Modeling Proton Exchange Membrane Fuel Cell Cathode Catalyst Layers with the Lattice-Boltzmann-Method-Direct-Numerical-Simulation Framework

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Abstract

In this work, a coupled Lattice-Boltzmann-Method and electrochemistry Direct-Numerical-Simulation model for a proton exchange membrane (PEMFC) electrode has been presented. One of the main challenges affecting study of the cathode catalyst layer (CCL) in PEMFCs is the lack of detailed understanding of species transport and how it affects electrochemical performance. Researchers have typically used high level approximations that oversimplify the microstructure of the CCL—these are known as macrohomogenous models. However, as the field has progressed, these idealizations have begun to show their flaws, especially in areas of improving catalytic performance with lower Pt-loadings and non-noble metal catalysts. Previously, the microstructure details needed to build an accurate mesoscale model have eluded researchers; however, with advances in tomography and focused-ion-beam scanning-electron-microscopy (FIB-SEM), creating these representations has become possible. Mesoscale modeling in the CCL has traditionally approached through either the Lattice-Boltzmann-Method (LBM) or electrochemistry coupled Direct-Numerical-Simulation (DNS). These models have been underutilized in the fuel cell community due to their complexity and resource intensiveness; however, with advances in parallel computing, this has become not only a possibility, but a necessity for modeling phenomena such as low platinum loadings and interfacial effects. With these new advances, a synergistic modeling approach can be taken that combines the advantages of each method. This can shed light on the transport and degradation phenomena in PEMFCs, particularly catalyst layer considerations and carbon support corrosion.

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Proton exchange membrane fuel cells (PEMFCs) are a promising, non-carbon dioxide producing energy conversion alternative that has the potential to dramatically alter the automotive industry.\textsuperscript{1,2} However, there are significant obstacles that have limited widespread utilization of this technology beyond small trials of buses and light-duty vehicles, such as increasing catalytic activity, reducing crossover, lower cost, durability, among others.\textsuperscript{3} The primary focus of the modeling work addresses the challenges of the cathode catalyst layer (CCL), since not only does this thin layer make experimental characterization extremely difficult, but also because the oxygen reduction reaction (ORR) is considered the most difficult reaction in common electrochemistry. One of the main problems affecting study of the CCL in PEMFCs is the lack of understanding of failure mechanisms and our relative difficulty in experimentally studying them.\textsuperscript{2,4-6} Specifically, at higher cathode potentials, the carbon support that platinum rests on begins to oxidize to form carbon dioxide, disconnecting the platinum from the support.\textsuperscript{5,7} These high potentials also cause the platinum to agglomerate by Ostwald ripening, which drastically decreases efficiency and cycle life.\textsuperscript{8,9}

The usual starting point for modeling has been a macrohomogeneous porous electrode model of the catalyst layer.\textsuperscript{10} In order to increase the surface area for heterogeneous electron transfer reactions, porous electrodes with small characteristic dimensions are used. As with all fuel cells, establishing and controlling the interface between phases in these porous electrodes is of paramount importance. The so called flooded-agglomerate model, an idealization that dates back to at least the 1960s,\textsuperscript{11} was introduced to represent better the complex structure of and processes in the electrode. As research has continued, however, the limitations of this idealization are surfacing; as a key example, the model fails to accurately predict the effect of platinum loading on mass-transfer resistance—it forecasts no effect, whereas experiments show a clear impact.\textsuperscript{4,12} However, despite this experimental confirmation, due to the complex structure of the electrode and its ~10-micron profile, it is quite difficult to do in operando studies. To counter this, previous work gives insight into the CCL microstructure with FIB-SEM (focused-ion beam scanning electron microscopy) to enable the use of mesoscale modeling techniques, an example of the geometry created from these is shown in Figure 1.\textsuperscript{5,13} The main objective of the current research is to expand upon the previous FIB-SEM work and fabricate a simulation framework to describe flow behavior and better understand performance failure mechanisms.\textsuperscript{5,13-15} As a preliminary study, here we study the effect of different current densities on water formation and its effect on oxygen transport in the catalyst layer; this will allow us not only to explore an important experimental parameter (the effect of current density on saturation levels), but also build a foundation for studying our goal problem: corrosion.

