Concentration Effects of Polymer Electrolyte Membrane Degradation Products on Oxygen Reduction Activity for Three Platinum Catalysts

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A rotating disk electrode (RDE) along with cyclic voltammetry (CV) and linear sweep voltammetry (LSV), were used to investigate the impact of two model compounds representing degradation products of Nafion and 3M perfluorinated sulfonic acid membranes on the electrochemical surface area (ECA) and oxygen reduction reaction (ORR) activity of polycrystalline Pt, nano-structured thin film (NSTF) Pt (3M), and Pt/Vulcan carbon (Pt/Vu) (TKK) electrodes. ORR kinetic currents (measured at 0.9 V and transport corrected) were found to decrease linearly with the log of concentration for both model compounds on all Pt surfaces studied. Model compound adsorption effects on ECA were more abstruse due to competitive organic anion adsorption on Pt surfaces superimposing with the hydrogen underpotential deposition (HUPD) region.

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System contamination in polymer electrolyte membrane (PEM) hydrogen fuel cells has been a growing area of interest in recent years due in large part to the potential detrimental effects inflicted on fuel cell performance and durability.¹ While system contamination typically originates from sources outside of the membrane-electrode assembly (MEA), e.g. fuel^{2,3} and air stream impurities⁴⁻⁶ as well as the degradation/chemical leaching of balance of plant components (i.e. structural materials and assembly aids),⁷⁻¹² there also exists the possibility that the MEA itself could lead to the formation of chemical impurities. Results from both in-situ and ex-situ studies have shown that as PEMs undergo chemical degradation, small molecules are released from the polymer network and can eventually be transported throughout the cell.^{13,14}

Previous studies showed that several chemical decomposition products were generated when perfluorinated sulfonic acid (PFSA) membranes were exposed to peroxides and hydroxyl radicals.^{13,15} In addition to the release of HF from either membrane type, two compounds in particular, both in the form of a diacid, perfluoro(2-methyl-3-oxa-5-sulfonic pentanoic) acid (DA-Naf) and perfluoro(4-sulfonic butanoic) acid (DA-3M) (shown in Figure 1), have been identified as the main degradation compounds of Nafion (Nafion is a registered trademark of DuPont) and 3M commercial PFSA membranes respectively.^{14,16}

In addition to losses in membrane conductivity and structural integrity due to PEM chemical degradation, the aforementioned degra-

dation products may also adsorb on the fuel cell electrocatalyst layer, leading to a loss in ORR activity and/or Pt ECA. To date, little effort has been put forth in determining the impact that PFSA chemical degradation compounds have on catalyst performance.

The work herein shows the effect of DA-Naf and DA-3M, in the form of model organic compounds on ECA and ORR activity via ex-situ CV and LSV experiments. In order to gain a broad understanding of Pt electrocatalysts, polycrystalline Pt, NSTF, and Pt/Vu catalysts were studied in a range of model compound concentrations (from 0.001 mM – 1 mM) that could realistically be found during fuel cell operation.¹⁷

Experimental

DA-Naf and DA-3M were obtained in their lithium salt forms from collaborators at 3M with a reported purity of >95% and the major trace component being LiF. No adsorption effects of LiF at any concentration relevant to this study were observed in an investigation using a polycrystalline Pt electrode (data not shown). Consequently, it was determined that the LiF impurity would pose minimal interference with model compound adsorption. All compounds were therefore used as received. Electrochemical experiments utilized 0.1 M perchloric acid electrolyte (diluted from 70% HClO₄ double distilled veritas grade, GFS Chemical) along with polycrystalline Pt and glassy carbon rotating disk electrodes (Pine Instruments).

Polycrystalline Pt electrode surfaces were prepared by polishing with 0.05 μM alumina slurry followed by rinsing and sonication in 18.2 MΩ water. NSTF (provided by 3M) electrodes were prepared by applying 10 μL of a catalyst ink (4.5 mL water, 0.5 mL IPA, bath sonicated in ice for 20 min, then horn sonicated in ice for 1 min, and dried at 40°C) to a glassy carbon surface at a Pt loading of 40 μg/cm². Pt/Vulcan carbon (Tec10V50E, Tanaka Kikinokogyo (TKK)) surfaces were prepared by applying 10 μL of a catalyst ink (7.6 mL water, 2.4 mL IPA, 40 μL Nafion ionomer, bath sonicated in ice for 20 min and dried at 40°C) to a glassy carbon surface at a Pt loading of 17 μg/cm². All RDEs used had a geometric surface area of 0.196 cm² and all CV and ORR current were normalized to this area.

