art system (55). Specifically, here we considered a symmetric cell design utilizing the VO$_2^+/VO_2^+$ redox couple. This redox couple is kinetically-sluggish (10, 56), offering an interesting platform for optimizing the balance between electrochemical performance (i.e., mass transfer and available surface area) and parasitic pumping losses (57). The physicochemical properties of the electrolyte and main operating conditions used as input in the electrochemical algorithm are shown in Table 2. These parameters were obtained from literature or have been experimentally determined as described in Section A2. To satisfy the dilute electrolyte assumption (i.e., migration is not considered in the iterative algorithm (58)), we operate the RFB cell at a relatively low vanadyl ion, VO$_2^+$, and pervanadyl ion, VO$_2^+$, with inlet concentrations of 100 mol m$^{-3}$ per species in an excess supporting electrolyte solution of 1000 mol m$^{-3}$ H$_2$SO$_4$. 
Table 2: Electrolyte and electro-kinetic properties for the VO$_2^+/VO_2^+$ vanadium chemistry.

<table>
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<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
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<tr>
<td>Density of the electrolyte in both half-cells</td>
<td>$\rho_l$</td>
<td>992 kg m$^{-3}$</td>
</tr>
<tr>
<td>Viscosity of the electrolyte in both half-cells</td>
<td>$\mu$</td>
<td>8.9 x 10$^{-4}$ Pa s</td>
</tr>
<tr>
<td>VO$_2^+$ diffusion coefficient in the electrode (59)</td>
<td>$D_{VO_2^+}$</td>
<td>2.11 x 10$^{-10}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>VO$_2^+$ diffusion coefficient in the electrode (59)</td>
<td>$D_{VO_2^{2+}}$</td>
<td>2.11 x 10$^{-10}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Inlet VO$_2^+$ concentration in both half-cells</td>
<td>$c_{VO_2^{2+},in}$</td>
<td>100 mol m$^{-3}$</td>
</tr>
<tr>
<td>Inlet VO$_2^+$ concentration in both half-cells</td>
<td>$c_{VO_2^{2+},in}$</td>
<td>100 mol m$^{-3}$</td>
</tr>
<tr>
<td>Supporting electrolyte concentration</td>
<td></td>
<td>1.0 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>Bulk electrolyte conductivity</td>
<td>$\sigma_l$</td>
<td>28 S m$^{-1}$</td>
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<tr>
<td>Cathodic transfer coefficient (19)</td>
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<tr>
<td>Anodic transfer coefficient (19)</td>
<td>$\alpha_a$</td>
<td>0.42</td>
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<tr>
<td>Reference concentrations of active species</td>
<td>$c_{ref}$</td>
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<td>Exchange current density (19)</td>
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<td>Electrolyte velocity</td>
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<td>Overpotential</td>
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3. Results and discussion

3.1 Proof of concept

We first explore the application of the developed methodology to a model cubic architecture for the VO$^{2+}$/VO$_2^+$ electrolyte. In this step, we study the evolution of the fitness and the resulting electrode microstructure operating at the conditions listed in Table 2. The progression of the fitness value throughout 1000 generations of the best performing microstructure in each generation is presented in Figure 3a, showing the remarkable improvement in network fitness of 75% (0.27 to 0.48, with a maximum achievable fitness of 0.603). This improvement is the result of a decrease in the required pumping power of 73% and an increase in the electrical performance of 42% (Figure 3b), which shows the potential of a coupled GA and PNM framework as a method to discover improved electrode morphologies.

For the studied system, the algorithm shows a higher tendency to optimize the pumping power than the electrochemical performance. The favored optimization of the pumping power is likely caused by three factors. First of all, the electrode microstructure is simulated using a flow-through configuration with a relatively low porosity of 54% compared to the typical porosity values (66-90%) in commercial electrodes (11, 15, 27, 60), which increases the pressure drop significantly compared to commercial electrodes with flow-by configurations. Secondly, the pore coordinates, number of pores, and the maximum allowable pore size within the electrode microstructure are fixed, which restricts the ability of the algorithm to further enhance the electrochemical power. Finally, the fitness function has a quadratic dependency on the fluid velocity as $Q \cdot \Delta P \propto v^2$ (equation (8)-(9), Hagen-Poiseuille), increasing the sensitivity of the algorithm towards the achievable hydraulic performance.
Figure 3: The results of the genetic algorithm for the VO$^{2+}$/VO$_2^+$ electrolyte, with: (a) the evolution of the algorithm over the number of generations by plotting the maximum fitness for each generation, (b) the maximum electrical performance and pumping power for each generation, (c) the pore size distributions of the first and final generation, showing the pore count and cumulative normalized volume distributions (divided in 2 $\mu$m pore sized bins), and (d) the polarization curve shown as the current density versus the potential, together with the activation and concentration overpotential contributions for the first and last generation.

