In Situ Characterization of the Catalyst Layer in a Polymer Electrolyte Membrane Fuel Cell

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In polymer electrolyte membrane fuel cells (PEMFCs), hydrogen is introduced through channels in a bipolar plate through a gas diffusion layer (GDL) into the anode catalyst layer, where the catalyst facilitates the dissociation of hydrogen into protons and electrons. The membrane sandwiched between the GDLs is able to freely conduct protons while remaining relatively impermeable to electrons. Thus, protons migrate across the membrane while electrons are conducted through an external circuit generating useful electrical power. Once the protons and electrons reach the cathode, they combine with oxygen in the presence of the catalyst to form water and heat, as shown in Fig. 1. PEMFCs are promising energy conversion systems for future automotive and stationary applications. However, efficient and sustainable energy conversion through a hydrogen economy places formidable demands on materials optimization as well as a better understanding of transport processes within the cell.1-3

Careful water and heat management throughout the cell is needed to maximize performance. Efficient removal of excess water is still a significant challenge, since the cathode side of the PEMFC is prone to liquid water formation due to electro-osmotic water transport across the membrane and water production from the oxygen reduction reaction (ORR). Unless instantaneously removed, this liquid water may fill the pores of the GDL, thus blocking the oxygen transport into the catalyst layer (CL). Condensed water can also cover the catalyst sites, rendering them electrochemically inactive. This phenomenon is known as "GDL/CL flooding." If excess liquid water accumulates in the flow channel, a water lens or band may form inside the channel, thereby clogging and shutting down the oxidizer flow. This latter condition is referred to as "channel flooding."4-7 It should be noted that under certain operating conditions of temperature and humidity, flooding can initiate in the GDL/CL and lead to channel flooding, while in some instances the channel flooding may occur first if the saturation condition is met there. The CL is the most complex and versatile component of a PEMFC, since it is the location of the "three-phase contact" and the bed for electrochemical reactions (Fig. 1). Interactions in this heterogeneous structure, where different phases coexist, are further complicated by the accumulation of liquid water.4-10

While the need for modeling liquid water formation and transport in PEMFCs has long been recognized,11-14 the role of the CL in water transport has not been explored in depth. Most cell and stack computational fluid dynamics models treat CLs as infinitesimally thin interfaces without structural resolution, which oversimplifies the fact that the catalyst layer has a finite thickness with distributed properties. Most models also do not account for the presence of liquid water at the CL interface, and consider its effect only on the conductivity and swelling of the membrane phase.

The complex and heterogeneous micro/nano structure of the CL, coupled with the fact that it is concealed behind the GDL within the cell, makes it a challenging task for both theoretical and experimental investigation. Experimental explorations of PEMFC flooding and water management have focused on liquid water formation in GDLs and flow channels, while usually ignoring the effect of flooding on...
the reactive surface in the catalyst layer. While in situ direct visualization has been widely used to study water dynamics, it has insofar been limited to channel flooding. On the other hand, neutron imaging provides a through-thickness integrated water content, making it difficult to distinguish the water amount at different penetration depths. The goal of our study is therefore to provide an insight into the mechanisms of water formation and transport in/on the CL. In the present work, liquid water dynamics on the CL are investigated by direct visualization in an operating fuel cell.

Experimental

The experimental setup, as shown in Fig. 1, consists of a catalyst-visible operational fuel cell, a microvisualization and imaging system, a gas supply and a 200 W test stand (Arbin Instruments) with controlled temperature, pressure, flow rate and relative humidity, an electronic load and a data acquisition system. The catalyst-coated membrane used in the catalyst-visible PEMFC was Nafion-based, 25 μm thick, with Pt catalyst loading of 0.3 mg/cm² on each electrode (Ion Power, Inc.). Sigracet SGL31BC by SGL Carbon Group was employed as the GDL. The cathode flow field of the experimental cell was made by chemically etching a 0.75 mm thick copper plate to form a 1 mm wide serpentine channel with 1 mm wide lands for current collection.

The anode flow field of the cell was a conventional graphite bipolar plate containing a single serpentine channel. The total active area of the test cell was 10 cm². The temperature-control system of fuel cell consisted of heaters in the end plates, and an adjustable-speed fan. The temperatures of the front and back of the fuel cell were controlled separately. In the front, the temperature sensor was located in the polycarbonate window and the heaters were placed around the window. The fuel cell was operated at 70°C, with fully humidified inlet air and hydrogen. The operating pressure was 2 atm (abs). In all experiments, ultrahigh purity (99.999%) hydrogen and standard dry air were used from compressed gas bottles.