Recently, LBM has evolved into a popular method for simulating fluid flows for complex geometries and interfacial dynamics that standard computational fluid dynamics (CFD) techniques, such as finite difference, finite element, and finite volume, struggle to solve.\textsuperscript{16,17} Unlike these CFD techniques, which discretize the macroscopic continuum equations explicitly, LBM’s fundamental quantity is the discrete-velocity distribution function shown below, which are called particle populations. These particle populations represent the density and the velocity $c_i$ with position $x$ and time $t$. The velocities have a

\begin{figure}
\centering
\includegraphics[width=\textwidth]{geometry.png}
\caption{Geometry created from the FIB-SEM data}
\end{figure}
corresponding weighting coefficient $w_i$, which form sets of \{c_i, w_i\}. In LBM, these sets are typically denoted DdQq, where d is the number of spatial dimensions the set covers, and q is the set’s number of velocities. For standard 3D LBM in PEMFCs and other disciplines, the D3Q19 set is typically used and is shown below in Figure 216-18.

\[
\rho(x, t) = \sum_i f_i(x, t) \quad [1]
\]
\[
\rho u(x, t) = \sum_i c_i f_i(x, t) \quad [2]
\]

Additionally, in each velocity set, there is a constant velocity $c_s$ that defines the equation of state in standard isothermal LBM: \( p = c_s \rho \), where \( p \) is the pressure and \( \rho \) is the density. This constant can be seen as the model’s speed of sound for compressible systems and, for all velocity sets in D3Q19, this is defined as \( c_s^2 \equiv \left( \frac{1}{3} \right) \) due to maintaining lattice rotational isentropy\textsuperscript{16}. Von Neumann stability analysis can be performed to give $\Delta x$ and $\Delta t$ that are the lattice spacing and time step, respectively. Furthermore, since the idea behind LBM is to collide these fictitious particles populations together, we need some way to understand collisions. This is done by the collision operator $\Omega_i$; while there are many different ones, the most common choice for Navier-Stokes (N-S) simulations on porous geometries is the multi-relaxation time (MRT) operator. This operator is a matrix representation of the relaxation times and is shown below\textsuperscript{19,20}.

\[
\Omega_i = -M^{-1}S[m(x, t) - m^{eq}(x, t)]\Delta t \quad [3]
\]

where \( M \) is the transformation matrix, \( S \) is a diagonal matrix of the \( q \) relaxation times, \( m \) are the individual moments, and \( m^{eq} \) is the equilibrium moments. Since the idea of the MRT operator is to relax the individual moments rather than the populations, there are as many relaxation times as there are moments – as an example, this corresponds to 19 for D3Q19. After this, one needs to collide these moments; a new moment \( m^*_k \) which is defined as follows:

\[
m^*_k = m_k - \omega(m_k - m_k^{eq})\Delta t \quad [4]
\]

One can transform back into population space with the following relationship:

\[
f^*_i = \sum_k M^{-1}_{ik}m^*_k \quad [5]
\]

Once we transform back into population space, we need to stream to the rest of the nodes in the system – this is done in the following way:

\[
f_i(x + c_i \Delta t, t + \Delta t) = f^*_i(x, t) \quad [6]
\]

Once one discretizes the Boltzmann equation and, after combining these definitions, we arrive at the Lattice Boltzmann Equation:
\[ f_i(x + c_i \Delta t, t + \Delta t) = f_i(x, t) + \Omega_i(x, t) \]  \[7\]

One cycle of the LBM algorithm is shown in Figure 3.16.

The advantage of this approach is that one no longer needs to explicitly discretize the underlying fluid flow equations and can instead derive them implicitly. This is achieved by doing Chapman-Enskog expansion around the Knudsen number to get N-S. Since the explicit approaches struggle to resolve the advection term in N-S, \((\mathbf{u} \cdot \nabla) \mathbf{u}\), this makes implicit schemes valuable, especially in areas of reactive and porous flow. While LBM has the ability to resolve some of the challenges in the CCL, such as accounting for the pore morphology and rigorously showing the flow profile, it is quite expensive computationally. However, this approach is inherently parallel, which makes this process run efficiently on clustered supercomputers.

