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Experimental Observations of Microstructure Changes in the Catalyst Layers of Proton Exchange Membrane Fuel Cells under Wet-Dry Cycles

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Microstructure changes of the catalyst layers in proton exchange membrane fuel cells (PEMFCs) lead to significant performance degradation and durability limitations, especially under dynamic loading condition; and they are investigated experimentally in this study simulating the effect of wet-dry cycles through water intrusion-evaporation and water flow-through-dehydration experiments, respectively. It is found that the cycling of water intrusion-evaporation processes significantly contributes to the growth of agglomerates as well as the formation of pinholes and cracks, causing irreversible losses of active surface areas and catalytic activity; in contrast, the cycling of water flow-through-dehydration experiments enlarges the large pores but changes very little the agglomerate sizes. This is because water tends to flow through the path of least resistance, that is, the large pores in the catalyst layers, leaving the other parts of the catalyst layers with relatively small pores less affected. These observations provide experimental evidence of microstructure changes and their forms for a better understanding of degradation in PEMFCs, especially under dynamic operating conditions.

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Proton exchange membrane fuel cells (PEMFCs) have reached the early stage of commercialization, and durability and cost still remain as the key technical challenges to their widespread applications. However, cost and durability are inter-related, and conventionally durability is favored at the expense of high cost through high loading of the expensive platinum catalyst.^{1,2} In addition, PEMFCs are found to degrade faster under dynamic load conditions than under static load conditions.^{3–6} Over the past several years, significant efforts have been devoted to investigating and understanding factors impacting PEMFC durability, especially under dynamic conditions.^{2,7,8} Because of the need of having high platinum loading to ensure lifetime, phenomena occurring within the catalyst layers of PEMFCs have been the subject of studies^{9–11} and water and heat management are the two critical issues for PEMFCs.^{12–14} Then it is interesting to consider the effect of water and heat cycling on the catalyst layers.

The catalyst layer is the place where electrochemical reactions occur, which is typically composed of catalyst, ionomer, and pore. The catalyst is for accelerating reaction rate and transporting electrons, while the ionomer is used to bind the catalyst particles and to provide pathways for proton transport;^{9,10,15} however, the protonic conductivity of the ionomer is highly sensitive to the water content in the ionomer – fully hydrated ionomer has the highest, while dry ionomer has the lowest conductivity for proton.¹⁶ Accompanied by this property, the volume of the ionomer changes sensitively with its water content, resulting in swell-shrinkage cycling with the hydration level. This can lead to the fatigue failure of the ionomer as the binding agent, causing catalyst particles to loose up and be carried out by the water transport. The catalyst currently utilized in PEMFCs is typically carbon supported platinum (Pt/C), which contributes a large portion of overall cost.^{1,17–24} The durability of the catalyst layers varies significantly when they are under different operating conditions.^{3,21,25} The required lifespan is about 5,000 h for passenger vehicles, 20,000 h for buses, and 40,000 h for stationary applications,^{3,4} but the actual lifespan for today's PEMFCs is short of the expectation, e.g., only

2,500–3,000 h for vehicles and 30,000 h for fixed power sources.^{5,6} It should be noted that the long lifetime is only achieved with regular interruptions of the operation to perform refresh procedures in order to eliminate reversible degradation losses.⁵ For a stationary fuel cell working at constant load conditions, the performance degradation can be as low as $1\text{--}2\ \mu\text{V} \cdot \text{h}^{-1}$,²⁶ however, the degradation rate would increase by orders of magnitude when the vehicular fuel cell is working under severe conditions including load, humidity, thermal, potential, and stress cycling.^{6,25} The difference in PEMFC durability between vehicles and stationary devices indicates that the operational condition is one of the most important factors that cause the PEMFC performance to irreversibly and rapidly decay.

Extensive experimental and theoretical studies have been made in an attempt to understand the degradation mechanisms of catalyst layers.^{2,7,26–29} Typical degradation modes can be Pt sintering and dissolution, carbon corrosion, and ionomer decomposition due to radical species attacks.^{30–32} The material degradation can cause the loss of catalytic activity, reduction in electronic and protonic conductivity, decrease in mass transport, and poor water management due to the deterioration of the pore structure.^{30,33} These malfunctions can become worse under vehicular operating conditions during which the cell components experience severe load, humidity, thermal, potential, and stress cycling due to frequent start-stop cycles and dynamic load responses.^{2,21,28,34,35}