The microvisualization system consists of an optical subsystem, image capturing and controlling subsystem, an objective lens, zoom lens assembly, and projection lens. In addition, small holes (about 0.5 mm) were introduced into the GDL to expose the underlying CL for visualization purposes. The anode flow field of the cell was a conventional graphite bipolar plate containing a single serpentine channel. The total active area of the test cell was 10 cm². The temperature-control system of fuel cell consisted of heaters in the end plates, and an adjustable-speed fan. The temperatures of the front and back of the fuel cell were controlled separately. In the front, the temperature sensor was located in the polycarbonate window and the heaters were placed around the window. The fuel cell was operated at 70°C, with fully humidified inlet air and hydrogen. The operating pressure was 2 atm (abs). In all experiments, ultrahigh purity (99.999%) hydrogen and standard dry air were used from compressed gas bottles.

The microvisualization system consists of an optical subsystem, image capturing and controlling subsystem, a cold-light source, and a compact XYZ translation stage. The optical subsystem (including an objective lens, zoom lens assembly, and projection lens) was carefully designed with a spatial resolution of 5 μm and a working distance of up to 10 cm. This key feature distinguishes it from a conventional microscope, which requires very small working distances to obtain higher magnifications. A high-resolution camera (Sony XCD-SX910) controlled by a PC is used to record the water dynamics on the exposed CL surface at up to 30 frames/s. Fiber optic goosenecks attached to an adjustable 150 W halogen cold light source (Volpi Intralux 5100) were used to illuminate the areas of interest.

Ex situ experiments.—A JSM-7400F field emission scanning electron microscope (FESEM) was used to examine CL morphology with a spatial resolution of 1.4 nm at 1 kV. Figure 2 shows a typical SEM image of the complex structure in the catalyst layer. Agglomerates comprised of carbon particles (ranging from 10 to 20 nm) with highly dispersed Pt catalyst (ranging from 1 to 10 nm) form agglomerates with a random pore distribution and length scales of the order of 100 nm. For high performance, the CL requires a sufficiently contiguous carbon matrix for good electron conductivity, and adequate Pt surface for electrochemical reaction, ionomer for proton transport, and pore space for oxygen transport. Although the materials comprising the CL have distinctly different individual wetting properties, the CL surface may be highly hydrophobic in nature due to its micro/nano roughness. A typical contact angle value of 168° was measured at room temperature.

Figure 2. (Color online) SEM image of a catalyst layer. Top right corner shows a schematic of agglomerates within the catalyst layer.

In situ observation of water dynamics on the CL.—Polarization curves of the catalyst-visible PEMFC under stoichiometries of 4/4, 2/2, and 1.5/1.5 at 1 A/cm² are shown in Fig. 3. The dashed lines represent the power density, and the solid lines represent the cell voltage. The curves more or less overlap at lower current densities, whereas the performance improves with flow stoichiometry at higher current density due to improved mass transport. Power density peaks at 0.6 W/cm² at a voltage of 0.45 V and stoichiometry of 4/4. Even at the low stoichiometry of 1.5/1.5, the maximum power density recorded was 0.45 W/cm² at 0.52 V. It shows that we were able to operate the cell at the current and power densities seen in industrial cells, thus capturing realistic transport phenomena. Al-
Figure 4. Typical image of in situ micro water droplet on the catalyst layer.

though exposing the CL surface will change the local capillary forces and the thermal boundary condition, we have tried to minimize these effects by keeping this region at the micro level. We have also confirmed that exposing the CL surface for micro visualization purposes does not influence the overall cell performance and durability.