![D3Q19 lattice structure schematic](image-url)

**Figure 2:** D3Q19 lattice structure schematic
The CCL is a complex, mesoporous, multi-phase system made up of carbon support, platinum catalyst, ionomer, and reactant gases as well as its liquid water product from ORR – this represents a challenging modeling question for computational fluid dynamics. Much of the work in the LBM field for PEMFCs has been trying to couple LBM with a macroscopic approach, such as DNS or FVM, to solve the electro-kinetics equations as well as balance equations. The alternative approach to modeling porous electrodes in fuel cells utilizes the aforementioned macrohomogeneous models incorporating volume averaging of characteristic phase properties and variables over a representative elementary volume (REV) containing statistically significant number density of particles. In this method, the intricate microscopic details of the pore structure are implicitly resolved and homogenization over the electrode volume is performed to obtain averaged geometric and transport properties like porosity, specific surface area, tortuosity, effective diffusivity, and effective conductivity. Typically, empirical correlations are used to describe the effective properties as a function of porosity and tortuosity of the porous medium. In this regard, FVM-based DNS performed over the fully resolved porous microstructure is an accurate, albeit computationally expensive, tool to study the influence of the microstructure on the species and charge transport processes occurring inside the porous media. Additionally, the relative ease of treatment of electrochemical reactions as source terms alongside transport in the DNS framework provides a mechanism to supplement the mesoscale multiphase air-water flow description in the CCL through LBM models. LBM modeling has matured well in treatment of liquid water and gaseous transport (oxygen, nitrogen and water vapor) through the CCL and can provide descriptors for liquid water flooding based surface coverage and corresponding electrochemically active surface area (ECSA) region information. This information can be fed to the DNS framework resulting in local electrochemical reactions-based source terms that account for the microstructure and flooding. The coupling approach can help discern local reaction hotspots and provide insights into flooding-based performance degradation. In these local hotspots, one should pay attention to the dimensionless numbers of the flow, primarily the Reynolds number \(10^4\), the Capillary number \(10^6\), and the viscosity ratio \(M(10^2)\). In this regime, one would expect to see capillary fingering in random directions as the water moves. Using these ideals, multiple papers have been published showing the movement of water throughout the catalyst layer using LBM. As for DNS, models can also incorporate degradation aspects, for example, carbon corrosion through deleterious corrosion kinetics and reaction source terms, providing so far unrealized avenues for gaining insight into cycling performances.

**Computational Methodology**

The main simulation attempted is flow of oxygen, nitrogen, water vapor, and liquid water through the FIB-SEM data. For this, a D3Q19 LBM simulation for free-surface flow using Smagorinsky MRT dynamics was conducted. As free-surface flow assumes the kinematic viscosity of the gas phase is functionally infinite compared to the liquid, a decoupled forced Shan-Chen (S-C) model for the multi-component air system was used, and a volume of fluid (VoF) approach was used to track the liquid/vapor interface. The Smagorinsky method is an eddy minimization method typically used in turbulence modeling that is a low-pass filtering of the Navier-Stokes equations, whereas MRT is used to properly model porous geometry as previously mentioned. The main idea behind the S-C model is to create pseudo-potentials to describe different components in the simulation.
– this is the standard multi-phase, multi-component model in the literature. The forced part of the model involves applying the physics to the problem, whether they be buoyancy, capillary pressure, among others. In LBM, boundaries are applied throughout the whole geometry; this means one needs to have a schema for all areas where the Boltzmann equation is solved and where it is not. To do this, the bounce-back system means that whenever the simulation reaches a solid boundary, it “bounces back” to the previous node and goes to the next wet-node where the system is solved. For both the gas and liquid phase in the x-y direction, periodic boundary conditions are used. These were chosen based on the FIB-SEM data: in the x/y dimensions, only a small portion is captured, whereas, in the z direction, the portion accounts for a significant fraction (between 30-40%). Once the simulation is set up, this is then iterated over until convergence in either the average energy or density of oxygen is reached.

To describe initial and boundary conditions in the z direction, one can split them for each of the components and phases of the fluid. Additionally, bounce-back criteria are applied to each phase so that the void space is filled with only one component. For the liquid, a 3-4% saturation random condition was applied to all open voxels throughout the geometry and is continuously generated randomly at some time constant, derived from Faraday’s law below. The reason for the randomly distributed condition is to mimic the unknown Pt distribution; as for other boundary conditions, the liquid is removed at the CCL/MPL boundary every second, and no flux is at the CCL/membrane bound.

\[ \tau = \frac{i n F \rho e L}{MW} \]  