The catalyst sintering or agglomerate size growth is one of the most important causes of the long-term performance degradation³⁶ because it occurs throughout the cell operation and will result in a steady decrease in electrochemical reaction area and catalyst activity.^{29,32} Two mechanisms for the agglomerate growth can be Ostwald ripening (OR) and particle migration and coalescence (PMC).³² OR is the phenomenon that small particles first break into atoms or molecules and then merge into large particles. In contrast, PMC involves the movement of small particles in a Brownian-like motion with subsequent coalescence leading to agglomerate growth. The agglomerate grows throughout the entire lifetime of PEMFCs, and the growth rate can be accelerated by severe working conditions.^{26,37} In comparison with steady operation (e.g., stationary devices), the vehicular fuel cell

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has to frequently change its output current density, voltage, and power to respond to the transient load cycling. For a specific fuel cell device, a sudden load change results in a significant change in chemical reaction rate as well as water and heat generation, making it difficult for effective thermal and water management. This type of degradation during cell operation cannot be avoided, but the degradation rate may be minimized with the proper design if the associated mechanisms and causes of the agglomerate growth are clearly identified and understood. Unfortunately, the processes of the catalyst sintering and agglomerate growth are still not fully understood.^{3,38} Experimental and simulation results indicate that many factors are involved including the cyclic changes of humidity and temperature, hydration levels, and crystallite migration.^{36,39,40}

In the pore regions of the catalyst layers, the water usually presents in either liquid or vapor forms, although a fraction of water can be adsorbed by the ionomer, which is beneficial for the ionic conductivity. The liquid water in the pores blocks the pathways of reactant transport, thus excess liquid water need be removed efficiently.⁴¹ Otherwise, the operational performance can be dramatically deteriorated by the water flooding problems.^{41–44} However, a proper amount of water vapor (or relative humidity) keeps the ionomer in the catalyst layers hydrated at the practical operating conditions. A well-hydrated ionomer can reduce the ionic resistance and facilitate the electrochemical reactions.¹³ It should be noted that a frequent hydrated and dehydrated working condition will cause the ionomer to swell and shrink during the dynamic loading operation.^{39,40} The dynamic swelling-shrinking cycling of the binding material may lead to the deformation and detachment of the catalyst particles. This indicates that water behaviors may have a significant impact on not only the transient operation but also long-term performance degradation due to potential structural damages.

Therefore, the objective of the present study is to experimentally investigate the microstructure changes of the catalyst layers in PEMFCs under the wet-dry cycles, simulating the practical dynamic working conditions. Two ex-situ experiments of water intrusion-evaporation and water flow-through-dehydration cycling are designed to investigate the impact of water production, transport, and removal in the catalyst layers of PEMFCs on the catalyst agglomerate growth. In the water intrusion-evaporation experiment, the catalyst layers are immersed in deionized (DI) water. External forces are applied to make water fill up all the pores, and then the water is removed by drying in vacuum conditions. Scanning electron microscopy (SEM) images are taken before and after the tests at various magnification levels for comparing the microstructures including agglomerate sizes, cracks, and pores. The second experiment involves water flow-through-dehydration cycling. The water is forced to pass through the porous samples with the help of a vacuum pump and then heated until totally dried on a hot vacuum plate. Similarly, the SEM images are taken before and after tests for comparing the microstructures including agglomerate sizes, cracks, and pores. Finally, the impact of in-situ accelerated stress test for consecutive 30 h cycling on cell performance, active surface area, and cell resistance are investigated.

Experimental

Catalyst layers preparation.—The catalyst layers used in the experiments are fabricated and deposited on a commercial porous gas diffusion layer (GDL, AvCarb GDS3250). The GDL is composed of a Teflon treated carbon fiber paper and a micro-porous layer (MPL) on one side (Thickness: 221.6 μm ; Porosity: 74.7%);¹⁰ the catalyst layer is fabricated by spraying the catalyst ink mixture on the top of MPL. The catalyst ink consists of three major ingredients: ionomer, catalyst, and solvent. Ionomer from Nafion solution (5 wt% Nafion PFSA) not only provides pathways for proton transport from reaction sites to the membrane but also bind the catalyst particles. The catalysts used are commercial TEC10V30E with the Pt weight ratio of 29.0% (nominally referred to as 30% Pt/C), and Pt is supported by carbon particles. The solvent is 2-propanol with a purity of 99.9%. The proper amount of Pt/C catalyst, Nafion solution, and 2-propanol are mixed. The mass fraction of Nafion in the solid components is maintained at

25%. The ink is then subjected to ultrasonic treatments for 60 minutes until all ingredients are uniformly distributed in the solution. After the inks are sprayed on the GDLs with Pt loading of 0.4 $\text{mg}\cdot\text{cm}^{-2}$, the catalyst layers are dried at 60°C. Nafion 211, as an electrolyte is then sandwiched between catalyzed GDLs. The active area of the membrane electrode assembly (MEA) is 45 cm^2 . The prepared MEA is hot pressed under 1,000 psi and 130°C, for 3 min.

