

Electrode Development and Characterization for Polymer Electrolyte Fuel Cell with Low to Zero Platinum Loading

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"All my brilliant plans foiled by thermodynamics. Damn you, Entropy!"
—Andy Weir, *The Martian*

This thesis is dedicated to my parents.

Abstract

Electrification of vehicles could enable the transportation sector to be more efficient with reduced emissions. Polymer electrolyte fuel cell (PEFC) vehicles powered by sustainably generated hydrogen fuel would be a viable replacement for internal combustion engines. PEFC powered vehicles are highly efficient and offer zero tailpipe emissions. State-of-the-art PEFCs rely on platinum (Pt) and platinum alloy catalyst nanoparticles supported on high surface area carbon black bound by ionomer. The high Pt loadings currently needed for the low-temperature acidic oxygen reduction reaction (ORR) incur significant costs due to the Pt raw material. Degradation of conventional carbon supported Pt electrodes remains a challenge for the commercialization of PEFCs. In the cathode, the ORR is sluggish and results in a large overpotential loss and hence reducing the Pt utilization. The strategy to make PEFC commercially viable is by reducing the cost through either reducing the amount of Pt in the electrode or replacing the Pt catalyst with alternative low-cost catalysts.

Ionomer binder in conventional electrodes needed for proton conduction introduces undesirable high oxygen transport resistance that further reduces the Pt efficacy. However, novel ionomer-free electrodes, which have an advantage of no ionomer film resistance, relies on water for proton conduction and thus hindering the performance and stability at dry conditions. Alternative electrode designs can potentially alleviate some of the problems in these high power density devices. This work presents an alternative composite Nafion nanofiber catalyst support electrode, in which the oriented nanofibers provide robust internal proton transport to a conformal Pt catalyst coating without impeding oxygen transport. The high-surface-area electrodes are prepared by solution casting Nafion onto a sacrificial template, and thin Pt films are deposited on the nanofibers using either physical vapor deposition or chemical vapor deposition. The electrochemical characterization of the nanofiber electrodes demonstrates the high current density and specific activity of this nanofiber approach relative to prior electrodes fabricated by depositing Pt directly onto other Nafion surfaces.

Even with the improved electrode architecture, the Pt raw material cost is still an obstacle. Hence, Pt group metal-free (PGM-free) PEFC cathodes are of significant interest for low-temperature ORR since they have the potential to reduce PEFC costs dramatically. The activity and durability of PGM-free catalyst have significantly improved in

the last 10 years. However, several challenges remain before they can become commercially viable. The PGM-free catalysts have lower volumetric activity and hence the PGM-free cathodes are thicker than Pt-based electrodes. Thus, they suffer from significantly greater gas and proton transport resistances that reduce the observed performance and robustness of operation. To better understand the efficacy of the catalyst and improve electrode performance, a detailed understanding of the correlation between electrode fabrication, morphology, and performance is crucial.

This dissertation reports the characterization of PEFC cathodes featuring a PGM-free catalyst using nano-scale resolution X-ray computed tomography (nano-CT) and morphological analysis. In this work, the pore/solid structure and the Nafion distribution was resolved in three dimensions (3D) using nano-CT for three PGM-free electrodes of varying Nafion loading. The particular PGM-free cathode being studied feature two distinct length scales of interest and was resolved using multi-resolution imaging in nano-CT. The associated transport properties were evaluated from pore/particle-scale simulations within the nano-CT imaged structure. These characterizations are then used to elucidate the microstructural origins of the dramatic changes in fuel cell performance with varying Nafion loading. The results show that this is primarily a result of distinct changes in Nafions spatial distribution. The significant impact of electrode morphology on performance highlights the importance of PGM-free electrode development in concert with efforts to improve catalyst activity and durability. To understand the potential distribution in the thick electrodes we utilize a novel experimental technique to measure the electrolyte potential directly at discrete points across the thickness of the catalyst layer and evaluate the ORR along the thickness of the catalyst layer. Using that technique, the electrolyte potential drop, the through-thickness reaction distribution, and the proton conductivity is measured and correlated with the corresponding Nafion morphology and cell performance.

At this stage of PGM-free catalyst development, it is also necessary to optimize these thick electrodes along with the catalyst. To address the significant transport losses in thick PGM-free cathodes (ca. > 60 μm), we developed a two-dimensional (2D) hierarchical electrode model that resolves the unique structure of the PGM-free electrode. The 2D computational model is employed to correlate the morphology and the electrochemical performance of the PGM-free electrodes. The model is a complete cell, continuum model that includes an agglomerate model representation of the cathode. A unique feature of the approach is the integration of the model with morphology and transport parameter statistics extracted from nano-CT imaging of the electrodes. The model was validated with experimental results of the PGM-free electrode with three levels of Nafion loading. We discuss the sensitivity of the PGM-free catalyst layer on the operating conditions and the morphological parameters to identify improved architectures for PGM-free cathodes. We employ the model to evaluate the targets for the volumetric activity of the catalyst. A notable finding is the impact of the liquid water accumulation in the electrode and the significant performance improvement possible if electrode flooding is mitigated.

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Chapter 1

Introduction

1.1 Motivation

In the past decade, the drastic growth in population has increased the energy demand. The emission of greenhouse gases has increased exponentially, and the largest fraction of the emissions is due to the consumption of energy by the Transportation sector [1]. Since transportation is responsible for roughly a third of carbon dioxide emissions [1], developing new zero emission vehicles is an important aspect of limiting global greenhouse gas emissions. Emissions of particles, apart from causing drastic climate change, also causes health-related problems [2]. A significant requirement for cleaner modes of transportation and reduced dependence on oil has yielded an interest in the electrification of vehicles which could reduce the demand on fossil fuels. Electric vehicles using polymer electrolyte fuel cells (PEFCs) provide zero tailpipe emission and a long range

with quick refueling option.

PEFCs are a promising energy conversion technology for a wide variety of transportation, portable, and stationary applications. PEFC vehicles fueled by sustainably generated hydrogen fuel would be a viable replacement for IC engines. PEFCs offer high power density, and high efficiency but there are still challenges to be solved before they are commercially viable. Although the manufacturing cost is decreasing, the current cost of \$55/kW is higher than the Department of Energy's target cost of \$30/kW by 2020 [3]. Nearly half of the cost is due to the raw material cost of platinum. Also, the utilization of the Pt in the electrode is low and reducing the Pt loading increases the oxygen transport losses due to increased flux at the ionomer film [4]. Unfortunately, meeting the cost targets for automotive PEFCs requires a significant reduction in the Pt usage in combination with approaches to reduce the local transport resistance at the Pt-ionomer interface, such that power density is not sacrificed in the name of low Pt loading [4, 5]. This dissertation work presents the characterization of a new promising catalyst which does not use the expensive Pt and provides an alternate approach to alleviate oxygen transport resistance in Pt-based electrodes.

1.2 Background

1.2.1 Polymer Electrolyte Fuel Cells (PEFC)

PEFCs are electrochemical energy conversion devices that combine oxygen and hydrogen to generate electricity, water, and heat. Figure 1.1a shows the different pathways for gas, ions, and electrons in a PEFC. The gas channels supply the reactants, hydrogen at the anode and oxygen/air at the cathode. The reactant gases diffuse through the diffusion media (DM) into the catalyst layer (CL). In anode CL, hydrogen oxidizes to form protons and electrons.



The proton migrates to the cathode CL through the polymer electrolyte membrane. The membrane consists of ionomer, Nafion, which conducts protons but is an electric insulator. Electron transport takes place through the conductive CL, DM and an external circuit to the cathode. In the cathode CL, shown in Figure 1.1b, the diffused oxygen has to dissolve further into the ionomer to react at the catalyst surface area with the proton and electron to generate electricity. The reaction also generates water and heat as by-products. The product water leaves through the cathode DM.



The DM consists of the gas diffusion layer (GDL) with a microporous layer (MPL)

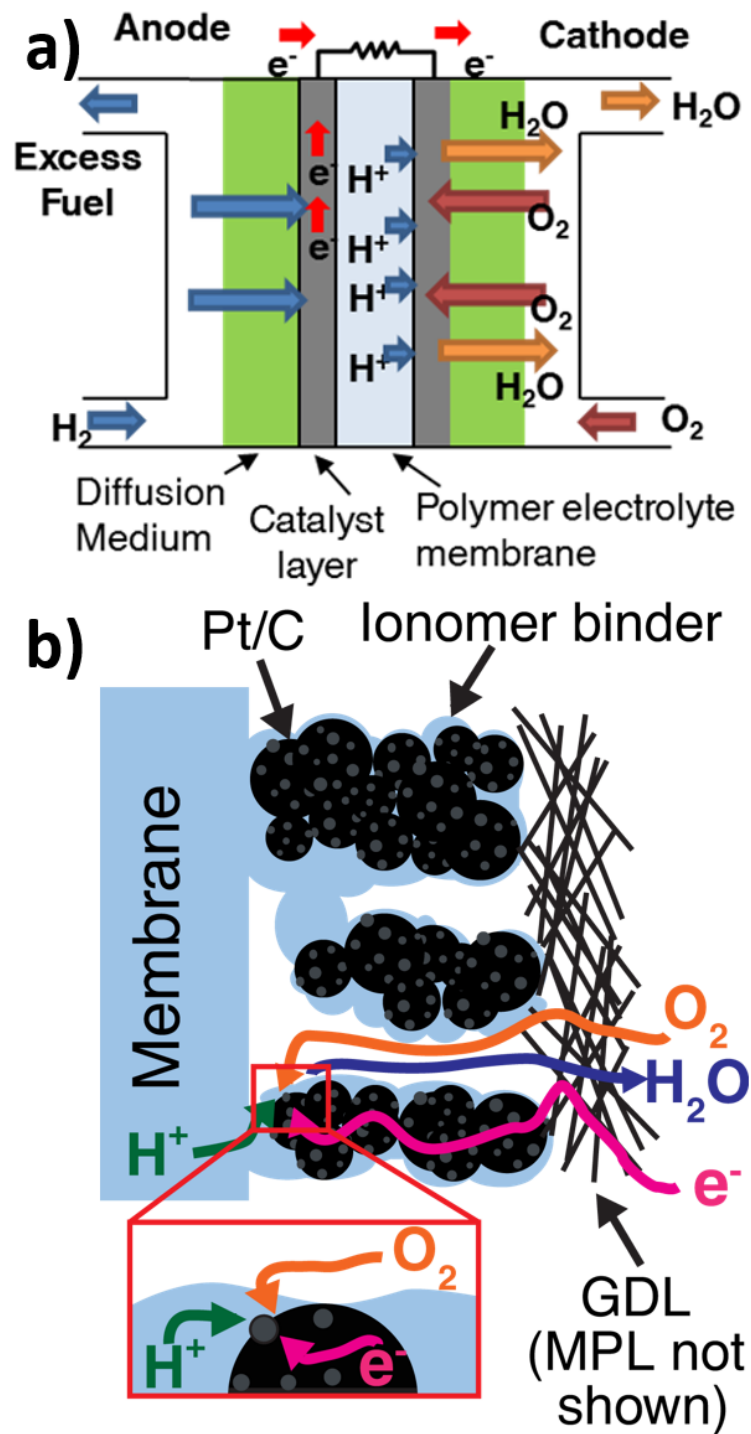


Figure 1.1: Schematic of polymer electrolyte fuel cell components and transport pathways. a) Gas and ionic species transport. b) Cathode of Pt/C based PEFC

backing. The GDL consists of carbon fiber paper or cloth coated with hydrophobic polytetrafluoroethylene (PTFE). MPL has a high surface area carbon with PTFE coating. MPL consists of a high hydrophobic medium and a good contact with the CL to prevent liquid water accumulation in the CL. The carbon in the GDL and MPL provides electronic conductivity. The pores in the diffusion of the reactants, and hydrophobic coating assists in the removal of liquid water from the CL to the gas channel.

1.2.2 Catalyst Layer

The CL is the most complex domain in a fuel cell. It has three different species of transport namely: ionic, electronic and fluid (gas and liquid water) as shown in Figure 1.1b. The majority of current research is focused on the cathode CL due to the sluggish oxygen reduction reaction (ORR) compared to the fast hydrogen oxidation reaction (HOR) in the anode [6]. The requirement for the catalyst to be active for ORR is that the binding energy for the adsorption of the reactant on the catalyst surface has to be intermediate (*i.e.*, neither strongly adsorbing or weakly binding). Platinum group metals (PGM) and its alloys exhibit highest activity for the ORR in the acidic medium [7].

Platinum Group Metal Catalyst

Conventional fuel cell CL consists of Pt nanoparticles supported on high surface area carbon bound by ionomer [6, 8]. Inset of Figure 1.1b shows the triple phase bound-

ary (carbon, Pt and Ionomer) where reaction occurs. The ionomer binder film around the Pt/C catalyst adds to the oxygen transport resistance, which reduces the Pt effectiveness and becomes significant for low Pt loading [9, 10]. Another challenge with Pt/C catalyst is that oxidation of carbon during startup and cell reversal degrades electrode performance, requiring restrictive operating procedures to mitigate damage. Pt loading in the cathode is much greater than in the anode due to sluggish ORR and is impeded further by mass transport limitations. Decreasing the loading of Pt in the cathode reduces the cell efficiency, and increases the relative impact of oxygen transport resistances thereby reducing performance. Unfortunately, meeting the target costs for automotive PEFCs requires reducing the Pt usage. Improving the performance, while minimizing the loading, requires the losses in the electrode to be limited to the reaction kinetic losses. This is a short-term mitigation strategy, as the Pt cost does not follow the economies of scale. This holds because Pt is a raw material and its cost is volatile in nature due to socioeconomic reasons.

Platinum Group Metal-Free Catalyst

For a long term strategy, the catalyst should be completely devoid of noble metals. As an alternative to thrifted Pt from the catalyst, a compelling approach to reducing PEFC costs is to use PGM-free catalysts prepared from nitrogen precursors, transition metals, such as iron and cobalt, combined with a carbon support. Initial PGM-free catalyst were fabricated using more expensive iron ($Fe - N_4$) or cobalt ($Co - N_4$) based macro-

molecules. The electrodes prepared from these PGM-free catalysts had a low activity and were less durable compared to Pt-based electrodes. The active site has not been elucidated yet, however, it is commonly assumed the active site is a $Fe - N_4$ moiety found at the edge of graphene planes in micropores [11]. With these materials, there is an opportunity to reduce electrode costs dramatically. Over the past decade, increasing interest in PGM-free catalysts for the ORR in low-temperature acidic media has led to notable improvements in the activity and durability [12, 13, 14, 15, 16, 17, 18]. In general, it has been observed that higher catalyst activity is due to increased carbon support surface area yielding the formation of more active sites in micropores [19]. However, due to the lower turnover frequency (TOF) of the active sites, the volumetric activity of PGM-free cathodes is lower than their Pt/Pt-alloy counterparts. Hence, to produce comparable power density, PGM-free cathodes are typically an order of magnitude thicker than Pt-based electrodes as shown in Figure 1.2. Unfortunately, thicker electrodes result in increased resistances to oxygen and proton transport, and non-uniform catalyst utilization [20]. Thus, to properly implement these catalysts with the present TOF, it is imperative that the electrode structure be optimized to reduce these losses. At present there is unclear understanding of the PGM-free catalyst as there is scarcity in work towards estimation of the TOF and active site density. Sahraie et al. estimated the active site density as well as the utilization of the metal centre using a combination of the CO adsorption/desorption and Mossbauer spectroscopy [21].

At present, the electrochemical testing of the PGM-free catalyst is done through rotating disk electrode (RDE) and rotating ring disc electrode (RRDE). RDE and RRDE

are helpful in understating the PGM-free catalysts electro-kinetics. However, due to the requirement of thicker electrodes for PGM-free catalyst, the effect of mass transport overpotential losses in the RDE/RRDE results is uncertain. Also, the performance differs while electrochemical evaluation of the PGM-free membrane electrode assembly (MEA) differs from the catalyst RDE testing. At this stage of PGM-free development, along with increasing the activity of the catalyst, the cathode morphology of the MEA should also be optimized. Understanding the correlation between the morphology and the performance of the thick PGM-free cathode is essential to improve the performance.

1.2.3 Catalyst Layer Morphology

Catalyst layer structure can significantly impact PEFC performance. In general, PEFC catalyst layers consist of a percolating network of the catalyst aggregates (Pt/C or PGM-free catalyst) bound by the ionomer. The specific structure depends on many factors, including the initial structure of the catalyst aggregates, ionomer loading, solvents, and the deposition process [22, 23]. Prior studies have shown that catalyst layer pore morphology and ionomer distribution significantly affect the performance of the electrode [24, 25, 26, 27]. The catalyst layer pores volume fraction (*i.e.*, porosity), tortuosity, pore size distribution, and wettability can impact the performance by altering the rate of gas transport as well as the liquid water retention and transport [28]. Also, it has been shown that the size distribution of the distinct dense regions of agglomerated catalyst particles can impact performance through the local microstructural transport resistance

[29].

The degree of ionomer infiltration into the catalyst agglomerates depends on the catalysts pore size distribution as well as the ionomer loading and its level of aggregation in solution. The ionomer distribution and ionomer loading can influence the ionic conductivity of the catalyst layer and hence the Ohmic overpotentials within the catalyst layer. Ionomer infiltration, apart from affecting the ionic conduction in the catalyst layer, adds additional gas transport resistance. It is necessary to understand the correlation between the electrode morphology, and its reaction kinetics and transport to improve the performance of the electrodes. Morphological characterization provides an understanding of the transport phenomena in the electrode, electrochemical evaluation is necessary to evaluate the performance of the catalyst or the electrode.

1.2.4 Fuel Cell Characterization

Polarization Curve

Polarization curve relates the fuel cell voltage to the current, as shown in Figure 1.3. The shape of the polarization curve helps in understanding the losses in the fuel cell. Polarization curve can be obtained by applying a constant current (Galvanostatic) and measuring the resulting voltage. Similarly, in potentiostatic mode, a constant voltage is applied and the resulting current from the cell is measured. Reversible voltage, E_{rev} , is the difference in the standard potential difference between cathode and anode. For

PEFC, E_{rev} is 1.23 V. Major losses in a PEFC can be categorized into activation (η_{act}), Ohmic (η_{Ohm}) and mass transfer over-potential (η_{mass}). The activation overpotential is the loss incurred by the reactants to overcome the activation barrier of the catalyst for the reaction to proceed. The cathode activation overpotential is the major source of loss in the fuel cell. The anode activation overpotential is usually minimal and neglected due to fast HOR. The Ohmic loss is due to the conductivity of protons across the membrane and the contact resistance at the various interfaces in the PEFC. Mass transport resistance occurs due to increase in the tortuosity of the gas transport pathway due the water generated at high currents flooding the pores of the catalyst layer with liquid water. Mass transport and ionic losses could be minimized with the optimized CL morphology [24, 25, 26, 27].

Although the polarization curve indicates the major loss that occurs it is hard to elucidate the losses as they overlap. Hence, the phenomenon or the source for the loss is difficult to identify purely based on the polarization curve. Other characterization techniques in conjunction with the polarization curve are typically used to understand the losses.

Cyclic Voltammetry

Cyclic voltammetry (CV) is a characterization technique to identify the electrochemical surface area (ECSA). CV is operated with fully humidified H_2 in the anode and N_2 in the cathode. Voltage is applied at a constant rate sweep from 0 V to 0.8 V and the current

response is measured. A typical CV is shown in Figure 1.4. In the forward sweep from 0 V to 0.8 V (top of the curve), the peaks below 0.4 V represent the desorption of H_2 from the Pt surface. The peak after 0.8 V is due to the oxidation of Pt. On the reverse sweep (bottom curve) from 0.8 V to 0 V, the peak around 0.8 V represents the reduction of Pt and the adsorption of hydrogen on the Pt shows up as peaks below 0.4 V. The region between 0.4 and 0.8 V represents the double layer region, which is the charging or discharging of the double layer capacitance at the metal-electrolyte interface. The area under the curve, $QH_{ads/des} [\mu C cm_{geo}^{-2}]$, due to the hydrogen reduction or oxidation represents the charge of the Pt adsorption/desorption on the Pt surface. The electrochemical

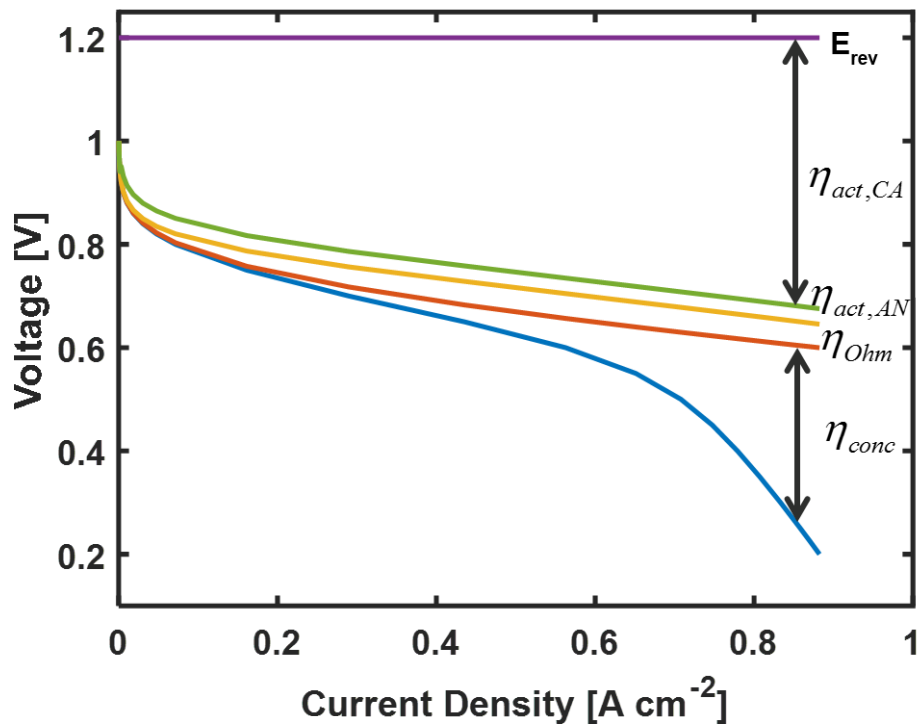


Figure 1.3: A standard fuel cell polarization curve with different overpotential losses

surface area (ECSA) [$cm^2_{Pt}g_{Pt}^{-1}$] is obtained using the equation

$$ECSA = \frac{QH_{ads/des}}{Q_{Pt}L} \quad (1.3)$$

where $L[mg_{Pt}/cm_{geo}^{-2}]$ is the Pt loading in the electrode and Q_{Pt} is the constant $210 \mu C cm_{Pt}^{-2}$. ECSA is an indication of the performance of the fuel cell. Higher ECSA indicates the higher amount of the Pt accessible for reaction. The CV also provides information about the H_2 crossover, which is the permeation of H_2 gas from anode to cathode through the membrane. H_2 crossover is measured by first identifying the center line of the double layer and measuring the shift in the line from zero current.

Computational Modeling

Computational models have been an invaluable tool in the critical understanding of the phenomena that occur inside the fuel cells, that cannot be easily understood or resolved through experiments. Predictive models also reduce the time in electrode development by reducing the amount of experiments required. Transport and electrochemical phenomena are studied by solving the mass, momentum, energy and charge conservation in the fuel cell domain in either one, two or three dimensions.

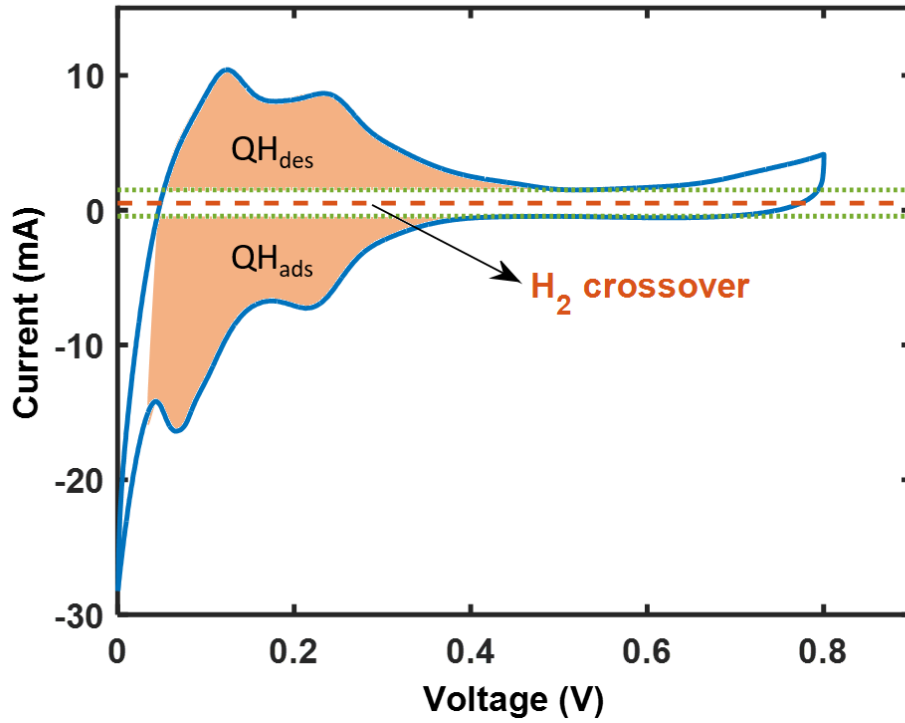


Figure 1.4: A standard CV for Pt based electrodes with H_2 and N_2 in the anode and cathode respectively. Area under the curve $QH_{ads/des}$ represents the charge during adsorption/desorption.

1.3 Related Work

1.3.1 Catalyst Architecture and Support

Several approaches have been reported to resolve the issues mentioned above without reduction of performance. For instance, improving the electrode structure, high surface area catalyst support, improved Pt architecture, and Pt-alloys with high activity [30, 31]. Ionomer and carbon-free electrodes can be used to reduce the oxygen transport

resistance and improve durability [32, 33]. Ionomer-free, thin-film Pt electrodes can be fabricated by depositing a thin film of catalyst, with lower loading of Pt onto the membrane or the diffusion medium, or a nano-structured support (*e.g.*, 3M's nano-structured thin-film (NSTF) electrodes [34]). Most of the reported ionomer free thin-film electrodes do not have the required performance with the exception of catalyst deposited on the diffusion media or a nano-structured support. In many of these cases, the thin-film electrodes are limited due to the low Pt surface area or proton conduction in the electrode. The roughness factor, the ratio of total surface area to the geometrical area, of thin-film catalyst surface should be high in order to increase electrochemically active surface area (ECSA). O'Hayre *et al.* [35] fabricated electrodes by sputtering Pt onto the surface of roughened Nafion membrane. They observed that the performance improved compared to a non-roughened membrane due to the higher roughness factor. NSTF electrodes featuring a high roughness factor catalyst support have exhibited high specific activity and high durability with reduced Pt loading [34]. Since the NSTF electrodes are ionomer free, they rely on water for proton transport. Unfortunately, flooding issues can arise at low temperatures due to the low pore volume in the thin electrodes [36]. A prior study has shown that an electrode thickness of at least a few micrometers is necessary to uptake liquid water during rapid increases in current density [37]. Other methods to increase the roughness factor of the membrane include laser bombardment [38] and pattern molding [39].

The catalyst support also crucially influences the Pt utilization, degradation, and performance of the ionomer free electrodes. Catalyst supports should have high sur-

face area necessary for better dispersion of Pt and electrochemical stability. Carbon nanotubes [40] and carbon nanofibers [41] have higher surface area than carbon black that leads to a reduction in Pt loading. In ionomer free electrodes, the ionic conductivity of the catalyst support can significantly influence the performance of the electrode [36, 42]. In these electrodes, the proton conductivity is dependent on water and requires higher relative humidity operating conditions which could be overcome by utilizing a proton conducting catalyst support. With this in mind, Aizawa *et al.* [43] sprayed Pt/C catalyst on micro-structured Nafion pillars (2 μm diameter, 3-10 μm height) with a roughness factor of 2 and observed minor improvement in performance. Zhang *et al.*[44] fabricated Nafion 115 nanowire array (85 nm diameter) by extruding through a porous membrane. Unsupported Pt nanowires and nanotubes fabricated by CVD or PVD have a high surface area of Pt, particularly the nanotubes, owing to the inner and outer surfaces [45, 46]. Galbiati *et al.* [47] fabricated Pt nanotube array by atomic layer deposition of Pt on anodized alumina oxide and coated the Pt nanotubes with ionomer. Half-cell studies of the Pt nanotubes showed increased specific activity. Similarly, Papandrew *et al.*[48] fabricated Pt nanotubes by vapor depositing conformal films of Pt nanoparticles within the pore structure of anodized alumina oxide followed by thermal treatments to induce grain growth. After the dissolution of the templates, the released nanotubes exhibited ORR activity comparable to polycrystalline Pt.

1.3.2 Morphological Characterization

Many of the prior observations of the CL morphology are based on fuel cell testing along with indirect characterizations of the CL structure, such as mercury intrusion porosimetry (MIP) [49] and Brunauer-Emmett-Teller (BET) gas adsorption measurements [50].

In addition to porosimetry, the catalyst layer structure is commonly evaluated by scanning electron microscope (SEM) or transmission electron microscope (TEM) imaging [51]. Although SEM imaging offers high resolution, it only provides external information from the exposed surface in a 2D image [51, 52, 53, 54]. TEM and related methods, such as scanning TEM (STEM), offer even higher resolution and can be extended to 3D tomography. However, the transmission imaging requires the sample to be very thin, on the order of 100 nm [51, 54, 55, 56]. Focused ion beam (FIB) milling, combined with SEM, can provide high resolution 3D morphology of the catalyst layer [53, 57]. However, FIB-SEM faces its own set of challenges. It is a destructive technique and differential milling rates for different materials can be intrusive [58]. For the reconstruction, there are also challenges in distinguishing the cutting plane surface from the background beneath the cut. Some groups have addressed this by adding high contrast material to ease segmentation [59]. As an alternative to electron microscopy, micro-scale (micro-CT) and nano-scale resolution X-ray computed tomography (nano-CT) can be used to image fuel cell components [53, 60].

1.3.3 X-ray Computed Tomography

X-ray computed tomography (CT) can provide quasi-destructive imaging of the fuel cell components [53]. CT is quasi-destructive as the imaging itself is non-destructive, some initial destructive sample preparation is necessary to fit the sample in the field of view (FOV). Because of the quasi-destructive nature of the CT sample, additional processing (staining) or other imaging methods (different contrast or resolution modes) studies can be performed on the same sample. For instance, we performed different contrast imaging of the same lithium-ion cathode to resolve the active and inactive phases. The multi-contrast imaging of lithium-ion is described in detail in Appendix E. CT operating conditions do not require a vacuum environment and also the non-invasive nature is ideal for *in-situ* as well as *in-operando* imaging of PEFC [61]. Advances in diffraction-based X-ray optics using monocapillary condensers and Fresnel zone plate objectives has led to X-ray CT imaging at resolutions of 50 nm and better. Epting *et al.* [60] previously demonstrated that nano-CT can be used to image the pore and solid structure of fuel cell catalyst layers, where the solid were the dense regions of Pt/C catalyst and ionomer. This was achieved on a lab-scale nano-CT system with an 8 keV rotating copper anode source and Zernike phase contrast. Zernike phase contrast imaging enables imaging of low atomic number (Z) materials that offer little contrast by traditional X-ray absorption [62, 63]. The low Z material contrast is achieved by inserting a gold phase ring between the zone plate and the scintillator, which phase shifts the undiffracted X-rays such that they interfere with sample diffracted X-rays, enhancing the image con-

trast, particularly of the pore/solid interface. The enhanced interface contrast is due to the halo artifacts of phase contrast, which consist of bright regions in the solid next to the interface and dark regions in the pore. A second artifact of Zernike phase contrast is shade off, where the intensity within the solid domains sufficiently far from the interface is not significantly different than that of the surrounding air, which can make segmentation difficult (although these algorithms exist to correct these images [64]). Epting *et al.* [60] showed that Zernike phase contrast of Pt/C catalyst materials and other materials with length scales on the order of a few hundred nm do not suffer from shade off in segmentation because at those scales, the halos overlap and provide enhanced contrast over the whole solid or pore region.

Three-dimensional imaging is useful beyond just qualitative correlations, as they can be used to extract morphological statistics, which can then be used to inform models [29]. They can also be directly used for the geometry in particle/pore-scale simulations [65, 66, 67]. For example, Litster *et al.* [65] used nanoscale resolution X-ray computed tomography of images of Pt/C catalyst layer for the geometry in pore-scale computational models to analyze and extract effective transport properties (*e.g.*, effective diffusivity and tortuosity).

1.3.4 Ionomer Imaging

In addition to imaging the pore morphology, there is great interest in imaging the ionomer distribution in PEFC catalyst layers in order to reveal the film thickness and

the level of ionomer heterogeneity. Conventional methods of studying ionomer distributions are by SEM with energy dispersive X-ray spectroscopy that images ionomers fluorine distribution and by STEM imaging that can directly map the ionomer distribution [56, 68, 69]. Another method of visualization is by staining the ionomer by ion exchanging the ionomers acid with a high Z cation for Z-contrast imaging. For example, Rieberer *et al.* [70], and Fujimora *et al.* [71] imaged Cs^+ stained ionomer films using TEM. Lopez-Haro *et al.* [72] imaged the stained ionomer that had adsorbed in solution onto single particles of carbon black support by 3D TEM tomography.

1.3.5 Continuum Scale Computational Model

The progress in macro-homogeneous continuum scale models for PEFCs has increased significantly [73]. There have been several published papers on the computational model for thin catalyst layer for PEFC [73][74][75][76][77][78]. The catalyst layer (CL) is the most complex to model or mathematically represent because of gas and ionic species coupled transport and ORR. Hence, CL requires a highly detailed physical model to capture the phenomena occurring in the CL accurately.

CL is commonly modeled as an interface [79] or discrete volume model [80] or an agglomerate model [81]. The interface model represents the CL as a boundary condition between the membrane and the MPL. It does not consider the transport losses or morphology of the CL. The discrete model considers the transport in the CL and uses standard Butler Volmer equation to represent the ORR in the CL. However, it does not

consider the O_2 dissolution or transport in the Nafion binder domain. The agglomerate model is more detailed in the description of the CL morphology. Sun et al. [81] developed an agglomerate model which is an analytical solution to the coupled diffusion and reaction in an ideal spherical agglomerate. The computational models published previously tend to use a single average representative diameter [81] or a gradient of diameter [75] or different sub-layers with each sub-layer represented by a single diameter [82] to represent the catalyst aggregate structure and do not consider the non-uniform distribution which exists in practical electrodes. Epting et al. [29] showed that distinct agglomerate dimensions contribute at different reaction rates. At high current density the fraction of smaller agglomerates contribution is greater because of its shorter diffusion time length and at low current density agglomerates of all size contribute similarly. Also considering the significant variation in the size seen in SEM images(1.1), the agglomerate model needs to be adapted for a non-uniform size distribution.

Numerous models have addressed the optimization of the catalyst layer, but these works are primarily for thin PGM based catalyst layers. Most of these models have a good agreement with the experiment. However, some of these models fit the transport parameters to validate the results to the experimental characterization. Very few models exist for thick electrodes and PGM-free electrodes [83]. It is crucial that the PGM-free electrodes models do not fit the transport models as they could result in non-physical properties.

1.4 Method

1.4.1 Improved Electrode Architecture

An ideal fuel cell electrode should have the following characteristics: low Pt group metal loading, high surface area, good corrosion resistance, high specific activity and low cost. In conventional Pt/carbon electrodes, the sluggish ORR at the cathode results in a large over-potential. The Nafion ionomer often used to bind Pt/C electrodes adds to the oxygen transport resistance [9, 10] and becomes a significant transport reduce for electrodes with low Pt loading [25]. In addition, Pt/C are problematic because oxidation of the carbon Pt support leads to degradation of the electrode and requires careful operating procedures to mitigate. One way to improve the ORR is to reduce the oxygen transport resistance by fabricating thin-film electrodes with extended surface catalyst and having no polymer electrolyte binder [84]. This approach yields high specific activity and low mass transport resistance. However, such electrodes can suffer from flooding due to low pore volume and high ionic resistances at lower relative humidity [36].

To address this we fabricated a novel catalyst support made of vertically oriented Nafion composite nanofibers that have high proton conductivity and high surface roughness. Pt is conformally deposited onto the nanofibers forming a high roughness factor electrode. Nanofibers were fabricated by casting a SiO_2 /Nafion composite solution onto a track-etched polycarbonate template to simultaneously form nanofibers and the solid

membrane. After etching away the template, a thin film of Pt was deposited directly onto the nanofiber side of the membrane. Pt was deposited either by physical vapor deposition or chemical vapor deposition.

1.4.2 Morphological and Electrochemical Characterization of the PGM-free

The activity and durability of ORR PGM-free have significantly improved in the past decade. However, in order to generate current densities comparable to conventional Pt cathodes, the lower volumetric activity requires the PGM-free cathodes to be an order of magnitude thicker. Increasing the electrode thickness increases the proton and oxygen transport resistance as well as makes the electrode more susceptible to liquid water flooding. Therefore, understanding the relationships between the cathode architecture and performance is crucial for optimizing the performance of thick-format PGM-free cathodes. Figure 1.5 summarize the framework use used to characterize and optimize the PGM-free electrode.

We characterize the PGM-free electrode based on Los Alamos National Labs cyanamide polyaniline iron (CM-PANI-Fe) catalyst. The electrodes have characteristics at two different length scales which are of importance to the model. There are large dense aggregate particles (500 nm - 10 μm) of the PGM-free catalyst with Nafion binder surrounded by large macropores. The dense aggregates are interspersed with micropores

(<500 nm). To resolve the features of the electrode, it is imaged using nanoscale resolution X-ray computed tomography (nano-CT) in multi-resolution, multi-contrast imaging modes. Zernike phase contrast imaging in two different resolution modes to resolve the solid and pores. First, large field of view (LFOV) resolution mode resolves the large

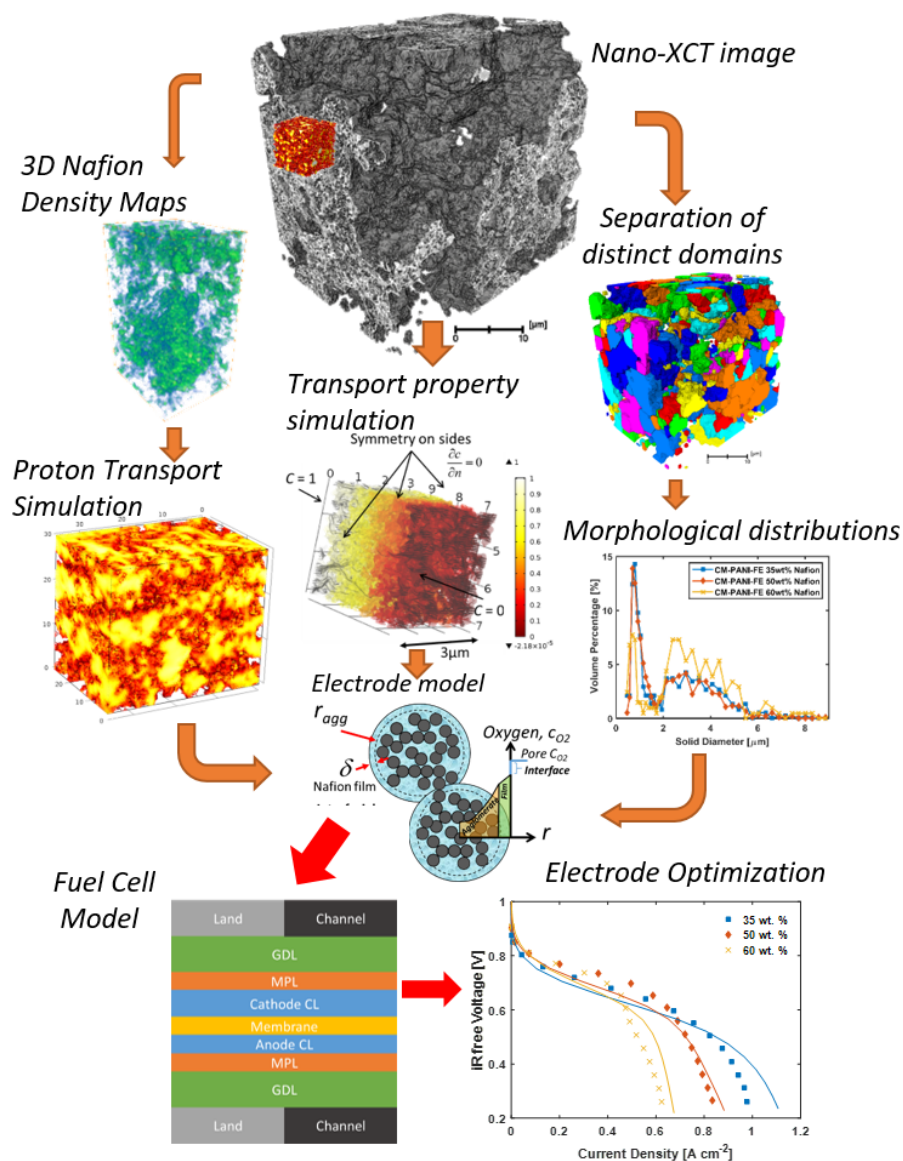


Figure 1.5: Framework for morphological and electrochemical characterization of the PGM-free electrode.

dense particles and the macropores. Second, high resolution (HRES) mode resolves the dense aggregates into intra agglomerates and micropores. Ionomer distribution was obtained by ion-exchanging the proton in the ionomer with higher X-ray attenuating cesium ions, Cs^+ .

Apart from morphological characterization, the nano-CT images are directly used to extract transport parameters. Pore scale model is performed on pore domain from nano-CT imaging of electrode with three levels of Nafion loading, to extract effective diffusivity in the micropores of the PGM-free catalyst. The Nafion domain is utilized for particle scale modeling of ionic conductivity. To validate the ionic conductivity obtained from the particle scale model, *in-situ* ionic conductivity is measured experimentally using microelectrode scaffold (MES) diagnostic as previously developed in our group for Pt electrode [20]. In addition we measure through-plane potential distribution to understand the ORR in the thick electrode.

We developed a hierarchical electrode model that resolves the unique structure of the PGM-free cathodes we studied. A unique feature of the approach is the integration of the model with morphology data extracted from nano-scale resolution nano-CT imaging of the electrodes. The hierarchical electrode model was integrated within a fuel cell model framework. The model is used to elucidate the losses in the thick PGM-free electrodes and optimal morphological parameters are identified. Further the model is used to predict the activity targets.

1.5 Scope of Thesis

This dissertation discusses the development of PGM and PGM-free electrode in PEFC, utilizing experimental and computational techniques. The dissertation is divided into six chapters. The first chapter is based on PGM electrode, the next four are dedicated to PGM-free electrode and the final chapters presents conclusions. Chapter 2 presents the electrochemical characterization new electrode architecture for thin film PGM electrodes. Chapter 3 presents the nano-CT imaging of catalyst, pore, and ionomer in PGM-free electrode and also pore —scale and particle —scale simulations directly on the imaging domain. Chapter 4 presents characterization using microstructured electrode scaffold for estimating the ionic conductivity of the PGM-free catalyst layer. Chapter 5 outlines the framework for the hierarchical model which utilizes the morphological and transport data from nano-CT imaging of the PGM-free electrode. Chapter 6 presents the application of the model in understanding and optimizing the performance of the PGM-free MEA. Final Chapter 7 presents the conclusion, contribution, and recommendation for future work. Appendix B&C presents the derivation of the agglomerate model and the Nafion film thickness. Appendix D presents the parameters used in the model described in Chapter 5. Appendix E presents the characterization of active and inactive phases the Lithium-ion battery cathode using nano-CT.

Chapter 2

Vertically Oriented Polymer Electrolyte Nanofiber Catalyst Support for Thin Film Proton-Exchange Membrane

2.1 Introduction

This chapter presents the fabrication and electrochemical characterization of a polymer electrolyte fuel cell (PEFC) cathode with ionic conducting nanofiber catalyst support for thin-film, extended surface electrode. The proton conducting support comprises of vertically oriented polymer electrolyte nanofibers with high roughness factor. The nanofiber supports are cast simultaneously with the membrane, forming a single ion

conducting component. Figure 2.1 shows the pathways for oxygen and protons in conventional Pt/C electrodes and the proposed nanofiber electrode. As Figure 2.1a shows, the oxygen reduction reaction (ORR) could occur on the air-Pt interface or the Nafion|Pt interface depending on the transport resistance of protons on the exposed Pt surface and that of oxygen in the Nafion, respectively.

The proposed benefits of this approach are:

- Removal of exterior Nafion films for better O₂ transport,
- Elimination of carbon supports,
- High activity, extended surface catalyst,
- Low tortuosity transport pathways,
- Single-step membrane and electrode support fabrication, and
- Adequate electrode thickness for water uptake during transients.

