Polymer electrolyte membranes (PEMs) are a critical cell component for polymer electrolyte membrane fuel cells (PEMFCs). The durability of PEMs is important because the life of PEMFCs is often determined by PEM failure. The chemical stability of PEMs has been discussed since the 1960s, notably by engineers and scientists at GE. LaConti proposed a chemical degradation mechanism for perfluorosulfonic acids (PFSA)s; oxygen molecules permeate through the membrane from the cathode and are reduced at the anode Pt catalyst to form hydrogen peroxide. Although PFSA membranes are stable in the presence of hydrogen peroxide, metal ions such as Fe2+ and Cu2+ in the catalyst layers greatly accelerate the membrane degradation rate by forming reactive oxygen species such as hydroxyl (HO·) and hydroperoxyl (HO2·) radicals.

\[
\begin{align*}
H_2O_2 + M^{2+} & \rightarrow M^{3+} + \cdot OH + OH^- \quad [1] \\
\cdot OH + H_2O_2 & \rightarrow H_2O + OOH^- \quad [2]
\end{align*}
\]

Since the reactive oxygen species are generated in the catalyst layer, the membrane degradation is greater with a supply of H2 and O2 in the catalyst layers. Liu et al. reported about the substantially short lifetime for Nafion membranes when H2 and O2 gases were supplied to the catalyst-coated membrane, while no degradation is detected when H2/O2 is decoupled to H2/N2 or N2/O2. Later, Burlatsky et al. suggested that an extended catalyst layer between the cathode and the membrane could consume reactive oxygen species to produce water, thereby mitigating the membrane degradation. The effect of gas permeability on membrane degradation has also been demonstrated. Sethuraman et al. compared the durability of wholly aromatic membranes, BPSH-35 and Nafion 112, under accelerated stress conditions. Although the BPSH-35 membranes showed poor chemical stability in ex-situ Fenton tests, the membrane electrode assemblies (MEAs) with BPSH-35 outlasted the MEAs with Nafion 112 in the open circuit voltage (OCV) and potential cycling tests under H2/O2 conditions due to the low gas-crossover rates of the BPSH-35 membrane.

Because the chemical degradation of membranes is related to the formation of reactive oxygen species in the catalyst layers and their diffusion through the membrane, electrodes, and gas diffusion layer, interactions between different MEA components become crucial for the assessment of the chemical stability of PEMs. The effects of electrocatalysts on PEM stability have been investigated. The chemical degradation of Nafion membranes were reduced by 50% when Pt/C catalyst was replaced with Pt-Co/C. Sulek et al. have also reported that Nafion lifetime could be extended by 65% when Pt/C catalyst was replaced with Pt-Ni/C. The effect of the gas diffusion electrode (GDE) on membrane stability has also been investigated. Kreimeier et al. reported that a membrane with a GDE exhibited better stability than the bare membrane when exposed to reactive oxygen species. The aforementioned examples suggest that membrane degradation in fuel cells are affected not only by the chemical stability of the membrane itself but also by the interactions with other MEA components. However, the electrode structural effect on PEM durability has been largely unexplored so far.

In this paper, the impact of the cathode structure on membrane stability is investigated. The structural change of cathodes were obtained by using long side chain (LSC) PFSA Nafion (EW = 1,000 g/mol, DuPont) and short side chain (SSC) PFSA Aquivion (EW = 830 g/mol, Solvay Solexis) and three different dispersing solvents (water-isopropanol, NMP, or glycerol) for the catalyst inks. Other MEA components and test conditions were held constant. The structural differences between LSC and SSC PFSA have been studied by Kreuer et al. They reported that SSC PFSA does not have any distinct differences in water and proton transport, yet provides better thermo-mechanical stability, which is anticipated due to the stability of the electrolyte/electrode interface. The effect of different catalyst dispersing solvents for electrode preparation has been also studied by Kim et al. The electrodes prepared from water-isopropanol solvent showed numerous large scale open cracks (>100 μm) while the electrodes prepared from glycerol and N-methyl pyrrolidone (NMP) exhibited distributed microcracks (<10 μm) and a crack-free structure, respectively. Based on this information, a series of MEAs having different cathode structures were fabricated and the durability of Nafion 212 membrane was examined by measuring the H2 crossover rate during a 2-hour OCV accelerated stress test (AST). Other relevant properties such as open circuit voltage (OCV) and polarization behaviors were examined as well. The membrane degradation process and the role of electrode structure on membrane degradation during OCV tests are discussed based on structural analyses by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS).
Experimental