Water intrusion-evaporation cycle.—A test station is designed, as shown in Fig. 1, to simulate water intrusion and evaporation processes in the catalyst layers, especially for the condition that the excess water is not removed effectively. In this experiment, water is first forced to wet pore regions and subsequently evaporated until totally dried. The factors of electrochemical reaction, frequent temperature variation, potential and stress cycling, and flowing water through the porous layers are excluded from the test. By investigating the microstructure changes before and after tests, the evidence of microstructure changes and their forms are identified.

In the water intrusion-evaporation test, DI water is first forced to penetrate into the porous catalyst layer structure and then evaporated. During the water intrusion stage, the catalyst layer is immersed in a bottle partially filled with DI water as shown in Fig. 1a. Due to the surface hydrophobicity, water cannot naturally intrude into all the pores, especially the small pores. Thus, a vacuum pump is employed to create a vacuum environment (-100 kPa) in the bottle so that all the pores are wetted by water as the gas in the pores is evacuated from the samples as bubbles. The catalyst layer samples are soaked in water for 60 minutes until no bubbles come out from the samples and all the pores are occupied by DI water. Subsequently, the wet samples are placed in a drying bottle, in which the samples are heated to 75°C. A vacuum environment is created by a pump to accelerate the drying process. The samples are dried for 60 minutes in order to remove all the water in the pores. The wet-dry cycle is repeated for 15 times in a row lasting for 30 h. Then SEM images of the catalyst layer surface before and after tests are taken and compared at different length scales.

Water flow-through-dehydration cycle.—A water-flooding test is designed, as shown in Fig. 2, to simulate water flow-through and dehydration processes in catalyst layers. The electrochemical reactions are excluded in the test. DI water is forced to pass through the catalyst layer from the top to the bottom. By identifying the microstructure changes after the tests, the evidence of the water flow-through on the PEMFC degradation is explored.

The testing process is divided into two major steps: water flooding and dehydration. The porous catalyst layer sits on a hot vacuum plate, which allows water or gas to pass. The hot plate is heated to 75°C (the typical operating temperature of cell operation), and a vacuum pump creates a negative pressure environment (-50 kPa) from the bottom of the hot plate. During the test, a thin film of DI water is placed on top of the catalyst layers. Due to the pressure difference created by the vacuum pump from the bottom, water flows through the catalyst layers continuously. The samples are then heated on the hot plate at 75°C until they are totally dried. The process lasts for 30 minutes. Finally, the water flow-through and dehydration process is repeated for 60 times, the total time being 30 h. The microstructure changes including particle distribution on the surface of the catalyst layers are observed and recorded by SEM.

Performance of membrane electrode assembly (MEA).—Performance tests are conducted at the temperature of 75°C, pressure of 75 kPag, and fully humidified hydrogen and air streams with the flow rates of 4.45 and 9 slpm, respectively. The electrochemically active surface area (ECSA) of the MEA is analyzed by in-situ cyclic voltammograms, with nitrogen and hydrogen supplied at the cathode and anode. The voltammogram is recorded at a scan rate of 0.05 $\text{V}\cdot\text{s}^{-1}$ at 80°C. Electrochemical impedance spectroscopy (EIS) measurements are performed under the same operating conditions as polarization curve. The EIS analyses are conducted at 0.70 V, at a frequency

(a) Catalyst layer wetting in water

(b) Catalyst layer drying in a vacuum bottle

Figure 1. Schematic of water intrusion and evaporation test for catalyst layers.

of 100 mHz to 100 kHz. The degradation of the catalyst layer is investigated through the accelerated stress test (AST) using a potentiostat, carried out by potential cycling between 0.6 and 0.96 V with a $50 \text{ mV} \cdot \text{s}^{-1}$ ramp rate for 30,000 cycles. After 30 h cycling, the tests are paused to evaluate the degradation by plotting polarization curves, cycling voltammogram, and impedance under the operating conditions discussed earlier.