Here we have used sacrificial template based solution casting to fabricate the nanofibers along with a solid membrane. After etching away the template, physical vapor deposition (PVD) or chemical vapor deposition (CVD) was used to deposit Pt catalyst on the freestanding nanofibers. In another variation prepared by PVD, a Pt pre-sputtered template was used to fabricate the electrode. The Pt transfers from the template to the bottom of the nanofibers surface after etching and, in addition, a thin layer of Pt was later deposited on the nanofibers. Nanofiber electrodes were compared to an electrode fabricated by PVD of Pt onto a planar, commercial Nafion membrane. Morphological

and electrochemical characterization of the nanofiber electrode were performed to evaluate the effects of surface roughness and catalyst coating method.

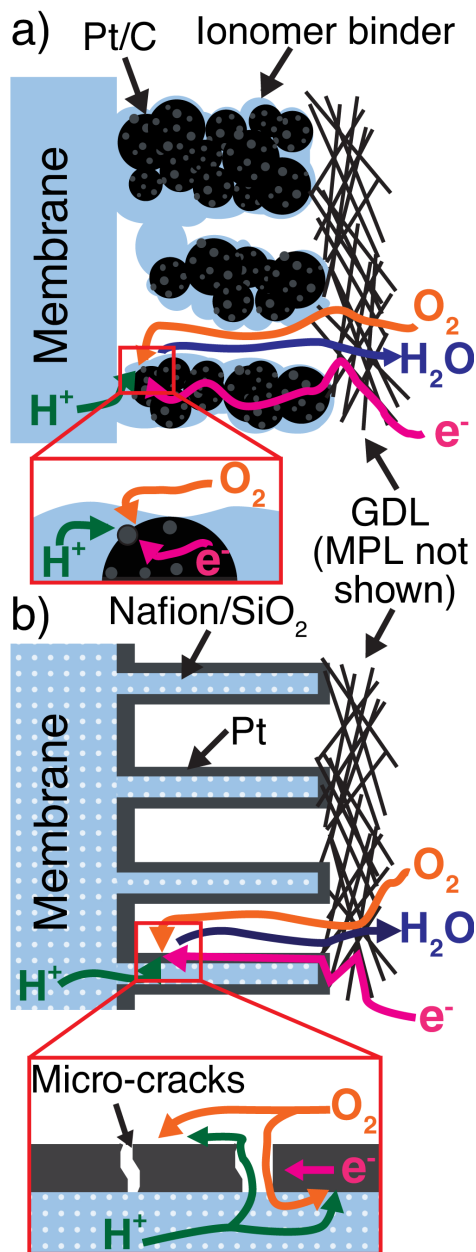


Figure 2.1: Schematic of species transport in a) Conventional Pt/C electrode; b) Polymer electrolyte nanofiber catalyst support electrode.

2.2 Nanofiber Electrode

We prepared nanofiber covered membranes by solution casting Nafion polymer electrolyte onto a commercial, low-cost sacrificial template (low cost relative to commercial Nafion membranes). The templates used were track-etched polycarbonate (TEP) membranes with 200 nm pore diameter and thickness of 10 μm , as shown in Figure 2.2a. The membrane pore dimensions dictate the resulting nanofiber diameter and length. The track-etched membrane is selected because of its highly aligned through-pores. The porosity of the TEP calculated from Figure 2.2a is 12.5 %. The TEP was commercially produced by random firing of charged particles at a polycarbonate sheet in a reactor, followed by controlled etching to generate the desired pore diameter. Because of the randomness of the manufacturing process the pores are randomly distributed as seen in Figure 2.2. Visualization of the pore domain using nano-scale X-ray computed tomography (nano-CT) showed a uniform pore diameter. However, the orientation of the pores is not exactly vertical and they are consistently angled 16-19° away from perpendicular to the surface plane, with some pores intersecting within the membrane.

Figure 2.3 shows the steps in the fabrication of the nanofiber electrodes through PVD and CVD from freestanding nanofibers. After casting, the ionomer template sample is annealed in a vacuum chamber to increase the mechanical strength of the cast composite solution [85, 86]. After annealing, the template is removed by chemical etching and then rinsed with deionized water. If subsequently dried in air, we found the surface tension of water caused the nanofibers to collapse, reducing the surface area for Pt de-

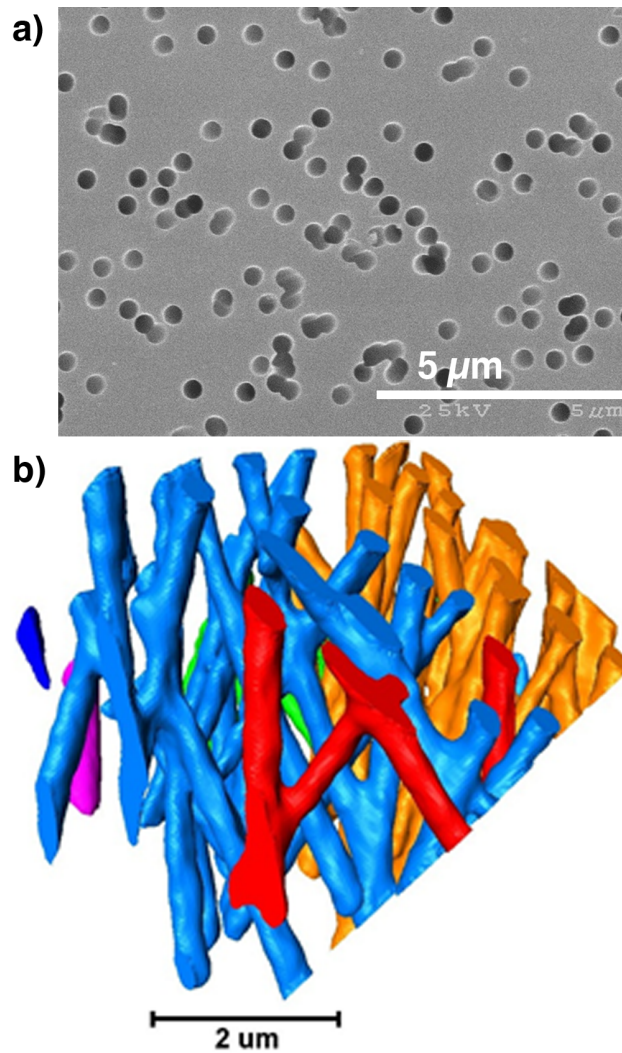


Figure 2.2: Visualization of TEP. a) SEM image of the track-etched polycarbonate membrane. The pores are 200 nm in diameter. The interpore distance varies because of the random distribution of the pores. b) nano-CT reconstruction of the pores of the track-etched polycarbonate membrane. The reconstruction shows directionality and the inclination of the pores.

position. To avoid structure collapse during drying, the sample along with water was rapidly frozen in liquid nitrogen and the water was then sublimated in vacuum [87]. In preparing aligned arrays such as these, there is a great possibility of fiber clumping when they are at high proximity to each other due to the fiber surface energy [88]. For a desired geometry, the amount of clumping can be reduced by increasing the Young's modulus of the fibers. To increase fiber strength and reduce clumping, we added silica (SiO_2) nanoparticles into the polymer electrolyte casting solution. Nanofibers fabricated from the composite solution had higher rigidity than compared to pure Nafion solution and prevented structure collapse. Prior work has also shown that Nafion/ SiO_2 composite membranes enable increased water retention [89].

Figure 2.4a shows the prepared nanofibers and Nafion membrane. The Nafion nanofibers match the diameter and length of the TEP pores (200 nm in diameter and 10 μm , respectively). However, they initially appear to be partially collapsed. In fact, they reflect the structure of the pores in the polycarbonate as evidenced by the nano-CT imaging and some nanofibers do collapse due to some proximity clumping. The non-porous, composite Nafion membrane that were casted simultaneously below the fibers were typically 40 μm thick. The surface roughness of the nanofibers estimated from the nano-CT, SEM, and the manufacturers specification was $21 \text{ m}_{\text{fiber}}^2 / \text{m}_{\text{planar}}^2$.

Nanofiber electrodes are fabricated from the nanofiber supports by depositing a thin film of Pt directly onto the nanofibers. High Pt coverage over the nanofibers is crucial for good ORR performance and Pt utilization. During PVD, the sputtering base is tilted,

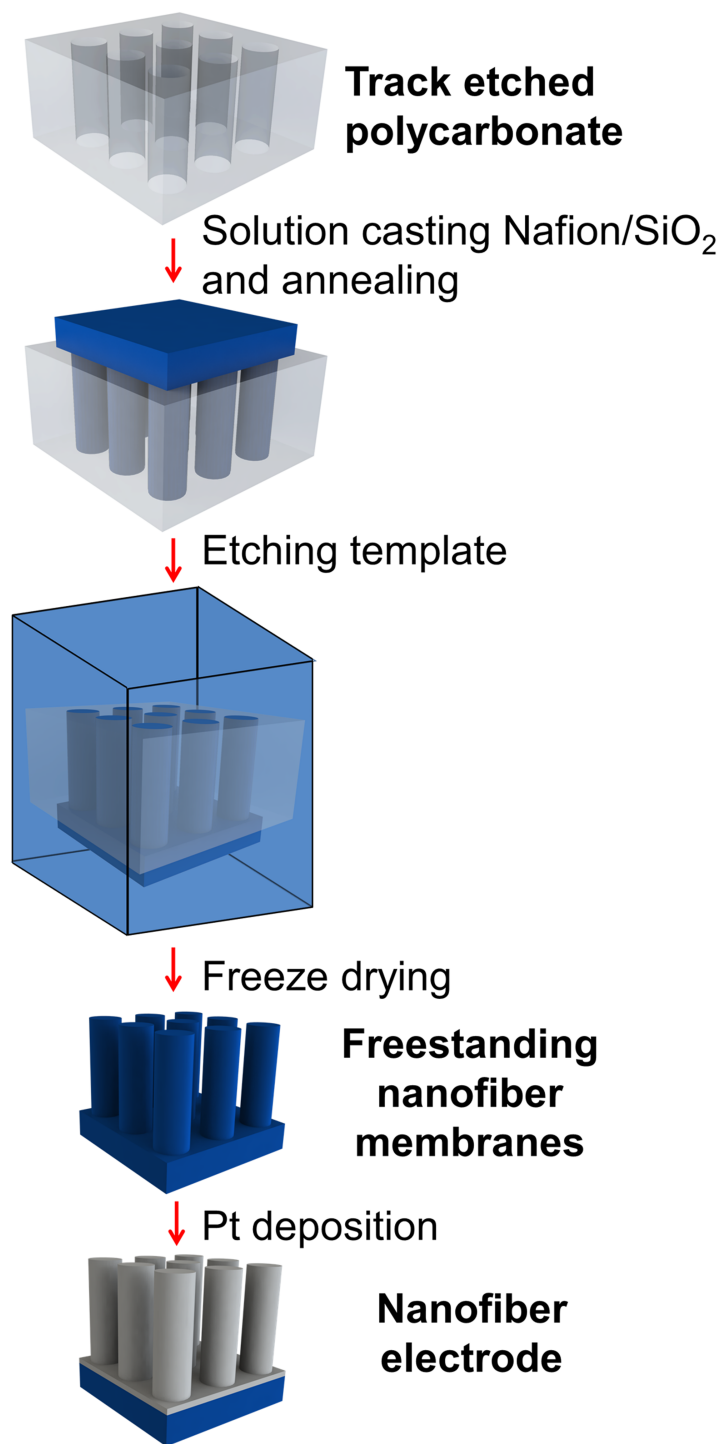


Figure 2.3: Schematic of the nanofiber electrode fabrication procedure.

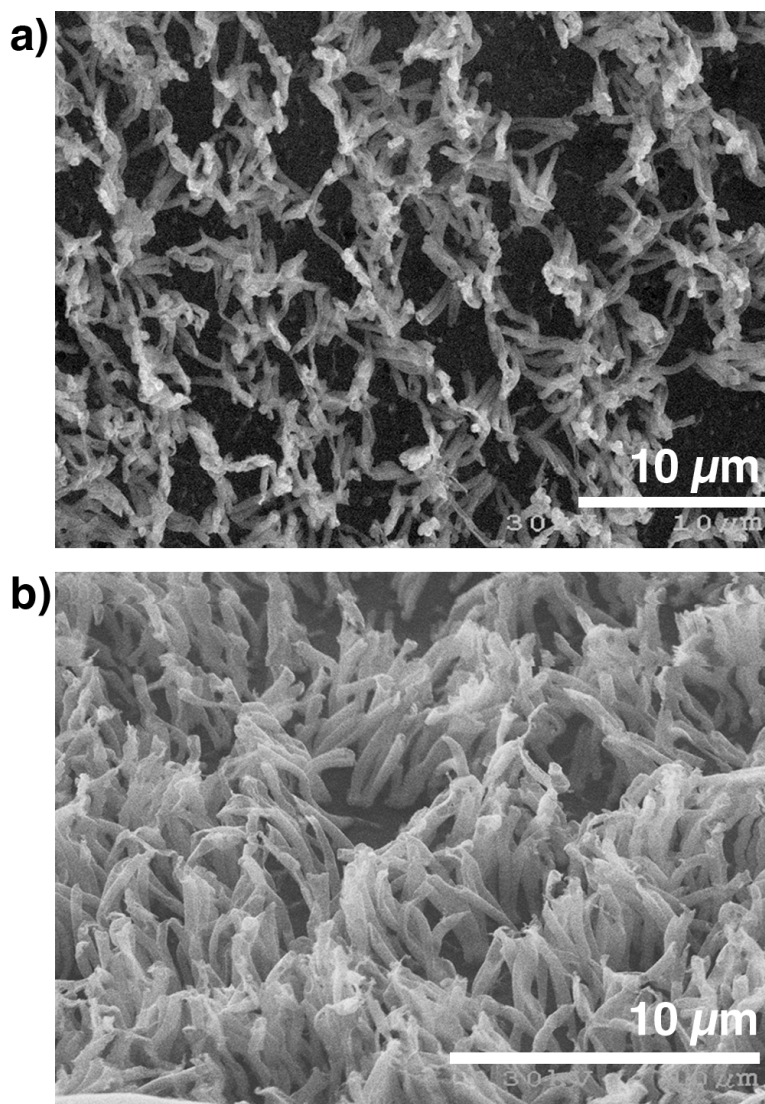


Figure 2.4: SEM images of free-standing Nafion composite nanofibers before Pt deposition. a) Top view. b) Side view.

at an angle of 15 degrees on both sides of the axis perpendicular to the sputtering base, to improve the distribution of Pt throughout the length of the nanofiber. However, given the line of sight nature of sputtering, it is unlikely the Pt properly coated the underside and membrane base of the fibers that could not be made visible. The other variation of the sputter deposited electrode addressed this issue by using the pre-sputtered TEP

that transferred Pt to the membrane surface and a small length of the nanofibers at their base. The electrode fabricated using pre-sputtered TEP template had a higher loading than the bare template because of the Pt transferred from the TEP. In the CVD process, platinum nanoparticles were deposited on the freestanding nanofibers from a Pt acetylacetonate precursor to form a conformal film of Pt on the nanofibers, an approach previously demonstrated for synthesizing Pt nanotubes [48] and electrodes for solid electrolyte systems [90, 91]. The membrane electrode assembly (MEA) was fabricated by adding a gas diffusion layer (GDL) to the cathode side and a conventional Pt/C gas diffusion electrode (GDE) for the anode as seen in Figure 2.5.

The performance of the nanofiber electrodes were compared to that of a commercial, planar Nafion 115 membrane with a cathode prepared by Pt PVD. The Nafion 115 MEA was prepared using the same combination of cathode GDL and anode GDE. The surface roughness of the Nafion 115 membrane is effectively 1, which is small compared to surface roughness of 21 for the nanofibers and provides normalization figures for evaluating the effects of surface area.

2.3 Experimental

2.3.1 Electrode fabrication:

A Nafion/SiO₂ composite solution was prepared by mixing 10 nm —20 nm SiO₂ particles (SigmaAldrich, St Louis, MO) with 20 wt. % Nafion solution (D2020, Ion Power,

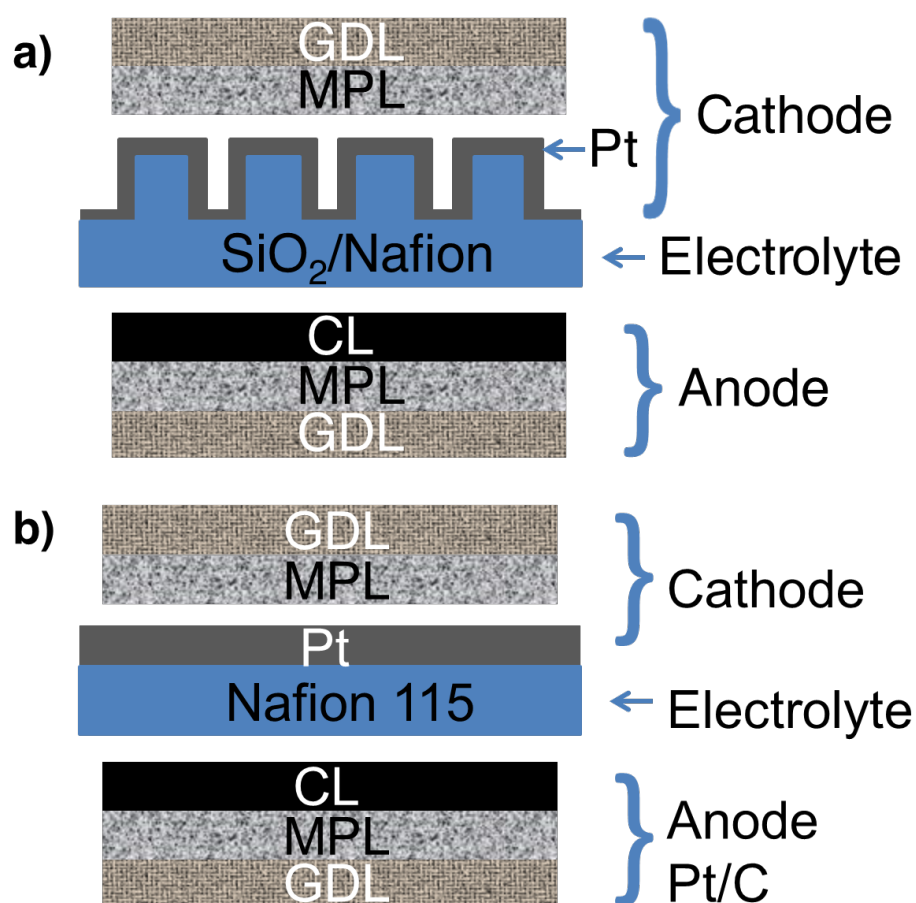


Figure 2.5: Schematic of MEA for a) nanofiber electrode. b) Nafion 115 electrode.

New Castle, DE). The resulting solution was 10 wt. % SiO_2 w.r.t. the weight of dry Nafion. The solution was then placed in an ultra-sonication bath for 30 min. After ultra-sonication, the composite solution was cast onto the 25 mm diameter TEP (E0225-MB, Structure Probe Inc., West Chester, PA). The solution was allowed to dry at room temperature for 24 hrs in a desiccator. The TEP was chemically etched by using methylene chloride (D37-1, Fisher Scientific, Pittsburgh, PA) for 5 min in an ultra-sonication bath. After etching the TEP, the Nafion nanofiber film was rinsed and stored in deionized water. The membrane was frozen along with the water by submerging them in liquid nitrogen. Subsequently, the frozen water was sublimated in a vacuum chamber under a pressure of 100 Pa. After freeze drying, a film of Pt was on the nanofibers by sputtering (PVD process) at an angle of 15 degrees on both sides perpendicular to the membrane. The sputtering conditions were 50 W DC and 25 sccm argon at 5 mTorr resulting in the deposition rate of 25 nm min^{-1} . The same conditions were used to sputter a 25 nm thick layer of Pt on the TEP for the MEA with pre-sputtered template. The Nafion 115 membrane was prepared by boiling the membrane for one hour each in the order of 3 wt. % hydrogen peroxide, deionized water, 0.5 M sulfuric acid, and deionized water. Under the same sputtering condition, Pt was deposited on one side of the Nafion membrane with a loading similar to bare template. The CVDNE was fabricated by depositing 1.4 mg of Pt on the free standing nanofibers in a N_2 -water vapor atmosphere from a platinum(II)(2,4)-pentanedionate ($\text{Pt}(\text{acac})_2$) precursor (Acros Organics). The nanofiber mat was fixed above a quantity of solid $\text{Pt}(\text{acac})_2$ in a deoxygenated and N_2 -flushed vacuum oven at an initial pressure of 0.3 bar. Temporal temperature varia-

tion induced the sequential sublimation and adsorption of the precursor molecules on and within the nanostructured mat followed by decomposition of the precursor to Pt⁰ at an ultimate temperature of at 160°C.

The anode GDE was prepared by painting a non-catalyzed gas diffusion layer (GDL) (SGL 24BC with micro porous layer (MPL), Ion Power) with in-house prepared Pt/C ink made of Pt/C catalyst (20% wt. Pt on carbon black, Alfa Aesar, Ward Hill, MA) and Nafion solution (D521, Ion Power, New Castle, DE). Pt loading for the anode was 0.4 $mg_{Pt}cm_{geo}^{-2}$ and the Nafion loading was 33% by weight. A non-catalyzed gas diffusion layer (GDL) (SGL 24BC with micro porous layer (MPL), Ion Power) was used in the cathode side. The MEA was assembled by stacking the components directly in the fuel cell hardware without hot pressing.

2.3.2 Fuel cell testing

Polarization curves

The active area of 1 cm² was masked from the electrodes using a gasket. The MEAs were tested using commercial fuel cell hardware (Scriber Associates, Southern Pines, NC). A fuel cell test stand (FCT-150 Biologic, France) was used to control temperature, humidity, and flow rate. Anode and cathode gases were H₂ and air, respectively. To condition the MEAs, voltages between 0.8 to 0.2 V was applied in decrements of 0.2 V, holding each voltage for 30 s at 80°C. This process was performed for 8 hrs and repeated

again after cooling the cell to room temperature.

Cyclic Voltammetry (CV)

The ECSA was measured using CV performed with fully humidified H_2 in the anode and N_2 in the cathode at 30°C. The measurements were done with a linear potential scan rate of 40 mV s⁻¹ between 0 and 0.8 V. Potentiostatic polarization curves were measured by holding potentials greater than 0.8 V for 60 s while potentials lower than 0.8 V were held for 10 min. The time averages of the last 30 s for potential greater than 0.8 V and the last 90 s for potentials lower than 0.8 V were used for plotting the polarization curves. Electrochemical impedance spectroscopy was performed at the end of each potential hold to obtain the high frequency resistance.

2.4 Results and Discussion

The resulting Pt loadings for the PVD nanofiber electrodes (PVDNEs) on the bare and pre-sputtered template electrodes were 0.036 and 0.089 $mg_{Pt}cm_{geo}^{-2}$ respectively. The loading on the Nafion 115 electrode was controlled to match the bare template electrode value of 0.036 $mg_{Pt}cm_{geo}^{-2}$. Pt thickness on the Nafion 115 electrode was 25 nm, which is also the theoretical thickness of Pt deposited by PVD on the nanofibers. Figure 2.6 shows an example of the Pt distribution around a Nafion nanofiber in a TEM image of the nanofiber arrays cross-section. As Figure 2.4 shows, we observe that the thickness

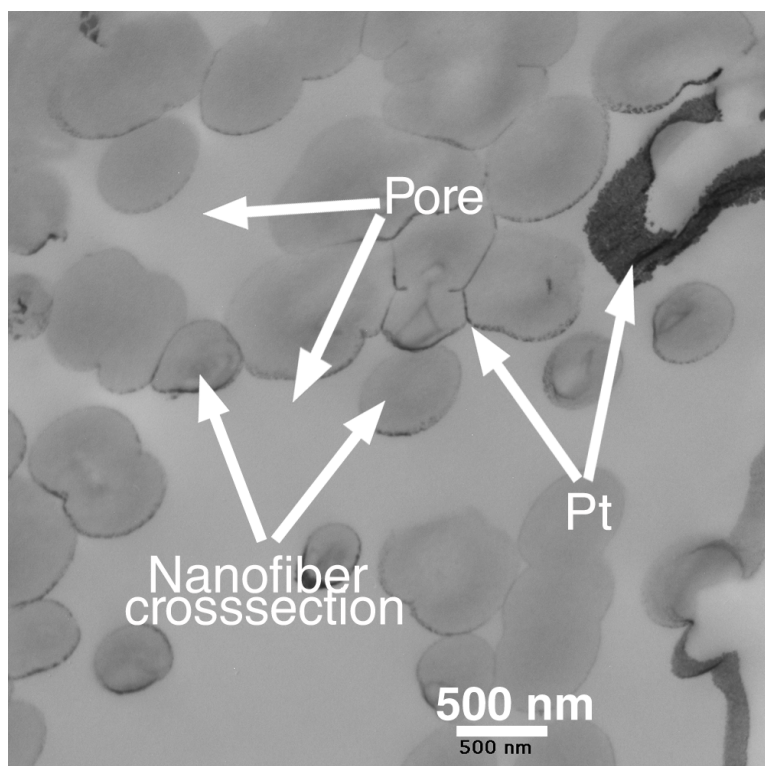


Figure 2.6: TEM image of a PVDNE, showing the Pt distribution around Nafion/SiO₂ nanofiber cross-section.

of Pt decreases when the distance between adjacent nanofibers decreases and the local support surface area increases. The TEM image also shows how the orientation of the nanofibers prevents the PVD coating of Pt on the underside of the nanofibers. As noted above, this is partially resolved by a pre-sputtered template. However, sputtering Pt onto the template does not deposit Pt at any meaningful distance into the TEP pores as was confirmed by nano-CT imaging of the pre-sputtered template.

Based on the observations above, it is evident that PVD did not provide high Pt coverage on the nanofibers. CVD is known to provide conformal deposition of metals on irregular surfaces, such as the unexposed parts of the nanofibers. A MEA with the

CVD nanofiber electrode (CVDNE) was assembled similar to the pre-sputtered and bare template electrode. The resulting loading on the CVDNE was $0.439 \text{ mg}_{\text{Pt}} \text{cm}_{\text{geo}}^{-2}$. From the loading and density of Pt, it was estimated that the theoretical non-porous thickness of the Pt on the nanofibers is approximately 108 nm. In future work, that thickness can be significantly reduced. Figure 2.7a and 2.7b show a CVDNE before assembly. We observe the coated nanofibers are partially fused together due to the notable thickness of this particular CVD coating. Figure 2.7c and 2.7d show a CVDNE and integrated membrane after electrochemical characterization and disassembly. We observed some nanofibers collapse, but the overall structure and thickness is intact. Figure 2.7c also shows the $40 \mu\text{m}$ thick cross-section of the integrated membrane that was cast with the nanofibers.

2.4.1 Cyclic Voltammetry

The ECSA of the electrodes was measured to study the resulting Pt active area surface and the corresponding surface roughness factor. The ECSA was calculated from the hydrogen desorption area of the CVs in Figure 2.8. The ECSA for bare and pre-sputtered template electrode are 6.5 and $10 \text{ m}_{\text{Pt}}^2 \text{g}_{\text{Pt}}^{-1}$, respectively, yielding surface roughness factors of 3.6 and $5.8 \text{ cm}_{\text{Pt}}^2 \text{cm}_{\text{geo}}^{-2}$, respectively. For comparison, our Nafion 115 electrode has an ECSA and surface roughness factor of $0.78 \text{ m}_{\text{Pt}}^2 \text{g}_{\text{Pt}}^{-1}$ and $2.1 \text{ cm}_{\text{Pt}}^2 \text{cm}_{\text{geo}}^{-2}$. The roughness factor of 2 is most likely a result of the hydrogen adsorption of both sides of the Pt film (air and Nafion interfaces) since protons are known to exhibit long range

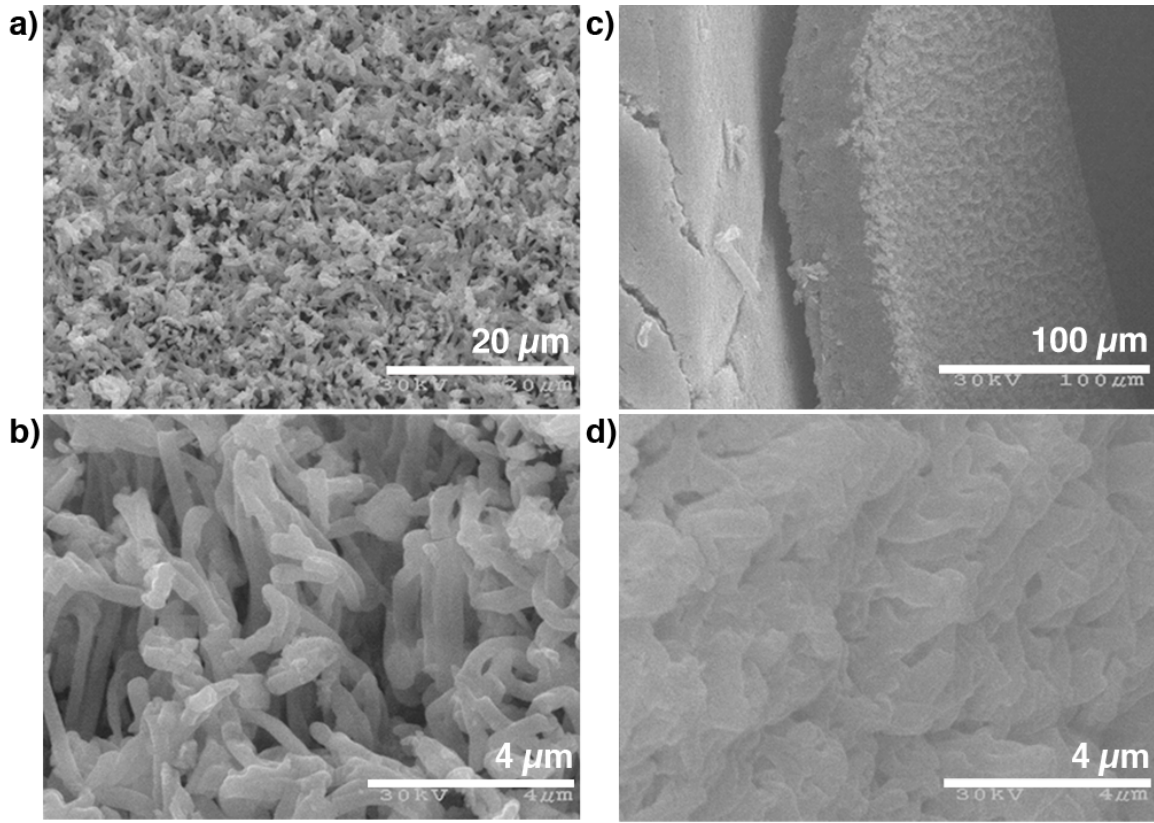


Figure 2.7: SEM images of the CVDNE electrode before testing. a) Top view of the nanofibers. b) SEM images of the CVDNE electrode after characterization: c) Membrane thickness of 40 μm . d) nanofibers are still intact after testing.

transport on continuous Pt surfaces that are not in contact with polymer electrolyte [92, 93]. The surface roughness for pre-sputtered template electrode is higher than the bare template since the former has better distribution and also has continuous film of Pt near at the bottom of the nanofibers along the membrane surface and the base of the nanofibers. The $2.2 \text{ cm}_{Pt}^2 \text{ cm}_{geo}^{-2}$ increase of roughness with the pre-sputtered template over the bare template is consistent with the large planar membrane surface area

(with Nafion 115 roughness) that would be coated using the pre-sputtered template and otherwise blocked by the nanofibers.

The CV results indicate that the Pt coating on the membrane surface of the DNE MEA has sufficient electronic connectivity to the GDL. However, that does not indicate the quality of the electronic connectivity on the nanofibers. It is also noted that the CV for the pre-sputtered template (Figure 2.8a) shows more distinct peaks corresponding to hydrogen adsorption at different Pt crystal sites. However, the distinct strongly adsorbed hydrogen (high potential) peak is not clearly distinguishable in the CVs for the bare template and Nafion 115 electrodes. Further investigation is necessary to interpret the behavior of the hydrogen adsorption/desorption peaks for bare template and Nafion 115 electrodes. For now, we suggest that surface state of the Pt interface transferred from the template is likely distinct from the outer surface prepared during PVD onto the Nafion. For example, we expected the transferred surface to be flatter and less disordered. Figure 2.8b shows the CV of the CVDNE electrode along with the pre-sputtered template PVDNE CV for comparison. From the hydrogen desorption area, we estimated an ECSA of $55 \text{ m}_{Pt}^2 \text{ g}_{Pt}^{-1}$, which is 9 times the higher than the pre-sputtered template electrode. The surface roughness is $240 \text{ cm}_{Pt}^2 \text{ cm}_{geo}^{-2}$, which is similar to that for conventional Pt/C catalyst based electrodes and consistent with prior uses of this CVD process in preparing Pt electrodes.

The ideal surface roughness of the nanofibers is 21, which is greater than 6 times higher in magnitude than the Pt surface roughness for the PVDNE with a bare template.

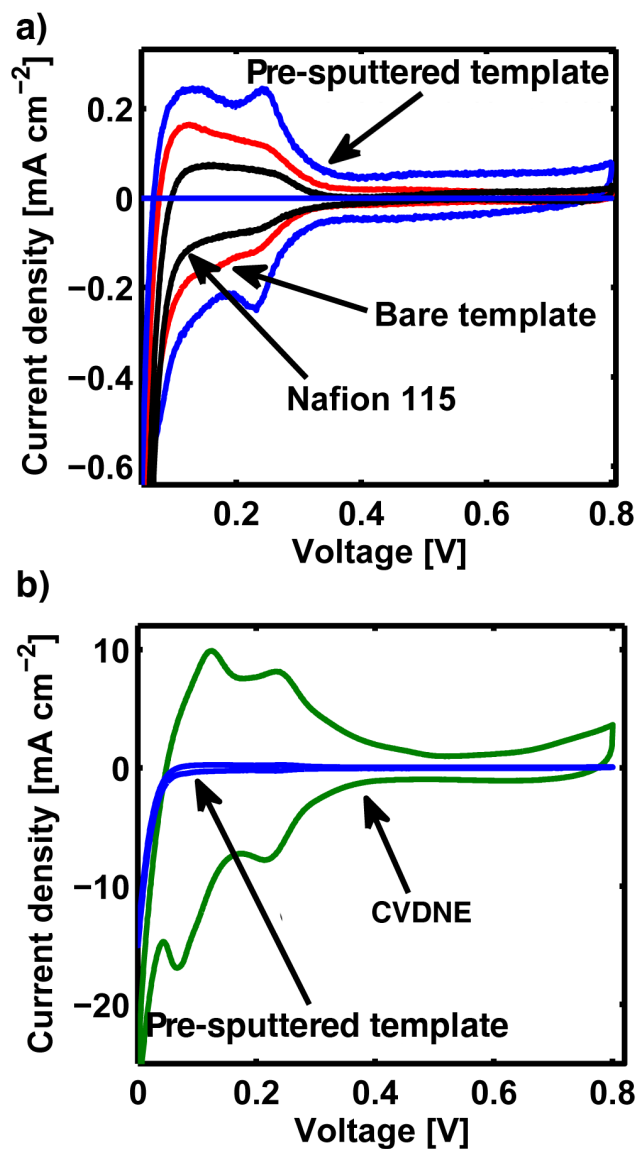


Figure 2.8: CV with the hydrogen crossover correction at 30°C and fully humidified gases. a) CV for the PVDNEs. b) Comparing CV of the CVDNE and the pre-sputtered template electrode. CVDNE has an ECSA of order of magnitude higher than the pre-sputtered template. The scan rate was 40 mV s⁻¹.

This suggests that the nanofibers are not well coated and/or the Pt is not electronically well connected. The situation is modestly improved with the pre-sputtered template, but the ideal surface area is still 4 times higher than the measured result. In dramatic contrast, the CVDNE provided an order of magnitude higher Pt roughness compared to the PVD coated nanofibers. Prior electron microscopy of the CVD Pt coating shows that coating is, in fact, porous and formed of fused Pt nanoparticles with high surface area [48, 90, 91]. There is an important distinction to be made at this point. The ECSA of the PVDNEs is a result of the external surface area of the dense films, whereas the ECSA of the CVDNE is a function of the volumetric Pt surface area within the internal volume of the porous CVD coating. This internal surface area is what causes the roughness factor of the CVDNE to be an order of magnitude higher than the ideal roughness factor of the nanofibers. Furthermore, this shows that the CVDNE ECSA is only a function of loading and not the support roughness. However, the CVDNEs cathode performance in a PEFC does depend on nanofiber roughness surface area since transport efficacy is not captured by these ECSA measurements.

2.4.2 Polarization Curves

We now present the PEFC operation characterization of the nanofiber electrodes. Here, the testing has been done with air and hydrogen feed gases, whereas much of the prior literature on sputtered thin-film Pt electrodes has included mostly polarization curve studies with oxygen instead of air, which increases apparent ORR activity and reduces

oxygen mass transport losses. The electrodes survived the different testing procedure discussed later in the experimental section. Figure 2.9a shows the polarization curves for nanofiber electrodes. The curves show that both of the PVDNEs perform better than the Nafion 115 electrode as expected due to the higher Pt surface area. The pre-sputtered template electrode generated a power density of $26 \text{ mW cm}_{geo}^{-2}$ at 0.6 V while bare template electrode generated, $13 \text{ mW cm}_{geo}^{-2}$ at 0.6 V, nearly half of pre-sputtered template (similar to ECSA difference). From Figure 2.9 we also observe that the Nafion 115 electrode performs 4-5 times lower than the nanofiber electrodes; generating $3.9 \text{ mW cm}_{geo}^{-2}$ at 0.6 V. It is clear there is a large activation over-potential for the PVDNEs. We suspect the high activation losses are due to a combination of a low specific activity of the untreated PVD Pt and the low ECSA. The composite membrane shows higher proton resistance as expected, about 3 times higher compared to a Nafion membrane. However, at these low currents the effect of Ohmic over-potential is small. Liquid water is also deteriorated the performance, and the cathode was operated at 150 kPa to create a pressure differential to drive water removal to the anode. High gas flow rates were also used to limit flooding.

The CVDNE was tested in the same condition as the PVDNEs. The CVDNE generated $106 \text{ mW cm}_{geo}^{-2}$ at 0.6 V, an order of magnitude higher than that for the PVDNEs. From Figure 2.9a, the CVDNE exhibited a lower activation over-potential as compared to the PVDNEs but was susceptible to flooding in the Ohmic region of the polarization curve. At high current density the performance improved. This performance increase at higher currents is consistent with the heat generated in the catalyst layer evaporat-

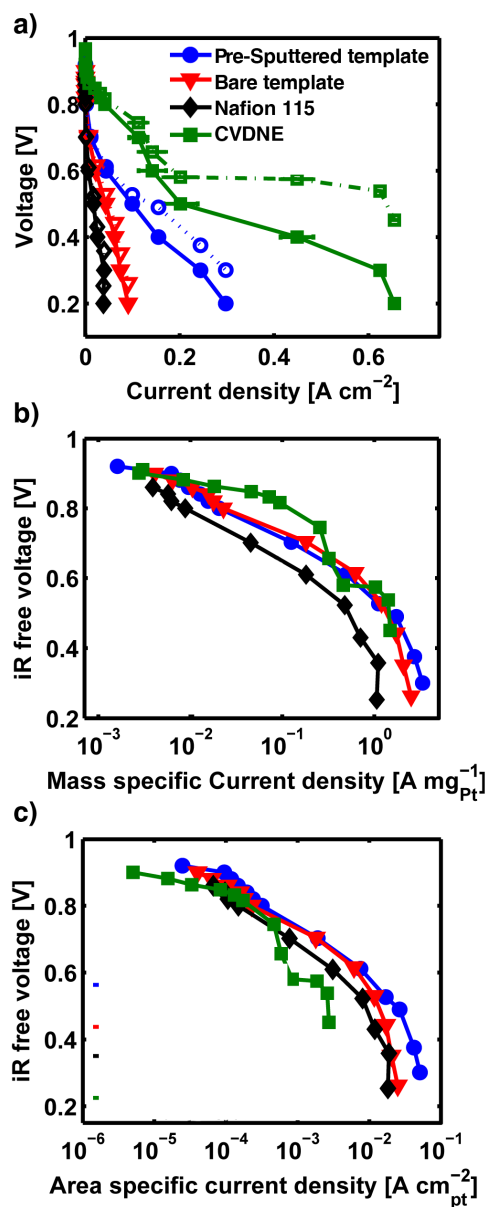


Figure 2.9: Fuel cell performance at 80°C, 100% relative humidity.

a) Polarization curves for the nanofiber electrode and the Nafion 115 electrode at a back pressure of 150 kPa in the cathode. Unfilled symbols are iR corrected polarization curves. b) Mass specific polarization curve. c) Surface area specific polarization curve.

ing liquid water that had accumulated in the electrode. This flooding and drying was also evident in the transients observed during operation. Water management is a pertinent issue for these film electrodes since they don't currently feature the hierarchical pore structure and mixed wettability of Pt/C electrodes. This issue could be potentially resolved by introducing hydrophobicity between the nanofibers.

Figures 2.9b and 2.9c compare the electrode polarization curves in terms of the mass and surface area specific activity. We observe that the two PVDNEs perform similarly on both mass and area basis, with the pre-sputtered electrode performing slightly better at high current density. Interestingly, we note that the Nafion 115 electrode performs worse even on a mass and area basis. This is likely due to an oxygen or proton transport resistance to Nafion—Pt or air—Pt interfaces, respectively. Performance of the pre-sputtered template electrode is similar to prior work on electrodes fabricated by sputtering Pt on membrane [33]. The CVDNE performed higher than prior reported work of electrode with Pt sputtered on a membrane with roughness factor 1 [35, 38]. It suggests the effect of the surface roughness on the performance is one of the considerable difference between the nanofiber electrode and the prior work. However, the performance of the nanofiber electrode is lower than reported for NSTF electrodes. Comparison of prior work to the nanofiber electrodes are presented in Table 2.1. Note, the Nafion 115 Pt PVD film was thicker than that for the other PVDNEs due to the reduced surface area, increasing the mass and charge transport resistances across the Pt film. When normalized to the mass of Pt in Figure 2.9b, the CVDNE performance was highest for potentials greater than 0.6 V, but below 0.6 V the performance deteriorates due to flood-

ing. With current density normalized by the Pt surface area (Figure 2.9c), the CVDNE performed notably lower than the PVDNEs in the activation region of the polarization curve. We suggest this is a result of the thick (100 nm), porous CVD coating used in this exploratory work, which could yield significant transport resistances in the coatings pores. Similar to the discussion above for the Nafion 115 electrode, the micropore structure of the thick CVD coating will severely restrict oxygen transport across the film. The thick layer may also contribute to increased ion transport resistance. The area specific polarization curve of the CVDNE is significantly lower than the other electrodes in the mass transport region. However, the geometric current density and actual water generation rate is much higher for this electrode, increasing the flooding and mass transport losses.

Regarding the transport resistances through the CVD coating, we put forth that the oxygen transport is more problematic than the ion transport. First, the small pores in the CVD coating are likely quite susceptible to flooding. Second, ion transport on continuous Pt surfaces has been shown to be quite facile, Work from McBreen *et al.*[98] and Paulus *et al.*[92] amongst others has shown that continuous films of Pt that extend beyond the contact with polymer electrolyte still participate in hydrogen adsorption and desorption CV measurements. Our recent work has shown that ORR could be quite active at significant distances away from the polymer electrolyte interface [93].

Table 2.1: Summary of PEM fuel cell electrode fabricated by Pt deposition directly on the membrane or extended surface.

Substrate	Pt loading	Surface roughness	Power Density at
	$[mg_{Pt}cm^{-2}]$	$[cm^2_{Pt}cm^{-2}]$	0.6 V $[mWcm^{-2}]$
Nafion[35]	0.04		18
Nafion[38]	0.2		4.5 with Pt black
Nafion[94]	0.014		0.25
Nafion[95]			3.8
Nafion[96]	0.04		0.15
Nafion[33]	0.084		26.4
NSTF[34]	0.15	14	600
NSTF[97]	0.15		750
Presputtered template	0.089	5.82	26.2
Bare template	0.039	3.63	13.4
CVDNE	0.439	240.04	106.1
Nafion 115 electrode	0.039	2.1	3.9

2.5 Summary

In this chapter we demonstrate a novel catalyst support comprising of high surface roughness vertically oriented polymer electrolyte nanofibers fabricated by solution casting onto a porous template. PVD and CVD were used for fabricating three different variations of the nanofiber electrode. The effect of surface roughness was compared to the electrode fabricated by depositing Pt directly onto Nafion 115. The CVDNEs had a higher useful coverage of Pt over the length of the nanofibers. The electrodes were characterized both morphologically and electrochemically. The surface roughness of Pt was higher by an order of magnitude for the CVDNE compared to the other electrodes. Analysis based on the polarization curves also showed that the CVDNE performed better than the PVD and planar variants. The results suggest that the Nafion nanofiber catalyst support electrode is a viable approach but necessitates further improvement by structure optimization.