In this, \( i \) is the current density, \( nF \) are the number of electrons and faraday’s constant, \( \rho \) is the porosity, \( L \) is the thickness of the electrode, and \( MW \) is the molecular weight – as an example, for 1000 mA/cm\(^2\), the time constant for filling is about 8s. For the nitrogen, an initial purge is applied to the system to mimic experimental conditions, whereas the bounds are a Dirichlet constant pressure at the MPL/CCL, and a no flux at the membrane. For oxygen, none is present at the beginning. As air is being flowed in, oxygen is consumed at a discrete point (defined by some multiple of the time constant) wherever water is formed at the random Pt sites. As for other bounds, a Neumann condition is at the MPL/CCL, and no flux condition at the membrane. Finally, for water vapor, there is initially no water vapor, a Dirichlet constant pressure at the MPL/CCL, and a no flux boundary at the membrane. As for the partial pressures tried, initially the temperature and pressure are 80 °C and 1 atm, meaning the partial pressures of nitrogen, oxygen, and water vapor at 100% RH are 42.1 kPa, 11.9 kPa, and 47.4 kPa, respectively.

With the DNS approach, the goal is to model the electrochemical effects that cannot be modeled effectively with LBM\(^{19,35-37}\). These effects include modeling the standard electroanalytic techniques such as polarization curves and reaction profiles, as well as diffusion profiles and their associated boundary conditions. As these are the equations most commonly seen in other PEMFC models, these can be directly compared to literature. In addition, both LBM and DNS models need to be verified to make sure their predictions are accurate – for LBM, this is done by comparing to the Leverett-J function as well as examining the effect of different contact angles\(^{38-40}\). The verification for DNS is not shown below, but LBM is in Figures 4 and 5.

Simulation Verification
For the LBM verification, the goal is to understand the relationship between capillary pressure and saturation inside of the CCL. This is typically done by looking at the capillary pressure versus saturation curve, which describes flow for some driving force between the wetting (contact angle less than 90° -- the ionomer and fluid components themselves) and the nonwetting phase (contact angle greater than 90° -- the carbon media and Pt). Capillary pressure is typically handled by looking the Young-Laplace equation below relating it to physical parameters:

\[ \Delta P = \frac{2\gamma \cos \theta}{a} \quad [9] \]

In this equation, \( \Delta P \) is the capillary pressure, \( \gamma \) is the surface tension, \( \theta \) is the contact angle, and \( a \) is the pore size. One typically determines capillary pressure experimentally with mercury porosimetry. For the kinds of pore sizes and contact angles in CCLs, capillary phenomena should start occurring around 2 MPa. However, these kinds of pressures in the CCL are extremely difficult to measure accurately with mercury porosimetry or any other method. As such, experimental literature values vary wildly for many of the CCL\textsuperscript{38-41} and are often shown by a model. This was used as the test case for LBM.

\[ \text{Capillary Pressure and Saturation Relationship} \]
\[ \text{Capillary Pressure vs Saturation Contact Angle} \]

**Figure 4:** (left) Leverett-J model predictions for packed spheres for a non-wetting contact angle and the LBM result. (right) Capillary Pressure vs saturation for different contact angles for the LBM model

As we can see here, the model results match the Leverett-J model fairly well for the series of packed spheres. The simulations only showed accurate behavior up to a saturation of approximately 65% -- this is sufficient because capillary pressures of this order of magnitude are never seen in fuel-cells. These results also match what we see from the Young-Laplace equation – especially what is seen at contact angles close to 90 degrees, where there is a three order of magnitude drop in capillary pressure.

Additionally, we tried to examine liquid profiles for the effects of capillary fingering as well as viscous displacement. The liquid profile is shown as a schematic in Figure 5 below.
**Figure 5**: Simulations of liquid water going through the FIB-SEM geometry at 1, 3, 6, 11, 13, and 20 MPa, respectively. The order is an inverted s.

These simulations visually show different steady state points on the capillary pressure vs saturation curve. In the first, the capillary pressure (1 MPa) is not enough for the fluid to penetrate the geometry – this can be predicted from the Young-Laplace equation, which predicts a capillary pressure of 1.97 MPa for a surface tension of 0.06128 N/m, a contact angle of 130°, and an average pore size of 40 nm. Once we go beyond this point, the liquid film begins to go beyond the initial state, at first fingering (shown in 3 and 6 MPa, continuing to 11 MPa) then filling the whole geometry (shown in 13 and 20 MPa in Figure 5). Beyond the 20 MPa mark, we begin to reach the third part of the curve, where it takes much higher capillary pressures to fill the geometry further – as mentioned, this is not important to PEMFC practitioners, as the capillary pressure will not get this high. As for dimensionless numbers, the three of interest are the Re, Ca, and the viscosity ratio, which were found to be $2.58 \times 10^{-5}$, $2.62 \times 10^{-6}$, and 56.6, respectively – these results were corroborated on the phase diagram from Mukherjee on the right of Figure 5.