The optimization procedure results in a final network with a bimodal pore size distribution (Figure 3c) consisting of longitudinal flow pathways composed of pores of the maximum allowable diameter to effectively transport the electrolyte throughout the network (Figure 4). These flow pathways are distributed over the entire length of the network in addition to clusters of smaller pores. The alignment of the pores and corresponding throats highlights the importance of pore positioning, as the placement of interconnected larger pores facilitates the formation of low hydraulic resistance pathways while the diffusion-dominated regions of smaller pores provide additional electrochemical surface area to increase the power output of the system. As a result of the optimization, the average pore diameter of the network increased (from 13.3 to 13.8 $\mu$m) while the average throat diameter decreased (11.7 to 10.6 $\mu$m), which combined with the bimodality (isolated large pores have an increased surface area (Figure A3, equation (5)) leads to an 47% surface-to-volume ratio increase compared to the initial network.
(Table A5), despite the constant network volume scaling. These observations are in line with the high performance and low pumping requirements seen in recently developed materials such as the electrodes prepared using non-solvent induced phase separation manufactured by Wan & Jacquemond et al. that consists of bimodal porous microstructures with a large interconnected backbone of macrovoids alternated by segments of smaller pores (61, 62). Furthermore, other authors observed that bimodal cloths have excellent transport properties while retaining high surface area (11, 63). This result emphasizes the need to further develop manufacturing methodologies to prepare precisely engineered aligned structures to improve cell performance and reduce pumping power costs.

Figure 4: The results of the genetic algorithm optimized for the VO$_{2}^{+}$/VO$_{2}^{+}$ electrolyte. The network structure of generation 1 and generation 1000 are shown together with the pore diameters with the flow in the y-direction and the thickness in the z-direction with the membrane facing to the top. In addition, the pore and throat diameters of generation 1000 are shown over each layer over the z-coordinate.

To gain insight into the absolute electrical performance of the generated structures, we performed a polarization sweep between 0 V to 1 V with 0.1 V increments (Figure 3d). The test reveals that, although the progression in the fitness function is significant, the absolute electrical performance (i.e., the electrochemical work that can be retrieved from the system ($P_{\text{max}} - P_{\text{el}}$)) of the generated networks is an order of magnitude lower in comparison to
literature values (64, 65). The low generated current can be explained by the lower internal surface area of the artificially generated electrode (0.8 x 10^4 m^2 m^{-3} for generation 1 and 1.2 x 10^4 m^2 m^{-3} for generation 1000) compared to commercial electrodes (~1 x 10^5 m^2 m^{-3}) (11, 66). This effect is amplified by the sluggish kinetics of the system (k_0 = 6.8 x 10^{-7} m s^{-1} (54, 56)), leading to high activation overpotential losses at 0.5 V. Operation at a higher overpotential (1 V) results in a higher contribution of the concentration overpotential on the overall system performance. Nonetheless, the generated structure, optimized for performance at 0.5 V, also shows a significant reduction of the concentration overpotential at 1 V, resulting in an increase in current density of 29% over 1000 generations. Consequently, after the evolution, the electrical performance at 1 V is 3.6 times greater than the required pumping power, instead of 1.4 times lower in magnitude as before the evolution. Figure 5 visualizes this ratio, with the demarcation of unity illustrating the trade-off between the electrochemical power (P_{max} - P_{el}) at a fixed overpotential and pumping power (11). Although in practical systems the pumping power represents a lower percentage of the generated electrical power (e.g., typically below 10%), we elected to start with model structures to focus on the fundamental understanding first. Future efforts should focus on initiating the optimization procedure with more representation porous network and more flexibility on the geometrical evolution.