Chapter 3

Resolving Electrode Morphology's

Impact on PGM-free Cathode

Performance using Nano-CT

3.1 Introduction

This chapter reports the use of nanoscale X-ray computed tomography (nano-CT) in characterizing the morphology and transport properties of PGM-free cathodes prepared using Los Alamos National Laboratories cyanamide-polyaniline-iron (CM-PANI-Fe) catalyst. The electrodes made with this catalyst typically exhibit a macro-scale hierarchical structure that is a result of the large ($1\text{-}10\ \mu\text{m}$) catalyst particles produced during syn-

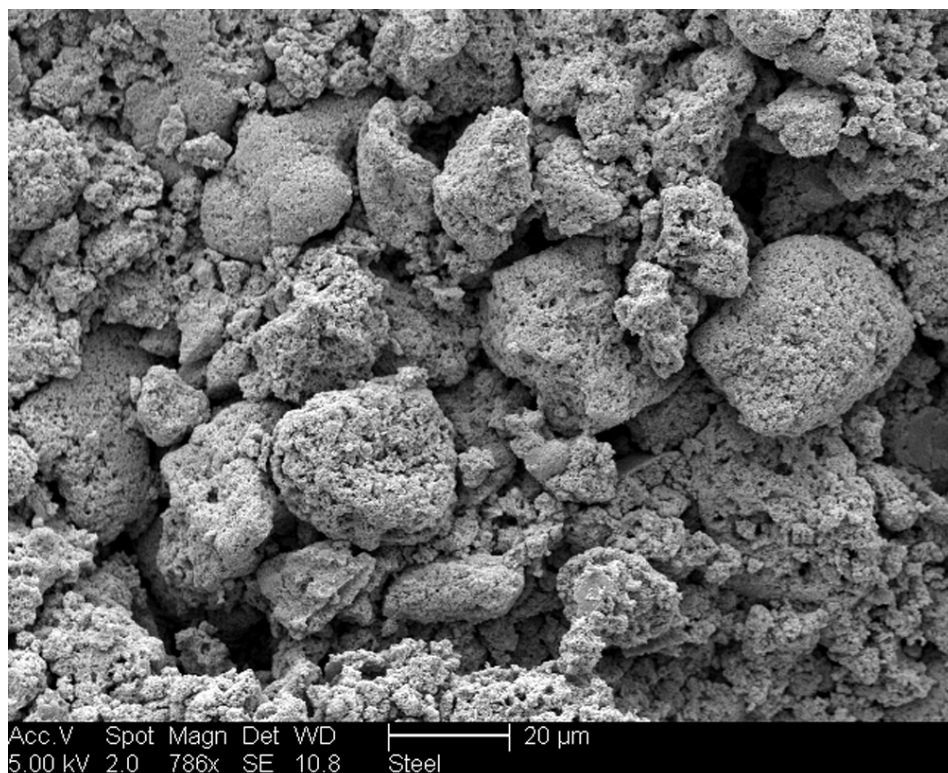


Figure 3.1: SEM image of a cathode prepared from the CM-PANI-Fe catalyst that yields a hierarchical structure due to the large porous catalyst particles that form large macro-pores between the particles.

thesis. The particles themselves are a hard fused network of the carbon support used in the preparation of the catalyst, which is similar in structure to a Pt/C electrode. Figure 3.1 shows an scanning electron microscopy (SEM) image of the top surface of an electrode prepared with this catalyst, where the large porous catalyst particles are clearly evident. This hierarchical structure is presumed to be one of the factors leading to the promising performance of these electrodes and their ability to achieve current densities greater than 1 Acm^{-2} at low fuel cell voltages when operating on atmospheric pressure

air. The electrodes studied here were prepared with three levels of Nafion loading (35, 50 and 60 wt. %) and their performance in fuel cells was experimentally characterized. These variations in Nafion loading dramatically alter fuel cell performance. The goal of the present analysis is two fold: 1) identify the origins of the impact of Nafion loading on fuel cell performance, and 2) extract detailed geometry, morphology statistics, and transport properties for future modeling studies.

For the present analysis, we carried out three separate nano-CT scans of each sample. We performed Zernike phase contrast scans at two levels of resolution and field of view so that we can resolve of the large particle structure as well as the pore structure within the particles. Our property estimations from the Zernike nano-CT images includes size distributions of pores as well as effective gas diffusivity and solid conductivity. Here we also report the first X-ray CT imaging of the ionomer distribution in fuel cell catalyst layers that we have achieved by ion-exchanging protons in the Nafion with Cesium (Cs^+) ions for contrast in a third scan using X-ray absorption contrast rather than phase contrast. We use the imaged ionomer distribution to simulate the proton transport and evaluate the effective conductivity. Finally, we discuss the correlation between the observed performance changes with variations in loading and the corresponding changes in catalyst layer structure.

3.2 Experimental

3.2.1 Catalyst and Electrode Preparation and Testing

Chung *et al.* [99] previously discussed the fabrication of the catalyst powder in detail. In brief, the catalyst powder was prepared by high-temperature heat treatment of dual nitrogen precursors (cyanamide and polyaniline) combined with a Ketjenblack carbon support and an iron salt ($FeCl_3$) followed by acid leaching in sulfuric acid and a second high temperature heat treatment. The cyanimide is included to assist in pore-forming and also serves as a nitrogen precursor for increased active site density. Catalyst inks were prepared by adding catalyst powder, isopropyl alcohol, de-ionized water and desired amount 5 wt. % Nafion solution (D521, Ion Power, New Castle, DE). The amount of Nafion suspension was varied to obtain catalyst layers with Nafion loadings of 35 wt. %, 50 wt. % and 60 wt. % while the amount of additional solvents, isopropyl alcohol (IPA) and deionized (DI) water, added was constant for all the three loadings. The catalyst ink was painted directly onto Nafion 211 membranes (Ion Power, New Castle, DE) to prepare catalyst coated membranes (CCMs) with a cathode catalyst loading of $4 \text{ mg}_{catalyst} \text{cm}^{-2}$. The thickness of resulting catalyst layers was approximately $100 \text{ }\mu\text{m}$. A 5 cm^2 membrane electrode assembly (MEA) was fabricated by using SGL 24BC gas diffusion layer (GDL) on the cathode side and a gas diffusion electrode (GDE, Johnson Matthey HiSPEC 9100) with a Pt loading of $2 \text{ mg}_{Pt} \text{cm}^{-2}$ was used for the anode. Polarization curves were measured with fully humidified H_2 and air supplied to the an-

ode and cathode, respectively, using flow rates of 200 sccm on both sides. The cell was operated at 80°C and 1.0 atm of partial pressure of H_2 and air (1.5 atm total pressure).

3.2.2 Nano-CT sample preparation

CCMs, prepared with the same catalyst and according to the same protocols as for fuel cell testing, were used to prepare samples for nano-CT imaging. For each sample, a small $500 \times 500 \mu m^2$ area of the CCM was cut using microscopy grade razor blades. The bare anode side of the membrane was mounted flat onto the top of a clothes pin head using epoxy. A laser micro-mill (ESI, QuikLaze 50ST2, Portland, OR) with a beam size of $1 \mu m$ accuracy was used to mill out a pillar of the catalyst layer. The milled pillar would remain within the field of view (FOV) of the nano-CT during rotation, which is desired for high quality reconstructions. Small gold particle fiducials were placed on top of the sample to correct for the sample drift during 3D reconstruction. This unstained version of the sample was used to image the solid and pore in the catalyst layer in Zernike phase contrast. Subsequently, the mounted samples were stained using a saturated solution of cesium sulfate (Cs_2SO_4 , Sigma-Aldrich, St. Louis, MO) in DI water (W2-20, Fisher Scientific, Pittsburgh, PA) for 78 hours to ion exchange protons in the Nafion with Cs^+ ions. The sample was then rinsed for five minutes in DI water to remove excess salt and avoid salt precipitation.

3.2.3 Nano-CT Imaging

The electrode architecture was imaged in 3D using a commercial, laboratory-scale nano-CT (UltraXRM L200, Xradia, Inc., Pleasanton, CA) with an 8 keV rotating copper anode X-ray source. The nano-CT has optics for two different resolution levels: 1) a large field of view (LFOV) mode with a voxel size of 64 nm and optical resolution of 120-150 nm within a 65 μm FOV, and 2) a high-resolution (HRES) mode with a voxel size of 16 nm and optical resolution of 50 nm within a 16 μm FOV. The nano-CT also has two different contrast modes for imaging: Zernike phase contrast and absorption contrast. Absorption contrast imaging mode provides contrast on the basis of material density and Z, whereas Zernike phase contrast provides images of low Z materials through the phase contrast artifacts as discussed earlier. The filtered back projection method was used to reconstruct the radiographs using proprietary software (Xradia, Inc., Pleasanton, CA). Reconstructed images were visualized using Avizo Fire (FEI Visualization Sciences Group, Burlington, MA).

For each sample, two Zernike phase contract scans were performed. The first was in the LFOV mode to resolve the macro-pore and catalyst particle structure and the second was a HRES scan of the micro-pores within the large catalyst particles. Due to the nature of Zernike phase contrast images of low Z materials, the image can only be distinguished into solid or pore, where the solid can be a mixture of materials that include carbon and Nafion. Absorption contrast with the LFOV optics was used to image the stained CCM to resolve the 3D distribution of the ionomer as well as any

remaining large Fe clusters.

3.2.4 Structural Morphology

Purely structural characterizations were performed using Avizo Fire and custom MATLAB (Mathworks, Natick, MA) code. The structural information provided here are the volume fractions (solid and pore), agglomerate size distribution (ASD), and pore size distribution (PSD). Unprocessed Zernike phase contrast images were converted to binary images by threshold segmentation. In order to generate PSDs for the entire hierarchical structure without double-counting intermediate pore sizes visible in both the LFOV and HRES images, the pores smaller than 500 nm in the LFOV images were closed (converted to solid) by a closing morphological operation prior to generating the hierarchical size distributions.

In generating the ASDs and PSDs, the region of interest (ROI) was the largest cuboid that could fit within the sample domain without entering the surrounding bulk air. The selected ROI for the solid region was divided into discrete agglomerates by using the bin-separate function in Avizo Fire, which separates domains based on concave interfaces between solid domains. The distribution was further processed using MATLAB to obtain the volume fraction for the distribution of the agglomerates. The pore size distribution was calculated based on inscribed spheres using custom MATLAB code.

3.2.5 Morphological Transport Properties

In addition to purely structural information, computed transport properties from the nano-CT images is valuable for directly evaluating the impact of structure on transport rates. These parameters typically result from evaluating transport processes within the electrode, in either the pore or solid domains, and evaluating the effective transport properties when considering the domain to be a representative elementary volume (REV). For the pore and solid domains, this includes the effective oxygen diffusivity, formation factor, and tortuosity. Also, from the ionomer distribution images, we use simulations to obtain the effective conductivity and tortuosity of the ionomer.

To obtain these parameters, pore/particle-scale finite element method (FEM) simulations were performed on the nano-CT images. The pore-scale simulation of gas transport follows that of Litster *et al.* [65], where a non-linear, conservative form of the Laplace equation for gas diffusion was solved:

$$\nabla \cdot (D_{pore} \nabla c) = 0 \quad (3.1)$$

where D_{pore} represents local diffusivity that is a function of location, and c is the concentration. The local diffusivity was calculated as a function of the local pore diameter because the pore diameters approach the mean free path of the gas and thus the diffusion is in the transition Knudsen diffusion regime where diffusion is further restricted by molecule-wall interactions. The spatially non-uniform diffusion coefficient based on local pore diameter was calculated using the Bosanquet formulation, which considers

Knudsen diffusion as a resistance in series with the molecular diffusion:

$$\frac{1}{D_{pore}} = \frac{1}{D_m} + \frac{1}{D_{kn}(d_{pore})} \quad (3.2)$$

where D_m is molecular diffusion which can be calculated as a function of temperature and pressure:

$$D_m = D_m^{ref} \left(\frac{T}{T_{ref}} \right)^{1.82} \left(\frac{p_{ref}}{p} \right) \quad (3.3)$$

The reference diffusion coefficient for oxygen used was $2.02 \times 10^{-5} \text{ m s}^{-1}$ at 298 K and 1 atm. The D_{kn} term is the Knudsen diffusion coefficient that is calculated from the local pore diameter:

$$D_{kn}(d_{pore}) = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi M}} \quad (3.4)$$

where R , T , and M represent the universal gas constant, temperature and molecular weight of oxygen, respectively. In the simulations of the cubic domains, the concentration on the inlet face was set to one and the opposite face was set to zero while the other adjacent faces were specified as no flux boundary conditions.

For electron conduction through the solid domain, the Laplace equation similar to Eq. 3.1 was used again but with D_{pore} replaced by a spatially uniform conductivity, σ , of 1 in the solid domain and 0 in the pore and c replaced with the electric potential, Φ . The specification of the boundary conditions were the same as the gas transport simulations.

Once a solution is obtained, the effective diffusivity can be calculated by the expres-

sion:

$$D_{eff} = \frac{J}{A} \frac{L}{\Delta c} \quad (3.5)$$

where J and A are the flux area integral and the area of the inlet, respectively, and L and Δc are correspondingly the distance and specified concentration difference between inlet and exit, respectively. The effective diffusivity can be related to the pores volume-average diffusion coefficient through the formation factor, k_f , using the formula:

$$D_{eff} = K_f \bar{D}_{pore} \quad (3.6)$$

where $\bar{D}_{pore}$ is volume-averaged diffusivity in the pores obtained by integration within the pore volume, V_{pore} :

$$\bar{D}_{pore} = \frac{1}{V_{pore}} \int_{V_{pore}} D_{pore} dV \quad (3.7)$$

The formation factor can also be expressed as a function of the pore volume fraction (porosity), ϵ , and tortuosity, τ :

$$K_f = \frac{\epsilon}{\tau} \quad (3.8)$$

and the effective diffusivity can be represented as:

$$D_{eff} = \frac{\epsilon}{\tau} \bar{D}_{pore} \quad (3.9)$$

Eq. 3.8 can then be used to extract a transport-specific tortuosity. As Litster *et al.* [65] discuss, the tortuosity can vary within a given geometry depending on the ratio of molecular diffusivity to Knudsen diffusivity, with tortuosity increasing with increased

Knudsen diffusion due to longer gas mean-free path conditions (lower pressure, higher temperature). Often, a power law scaling of effective diffusivity with volume fraction (*i.e.*, the Bruggeman correction) is used to model the increased tortuosity with lower volume fractions:

$$D_{eff} = \varepsilon^\alpha \bar{D}_{pore} \quad (3.10)$$

The symbol α in Eq. 3.10 is the Bruggeman factor, where higher values indicate high tortuosity and a higher sensitivity of the tortuosity to volume fraction.

The transport properties of the Nafion ionomer in the catalyst layers were also extracted from particle-scale simulations. The intensity from the absorption contrast imaging was used to assign the local volume fraction of Nafion and the resulting local conductivity. The proton conduction was simulated using the following non-linear, conservative form of the Laplace equation for spatially varying conductivity:

$$\nabla \cdot (\sigma_{local} \nabla \phi) = 0 \quad (3.11)$$

The intensity of the stained Nafion from the X-ray absorption directly correlates to the density of cesium ions within each reconstructed voxel through the partial volume effect in X-ray absorption computed tomography. The density of the Cesium is assumed to be proportional to the density of the sulfonic group in Nafion, assuming complete ion exchange and zero excess cesium retention. The results discussed later indicate these assumptions are acceptable. Estimating the Nafion volume fraction was eased by the presence of dense Nafion domains that provide the intensity for bulk Nafion. Given that the absorption signal intensity was negligible outside of the domains with-

out Nafion (*i.e.*, the air surrounding the sample), the volume fraction of Nafion, ε_N , could be approximated as:

$$\varepsilon_N = I/I_{bulk} \quad (3.12)$$

where I_{bulk} is the average intensity within a specified bulk Nafion domain within the image.

The spatially-varying, local conductivity was calculated from bulk Nafion conductivity, σ_{bulk} , using the following expression that features a Bruggeman correction to reflect the tortuosity of the Nafion at length-scale below the resolution of the nano-CT image (*e.g.*, the tortuous Nafion distribution within the small meso-pores and micro-pores of the catalyst particles):

$$\sigma_{local} = \varepsilon_N^{1.5} \sigma_{bulk} \quad (3.13)$$

Bulk conductivity value of 10 Sm^{-1} is used assuming fully hydrated Nafion film. The Nafions volume average effective conductivity, formation factor, and tortuosity are calculated in a similar fashion as those properties for gas diffusion. The resulting effective conductivity can be used to calculate the tortuosity using the expression:

$$\sigma_{eff} = \frac{\bar{\varepsilon}_N}{\tau} \sigma_{bulk} \quad (3.14)$$

where $\bar{\varepsilon}$ is volume fraction that is obtained by integrating the local volume fraction.

$$\bar{\varepsilon}_N = \frac{1}{V_{ROI}} \int_{V_{ROI}} \varepsilon_N dV \quad (3.15)$$

In our analysis and visualizations, the local current density was computed using the

gradient of potential as shown:

$$i = \sigma_{local} \nabla \phi \quad (3.16)$$

3.2.6 Numerical Method

The pore and particle scale transport property simulations were done using commercial FEM software (COMSOL Multiphysics v5.1, Comsol Inc., Burlington, MA). For the pore and solid domain simulations, segmented and binarized nano-CT data of the respective domains were used to generate a tetrahedral mesh using mesh generation in Avizo Fire that could be imported into COMSOL. For the local diffusion coefficient, D_{pore} , we first calculate local pore diameter in MATLAB using the method previously described by Litster *et al.* [65]. In brief, the pore diameter was calculated by using opening morphological operation on a spherical kernel. The diffusion coefficient was imported into COMSOL as a look-up table. For the proton conduction simulations, the normalized Nafion intensity data over the entire cubic domain from Avizo Fire was imported into COMSOL as a look-up table for computing local conductivity, and the tetrahedral mesh was generated in COMSOL for the entire cubic domain. The number of mesh elements was refined until our grid convergence criteria were met.

3.3 Results

The following results present the characterization of the three electrodes prepared from the PGM-free catalyst with Nafion loadings of 35, 50, and 60 wt. %. We briefly present the fuel cell performance, with a more in-depth experimental catalyst synthesis and electrochemical performance evaluation being beyond the scope of the present study. Next, the fuel cell performance results are followed by the imaging data and a detailed characterization of the morphological and transport properties. We use the fuel cell electrochemical performance results to elucidate the observed performance changes with Nafion loading. A further use of these results is in assigning accurate microstructure properties in fuel cell performance simulations.

3.3.1 Fuel cell Performance

Figure 3.2 shows the polarization curves for the CM-PANI-Fe electrodes with Nafion loadings of 35, 50 and 60 wt. %. Depending on the Nafion loading, there are significant differences in both the kinetic (high voltage) and mass transport (high current) regions of the polarization curves. The changes in the mass transport region are consistent with past observations with varying Nafion loading in Pt/C electrodes, where mass transport losses and water flooding increase with greater Nafion loading [100]. A distinct feature of the mass transport region in these curves, particularly in the 50 and 60 wt. % cases, is linear slope with little curvature. Typically, the dV/dI slope become

progressively steeper at higher currents. A similar polarization curve feature of a linear mass transport region was observed by Hess *et al.* [20] for ultra-thick Pt/C cathodes. In that work, potential measurements across the cathode thickness were used to show that this linear, low curvature, mass transport region is due to a fully-flooded cathode that severely hinders O_2 transport into layer. The O_2 starvation results in a large Ohmic drop through the catalyst layer to the MPL interface where ORR was still active. The Ohmic loss through the cathode yielded the apparent second Ohmic slope in the fuel cell polarization curves. This observation was recently confirmed on these PGM-free catalyst layers using the same microstructured electrode scaffold measurements of potential distribution [101].

The kinetic region of the polarization curves also shows a significant change with the increase in Nafion loading from 35 to 50 wt. %, with an apparent suppression of the catalyst activity with 35 wt. %. Although, very low Nafion loading has been shown to lower activity in Pt/C cathodes, the value of 35 wt. % is typical of an optimum amount for Pt/C catalyst [100]. Thus, this significant reduction in current at 0.8 V with 35 wt. % is initially quite surprising. These results will be investigated in the following results and discussions of the structure and transport characterization.

3.3.2 Nano-CT imaging

Figure 3.3 shows the nano-CT images of the PGM-free electrode hierarchical structure from the LFOV and HRES Zernike phase contrast scans. Figure 3.3a shows orthogonal

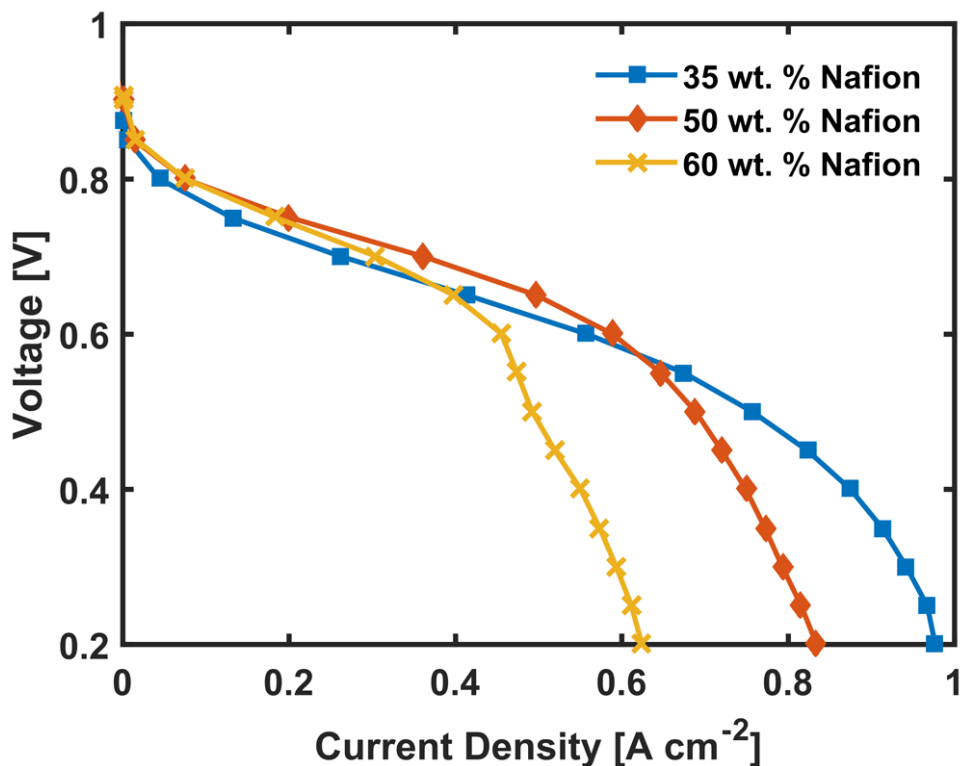


Figure 3.2: Polarization curves for CM-PANI-Fe cathodes with 35, 50, and 60 wt. % Nafion loading. The cell was operated at 80°C with air and hydrogen both at 100 % relative humidity and 1 atm.

virtual slices through the raw reconstructed LFOV image for the 35 wt. %, whereas Figure 3.3b shows the image after filtering to enhance the solid domain contrast and close the smaller pores (<500 nm), which are characterized in the HRES scans. Figure 3.4 the corresponding images for 50 and 60 wt. %. A benefit of nano-CT imaging is that it resolves the 3D interior pore space. These images show that the large particles seen in the SEM image (Figure 3.1) result large interior pores that are in the 1-10 μm size range. The large dense agglomerates in Figure 3.3b are themselves comprised of smaller pores. The HRES scan shown in Figure 3.3c is able to resolve the intra-particle pores with diame-

ters larger than 50 nm. The processed images in Figure 3.3b and 3.3c were segmented by manual thresholding for the computation of the hierarchical morphology and transport properties. The segmentation was verified by visually inspecting the boundaries with the gray scale virtual slices. Figure 3.5 shows the HRES Zernike phase contrast raw slices and the corresponding binary segmented images.

3.3.3 Structural Morphology

The volume fractions for both the pore and solid domains were calculated separately from LFOV and HRES images. The pore space remaining after closing the small <500 nm pores in the LFOV image (Figure 3.3b) are termed the macropores, and for convenience the sub-500 nm pores from the HRES images are termed micropores. In this way, the two pore sizes are distinctly characterized from the two Zernike phase contrast scans. Table 3.1 shows the porosity for the macropores and micropores in electrodes with three different Nafion loadings. The micropore porosity were similar in all the three different electrodes while the macropores show significant variation in pore volume fraction, likely due to variance from the large size of the macropores relative to the FOV and cathode thickness. Porosity obtained in the segmented LFOV images is termed macro and in HRES is micro. By assuming the micropore porosity is typical of the catalyst particles, the total porosity of the catalyst layer for all pores > 50 nm can be approximated by the expression:

$$\varepsilon = \varepsilon_{macro} + \varepsilon_{solid}\varepsilon_{micro} \quad (3.17)$$

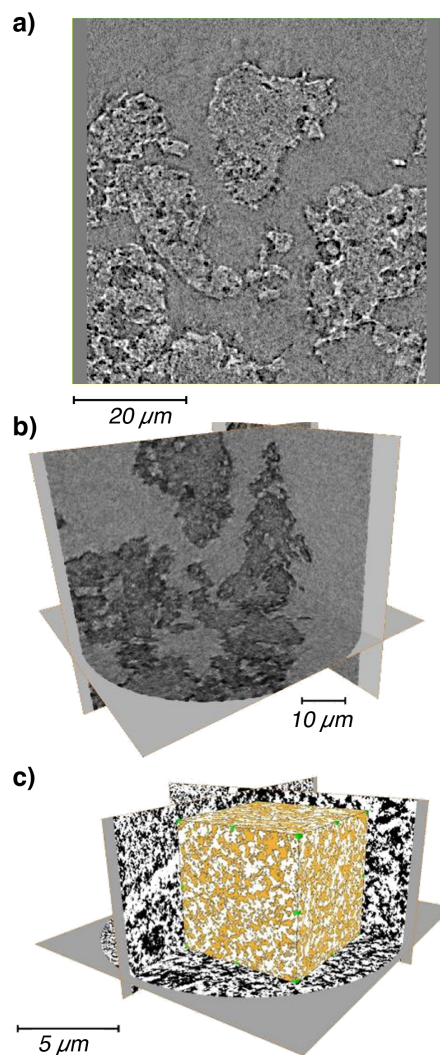


Figure 3.3: The hierarchical structure of the CM-PANI-Fe electrodes. Virtual slice of the PGM-free catalyst layer with 35 wt.% Nafion loading in LFOV imaging with 120 nm resolution a) before image processing and b) after image processing and morphological closing. c) HRES (50 nm resolution) imaging of the pores within the catalyst.

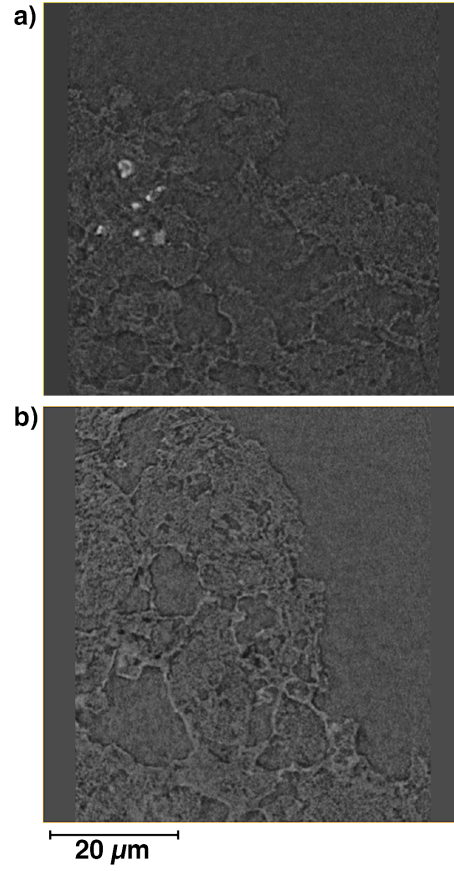


Figure 3.4: Nano-CT LFOV virtual slices of the PGM-free catalyst layer with a) 50 wt. % and b) 60 wt. % Nafion loading

where ε_{solid} is the macro-scale solid volume fraction from the processed LFOV image:

$$\varepsilon_{solid} = 1 - \varepsilon_{macro} \quad (3.18)$$

The derivation of the effective porosity is shown below:

$$v_{pore} = v_{macro} + v_{micro} \quad (3.19)$$

where v is volume and subscripts pore, macro and micro are effective pore, macro-pore

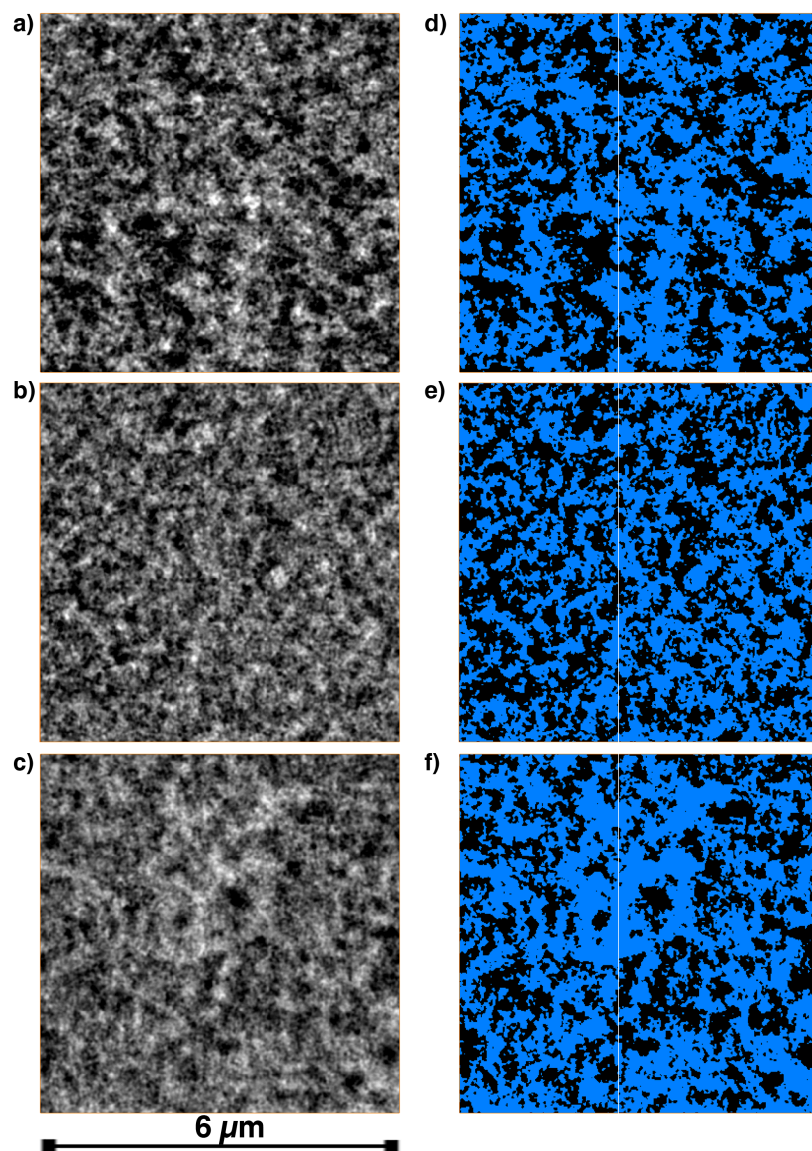


Figure 3.5: Segmentation of Nano-CT data. Raw grey scale virtual slice for a) 35, b) 50 and c) 60 wt. % Nafion loading and the corresponding segmented binary image d) 35, e) 50, and f) 60 wt. % Nafion loading. In the segmented image, blue corresponds to solid domain and black corresponds to pore domain.

and micro-pore respectively. Porosity of the catalyst layer is defined as

$$\varepsilon_{pore} = \frac{v_{pore}}{v_{total}} \quad (3.20)$$

Combining Eq. 3.19 and Eq. 3.20 we obtain

$$\varepsilon_{pore} = \frac{v_{macro} + v_{micro}}{v_{total}} = \frac{v_{macro}}{v_{total}} + \frac{v_{micro}}{v_{total}} \quad (3.21)$$

In first term in Eq. 3.21 represent the micro-porosity.

$$\varepsilon_{pore} = \varepsilon_{macro} + \frac{v_{micro}}{v_{total}} \frac{v_{solid}}{v_{solid}} = \varepsilon_{macro} + \frac{v_{micro}}{v_{solid}} \frac{v_{solid}}{v_{total}} \quad (3.22)$$

Porosity obtained in HRES imaging is presented by

$$\varepsilon_{micro} = \frac{v_{micro}}{v_{solid}} \quad (3.23)$$

where v_{micro} is the volume of pore in obtained from HRES, v_{solid} is the total volume of dense agglomerates. By combining Eq. 3.22 and Eq. 3.23 one obtains Eq. 3.17.

In general, volume normalization of any pore volume specific parameter ζ , which

Table 3.1: Structural parameters computed from Nano-CT imaging.

Nafion wt. %	Macro-porosity, ε_{macro} [-]	Micro-porosity, ε_{micro} [-]	Total Porosity, ε [-]
35	0.4	0.47	0.68
50	0.17	0.49	0.58
60	0.21	0.46	0.57

exists at both length scales can be expressed assuming linear mixing as:

$$\zeta = \frac{\zeta_{macro}\varepsilon_{macro} + \zeta_{micro}\varepsilon_{micro}\varepsilon_{solid}}{\varepsilon} \quad (3.24)$$

Figure 3.6 presents 3D renderings of the solid domains from the LFOV and HRES images. Figures 3.6a,b show the segmented images and Figures 3.6c,d show the corresponding solids after the binary separation process with labeling by color. The benefit of the separated solids is that it allows us to generate ensemble statistics for the solids domain, which include length-scale and surface-area distribution. Here we report an effective diameter length scale, d , distribution for the solids that is based on the volume, V , to surface area, S , ratio (see Eq. 3.25) because the coupled transport and roughly first order reaction causes the ORR to concentrate towards the particle surface when transport limited, making this an appropriate length scale. Figure 3.7 shows the segmented volume and the corresponding separated volume for three levels of Nafion loading.

$$d = \frac{6V}{S} \quad (3.25)$$

Figure 3.8 shows the distributions of solid and pore effective diameters for the different Nafion loadings. The distributions have been normalized by the porosities such that volume percentage reported for each size is the percentage of volume of that particular quantity (*e.g.*, Figure 3.8a shows each macropore diameter bin as a percentage of the total macropore volume). From the macro-scale solid distribution in Figure 3.8a, we observe two distinct modes in the size distribution. The smallest mode is strongly centered around $0.8 \mu m$ and reflects the small separated solids in Figure 3.8c. This is not an artifact of voxel resolution, as the voxels are more than an order of magnitude smaller; it

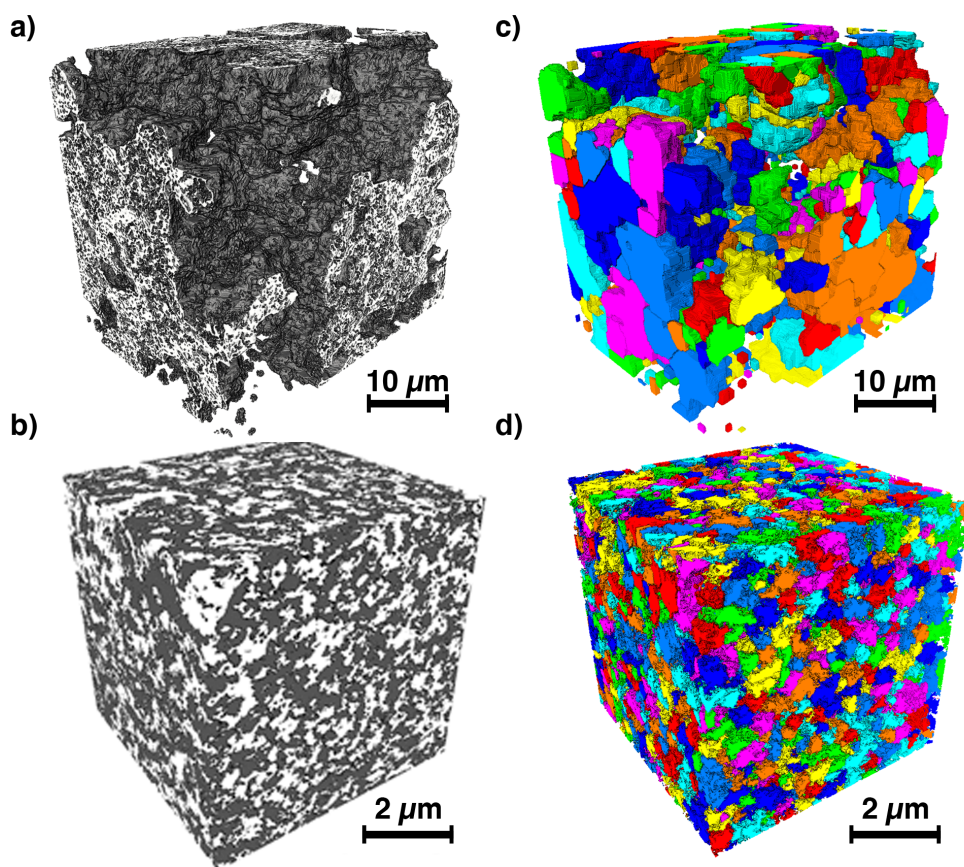


Figure 3.6: 3D rendering of the nano-CT image of the PGM-free electrode in a) LFOV and b) HRES. c) and d) show the respective images after segmentation, and morphological separation with color labeling.

is a result of distinct small solid domains that have been separated. The second, broader mode is centered around $3\text{--}4\ \mu\text{m}$ and reflects the abundance of large solids. There is also an evident shift of the larger solid domains to slightly large sizes when the amount of Nafion was increased from 50 to 60 wt. %, whereas there is little difference between 35 and 50 wt. %. As Figure 3.6b shows, the HRES scans solid domain size distribution is bimodal distribution with a main mode at roughly 200 nm and there is a minor mode at

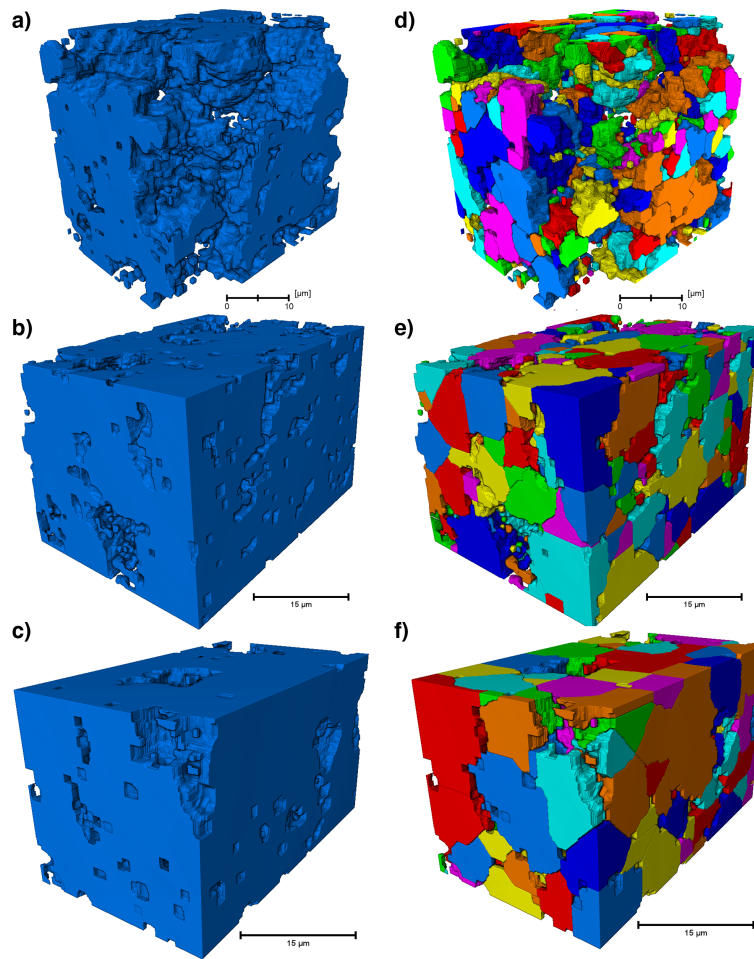


Figure 3.7: Segmentation and agglomerate separation of the PGM-free electrodes. The segmented 3D rendering for a) 35, b) 50 and c) 60 wt. % Nafion loading. The corresponding separated agglomerates for d) 35, e) 50, and f) 60 wt. % Nafion loading.

roughly 80 nm due to small separated solids. In this size distribution, there is a minor shift to larger solids with 60 wt. % Nafion.

Figures 3.8c,d present the macropore and micropore PSDs with the diameters computed from inscribed spheres. From the macropore PSD, we observe log-normal type

distributions with a single mode at approximately $1.8 \mu\text{m}$ and a large skew to larger pores. There is a minor shift to a greater proportion of smaller pores with the addi-

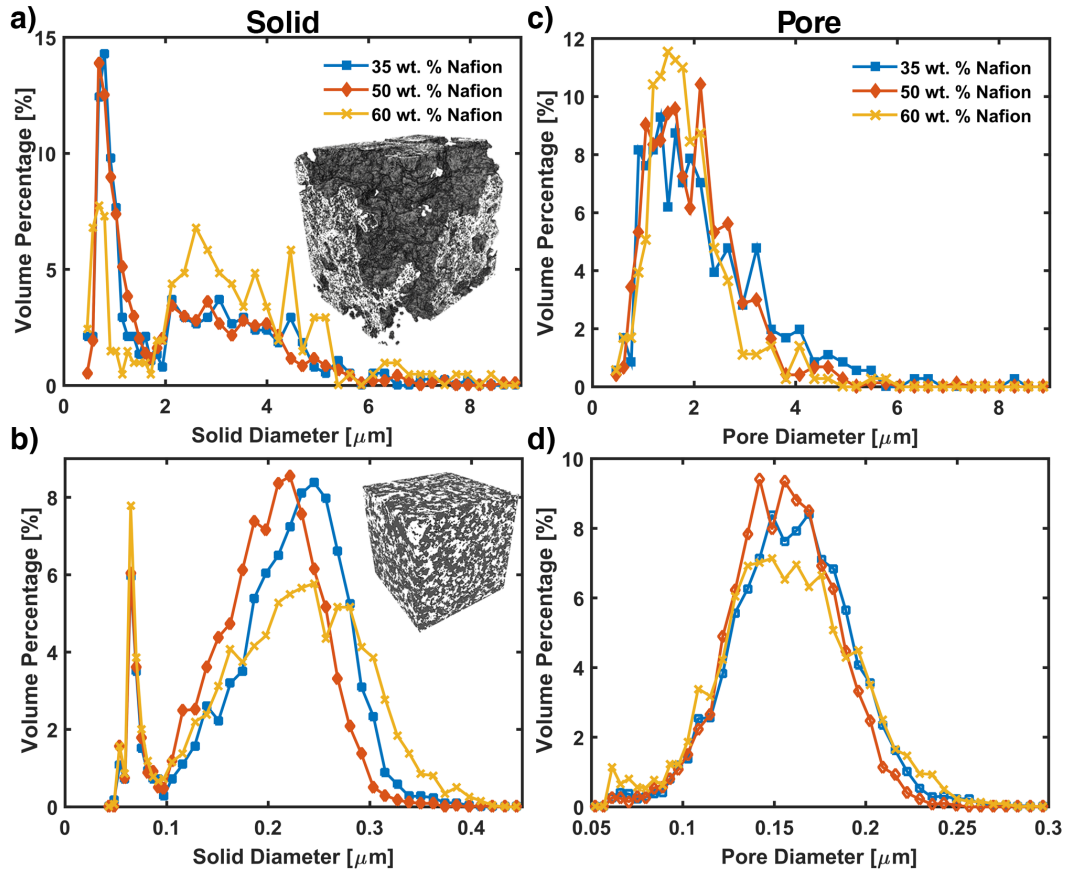


Figure 3.8: Size distribution of CM-PANI-Fe electrodes with varying Nafion loading. Solid (a & b) and pore (c & d) size distributions from the large field of view (a & c) and high resolution (b & d) nano-CT scans of the hierarchical PGM-free electrode. The internal features of the dense agglomerates were better resolved in the HRES images. Hence, the internal characteristics (pore diameters smaller than 500 nm) were removed from the LFOV images after which the size distribution was obtained.

tion of Nafion. In contrast, the micropore size distribution is largely unaffected by the addition of Nafion, with all three electrodes having a single mode and a symmetric Gaussian-like distribution around 160 nm. Note, one should use caution is trying to relate the solid and pore size distribution presented here as they are based on different length scale formulations.

3.3.4 Effective Gas Transport Properties

We now present the analysis of effective gas transport properties within the micropores using pore-scale simulation. A corresponding study of the macropores is not possible given the length-scale of the pores is too large to properly define a representative elementary volume (REV) within the LFOV field of view or even across the electrode thickness. For the micropore gas transport, a cubic ROI with 6 μm side lengths was selected within the dense particle domain. To generate statistical distributions of REV properties, the cube was further subsampled into eight cubes with 3 μm sides. The gas transport simulation was performed for all the eight subsamples to evaluate heterogeneity and develop correlations between porosity and effective diffusivity.