Figure 4 shows a typical image of micro droplets on the cathode catalyst layer (CCL) in an operating fuel cell. The bright parts are due to the reflected lights on the droplets. Liquid water formation on the CCL surface is governed by multiple processes and reactions, which mainly include: water production due to ORR, electroosmotic water transport across the membrane, diffusion, and phase change due to local evaporation and condensation. Initially, water droplets were observed with diameters ranging from 2 to 5 μm, which are considered to condense preferentially on less hydrophobic sites. The droplets are held onto the site by surface tension as they grow and coalesce. Their geometries are governed only by surface tension due to the small Bond number, Bo, defined as follows

\[ Bo = \frac{\Delta \rho g d^2}{\sigma} \]  

where \( \Delta \rho \) is the density difference between the liquid and the gas, \( g \) is the gravitational acceleration, \( d \) is the droplet diameter, and \( \sigma \) is the surface tension. Because of the super hydrophobic nature of the CL surface, the droplet can be described as a spherical cap. If the contact angle hysteresis and the condensation during coalescence are neglected, the newly formed droplet radius, \( r \), and the covered area of the CL surface, \( S \), can be calculated as

\[ r = \left( \frac{1}{\pi} \sum_{i=1}^{n} r_i^3 \right)^{1/3} \]
\[ S = \pi (r \sin \theta)^2 \]

where \( r_i \) is the radius of the \( i \)th coalescing drop, and \( \theta \) is the contact angle. Liquid water coverage area reduces by 20% when two drops of the same radius coalesce. This mechanism therefore enables higher utilization of the catalyst and further mitigates the flooding due to the increased reaction area, which is discussed later.

After they are removed by evaporation or capillary force or by drag force due to the flow, new droplets of water are observed to appear and grow on the same preferential locations on the CL surface, while the cell is held under constant operating conditions. Re-starting the cell with the same operating condition resulted in a similar droplet distribution pattern. Our observations revealed four possible pathways of water dynamics on the CL surface: (i) After a droplet forms, it continues to grow until it is removed by the drag force due to the flow; (ii) droplet formation and growth are followed by complete evaporation; (iii) evaporation occurs as soon as the liquid drop is formed, before it has a chance to grow; or (iv) no droplet formation was observed at some of the sites on the CL. It should be noted that small droplets in the hole will be shaded to some extent from the local flow velocity, whereas larger droplets could be removed by drag forces. Droplet removal by drag forces is enhanced by the strongly hydrophobic nature of the CL surface. More research is needed to analyze this in a quantitative fashion, as the water dynamics at the CL depends not only on the local temperature and water partial pressure, but also on the thickness, composition, and pore morphology of the CL.

It should be noted that the CL in a conventional cell would be covered completely by the GDL. Therefore, instead of being carried away by the drag force, the growing droplets would eventually be wicked away through the GDL pores, while condensation would continue throughout the GDL. Studies of channel flooding have shown that the droplets periodically emerge and grow at preferential sites on the GDL surface in the flow channel. It is therefore reasonable to assume that such repeatable liquid water behavior on the GDL is caused by combined effects of the GDL structure and the preferential droplet growth locations on the underlying CL surface. Hence, the micro-visualization technique could help to estimate the in situ condensation rate within the GDL as the difference between the liquid water evolution rates on the CL, and the neighboring GDL surface sites. Furthermore, by identifying the pattern of the preferential sites for water formation on the CL, one could utilize this information to design the GDL/CL interface for efficient water removal.

Role of the CL pore size and wetting property.— Since the present experimental approach allows us to study water behavior on the CL surface only, we can employ a classical model to discuss the water evolution in the interior of the CL. Although simplified, this approach can explain why some sites on the CL surface are more prone to liquid water formation than the others. The catalyst layer can be modeled as a porous medium with a characteristic pore size and wetting properties. The saturated vapor pressure, \( P_{sv} \), in a pore of radius \( r \) can be estimated by the Kelvin equation as follows

\[ \ln \left( \frac{P_{sv}}{P_0} \right) = -\frac{2\sigma M_w \cos \theta}{r \rho_w RT} \]  

where \( P_0 \) is the saturated vapor pressure over a flat surface, \( \sigma \) is the surface tension, \( \theta \) is the contact angle along the pore wall, \( R \) is the gas constant, \( T \) is the absolute temperature, \( M_w \) is molecular weight of water, and \( \rho_w \) is the density of water. Once condensed, water is transported through the pore via capillary pressure, accompanied by condensation/evaporation. The capillary pressure, \( P_c \), in a cylindrical pore is determined by pore radius, \( r \), fluid and substrate properties, and can be calculated as

\[ P_c = P_{nw} - P_w = -\frac{2\sigma \cos \theta}{r} \]  

where \( P_{nw} \) and \( P_w \) are the pressure of the nonwetting phase and wetting phase, respectively.