3.2 Parametric evaluation

In this section, we study the impact of variations in the operating conditions and electrolyte properties on the evolution of the electrode morphology and its performance. A systematic evaluation was conducted by modifying the velocity (to 20 or 0.1 cm s^{-1}), exchange current density (to 1 x 10^4 or 1 x 10^{-4} A m^{-2}), or overpotential (to 1 or 0.1 V) as shown in Figure 5, to represent different fluid transport regimes, redox chemistries, or potential operating conditions, respectively. We found that the variation of the tested parameters has two distinct effects on the network evolution: both the exchange current density and overpotential directly influence the generated electrical power, while the electrolyte velocity impacts the formation of longitudinal flow pathways and thus pressure drop.

In the following sections, we discuss the overarching trends that were extracted from the set of parameters runs. First, an evaluation of the trade-off between the pumping and electrochemical power for the initial and final networks is presented. Subsequently, the formation of longitudinal flow pathways is discussed. Finally, an analysis on the distribution of
available surface area is described. A detailed overview of the individual results for the studied systems can be found in Section A4.

3.2.1 System performance

The tradeoff between the required pumping power and the generated electrical power of the initial and final networks is shown in Figure 5. For all evaluated systems, the evolution over 1000 generations results in an improved fitness, shifting the network performance towards a more efficient operational regime. An interesting result to emerge from the study is that the relative increase in electrical power and pumping power are relatively unaffected by the applied changes in the operating conditions and electrolyte properties. In all cases, we find that the reduction in pumping power (70-73%) is the predominant factor for the improvement in the network fitness compared to the improvement in the electrochemical performance (22-48%). Moreover, all studied systems feature a morphological shift towards a bimodal pore size distribution, resulting in an improved fitness, electrical performance, pumping requirement, and surface area (41-49%).

The results of the parametric evaluation show that the obtained relative increase (0.4-344%) and the absolute values of the fitness function heavily depend on the operating conditions and electrolyte properties. Especially, the reduction in reaction kinetics (decrease of the exchange current density from 0.39 to $1 \times 10^{-4}$ A m$^{-2}$) affecting the electrochemical power of the system, and the increase in electrolyte velocity (from 1.5 to 20 cm s$^{-1}$) affecting the required pumping power, have a detrimental effect on the performance of the system. Although this observation is relevant in the search for optimized conditions for most efficient system operation (33), the current study did not focus on finding the optimal operating conditions for specific applications (e.g., for vanadium RFBs), but we aim to demonstrate the potential of the optimization platform over a range of operating and electrolyte conditions. We envision that this methodology can serve as a basis to undertake further research that focuses on the optimization of electrode geometries for specific operational design cases (e.g., on distinct redox chemistries or other electrochemical technologies).
Figure 5: The pumping power versus electrical power ($P_{\text{pump}} - P_{\text{el}}$) for the first and last generation for the seven different systems: the reference, lower velocity (to 0.1 cm s\(^{-1}\)), higher exchange current density (to $1 \times 10^4$ A m\(^{-2}\)), higher overpotential (to 1 V), lower overpotential (to 0.1 V), higher velocity (to 20 cm s\(^{-1}\)), and lower exchange current density (to $1 \times 10^{-4}$ A m\(^{-2}\)) system. The dashed line and shaded region indicate a demarcation of unity.

3.2.2 Longitudinal flow pathways
The inlet velocity of the electrolyte critically affects the trade-off between the system’s pressure drop (Hagen-Poiseuille) and reactant depletion effects, where higher velocities result in improved mass transfer at the cost of larger hydraulic requirements. However, a further increase in the operating velocity from 1.5 cm s\(^{-1}\) to 20 cm s\(^{-1}\) (Figure A17) does not result in a significant change in the number of longitudinal transport pathways. This can be explained by considering the ratio between the pumping and electrochemical power of the reference system.

The pumping power required for the first generation is an order of magnitude higher than the electrochemical output of the system (Figure 5). Therefore, the algorithm puts a larger emphasis on reducing the pressure drop and there is limited opportunity to further optimize the pressure drop when changing the velocity from 1.5 cm s\(^{-1}\) to 20 cm s\(^{-1}\). As a result, similar final morphologies are formed for both systems. Similarly, only a slight improvement in longitudinal flow paths was found for the lower overpotential case (0.1 V, Table 3, Figure A14).