**Results and Discussion**

Once these validations were complete, the current density tests were completed for the PEMFC CCL models – these were doing LBM simulations for liquid water, air, and water vapor transport through the FIB-SEM geometry for current densities ranging from 10 mA/cm$^2$ to 1500 mA/cm$^2$. These were chosen to get a range of different current densities seen on a typical polarization curve; these profiles for oxygen transport are shown in Figure 6. Profiles are shown for the beginning of the simulation, an intermediate step, and finally for the final dynamic steady state.

100 mA/cm$^2$
Figure 6: Oxygen distribution through the geometry at 1.6 s, 64 s, 96 s and 123.2 s for current densities 100, 500, and 1000 mA/cm² (160 s). (top row) Oxygen distribution through the geometry at 1.6 s, 64 s, and 123.2 s for 100 mA/cm² (middle row) Oxygen distribution through the geometry at 1.6 s, 64 s, and 123.2 s for 500 mA/cm² (bottom row) Oxygen distribution through the geometry at 1.6 s, 64 s, and 123.2 s for 1000 mA/cm²

Since the liquid and gas phase have been decoupled with the free-surface simulation, the gas-phase is shown separately below in Figure 6 for a few different time steps. From these simulations, one can see that as the liquid continues to fill up the geometry, increasingly less oxygen can flow through the geometry – one can see the significantly reduced oxygen content in the later simulations, especially at higher current densities. This is expected from experimental results due to concerns of flooding. However, if we examine the dynamic steady state reached towards the end of the simulation, we can see we see almost no saturation where larger current densities are completely full. This is due to the time constant for smaller current densities is much larger than it would be for smaller current densities – the simulation converges before this level of saturation is reached. We can also see that there is larger partial pressure of oxygen in the geometries as the current density increases, specifically around the MPL/CCL boundary. This may be due to the liquid water beginning to block access to the membrane, meaning there is a build-up of pressure in the pore movement of oxygen. For the peak levels of saturation, we typically see saturation levels peak (around 90%) at this same point where this local build-up of pressure is. To examine this, the local saturations were analyzed per distance from the membrane in the CCL, which are shown for two of the current densities in Figure 7. Additionally, we do see a variation in the local saturation profile for different current densities. As the saturation levels reached are quite high, further tests need to be run to ascertain if this phenomenon is not an artifact of the simulation.
Figure 7: Saturation vs distance from the 100 and 500 mA/cm\(^2\) simulations for the first 40 timesteps, at intervals of 1.6 s for a total of 64 s (left) 100 mA/cm\(^2\) (right) 500 mA/cm\(^2\)

Conclusions

This work suggests that the LBM-DNS mode can be the chief method for CCL analysis not just in water management, but also in areas of electrochemical phenomena incorporation and interfacial effects. The current density test gives better insight for understanding local saturation and what factors impact the transport of oxygen to the catalyst layer. A better understanding of the CCL response to various operating parameters is essential for advanced PEMFCs, especially with lower Pt-loading or non-noble metal catalysts modeling being active areas of need in the PEMFC community. The model is distinguished from the rest of the literature because it is the first to use tomography and mesoscale modeling techniques to render the CCL rather than stochastic reconstruction for model predictions. This allows the field to move beyond simply ignoring the microstructure seen in the macrohomogenous model. In the past, there has been resistance to using these methods due to their computationally intensive nature and the lack of availability of microstructures; however, we’ve shown that these are gradually being lifted. Ideally, when the field of LBM-DNS modeling in PEMFCs is more mature, the simulations can take experimental data for quantities such as contact angle, capillary pressure, and coverage and give researchers not only a better idea of what occurs in the catalyst layer through reduced-order models, but also design better PEMFCs. Also, given the complexity of the models and the paucity of open source codes, more collaboration in the PEMFC community and renewed impetus towards openly shared and developed code can foster innovative insights into CCL physics. These will help us design and model PEMFC that can successfully innovate the next generation of energy storage devices.

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References


Klingele, M., Zengerle, R. & Thiele, S. Quantification of artifacts in scanning electron microscopy tomography: Improving the reliability of calculated transport parameters in energy applications such as fuel cell and battery electrodes. J Power Sources 275, 852-859 (2015).