Results and Discussion

Catalyst layer samples with the same composition are separately tested under water intrusion-evaporation cycles and water flow-through and dehydration cycles, respectively. The water treatments for both experiments are 30 h, and their effects on the microstructure changes are investigated through SEM imaging before and after tests.

Effect of water intrusion-evaporation cycles.—Fig. 3 shows the scanning electron micrographs of the catalyst layers before and after the wet-dry cycling tests. As can be seen, some new cracks can be found after 15 cycles of water intrusion and evaporation processes. These large cracks can be as long as $\sim 100 \mu\text{m}$ (see Points a3 and b3 in Figs. 3a and 3b, respectively). The water intrusion and evaporation can also cause some ‘islands’ at the edge of some existed cracks (see Points a1 and b1). Another interesting finding is that some cracks are filled with smaller particles (see Points a2 and b2). These particles may have come from the walls of the cracks or neighboring pores. It should be noted that the SEM images after water

intrusion-evaporation cycling appear brighter, which is likely due to changes in the samples themselves – the reduction in the electric conductivity of the samples involved, arising from the ionomer swelling/shrinking cycling associated with the water cycling.

During the water intrusion process, ionomer adsorbs water molecules when the pores are filled with water. The wetting or hydration process causes the ionomer to swell. During the water evaporation process, a portion of liquid water becomes vapor and the remaining liquid water redistributes in the pores. Further, ionomer loses water and becomes dehydrated. The drying or dehydration process causes the ionomer to shrink. The hydration and dehydration of the ionomer due to water intrusion and evaporation in the pores of the catalyst layers lead to the expansion and shrinkage of the ionomer, which is serving as the binding agent for the catalyst particles; thus initiating the formation, propagation, and growth of cracks, and making some catalyst particles unstable. Further, the loose particles may be combined with and merge into other particles through OR and PMC, forming larger agglomerates and reducing the chemical reaction areas and catalytic activity.

Fig. 4 presents the surface of the same catalyst layer under the same wet-dry cycles at 2,000x magnification levels. After water intrusion and evaporation cycling, the catalyst layer surface becomes rough. Some deeper holes can be found throughout the catalyst layer together with some micro-cracks. The water intrusion and removal cycling, with the repeated swell and shrinkage of the ionomer, might loose and lose some particles that are not well-bonded. The relocation of loose particles results in deep pinholes and micro-scale cracks. When Pt/C particles are removed, the pores become larger and even propagate

(a) Water flow-through a catalyst layer

(b) Water dehydration on hot vacuum plates

Figure 2. Schematic of water flow-through and dehydration test for catalyst layers.

(a) Before tests

(b) After tests

Figure 3. Scanning electron micrographs, at 100x magnification, of the catalyst layer (30% Pt/C, 0.4 mg.cm⁻² Pt loading, and 25 wt% Nafion) before and after 15 wet-dry cycles involving repeated water intrusion and evaporation processes.

into deep holes. The remaining ionomer trends to agglomerate, which will dramatically reduce electrochemically active surfaces.

When the surface is enlarged to 10,000x magnification, as shown in Fig. 5, micro-cracks can be clearly identified (~2 μm wide and ~10 μm long). More and larger particle agglomerations can be found in the image. Some of the large agglomerations have a diameter of 2–3 μm and some of them seem isolated, which might lead to a poor electric and ionic connectivity. These structural changes might also make the isolated particles electrochemically inactive, and the agglomerate size changes are irreversible which gradually reduces the long-term PEMFC performance. It is also a clear presentation of some large pores formed at the water intrusion and evaporation cycling.

Coarse agglomerates and deep pinholes can be clearly observed when the images are enlarged further at 20,000x magnification level

(See Fig. 6). Before the tests, the agglomerate size is about 0.1 μm, while after the tests, more agglomerates with a diameter larger than 0.5 μm can be observed. The increase in agglomerate size will definitely reduce the chemical reaction surface areas. In addition, the deep pinholes can be clearly identified due to water intrusion and evaporation. These holes are likely the result that a large portion of particles is taken away from the original samples by water during the wet-dry cycling tests, which leads to a great loss in electrochemically active areas. These washed-away particles either merge into other agglomerates causing agglomerate growth or trapped in cracks as observed in Fig. 3. Due to particle wash-away and agglomerate growth, the pores become significantly larger as well.