Figure 3.9 shows the results for the 35 wt. % cathode when the temperature and pressure for the simulation were specified as 80°C and 1 atm. Figure 3.9a shows the local diffusion coefficient, calculated using the Bosanquet formula shown in Eq. 3.2, where the larger pores feature significantly higher diffusion coefficients. Figure 3.9b shows the resulting 3D oxygen concentration distribution as well as streamlines of the

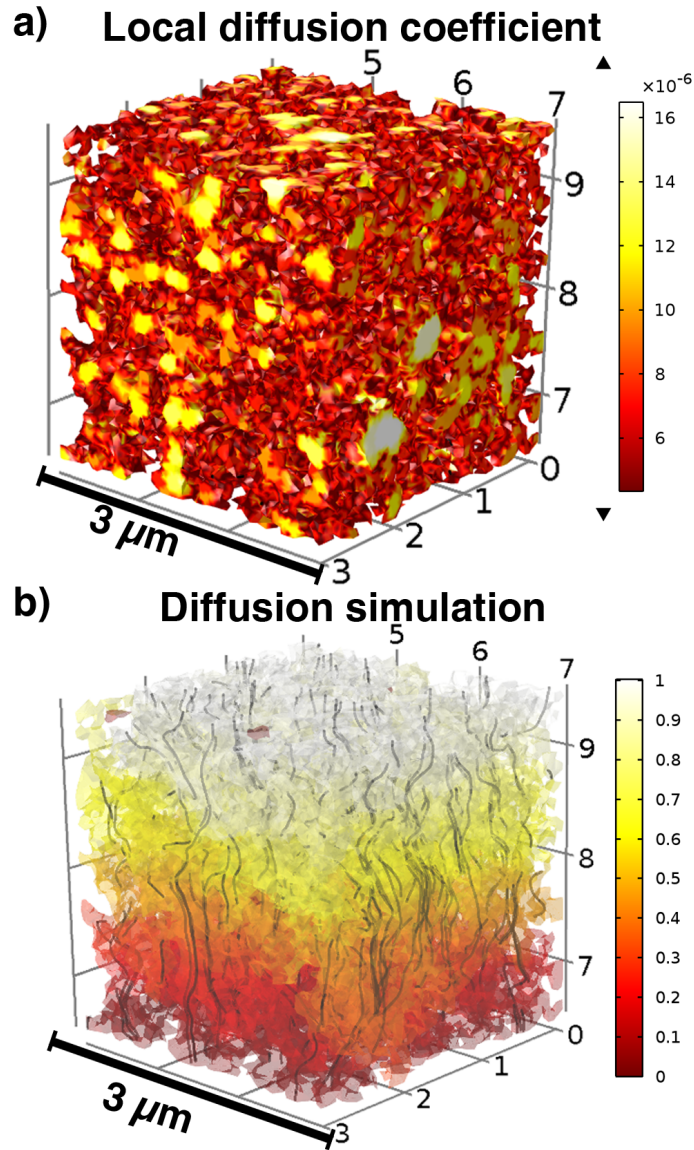


Figure 3.9: Effective transport property estimation for the micropores of the 35 wt. % electrode. a) Local diffusion coefficients within the pores. b) Oxygen concentration and flux streamlines of oxygen diffusion.

oxygen flux that highlight the tortuous oxygen path.

Figure 3.10a shows the formation factor for O_2 transport for the different subsamples

of each of the three different Nafion loading PGM-free electrode. The linear sensitivity does not hold for porosity porosity due to the increased tortuosity as the porosity decreases towards the percolation limit. There is also the additional effect of lower porosity being correlated with smaller pores and the greater influence of Knudsen diffusion that increases tortuosity. The formation factor was calculated for the solid domain representing the electron transport in the catalyst domain. Figure 3.10b presents the formation factor *vs.* solid volume fraction. The gas micropore tortuosity and the Bruggeman factor were also calculated for the using Eq. 3.8 and Eq. 3.9, respectively, with the average values reported in Table 3.2.

Table 3.2: Morphological transport properties computed from Nano-CT and pore scale diffusion simulation.

Nafion wt. %	Micro Porosity, ε_{micro} [-]	Micropore Formation Factor, κ_f [-]	Micropore Diffusion Coefficient, D_{eff} [m/s]	Bruggeman Factor, α	Micropore Tortuosity, τ [-]
35	0.47±0.02	0.19±0.02	1.90±0.17 x10 ⁻⁶	2.16±0.17	2.44
50	0.49±0.03	0.21±0.04	1.96±0.38 x10 ⁻⁶	2.19±0.05	2.37
60	0.46±0.02	0.17±0.03	1.69±0.33 x10 ⁻⁶	2.29±0.12	2.75

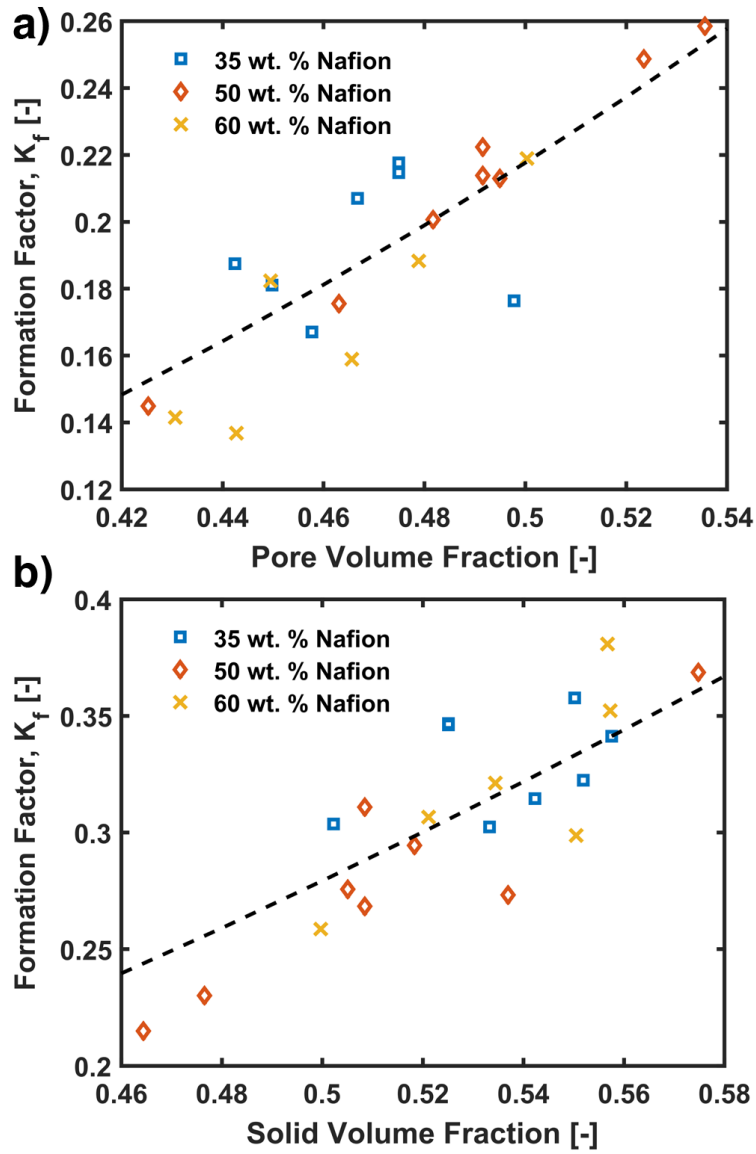


Figure 3.10: Formation factor vs. volume fraction for PGM-free electrodes with varying Nafion loadings for both the a) pore and b) solid domains. Simulations were performed for 80°C and 1 atm.

3.3.5 Water Retention Curves

It is commonly observed that thick PGM-free cathodes are highly prone to liquid water flooding of the pores that severely restricts oxygen transport. Thus, their liquid water uptake and transport characteristics are of key importance. Here, we use the pore size distributions of the electrodes to approximate their water retention curves, which are correlations between the static liquid water saturation (*i.e.*, fraction of pore volume filled with water) and the capillary pressure, where capillary pressure is defined as the pressure difference between non-wetting phase (air) and the wetting phase (water). In this analysis, we assume that the electrode is perfectly wetting due to the hydrophilic nature of the carbon and Nafion once wetted. In this case, the capillary pressure, p_c , in a given partially filled pore can be calculated from the pore radius using the Young-Laplace equation:

$$p_c = \frac{2\gamma}{r_c} \quad (3.26)$$

where γ is the surface tension of the wetting liquid and r_c is the pore radius. The surface tension was assumed to be a constant value of 0.625 Nm . To parameterize the curves, a log-normal distribution was fitted to the pore size distributions in Figure 3.8 to extract the mean radius, r_m , and the standard deviation of the pore size distribution, σ_{psd} . We can then define the saturation of the hydrophilic pores at any given p_c as the summation of the volume fraction of pores with a radius less than r_c . In this man-

ner, prescribing a log-normal description of the pore size distribution yields the Van Genuchten water retention curve [102], which is expressed as

$$s = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{\ln(r_c/r_m)}{\sigma_{psd}\sqrt{2}} \right) \right] \quad (3.27)$$

where s is the saturation for a corresponding pore radius r_c that can be related to capillary pressure using Eq. 3.26. The fitting of the log-normal curves and the generation of the water retention curve was performed separately on the macropore and micropore size distributions to provide a hierarchical description of the water saturations. In other words, the saturation of the macropores and micropores can be independently computed. Table 3.3 lists the Van Genuchten water retention parameters.

By combining the macropore and micropore water retention curves, an overall water retention curve can be approximated. The total saturation in the catalyst layer is then calculated from the expression:

$$s = \frac{s_{macro}\varepsilon_{macro} + s_{micro}\varepsilon_{micro}\varepsilon_{solid}}{\varepsilon_{macro} + \varepsilon_{micro}\varepsilon_{solid}} \quad (3.28)$$

Figure 3.11 shows the overall water retention curve constructed using Eq. 3.28 and the

Table 3.3: Parameters for the water retention curves.

Nafion wt. %	Micropore, $r_m [\mu m]$	Micropore, σ_{psd}	Macropore, $r_m [\mu m]$	Macropore, σ_{psd}
35	0.078	0.19	0.87	0.50
50	0.075	0.19	0.83	0.41
60	0.074	0.28	0.78	0.37

separate micropore and macropore expressions for saturation as a function of capillary pressure using Eqs. 3.26 and 3.27 with the parameters listed in Table 3.3. As these curves show, with increasing water content, the micropores fill at a relatively constant capillary pressure followed by a steep decline in the capillary pressure and then a less steep decline in capillary pressure as the macropores fill. The higher slope in the macropore region in comparison to the micropores is due to the wider standard deviation of macropores relative to their mean, *i.e.*, the broader the pore size distribution, the greater the variation in capillary pressure with saturation. The saturation value for the transition from micropore filling to macropore filling is a function of the macropore porosity, which is why the more macroporous 35wt. % Nafion sample shows a transition to macropore filling at a notably lower overall saturation.

Figure 12 shows the water retention curves for the PGM-free electrodes with varying Nafion loading for micropore and macropore separately. From Figure 3.12, the fit shows good agreement with the data for the micropores. While at higher saturation (≥ 0.95) or lower capillary pressure, the fit was unsatisfactory for macropores. This shift from fit was due to the higher pore diameter causing a longer tail in the distribution causing the deviation from the Van Genuchten correlation.

3.3.6 Nafion Distribution

In this section, we discuss the nano-CT imaging of the cesium stained electrodes used to study the 3D Nafion ionomer distribution in the PGM-free cathodes. The intention

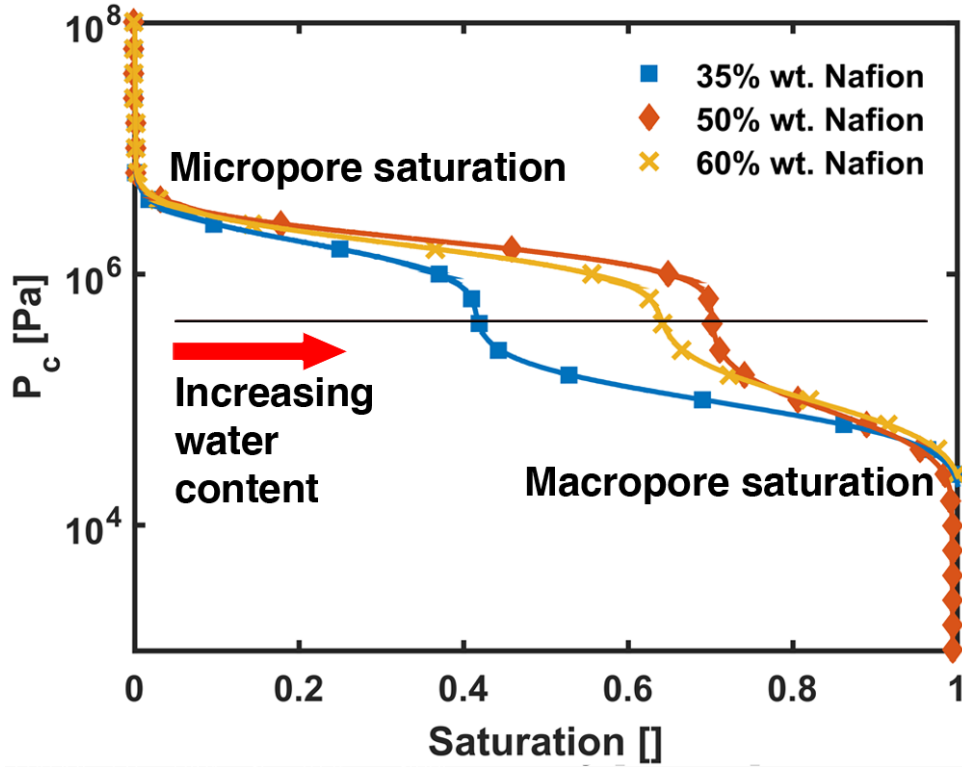


Figure 3.11: The water retention curves for combined micropore and macropore for the PGM-free electrodes with 35 wt. %, 50 wt. %, and 60 wt. % Nafion loading electrodes.

being to further elucidate the causes for the Nafion loading variations impact on performance. In these cases, X-ray absorption contrast is used to distinguish the Cs^+ stained Nafion. For a consistent, quantitative comparisons between the nano-CT images of catalyst layers with different Nafion loadings, the X-ray intensity, I_{X-ray} , was normalized using the intensity within the solid gold fiducial particle, I_{gold} , and the surrounding air, I_{air} , using the equation below:

$$I = \frac{I_{raw} - I_{air}}{I_{gold} - I_{air}} \quad (3.29)$$

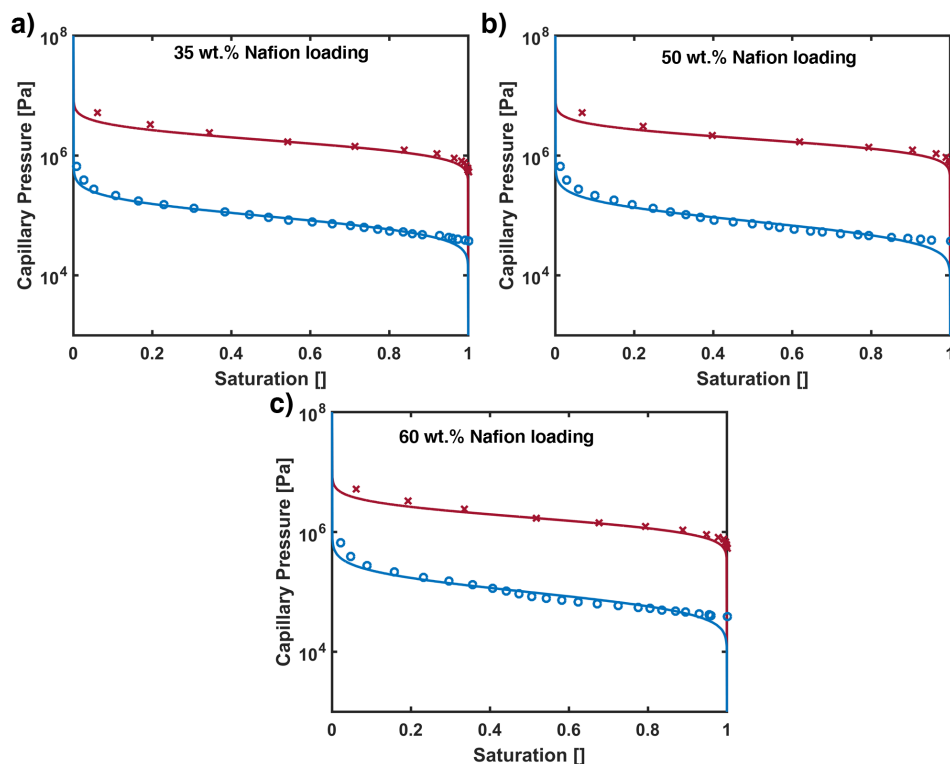


Figure 3.12: The water retention curves for the a) 35 wt. %, b) 50 wt.%, and c) 60 wt. % Nafion loading electrodes. Water retention curves for calculated separately the micropores (shown as circles) and macropores (shown using cross) in the electrode. The continuous lines represent the Van Genuchten correlations generated by fitting a log-normal distribution to the nano-CT characterized pores size distributions shown in Figure 3.8.

Figure 3.13 shows the absorption contrast images of the 50wt. % Nafion sample before and after the cesium staining. Both of these images have been normalized according to Eq. [24], thus the color intensity values in each image corresponds to the same X-ray absorption. As this comparison shows, there is little absorption contrast prior to staining,

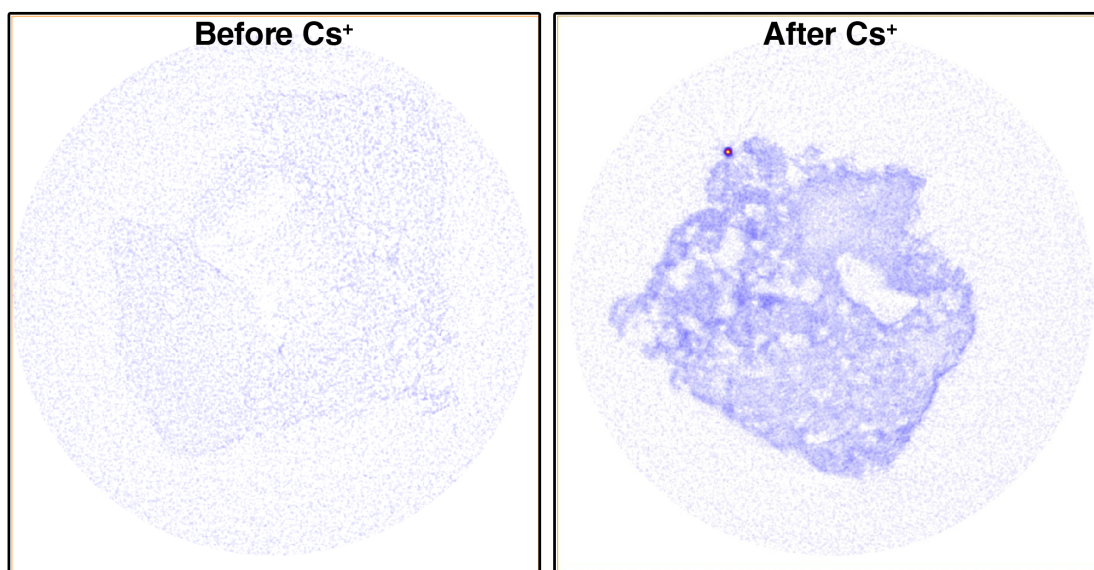


Figure 3.13: Absorption contrast virtual slices of the same 50wt. % Nafion cathode sample, before and after staining the Nafion with cesium ions.

with the exception of some dispersed iron agglomerations that are easily distinguished by significantly higher absorption than the stained Nafion.

Figure 3.14 shows reconstructed virtual slices for the catalyst layer with 50 wt. % Nafion loading for imaging in both the absorption (Figure 3.14a) and Zernike phase contrast (Figure 3.14b) modes at the same in-plane cross-section. As Figure 3.14b shows, the Zernike phase contrast can distinguish the pore from the solid, but cannot clearly distinguish the Nafion due to low Z-contrast with phase contrast imaging. In comparison, the absorption contrast image in Figure 3.14a shows the stained cesium distribution that is distinct from the electrode structure in Figure 3.14b. In the following presentations of the Nafion distributions, we provide evidence that this is specifically the staining of the

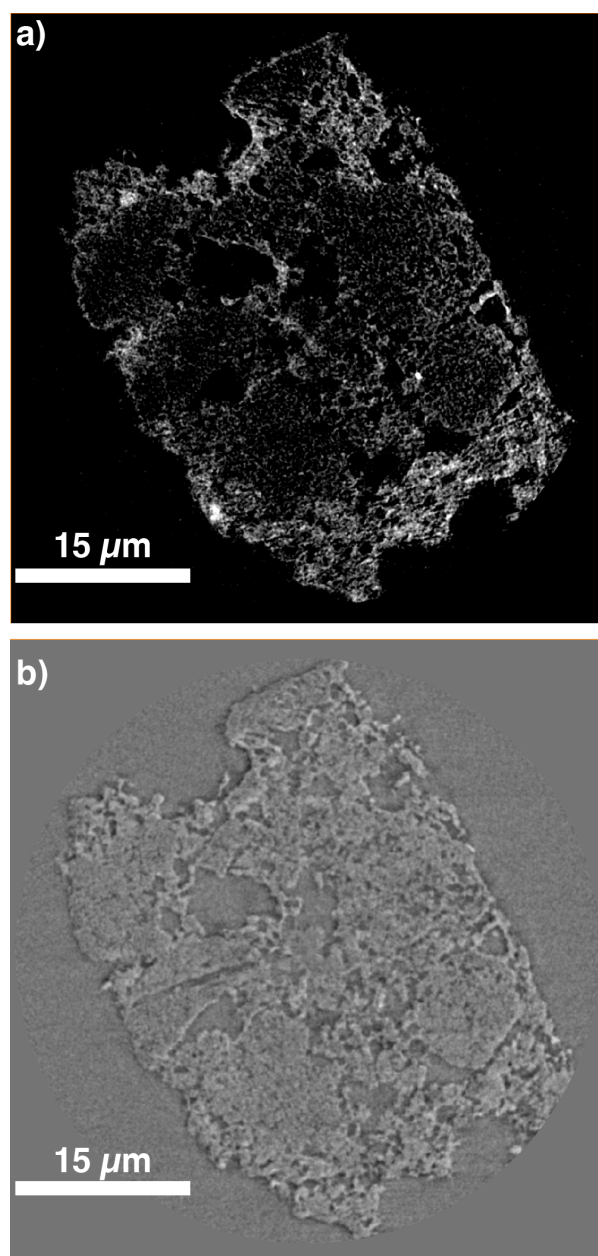


Figure 3.14: Nano-CT imaging of cesium stained electrode with 50 wt. % Nafion loading. Virtual reconstructed slices in a) absorption and b) Zernike phase contrast imaging mode.

Nafion by ion-exchange and not cesium adsorption on the carbon surfaces.

Figures 3.15a-c shows the normalized virtual slices in absorption contrast mode for the PGM-free catalyst layer with 35, 50, and 60 wt. % Nafion loading, respectively. Figures 3.15d-f show the corresponding 3D volume renderings of the absorption images. The color intensity in the normalized images is directly proportional to the volume average X-ray absorption coefficient and density within each voxel. Using the results in Figure 3.13 as justification, we can assign this intensity to the density of cesium ions and the Nafion acid site density. Note that in these images, we only show a region of interest from within the sample to exclude artifacts of the laser milling, which may leave additional films of stained Nafion on the exterior of the sample.

The results in Figure 3.15 show significant changes in the Nafion distribution and morphology with changes in the loading. The 50 wt. % Nafion loading images show a relatively uniform distribution of Nafion within the catalyst particles (also evident in Figure 3.14). The larger regions without any absorption signal are the areas of the large macropores where no Nafion exists. In contrast, with the reduction in Nafion loading to 35 wt. %, the morphology dramatically changes, with large dense agglomerates of Nafion forming outside of the catalyst particles and little Nafion penetration into the particles. Because of this unexpected and significant difference, the 35 wt. % sample preparation and imaging was repeated to confirm this anomalous morphology was consistent. Another significant morphology change was observed with the increase in Nafion loading from 50 to 60 wt. %, where the greater loading yielded thick layers (200-500 nm) of Nafion on the outside of the catalyst particles. The minor amounts of dispersed iron agglomerates that were not removed by the acid leaching are clearly

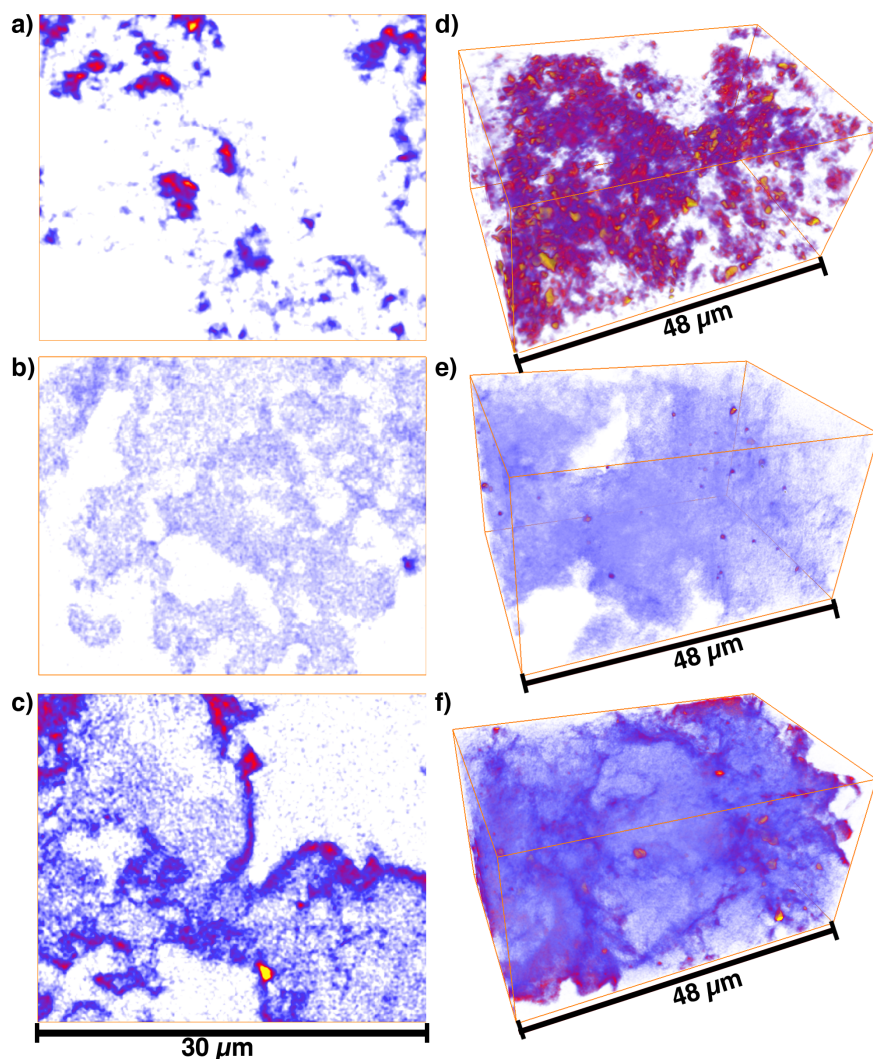


Figure 3.15: Segmented slices and 3D rendering Nafion domain in absorption contrast imaging mode. In-plane slice of the PGM-free catalyst with a) 35 wt. %, b) 50 wt. %, and c) 60 wt. % Nafion loading and 3D volume renderings of Nafion distribution for an electrode with Nafion loading of d) 35 wt. %, e) 50 wt. %, and f) 60 wt. % Nafion loadings. The intensity of color shows the local density of Nafion plus some minor Fe agglomerations.

evident in the 3D rendering of 50 wt. % Nafion images.

3.3.7 Effective Conductivity

Using the 3D Nafion distribution images, we performed particle-scale simulations of proton transport in the Nafion domain. As discussed earlier, the normalized Nafion intensity from the absorption contrast was directly correlated to the local Nafion volume and conductivity. Here we assumed a bulk conductivity value of 10 Sm^{-1} assuming fully hydrated bulk Nafion since the fuel cell performance measurements were performed with fully-humidified gases.

To illustrate the translation of ionomer distribution to conductivity with the model, Figure 3.16 shows a rendering of the Nafion conductivity distribution for the 50 wt. % Nafion loading electrode. This distribution is achieved by interpolating the intensity values from an exported look up table, at the nano-CTs 65 nm voxel resolution, to the nodes of the FEM mesh. Note, the resolution of the conductivity data is below that of the images since an initially coarse grid is only refined until the level of refinement no longer influences the predicted conductivity. In this particular sample, there was a very large macropore, a common characteristic of these electrodes, which results in a large area of negligible conductivity in the simulation.

Figure 3.17 shows the resulting local proton current density in the electrode with the different Nafion loadings, where brighter surfaces indicate higher currents. Note, these

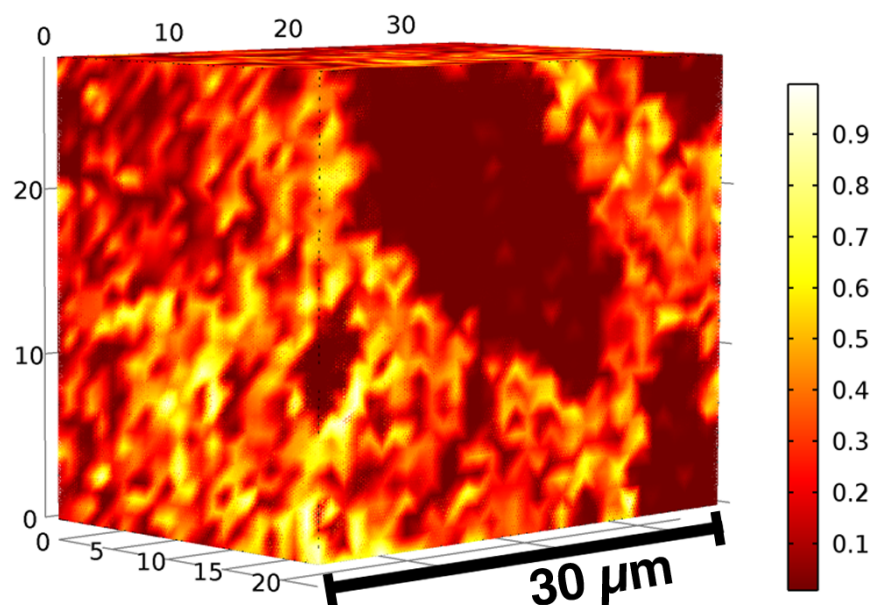


Figure 3.16: Proton conductivity distribution for the 50 wt. % electrode as interpolated within the FEM simulation using the Nafion spatial distribution from the absorption contrast imaging.

simulations are performed for a constant potential difference and thus the integrated surface current is not equal among the three simulations. All of the figures use the same color value range for the current density. Figure 3.17a shows a high current being carried through the dense agglomerates of Nafion (see Figure 3.15a). In contrast, Figure 3.17b shows that for the 50 wt. % case the current density is mostly uniform across the carbon particles. However, there is a large area devoid of current because of the large macropore. Figure 3.17c shows the similar uniform current within the carbon particles for 60 wt. %, but also regions of higher current in the thick Nafion film domains. In this image, the high current in the films is most evident on the right hand side of the front

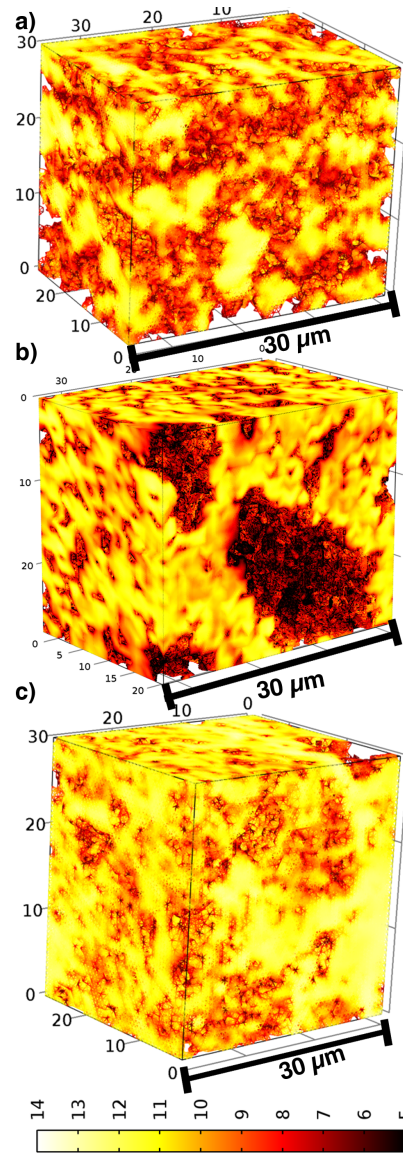


Figure 3.17: Local proton current density (A m^{-2}) distributions from simulations of the a) 35 wt. %, b) 50 wt. %, and c) 60 wt. % Nafion loading samples.

face.

Table 3.4 shows the resulting parameters from the particle-scale proton transport simulations. The values of effective conductivity on the order of 1 Sm^{-1} are consistent

Table 3.4: Structural parameters computed from Nano-CT imaging.

Nafion wt. %	Effective conductivity σ_{eff} [S/m]	Nafion volume fraction, ε_{Nafion} [-]	Tortuosity, τ [-]
35	0.75	0.24	3.17
50	0.73	0.2	2.83
60	1.66	0.33	2.01

with direct measurements in catalyst layers [20]. Because of the large macropore in the 50wt. % sample, its results are somewhat anomalous relative to the 35 and 60 wt. % results. For instance, because of this large macropore in this select region of interest, the estimated Nafion volume fraction is actually slightly lower than that of the 35 wt. % case. However, the more instructive trend is the decreasing tortuosity of the Nafion with its increasing loading. The 35 wt. % case exhibits a high tortuosity because of the dispersed, dense Nafion agglomerates that are poorly connected. In contrast, the 60 wt. % case presents a low tortuosity because the dense Nafion films do not feature any significant sub-resolution tortuosity and carry significant current.

3.4 Discussion

We now discuss the correlation between the experimentally observed fuel cell performance changes with Nafion loading with the characterizations from nano-CT imaging.

To review, the 35 wt. % electrode exhibited the highest currents in the mass transport region of the polarization curve (cf. Figure 3.2) relative to the 50 and 60 wt. % cases. However, it exhibited notably lower current in the high voltage, kinetic region of the curves. The 50 and 60 wt. % Nafion cathodes presented similarly high currents in the kinetic region, but the 60 wt. % Nafion showed excessive electrode flooding, resulting in a notable second Ohmic slope.

We can first investigate the effect of the Nafion loading on the properties related to gas transport. From the micropore size distributions (cf. Figure 3.8) and O_2 transport simulations (cf. Figure 3.10), the variation in the Nafion infiltration into the catalyst micropores, as observed in the absorption images of the stained samples, has a negligible effect on the micropore size distribution and the dry gas diffusion coefficients. In contrast, the 35 wt. % electrode exhibited a significantly higher macropore porosity, which could support the observed lower mass transport resistance. The increased macropore porosity may be an impact of the large Nafion agglomerates distributed through the electrode, which may act to further open the structure. From the LFOV solid size distribution, we see the 35 wt. % particle size distribution is effectively the same as the 50 wt. % case although it had notably lower macropore porosity. The lower coverage of the carbon catalyst by Nafion in the 35 wt. % case could increase the hydrophobicity of the pores and reduce flooding. This argument is supported by comparing the 50 and 60 wt. % cases. Despite them having roughly the same macroporosity, the 60 wt. %, case show significantly greater flooding in the polarization curve. The key difference between these samples is the thick Nafion films in the 60 wt. % case, which are visible in

absorption contrast images (cf. Figures 3.15c,f) and yield larger diameters for the dense solid domains (cf. Figure 3.8a). These thick Nafion films will yield highly hydrophilic pores once the pores are wetted by the condensed product water because of the smooth surface of bulk Nafion and the low contact angle of liquid water on saturated Nafion [103]. There is also a reduction of the pore volume associated with the largest pores (*i.e.*, the least wettable of the hydrophilic pores). With near complete flooding of the pores, the distance that O_2 can adequately diffuse through the electrode becomes significantly shorter than the cathode thickness and regions of the cathode near the membrane become inactive and behave as an additional layer of low conductivity membrane 13. This behavior is evident in the second Ohmic slope of the experimental polarization curves, particularly the 60 wt. % case.

We now discuss the change in apparent activity with increasing the Nafion loading from 35 wt. % to 50 wt. %. Considering the electrodes were prepared with the same catalyst batch following the same procedures, but just changing the amount of Nafion ionomer suspension added, we can begin by asserting that the difference is not a result of different intrinsic catalytic activity. Instead, it should be due to morphology changes incurred by the different added amounts of Nafion. Since the pore and solid size distributions and porosities are similar enough between all three cases it is unlikely that the difference in current at these high potentials is a result of the pore-scale transport. In addition, the estimated effective proton conductivity of 35 wt. % sample is similar to the two other electrodes and the low activity is not likely a result of poor proton conduction across the electrode. The most striking difference that relates to activity is the

poor infiltration of Nafion within the micropores in catalyst particles in the 35 wt. % case. Relative to the 50 and 60 wt. % cases, there is negligible Nafion content within particles in the 35 wt. % case and most of the ionomer resides in the large bulk Nafion agglomerates. Thus, we should expect large Ohmic drops for proton transport locally within the large catalyst particles as well as low proton reactant activity at the active sites within the particles, which would be interpreted as a reduced apparent exchange current density in an electrochemical analysis.

The origin of the stark change in Nafion morphology when reducing Nafion loading to 35 wt. % is attributed to a notably higher catalyst to total solvent mass ratio lower amount of ionomer suspension was added in the case. With increasing Nafion loading, the mass ratio of catalyst to total solvent decreases. At roughly, 50 wt. % it appears the particles reach an apparent saturation with Nafion and with the increased Nafion loading to 60 wt. %, the excess Nafion accumulates as films on the catalyst particle surface. Subsequent analyses in using 35 wt. % Nafion with additional solvent has shown a significant reduction in Nafion agglomeration.

In future work, these characterizations can be used in the development of cathode and PEFC models that accurately reflect the impact of the PGM-free electrode microstructure on fuel cell performance. Also, such modeling allows the separation and quantification of the overpotentials associated with each transport resistance, such as the through-plane O_2 transport versus the radial transport within the catalyst particles. Furthermore, the multi-resolution, multi-contrast mode images can be used for the di-

rect simulation of transport and reaction within these electrode structures.

Finally, a key finding of this work has been the importance of the electrode fabrication and resulting microstructure when evaluating the performance of PGM-free catalysts when evaluated in a fuel cell. Given the potential impact of a PGM-free catalyst cathode on fuel cell commercialization, significant work should be done to advance these systems. First and foremost, these catalysts require advances in materials and synthesis for improved TOF and durability, which have been a consistent goal in the past. However, with the significant recent advances in activity and durability, greater attention to electrode architecture, fabrication, and performance is needed to properly understand the present state of catalyst performance in optimized electrodes, as well as to construct accurate models for setting catalyst synthesis targets based on fuel cell performance metrics. For example, with careful consideration of electrode architecture and transport processes, refined catalyst synthesis targets such as active site density and pore-size distributions can be established.

3.5 Summary

In this chapter, PGM-free cathodes were characterized using nano-CT imaging and transport simulations to elucidate the fuel cell performances sensitivity to Nafion ionomer loading with these promising catalysts. The hierarchical architecture of these electrodes was resolved by using different imaging resolutions and the solid, pore, and Nafion do-

main components were distinguished by separate imaging in Zernike phase contrast and absorption contrast with the aid of cesium staining of the ionomer. Three cathodes with different Nafion loadings were characterized. Purely structural characteristics, including porosity, agglomerate, and pore size distribution were obtained by image processing. Pore-scale finite element simulations using the nano-CT images were performed on three domains (catalyst, gas, and Nafion) to study the electronic, gas, and ionic transport. Morphological transport parameters like formation factor, gas transport tortuosity, and Nafion tortuosity were obtained. The significant change in measured fuel cell performance with these changes in Nafion loading were attributed to significant changes in the Nafion distribution with increasing amounts of Nafion. At the lowest loading of 35 wt. %, the low observed activity was attributed to the poor infiltration of the Nafion ionomer into the catalyst particles. In contrast, with the highest level of Nafion loading (60 wt. %), the build of excess Nafion as films on the outside of the catalyst particles made for macropores pores with greater water retention, resulting in severe flooding. The severe flooding is evident in the second Ohmic slope of the experimental polarization curve, which results from a majority of the protons having to be conducted across a fully-flooded thickness of inactive cathode that behaves like an additional low conductivity membrane.

Chapter 4

In-situ through-plane measurements of ionic conductivity and ionic potential distributions in PGM-free electrode

4.1 Introduction

The Nafions loading and spatial distribution can significantly influence the electrodes ionic conductivity and the catalyst effectiveness in the PGM-free electrode. In the thick PGM-free cathode the electric potential drop through the Nafion across the electrode thickness can yield significant performance loss. Due to the extreme thickness of the PGM-free cathodes, existing in-situ techniques (*e.g.*, electrochemical impedance spec-

troscopy) cannot be used to measure the conductivity during operation due to large non-uniformities in properties and reaction rates. *In-situ* ionic conductivity and through-plane potential distribution are measured using microelectrode scaffold (MES) diagnostic as previously developed in our group for a Pt electrode [20]. MES consists of a cylindrical working electrode (cathode), a counter electrode (anode) and an electrolyte layer as shown in Figure 4.1. Eight different discrete sensing layers with H_2 reference electrodes are placed through the thickness of the cathode at its perimeter, enabling spatiotemporal measurement of the Nafion potential as a function of the distance from the membrane. Spatially, the slope and the rate of slope change provides us with a measure of the ORR distribution across the electrode. Ionic conductivity is additionally measured using a four wire resistance measurement technique [104]. The potential drop across the sense layer is measured while applying a small perturbation current to the reference electrode for H_2 pumping to the anode. MES can potential be used to validate or provide input to the model framework presented in the next two chapters.

4.2 Experimental

4.2.1 PGM-free Catalyst Powder and Ink

The present work employs cyanamide-polyaniline-iron (CM-PANI-Fe) as the ORR catalyst previously reported in the previous chapter. Briefly, a high surface area catalyst powder was prepared by high-temperature treatment followed by acid leaching

of cyanamide, polyaniline and iron acetate precursors. The catalyst ink for the MES measurements was prepared by mixing and ultrasonicing the catalyst powder with a Nafion ionomer solution, deionized water, and isopropyl alcohol (IPA) such that the resulting Nafion loading is 50 wt. %.

4.2.2 MES Fabrication

The MES is based on a substrate of alternating Nafion sense layers and Kapton insulating layers. The Nafion sense films were fabricated by spin coating 15 wt. % Nafion solution, prepared by diluting 20 wt. % Nafion solution (D2020, IonPower, New Castle, DE) with deionized water and IPA, on a 7.5 μm thick Kapton film. The Nafion-coated Kapton films were cut into the desired shape, i.e., square shape with a protruding tab for contact with a hydrogen reference electrode (HRE). Eight sense films were stacked such the each protruding tab was aligned to a HRE in the fuel cell hardware as shown in Figure 4.1. The stack was hot-pressed, with the addition of an un-coated Kapton film for ionic isolation from the membrane, at 50 psi and 125°C for 8 min. The thickness of the hot pressed films was 86.3 μm , consistent with a Nafion film thickness of approximately 2 μm . A 200 μm diameter through hole was cut at the center of the stack using the laser mill. Nafion 115 membrane was cut to match the square of the stack and hot pressed together with the same condition as the before. The catalyst ink was hand painted into the hole until it was filled. Commercial gas diffusion electrodes (GDE) were used for the anode and the HREs, while a commercial gas diffusion layer (GDL) (SGL 24BC,

IonPower, New Castle, DE) was used on the cathode side.