Electrochemical measurements were taken using an Autolab PG-STAT302N. A reversible hydrogen electrode (RHE) and a platinum mesh were used as the reference and counter electrode respectively. Experiments were performed at room temperature in a custom glass electrochemical cell purged with either 99.9999% pure nitrogen or 99.998% pure oxygen (Matheson Tri Gas). After baseline ECA and ORR activity were attained, a small aliquot (ca. 1 mL) of an aqueous solution containing the model compound of interest was injected into the electrochemical cell (containing 140 mL of electrolyte) to yield the desired contaminant concentration. The working electrode was

Figure 1. Chemical structures of studied diacid model compounds representing Nafion (DA-Naf) and 3 M (DA-3M) PEM chemical degradation products.

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rotated at 2500 rpm in order to quickly disperse the contaminant and achieve steady-state, and ECA (obtained through integration of the HUPD region) and ORR activity measurements for the contaminated electrode were subsequently performed. Model compounds were injected during a continuous low potential partial CV scan (0.04 V – 0.55 V), under purge of nitrogen for a predetermined amount of time (ca. 2.5 min) in order to allow the injected contaminant to adsorb and equilibrate onto the working electrode surface. Note, the low potentials also initially maintain the chemical integrity of the injected species by preventing their possible oxidation at higher potentials. All CV scans were performed at a scan rate of 50 mV/s. After a full CV of the contaminated Pt electrode was obtained, the electrochemical cell was purged with oxygen, and ORR activity subsequently measured. All ORR measurements were performed at a scan rate of 20 mV/s, sweeping anodically, and were IR corrected. ORR catalyst activity current was measured at 0.9 V as is the convention within the electrochemistry community. Diffusion limitations with regards to oxygen reduction are not a concern in this case, since the potential at which the kinetic current is measured falls well beyond that of the diffusion limiting current (<0.7 V) of the ORR linear sweep (while rotating the RDE at 1600 rpm). Please note that at the elevation of our laboratory (~ 6000 ft above sea level) the atmospheric pressure is merely ~ 82 kPa, resulting in a lower oxygen concentration in our electrolyte and a subsequently lower limiting current range ($4\text{--}5$ mA/cm²_{elec}) than is typically seen for RDE work performed at sea level ($5\text{--}6$ mA/cm²_{elec}). After the CVs were recorded and the ORR activity obtained, the model compound concentration was increased and the experiment repeated in order to maintain identical cell conditions. Model compound concentrations were increased incrementally by an order of magnitude from 0.001 mM to 1 mM in all experiments in order to bracket the concentration range suspected to be present in operating fuel cells.¹⁷ Limited reproducibility experiments have shown standard deviations of current measurements to be on the order of $\pm 5\%$ in regards to model compound adsorption. Finally, current measurements at all concentrations were corrected for any losses observed during “blank” trials, where the same protocol sequence was performed under identical conditions using clean electrolyte without any organic compounds added.

Results and Discussion

DA-Naf/DA-3M adsorption characteristics.— Polycrystalline Pt, Pt/Vu, and NSTF were investigated in order to encompass both fundamental and practical catalyst surfaces, and the significant differences in Pt atomic structure among the three electrode surfaces. With surfaces being close to atomically flat, polycrystalline Pt electrodes have both the lowest roughness factor (cm²_{Pt}/cm²_{elec}) and hence the lowest number of total Pt sites. Polycrystalline Pt surfaces are inherently unsupported, represent the most fundamental surface of this study, and have the highest ORR activity per site.¹⁸ The Pt/Vu electrodes perhaps represent the most relevant of the three due to the ubiquitous use of Pt supported carbon materials in state-of-the-art MEAs. Since the catalyst material consists of Pt nanoparticles (2–3 nm) supported on Vulcan carbon, the Pt/Vu surfaces have the highest ECAs of this study and the lowest observed intrinsic ORR activity per Pt site.¹⁸ NSTF, representing Pt extended surfaces, are hybrid structures featuring characteristics of both polycrystalline Pt and Pt/Vu. The NSTF Pt surface structure consists of thin Pt films coated on organic whiskers. This results in ECAs on the same order of magnitude as Pt/Vu surfaces and ORR activities approaching those for polycrystalline Pt surfaces.¹⁹ It is our hope that by examining the contamination effects of these specific surfaces, we can glean information about the severity of ORR poisoning in relation to initial Pt activity and Pt structure.

For all Pt electrode surfaces studied, it can be seen from Figures 2–3 that the presence and concentration of model compounds DA-Naf and DA-3M have a direct impact on both the Pt CV and the ORR polarization curves. Impact on ORR performance began to appear at 0.01 mM for all surfaces, while changes in CV began to appear at a

concentration of 0.1 mM. The greatest impacts was realized at 1 mM for all electrocatalysts.