Preparation of ionomer dispersion.— Ionomer dispersions were prepared by the direct dispersion technique that we developed.16,17 First, PFSA membranes were converted to the Na\(^{+}\) form by placing Nafion 212 in boiling 0.5 M NaOH solution for 90 min. Subsequently, the Na\(^{+}\) form membranes were placed in de-ionized water at 80° C for 90 min in order to remove the residual NaOH. The membranes were then dried at 60° C for 30 min followed by dissolving in the desired solvent at an elevated temperature. Three solvent systems were used; water-isopropanol (1:1 volume ratio), NMP, and glycerol. For the water-isopropanol solution, a closed pressure vessel was used to maintain solvent composition at 210° C for 3 hours. For NMP and glycerol, commercial vials with Teflon cap were used. The vials were heated in a convection oven at 110° C (NMP) and 210° C (glycerol) for 3 hours, respectively. Clear liquid solutions were obtained without any residual solid polymer. The solid content of the dispersions was 2.5 wt%.

MEA fabrication.— Carbon supported Pt catalyst (20 wt% Pt/C, BASF) was used for both anode and cathode catalyst layers. For the anode catalyst layer, the Pt/C catalyst powder (0.0625 g) was mixed with commercial 5 wt% Nafion dispersion (1 g). Glycerol (0.5 g) and 1 M tetrabutylammonium hydroxide (TBAOH) in methanol (20 μL) were added into the vial and stirred for more than 12 hours to make the standard ink slurry. TBAOH was added to convert the Nafion from the proton to the TBA\(^{+}\) form, which may enhance the interfacial adhesion between membrane and electrode during hot pressing.18,19 For the cathode catalyst layer, the catalyst to ionomer weight ratio was adjusted for the optimum performance. The catalyst to ionomer ratio for all electrodes, except glycerol-processed electrodes, was 5:2. The catalyst to ionomer ratio for glycerol processed electrodes was 5:1.7. To make the cathode catalyst ink slurry, the Pt/C electro-catalyst powder was mixed with the ionomer dispersion prepared by the direct dispersion technique. The ionomer dispersion consists of ionomer and the dispersing solvent without any other additives. The catalyst slurry was painted onto a 5 cm² decal substrate and dried at 140° C for 1 hour. The painting/drying of catalyst layers continued (usually 4 paintings) until the Pt loading reached 0.2 mg/cm². The decal-painted electrodes were then transferred onto the Na\(^{+}\) electrolyte solution to convert the MEA to the acid form of the MEAs. Ta-hydrogen gas flow at the cathode outlet was measured using a bubble flowmeter at room temperature. The morphology of the electrodes both before and after life tests was examined by scanning electron microscopy (SEM, FEI Inspect) operated at 20 kV of accelerating voltage. Samples were prepared by cutting a section of the catalyst from the MEA, then mounting it on SEM stubs with conductive tape.

Results and Discussion

PEM degradation.— Effect of Cathode Ionomer Type.— The initial PEMFC performance of LSC-W/A and SSC-W/A MEAs was 20 psig under fully hydrated conditions. For the cell break-in, 0.7 V of cell voltage was applied for at least 12 hours. After the break-in procedure, the OCV test was performed at a cell temperature of 90° C using US Fuel Cell Council, Single Cell Test Protocol.20 During the OCV test, H₂ (70 sccm) and air (165 sccm) were flowed into the cathode and anode, respectively, each at 30% RH and 21.8 psig of back pressure. H₂-air fuel cell polarization curves of the MEAs were generated at 80° C under fully humidified conditions with constant flow of H₂ (200 sccm) and air (500 sccm) at 30 psig of back pressure. The high frequency resistance (HFR) of the cell was measured while obtaining the polarization curve. In order to choose the frequency that minimizes the capacitance, a sinusoidal wave perturbation between 2 and 10 kHz was applied to the fuel cell load before obtaining polarization curves. The chosen single frequency, i.e. 3,333 Hz, was used for the HFR measurement. The same conditions were used for generating EIS, obtained under 10 mA of amplitude from 10,000 to 1 Hz of frequency at the cell current of 1, 3, 5, and 7 A. The H₂ crossover current was collected from cyclic voltammograms (CVs) which were measured from 0.06 to 0.5 V (vs Dynamic Hydrogen Electrode, DHE) with a 5 mV/s scan rate. The CVs were run with H₂ (50 sccm) and N₂ (50 sccm) flowing into the anode and cathode at a fuel cell temperature of 70° C under fully hydrated conditions. The N₂ crossover was measured with N₂ flowing into the anode. The N₂ flow at the cathode outlet was measured using a bubble flowmeter at room temperature. The morphology of the electrodes both before and after life tests was examined by scanning electron microscopy (SEM, FEI Inspect) operated at 20 kV of accelerating voltage. Samples were prepared by cutting a section of the catalyst from the MEA, then mounting it on SEM stubs with conductive tape.

