Report of the 7th Meeting of the Transport Modeling Working Group

May 22 and 23, 2014

The Transport Modeling Working Group (TMWG) met over 1.5 days at the end of May at Lawrence Berkeley National Laboratory. The chosen topics were to discuss multiphase flow with a focus on the diffusion media and the nexus between durability and transport modeling. The format was similar to previous meetings with ample time for discussion led off by a few presentations pertinent to the topic at hand. Both core TMWG participants as well as some experts and collaborators were invited to attend.

Multiphase Flow

A key issue that still confronts understanding and predicting fuel-cell behavior is multiphase flow and really the correct boundary conditions and interfacial phenomena. At the meeting, Dr. Iryna Zenyuk presented some modeling and experimental studies focused on the importance of the MPL/CL interface where water accumulation can occur due to the inherent roughness of the interface. Using a model based on explicitly accounting for the 5 micrometer interface, it was shown how liquid-water can imbibe and accumulate. Experimentally milled MPLs demonstrated increased performance due to their preferential water-removal characteristics. Key questions that arose are what are the transport properties of the interface, what is its inherent water capacitance, and how does the interface impact performance at different conditions.

In a complementary talk, Dr. Anthony Santamaria discussed the GDL/channel interface and the importance of knowing how to treat this interface in terms of modeling (i.e., what is the correct boundary condition). He presented some experimental studies on adhesion force and breakthrough for GDLs, and the force-balance approach for the modeling. Key questions here were what about smaller channels where lands and walls become more important (e.g., wicking), how critical is repeated wetting versus using new samples for breakthrough, and how do droplets impact performance at the anode where the mass-averaged velocities are often lower.

The subsequent discussion on interfaces highlighted the importance of interfaces yet the fact that they are not well characterized or understood, including such ones as the GDL/MPL which can be a very diffuse interface. This also brought comments about how heterogeneous the various materials like GDLs are, and thus one needs a multiscaling approach to understand how factors including PTFE heterogeneity can impact performance. Similarly, some comments concerning whether one needs transient models and studies versus steady state were made, with no strong agreement beyond that a time-scale analysis should be done to see if one can assume pseudo-steady-state behavior of some stochastic phenomena.

Discussion also centered around how to treat interfaces mathematically with explicit regions, microscopic submodels, or just interfacial boundary conditions. It was decided that some kind of specific modeling approach for the interfaces is required including the development of effective properties. This is also important when interfaces evolve such as under compression in the operating cell. Similarly, there is still a need for sufficient diagnostics to interrogate interfaces as well as examine their

importance in terms of lateral versus through-plane transport. Comparisons between GDEs and CCMs should also be evaluated. A short discussion of other interfaces such as membrane/catalyst layers was also discussed as a possible area for further research. Finally, comments about tying interfaces and durability were made including how blocking by droplets or water in the interfaces could result in local fuel starvation and other degradation mechanisms.

The next presentation was given by Prof. Jeffrey Gostick who focused on examining GDL modeling. He showed that one cannot assume local equilibrium and that characteristics such as capillary pressure–saturation relationships which are measured across a GDL can be applied locally. This is especially true since they are measured in the absence of the gradients that occur during operation (i.e., where the distribution of water is key); thus, one needs better approaches for the GDL than an entirely macroscopic one. Some possible approaches including pore-network modeling or statistical correlations with flat profiles were discussed, with the keys being to understand the true limiting phenomena and model that with high fidelity. For example, Darcy's law and related descriptions are not really valid if the process is entirely stochastic and based on capillary phenomena that include percolation. Another key concept to come out was the need for defining representative volumes that could be used for models including their characteristic parameters.

The above presentations also led to a discussion of effective properties. In particular, it was noted that there is a need to rank and identify the critical properties. For example, Dr. Gu commented that droplet coverage at the GDL/channel interface is not critical as it only accounts for a few mV in potential drop due to lateral flow in the GDL. It was agreed that for dry conditions, the community has a good handle and understanding of effective transport properties, but not so under humid conditions, low temperatures, or after degradation. In this latter case, it was noted that one does not necessarily know the state of the material anymore. Finally, issues such as error propagation in models due to the properties used as well as sensitivity towards certain properties has not been, but should be, studied.

Durability

The second day focused on the nexus between durability and transport, especially in terms of modeling. The initial presentation was given by Dr. Rod Borup, who presented on durability experiments and ASTs. He noted how transport changes as a function of durability due to changes in material and transport properties. It was noted that there is still a need to correlate real-world data with ASTs and derive acceleration factors. In addition, while some ASTs have been modeled explicitly (e.g., catalyst dissolution), others are only modeled in terms of their impact by comparing beginning and end of test performance. The issue of increased transport losses at low catalyst loadings was also discussed. Also, the impact of heterogeneities on performance was again highlighted as a research need. Finally, some comments about the need to model morphological changes with time and history with performance were made. Dr. Borup also highlighted possible issues with membrane chemical-degradation mitigation additives not staying where they initially existed before testing.

In terms of modeling durability and transport, Dr. Rajesh Ahluwalia and Prof. Kunal Karan presented on multistep Pt kinetics and reactions including dissolution and oxide formation. Here the key is to

determine the local concentrations of intermediates that may result in membrane degradation or other deleterious effects if they can be transported away from the generation site. It was shown that many of the durability phenomena depend on liquid water, which is a direct result from transport phenomena within the cell. It was shown how one can utilize a large data set to derive empirically key parameters, and again the impact of increasing mass-transport limitations as the Pt surface area is decreased due to degradation was highlighted.

Prof. Erik Kjeang and Dr. Ahmet Kusoglu presented on membrane degradation and durability modeling. They highlighted the synergistic interactions between transport and durability, where increased crossover results in more membrane attack. Similarly, it was discussed that there is a need to account for these synergistic interactions and how properties change during operation and not just beginning and end of life since they impact the degradation rates and phenomena. Transport phenomena was also shown to be key in controlling Pt band formation and location. The keys here are to model and link membrane degradation and transport through MEA models to get distributions for chemical stressors as well as for combined chemical/mechanical durability. For the latter, it was shown how mechanics models can be used to predict void growth in the membrane due to humidity cycling. Some discussion again on whether interfaces are key for durability as well as transport was made. Ensuring discussion also highlighted the need for predictive life models, where beginning and end of life was not seen as sufficient and synergistic effects are important as well as changes over time of material structure and properties. Finally, it was again noted that most durability concerns are related to the location of liquid water, and thus are integrally tied to transport models and studies.

Next Steps

Final discussion centered around the TMWG, were again everyone agreed that it was a well-structured and useful meeting. Those attending it for the first time enjoyed the amount of discussion and the duration of 1.5 days that allowed for good interaction and collaboration. It was agreed that it should continue to be held alone and not as part of a conference where there are too many distractions. However it was suggested to make it more of an open meeting and also invite more speakers (including from other communities), although while still striving to maintain a smallish group (~20) that allows for discussions and honesty.

For the next meeting, it was suggested to focus on catalyst layers including more characterization and microstructural talks to complement the usual continuum modeling and thin-film working group report.