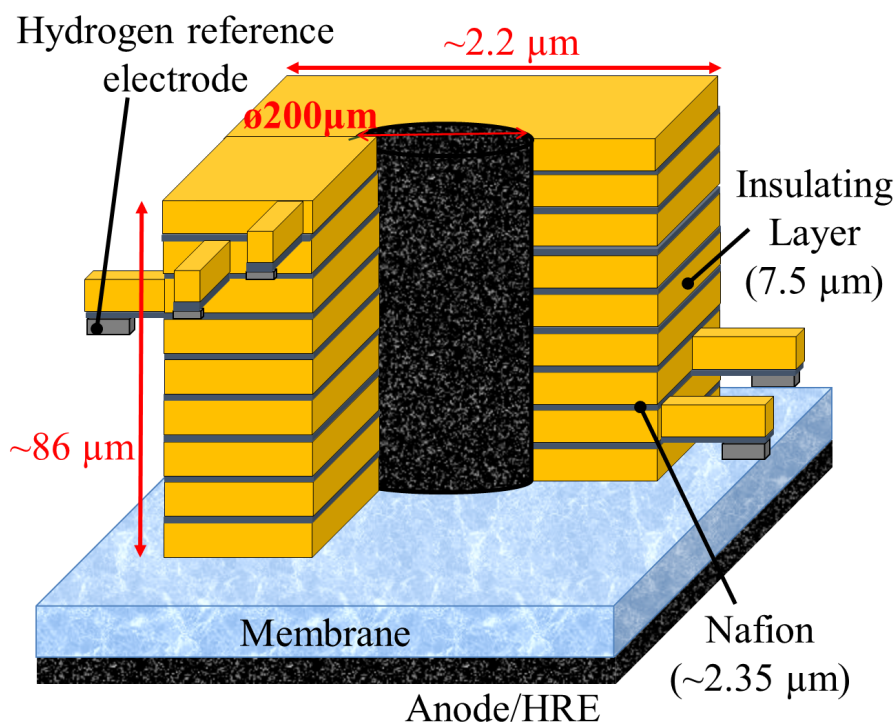


Figure 4.1: Schematic of an MES with eight alternating layers of insulating Kapton and Nafion film. Each sense layer has protruding tab with H_2 reference electrodes enabling *in-situ* measurement of the Nafion potential and proton conductivity.

4.2.3 MES Hardware

The custom fuel cell hardware used for the MES experiments was described previously by An *et al.* [104]. In brief, the anode flow field plate was modified to position eight reference electrodes around the anode. Printed circuit board in contact with the anode and the reference electrodes act as the anode current collector. A fuel cell test stand

(FCT-150, Biologic, France) was used to control the flow rate and humidity of the gases. The fuel cell voltage and the current were controlled and measured respectively by a potentiostat (SP-150, BIO-logic, Knoxville, TN). The potential at the sense layers were measured using a data acquisition system (National Instruments, Austin, TX).

4.2.4 Polarization Curve

The MES polarization curves were obtained galvanostatically. Each potential were applied for 60 seconds for greater than 0.7 V in steps of 0.02 V. For lower than 0.7 V, the potential was applied for 10 minutes in steps of 0.1 V. Last 20 % of the measured current in each step was averaged. The cell temperature and pressure was 80°C and 1 atm respectively.

4.2.5 Potential Measurement

The electrolyte potential was measured using the HREs connected to the MES sense layers. A data acquisition system was used to simultaneously record the potentials at sense layers located at the different discrete location through the thickness of the electrode as shown in Figure 4.2a. Fuel cell potential was applied in steps using a potentiostat. Each potential was held for 10 s.

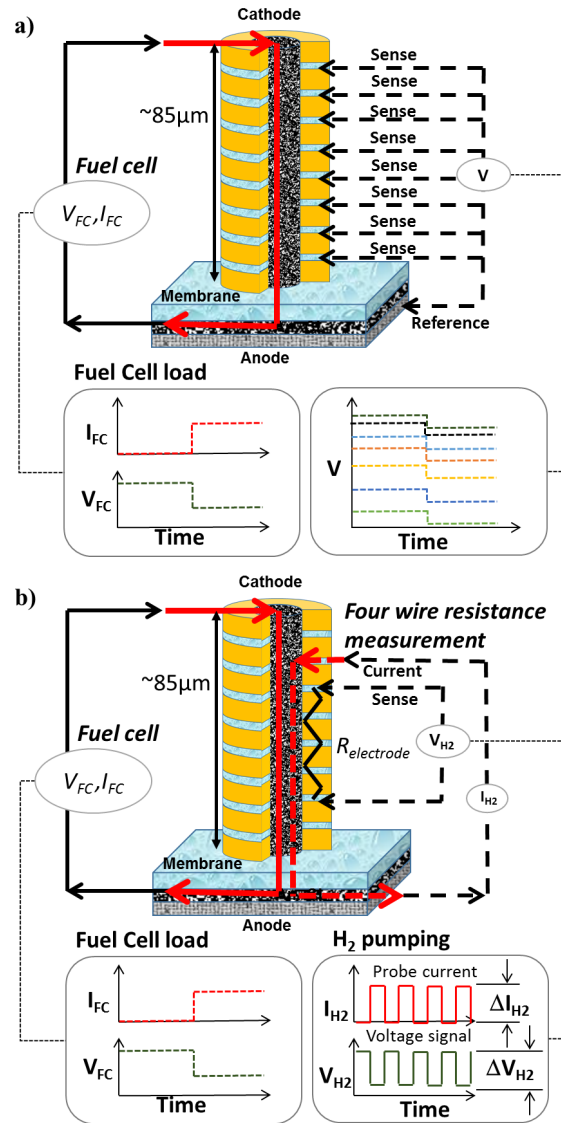


Figure 4.2: Schematic of the spatiotemporal measurement using MES. a) Ionic potential measurement at different locations through the thickness of the electrode. b) *In-situ* conductivity measurement using four wire measurement technique.

4.2.6 Conductivity Measurement

The ionic conductivity of an operating electrode was measured during the fuel cell operation by a modified four wire measurement technique. A potentiostat was used to apply a potential and record the corresponding fuel cell current. A second potentiostat applied a small DC perturbation H_2 pumping current between the anode and a reference electrode attached to a sense layer close to the GDL (7th electrode from the membrane) (see Figure 4.2b). The perturbation current was small as to not affect the fuel cell operation. The corresponding potential drop was measured between the 2nd and 6th sense layer from the membrane. The resistance of the catalyst layer was calculated by:

$$R = \frac{\Delta V_{H_2}}{\Delta I_{H_2}} \quad (4.1)$$

where ΔV_{H_2} is the applied perturbation current and ΔI_{H_2} is the measured potential drop. Similarly the conductivity was calculated using:

$$\sigma = \frac{L}{RA} \quad (4.2)$$

where A is the electrode area and L is the center to center distance between the 2nd and 6th sense layer from the membrane.

4.3 Results and Discussions

We now present the results of using the MES experimental apparatus to study the through-plane reaction distribution in a thick PGM-free cathode. Key areas of interest

are sensitivity of the reaction to hydration. It is often observed that with thick PGM-free cathodes, the mass transport regime often features steep linear polarizations, similar to a large Ohmic loss (a second Ohmic slope). Such a feature is observed in the 60 % wt. curve in Figure 3.2, where the mass transport loss resembles a significantly increased Ohmic loss at higher currents rather than the typical shape observed at 35 wt. %. We use the MES experiments to investigate the origin of this polarization curve feature. We also use the MES apparatus to measure the electrodes electrolyte conductivity during operation with internal water generation.

4.3.1 Polarization Curve

Figure 4.3 shows the polarization for the 50 wt. % Nafion loading sample at 50 %, 80 %, and 140 % RH in the cathode. The 140% relative humidity (RH) is based on dew point and ensures fully saturated gases. During all the tests, the anode was maintained at 80% RH. Due to the small diameter of the MES holes area compared to the Nafion membranes area, the water activity in the membrane and at the cathode|membrane interface will be largely dominated by the 80% RH of the anode gas stream. Thus, the activation region and the initial Ohmic region of the curves do not show a significant variation due to changes in the cathodes air RH. However, the mass transfer regions show a large variation in the performance due to the restricted water removal through the Nafion membrane and accumulation of liquid water in the cathode at higher RH and currents. The 50 % RH curve is dominated by activation and Ohmic losses and no

apparent mass transport loss. At 80 % RH, there is slight reduced Ohmic loss, but also the onset of some mass transport loss. At 140 % RH, the second Ohmic slope described above is observed.

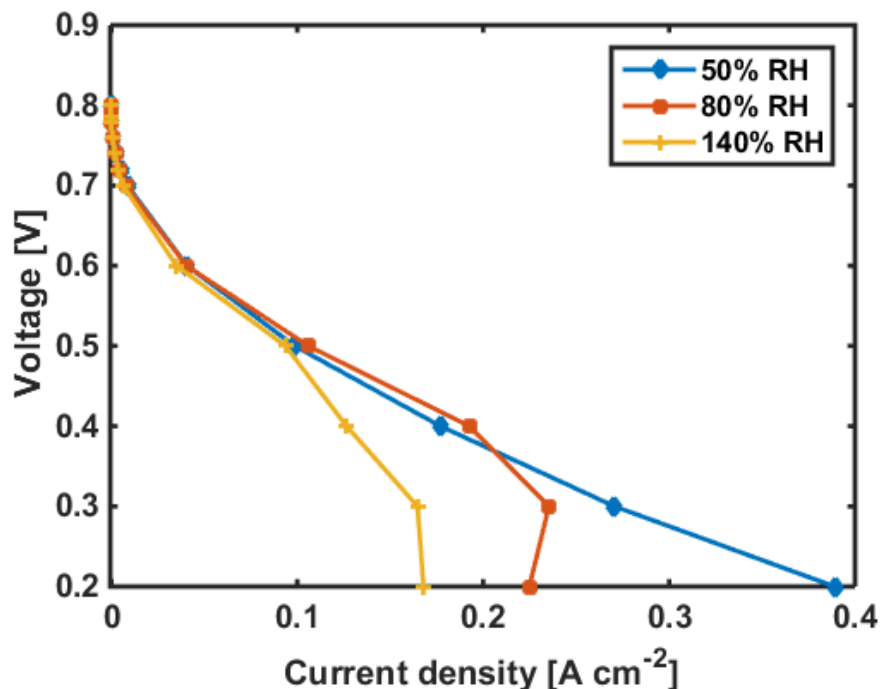


Figure 4.3: Polarization curves for CM-PANI-Fe 50 wt. % Nafion loading using the MES. Anode Pt loading was $0.35 \text{ mg}_{Pt}\text{cm}^{-2}$ at three cathode RH levels. Anode RH was 80 %. The anode/cathode gas flow rates were 200/200 sccm.

4.3.2 Nafion Potential Distribution

Figure 4.4a shows the time vs. measured potential at each of the sense layers. The potential measured at the sense layer reference electrodes are with respect to the fuel cell

anode as shown in Figure 4.4b. It can be seen from the time series that the magnitude of the potential difference between the sense layers increases with decreases in fuel cell voltage because the higher currents yielded higher Ohmic drop across the electrode. The primary reason for the potential difference between two sense layers is due the ohmic drop within that section of the sense layers. Thus, the greater the difference in potentials between adjacent sense layers, the larger the local proton current through the electrode. Decreases in the potential difference moving from the membrane to the GDL is consistent with reducing proton current as the protons are consumed by the ORR.

The plot of the potential drop vs. the thickness of the electrode was obtained by averaging the last 25 % of the potential drop in time series for each sense layer. Figure 4.5 shows potential distribution normalized by current density across the electrode at 0.2 V. The curves are normalized so the shape of the curve can be better compared since the different currents obtained at the same potential caused shifts in the raw potential at the different RH levels of 50, 80, and 140 %. The potential curves in certain cases exhibit a linear profile while a non-linear curve in other instances. The slope of the curve indicates the proton current:

$$i_{H^+} = -\sigma_{ionic} \frac{d\Phi}{dZ} \quad (4.3)$$

while σ_{ionic} is the ionic conductivity and i_{H^+} is the proton/ionic current. The curvature indicates the ORR:

$$i_{H^+} = -\frac{d}{dZ} \left(\sigma_{ionic} \frac{d\Phi}{dZ} \right) \quad (4.4)$$

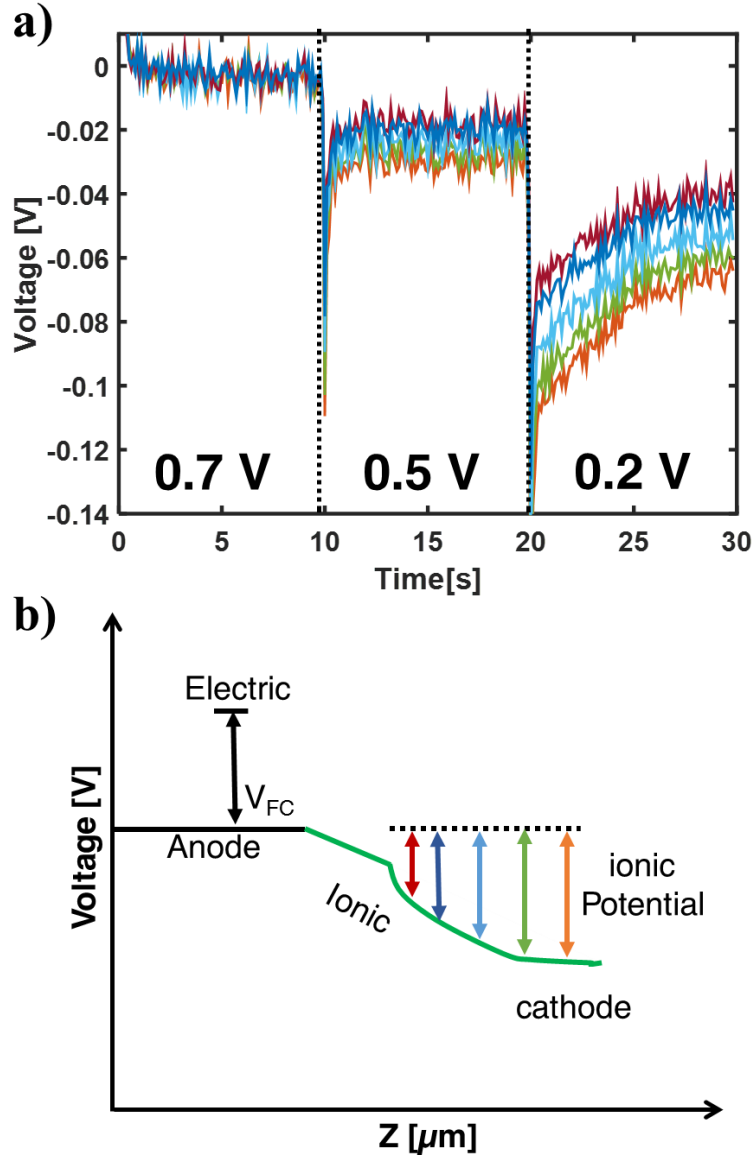


Figure 4.4: a) Time series of ionic potential measures at different sense layer. Fuel cell potential is held at 0.7 V, 0.5V, and 0.2V for 10 seconds. b) Schematic of the measured ionic potential at sense layer with respect to the fuel cell anode voltage.

At 50 % RH, we observe the distribution is flat in the last 30 μm next to GDL, consistent with little ORR because Ohmic losses concentrate the ORR near the membrane. The more linear potential distribution at high RH is due to the ORR reaction shifting towards the location near the MPL due to either oxygen transport resistance or flooding in the catalyst layer. In the case of flooding, a considerable portion of the cathode catalyst layer away from the MPL acts like a membrane with poor conductivity causing a huge ohmic resistance. Thus, the origin of the second Ohmic slope is the complete flooding of the cathode making it largely inactive except for a thin region adjacent to GDL.

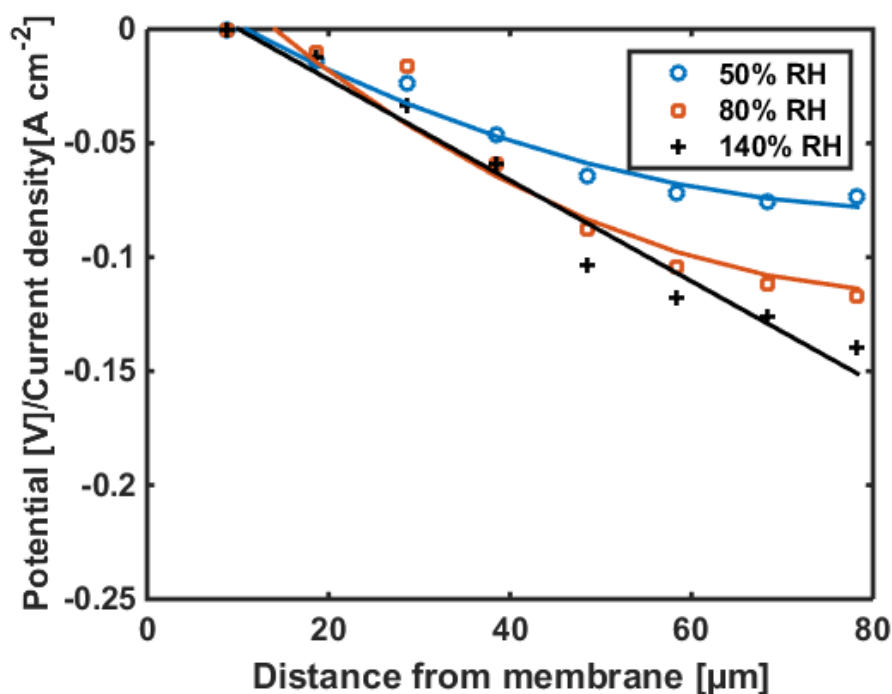


Figure 4.5: Current density normalized electrolyte potential distribution through the thickness of the electrode for CM-PANI-Fe 50 wt. % Nafion loading.

4.3.3 Ionic Conductivity

Figure 4.6 shows the *in-situ in-operando* measured catalyst layer conductivity using the modified four wire resistance measurement technique. Figure 4.6a shows conductivity increases with increase in RH at open circuit voltage (OCV). During the fuel cell operation at 50 % and 80 % RH, ionic conductivity plotted in Figure 4.6b is consistently around 0.6 Sm^{-1} at all fuel cell potentials. This likely because of the large water reservoir in the adjacent membrane with fixed water activity matching the 80 % in the anode. In the case of 140 % RH, the conductivity increases with increased in current density at lower potential. This suggests significant uptake of water generated by the ORR increases the proton conductivity in the catalyst layer. This is also supported by the fact that conductivity is notably higher during operation than at equilibrium in the OCV condition without water generation.

Average conductivity value of 0.6 Sm^{-1} from the MES measurement for 50 wt. % electrode is comparable to the value of 0.75 Sm^{-1} calculated using particle scale simulation on the ionomer domain image from nano-CT. Lower value from MES is expected as the anode RH is fixed at 80 % RH.

4.4 Summary

This chapter presents a novel in-situ experimentation to investigate the proton conduction in thick PGM-free electrodes. Using the MES experimental setup, the ionic potential

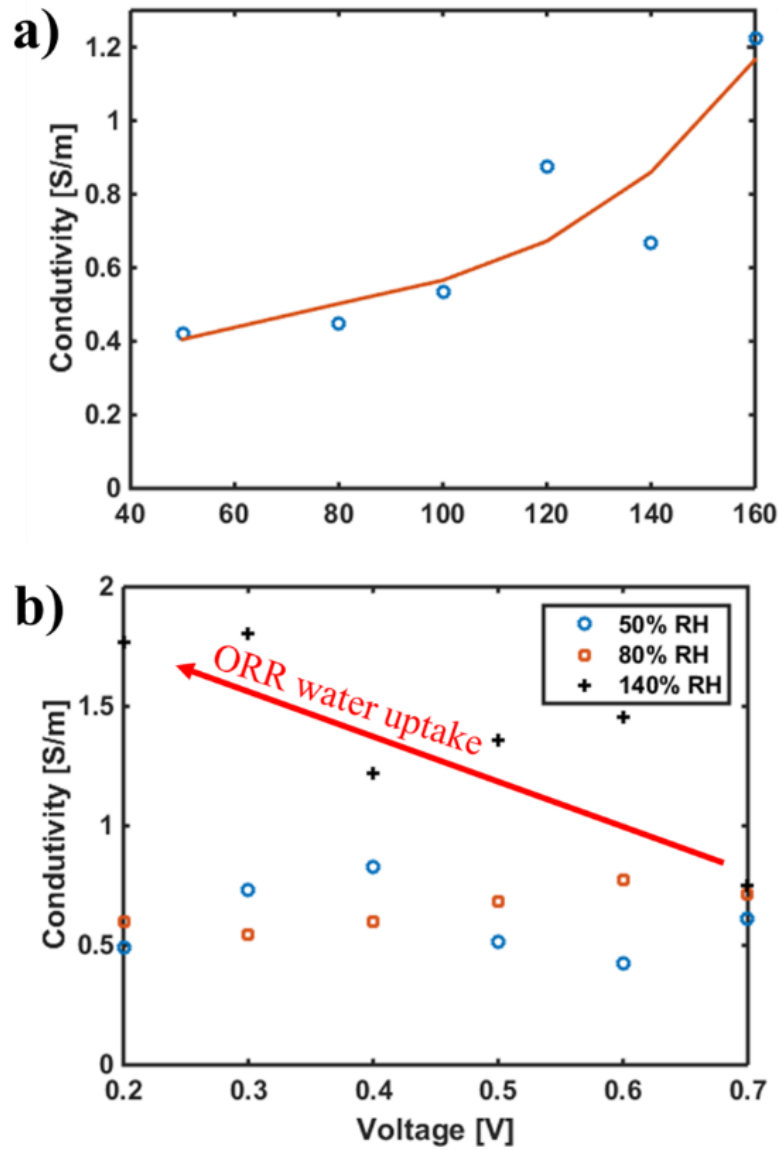


Figure 4.6: The ionic conductivity of CM-PANI-Fe 50 wt. % Nafion loading electrode. a) Effect of the RH on conductivity at OCV. b) Conductivity as a function of both RH and fuel cell operating voltages. The anode RH was 80 % in all cases.

is measured at discrete points through the thickness of the electrodes to infer the ORR current density distribution across the electrode. We observe the ORR focused near

the membrane in drier conditions, while at high RH the ORR is highly concentrated at GDL interface. The second Ohmic slope observed in the polarization curve is due to the flooding in the CL and the subsequent shift in ORR. The proton conductivity measurements show that conductivity is quite sensitive to RH as well as the rate of ORR water generation. Proton conductivity calculated from MES and the simulated value from the simulation in the last chapter is similar.

Chapter 5

Modeling Electrochemical Performance of the Hierarchical Morphology of PGM-free Catalyst

5.1 Introduction

This chapter presents the model framework for the PGM-free electrodes based on cyanamide polyaniline iron (CM-PANI-Fe) catalyst. Chapter 3 presented the morphological characterization of the CM-PANI-Fe electrode with different Nafion loading used in the model. The electrodes have characteristics at two different length scales which are of importance to the model. There are large dense aggregate particles (500 nm - 10 μm) of

the PGM-free catalyst with Nafion binder surrounded by large macropores. The dense aggregates are interspersed with micropores (<500 nm). The electrode is imaged using nanoscale resolution X-ray computed tomography (nano-CT) in multi-resolution, multi-contrast imaging modes to resolve different domain (catalyst, ionomer, and pore) features at the two different length scales. To understand the difference in performance for the electrodes with different Nafion loading, a detailed model which is morphologically consistent is developed.

5.1.1 Hierarchical Model

Figure 5.1 shows the implementation of the hierarchical morphology of the electrode in the model. The large dense catalyst aggregates imaged from large field of view (LFOV) was used to define the agglomerate and the macropore structure. The high resolution (HRES) imaging of the dense aggregates was used to define the internal morphology of the agglomerates. The transport through the PGM-free electrode was modeled as parallel transport via micropore and macropore. We model the spatially distributed reaction in the dense aggregates using the agglomerate model. We used the distribution of the agglomerates diameter, extracted from nano-CT imaging, in the agglomerate model. Effective diffusivity in the micropores was obtained from the pore-scale simulation on the internal pore morphology from the HRES nano-CT imaging. The ionic conductivity, volume fraction, and the tortuosity of the Nafion binder are obtained from the particle scale simulation on the Nafion domain.

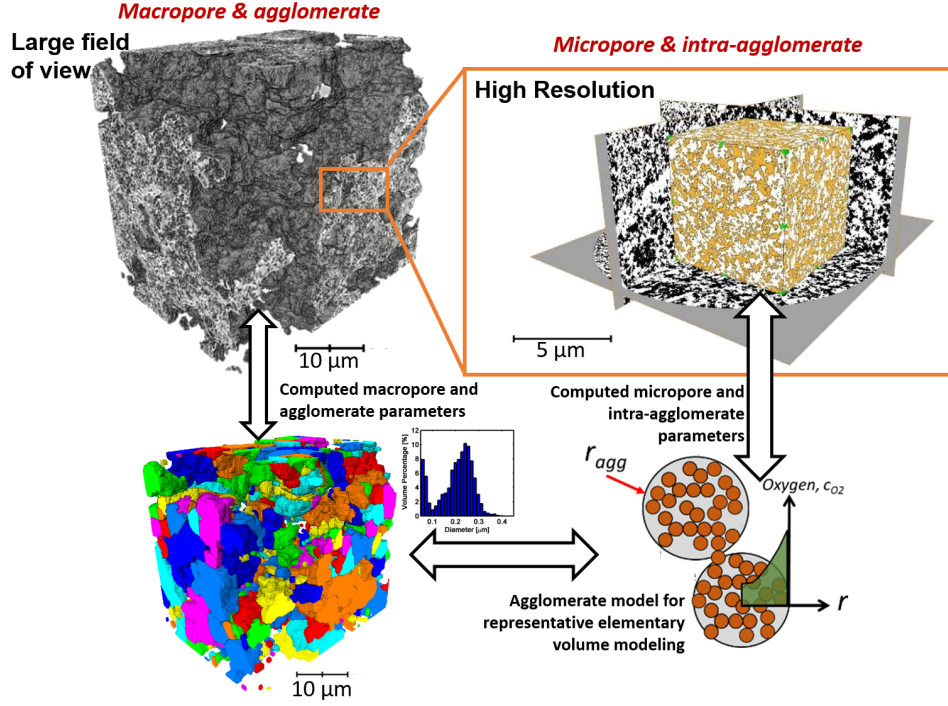


Figure 5.1: Hierarchical morphology implementation in PGM-free electrode model. The macropores and large dense agglomerates are imaged with LFOV scan, while HRES imaging resolves the internal morphology of denser porous solid domains. The morphology and transport properties extracted from both the scans are implemented into an agglomerate model used for representative elementary volume modeling.

In the present analysis, we used two-dimensional computational model to associate the relation between the morphology and the electrochemical performance of the different Nafion loading of the PGM-free electrode. The morphological and transport statistics extracted from the nano-CT imaging of the CM-PANI-Fe electrode with different Nafion loading was used as input. Agglomerate model with the distribution of the cat-

alyst aggregates from nano-CT is used to model the catalyst layer. We validated the model with the experimental polarization curves and elucidated the performance difference observed in the different loading electrodes.

5.2 Model Description

This section describes the governing equations and the framework for the model used for this study. The model is two-dimensional land-channel cross-sectional model and resolves multi-phase transport. Figure 5.2 shows the geometry of different domains and the domains associated with the parameters being modeled. The model domains include land, channel, gas diffusion layer (GDL), microporous layer (MPL), anode catalyst layer (CL), cathode catalyst layer (CL), membrane (MEM). Gas and liquid transport are modeled in the porous media (PM) which include the GDL, MPL, and the CL. In addition to modeling water vapor and liquid water, a separately dissolved water phase is considered, which represents the water absorbed in the ionomer binder and membrane. Ionic charge is conserved in the CL and MEM. The electron charge conservation is modeled in all the domains except the MEM. Table 5.1 describes the geometry dimensions of the different domains as well the material properties. Table 5.1 also indicates the various phases associated with each domain. The governing equations conserved and the source terms are represented in Table 5.2 and 5.3.

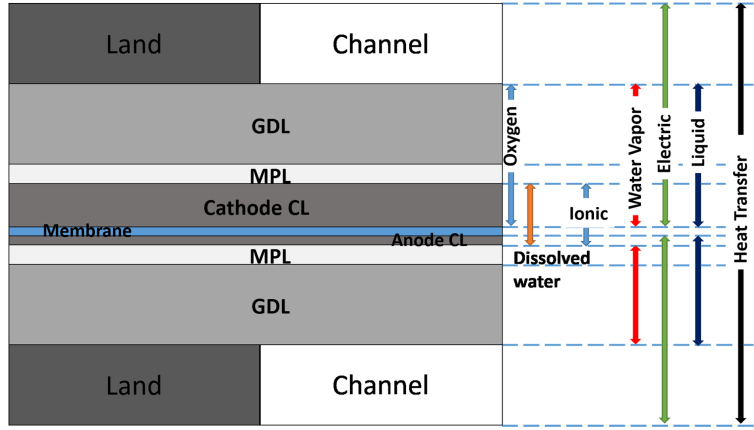


Figure 5.2: 2D land channel cross-sectional sandwich model domain and the species associated with each domain.

Table 5.1: Model domain dimensions and the phases in each domain.

Domain		Phases	Thickness [μm]	Length [μm]	Material
Land		T	200	500	Graphite
Channel		G,T	200	500	
GDL		G,T,L	190	1000	SGL 24 BC
MPL		G,T,L	45	1000	SGL 24 BC
Anode CL		G,T,L,DW	25	1000	Pt/C
Membrane		DW	25	1000	Nafion 211
Cathode CL	35 wt. %	G,T,L,DW	80	1000	Present
	50 wt. %		110	1000	work
	60 wt. %		120	1000	

Table 5.2: Governing equations and the domains they are modeled

in.

Species	Domain	Governing Equations
Ionic Current density	ACL, MEM, CCL	$\nabla \cdot i_{ionic} = S_i^{rxn} \quad (5.1)$
Ionic Potential	ACL, MEM, CCL	$i_{ionic} = -\sigma_{ionic}^{eff} \nabla \Phi_{ionic} \quad (5.2)$
Electric Current Den- sity	GDL, MPL, ACL, CCL	$\nabla \cdot i_{electric} = S_i^{rxn} \quad (5.3)$
Electric Potential	GDL, MPL, ACL, CCL, Land	$i_{electric} = -\sigma_{electric}^{eff} \nabla \Phi_{electric} \quad (5.4)$

Gas Species Concen- GDL, MPL, ACL,

tration

CCL

$$\nabla \cdot (-D_i^{eff} \nabla c_i) + u \cdot \nabla c_i = S_i^{rxn} + S_i^{phase} + S_i^{DW} \quad (5.5)$$

Gas flux

GDL, MPL, ACL,

CCL

$$N_i = -D_i^{eff} \nabla c_i + u c_i \quad (5.6)$$

Dissolved Water con- ACL, MEM, CCL
centration

$$\nabla \cdot \left(-D_{DW} \nabla c_{DW} - \frac{5}{44} \frac{c_{DW} \sigma_{ionic}}{vF} \nabla \Phi_{ionic} \right) = S_{DW} \quad (5.7)$$

Dissolved Water Flux ACL, MEM, CCL

$$N_{DW} = -D_{DW}^{eff} \nabla c_{DW} \quad (5.8)$$

Gas Pressure GDL, MPL, ACL,

CCL

$$\nabla \cdot \left(-\frac{\rho_i k_i^{eff}}{\mu_i} \nabla P_G \right) = S_i^{rxn} + S_i^{phase} + S_i^{DW} \quad (5.9)$$

Liquid Pressure GDL, MPL, ACL,

CCL

$$\nabla \cdot \left(-\frac{\rho_i k_i^{eff}}{\mu_i} \nabla P_L \right) = S_i^{phase} \tag{5.10}$$

Temperature

GDL, MPL, ACL,

CCL, Land, MEM

$$\rho_i C_{p,i} u \cdot \nabla T + \nabla \cdot \left(-k_{T,i}^{eff} \nabla T \right) = S_i^{rxn} + S_i^{phase} + S_i^{joule} \tag{5.11}$$

Table 5.3: Source terms for the governing equations.

Source Term		Domain					
		Land	GDL	MPL	ACL	CCL	MEM
Ionic	S_i^{rxn}				i_{HOR}	$-i_{ORR}$	
Electric	S_i^{rxn}				$-i_{HOR}$	i_{ORR}	
Oxygen	S_i^{rxn}					$\frac{-i_{ORR}M_{O_2}}{4F}$	
Hydrogen	S_i^{rxn}				$\frac{-i_{HOR}M_{H_2}}{2F}$		
Water Vapor	S_i^{rxn}					$\frac{i_{ORR}M_{H_2O}}{2F}$	
	S_i^{phase}		R_{phs}	R_{phs}	R_{phs}	R_{phs}	
	S_i^{DW}				R_{AD}	R_{AD}	
Dissolved Water	S_i^{DW}				$-R_{AD}$	$-R_{AD}$	
Gas Pressure	S_i^{rxn}				$\frac{-i_{HOR}M_{H_2}}{2F}$	$\frac{-i_{ORR}M_{O_2}}{4F} +$ $\frac{i_{ORR}M_{H_2O}}{2F}$	
	S_i^{phase}		R_{phs}	R_{phs}	R_{phs}	R_{phs}	
	S_i^{DW}				R_{AD}	R_{AD}	

Liquid Pressure	S_i^{phase}	$-R_{AD}$	$-R_{AD}$	$-R_{AD}$	$-R_{AD}$	
Temperature	S_i^{rxn}			$i_{HOR}\eta_{anode}$	$i_{ORR}(\eta_{cathode} + \Pi)$	
	S_i^{phase}	$-\Delta H_{fg}R_{phs}$	$-\Delta H_{fg}R_{phs}$	$-\Delta H_{fg}R_{phs} - 43740R_{AD}$		
	S_i^{joule}	$\frac{i_{elec}i_{elec}}{\sigma_{elec}^{eff}}$	$\frac{i_{elec}i_{elec}}{\sigma_{elec}^{eff}}$	$\frac{i_{elec}i_{elec}}{\sigma_{elec}^{eff}}$	$\frac{i_{electric}i_{electric}}{\sigma_{electric}^{eff}} + \frac{i_{ionic}i_{ionic}}{\sigma_{ionic}^{eff}}$	$\frac{i_{ionic}i_{ionic}}{\sigma_{ionic}^{eff}}$

Table 5.4: Model parameter equation.

Parameters	Governing Equations
Energy	
Effective thermal conductivity, $k_{T,i}^{eff}$	$k_{T,i}^{eff} = (1 - \varepsilon_i) k_{T,i}^{solid} + \varepsilon_i (Sat_i k_{T,i}^{liquid} + (1 - Sat_i) k_{T,i}^{gas}) \quad (5.12)$
Gas and Liquid transport	
Diffusion Coefficient D_{ij}	$D_{jk} = \frac{a}{P_G} \left(\frac{T}{(T_{C,j} T_{C,k})^{1/2}} \right)^b (P_{C,j} P_{C,k})^{1/3} (T_{C,j} T_{C,k})^{5/12} \left(\frac{1}{M_j} + \frac{1}{M_k} \right)^{1/2} \quad (5.13)$
Saturation, Sat	$Sat_{wp} = \left(1 + \left(\frac{P_C}{P_{CB}} \right)^n \right)^{-m} \quad (5.14)$
Rate of Evaporation, R^{evap}	$R_i^{evap} = k_{evap} \varepsilon_i \rho_{H_2O} S_i (P_{sat} - P_{H_2O}) \quad (5.15)$

Rate of condensation, R^{cond}

$$R_i^{cond} = k_{cond} \varepsilon_i (1 - S_i) \left(\frac{\chi_{H_2O,i} M_{H_2O}}{RT} \right) (P_{H_2O} - P_{sat}) \quad (5.16)$$

Saturation Pressure, P_{sat}

$$P_{sat} = -2864.4 + 411.24(T - 273) - 10.554(T - 273)^2 + 0.16636(T - 273)^3 \quad (5.17)$$

Ionomer: Water and Pro-

ton transport

Ionic Conductivity, σ_{ionic}

$$\sigma_{ionic} = \sigma_l^{303K} \exp \left(1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right) \quad (5.18)$$

$$\sigma_l^{303K} = -7.577 \times 10^{-5} \lambda^4 + 4.24 \times 10^{-3} \lambda^3 - 8.415 \times 10^{-2} \lambda^2 + 1.138 \lambda - 2.012 \quad (5.19)$$

Water Diffusion Coeffi-

cient, D_{DW}

$$D_{DW} = 1 \times 10^{-10} [2.594 - 0.3371\lambda + 0.02691\lambda^2 - 6.828 \times 10^{-4}\lambda^3 \\ + 1.22 \exp \left(- \left(\frac{\lambda - 3.045}{0.5956} \right)^2 \right) - 259.4 \exp (-1.686\lambda - 2)] \quad (5.20) \\ \times \exp \left[2416 \left(\frac{1}{303} - \frac{1}{T} \right) \right]$$

Ionomer equilibrated wa-

ter, λ_{eq}

$$\lambda_{eq} = 0.043 + 17.81\varphi - 39.85\varphi^2 + 36\varphi^3 + (22 - 14)Sat \quad (5.21)$$

$$\varphi = \frac{c_{H_2O}RT}{P_{sat}} \quad (5.22)$$

Adsorption / Desorption

rate

$$h_{AD} = \frac{k_A}{2} \left(1 - \frac{|c_{DW} - \nu\lambda_{eq}|}{c_{DW} - \nu\lambda_{eq}} \right) + \frac{k_D}{2} \left(1 + \frac{|c_{DW} - \nu\lambda_{eq}|}{c_{DW} - \nu\lambda_{eq}} \right) \quad (5.23)$$

$$k_{A,D} = a_{agg} k_{A,D}^{ref} \exp \left(- \frac{E_{AD}}{RT} \right) \quad (5.24)$$

Reaction Kinetics

Overpotential, η

$$\eta_a = \Phi_{electric} - \Phi_{ionic} \quad (5.25)$$

$$\eta_c = \Phi_{ionic} - \Phi_{electronic} + \bar{U}_{ORR} \quad (5.26)$$

Open circuit potential,

$\bar{U}_{ORR}$

$$\left[-2.154e^{-5} (-70650 - 8T \log(T + 92.84T)) - 0.5RT \log \left(|8.205e^{-5} c_{O_2} T|^{-0.5} \right) \right] / F \quad (5.27)$$

Effectiveness factor, E_i

$$E_r^i = \frac{1}{\phi_i} \left(\frac{1}{\tanh(3\phi_i)} - \frac{1}{3\phi_i} \right) \quad (5.28)$$

Thiele Modulus, ϕ_i

$$\phi_i = \frac{r_{agg}^i}{3} \sqrt{\frac{k_c}{D_{O_2}^{eff}}} \quad (5.29)$$

Henry's constant, H

$$H = 26.8 \times 10^{-3} \exp\left(\frac{5210}{R} \left(\frac{1}{T} - \frac{1}{323}\right)\right) \quad (5.30)$$

Diffusion coefficient in

Nafion, D_{NO_2}

$$D_{NO_2} = 4.38 \times 10^{-6} \exp\left(-\frac{25 \times 10^{-3}}{RT}\right) \quad (5.31)$$

Agglomerate per unit vol-

ume, a_{agg}^i

$$a_{agg}^i = \frac{3(1 - \varepsilon_s)}{(r_{agg}^i + \delta)} \quad (5.32)$$

5.2.1 Gas and liquid water transport

Mass and momentum are conserved in the PM for oxygen, and water vapor using Ficks law and Darcys law shown in Eq. 5.5, Eq. 5.6 and Eq. 5.9 Liquid water is also modeled in the PM using Darcys law (Eq. 5.10). The effective diffusion coefficient, $D_{jk,i}^{eff}$, is calculated as shown below:

$$D_{jk,i}^{eff} = \frac{\varepsilon_i}{\tau_i} D_{jk} \quad (5.33)$$

where τ_i is the tortuosity of the medium i and D_{jk} is the molecular diffusion coefficient of species j in k . For GDL and MPL, the diffusion coefficient is calculated using Eq. 5.13, while for CCL domain diffusion coefficient is calculated to represent the hierarchical morphology and is shown in the hierarchical morphology section. In Eq. 5.13, P_C , T_C and M_j are critical pressure, critical temperature and molecular weight of species j . The exponents a , b , and the critical point values are reported in the appendix D. The effective gas permeability, k_i^{eff} , is a product of the saturated permeability k_i^{sat} and the relative permeability, k_i^{rel} .

$$k_i^{eff} = k_i^{sat} k_i^{rel} \quad (5.34)$$

Relative permeability is dependent on the saturation, Sat , of the porous media. Relative permeability for gas is $k_i^{rel} = (1 - Sat_i)^3$, while for liquid water is $k_i^{rel} = Sat_i^3$.

The saturation, Sat (Eq. 5.14), in each domain is determined by water retention curve which relates the saturation to capillary pressure, P_{Cap} , defined as

$$P_{Cap} = P_{nw} - P_w \quad (5.35)$$

where nm and w are representing non-wetting and wetting phase. Van Genuchten water retention curve model is used for the capillary pressure and saturation correlation [105]. The fitting parameters P_{CB} , n , and m are reported in appendix D. The effective saturation is incorporated as

$$Sat = \frac{Sat_{wp} - Sat_{res}}{1 - Sat_{res}} \quad (5.36)$$

where S_{res} is the residual saturation and in this work, it is assumed to a value of 0.1. The water vapor condensation and liquid water evaporation are implemented as source terms in Eq. 5.5, 5.9 and 5.10. Rate of phase change in domain i is represented as

$$R_i^{phase} = R_i^{evap} switch + R_i^{cond} (1 - switch) \quad (5.37)$$

where R_i^{evap} and R_i^{cond} is the rate of evaporation and condensation respectively as is incorporated as shown in Eq. 5.15 and Eq. 5.16. In both the rate equations, P_{sat} is the saturation pressure (Eq. 5.17) and $switch$ is a mathematical operator defined as

$$switch = \frac{1}{2} \left[1 + \frac{P_{H_2O} - P_{sat}}{|P_{H_2O} - P_{sat}|} \right] \quad (5.38)$$

5.2.2 Heat Transfer

Temperature of each domain and phases is obtained by solving energy balance shown in Eq. 5.11. Along with heat due to the electrochemical reaction, water vapor condensation and liquid water evaporation are added as source terms for the energy conservation. Heat due to adsorption or desorption of water dissolved in Nafion is also accounted for in the energy conservation. Effective thermal conductivity, $k_{T,i}^{eff}$, in the PM is volume

averaged mixture of the solid and fluid thermal conductivity as shown in Eq. 5.12. In Eq. 5.12, ε_i and Sat_i is the porosity and the saturation of domain i .

5.2.3 Ionomer

Proton and ionomer dissolved water are modeled in the membrane domain and ionomer binder in CL domain using Eq. 5.2 and Eq. 5.7. The ionic conductivity is calculated in the model includes both water vapor and liquid equilibrated conditions as shown in Eq. 5.18. The ionic conductivity of the membrane and the Nafion CL using the equation below

$$\sigma_i^{ionic} = \frac{\varepsilon_i}{\tau_i} \sigma_{ionic} \quad (5.39)$$

where ε_i and τ_i are the volume fraction and the tortuosity of the Nafion respectively in the domain i . The value of the volume fraction and the tortuosity in the membrane is 1, while these parameters for the CCL are obtained from the The diffusion coefficient of the absorbed water (Eq. 5.20) from the measurements of Zawodzinski *et al.* [106] is implemented as a continuously differentiable correlation for the diffusivity. Water absorbed in the Nafion is in equilibrium condition with water vapor. This is implemented as a source term as shown below.

$$R_{AD} = h_{AD} (c_{DW} - \nu \lambda_{eq}) \quad (5.40)$$

where λ_{eq} is membrane equilibrated water (Eq. 5.21) and h_{AD} is the rate of absorption or desorption (Eq. 5.23).

5.2.4 Catalyst layer

Electron charge conservation is modeled in all domains except membrane using Eq. 5.3. In ACL, catalyst layer is based on Pt/C and the HOR is represented by standard Butler-Volmer equation as shown below:

$$i_{HOR} = i_{HOR}^{ref} a_{Pt} P_{H_2} \left[\exp \left(\frac{\alpha_a F}{RT} \eta_a \right) - \exp \left(-\frac{\alpha_a F}{RT} \eta_a \right) \right] \quad (5.41)$$

where i_{HOR}^{ref} is the reference exchange current density, a_{Pt} is the electrochemically active Pt surface area in the anode and α is the charge transfer coefficient. η_a (Eq. 5.25) is the anode overpotential, which is the potential difference between electric and ionic.