Table I. Cathode compositions, dispersion solvents, and sample codes of MEAs.

| Sample code | Ionomer | Dispersing solvent |
|-------------|---------|-------------------|
| LANL Standard | Nafion | Water, isopropanol, 1-propanol, glycerol\(^a\) |
| LSC-W/A | Nafion | Water-isopropanol (1:1 vol. ratio) |
| LSC-NMP | Nafion | NMP |
| LSC-glycerol | Nafion | Glycerol |
| SSC-W/A | Aquion | Water-isopropanol (1:1 vol. ratio) |
| SSC-NMP | Aquion | NMP |
| SSC-glycerol | Aquion | Glycerol |

\(^a\)water: 16 wt%, 1-propanol: 16 wt%, isopropanol: 16 wt%, glycerol: 51 wt%, and a trace of methanol.

Figure 1. (a) Initial i-V curves and high frequency resistance (HFR) of H₂-air fuel cells of LANL Standard, LSC-W/A, and SSC-W/A; (b) Nyquist plots of the fuel cells measured at 0.6 and 1.4 A/cm².

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examined before OCV testing (Figure 1a). LSC-W/A exhibited a comparable performance with the LANL Standard control, suggesting that the cathode prepared from the in-house Nafion dispersion had similar characteristics to the cathode prepared from the commercial Nafion dispersion. It was noted that there was a slightly lower performance for SSC-W/A compared to LSC-W/A in the current range from 0.5 to 1.7 A/cm². The Nyquist plots measured at 0.6 A/cm² indicate that SSC-W/A has a higher ohmic resistance (0.31 Ω⋅cm² for SSC-W/A vs. 0.28 Ω⋅cm² for LSC-W/A) yet lower charge transfer resistance compared to LSC-W/A (Figure 1b Top). The higher ohmic resistance of SSC-W/A is probably due to limited water transport in the SSC-W/A cathode that leads to only partial hydration of the membrane. The lower charge transfer resistance of SSC-W/A is possibly caused by the greater proton conductivity of the SSC binder as we observed that the proton conductivity of the SSC ionomer at 80°C was ~50% greater than that of the LSC ionomer. The Nyquist plots measured at 1.4 A/cm² show that SSC-W/A has a higher mass transport resistance at low frequency (Figure 1b Bottom). This suggests that O₂ transport in the SSC-bonded cathode is lower than that in the LSC-bonded cathode. Springer et al. reported that the low frequency impedance originates from the oxygen access limitation caused by the gas diffusion backing of the fuel cells. However, in our case; the lower gas transport originates from the oxygen access limitation caused by the gas diffusion layer (GDL) since the same GDLs for both MEAs were used.