From the above observations, it is evident that water intrusion and evaporation cause agglomerate size to increase after the

(a) Before tests

(b) After tests

Figure 4. Scanning electron micrographs, at 2,000x magnification, of the catalyst layer before and after 15 wet-dry cycles involving repeated water intrusion and evaporation processes.

(a) Before tests

(b) After tests

Figure 5. Scanning electron micrograph, at 10,000x magnification, of the catalyst layer before and after 15 wet-dry cycles involving repeated water intrusion and evaporation processes.

wet-dry cycles. Such water intrusion and evaporation processes occur in PEMFCs as a part of the PEMFC operation, such as frequent start and stop operation.

Effect of water flow-through-dehydration cycles.—In this test, the effect of water flow-through on the microstructure changes of catalyst layers, e.g., agglomerate growth and the formation of pinholes and cracks, are investigated. The water is forced to flow through the catalyst layers via a vacuum pump from the bottom of the catalyst layers.

Fig. 7 compares the scanning electron micrographs of the catalyst layers before and after water flow-through and dehydration tests at the same location. As can be seen, the water flow-through and dehydration does not change the cracks significantly. Some of the existed cracks propagate and are enlarged after the water flooding tests. Some of the particles that are not well-bonded by the ionomer near or in the cracks are washed away. This will cause a loss of catalysts and a reduction of connection between particles, leading to a loss of the electrochemical areas and an increase in electronic and ionic resistance.

Higher magnifications of SEM images indicate the agglomerate size is hardly affected by the water flow-through tests (See Fig. 8).

In comparison with the water intrusion-evaporation cycling, the water in flow-through and dehydration cycling tests tend to flow through large pores and cracks due to flow through pores with least resistance. Therefore, the water rarely penetrates into the microporous regions because water cannot easily flow through the small pores as compared with the large pores. Due to the relative lack of ionomer hydration and dehydration within the agglomerates, the well-bonded agglomerates are not subject to frequent ionomer swell and shrink. In other words, the majority of the forced flowing water passes through the large pores or cracks, and the microporous regions are marginally affected. This explained why the flowing water does not impact the agglomerate growth in comparison with the water intrusion-evaporation cycling tests. However, those unstable particles may be taken away by the flowing water, and cracks will continue to propagate due to the water flow, resulting in the formation of even larger pores in comparison.

Fig. 9 presents schematically the impact of water behaviors involving water intrusion-evaporation cycling and flow-through-dehydration cycling on the agglomerate growth after 30 h of water treatments. During the water intrusion-evaporation cycling, the catalyst agglomerate growth can be clearly observed after tests. However, little observable agglomerate growth can be found after the water flow-through and

(a) Before tests

(b) After tests

Figure 6. Scanning electron micrographs, at 20,000x magnification, of the catalyst layer before and after 15 wet-dry cycles involving repeated water intrusion and evaporation processes.

Figure 7. Scanning electron micrographs, at 100 x magnification, of the catalyst layer before and after 60 wet-dry cycles involving repeated water flow-through and dehydration processes.

dehydration tests. These findings indicate that if excess water can be efficiently removed, it will not only improve dynamic performance but also slow down performance degradation. In other words, if the accumulated water in the catalyst layers is not timely repelled during operation, water may have to flow through micropores, leading to a significant increase in agglomerate size and a decrease in PEMFC lifetime.

In order to investigate the degradation of the catalyst layers, accelerated stress test (AST) is applied during PEMFC operation to determine the losses in the electrochemically active surface area (ECSA) and performance. Ideally, it would be nice to use the same catalyst layer samples for both ECSA analysis and the two ex-situ wetting/drying cycles presented earlier, and then conduct the ECSA analysis again for the changes in the ECSA before and after the wetting/drying cycles. However, after the ECSA analysis for the entire MEA, it is difficult, if possible at all, to separate the catalyst layers without any possible damages (microscopically and macroscopically) for the two ex-situ wetting/drying cycle tests. Therefore, in the present study several catalyst layer samples were made nominally identical, and some samples were made into the entire MEA for the ECSA analysis given below, while some other samples were used for the two wetting/drying cycle tests given earlier.

