Title: Towards bottom-up design of porous electrode microstructures – An approach coupling evolutionary algorithms and pore network modeling

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Porous electrodes are performance- and cost-defining components in modern electrochemical systems such as redox flow batteries, fuel cells, and electrolyzers. They must facilitate mass transport, provide surfaces for electrochemical reactions, and conduct electrons and heat. Thus, understanding and optimizing the porous electrode microstructure offers a promising pathway to cost reduction by increasing power density (*1*). However, our current arsenal of materials is limited to fibrous carbonaceous electrodes that were developed for low temperature fuel cells and are now repurposed to emerging systems (i.e., redox flow batteries), which fundamentally limits the performance. The empirical design of electrodes is time- and resource-intensive which limits exploration of the wider design space. To accelerate progress, microstructure-informed multiphysics simulations can be leveraged to aid the theoretical understanding and design of advanced electrode architectures but has primarily focused to the investigation of existing, carbon-fiber-based electrodes (*2–4*). In this work, we explore the following scientific question: Can we deploy three-dimensional simulations in combination with evolutionary algorithms to enable bottom-up artificial generation of porous electrodes?

In the first part of this talk, I will discuss the modeling framework and experimental validation. Using a pore network modeling open-access platform (OpenPNM) (*4, 5*), we built a microstructure-informed, electrolyte-agnostic simulation framework. In this work, we focus on redox flow batteries as an application case. The model utilizes a network-in-series approach to account for species depletion over the entire length of the electrode, thus enabling the simulation of large electrode sizes (17 mm x 1 mm x 210-400 μm). To validate the robustness of the modeling framework, we performed symmetric flow cell experiments for two distinct electrolytes - an aqueous Fe^{2+}/Fe^{3+} and a non-aqueous $TEMPO/TEMPO^+$ - and two types of porous electrodes – a Freudenberg carbon paper and an ELAT carbon cloth - (Figure 1a). The dry electrode microstructures were obtained with X-ray computed tomography and converted into a network of spherical pores and cylindrical throats using the SNOW algorithm (*6*). The electrochemical model is solved for the electrolyte fluid transport and couples both half-cells by iteratively solving the species and charge transport with low computational cost (-1 – 0 V, with -0.05 V step intervals takes 60-120 min on an Intel® Core(TM) i7-8750H CPU). The electrochemical performance of the non-aqueous electrolyte was well captured by the model without fitting parameters, allowing rapid benchmarking of porous electrode microstructures. For the aqueous electrolyte, we find that incomplete wetting of the electrode results in overprediction of the electrochemical performance. To account for incomplete wetting, we successfully employ a fitting parameter to account for the near-surface mass transfer coefficient (*7*).

In the second part of the talk, I will describe a genetic algorithm that optimizes porous electrode microstructures from the bottom-up by coupling the pore network modeling framework with an evolutionary algorithm. Our goal is to optimize electrode microstructures by only having the electrolyte chemistry and flow field geometry as inputs. The microstructure evolves driven

by a fitness function that minimizes pumping power requirements and maximizes electrochemical power output. The analyzed systems show significant improvement of the networks' fitness, which increased by 30-400%. For flow-through flow fields, the pumping requirements are dominant and were reduced by 60-70%, resulting in a bimodal pore size distribution with large-pore longitudinal electrolyte flow pathways (Figure 1b). Additionally, the surface area at the membrane-electrode interface is increased for all systems, resulting in an increased electrochemical performance of 3-8%. The presented framework offers great potential for predictive design of electrode microstructures tailored for specific redox chemistries and reactor architectures, which will accelerate and broaden the design and fabrication process of advanced electrode structures. While applied to flow batteries here, this methodology can be leveraged to advance other electrochemical systems by adapting the relevant physics.
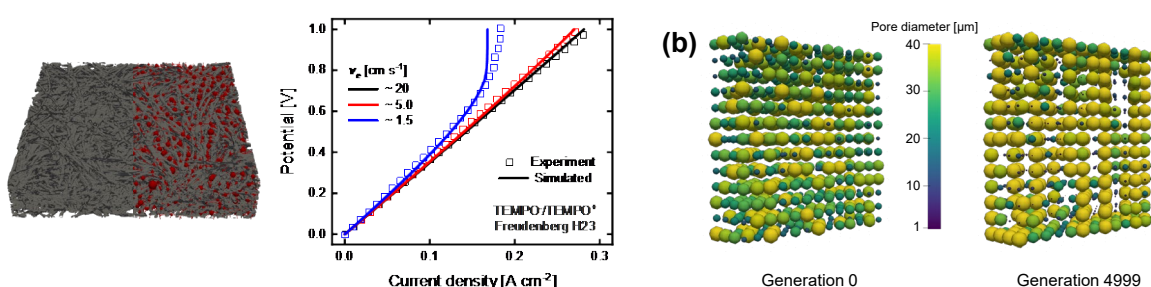
of the processed x-ray tomography images overlaid with the extracted pore network, and the comparison of the polarization nental data with a non-aqueous TEMPO⁻/TEMPO⁺ (0.2 M TEMPO⁻/TEMPO⁺ in 1 M TBAPF$_6$ in MeCN) electrolyte at inlet ⁻¹, for the Freudenberg H23 electrode. **(b)** The results of the genetic algorithm visualizing the network structure and pore ration 4999, where the flow is from the bottom to the top and the membrane is facing to the front-right corner.

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