To model the PGM-free CCL, the agglomerate model is used to capture and predict the combined transport and electrochemistry. Agglomerate model is an analytical solution to the coupled diffusion and reaction in an ideal spherical agglomerate [81]. The advantage of the agglomerate model is that it captures transport losses within the microstructure implicitly. The current density for a single diameter is

$$i_i^{ORR} = 4F \frac{P_{O_2}}{H} f_i^i \left[\frac{1}{E_r^i k_c \varepsilon_{agg}} + \left(\frac{r_{agg}^i{}^2}{k_{int} (r_{agg}^i + \delta)^2} + \frac{r_{agg}^i \delta}{(r_{agg}^i + \delta) D_{NO_2}} \right) \left(\frac{f_i^i}{a_{agg}^i} \right) \right]^{-1} \quad (5.42)$$

and the effective current density is a summation of all the diameter weighted by the volume fraction. Figure 3.8 shows the distribution of the agglomerate diameter obtained from nano-CT for three different Nafion loadings.

$$i_{ORR} = \sum_i f_i i_i^{ORR} \quad (5.43)$$

In Eq. 5.42 F , H , and P_{O_2} represent Faradays constant, Henrys constant (Eq. 5.30) and partial pressure of oxygen respectively. E_r^i , f_i , and a_{agg}^i is the effectiveness factor, volume

fraction, and agglomerate surface area per unit volume respectively of an agglomerate with radii r_{agg}^i . δ is the Nafion film thickness, D_{NO_2} (Eq. 5.31) is the diffusivity of O_2 in the Nafion and ε_{agg} is the agglomerate ionomer fraction. k_c is the ORR rate constant defined using standard Butler-Volmer equation as shown below:

$$k_c = \frac{R_s J_s}{4F \varepsilon_{agg} c_{O_2}^{ref}} \left[\exp \left(\frac{\alpha_c F}{RT} \eta_c \right) - \exp \left(-\frac{\alpha_c F}{RT} \eta_c \right) \right] \quad (5.44)$$

where $R_s J_s$ is the electrochemically active site density multiplied by activity per site, ε_{agg} is the electrodes volume fraction of agglomerates not including ionomer film, $c_{O_2}^{ref}$ is the reference oxygen concentration associated, α_c is the cathodic charge transfer coefficient, n is the number of electrons transferred in the rate-limiting step of the reaction, and η_c (Eq. 5.26) is the representative local cathode overpotential. Active site density, R_s , and activity per site, J_s , is not clearly estimated for the PGM-free catalyst. Hence, the $R_s J_s$ parameters are fit at 0.8 V from the experimental polarization curve. Effectiveness factor, E_r^i (Eq. 5.28), is the ratio of actual reaction rate to the ideal reaction rate. Thiele modulus, ϕ_i (Eq. 5.29), represent the ratio of the diffusion rate to reaction rate. Both effectiveness factor and Thiele modulus represent the contribution of an agglomerate of radii, r_{agg}^i , at a given rate. In Thiele modulus, the effective diffusion in the agglomerate, $D_{O_2}^{eff}$, is corrected for the saturation in the micropore as follows

$$D_{O_2}^{eff} = (1 - Sat_{micro})^{1.5} D_{O_2}^{micro} \quad (5.45)$$

where Sat_{micro} and $D_{O_2}^{micro}$ is the saturation and diffusion coefficient in the micropore respectively.

5.2.5 Boundary conditions

The flux of protons is zero at the MPL|CL interface and is represented as below

$$\bar{n} \cdot \nabla \phi_l|_{CL/MPL} = 0 \quad (5.46)$$

The electric potential on the anode plate is set to the 0 V, while the cathode plate is held potentiostatic at the V_{FC} .

$$\Phi|_{Anode} = 0 \quad (5.47)$$

$$\Phi|_{Cathode} = V_{FC} \quad (5.48)$$

The relative humidity of both anode and cathode gas feeds are at 100 % unless specified.

The water vapor concentration at the channel|GDL interface is

$$c_{H_2O}|_{A,C} = \frac{P_{sat}RH_{A,C}}{RT} \quad (5.49)$$

Similarly, the oxygen concentration at the channel|GDL is set as

$$c_{O_2}|_{Ch|GDL} = \frac{\chi (P_{cathode} - P_{sat}RH_C)}{RT} \quad (5.50)$$

where $\chi = 0.21$ if the cathode feed is air and $\chi = 1$ for pure O_2 cathode feed. The flux of gas species across the membrane is zero.

$$\bar{n} \cdot (D_i^{eff} \nabla c_i)|_{CL|MEM} = 0 \quad (5.51)$$

Nafion dissolved water flux at the CL|MPL interface is set to zero.

$$\bar{n} \cdot \left(D_{DW} \bar{\nabla} c_{DW} + \frac{5}{44} \frac{c_{DW} \sigma_{ionic}}{\nu F} \nabla \Phi_{ionic} \right) \Big|_{CL/MPL} = 0 \quad (5.52)$$

Gas inlet pressure is set to the feed pressure and inlet liquid pressure such that the capillary pressure at the Channel|GDL interface corresponds to the saturation value of 0.0025.

$$P_G|_{CH|GDL,A} = P_{anode} \quad (5.53)$$

$$P_G|_{CH|GDL,C} = P_{cathode} \quad (5.54)$$

$$P_L|_{CH|GDL:A,C} = P_{G:A,C} - 3E - 3[Pa] \quad (5.55)$$

Temperature of the model at the outside edge of the land was

$$T_{A,C}|_{Land} = T_{A,C}^{initial} \quad (5.56)$$

where $T^{initial}$ is the temperature of the anode/cathode feed gas temperature. The convection of the gas inlet feed is implemented as

$$\bar{n} \cdot (k \nabla T)|_{CH|GDL,CH|Land} = h_{A,C} (T_{amb} - T) \quad (5.57)$$

where $h_{A,C}$ is the convective heat transfer coefficient. To generate the polarization curve V_{FC} is varied from 1 V to 0.8 V in 0.02 V steps and 0.8 to 0.2 V in steps of 0.05 V.

5.2.6 Hierarchical model

In addition to the diameter distribution, the hierarchical agglomerate model includes the volumetric ORR activity, effective diffusion coefficient, and permeability from the nano-CT characterization. In the previous agglomerate models for the Pt-based electrode, the volumetric ORR is included as a function of the active surface area and ex-

change current density for Pt. In this work for the PGM-free electrodes, we implemented it as volumetric active site density, R_s , multiplied by active site activity, J_s . Since both R_s and J_s for the PGM-free catalyst are still unclear, the parameter $R_s J_s$ is the only fitting parameter in the model.

Pore-scale simulation obtains the effective O_2 diffusion coefficient inside the microstructure of the agglomerates in the pore domain obtained from HRES imaging. We calculate the local diffusion coefficient using Bosanquet formulation which series resistance of molecular and Knudsen diffusion. The effective diffusivity is obtained by simulating Laplace equation with the local diffusion coefficient. This is important to include the distribution local pore diffusivity to calculate the effective tortuosity accurately. Similarly, for the larger macropores obtained from LFOV imaging the Knudsen diffusion is neglected as the pore sizes are generally in the range of $1 \mu m$. The effective diffusion coefficient for the CCL is calculated as a volume normalization as shown

$$D_{CL}^{eff} = \frac{D_{macro}\varepsilon_{macro} + D_{micro}^{eff}\varepsilon_{micro}(1 - \varepsilon_{macro})}{\varepsilon_{CL}} \quad (5.58)$$

where D is diffusion coefficient and ε is pore volume fraction. The subscripts micro and macro represent micropore and macropore respectively. The effective properties of the CL are determined by volume averaging properties from both micropore and macropore. For instance, any pore volume specific parameter ξ^{eff} can be volume normalized for the CL as

$$\xi_{CL}^{eff} = \frac{\xi_{macro}\varepsilon_{macro} + \xi_{micro}\varepsilon_{micro}(1 - \varepsilon_{macro})}{\varepsilon_{CL}} \quad (5.59)$$

We calculate the saturation in the micropore and macropores separately to model the

difference in accumulation of the water in the small pores in the agglomerates and the macropores. The pore size distribution obtained from the nano-CT imaging is used to fit a log-normal distribution to obtain a relation between the capillary pressure and saturation [102]. Both the micropore and macropore is assumed to be hydrophilic because of Nafion and the graphitized carbon in the electrode. Therefore, the micropores are flooded first, and water then floods the macropores. The saturated permeability is obtained using Carman-Kozeny relationship [107] and is corrected for gas and liquid phase using the Eq. 5.34. The effective permeability for the CCL is calculated using Eq. 5.59. The water retention curves suggest that the electrode should be flooded for the water to transport to the highly hydrophilic MPL. However, this is not the only requirement for water transport across the cathode. A sufficient temperature gradient across the GDL to the CL can cause the water to evaporate in the CL and then condense in the GDL.

5.2.7 Numerical Method

Charge, mass and energy conservation are modeled using second order discretization in commercial FEM package (COMSOL Multiphysics v5.1, Comsol Inc., Burlington, MA). The model was run in steady state condition. The potentiostatic parametric sweep was run in COMSOL interface, while the results were exported through MATLAB (Mathworks, Natick, MA). The mesh generated had 34400 triangular elements. The mesh density is higher in the both the CL and membrane domain. The density of mesh is also

higher at the CL|MPL and CL|MEM interface.

5.3 Result and Discussions

5.3.1 Base case

This section discusses the baseline scenario for validation of the model. The experimental data of the CM-PANI-Fe electrodes with the 35, 50, and 60 wt. % Nafion loading is presented previously by Zelenay *et al.* [108]. Figure 5.3 presents both the experimental and model results for CM-PANI-Fe with 35 wt. % Nafion loading with different pure O_2 partial pressures. The current density at 0.8 V for the 2 atm partial pressure case was matched between the experimental and model results to fit the $R_s J_s$ parameter. The potentials above 0.8 V have parasitic losses and lower current density. While the potentials below 0.8 V are less activity dependent as Ohmic and mass transport losses increases. Hence 0.8 V was chosen as the potential for fitting the parameter $R_s J_s$. In Figure 5.3, for the 0.3 and 1 atm partial pressure cases the fit parameter, $R_s J_s$, was not modified. The polarization curve from the model shows an excellent agreement in trend with the experimental data.

Figure 5.4 shows the model prediction for CM-PANI-Fe cathode with varying Nafion loading with air as the cathode gas. For the 35 wt. % loading, the value of $R_s J_s$ was not varied. For 50 and 60 wt. % loading the morphological and transport properties

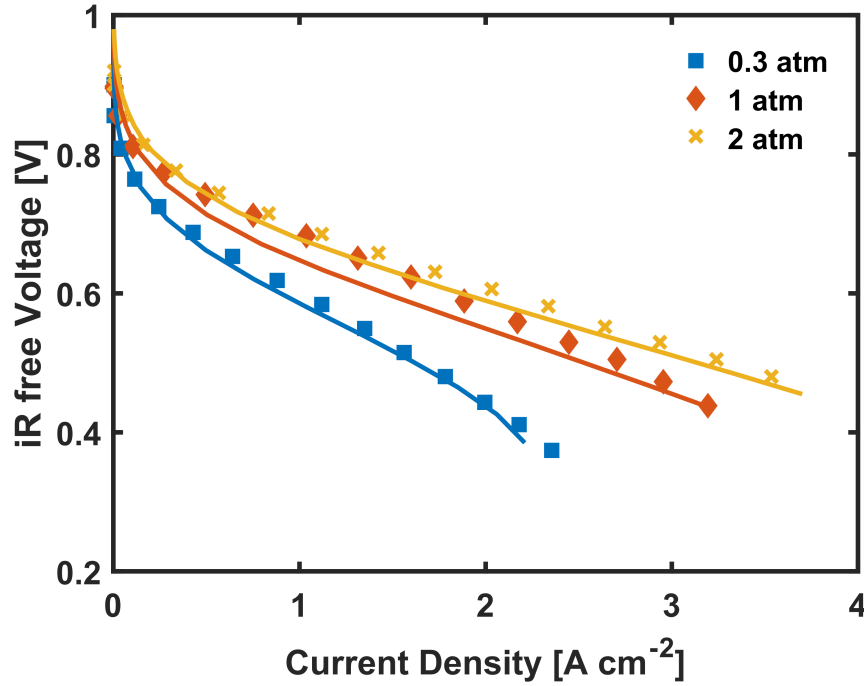


Figure 5.3: . Polarization curve for CM-PANI-Fe with 35 wt. % Nafion loading electrode. The symbols are for experimental results [37] and the line represents the model results. The simulation parameters match the experimental of 80°C and 100 % RH feed with H_2/O_2 in anode/cathode.

obtained from nano-CT imaging is incorporated. Due to the difference in activity observed in higher Nafion loading owing to the Nafion distribution, the $R_s J_s$ parameter was refit at 0.8 V for the 50 and 60 wt. % loading electrode. The model is able capture the trend in morphological change due to the increase of Nafion loading. The hierarchical agglomerate model is also able to capture the second Ohmic slope, in 50 and 60 wt. % loading electrode, which is a trait of flooding in the thick electrode. In both the O_2 and air case, the model prediction of the current density at the Ohmic region is lower than

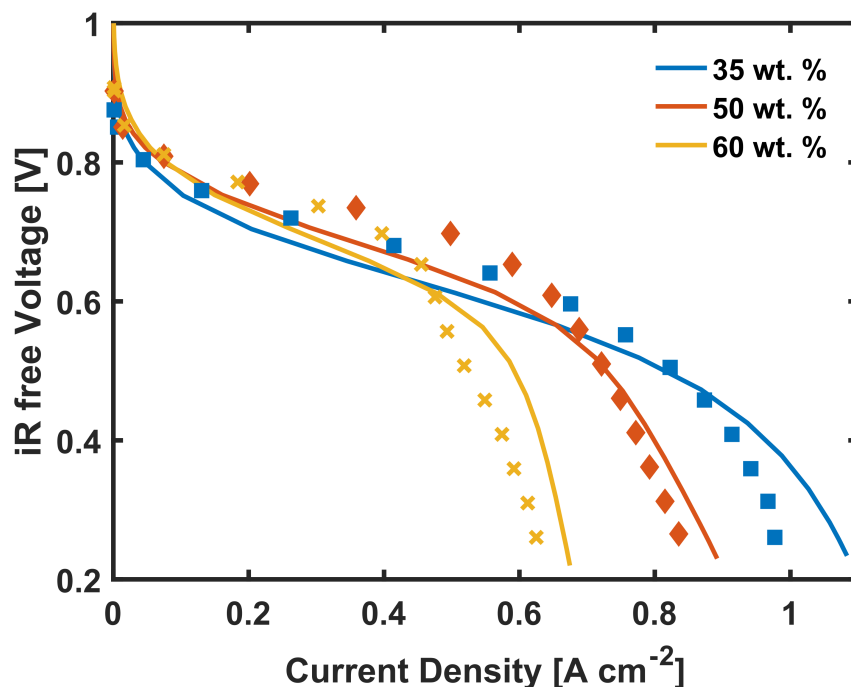


Figure 5.4: Experimental and model polarization curves for CM-PANI-Fe cathodes with 35, 50, and 60 wt. % Nafion loading. The cell was operated at 80°C with air and H_2 both at 100 % relative humidity and 1 atm. The symbols are for experimental results (Figure 3.2) and the line represents the model results.

the experimental values. This is due to the early onset of flooding based on the water retention curve. The Young-Laplace equation in the model is used independently of the contact angle for the water retention curve in the CL in the model. The wide variation of the Nafion distribution in the three loadings makes it difficult to estimate an accurate contact angle. Increasing the contact angle more hydrophobic reduces the flooding at the higher potential increasing the current density at the Ohmic region.

5.3.2 Voltage Losses

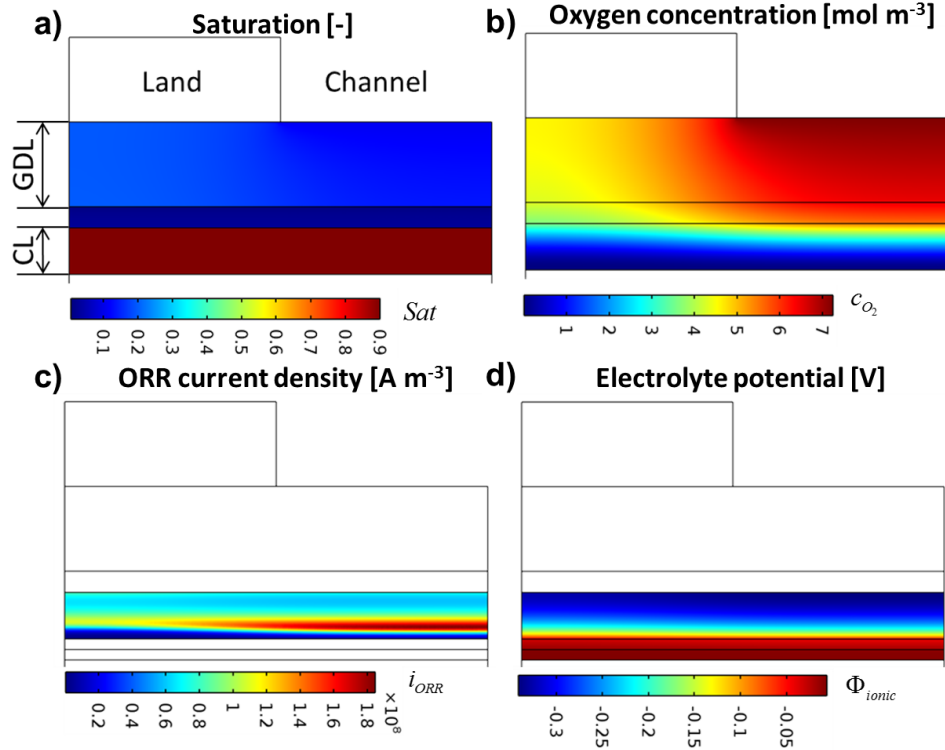


Figure 5.5: 2D spatial distribution in the cathode at 0.4 V for 50 wt. % Nafion loading electrode. a) Liquid water saturation. b) Oxygen concentration [mol/m³]. c) ORR current density [A/m²]. d) Ionic potential [V]. The voltage loss is a flooding induced ohmic loss.

This section discusses the loss in performance and the second Ohmic slope observed. The difference in the current density at the mass transfer region can be attributed to the difference in flooding and the morphological changes due to Nafion distribution. In the 50 and 60 wt.% the decrease in the pore size, due to Nafion infiltration into the micropores, increases the oxygen transport resistance and also makes the pores more susceptible to flooding. Figure 5.5a shows the saturation of 50 wt. % Nafion loading

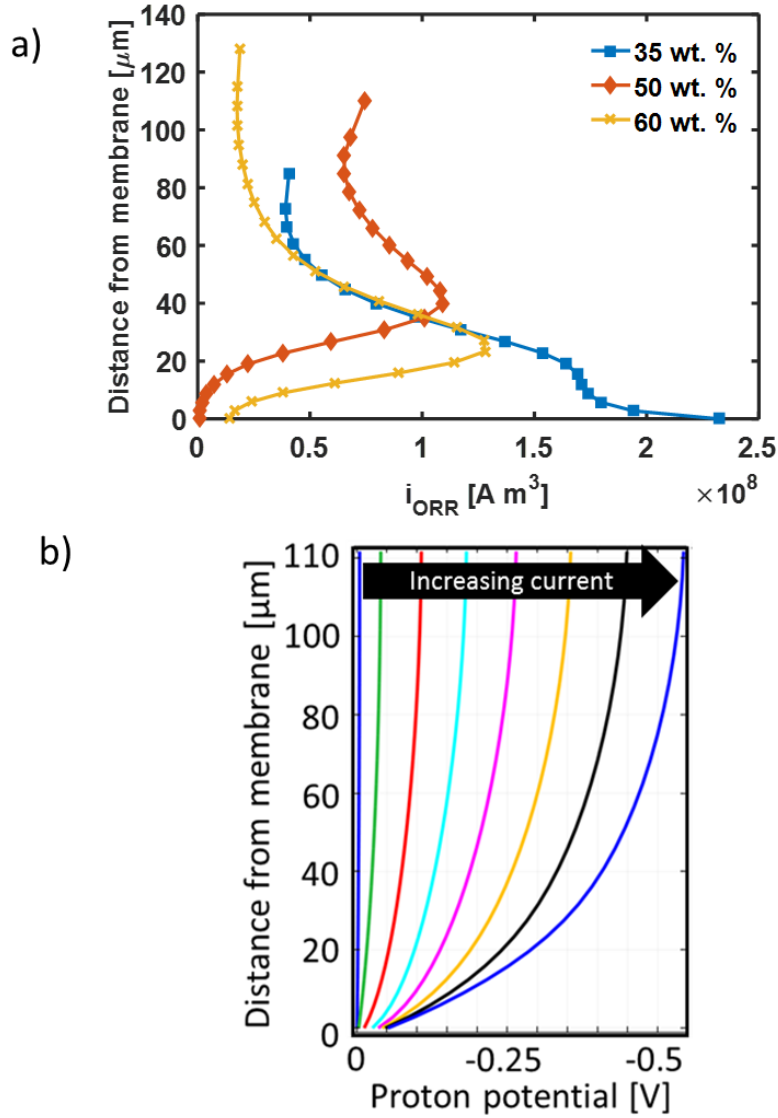


Figure 5.6: a) Through-plane ORR distribution for different Nafion loading of the CM-PANI-Fe electrode at 0.2 V. b) Through-plane ionic potential in the CCL at different voltages for 50 wt.% Nafion loading electrode.

electrode at 0.4 V. The CCL is completely flooded at high current densities. Figure 5.5b shows the O_2 distribution in the cathode. The liquid water flooding starves the CL of

oxygen and hence, the reactions shifts away from membrane at high current density. In the flooded region the CL acts as a low conductivity proton conductor. Figure 5.5d shows that high current density the Ohmic loss due to flooding is approximately 400 mV. In the catalyst layer the apparent mass transfer loss, which is shown as second Ohmic slope, is due to Ohmic loss through liquid flooded electrode. The large Ohmic drop is due to the flooded electrode acting as a poor proton conductor. Figure 5.6a shows the ORR in the through plane CL cross-section. The 35 wt. % Nafion loading electrode has a higher utilization of the CL while the 50 and 60 wt. % electrode has an initial 15 μm from the membrane unutilized. Figure 5.6a shows the through ionic potential drop in the CL for 50 wt. % Nafion loading electrode at different operating voltages.

All the further analysis is done for the 50 wt. % Nafion loading because of the lower activation losses and the optimization of the electrode structure can improve the performance in the mass transfer region. Figure 5.7 shows the overpotential loss in 50 wt. % electrode due to the resistance in different domains. We identify the potential gain by setting the various resistance parameters to zero individually and subtracting from the base case polarization. The different resistances have a non-linear relationship. The effect of liquid water is studied by computationally setting the saturation to zero. The diffusion coefficients in different domains were multiplied by a large factor to make the transport resistance to zero. The effect of liquid water is the highest losses that occur in the cathode, while the diffusion and ionic conductivity in the CL are the second largest loss. This indicated the losses in the CL could be mitigated by better distribution and

infiltration of Nafion, which influences the pore size, ionic conductivity, and the contact angle. Similarly improving the diffusion in the GDL and MPL can also improve the losses at the mass transfer region by about 250 mV. A different GDL with increased diffusion coefficient and water removal capability can improve the performance of the electrode. Diffusion in the Nafion film surrounding the agglomerate and diffusion in the micropores in the agglomerate shows minimal or no effect on the performance. Once the flooding is mitigated, the other resistances would become significant, and there is a significant effect of the Nafion distribution through ionic conductivity and diffusion in the micropores.

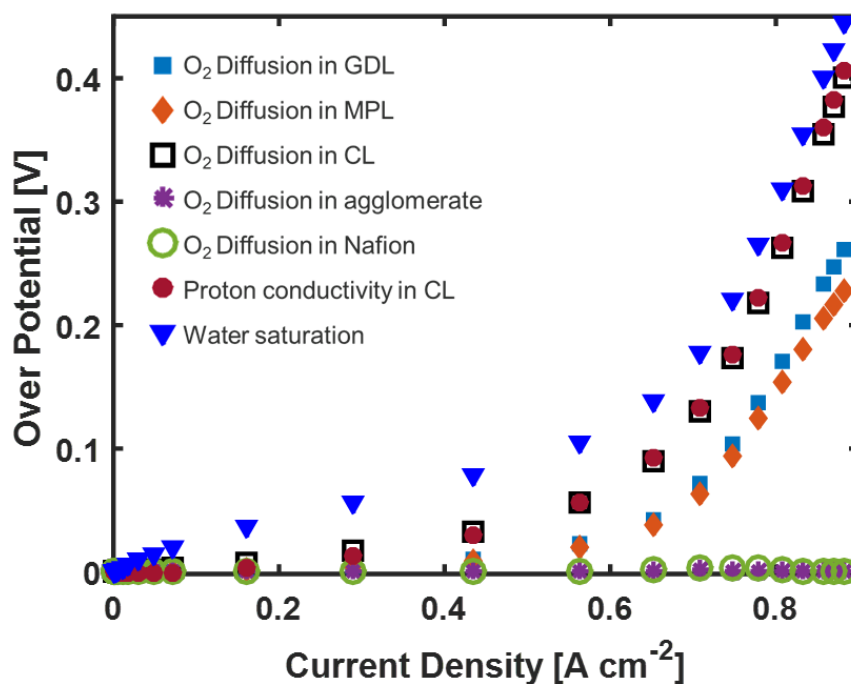


Figure 5.7: Voltage gain due to different resistance in the electrode for the 50 wt. % Nafion electrode. The model was operated with H_2 and air fully humidified gas at 80°C and 1 atm partial pressure.

5.4 Summary

This chapter presents an electrochemical model framework to characterize the electrochemical performance of PGM-free electrodes. Parameters extracted from using multi-resolution multi-contrast mode in nano-CT is used to inform the model of the hierarchical architecture of the PGM-free electrode. The model is validated against the experimental evaluation for PGM-free electrodes three different Nafion loadings (35, 50, and 60 wt. %). The model can accurately predict the trend and is able to capture the transport losses in the fuel cell. The large Ohmic drop observed in the higher Nafion loading (50 and 60 wt. %) is due to flooding induced ionic potential loss. Different resistance is compared and is found to have a non-linear relationship. Mitigating liquid water saturation, ionic conductivity, and the diffusion in the CL can significantly improve the performance of the electrode.

Chapter 6

Parametric Study of the PGM-free Electrode Morphology

6.1 Introduction

This chapter uses the model described in chapter 5 for a parametric study on the electrode morphology's significance on the electrochemical performance. Parametric study on various operating conditions and morphological parameters is performed and compared to the base case for the 50 wt. % Nafion loading. Wettability, catalyst loading, Nafion distribution is studied in detailed to understand the effect of water saturation, thickness and Nafion loading. Size distribution effect is studied using the model by changing the diameter distribution from the nano-CT to a single representative diam-

eter. The present analysis not only provides a model for characterization but also provide actionable goals and targets for improvement of the PGM-free catalyst. Finally, we discuss the effect of the different parameters on theoretically improved catalyst activity electrode. We also present an experimental study on the a hydrophobic cathode to study the effect of liquid water saturation.

6.2 Model Results

6.2.1 Parameter Sensitivity

Different morphological and operating parameters were systematically varied in the 50 wt. % Nafion loading electrode under realistic conditions to find optimal parameters. The wettability of the cathode catalyst layer (CCL) has the highest effect of power density. At 0.7 V, increasing the operating pressure and Nafion conductivity increases the power density by 50 mWcm^{-2} . At the voltage corresponding to maximum power, decreasing the thickness increases the power density by approximately 100 mWcm^{-2} . Other morphological parameters like volume fraction and tortuosity of pore and Nafion domain show an increase of less than 50 mWcm^{-2} . Diffusion in Nafion and tortuosity of Nafion volume fraction have a minimal improvement in power density. The following sections discuss a few parameters in detail.

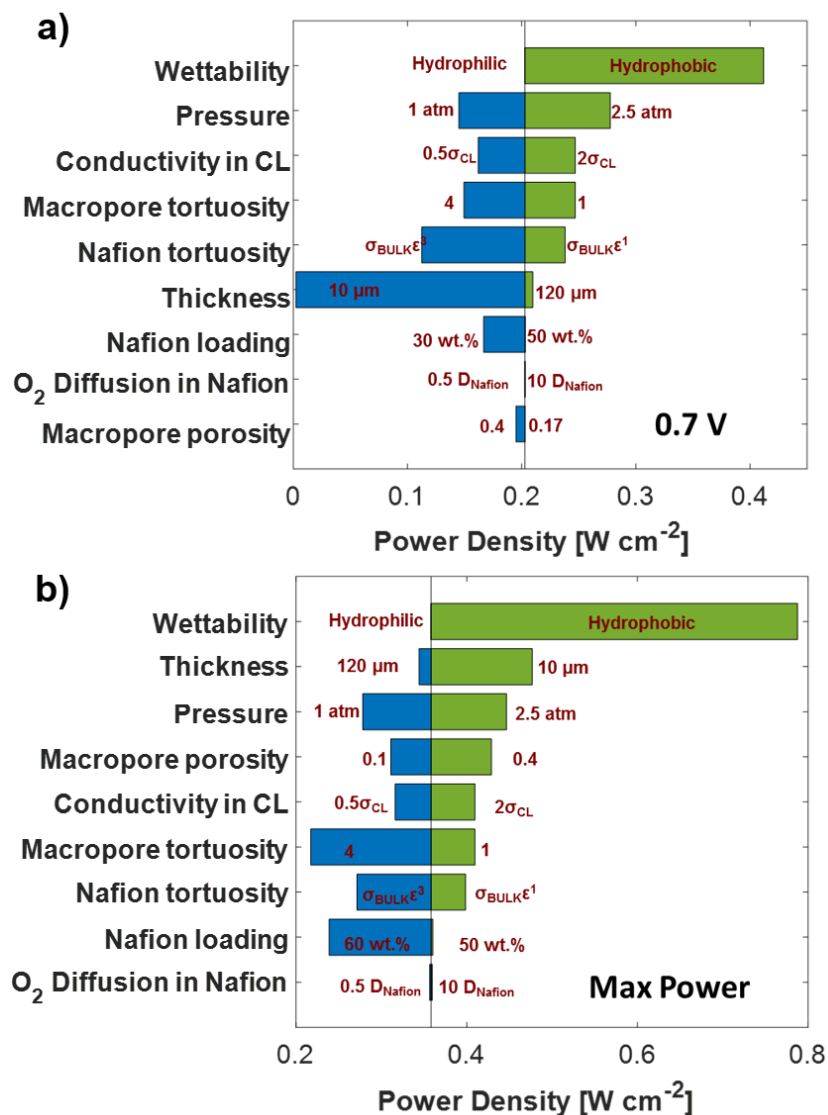


Figure 6.1: Parameter sensitivity for different morphological and operating conditions at a) 0.7 V and b) voltage corresponding to maximum power. The base case is the CM-PANI-Fe 50 wt. % Nafion loading electrode fully humidified air and H_2 at 80°C and 1.5 atm total pressure.

6.2.2 Wettability

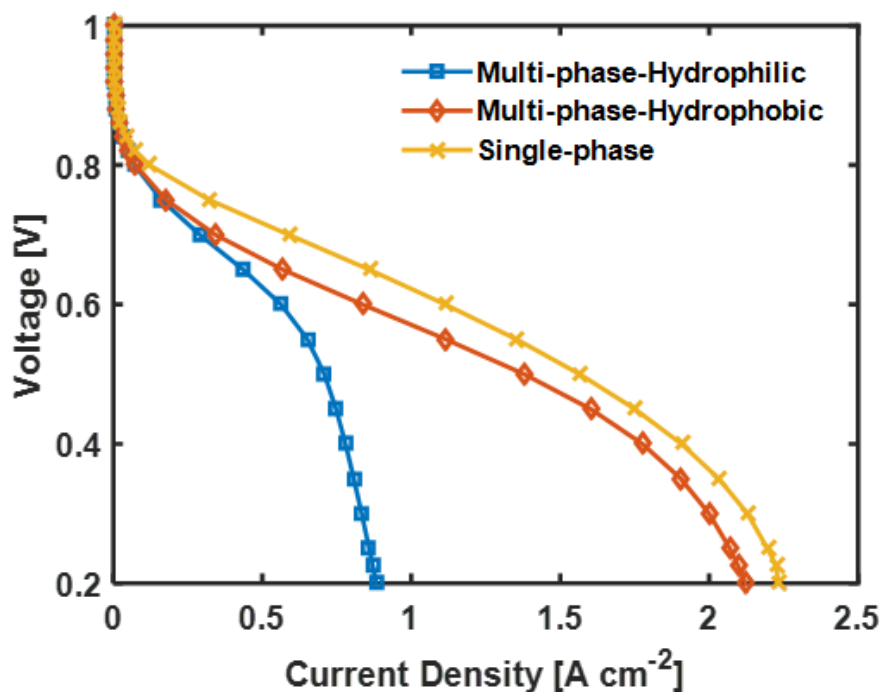


Figure 6.2: Effect of wettability on the 50 wt. % Nafion loading CM-PANI-Fe electrode. The simulation was run at 80°C and 100 % RH H_2 and air feed gas at 1 atm partial pressure.

This section discusses the effect of liquid water on the performance of the PGM-free electrode. Figure 6.2 shows the effect of wettability of the electrode for the 50 wt. % Nafion loading electrode. The base case is the multiphase simulation with hydrophilic wettability. The effect of water saturation was studied by computational setting the saturation to zero in the single-phase case. Removing liquid water shows significant improvement in the performance at all potentials below 0.8 V. In the mass transfer region, the current density is nearly doubled. Maintaining zero saturation is a practical

difficulty in the low-temperature fuel cells. However, fabricating the electrode with a hydrophobic wettability is possible by adding either dimethyl silicone oil (DSO) [109] or polytetrafluoroethylene (PTFE) [110]. The hydrophobic electrode is shown to have improved mass transport by reducing flooding. In the model, wettability is changed by changing the contact angle in the Young-Laplace equation to the hydrophobic region (180°). The macropore is changed to hydrophobic while the micropore still is hydrophilic. This is a realistic assumption because the hydrophobic domain has a lower chance of infiltration into the micropore. The hydrophobic cathode performs lower than the condition of no liquid water (single phase) but higher than the hydrophilic cathode. The actual performance of the hydrophobic cathode will be lower than the model prediction as the volume fraction of the hydrophobic domain is not considered in the model.

6.2.3 Thickness / Catalyst Loading

This section discusses the effect of the thickness of the CCL. Reducing the thickness of the CCL reduces the loading hence the active site density. While reducing the reducing except the thickness, other morphological parameters are kept constant. Figure 6.3 presents the polarization curve for varying thickness/catalyst loading. This is reflected in lower performance in the activation region with reducing thickness. Reducing the thickness of the electrode reduces the mass transport losses and thereby increasing the current density at a lower potential. While reducing the thickness of the electrode, mor-

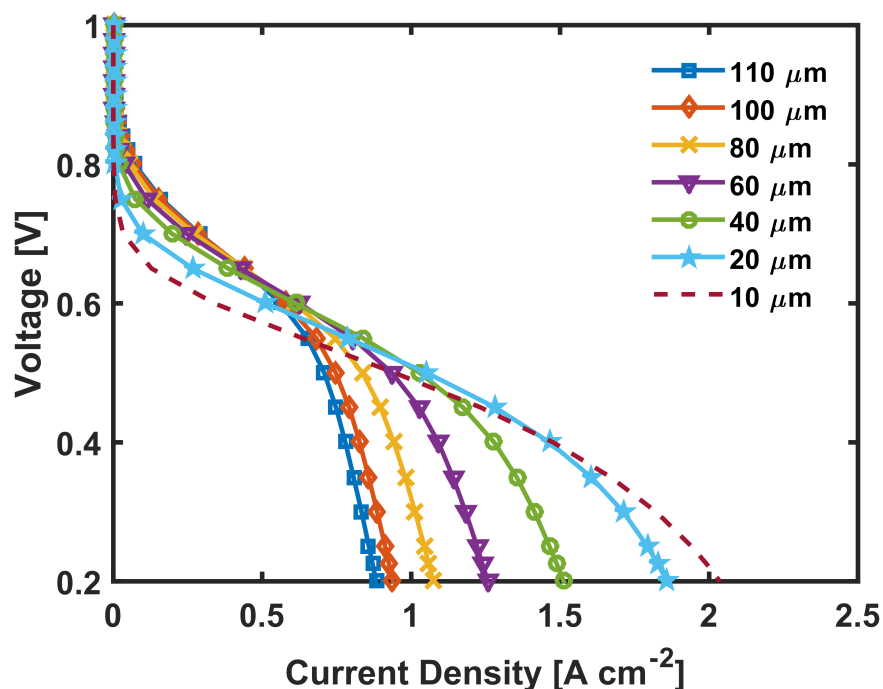


Figure 6.3: Effect of thickness on the 50 wt. % Nafion loading CM-PANI-Fe electrode. The simulation was run at 80°C and 100 % RH H_2 and air feed gas at 1atm partial pressure.

phological parameters were constant including the active site density and activity. If the thickness is reduced by decreasing the porosity, performance in the activation region would remain similar to the base case but decrease in performance decrease can be expected in the mass transfer region due to increased oxygen transport resistance.

6.2.4 Nafion Loading

In this section the effect of the Nafion loading and distribution is studied. The Nafion volume fraction and distribution is calculated assuming uniform distribution unlike the

base case 35 wt. % Nafion loading (Figure 3.15). The other assumptions for calculating the Nafion volume fraction and the film thickness are

- For loading below 50 wt.%, only the micropores inside the agglomerate are infiltrated with Nafion, and there is no Nafion film formation on the agglomerate.
- The film growth happens for Nafion loading greater than 50 wt. %.
- Volume fraction of the micropore and macropore are corrected accordingly to the increase in Nafion volume fraction as well as film thickness growth.

The Nafion volume fraction, ε_{Nafion} , in the agglomerate is

$$\varepsilon_{Nafion} = \begin{cases} \frac{M_{Nafion}}{\rho_{Nafion} L_{CCL}}, & y_{Nafion} < 0.5 \end{cases} \quad (6.1)$$

$$\varepsilon_{Nafion} = \begin{cases} \frac{M_{Nafion,50wt}}{\rho_{Nafion} L_{CCL}}, & y_{Nafion} > 0.5 \end{cases} \quad (6.2)$$

where ρ_{Nafion} , L_{CCL} , and y_{Nafion} are the density of Nafion, thickness of the cathode catalyst layer, and the Nafion wt. % respectively. Mass of Nafion, M_{Nafion} , is calculated as

$$M_{Nafion} = \frac{M_{catalyst} y_{Nafion}}{(1 - y_{Nafion})} \quad (6.3)$$

The film thickness, δ_{film} , is similarly calculated as

$$\delta_{film} = \begin{cases} 0, & y_{Nafion} < 0.5 \end{cases} \quad (6.4)$$

$$\delta_{film} = \begin{cases} \frac{\varepsilon_{Nafion} - \varepsilon_{Nafion,50wt}}{\varepsilon_{solid} SA}, & y_{Nafion} > 0.5 \end{cases} \quad (6.5)$$

where ε_{solid} is solid volume fraction and SA is the surface area of the agglomerate obtained from nano-CT imaging.

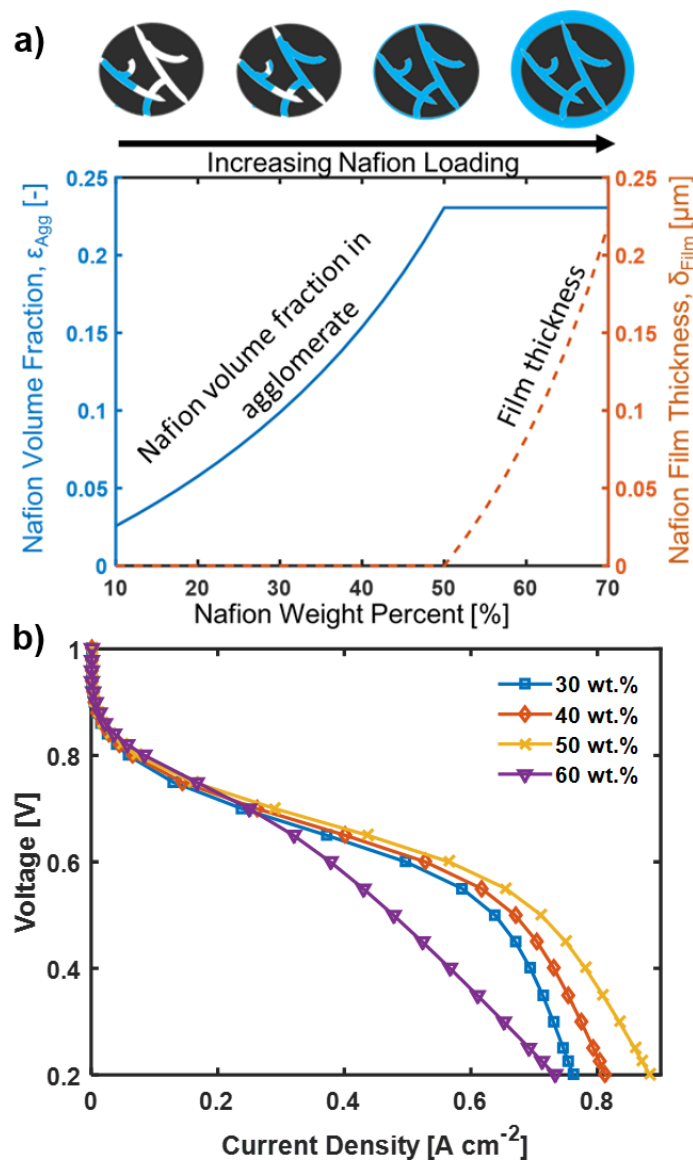


Figure 6.4: Theoretical performance of CM-PANI-Fe electrode with varying Nafion loading. a) Nafion volume fraction and film thickness as a function of the Nafion loading. b) Polarization curve with Nafion loading from 30 wt. % to 60 wt. %.

These assumptions are based on the Nafion imaging using nano-CT for 35, 50 and 60 wt. % Nafion loading electrodes (Figure 3.15). Based on the hypothesis, the Nafion

volume fraction inside the agglomerate increase till 50 wt. % and then remains constant, while the excess Nafion forms a film around the agglomerates. Figure 6.4 a shows the Nafion volume fraction and the film thickness as a function of Nafion loading. Figure 6.4b shows the resulting polarization curve for varying Nafion loading. The current density at the activation region increases with increasing Nafion loading. In the mass transfer region, the current density for the different loading shows an optimal Nafion loading of 50 wt. %. The 30 wt. % theoretical loading electrode shows higher activation than the similar Nafion loading of 35 wt. % base case but there is a performance decrease at mass transfer region compared to the baseline scenario due to the decrease in the micropore volume fraction. The 60 wt. % Nafion loading shows a significant Ohmic drop than observed in baseline scenario which is due to the assumption of constant thickness and decrease in macroporosity. Therefore, for these thick PGM-free electrodes 50 wt. % is an optimal loading which is higher than the usual 30-35 wt. % Nafion loading in the thin film PT electrodes.

6.2.5 Agglomerate size distribution

This section discusses the effect of using the distribution of ASD versus a single representative diameter. Figure 6.5a shows the ASD for the 50 wt. % loading electrode as well as the mean and mode of the distribution. The mean and mode diameter of the distribution are $0.9\ \mu m$ and $2\ \mu m$ respectively. In addition, the average diameter observed from the SEM is $6\ \mu m$ (Inset of Figure 6.5). The distribution in the agglomerate model

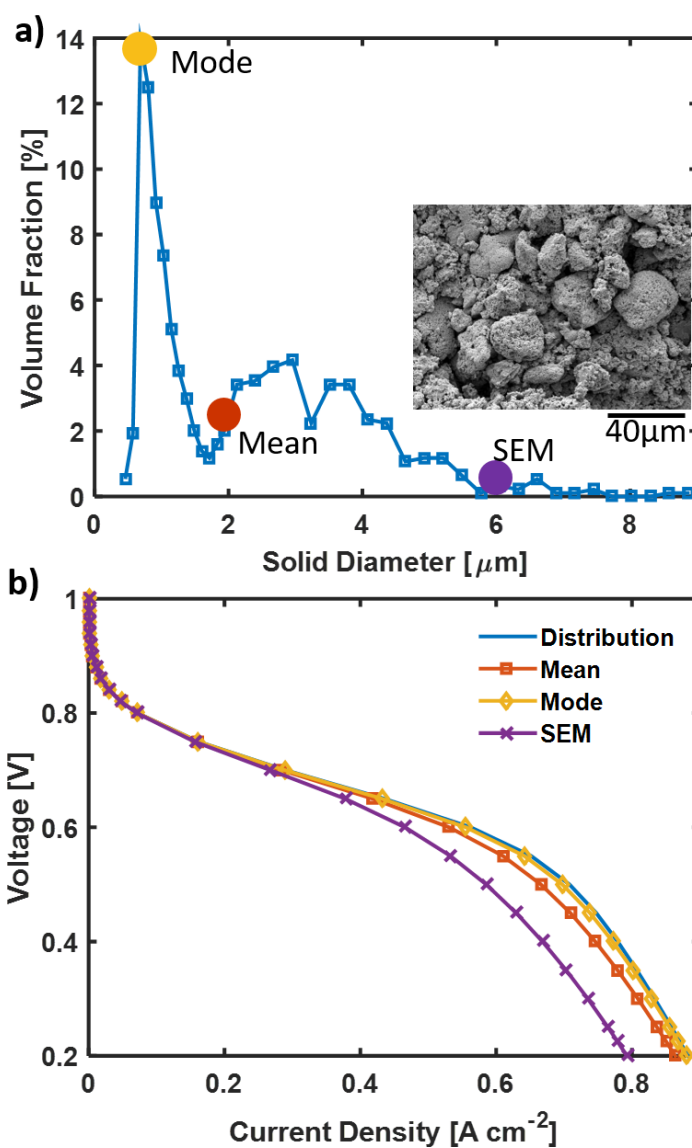


Figure 6.5: a) CM-PANI-Fe 50 wt. % Nafion loading agglomerate distribution. Inset: SEM of the 50 wt. % Nafion loading CL. b) The polarization curves predicted using the model for the distribution and the single representative diameters. The model was simulated at 80°C and fully humidified H_2 and air at 1 atm partial pressure.

is implemented using Eq. 5.43. The single diameter case simulations were run setting the volume fraction of the corresponding diameter to 1 and the rest to zero. Figure 6.5b shows the resulting polarization curve comparison for the distribution and single diameter. For the current activity, the polarization curve difference for the distribution and the mode case is very low. Similarly, for the mean from the distribution and the average diameter from SEM there is no difference in the activation region. While at the mass transfer region, the performance is lower than the distribution case. This indicating that at the high current densities, the contribution of the smaller agglomerates around the mode is greater than the contribution of the larger agglomerates above the mean of the distribution. Therefore, the preferred size of the agglomerates would be lower than the mode of the distribution, but decrease in agglomerate size would also reduce the pore size.