Figure 2 shows the OCV test results for LSC-W/A and SSC-W/A. The OCV values gradually decreased over time, suggesting that the PEMs for both MEAs had degraded. SSC-W/A shows slightly less OCV decay than LSC-W/A, ca. the OCV decay rate: −1.8 mV/h for SSC-W/A vs. −2.6 mV/h for LSC-W/A. The reduction of the H₂ crossover current density of SSC-W/A is also less than that of LSC-W/A after 200 hours of OCV testing (Figure 2b). The changes of the H₂ crossover current density, however, show non-linear behavior: more H₂ crossover change during the last 100 hours compared to the first 100 hours. Furthermore, the increase of H₂ crossover seems to be related to i-V curve measurements taken during OCV testing. During the interval of the OCV test, we normally ran ten i-V curves in the potential range of 1.0 to 0.2 V with a step voltage of 0.05 V per 30 seconds. Without i-V curve measurements, the H₂ crossover rate increase is notably less. This suggests that cathode structural change during i-V curve measurements may accelerate the H₂ crossover. Since those MEAs showed a stable performance with multiple i-V curve measurements without OCV tests, the H₂ crossover change associated with i-V curve measurements seems to only assist the PEM failure which had been initiated by the OCV test. With ten i-V curve measurements after the first 100 hours of OCV testing, the H₂ crossover current densities of LSC-W/A and SSC-W/A after 200 hours of OCV testing reached 160 and 109 mA/cm²geo, respectively. Figure 2c and 2d show the polarization curves of LSC-W/A and SSC-W/A over the course of OCV testing. The change of polarization curves are characterized in two metrics; one is the OCV value and the other is current density at low cell voltage, ca. at 0.4 V. The OCV of LSC-W/A decreases from 0.96 V (initial) to 0.88 V (100 hours) to 0.54 V (200 hours). The OCV of SSC-W/A decreases from 0.95 V (initial) to 0.90 V (100 hours) to 0.84 V (200 hours). The non-linear behavior of OCV measured from the i-V curves is qualitatively in good agreement with the H₂ crossover current density results. In other words, the OCV values from the polarization curves after 200 h OCV tests are higher than those recorded at the end of the 200 hours OCV test, indicating that the OCV value recorded at the end of the test may be affected by other factors such as catalyst oxidation and thus cannot be used as a metric for PEM degradation. The cell current density at low cell voltage also decreases after 200 hours of OCV testing. At 0.4 V, the cell current density of LSC-W/A decreases from 1.87 A/cm² (initial) to
processed cathodes exhibit less OCV decay than the MEAs with water-isopropanol-processed cathodes (Figures 4a and 4b). The H2 crossover current density of the MEAs with NMP-processed cathodes show a non-linear behavior similar to the MEAs with water-isopropanol-processed cathodes. The H2 crossover current density for all MEAs maintained a relatively low level ca. < 5 mA/cm2 for the first 40 hours of the OCV tests then substantially increased as the experimental time increased. At the end of the OCV tests, the H2 crossover current densities showed a clear trend, depending on the ionomer type and cathode processing solvent: LSC-W/A (160 mA/cm2 (geo)) > SSC-W/A (109 mA/cm2 (geo)) > LSC-NMP (67 mA/cm2 (geo)) > SSC-NMP (36 mA/cm2 (geo)) > LSC-glycerol (2.3 mA/cm2 (geo)) > SSC-glycerol (0.8 mA/cm2 (geo)). The H2 crossover values of LSC-W/A and SSC-glycerol were differences by a factor of 100 after 200 hours of OCV testing. Considering that the same Nafion 212 membranes were used for all of the MEAs, the data indicates that the effect of the cathode structure on PEM degradation is substantial.

Figure 5 shows the H2/air polarization curves, HFR, and OCV values of the NMP- and glycerol-processed MEAs. The cell HFR did not significantly change after 200 hours of OCV testing. This suggests that the interfacial adhesion between Nafion 212 and the cathodes prepared from different solvents is good without adding TBAOH solution in the catalyst inks.22,23 The OCV of the MEAs with NMP-processed cathodes decreases during OCV testing. In contrast, the OCV values of the MEAs with glycerol-processed cathodes are stable even after 200 hours of OCV testing. The OCV values from the polarization curves after 200 hours of OCV testing show a consistent trend with H2 crossover behavior: LSC-W/A (0.54 V) < SSC-W/A (0.83 V) < LSC-NMP (0.86 V) < SSC-NMP (0.89 V) < LSC-glycerol (0.93 V) < SSC-glycerol (0.95 V). These results indicate that the MEAs with glycerol-processed cathodes have superior PEM durability compared to the MEAs with NMP-processed cathodes. The MEAs with water-isopropanol-processed cathodes showed the least PEM durability. The current density at low cell voltage obtained from i-V curves again does not show the same behavior as OCV or H2 crossover current density. For example, the current density of LSC-NMP, LSC-glycerol and SSC-glycerol at low cell voltage increased after 100 hours of OCV testing then decreased after an additional 100 hours of OCV testing, while the OCV and H2 crossover current exhibited monotonic changes. This confirms that there are other major contributing factors playing a major role in fuel cell performance durability. In a previous study, it was identified that this type of cathode performance change, i.e. improved performance before dropping off, originated from a cathode structural change.25 Note that the improving fuel cell performance has little to do with the ohmic contribution due to possible membrane thinning as shown in the iR-corrected cell potentials are shown in Figure 5. In general, glycerol-processed cathodes show more positive structural change than NMP-processed cathodes. Water-isopropanol-processed cathodes did not show a positive cathode structural change. Adding these structural effects, MEAs with glycerol-processed cathodes showed no deteriorated cell performance after 200 hours of OCV testing.