The exchange current density dictates the intrinsic rate of the electrochemical reaction for a given electrolyte-electrode pair. Thus, decreasing this parameter to $1 \times 10^{-4}$ A m\(^{-2}\) shifts the battery operation to a more kinetically limited regime (Figure A19d). Under these conditions (Table 3, Figure A20), we find that the optimization algorithm does not yield notable improvements, which we hypothesize is due to the very low starting performance (0.1 mA cm\(^{-2}\) at an overpotential of 1 V). In contrast, for the higher exchange current density system
(1 x 10^4 A m\(^{-2}\)), better connected flow pathways emerge (Table 3, Figure A8) which is a result of the higher drive of the algorithm to reduce mass transfer resistance under facile kinetics.

Table 3: The number of longitudinal flow paths in the artificial electrode consisting of \(\geq 6\) and \(\geq 10\) connected pores of a pore diameter \(>30\) \(\mu\)m with a maximum pore size of 38 \(\mu\)m. Together with the relative increase in surface area at the electrode-membrane interface over 1000 generations.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Longitudinal flow paths [nr]</th>
<th>Relative increase of surface area at the electrode-membrane interface [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\geq 6) (46%)</td>
<td>(\geq 10) (77%)</td>
</tr>
<tr>
<td>Lower velocity</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>Higher exchange current density</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>Higher overpotential</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Lower overpotential</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>Higher velocity</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>Lower exchange current density</td>
<td>9</td>
<td>5</td>
</tr>
</tbody>
</table>

3.2.3 Distribution of available surface area

The redistribution of surface area is critical for the performance of systems that have a dominant electrochemical power over pumping power (Figure 5), such as the lower velocity and higher exchange current density system. For these cases, we observe a redistribution of surface area towards the membrane-electrode interface. To quantify this trend, we compare the pore surface area of the electrode layer closest to the membrane with the total surface area increase in the system (Table 3, Section A4).

For the lower velocity (0.1 cm s\(^{-1}\)), the pumping power required is strongly reduced and the electrochemical power of the system governs the evolution of the fitness, which favors the optimization of the ohmic currents and kinetic activity in the cell (Figure 5). The evolution of the network indeed stimulates the electrochemical performance of the cell, as we observed a 10% increase in surface area at the electrode-membrane interface with respect to the baseline (see Table 3, Figure A6). This finding is in agreement with our previous study, where we found that the pores in the region closest to the membrane surface are predominantly responsible for the current generated in the system (27), which is in line with the design principle of a zero-gap electrochemical cell (67). Similarly, for the higher exchange current density system, the facile kinetics result in a dominant contribution of the electrochemical performance to the fitness evolution (Figure 5). The improved kinetics of the system results in the emergence of mass transfer limitations (Figure A7d) at an overpotential of 0.5 V, which is counteracted by an increase in, and improved distribution of, surface area in the electrode (Figure A9).
Interestingly, both the higher and lower overpotential systems also show a redistribution of accessible surface area towards the membrane (Figure A12 and A15). For the higher overpotential (1 V) this can be expected as the electrical power becomes more dominant over the generations (Figure 5).

In summary, the developed computational framework efficiently optimizes electrode microstructures for a wide range of operating conditions relevant to redox flow batteries. In line with current experimental understanding, we find that the bottom-up design results in microstructures with bimodal pore size distributions, pore size gradients, and interconnected transport pathways. In this proof-of-concept study, we elect to leverage model simplified geometries to elucidate fundamental microstructure-performance traits that can inspire new material concepts and inform more advanced computational platforms. Although beyond the scope of this work, future studies should consider more realistic electrode structures and manufacturability constrains as part of the evolution.
Conclusion
In this study, we developed a bottom-up computational approach to optimize the electrode microstructure of redox flow battery electrodes using a coupled genetic algorithm and electrochemical pore network model. We demonstrated that the framework offers a powerful tool to optimize the performance of flow battery electrode microstructures under a wide range of operating conditions. A proof-of-concept study was presented, applying the GA to randomly generated cubic networks using the VO$_{2+}$/VO$_2^+$ vanadium chemistry and a flow-through geometry, at a velocity of 1.5 cm s$^{-1}$ and an overpotential of 0.5 V. The algorithm optimized the structures using a fitness function that enhances the electrical power output and reduces the hydraulic requirements, resulting in a fitness increase of 75% (from 0.27 to 0.48 with a maximum fitness of 0.603). The improved performance was attributed to the formation of a bimodal porous structure with interconnected longitudinal pathways with larger pores, which decreased pumping requirements (-73%), and increased electrode internal surface area (47%), which enhanced the electrical power output (42%). In addition, we performed a parametric evaluation that highlighted the response of the network evolution under a wide range of electrolyte and operating conditions. Based on the trade-off between the electrical power and the pumping power, the algorithm emphasizes either the optimization of the flow geometry or the distribution of the available surface area. Operation at a higher velocity, lower overpotential, or a higher exchange current density resulted in better connected longitudinal flow paths compared to the reference system, reducing the hydraulic requirements. Operation at a lower inlet velocity or higher exchange current density resulted in a redistribution of the surface area close to the electrode-membrane interface, enhancing the electrochemical power output.