6.2.6 Parametric study of the catalyst activity

In this section, we discuss the density or activity of the active site improvement needed to achieve the power density targets. Figure 6.6 shows the multiplication factor to the $R_s J_s$ parameter versus thickness of the CCL. The optimal thickness of the CCL decreases with increase in the activity or site density for operating voltages of 0.7 V and 0.6 V. Lowering the thickness of the electrode when operating at 0.5 V and operating at maximum power is preferred because of reduced mass transport losses. Strategic analysis showed an intermediary target of 475 mW cm^{-2} rated power is required for PGM-free electrodes

to be cost effective. Figure 6.6a shows that to achieve the power density target, a 40 times increase in either the active site activity or the activity per site is needed. The optimal thickness for 40 times increase in volumetric activity at 0.7 V is 47.5 μm while at 0.6 V is lower than 20 μm . At 0.5 V and the voltage corresponding to maximum power, the optimal thickness, shown in Figure 6.6c and 6.6d, is below 20 μm . At rated power, 15 times increase in the volumetric activity can significantly improve the power density at 0.7 V by a factor of 4. The site density can also be increased by increasing the utilization of the metal site. Sahraie *et al.* estimated that only 20 % of the iron metal centres are ORR active in acidic medium [21]. The active iron sites corresponds as 1 wt. % of

Increase in half wave potential for the catalyst, $E_{1/2}$, is calculated using the following equation:

$$E_{1/2,2} - E_{1/2,1} = \left(\frac{RT}{\alpha F} \right) \log \left(\frac{i_2}{i_{o,2}} \frac{i_{o,1}}{i_1} \right) \quad (6.6)$$

Assuming the same catalyst loading for the calculation which would leads to the same limiting current. Hence the current density corresponding to the half wave potential is same, *i.e.*, $i_1 = i_2$. In Eq.6.6 the value of α , R , and T are 0.5, 8.314 [$JK^{-1}mol^{-1}$], 353 [K] respectively. For 15 times increase in volumetric activity ($i_{o,2} = 15i_{o,1}$), the overpotential at the have wave potential decreases by 0.16 V. For the *CM - PANI - Fe* catalyst the current half wave potential, $E_{1/2}$, is 0.77 V [108] and increasing the volumetric activity by 15 times increased the $E_{1/2}$ to 0.93 V, which is comparable to Pt-based electrodes.

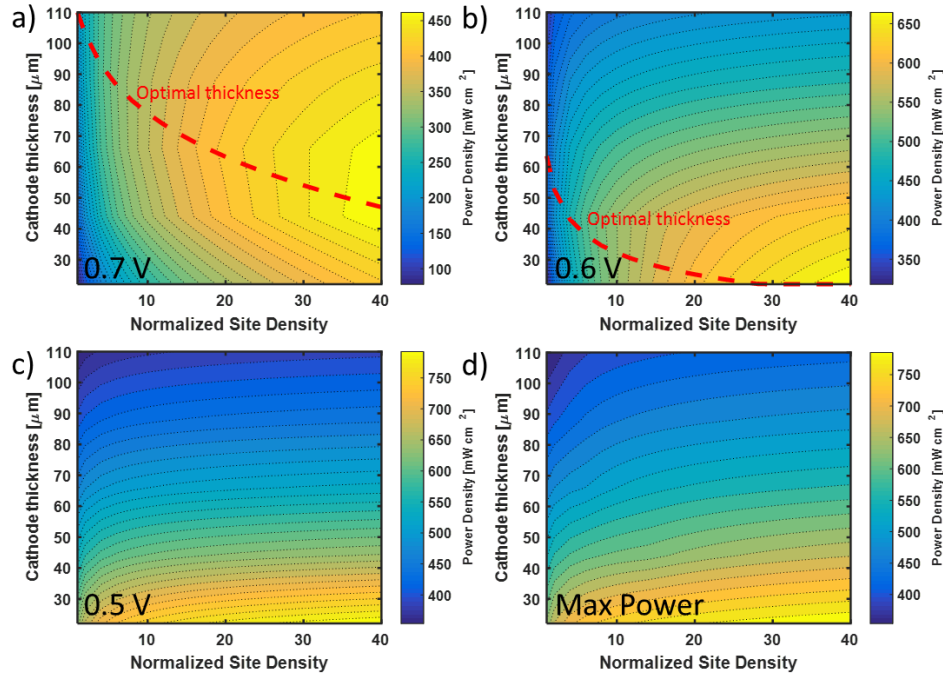


Figure 6.6: The power density of 50 wt.% Nafion cathode as a function of site density and thickness at a) 0.7 V, b) 0.6 V, c) 0.5 V, and d) voltage corresponding to maximum power. The optimal thickness is shown in dashed line.

6.2.7 Improved activity catalyst

This section discusses the difference in performance of the catalyst with increased activity or site density for 50 wt. % Nafion loading electrode. The $R_s J_s$ parameter is increased by a factor of 10. The morphological parameters were constant for the new electrode except the thickness of the CCL, which is $35 \mu m$ based on the optimal thickness estimation at 0.6 V from Figure 6.6b. Figure 6.7a shows the comparison between the electrode with the current activity and increased activity. Figure 6.7b shows the voltage gain due to

different resistances for the increased activity catalyst. The effect of flooding still has the highest effect in the improved activity catalyst. Unlike the current activity (Figure 5.7), the resistance shows similar voltage gain at the high current density. At the lower current density or higher potentials, ionic conductivity, and effect of water shows a 50 mV increase. If the effect of flooding is mitigated other losses in the GDL, MPL, and the CL becomes significant.

Figure 6.8 shows the parametric study of the various morphological parameters for the improved activity catalyst. Even in the improved activity catalyst, the wettability shows the highest effect of improvement in performance. Unlike the current activity catalyst, other morphological and operating parameters show significant improvement at 0.7 V. Increase in macropore porosity reduces the performance as the thickness of the CL increase with an increase in macropore porosity. Nafion distribution and infiltration is crucial to the performance as it controls the wettability, conductivity, and oxygen transport. However, diffusion in the Nafion and into the agglomerate do not affect the performance even with the increase in the volumetric activity.

Figure 6.9 shows the model prediction for using the distribution and the single representative diameter in the agglomerate model for the improved activity catalyst. The single representative diameter of mode and mean case from the nano-CT distribution have higher mass transport losses than the distribution. The average from the SEM case has lower performance because of the transport losses due to the higher diameter at lower potentials. For the current activity or site density, the agglomerate sizes do not

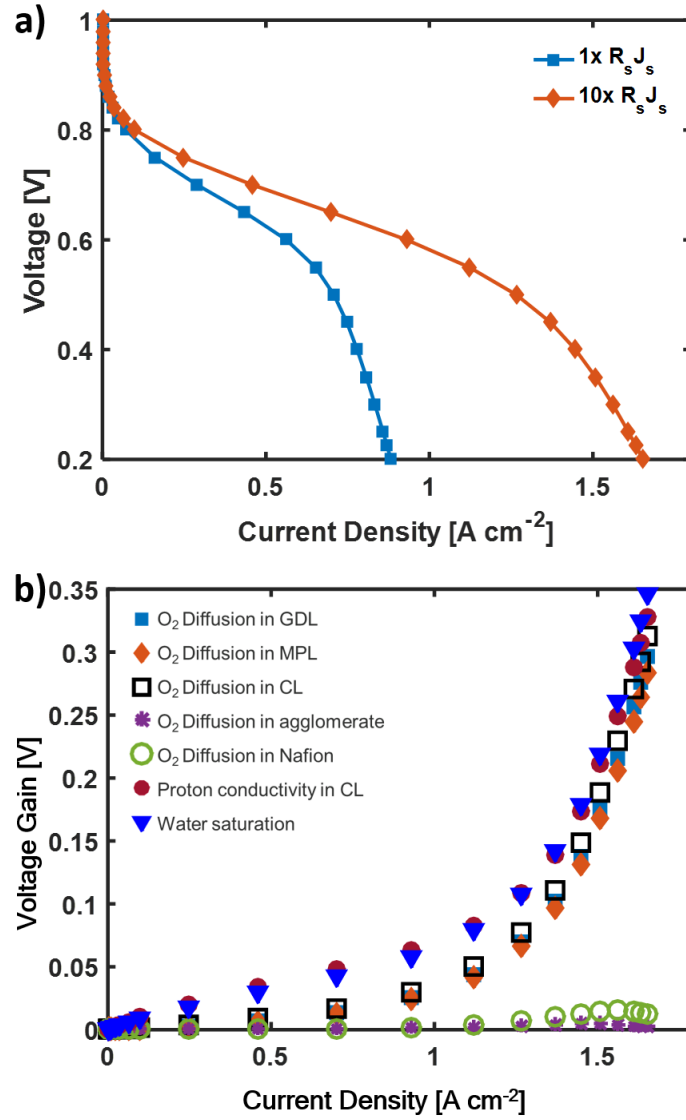


Figure 6.7: a) Polarization curve for current and the improved activity. b) Voltage gain due to different resistance in the improved activity catalyst.

vary the performance but once the activity or site density is increased the agglomerate diameter distribution becomes critical. If the activity of the catalyst is improved the agglomerate size of a few hundred nanometer is preferred as the even the mode of the

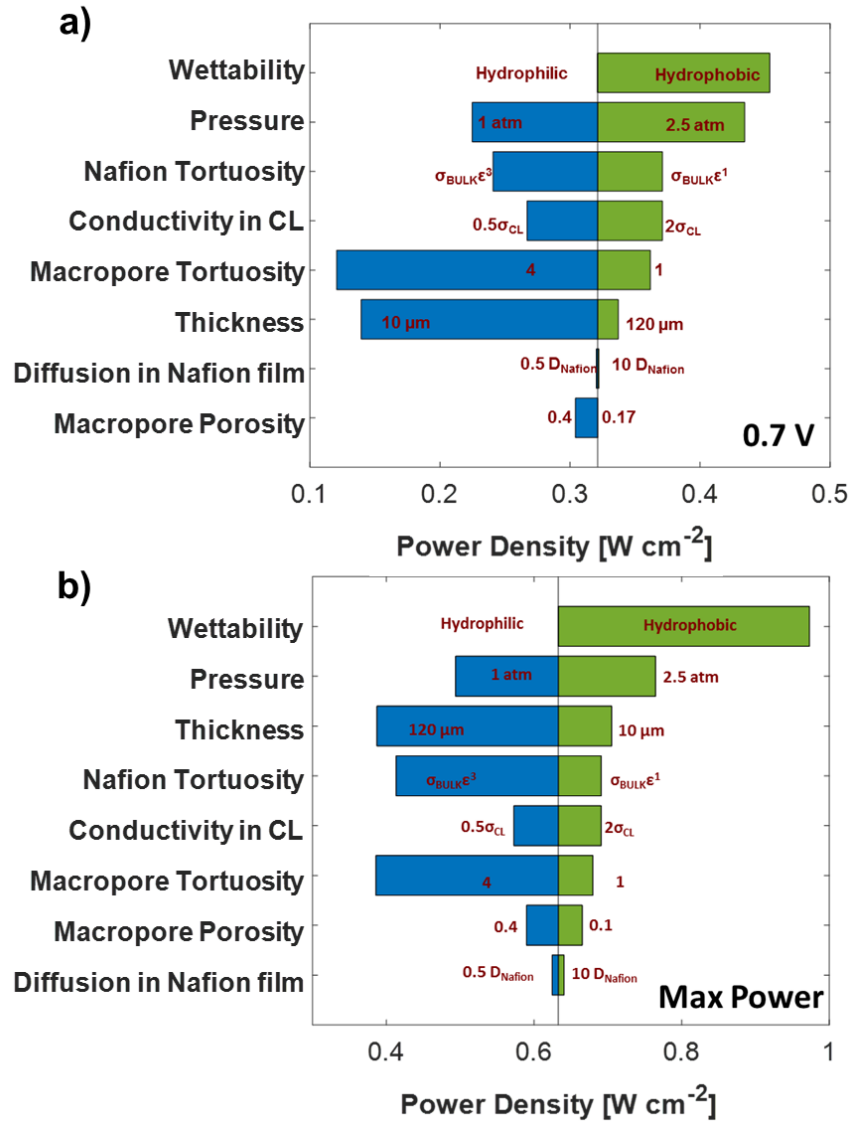


Figure 6.8: Parameter sensitivity for different morphological and operating conditions for the improved activity catalyst at a) 0.7 V and b) the voltage corresponding to maximum power.

distribution showed mass transport limitation. While reducing the size of the diameters, the macropore porosity should be maintained similar to the base case as decreasing the pore volume fraction reduces the oxygen diffusivity.

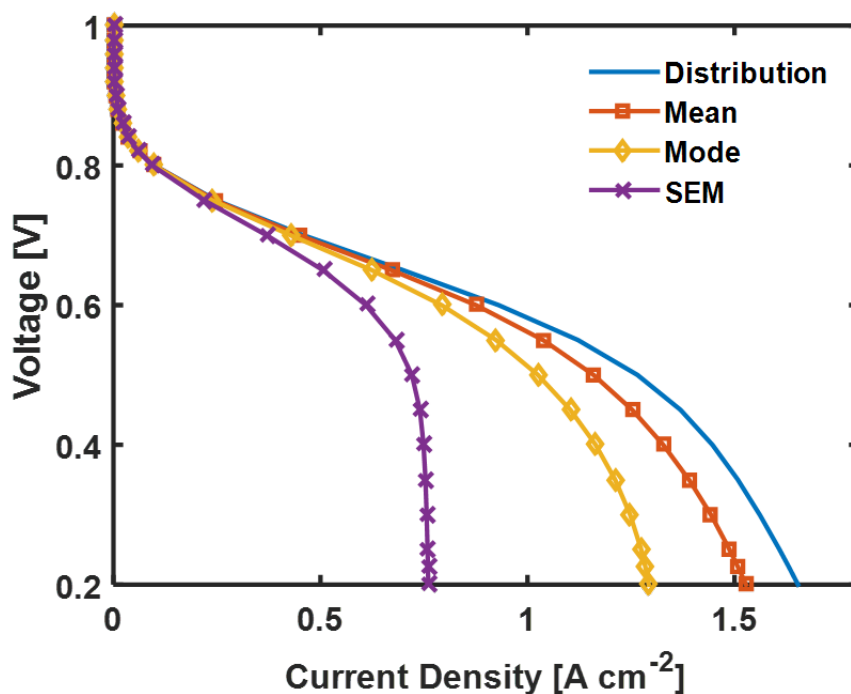


Figure 6.9: Model prediction of the improved activity catalysts polarization curve for an agglomerate model with distribution and single representative diameter.

6.2.8 Theoretical size distribution

Based on the polarization curve from Figure 6.5 there is an optimal agglomerate and pore size distribution which can increase the performance of the electrode. To generate the distribution of agglomerate and pore diameters, a bimodal log normal distribution (Eq. 6.7) is fit to the 50 wt. % Nafion loading electrodes ASD and PSD respectively (Figure 3.8). In Eq. 6.7, μ and σ are the mean and standard deviation. And f_1 is the fraction of the first modal distribution. Table 6.1 shows the multiplication factor to μ_1 and μ_2 , and the fraction, f_1 , value used to generate 4 different theoretical distributions. Figure 6.10

shows the different distribution for agglomerates and pores generated by varying μ_1 , μ_2 , and f_1 . Similarly, for the pore size distribution, the corresponding parameters were changed according to the agglomerate size distribution. The water retention curve was generated using the PSD, using the Van Genuchten model described in section 3.5 of chapter 3. In this study, thickness, porosity and the Nafion volume fraction were constant.

$$f_{dis} = \frac{f_1}{x\sigma_1\sqrt{2\pi}} \exp\left[\frac{\log(x) - \log(\mu_1)}{\sqrt{2}\sigma_1}\right] + \frac{(1-f_1)}{x\sigma_2\sqrt{2\pi}} \exp\left[\frac{\log(x) - \log(\mu_2)}{\sqrt{2}\sigma_2}\right] \quad (6.7)$$

Figure 6.11 shows the resulting polarization curve from the model simulation for the different distributions. Polarization curve for the distribution 1, 2, and 3 are similar to the nano-CT distribution while the 4th distribution shows mass transport losses. For the current activity of the PGM-Free catalyst the distribution with mean diameter around 1 μm . The distribution around mean diameter, distribution 4, shows mass transport losses which is due to the larger agglomerates. The performance of the distribution 1-3 would vary as the macroporosity would change with the distribution and macroporosity can affect the performance, as seen in Figure 6.1. The current activity of the PGM-free is low such that the distribution centered around 1 μm has similar effectiveness factor at high current densities. For the improved activity it shows the higher performance loss at mass transfer region.

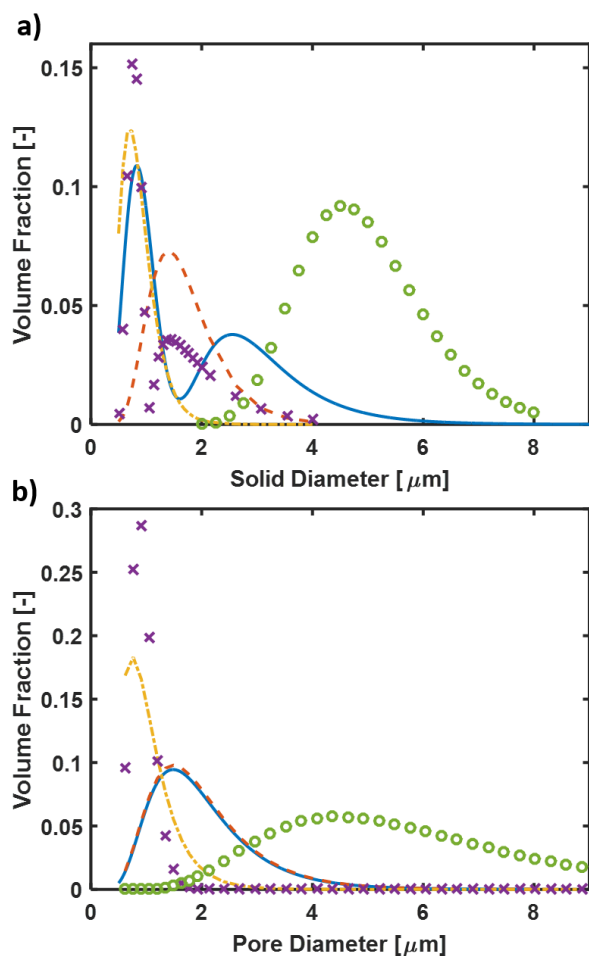


Figure 6.10: Distributions generated based on the distribution from nano-CT reconstruction of CM-PANI-Fe 50 wt. % Nafion loading electrode. Theoretical a) agglomerate size distribution and b) pore size distribution.

6.3 Hydrophobic Cathode

This section discuss the experimental evaluation of the PGM-free electrode with varying wettability of the catalyst layer. We fabricated hydrophobic cathode by adding PTFE particles of two different diameters to vary the surface area of the hydrophobic domain.

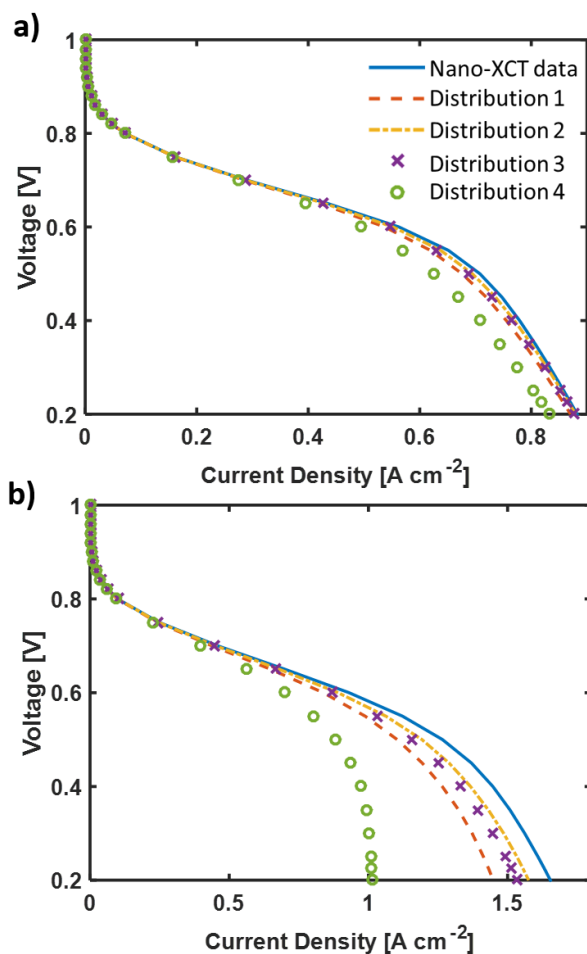


Figure 6.11: Polarization curve from the model for the theoretical size distribution shown in Figure 6.10. Model prediction with a) the current volumetric activity b) 10 times increment to the current volumetric activity.

The PTFE particle loading was 0.6 times the catalyst loading to ensure a percolating network of the hydrophobic domain.

6.3.1 PGM-free Ink

The catalyst ink was prepared by mixing and ultrasonicing the catalyst powder with a Nafion ionomer solution, deionized water, and isopropyl alcohol (IPA) such that the resulting electrode is 50 wt. % Nafion loading. The ink is painted on GDL (SGL 24BC with micro porous layer (MPL), Ion Power). PTFE particles of two different sizes (0.2 and 3 μm) are added to base ink and painted on a similar GDL to generate the hydrophobic GDE. The resulting catalyst loading is 5 $mg_{cat}cm_{geo}^{-2}$ and the PTFE loading in the hydrophobic cathode is 3 $mg_{cat}cm_{geo}^{-2}$. In the anode, a Pt/C GDE is used with a Pt loading of 0.3 $mg_{Pt}cm_{geo}^{-2}$.

Table 6.1: Agglomerate and pore size distribution parameters for the theoretical distribution using log-normal fit.

Distribution	Multiplication factor to μ_1	Multiplication factor to μ_2	f_1
1	x1	x1	1
2	x0.5	x1	1
3	x0.5	x1	0.5
4	x3	x1	1

6.3.2 Polarization Curve

The polarization curves were obtained galvanostatically. Each potential were applied for 60 seconds for greater than 0.8 V in steps of 0.02 V. For lower than 0.8 V, the potential was applied for 10 minutes in steps of 0.1 V. Last 20 % of the measured current in each step was averaged. The cell temperature and pressure was 80°C and 1 atm respectively. A fuel cell test stand (FCT-150, Biologic, France) was used to control the flow rate and humidity of the gases. The fuel cell voltage and the current were controlled and measured respectively by a potentiostat (SP-150, BIO-logic, Knoxville, TN).

Figure 6.12 shows the polarization for both the hydrophilic and hydrophobic cathode. In the activation region, both the hydrophobic cathode have increased performance but there is no increase performance in the mass transport region. The increase in the activation region might be due to the removal of water which makes the active site more accessible and hence increasing the active site density. But at the mass transport region, the decrease or no improvement in performance is due to the increase in thickness of the catalyst layer due to additional PTFE particles. It is unclear on the effect of the Nafion distribution in the CL due to the addition of the PTFE.

6.4 Summary

This chapter employs the model framework described in previous chapter for a parametric study of PGM-free electrode's morphological parameters. Effect of the wettabil-

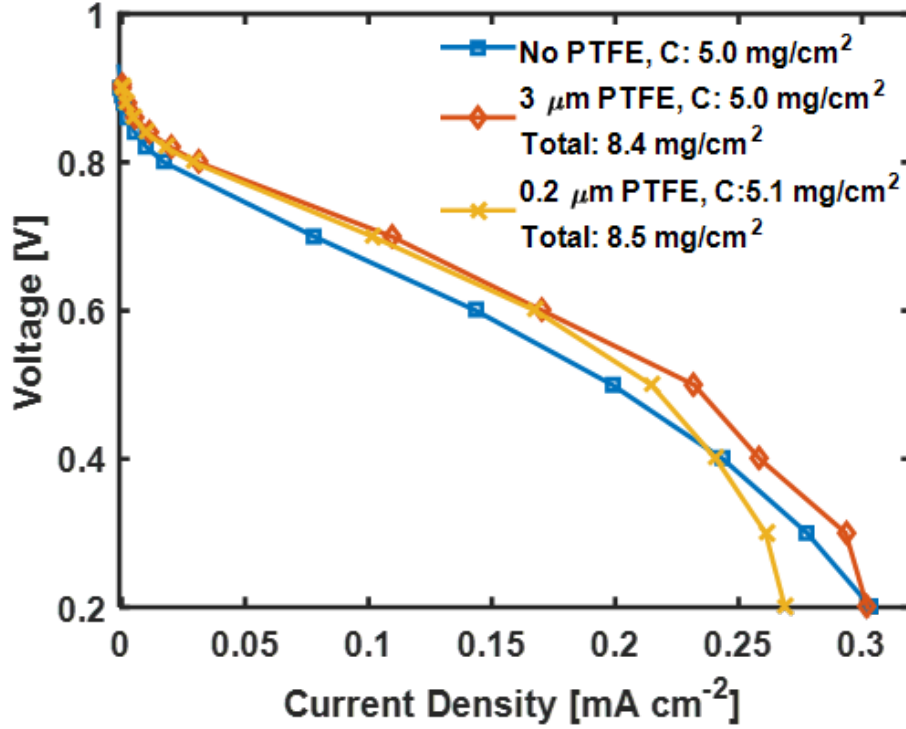


Figure 6.12: Experimental polarization curve at 80°C and 1 atm to study the effect of the wettability of the CL. The wettability is changed by adding PTFE particles.

ity, thickness, and Nafion loading is studied in detail. Single representative diameter and the distribution of the agglomerate diameter is implemented in the agglomerate model to understand the agglomerate size effects. Increase in the volumetric activity required to achieve power density targets is identified using parametric variation of the $R_s J_s$ parameter and the thickness. Also, parametric sensitivity on a theoretical improved activity electrode is studied. We also predict the optimal size distribution required for improved performance. Wettability of the CL was varied by adding PTFE particles to the 50 wt % Nafion loading catalyst ink. The hydrophobic cathode showed

improve performance in the activation region as more active sites were accessible due to removal of water.

Chapter 7

Conclusion, Contributions and Future Work

7.1 Conclusion and Contribution

7.1.1 Vertically Oriented Polymer Electrolyte Nanofiber Catalyst Support for Thin Film Electrodes

This chapter presented a novel catalyst support fabricated from polymer electrolyte. The vertically oriented high surface roughness nanofibers fabricated by solution casting ionomer solution onto a porous template. The sacrificial template used was a low cost track etched polycarbonate. We fabricate the membrane along with the nanofibers

which had a surface roughness factor of 21. Platinum (Pt) was deposited on the nanofiber side by physical vapor deposition (PVD) and chemical vapor deposition (CVD) to fabricate three different variations of the nanofiber electrode. The effect of surface roughness was compared to the electrode fabricated by depositing Pt directly onto flat membrane. The nanofiber electrodes fabricated through PVD showed incomplete coverage of the nanofibers which was inferred from the electrochemical surface area (ECSA). In another variation of the PVD nanofiber electrode, the template was pre-coated with Pt before solution casting to enhance the Pt coverage near the base of the nanofibers. PVD deposition of Pt on the template improved the ECSA and the performance of the nanofiber electrode but the Pt roughness was still lower than the nanofiber roughness. PVD process deposits the Pt on only one side of the Pt due to the orientation and does not cover the underside of the nanofiber. Even the deposition on the template does not coat any meaningful distance into the pores. Pt deposition using CVD were able to provide a higher coverage of the nanofibers. Also, the annealing process after CVD deposition provided additional roughness to the deposited Pt. The nanofiber electrodes were characterized electrochemically using cyclic voltammetry (CV) and polarization curves. ECSA was an order of magnitude higher for the chemical vapor deposited nanofiber electrode (CVDNE) compared to the other electrodes. The Nafion 115 electrode had a Pt roughness of 2 indicates Pt roughness on the flat surface. The polarization curve showed the three variants of nanofiber electrodes performed better than the planar variant. CVDNE performed better than the bare and pre-sputtered template nanofiber electrode but suffers from severe flooding. The results suggests that the nanofiber cat-

alyst support improves performance and is a viable approach. The performance of the CVDNE is higher than previously fabricated electrode by direct Pt deposition on membrane.

7.1.2 Resolving Electrode Morphology's Impact on PGM-free Cathode Performance

In this chapter, platinum group metal-free (PGM-free) cathodes were characterized using nanoscale resolution X-ray computed tomography (nano-CT) imaging and transport simulations to elucidate the fuel cell performances sensitivity to Nafion ionomer loading with these promising catalysts. The hierarchical architecture of these electrodes was resolved by using different imaging resolutions and the solid, pore, and Nafion domains were distinguished by separate imaging in Zernike phase contrast and absorption contrast with the aid of cesium staining of the ionomer. Three cathodes with different Nafion loading (35, 50, and 60 wt. %) were characterized. Purely structural characteristics, including porosity, agglomerate, and pore size distribution was obtained by image processing. Significant difference is observed in the ionomer distribution for different loading. 35 wt. % loading had sparse distribution and low infiltration into the micropores. 50 and 60 wt. % loading electrode had a higher infiltration into the micropore and a more uniform distribution. The excess amount of Nafion in 60 wt. % leads to film growth outside the dense agglomerates. Water retention curve for both the micropore and macropore is obtained using Van Genuchten model which is a log-normal fit to the

pore size distribution. Pore/particle-scale finite element simulations using the nano-CT images were performed on three domains (catalyst, gas, and Nafion) to study the electronic, gas, and ionic transport. Morphological transport parameters like formation factor, gas transport tortuosity, and Nafion tortuosity were obtained. The significant change in measured fuel cell performance with these changes in Nafion loading were attributed to significant changes in the Nafion distribution with increasing amounts of Nafion. At the lowest loading of 35 wt. %, the low observed activity was attributed to the poor infiltration of the Nafion ionomer into the catalyst particles. In contrast, with the highest level of Nafion loading (60 wt. %), the build of excess Nafion as films on the outside of the catalyst particles made for macropores pores with greater water retention, resulting in severe flooding. The severe flooding is evident in the second Ohmic slope of the experimental polarization curve, which results from a majority of the protons having to be conducted across a fully-flooded thickness of inactive cathode that behaves like an additional low conductivity membrane.

7.1.3 *In-situ* through-plane measurements of ionic conductivity and ionic potential distributions in PGM-free electrode

This chapter demonstrated the use of a novel *in-situ* experimentation to investigate the proton conduction and the ionic potential distribution in thick PGM-free electrodes. Microstructured electrode scaffold (MES) with 8 sense layers were fabricated with a total height of 86 μm . Using the MES experimental setup, the ionic potential was measured

at discrete points through the thickness of the electrodes using the sense layers to infer the oxygen reduction reaction (ORR) current density distribution across the electrode. We observe the ORR focused near the membrane in drier conditions, while at high relative humidity (RH) the ORR shifts towards the CL|MPL interface. The ionic potential measurements provides experimental evidence for the observed second Ohmic slope due to flooding induced Ohmic loss in higher Nafion loading. *In-situ in-operando* proton conductivity is measured using four-wire measurement. The proton conductivity measurements show that conductivity is quite sensitive to RH as well as the rate of ORR water generation. The value of proton conductivity calculated using the particle scale simulation from chapter 3 and using MES are similar for the 50 wt. % Nafion loading PGM-free electrode. The polarization curve and the ionic potential measurement at the high RH provided experimental verification of the second Ohmic slope.

7.1.4 Modeling Electrochemical Performance of the Hierarchical Morphology of PGM-free Electrode

This chapter describes the framework for the morphologically consistent hierarchical model for thick PGM-free electrodes. Statics from the hierarchical morphology of the electrodes resolved using multi-resolution, a multi-contrast mode in nano-CT was implemented as input to the model. Transport simulation of the gas diffusion and proton conduction at the pore/particle-scale was also used to inform the model. The model prediction for PGM-free electrodes three different Nafion loading (35, 50, and 60 wt.

%) are consistent with the experimental evaluation of the electrode. From the model, the ORR at high current density occurs closer to the microporous layer (MPL) for high Nafion loading leading to under utilization of the catalyst. The large Ohmic drop observed in the higher Nafion loading (50 and 60 wt. %) is due to the ionic potential drop caused by shift in the ORR away from the membrane due to severe flooding of the electrode. In the flooded region of the catalyst layer (CL), the flooded region of the CL acts as a very low proton conducting membrane. We studied the losses in the 50 wt. % Nafion loading electrode by individually setting the resistances to zero. At the current volumetric activity, The liquid water management mitigation is crucial to the improvement in performance of the electrode. Nafion distribution is also crucial as it affects the ionic conductivity, the pore size, and wettability. The gas diffusion layer (GDL) and MPL could also provide improvement in performance in high current densities.

7.1.5 PGM-free Electrode Morphological Optimization

This chapter utilized the model framework described in chapter 5 to understand the losses, and identify the optimal morphological and operating parameters. Parameter sensitivity to operating conditions and morphological characteristics show the highest performance improvement to flooding mitigation. Varying the wettability of the electrode from hydrophilic to hydrophobic shows a huge improvement in performance of the electrode in the mass transport region due to improved O_2 diffusion. Varying the thickness/loading of the CL showed decrease in performance in the activation region

but improvement in the mass transport region. Considering uniform distribution of Nafion, theoretical prediction of the Nafion distribution showed highest performance 50 wt. % Nafion loading. Using the diameter from agglomerate size distribution in the agglomerate model showed higher performance compared to a single representative diameter as it can capture most of the losses in the catalyst layer at all operating voltages. Parametric study on the power density by varying the $R_s J_s$ parameter and the thickness showed the power density target at 0.7 V can be achieved with 15 times increase in either the active site density or the activity per site. There also exists an optimal thickness of the catalyst layer with an increase in the volumetric activity. With ten times increase in the volumetric activity and at the optimal thickness of the catalyst layer, flooding still causes the highest loss in the performance. Based on the morphological observation fabrication of the a commercial sample led to better distribution of Nafion and the model prediction of the performance of the commercial sample was similar to the experimental evaluation. Hydrophobic PGM-free CL was fabricated by adding polytetrafluoroethylene (PTFE) particles to the 50 wt % Nafion loading catalyst ink. The hydrophobic cathode showed improve performance in the activation region as more active sites were accessible due to removal of water.

7.2 Future Work

7.2.1 Vertically Oriented Polymer Electrolyte Nanofiber Catalyst Support for Thin Film Electrodes

The results indicate the effect of the surface roughness of the catalyst support. Fabricating the nanofibers with a higher surface roughness, by increasing the aspect ratio, compared to the present roughness could further improve the performance. In addition, the roughness of the electrodes can be optimized in terms of orientation, and areal density. To improve the ionic conductivity of the nanofibers and the membrane, high conductive or low equivalent weight ionomer solution can be used for solution casting instead of the 20 wt. % Nafion solution.

The electrochemical characterization were conducted at fully humidified conditions at 80°C. To compare with NSTF, the nanofibers should be extensively characterized at different relative humidity and temperature. In light of the observed flooding losses in the nanofiber electrodes and indicated transport losses in the CVD films, we suggest that significant improvements in performance (geometric and gravimetric) are possible for the chemical vapor deposited nanofiber electrodes. In contrast, PVD does not appear to be a viable option for these high aspect ratio fibers. The two fundamental approaches to improving the CVDNE performance is by optimizing the CVD coating thickness such that it is just thick enough to coat the fibers conformally. A significant performance improvement could also be achieved by including a hydrophobic component to prevent

the buildup of water in the large hydrophilic pores between the fibers. Recent work on other extended surface metal electrodes has shown the addition hydrophilicity to dramatically increase performance and robustness of operation [97, 111]. Recently, passive water management using a modified GDL (without an MPL and a hydrophobic coated layer) has improved the flooding and operation at different temperature and relative humidity [112, 113]. The modified GDL improves back diffusion in the membrane and enables water removal through the anode.

7.2.2 Resolving Electrode Morphology's Impact on PGM-free Cathode Performance

Nano-CT Imaging

The degradation and durability are a vital consideration factor for the PGM-free electrodes commercial use. The PGM-free electrodes that were used for morphological characterization using nano-CT were all pristine or uncycled MEAs. Nano-CT imaging of an electrochemically cycled sample and comparing the electrode morphology to that of the pristine sample would lead to an understanding of the degradation mechanism. Also, visualization of ionomer distribution in both the pristine and cycled sample would identify ionomer degradation if any.

Several research groups have shown *in-operando* micro-CT imaging of water diffusion in the GDL [114] and also shown microstructural changes while cycling for a bat-

tery [115]. There are several published works of water visualization in PEFC which resolved at microscale using computed tomography (micro-CT). At this resolution, only the length scales of the pores in the GDL can be visualized. Since the scan time is longer using nano-CT, it does not suit the water visualization in CL but can be used for degradation studies. Due to the requirement that the sample being imaged should remain within the FOV, the setup for *in-situ* degradation would require a capillary type fuel cell configuration. Packing a capillary, which is X-ray transparent, of inner diameter less than 50 μm with the catalyst ink and we can fabricate an air breathing capillary fuel cell. The sample can be imaged at the pristine state as well as after cycling at the same location. This build can be used for the *in-situ in-operando* operation. This enables the study of the PGM-free electrode operation in 4D (spatial + time), provide an idea for the degradation or change in electrode morphology.

Nafion Distribution

Nafion distribution and Nafion loading affect the morphology and performance of the PGM-free electrode. Nafion solvent solution can significantly impact the final morphology of the catalyst layer [116]. Recently, a single non-aqueous Nafion solvent is shown to improve the performance and also the durability of the electrode [117]. Fabricating PGM-free cathode with different Nafion solvent and conducting similar analysis shown in chapter 3 could improve the morphology of the electrode. Figure 5.7 shows that ionic conductivity could improve the performance of the electrode significantly. Using high

conductive or low equivalent weight ionomer as binder for the CL would reduce the voltage loss due to the proton conduction.

7.2.3 Modeling Electrochemical Performance of the Hierarchical Morphology of PGM-free Electrode

One of the major assumptions in the agglomerate model is the uniform coverage of the Nafion. In practical electrodes, the Nafion coverage is non-uniform (Figure 3.15), and the agglomerate model should be modified to incorporate the non-uniform coverage. The pore-scale particle scale simulation can be extended to include the electrochemical reaction in 3D. Combining the pore, catalyst and Nafion domain for direct 3D modeling, could resolve the losses. This could resolve the coupling between the transport and electrochemical reaction at the local microstructure. This could additionally optimize the agglomerate structure size for the PGM-free cathode. Similarly to the 2D hierarchical model, the 3D model framework could be extended to the Pt based electrodes using the 3D transmission electron microscopy (TEM) images.

Also, the model framework could be extended to Pt-based cathodes. The primary structure of the Pt carbon based electrodes is less than 50 nm which is below the resolution of the nano-CT. This requires advanced TEM to characterize the primary and secondary pore in 3D. Morphological and transport statistics extracted from TEM could be used to inform the model.

7.2.4 PGM-free Electrode Morphological Optimization

The effect of relative humidity should be studied using the hierarchical model. The current model was investigated with fully humidified gases which are not the conditions for standard automotive fuel cell stacks, which are operated at low RH. To incorporate the effect of RH, the parameter $R_s J_s$ need to be fit to few experimental data of different operating RH to extrapolate a correlation for the activity to RH. This is necessary due to the observation of increased performance in the hydrophobic cathode due to increased the active site density attributed to removal of water. Also, the effect of temperature should be studied using the model.

Although adding PTFE to the CL to alter its wettability, showed improved performance in the activation region, the resulting thickness was higher than the base case (*i.e.* no PTFE in the CL). A better method of changing the wettability would be to the functionalize the carbon to tune its wettability. This can improve the performance of the electrode even at high current density as the thickness of the electrode is not increased.

From both MES and computational model, the catalyst utilization near the membrane is low and flooding causes a large electrolyte potential loss in the CL. Increasing the contact between the membrane and catalyst layer increases the utilization and reduce the electrolyte potential loss. This is achieved by increasing the roughness, ratio of total surface area to the projected geometrical area, of the membrane. Aizawa et al. [43] fabricated membrane with pillars with a diameter of a few micrometer. Figure 7.1a shows the computational model domain used in the simulation for studying the

effect of the patterned membrane. Figure 7.1b shows the initial polarization curve for both flat and patterned membrane. There is a performance increase in all the region and a notable decrease in Ohmic losses for the structured membrane. The inset shows the 2D distribution of electrolyte potential for the electrode with both the membrane. The flat membrane electrode has a huge electrolyte potential drop which is due to the shift in ORR away from the CL|MEM interface. However, in the patterned membrane electrode, the ionic potential drop is lowered which is also observed as the increase in performance at the lower potentials. The catalyst utilization is higher for the structured membrane as it has 25% lower catalyst loading. The computational model can be used for a parametric study on the diameter, height, and pitch of the pillars for the optimal performance. Based on the parametric study on the model, the patterned membrane could be fabricated for electrochemical testing, using similar fabrication techniques employed in chapter 2 and Aizawa et al. [43].

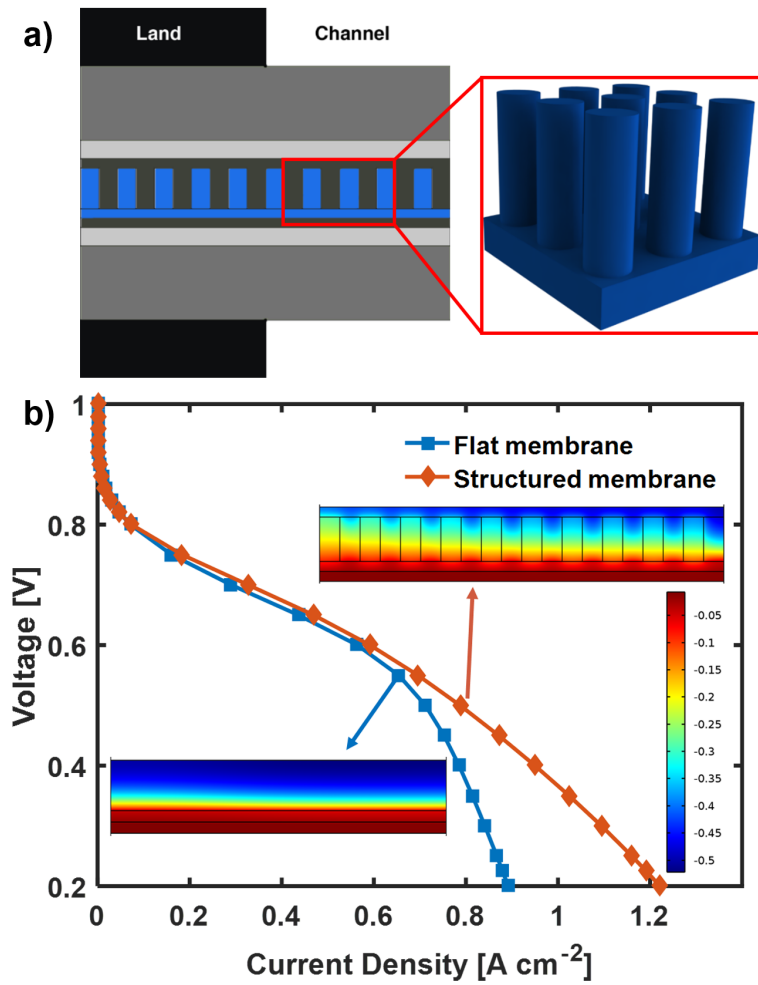


Figure 7.1: Effect of pattern structured membrane compared to flat membrane. a) Shows the computational domain. Inset shows the 3D rendering of the pillar membrane. b) Polarization curve for flat and pillar membrane. Inset shows the 2D distribution of electrolyte potential.