**PEM degradation mechanism.—** PEM Thinning vs Pinhole Formation.— It has been reported that membrane thinning due to the PEM degradation directly causes increased H2 crossover24–26; this indicates that the degradation process occurs uniformly throughout the active area of the MEAs. In order to see whether the PEM degradation process occurs uniformly, we examined a cross-section of the MEAs before and after OCV testing by SEM and measured the membrane thickness change. There are no noticeable thickness variations between center and edge parts of the MEAs. Figure 6 shows that the thickness of membranes before OCV testing is 44 ± 1 μm. After 200 hours of OCV testing, the membrane thickness for all MEAs ranges from 35 to 41 μm with similar thickness variations. Since the thickness of all MEAs decreased after the AST, it may be considered that the membrane thinning causes the OCV change and H2 crossover. However, this is not consistent with the degradation results; note that the MEAs with water-isopropanol-processed

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**Figure 3.** Initial i-V curves comparison of (a) LSC- and (b) SSC-MEAs.

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**Effect of cathode dispersing solvent.—** In this section, the effect of the cathode dispersing solvent on membrane durability is investigated. The initial performance of MEAs with water-isopropanol-, NMP- and glycerol-processed cathodes were compared (Figure 3). The MEAs with NMP-processed cathodes display similar initial performances to those prepared from water-isopropanol. However, the MEAs with glycerol-processed cathodes show substantially inferior performance, particularly at low cell voltage. Based on our previous microscopic analysis, the increased performance obtained by the MEAs with a water-isopropanol- or NMP-processed cathode is attributed to the easy access of gaseous oxygen to the catalyst sites through the relatively coarse electrode structure.15 For glycerol-processed cathodes, a slightly lower ionomer composition in the catalyst layer improves the initial performance, although the performance at low cell potential does not reach the levels of other MEAs. Since the glycerol-processed cathodes showed better performance with a Pt to ionomer ratio of 5:1.7, those MEAs were tested for the PEM degradation study.

Figure 4 shows the OCV test results of the MEAs prepared from three dispersing solvents. The MEAs with NMP- and glycerol-
Figure 4. OCV changes for (a) LSC- and (b) SSC-MEAs. Changes in H₂ crossover current density of (c) LSC- and (d) SSC-MEAs.

Figure 5. Fuel cell polarization plots after OCV testing, (a) LSC-NMP, (b) LSC-glycerol, (c) SSC-NMP, and (d) SSC-glycerol electrodes (numbers in parentheses are the OCV values).
cathodes exhibit less thickness reduction in spite of the greater PEM degradation. Furthermore, MEAs with glycerol-processed cathodes show more thickness reduction. The obvious contradiction between the thickness change and the degradation results suggests that thickness reduction may be irrelevant to PEM degradation during OCV testing and the reduced PEM thickness may be caused by cell compression or Nafion creep during OCV testing. The lack of the correlation between membrane thinning and degradation is also supported by the cell HFR after 200 hours of OCV testing (Figure 2 and Figure 5); HFR values of all tested MEAs are similar in spite of the significant differences in H2 crossover current.