Looking forward, we propose to further improve the geometrical flexibility by integrating flexible placement of pores and starting the evolution from more complex microstructures. Furthermore, the implementation of code parallelization would greatly improve the algorithm’s speed. Future efforts should incorporate manufacturability constraints into the optimization pipeline to ensure that the resulting structures can be synthesized. This study is the first step towards a computational design platform to accelerate the design and fabrication of porous architectures and we hope to inspire adjacent fields (e.g., computational scientists, mathematicians, mechanical engineers) to contribute to these developments. Although the methodology is applied to redox flow batteries here, the proposed framework can be tailored to any specific porous electrode in convection-enhanced electrochemical technologies (e.g., fuel cells, electrolysis, and separations).
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Competing Interests
The authors declare no conflict of interest.

Credit statement
R.v.G. and M.v.d.H. contributed equally to this work. R.v.G. developed the numerical model and contributed to the conceptualization, methodology, formal analysis, investigation, writing-original draft, writing-review and editing, and visualization, M.v.d.H. contributed to the conceptualization, methodology, experimental work, parametric study, formal analysis, investigation, data curation, writing-original draft, writing-review and editing, and visualization. M.A.S. contributed to model review and debugging, and writing-review and editing. J.G. contributed to supervision and writing-review and editing. Finally, A.F.C. contributed to the conceptualization, methodology, funding, resources, writing-original draft, writing-review and editing, project administration, and supervision.
### Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA</td>
<td>Genetic algorithm</td>
</tr>
<tr>
<td>PNM</td>
<td>Pore network model</td>
</tr>
<tr>
<td>RFB</td>
<td>Redox flow battery</td>
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</tbody>
</table>

### List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>First index</td>
<td>-</td>
</tr>
<tr>
<td>Δ𝑃</td>
<td>Pressure drop</td>
<td>Pa</td>
</tr>
<tr>
<td>𝑀𝑝</td>
<td>Pore internal surface area</td>
<td>m²</td>
</tr>
<tr>
<td>𝑀𝑇</td>
<td>Throat internal surface area</td>
<td>m²</td>
</tr>
<tr>
<td>𝜂</td>
<td>Mutation value</td>
<td>-</td>
</tr>
<tr>
<td>𝑑</td>
<td>Diameter</td>
<td>m</td>
</tr>
<tr>
<td>𝐸</td>
<td>Overpotential</td>
<td>V</td>
</tr>
<tr>
<td>𝐼</td>
<td>Generated total current</td>
<td>A</td>
</tr>
<tr>
<td>𝑘⁰</td>
<td>Kinetic rate constant</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>𝐿𝑇</td>
<td>Throat length</td>
<td>m</td>
</tr>
<tr>
<td>𝑛𝑝</td>
<td>Final index</td>
<td>-</td>
</tr>
<tr>
<td>𝑁𝑇</td>
<td>Number of throats</td>
<td>-</td>
</tr>
<tr>
<td>𝑃</td>
<td>Power</td>
<td>W</td>
</tr>
<tr>
<td>𝑄</td>
<td>Electrolyte flow rate</td>
<td>m³ s⁻¹</td>
</tr>
<tr>
<td>𝑆𝑝</td>
<td>Pore seed</td>
<td>-</td>
</tr>
<tr>
<td>𝑆𝑇</td>
<td>Throat cross-sectional area</td>
<td>m²</td>
</tr>
</tbody>
</table>

### Greek

- 𝜂: Pumping energy efficiency
- ξ: Fitness
- 𝜎: Mutation range

### Superscripts

- 𝑀: Mutated
- 𝑜: Old

### Subscripts

- 1: Generation 1
- 1000: Generation 1000
- losses: Losses
- cell: Open circuit cell
- el: Electrochemical
- 𝑀: Mutated
- 𝑚: Membrane
- max: Thermodynamic maximum
- pump: Pumping
- SA: Surface area
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