Appendix A

Abbreviations and Symbols

Abbreviations

3D Three Dimensions

CL Anode Catalyst Layer

ASD Agglomerate Size Distribution

BET BrunauerEmmettTeller

CL Cathode Catalyst Layer

CCM Catalyst Coated Membrane

CL Catalyst Layer

CT Computed Tomography

CV Cyclic Voltammetry

CVD Chemical Vapor Deposition

CVDNE CVD Nanofiber Electrodes

DI Deionized

DM Diffusion Media

DW Dissolved Water

ECSA Electrochemically Active Surface Area

FIB Focused Ion Beam

FOV Field of View

G Gas

GDE Gas Diffusion Electrode

GDL Gas Diffusion Layer

HOR Hydrogen Oxidation Reaction

HRE Hydrogen Reference Electrode

HRES High-Resolution

IPA Isopropyl Alcohol

L Liquid

LFOV Large Field of View

MEA Membrane Electrode Assembly

MEM Membrane

MES Microstructured Electrode Scaffold

MIP Mercury Intrusion Porosimetry

MPL Micro Porous Layer

nano-CT Nano-scale X-ray Computed Tomography

NSTF Nano-Structured Thin-Film

OCV Open Circuit Potential

ORR Oxygen Reduction Reaction

PEFC Polymer Electrolyte Fuel Cell

PGM-free Platinum Group Metal-Free

PM Porous Media

PSD Pore Size Distribution

Pt Platinum

Pt/C Pt/Carbon

PTFE Polytetrafluoroethylene

PVD Physical Vapor Deposition

PVDNE PVD Nanofiber Electrodes

RDE Rotating Disk Electrode

REV Representative Elementary Volume

RH Relative Humidity

ROI Region of Interest

RRDE Rotating Ring Disk Electrode

SEM Scanning Electron Microscope

TEM Transmission Electron Microscope

TEP Track-Etched Polycarbonate

TOF Turnover Frequency

Greek symbols

a_{agg}^i agglomerate surface area per unit volume

α Charge transfer Efficient

Z Atomic Number

J_s Activity per Active Site

A Area

α Bruggeman factor

CM-PANI-Fe Cyanamide-Polyaniline-Iron

c Concentration

P_C Critical Pressure

T_C Critical Temperature

Cs^+ Cesium Ion

i Current Density

D_{ij} Diffusion Coefficient

D_{kn} Knudsen Diffusion coefficient

D_m Molecular Diffusion coefficient

D_{pore} Diffusion coefficient of local pore

E_r^i Effectiveness Factor

η Overpotential

i_{HOR}^{ref} Reference Exchange Current Density for Pt on Ionomer

F Faraday's Constant

k_f Formation Factor

J Flux area integral

δ Film Thickness

R Universal Gas Constant

H Henry's constant

L Length

M Molecular Weight

k_c ORR rate constant

P_{Cap} Capillary Pressure

Φ Potential

r_{agg}^i Agglomerate radius

R_s Active Site Density

σ Conductivity

S Source or Sink in domain i

γ Surface Tension

T Temperature

τ Tortuosity

ε_i Volume Fraction/Porosity

f_i Volume Fraction

Subscripts and superscripts

<i>AD</i>	Adsorption/Desorption
<i>agg</i>	Agglomerate
<i>i</i>	Domain
<i>DW</i>	Dissolved water
<i>eff</i>	Effective
<i>H₂</i>	Hydrogen
<i>HOR</i>	Hydrogen oxidation reaction
<i>ionic</i>	Ionic/Proton
<i>Joule</i>	Joule heating
<i>O₂</i>	Oxygen
<i>ORR</i>	Oxygen reduction reaction
<i>Phs</i>	Phase change
<i>rxn</i>	Reaction
<i>res</i>	Residual
<i>wp</i>	Wetting phase

Appendix B

Agglomerate Model Derivation

This appendix presents the derivation of the agglomerate model, used in chapter 5, for PGM-free electrodes.

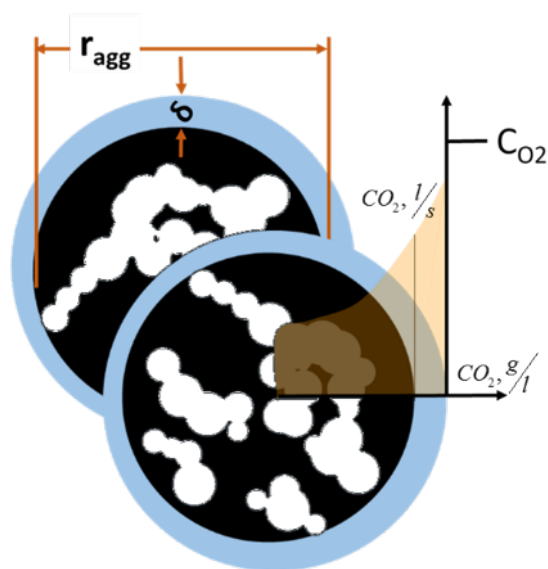


Figure B.1: Schematic of a single agglomerate with the Nafion film.

Flux at any point in the agglomerate at a radius r from the center:

$$N_{O_2} = -D \frac{\partial C_{O_2}}{\partial r} \quad (B.1)$$

Flux at point with radius r times its spherical area is constant:

$$-D (4\pi r^2) \frac{\partial C_{O_2}}{\partial r} = N_{O_2, l/s} (4\pi r_{agg}^2) = C_1 \quad (B.2)$$

On integration Eq. B.2:

$$C_{O_2} = \frac{C_1}{4\pi D r} + C_2 \quad (B.3)$$

Applying the boundary conditions At $r = r_{agg}$, $C = C_{l/s}$

and at $r = r_{agg} + \delta$, $C = C_{g/l}$ gives

$$C_1 = 4\pi D \frac{(r_{agg} + \delta) r_{agg}}{\delta} [C_{O_2, l/s} - C_{O_2, g/l}] \quad (B.4)$$

Substituting C1 from Eq. B.4 in Eq. B.1

$$N'_{O_2, l/s} = -D \frac{\partial C}{\partial r} \Big|_{l/s} = D \frac{(r_{agg} + \delta)}{r_{agg}} \left[\frac{C_{O_2, l/s} - C_{O_2, g/l}}{\delta} \right] \quad (B.5)$$

IN the case of Pt based electrodes a interfacial resistance beteen Pt|ionomer is incorporated to reflect the additional resistance observed due to the thin ionomer film. For thhe PGM-free electrodes this resistance is not incorporated and hence at

$$C_{O_2, g/l} = C_{eq} \quad (B.6)$$

where C_{eq} is the equilbirum concentration of O_2 dissolved in the ionomer. General equation for of flux in the agglomerate.

$$\nabla \cdot N_{O_2} - a_{agg} N'_{O_2} = 0 \quad (B.7)$$

$$\nabla \cdot N_{O_2} + \sum_i R_{O_2}^i = 0 \quad (B.8)$$

$$\Rightarrow N'_{O_2} = - \sum_i \frac{R_{O_2}^i}{a_{agg}^i} \quad (B.9)$$

Agglomerate volume current density is

$$R_{O_2}^i = R r e^i \varepsilon_{agg}^i \quad (B.10)$$

and

$$R r e = E_r k_c C_{O_2, l/s} \quad (B.11)$$

Combining Eq. B.10 and Eq. B.11

$$\Rightarrow R_{O_2}^i = E_r^i k_c \varepsilon_{agg}^i C_{O_2, l/s}^i \quad (B.12)$$

Combining Eq. B.9 and B.12

$$N'_{O_2, l/s} = -k_c \sum_i \frac{E_r^i \varepsilon_{agg}^i C_{O_2, l/s}^i}{a_{agg}^i} \quad (B.13)$$

Combining Eq. B.5 and B.13 we get

$$C_{O_2, l/s}^i \left[1 + \frac{E_r^i k_c \varepsilon_{agg}^i r_{agg}^i \delta}{a_{agg}^i D (r_{agg}^i + \delta)} \right] = C_{O_2, l}^i \quad (B.14)$$

Combining Eq. B.6 and B.14

$$C_{O_2, l/s}^i + \left(\frac{E_r^i \varepsilon_{agg}^i k_c}{a_{agg}^i} \right) \left(\frac{r_{agg}^i \delta}{(r_{agg}^i + \delta) D} \right) C_{O_2, l/s}^i = C_{eq}^i \quad (B.15)$$

Rearranging

$$C_{O_2, l/s}^i = \frac{C_{eq}^i}{E_r^i k_c \varepsilon_{agg}^i} \left[\frac{1}{E_r^i k_c \varepsilon_{agg}^i} + \left(\frac{r_{agg}^i \delta}{(r_{agg}^i + \delta) D} \right) \left(\frac{f^i}{a_{agg}^i} \right) \right]^{-1} \quad (B.16)$$

Electric current conservation

$$\nabla \cdot i = -4F \nabla \cdot N_{O_2} = 4F \sum_i Rr e^i \varepsilon_{agg}^i = 4F \sum_i Rr e^i \varepsilon_{agg} f^i \quad (B.17)$$

and also

$$\varepsilon_{agg}^i = \varepsilon_{agg} f^i \quad (B.18)$$

Combining Eq. B.12, and B.17

$$\nabla \cdot i = 4F \sum_i E_r^i k_c \varepsilon_{agg} f^i C_{O_2, l/s}^i \quad (B.19)$$

Substituting Eq. B.16 in Eq. B.19

$$\nabla \cdot i = 4F \sum_i E_r^i k_c \varepsilon_{agg} f^i \frac{C_{eq}^i}{E_r^i k_c \varepsilon_{agg}} \left[\frac{1}{E_r^i k_c \varepsilon_{agg}} + \left(\frac{r_{agg}^i \delta}{(r_{agg}^i + \delta) D} \right) \left(\frac{f^i}{a_{agg}^i} \right) \right]^{-1} \quad (B.20)$$

Simplifying and substituting $C_{eq} = \frac{P_{O_2}}{H}$ in Eq. B.20

$$\nabla \cdot i = 4F \sum_i f^i \frac{P_{O_2}}{H} \left[\frac{1}{E_r^i k_c \varepsilon_{agg}} + \left(\frac{r_{agg}^i \delta}{(r_{agg}^i + \delta) D} \right) \left(\frac{f^i}{a_{agg}^i} \right) \right]^{-1} \quad (B.21)$$

Reaaranging Eq. B.21

$$\nabla \cdot i = 4F \frac{P_{O_2}}{H} \sum_i f^i \left[\frac{1}{E_r^i k_c \varepsilon_{agg}} + \left(\frac{r_{agg}^i \delta}{(r_{agg}^i + \delta) D} \right) \left(\frac{f^i}{a_{agg}^i} \right) \right]^{-1} \quad (B.22)$$

Appendix C

Nafion Film Thickness Estimation

This appendix presents the derivation of the equation used to calculate the Nafion film thickness in the agglomerate model.

Mass of Nafion

$$M_N = \frac{M_c y_N}{(1 - y_N)} \quad (\text{C.1})$$

where M_c is mass of catalyst, and y_n is the weight percentage of Nafion. Volume fraction of Nafion

$$\varepsilon_N = \frac{M_N}{\rho_N L} = \frac{M_c y_N}{(1 - y_N) \rho_N L} \quad (\text{C.2})$$

where ρ_N is density of Nafion, and L is thickness of catalyst. Volume fraction of Nafion agglomerate thickness

$$\varepsilon_{N\delta} = \varepsilon_{agg} \delta S_{agg} \quad (\text{C.3})$$

where ε_{agg} is the volume fraction of agglomerate including the Nafion film and mir-

porosity, δ is Nafion film thickness, and S_{agg} is the surface area per volume of the agglomerate. Volume fraction of agglomerate without Nafion film

$$\varepsilon_{agg,nf} = \varepsilon_{agg} - \varepsilon_{N\delta} = \varepsilon_{agg} (1 - \delta S_{agg}) \quad (C.4)$$

Volume fraction of Nafion in micropore

$$\varepsilon_{agg,nf} \varepsilon_{N\mu p} = \varepsilon_N - \varepsilon_{N\delta} \quad (C.5)$$

$$\varepsilon_{N\mu p} = \frac{\varepsilon_N - \varepsilon_{N\delta}}{\varepsilon_{agg,nf}} = \frac{\left(\frac{M_c y_N}{(1-y_N) \rho_N L} \right) - (\varepsilon_{agg} \delta S_{agg})}{\varepsilon_{agg} (1 - \delta S_{agg})} \quad (C.6)$$

We assume that Nafion volume fraction in the micropore is constant and Nafion thickness for 35 wt

$$\varepsilon_{agg,nf}^x \varepsilon_{N\mu p}^{35} = \varepsilon_N^x - \varepsilon_{N\delta}^x \quad (C.7)$$

where x is the Nafion weight percentage, and $\varepsilon_{(N\mu p)}^{35}$ is the Nafion volume fraction in the micropore. Nafion film thickness for x Nafion weight percentage

$$\varepsilon_{N\mu p}^{35} \varepsilon_{agg}^x (1 - \delta^x S_{agg}^x) = \left(\frac{M_c^x y_N^x}{(1-y_N^x) \rho_N L^x} \right) - (\varepsilon_{agg}^x \delta^x S_{agg}^x) \quad (C.8)$$

$$\delta^x = \frac{\left(\frac{M_c^x y_N^x}{(1-y_N^x) \rho_N L^x} \right) - (\varepsilon_{N\mu p}^{35} \varepsilon_{agg}^x)}{\varepsilon_{agg}^x S_{agg}^x (1 + \varepsilon_{N\mu p}^{35})} \quad (C.9)$$

Appendix D

Hierarchical Model Parameters

Table D.1: Water retention curve parameters for the Van Genuchten model

Domain	Parameters		
	$P_{CB} [atm]$	n	m
GDL	0.0802	3.5	0.6489
MPL	8.443	2.211	0.5477
ACL	0.06	3.5	0.6

Table D.2: Parameter values used in the Model

Source Term	Value	Description
$a_{nonpolar}$	2.745E-4 [$atmcm^2/s$]	
a_{polar}	3.64E-4 [$atmcm^2/s$]	
AED	25000[J/mol]	Activation energy for diffusion
M_{Air}	28.97 [g/mol]	Molecular Weight of Air
μ_{Anode}	1.1E-5 [Pa s]	Anode Viscosity
a_{Pt}	$A_s M_{Pt} / L_{ACL}$	anode specific area
A_s	32.1819 [m^2/g]	specific catalyst area m^2/g
$b_{nonpolar}$	1.823	
b_{polar}	2.334	
$C_{p,f}$	1006 [J/(kg K)]	Specific heat capacity of fluid
$C_{p,s}$	885 [J/(kg K)]	Specific heat capacity of solid
$\mu_{Cathode}$	20.59E-6 [Pa*s]	Cathode Viscosity
v	1800 [mol/m^3]	SO_3^- concentration in Nafion
$c_{H_2}^{ref}$	40.88 [mol/m^3]	
$c_{H_2O}^{anode}$	$\rho_{an} P_{sat}^{anode} / P_{an}$	Anode water vapor concentration
$c_{H_2O}^{cathode}$	$\rho_{cat} P_{sat}^{cathode} / P_{cat}$	Cathode water vapor concentration
k_{CL}	7.55e-10 [cm^2]	ACL permeability

$c_{N_2}^{cathode}$	$(1-0.21)\rho_{cathode}(1-$ $P_{sat}^{cathode} / P_{cathode})$	
$c_{H_2}^{cathode}$	$0.21*\rho_{cathode}(1-$ $P_{sat}^{cathode} / P_{cathode})$	Ambient oxygen concentration
$c_{O_2}^{ref}$	0.85 [mol/m ³]	
∇G	-5209.69 [J/mol]	Free energy of dissolution
ρ_{anode}	$P_{anode}/(RT_{cell})$	anode density
$\rho_{cathode}$	$P_{cathode}/(RT_{cell})$	Cathode density
E_{ad}	30000 [J/mol]	Activation energy, vapor ads des
$\sigma_{CL}^{electric}$	200 [S/m]	CL electric conductivity
$\sigma_{GDL}^{electric}$	300 [S/m]	GDL layer electric conductivity
$\sigma_{MPL}^{electric}$	200 [S/m]	MPL electric conductivity
F	96487 [C/mol]	Faraday's constant
k_{GDL}	1.5e-9 [cm ²]	GDL permeability
$\rho_{graphite}$	2.15 [g/cm ³]	Graphite density
δH_{fg}	2260 [kJ/kg]	
H_{ref}	26851.125 [Pam ³ /mol]	Reference Henry's constant
i_{HOR}^{ref}	535 [mA/cm ²]	Anode exchange current
k_A	$k_D/10$	vapor absorption coefficient
k_D	0.01*2.8 [m/s]	vapor desorption coefficient

$k_{T,vapor}$	0.62 [W/m/K]	Thermal Conductivity water vapor
$k_{T,water}$	0.61 [W/m/K]	Thermal Conductivity liquid water
k_{cond}	1e6 [1/s]	Condensation phase Change constant
k_{evap}	1e-2 [1/(atm*s)]	Evaporation phase Change constant
ρ_{mem}	1.58 [g/cm ³]	Membrane density
M_{H_2}	2e-3 [kg/mol]	Hydrogen molar mass
M_{H_2O}	18e-3 [kg/mol]	Water molar mass
M_{N_2}	28e-3 [kg/mol]	Nitrogen molar mass
M_{O_2}	32 [g/mol]	Oxygen molar mass
k_{MPL}	3.3E-10 [cm ²]	MPL permeability
m_{Pt}	0.4 [mg/cm ²]	pt loading
P_{CH_2}	12.8	Critical Pressure H2
P_{CH_2O}	218	Critical Pressure H2O
P_{CN_2}	33.5	Critical Pressure N2
P_{CO_2}	49.8	Critical Pressure O2
ρ_{solid}	1100[kg/m ³]	Solid Density
T_{CH_2}	33.2	Critical Temperature H2

T_{CH_2O}	647.3	Critical Temperature H2O
T_{CN_2}	126	Critical Temperature N2
T_{CO_2}	154	Critical Temperature O2
$k_{T,air}$	0.027 [W/m/K]	Air thermal conductivity
$k_{T,CL}$	2.7 [W/m/K]	CL thermal conductivity
$k_{T,GDL}$	4.2 [W/m/K]	GDL thermal conductivity
$k_{T,Graphiter}$	128 [W/m/K]	Graphite thermal conductivity
k_{T,H_2}	0.1805 [W/m/K]	H_2 thermal conductivity
$k_{T,Mem}$	0.67 [W/m/K]	Membrane thermal conductivity
$k_{T,MPL}$	2.7 [W/m/K]	MPL thermal conductivity
τ_{ACL}	3.2	CL Gas Tortuosity Factor
τ_{GDL}	2	GDL Gas Tortuosity Factor
τ_{MPL}	3	MPL Gas Tortuosity Factor
ρ_{water}	1000 [kg/m^3]	Water density
μ_{water}	5E-3 [$g/(cms)$]	Water Viscosity

Appendix E

Multiple imaging mode X-ray computed tomography for distinguishing active and inactive phases in lithium-ion battery cathodes

E.1 Introduction

High resolution computed tomography (CT) is a valuable tool in the research and development of electrochemical energy materials as it provides a better understanding of 3D connectivity and internal structure. CT has been used in previous studies to char-

acterize polymer electrolyte fuel cell [29, 60], solid oxide fuel cell [118], and li-ion battery electrodes [119]. The microstructure of Li-ion electrodes significantly influences the battery performance through the resulting interfacial areas, material connectivity, and the transport length scales. Computational modeling can be a useful approach to understanding the impact of microstructure and 3D CT reconstructions of the electrode provide an important geometry input to these models [120]. For an accurate representation of the morphology of the battery electrode, the model should include realistic 3D reconstruction of all the three domains of the electrode: the active material, conductive additive and polymeric binder, and the electrolyte pore domain.

Prior work on 3D X-ray imaging of electrode microstructure has mainly resolved the active material, with the remainder of the volume being a combination of pore, conductive additive, and binder. This is due to the small length scale and low absorption of the low atomic number (Z) additive phases; photoelectric X-ray absorption is highly sensitive to Z [121]. Neglecting the additives can significantly diminish the quality of transport property estimation [122]. Zielke et al., considered all the three domains; using X-ray CT to reconstruct the active material and a statistical model to generate the binder phase [123]. Zernike phase contrast imaging modes in X-ray CT have been used by Chen-Wiegart et al., to identify the carbon additives, but without quantitative analysis [124]. An alternate method to reconstruct the electrode is through focused ion beam-scanning electron microscopy (FIB-SEM) [120, 125, 126, 127]. One drawback of FIB-SEM is in obtaining good contrast between the cutting plane and the solid behind pore openings, which poses a challenge for segmentation. In addition, FIB milling can dam-

age and distort fine polymer features [128], although advanced embedding techniques and very low currents can potentially resolve these issues. Depending on sample microstructure, multi-length scale imaging may be required for accurate characterization, which can be achieved with X-ray CT as demonstrated by Shearing et al. [129]. X-ray CT techniques can enable non-destructive ex-situ and in-situ studies of the cathode for degradation and morphological changes [115, 130, 131]. In the case of nano-scale resolution X-ray CT, although the imaging itself is non-destructive, some initial destructive sample preparation is necessary to fit the sample in the field of view (FOV). Similarly, specialty in-situ cells must be prepared for in-situ imaging.

This work presents a technique to reconstruct the three material domains of a Li-ion cathode by 50 nm resolution nano-CT with separate absorption and Zernike phase contrast images. In absorption contrast mode, the X-rays are well-attenuated by the high Z elements (e.g., transition metal-based active material). Alternatively, Zernike phase contrast additionally visualizes the low Z conductive additive and binder. Zernike phase contrast enhances low-Z material imaging by inserting a phase ring that generates an image based on the interaction of diffracted and undiffracted X-rays [62]. The leakage of the diffracted wave through the phase ring generates halo artifacts when reconstructed, enhancing the contrast at the interface. This aids in segmentation of low Z, nanostructured materials [60]. Unfortunately, contrast between materials with different Z is significantly reduced in Zernike phase contrast. By combining information from the two imaging modes into a single 3D image, we can confidently separate the additives from the active material. The distribution of the additives between the active material parti-

cles provides important information for analyzing electrical and structural connectivity.

E.2 Nano-CT Imaging

E.2.1 Sample Preparation

The sample we present is a commercially available LiCoO_2 cathode with carbon black conductive additive and polyvinylidene fluoride (PVDF) binder (MTI Corporation, Hefei, Anhui, China). The electrode was composed of 95.7 % LiCoO_2 , 2 % carbon black, and 2.3 % PVDF by weight. Figure E.1a presents scanning electron microscope (SEM) images of the cathode. We prepared the sample for imaging by removing the current collector from the electrode and using microscopy grade razor blades to cut triangular samples, as shown in Figure E.1b. The triangular sample enables the entire sample to remain within the X-ray FOV during sample rotation. The sample was mounted on a pin using epoxy, with the triangular tip pointing away from the pin and into the X-ray FOV.

E.2.2 X-ray Computed Tomography

The sample was imaged using a nano-CT (UltraXRM-L200, Xradia Inc., Pleasanton, CA) with an 8 keV rotating copper anode X-ray source, a monocapillary condenser, and a Fresnel zone plate objective, as well as an optional gold phase ring for Zernike phase contrast. Based on density and Z the absorption attenuation lengths of LiCoO_2 and

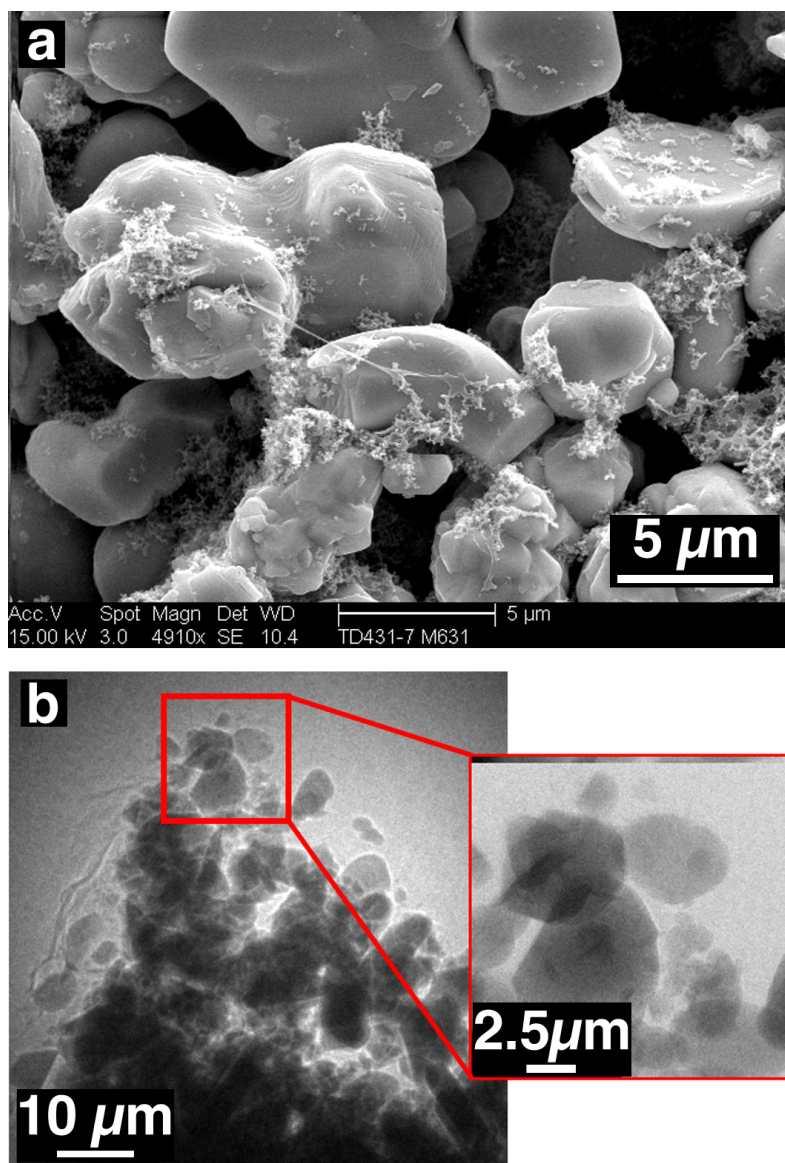


Figure E.1: SEM images and triangular sample. a) Scanning electron microscope images of LiCoO₂ cathode. b) Large field of view radiograph of the LiCoO₂ sample. (Overlay) high resolution radiograph of region of interest.

carbon for X-rays at 8 keV are 10 and 10,000 μm, respectively. Thus, in absorption mode the carbon will be indistinguishable from the pores and the LiCoO₂ signal will be well-

attenuated. Figure E.1b shows an absorption contrast radiograph in a large FOV mode with a lower 150 nm resolution. A high resolution CT scans with 50 nm resolution (16 nm voxels) and a 16 μm FOV were performed on a region of interest at the tip of the sample. A total of 451 projections with 200 s exposure times were obtained by rotating the sample over 180 degrees. A commercial filtered back projection algorithm (Xradia Inc., Pleasanton, CA) performed the 3D reconstruction. The nano-CT data was visualized using Avizo Fire (FEI Visualization Sciences Group, Burlington, MA) and custom Matlab (Mathworks, Natick, MA) codes were used to separate the domains.

E.3 Result and Discussion

Figure E.2 shows radiographs for both absorption contrast (a) and Zernike phase contrast (b) modes. In the absorption contrast radiograph, only the higher Z LiCoO_2 particles are visible. When using the Zernike phase contrast optics the image also shows the additives. Herein, we do not identify the separate conductive carbon additive and binder domain since the absorption coefficient of the two materials are similar and since we expect the binder to be present as films thinner than the instrument's resolution.

After imaging the electrode in both imaging modes, we used the following procedure to generate a 3D image with separate domains for the active material and the additives. First, separate 3D volumes were reconstructed from the radiograph projections in each mode. In processing the images, the unprocessed reconstructed volume's inten-

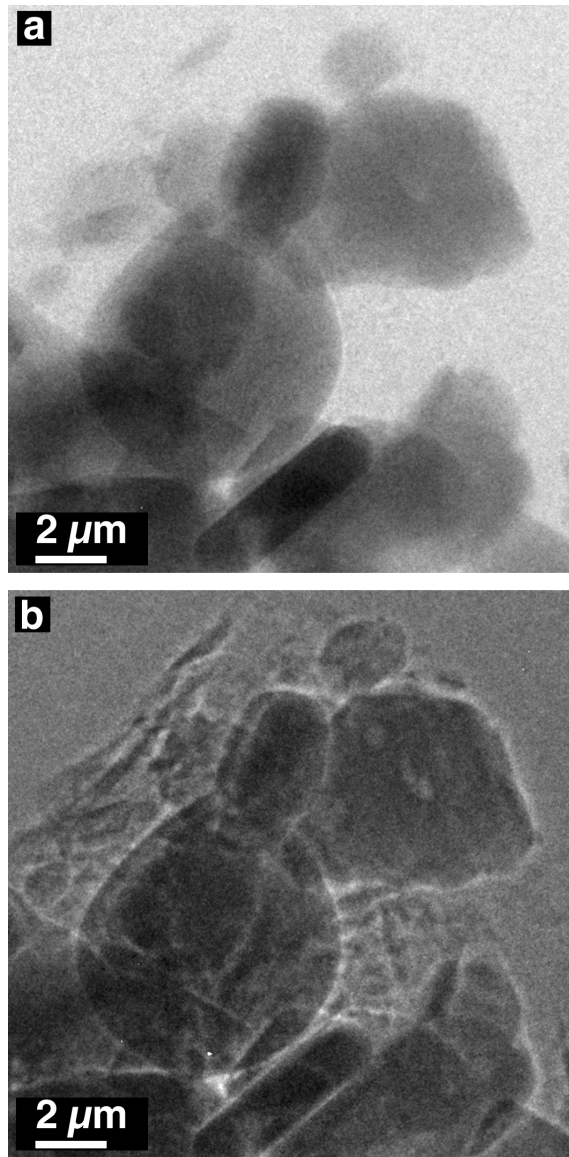


Figure E.2: High resolution transmission radiographs of the Li-ion battery cathode. (a) Absorption contrast imaging showing the LiCoO_2 particles. (b) Zernike phase contrast imaging showing the additives and the LiCoO_2 particles.

sity histograms were equalized to distribute the intensity uniformly. Then each data set was segmented into solid and pore using binary thresholding. In absorption contrast

the solid is only the LiCoO_2 particles, whereas in Zernike phase contrast the solid is the LiCoO_2 particles and the additives. Figure E.3 shows representative radiographs and their binary segmented slices in both imaging modes. To generate a 3D image of only the additives, the absorption contrast image was subtracted from the Zernike phase contrast image to remove the LiCoO_2 particle volumes. Thus, the result are two 3D images, one of the additives and one of the LiCoO_2 . Those two images were then combined into one image with three domains (LiCoO_2 , additives, and pore). Figure E.4 shows the reconstruction of the LiCoO_2 and additives. The reconstruction shows that 66% of additive is disconnected (floating islands), an artifact of the 50 nm resolution where some of the finest necks in the additives chains are not resolved. One approach to correcting this is to use a standard closing morphological operation to reconnect nearby particles. After this process the percentage of floating islands decreased to 44% by volume of the additives.

Useful statistics from this data are the percent area of the active material particles covered by the additives and the distribution contact patch areas. However, Zernike phase contrast mode introduces artifacts around the high Z LiCoO_2 particles that challenge this computation [62]. The artifacts are halos of low image intensity voxels (one or two voxels thick) around the high image intensity particles that appear as void in the segmented image. This results in an artificial gap between the active material and the additives in the combined image. Figure E.5 presents the computational process we used to correct this artifact. The binary data of both the LiCoO_2 particles and the additives are dilated separately to the voxel length of the artifact. After dilation, binary data

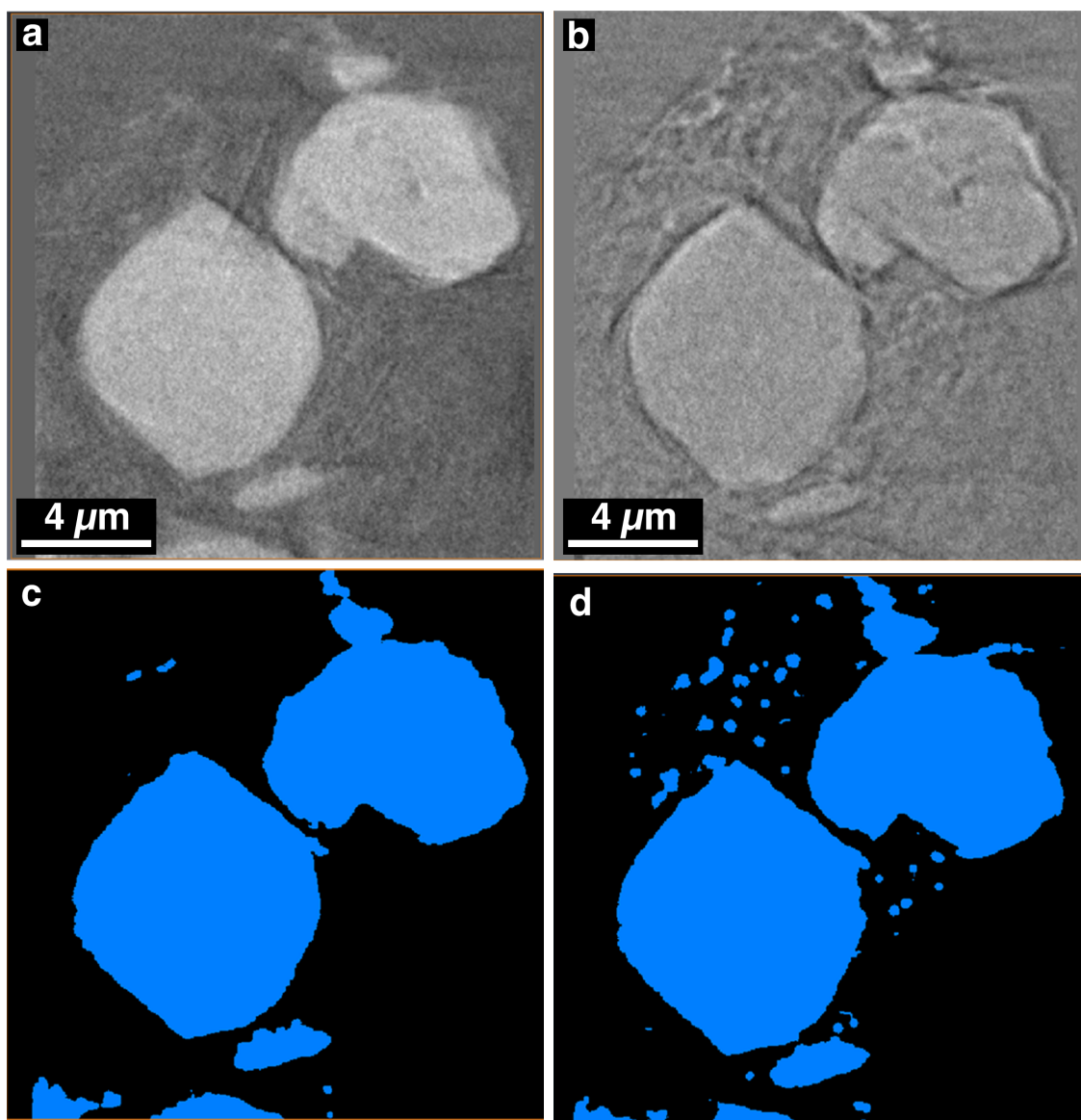


Figure E.3: Reconstructed slices for a) absorption contrast, b) Zernike phase contrast and their corresponding binary segmented slices for c) absorption contrast, d) Zernike phase contrast. Each slice represents a 16 nm thick volume.

of both domains are added to obtain a ternary data set. In the ternary data, the highest value represents the overlapping volumes of the interface with corresponding surface

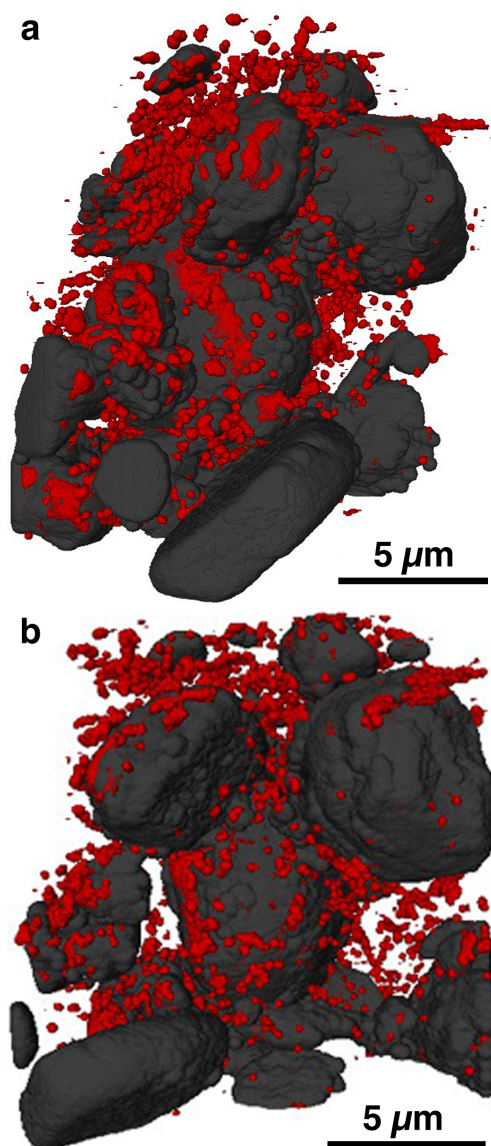


Figure E.4: 3D reconstruction of the Li-ion cathode. a) In-plane and b) through-plane view of the reconstructed Li-ion cathode. The LiCoO₂ particles (dark) and the additives (bright) are distinguished by combining absorption and Zernike phase contrast imaging modes.

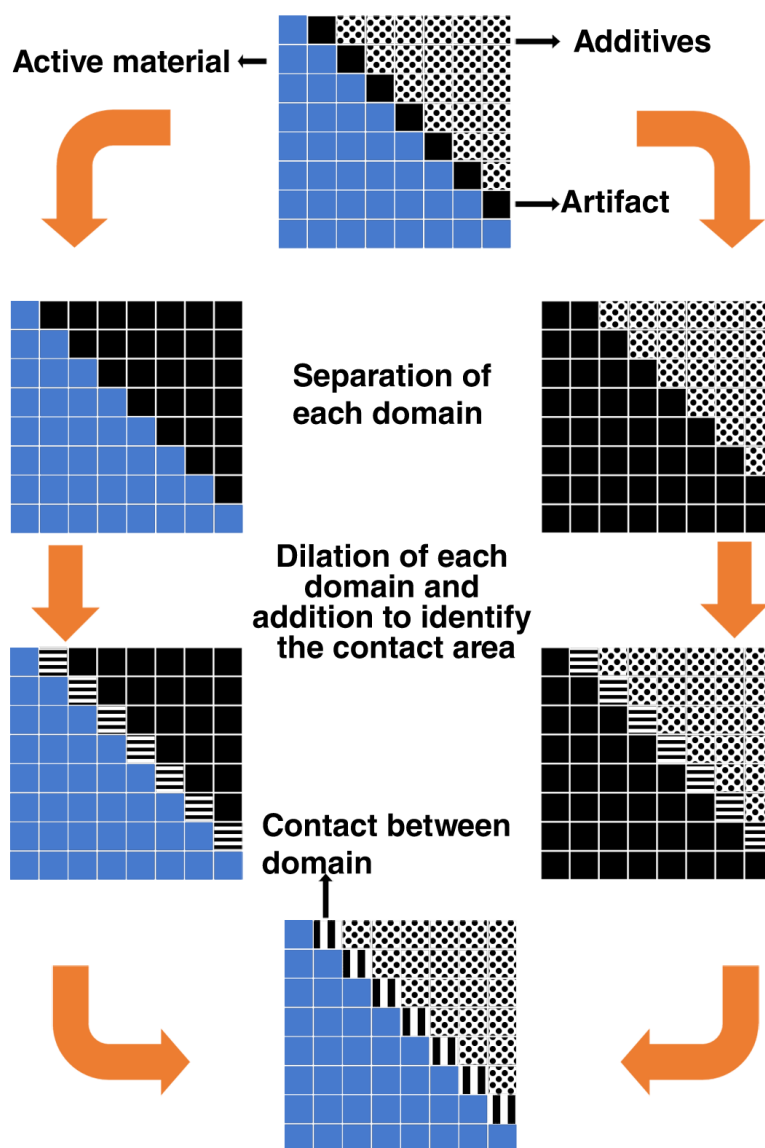


Figure E.5: Schematics for contact area determination. Each domain is individually dilated and added to identify the contact surface area between the active material and the additives.

areas that are approximately twice the surface areas of contacts between the LiCoO_2 particles and the additives.

In analyzing the 3D data, we observe an active material volume of 95% of the total

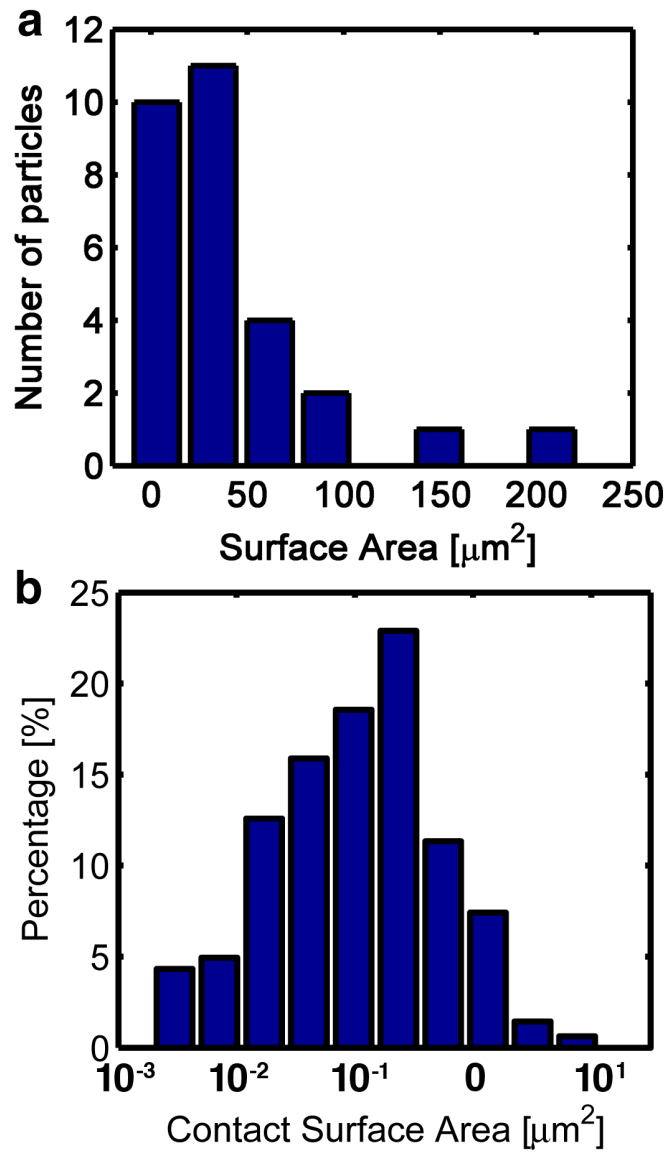


Figure E.6: a) Active material surface area distribution. b) Variation in contact area between the active material and the additives.

solid volume which reduced to 94% upon the closing operation described above, which is similar in magnitude to the manufacturer's specification of 89%. The small sample size and material in-homogeneity are likely responsible the difference. Prior imaging by FIB-SEM reported results of 87% [122] and 80% [127] for the active material volume

percentage. But those electrodes featured different materials and relative composition. The former is a custom made Li-ion cathode with a composition of 86.3% LiCoO_2 , 5% carbon black, and 8.7% PVDF by volume while the latter is a commercial VARTA LIC 18650 WC lithium-ion battery. The surface area distribution of the LiCoO_2 particles was computed using the marching cube algorithm in Avizo Fire and is shown in Figure E.6a. The particle microstructure is not homogeneous and consists of several small particles with high volumetric surface area. The total surface area of the LiCoO_2 particles is $1156 \mu\text{m}^2$, with a volume specific surface area of $1.9 \mu\text{m}^{-1}$. This volume specific surface area is comparable to the average value of $2.0 \mu\text{m}^{-1}$ for LiCoO_2 reported by Wilson et al., as obtained by FIB-SEM [126]. The surface area of the additives is $629 \mu\text{m}^2$ with a volume specific surface area of $16.2 \mu\text{m}^{-1}$. The total surface area of contact between the LiCoO_2 particles and the additives is $90 \mu\text{m}^2$, which amounts to a 7.9 % coverage of the active material surface. Figure E.6b shows a histogram of contact surface areas. The distribution of the additives is sparse and highly heterogeneous as seen from the SEM images in Figure E.1a and this is reflected in the distribution of the contact surface areas, which spans many orders of magnitude. The peak of the distribution is for a contact area of $0.2 \mu\text{m}^2$, which is equivalent to 780 voxel faces in the 3D reconstruction.

E.4 Conclusion

Nano-CT has been used to image a commercial LiCoO_2 cathode. Using different contrast imaging modes, we separately resolved both the additives and the LiCoO_2 parti-

cles with 50 nm resolution. The 3D image was used to quantify some key morphological characteristics of the cathode material, including the additives spatial distribution and the corresponding size distribution of contact area between the active material and the additives. The size and spatial distribution of these contact patches will influence the electrical current pathways and contact resistance, which is an area of our future study. In addition, the 3D material-segmented data is a useful input for the computational simulation of batteries at the particle scale.

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