If PEM degradation occurs non-uniformly, membrane failures may occur at catalyst layer edges because the catalyst edges used in many commercial fuel cells are not strong enough to resist either the sharp edges of the GDL or the stresses present in the region that is unsupported between the GDL and the gasket. In order to determine whether pinholes were generated near the catalyst edge or the active area, the N2 gas crossover was measured in two MEA configurations (adding an additional Teflon layer to either the center or the edge of the MEAs after the OCV AST). Both MEA configurations had the identical surface area, 2.5 cm2. Figures 7a and 7b show the total N2 crossover in MEAs after 200 hours of OCV testing without the Teflon layer as a function of the inlet N2 flow rate. LSC-W/A shows the highest N2 crossover rate while SSC-glycerol shows the lowest N2 crossover rate, which is consistent with the H2 crossover current results. Figure 7c compares the N2 crossover flow in LSC-W/A using the two MEA configurations. The N2 crossover rates through the catalyst layer edging and the center part of the active area are 65% and 35%, respectively. This data indicates that gas crossover occurs not only through the catalyst edge but also through the center of the catalyst active area, even though the MEA edge is considered to be weaker compared to the center part of the MEA active area. The MEA edge failures reported in literature are therefore likely due to the poorer mechanical properties of thinner PEMs, ca. 10 to 24 μm. The thicker version of PEM (Nafion 212, 50 μm thick) that was used for the OCV testing may prevent premature catalyst edge failure to a certain degree.

Electrode morphology.— If PEM degradation does not occur throughout the active surface yet in focused local areas, local hot spot and/or pinhole formation generated from the non-uniformity of cathode structures would be the major cause of OCV reduction. Figure 8 shows the SEM images of cathodes prepared from LSC-W/A and SSC-W/A. With higher magnification, Figures 8b and 8d, the morphological features for both cathodes seem to be similar. However, with lower magnification, Figures 8a and 8c, a difference is noted: the LSC-W/A cathode has larger macro-scale cracks (40 to >100 μm) compared to the SSC-W/A cathode (∼10 μm). In literature, electrode crack formation has been discussed in various aspects. Most reports suggest that electrode crack formations have a detrimental impact on fuel cell performance due to destroying the three-phase interface, a buckling deformation, pin-hole formation in the membrane, and/or inhibiting multi-phase transport. A few papers, on the other hand, report that crack formation can also benefit the cell performance by facilitating the access of gaseous reactants to the reaction site.

Further structural analysis was performed on cathodes prepared from different dispersing solvents. Figure 9 shows the effect of dispersing solvents on the morphology of SSC-bonded cathodes. While the water-isopropanol-processed cathode (Figure 9a) has macro-scale cracks (∼10 μm), NMP- and glycerol-processed cathodes (Pt/C to ionomer ratio: 5:1.7) processed cathodes (Figures 9b and 9c) show crack-free and uniform electrode structures (though the cathode from glycerol has slightly better uniformity since the cathode prepared from NMP has more dark areas). The cathode prepared from glycerol (Pt/C to ionomer ratio: 5:2) (Figure 9d) also shows crack-free and uniform electrode structure, yet it has a notably less porous structure. The lower porosity of SSC-glycerol (Pt to ionomer ratio = 5:2) is thought to be responsible for the poor initial polarization behavior as shown in Figure 3b. Since both NMP- and glycerol-processed cathodes have more thickness variation are denoted.
Figure 7. N₂ crossover flow after 200 hours of OCV testing of MEAs using (a) LSC ionomer, (b) SSC ionomer, and as a function of (c) MEA location.

crack-free structures, pinhole formation via macro-crack formation does not necessarily explain the PEM stability difference between the SSC-NMP and SSC-glycerol.

Impedance analysis.—EIS analysis was performed for the further investigation of electrode effect on PEM degradation. Figure 10 shows the Bode plots of the MEAs before OCV testing in the frequency range of 1–10,000 Hz at 1.0 A/cm². It is noted that the resistance of MEAs with glycerol-processed cathodes are higher at the low frequency range ca. 1 to 100 Hz. This explains the limited O₂ transport of the glycerol-processed cathodes. The glycerol-processed cathodes with a Pt to ionomer ratio of 5:2 show greater O₂ transport resistance as expected. Noteworthy is that the O₂ transport resistances of LSC-W/A and SSC-W/A are comparable in spite of the much larger macro-crack formation of LSC-W/A, which explains the comparable polarization shown in Figure 1a. When water-isopropanol-processed cathodes are compared with NMP-processed cathodes, the irrelevancy of micro-crack on O₂ transport becomes clearer, i.e. the similar gas transport resistance of NMP-processed cathodes without macro-crack formation. This suggests that the PEM durability does not necessarily correlate well with cathode O₂ permeability. We believe that the relatively good O₂ transport through NMP-processed cathodes is via a uniformly distributed open pore structure, possibly with much smaller length-scale.