The active area and performance losses are tracked after the 30 h AST cycling. In-situ cyclic voltammetry is applied based on the US DOE protocol, at a cell temperature of 80°C and relative humidity of 100%. Fig. 10 shows the cyclic voltammograms for the hydrogen adsorption/desorption. The ECSA is calculated as follows:

$$ECSA = \frac{Q_{ads}}{Q_{ref} \cdot m_{Pt}}$$

where Q_{ads} and Q_{ref} are the charge of hydrogen adsorption and the adequate charge for the monolayer adsorption on Pt surface, respectively. Pt loading is presented by m_{Pt} . Both voltammograms have common shapes for hydrogen adsorption and desorption on the Pt nanoparticles. However, the voltammogram after cycling presents the smaller peak under hydrogen adsorption and desorption areas. The calculated ECSAs are $34 \text{ m}^2 \cdot \text{g}^{-1}$ and $16 \text{ m}^2 \cdot \text{g}^{-1}$ for MEA before and after cycling, respectively. Lower ECSA can be related to the dissolution, and detachment of catalyst particles after 30 h AST cycling. In addition, it can be seen that the CV curves shift to the positive current density at high potential region which can be attributed to the Pt oxide formation in high potential, and hydrogen cross over in the cell.^{45,46}

The ohmic and mass transfer resistances are important factors that significantly affect the cell performance. In-situ electrochemi-

cal impedance spectroscopy (EIS) is applied before and after 30 h cycling to understand the dominant factor in catalyst degradation. Fig. 11 presents the impedance spectra in the form of Nyquist plots under the cell temperature and back pressure of 75°C and 35 kPag, respectively. In the spectra, the ohmic resistance is represented by the point where a high-frequency arc intersects the real axis, while the charge transfer resistance is represented by a low-frequency arc. It can be seen that the ohmic resistance is slightly increased after 30 h cycling. This increase can be attributed to the ionomer degradation and thinning in the catalyst layers^{47,48} and Pt detachment and deposition on membrane²⁶ which increase the ionic resistivity. However, the charge transfer resistance is substantially increased after 30 h, which can be shown by the increase in the diffusion resistance.

Fig. 12 is obtained by generating the polarization and power density curves before and after 30 h cycling. The tests are conducted at the cell temperature and pressure of 75°C and 35 kPag. Fully humidified hydrogen and air streams with the flow rate of 4.45 and 9 slpm are supplied to the anode and cathode side, respectively. It can be seen that the open circuit voltage (OCV) of the MEA is 0.92 V before cycling and then reduced to 0.89 V after cycling. This drop in OCV can be related to the loss of catalyst active surface area, degradation and thinning of ionomer in the catalyst layers, Pt oxidation, detachment and deposition on the membrane, and hydrogen crossover through the membrane.^{26,45–48} In addition, at the fixed voltage of 0.6 V, the current density is dropped by 33% after cycling, and by increasing the voltage this gap is improved. At the high concentration region, at the constant current density of $2.3 \text{ A} \cdot \text{cm}^{-2}$, the voltage is dropped by 54%. In addition, the maximum power densities of MEA before and after cycling are $0.82 \text{ W} \cdot \text{cm}^{-2}$ and $0.61 \text{ W} \cdot \text{cm}^{-2}$, respectively. These results clearly demonstrate the catalyst degradation under 30 h AST cycling.

Conclusions

In this study, ex-situ experimental observations of microstructure changes of catalyst layers in proton exchange membrane fuel cells (PEMFCs) have been made under the wet-dry cycling involving water intrusion-evaporation and water flow-through and dehydration processes. The microstructure changes at different length scales are captured by scanning electron microscopy (SEM). The results indicate that the cycling of water intrusion and evaporation processes leads to the considerable growth of the catalyst agglomerates, together with the formation of pinholes and cracks. These structural changes will result in irreversible loss of the active surface area and catalytic activity,

Figure 8. Scanning electron micrographs of the catalyst layer before and after 60 wet-dry cycles involving repeated water flow-through and dehydration processes, at various magnification levels.

causing long-term performance degradation. The water-flow-through-dehydration cycling does not yield significant observable agglomerate growth. This is likely because water tends to flow through the large pores in the catalyst layers, while the remaining parts of the catalyst layers with relatively small pores are less affected. These observa-

tions help understand PEMFC performance degradation, especially why dynamic load conditions significantly reduce PEMFC lifespan in comparison to static load conditions; and also provide insight into the importance of water management for PEMFC performance and durability.

Figure 9. Schematic of the effect of water behaviors on the catalyst agglomerate growth after 30 h of water wet-dry cycling treatments: water intrusion-evaporation cycling and water flow-through-dehydration cycling.

Figure 10. Cyclic voltammogram of the MEA before and after cycling.

Figure 11. Impedance spectra of the MEA before and after cycling.

Figure 12. Polarization and power density curves of MEA before and after cycling.

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