The CCL contains a mixture of hydrophobic and hydrophilic pores. The hydrophilic pores are mainly due to ionomer in CCL, while the cluster structure of the ionomer, as shown in Fig. 2, can be simplified as hydrophilic pores. Figure 5 plots the relation of \( P_{nw}/P_0 \) and \( P_c \) with contact angle and pore radius. The dashed line represents the saturated pressures ratio, while the solid line gives the capillary pressure. It is readily seen that the effect of the pore, be it hydrophilic or hydrophobic, becomes more pronounced as the pore radius decreases. For hydrophilic surfaces (contact angle >90°), both the saturated vapor pressure and capillary pressure will in-
crease with contact angle. This suggests that higher vapor pressures are required to condense water in a hydrophobic pore. Once condensed, water preferentially flows into larger hydrophobic pores, and sites with lower contact angles, since they require a smaller capillary force. For hydrophilic surfaces (contact angle < 90°), both the saturation pressure and capillary pressure decrease as contact angle and pore radius are decreased. Therefore, partial pressure of water required for condensation in a hydrophilic pore is smaller than the saturation pressure over flat or hydrophobic surfaces. The negative values of the capillary pressure indicate that liquid water will wick into a hydrophilic pore spontaneously. It should be noted that the Eq. 3 and 4 require curvature of the liquid-gas interface to be well defined, which might not be the case in the innermost regions of the CL. However, surface regions have sufficient pore size well defined, which might not be the case in the innermost regions of the CL. However, surface regions have sufficient pore size (Fig. 2), thus justifying the use of the equations. They offer a clear physical explanation for the two-phase dynamics in porous media.

We can now clarify the liquid water evolution on the CL surface observed in our experiments using the schematic in Fig. 6. Water is produced at the active sites on the pore walls. Water will gradually accumulate on the membrane side (bottom ends of the pores), either by moving through the membrane from the anode side, or by generation due to reactions in the CCL. For simplicity, we will assume that the pore is isothermal. Water will first condense and/or flow in the hydrophilic pores (Fig. 6A) and flood the catalyst sites therein. As liquid water continues to accumulate on the membrane side and the hydrophilic pores are flooded, water will eventually penetrate into the largest hydrophobic pores (Fig. 6B) when the capillary pressure reaches a critical value (given by Eq. 4). Since water vapor is produced all along the pore and can only be evacuated at its end, the water vapor pressure increases along the pore as one moves away from the membrane surface. Liquid water can form a plug in the middle region along the pore (Fig. 6C) thus starving the trapped section of reactant gas. In a smaller hydrophobic pore, there is no initial pore blockage, although droplets might evolve on the pore wall (Fig. 6E) in a manner similar to the one observed previously on the CL surface in Fig. 4. The coalescence of droplets will help reduce the liquid-coverage area along the pore wall (Eq. 2) and alleviate flooding. Clearly, this mechanism is beneficial only until the coalescing droplets block the entire pore cross section, when we retrieve the situation shown in Fig. 6C. The smallest hydrophilic pores (Fig. 6E) will be least prone to flooding. Although the schematic does not account for local temperature changes due to the reaction, nor does it consider how the water is removed once it reaches the pore end at the CL/GDL interface, it provides an insight into the mechanisms that culminate in droplet emergence from the openings on the CL surface observed in our experiments.

After droplets are formed on the CCL, some of them grow due to capillary transport and condensation, and coalesce with other droplets. At the critical detachment diameter (defined for the GDL surface in Ref. 4), the drag force overcomes the surface tension adhesion force, and the droplets detach from the surface and are carried away by the gas stream. Subsequently, new droplets were observed to re-emerge on the same sites. Other droplets are removed by evaporation.

The time evolution of liquid water on a CL surface under constant operating conditions is depicted in Fig. 7, where the time interval between the frames shown is 0.5 s. It can be observed that the catalyst layer exhibits uneven water droplet growth and evaporation rates. From 0 to 0.5 s, droplet A at the top right image region grows faster than the other droplets in the image. After 0.5 s, droplets at the top right image region disappear very quickly due to evaporation. On the other hand, droplet B grows and evaporates more slowly than those in the droplet A region. We can infer from these
images that the evaporation rate varies spatially over the observed area. Evaporation results from a combined effect of the variations in local temperature and saturation level. Further evaporation removes all the droplets as shown in the frame at 1.5 s. Note that the maximum size of the evaporating drops changes with time and location in the view window. The droplets in some areas disappeared soon after their formation on the CL, while others continued to grow for a while before gradually evaporating.