EIS analysis during OCV testing gives further information on the structural robustness of electrodes. Figure 11 shows the Nyquist plots of the MEAs before and after OCV testing at 1.0 A/cm² in the frequency range of 1 to 10,000 Hz. For the MEAs with water-isopropanol- and NMP-processed cathodes, the impedance at the
low frequency range notably increased as the OCV testing proceeded. However, for the MEAs with glycerol-processed cathodes, the impedance at the low frequency range did not change much over time. The low frequency impedance of SSC-glycerol even slightly decreased after 200 hours of OCV testing, indicating that O$_2$ transport through the glycerol-processed cathodes did not change thereby maintaining their initial three-phase interface. Meanwhile, O$_2$ transport in water-isopropanol- or NMP processed-cathodes gradually changed during OCV testing. Maintaining the initial three-phase interface during OCV testing may be important for uniform cell current generations which in turn minimize PEM degradation. The three-phase interface plays a role in the cell degradation observed while obtaining i-V polarization curves. When i-V polarization curves were taken, the increased cell current and the resultant water generation at the cathode caused changes in the three-phase interface, resulting in increased H$_2$ crossover through the PEM. One may argue that since the current density of MEAs with glycerol-processed cathodes during i-V curve measurements was less than that of other MEAs, the overall PEM degradation of glycerol-processed cathodes was less. However, this is not the case because the H$_2$ crossover current density of SSC-NMP without i-V curve measurements was found to be still higher than that of SSC-glycerol with i-V curve measurements i.e. 28 mA/cm$^2$ vs. 0.8 mA/cm$^2$. The EIS analysis cannot explain the superior PEM durability of NMP-processed cathodes compared to water-isopropanol cathodes because both showed comparable change. However this can be explained by the fact that water-isopropanol-processed cathodes have non-uniform structures from the beginning. As we discussed, the existence of macro-cracks do not necessarily impact O$_2$ transport (and the low frequency impedance), yet less uniform cell currents are likely generated. The superior PEM durability shown in SSC-bonded cathodes over LSC-bonded cathode can be explained also by the electrode robustness aspect. As previously indicated, SSC ionomers are less likely to undergo structural change due to two major reasons. First, there are more physical crosslinking between sulfonic acid groups in SSC ionomers due to the higher sulfonic acid concentration, which restrains the chain mobility and increases the softening temperature. Second, there are more polymer chain entanglements, i.e. a lower degree of phase separation, in SSC ionomers during solvent casting due to the shorter side chain length, thus improving the morphological stability. However, further studies on electrode structural differences induced from SSC and LSC ionomers are needed.

In summary, our electrode characterization supports that PEM degradation is accelerated by non-uniform cathode structures and structural instability during OCV testing. Our results are consistent with the direct observation of local hot spots by Zhang et al. They showed that aged MEAs after OCV testing have hot spots during oxygen and hydrogen reactions, although the majority of the membranes are still in normal condition. The relationship between electrode uniformity and PEM degradation also explains the abrupt deterioration of the MEA performance after the i-V measurements where the
increased cell current and the resultant water generation at the cathode caused changes in the three-phase interface.

Conclusions

This study shows that not only the chemical stability of Nafion itself but also cathode structures strongly impact the PEM stability. Using different ionomeric binders and cathode processing solvents shows that the H2 crossover rate in Nafion 212 can be 200-fold different after 200 hours of OCV testing. Microscopic and impedance analysis indicate that cathode structural uniformity is the major contributing factor for PEM durability. The change of the cathode three-phase interface and non-uniform current generation during OCV testing causes PEM degradation at local focused areas. The O2 permeation rate of the cathode plays a less critical role in PEM degradation. SSC ionomeric binder and glycerol solvent limit O2 transport to a certain degree resistance to structural changes during OCV testing. However SSC binder and glycerol solvent limit O2 transport to a certain degree which adversely impacts the fuel cell performance. This study emphasizes the role of cathode structure on PEM durability. Electrode structure should be considered a crucial parameter for PEM durability in addition to the chemical stability of PEMs.

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