Evaporation is definitely desirable in water management of the PEMFC. Once liquid water arrives in the GDL and the flow field, it is almost impossible to vaporize it. Furthermore, greater propensity for liquid water accumulation is anticipated in the CL areas covered by the GDL, since evaporation on the exposed CL portions is promoted by the gas flow directly over the droplets. This makes evaporation an even more important mechanism for water removal from the CL/GDL interface. Only the CCL possesses the ability to generate heat from electrochemical reactions and facilitate water removal by phase change. One of the future challenges will be to enhance evaporation in/on the CCL by coupling it with an approach to characterize its thermal properties as well. Based on our present technique, this might be achieved by adding an IR thermal imaging system to our experimental setup.

Relating fuel cell activity to droplet dynamics on CL.—Figure 8 gives the cell voltage and the corresponding liquid water distributions on the CL at current densities of 0.4 and 0.8 A/cm² with an H₂/air stoichiometry of 1.5/1.5. It is observed that at higher current density as shown in Fig. 8. As the current density increases, local capillary equilibrium shifts towards smaller pores due to more water accumulation. More pores of the CCL will also be flooded, thus failing to transport reactants to the catalyst sites, as shown in Fig. 6A-C. CL flooding causes the voltage oscillations at higher current density, while the voltage drops from 0.72 to about 0.58 V. Under each constant current density operating condition, the distributions of the droplet size and centers evolve in correlated fashion, exhibiting similar patterns of droplet dynamics.

The net water transport coefficient, which is widely used in water management calculations, is a dynamic variable of the membrane. It is a function of the current density, temperature, humidity, flow rate, membrane properties, and the CL. Its value has so far been determined by ex situ measurements, while neglecting some of the variables (e.g., current density). By developing proper image processing techniques, the local water accumulation rate on the CL surface can be found based on the video recordings with the present technique. This could be done by incorporating the water accumulation rate with the current density and the specified area into Eq. 5. Therefore, the microvisualization technique offers the possibility of estimating in situ the net water transport coefficient and its distribution across the cell. Further research is under way to characterize this coefficient.

Conclusion

In situ visual characterization of the CCL is performed by exposing microdroplet behavior on the CL surface in a catalyst-visible transparent PEMFC. Water removal by evaporation was identified as a distinguishing ability of the CL. Hence, one of the future challenges will be to exploit this mechanism to improve water management within the cell. Our results also indicate that reducing the pore size and increasing hydrophobic property preferentially retains water in the gas phase (Fig. 6E) and alleviates flooding within the CCL. By optimizing the thickness of the CL, one could further reduce the possibility of transport blockage in the pore (Fig. 6C). For efficient catalyst utilization, the CL should have an optimal distribution of hydrophobic and hydrophilic pores, such that the hydrophobic pores facilitate gaseous transport of reactants and products, while hydrophilic pores would remove the excess water as liquid. Our model also suggests that a gradual reduction of pore radius and/or increase of temperature away from the membrane will reduce condensation and flooding.

The experimental technique presented here identifies the CCL regions and operating conditions for which condensation and flooding become critical. It provides guidelines for alleviating these problems by design and fabrication of the CL structure less prone to flooding, and by careful choice of operating conditions. The overall cost can be reduced without compromising performance by maximizing the catalyst area usage through the efficient water management.

Although not yet exploited in detail, CL microvisualization offers various possibilities for further investigation of the complex processes involved in the water transport in a PEMFC. The technique could be used to estimate the condensation rate within the GDL across the cell. Liquid water behavior on the GDL surface within the flow field channel is shown to be promoted by the periodic water evolution on the underlying CL surface. Microvisualization results could therefore be useful when designing the GDL material to mitigate the excess water accumulation on the CL/GDL interface. In addition, it provides the means for evaluating the net water transport coefficient, widely used in the fuel cell modeling. Extending the current work to include thermal effects on water dynamics in a PEMFC will provide better understanding of phase change and heat-transfer within micro/nano pores of the catalyst layer.

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