Similar adsorption characteristics were observed with both model compounds for all Pt surfaces, with the only digression occurring at high concentrations (1 mM) of DA-Naf. In regards to CV scans, polycrystalline Pt and NSTF surfaces showed close to identical model compound adsorption behavior while the Pt/Vu surface exhibited attenuated effects comparatively. Symmetric increases in current observed in the HUPD region for both the anodic and cathodic scans, as shown in Figures 2 and 3(a–c), indicates charge transfer for both compounds begins in the low potential region (ca. 0.3 V), close to the point of zero charge (pzc) of Pt (~ 0.285 V)²⁰ and superimposing on the hydrogen adsorption/desorption currents (although initial adsorption may proceed at lower potentials). Symmetry of the adsorption/desorption peak provides evidence of a reversible adsorption process. Model compound adsorbates also appear to become displaced by oxides as higher potentials are approached, as indicated by the minimal change in shape of the oxide formation CV region. Shifts in oxidation onset toward higher potentials as model compound concentration increased suggests adsorbates present on the surface were able to hinder oxide formation before eventually becoming displaced. Shifts toward lower potentials of the HUPD peak at ca. 0.3 V with increasing model compound concentration gives evidence for competitive adsorption between the model adsorbates and hydrogen atoms. This potential shift of the HUPD peak is most clearly observed for the polycrystalline Pt and NSTF surfaces and with both compounds, suggesting a more facile adsorption mechanism involving either the distribution of crystal facets among the three surfaces or the specific geometries of the more planar, extended Pt surfaces.

No electrochemical stripping experiments were carried out in this study. Although experiments such as CO or Cu stripping can provide surface area information, in this case the weakly adsorbed organic compounds would likely be displaced by the probe CO or Cu. If full displacement occurs, then the surface area measured would be the same as that of the baseline HUPD integration. As a consequence no new information would be obtained from stripping measurements, since adsorption is already established by the superimposing currents (measured as an increase in current) in the HUPD region of the CV.

Adsorption likely occurs through the carboxylate anion, found in both compounds, forming a bridged structure with both oxygens at the surface. Such a mechanism has been shown by other groups to be the primary mode of bonding for carboxylic acids with metal surfaces.^{21–23} Given the similar structural nature of DA-Naf and DA-3M (see Figure 1), the correlation of their adsorption characteristics should not be surprising. However as mentioned, effects shown in the voltammograms for all three Pt surfaces with DA-Naf present at 1 mM did showcase the subtle differences between the two compounds and were most likely indicative of increased molecular interactions due to the ether functionality found in DA-Naf.

Structurally, the only difference between DA-Naf and DA-3M is the presence of an additional ether and fluoromethyl group. Although it would be difficult sterically, the ether functionality found in DA-Naf could affect the adsorption of said compound in the examined potential window if it were able to reach the electrode surface. Studies investigating the hydrocarbon dimethyl ether (DME) have shown that the current in the HUPD region decreased through adsorption on Pt electrodes as well as destructive chemisorption at higher potentials.^{24–26} DA-Naf results did not indicate any destructive chemisorption, due to the lack of additional CV peaks associated with dehydrogenation (defluorination in this case) and intermediate formation commonly found for DME oxidation. The shift of CV current in the double-layer region along with an alteration of the oxide formation region observed at 1 mM (see Figure 2a–c) suggests a greater adsorption interaction is taking place for the DA-Naf, compared to the non-ether containing DA-3M species (Figure 3a–c). Greater strength of the C–F bond (compared to C–H) adds to the stability of the compound and may prevent further decomposition upon adsorption to

Figure 2. Voltammograms (a-c) and ORR polarization curves (d-f) of polycrystalline Pt (top row), NSTF (middle row), and Pt/Vu (bottom row) electrodes in the presence of DA-Naf at increasing concentrations. Baseline curves (black dash), 0.01 mM (gray dash), 0.1 mM (gray solid), 1 mM (black solid).

the electrode surface.²⁷ In a study investigating adsorption of fluorinated ethers on metal and metal oxide surfaces, it was determined that adsorption of perfluorodiethyl ether on a Pt(111) surface was weaker than its hydrogenated counterpart.^{28,29} Furthermore, the compound was shown to reversibly adsorb exclusively by Van der Waals forces on both Pt(111) and ZrO_2 surfaces without decomposition.^{28,29} The difference in adsorption energy between the fluorinated and hydrogenated structures was attributed to increased steric hindrance of the ether O by the larger fluoromethyl groups and also to the depletion of electron density at the oxygen lone pair by the fluorine atoms.²⁸⁻³⁰

Perhaps the greatest disparity in adsorption processes occurring for DA-Naf compared with DA-3M can be seen in Figure 4, which shows partial CV (low potential) scans for all studied catalyst surfaces. Due to the competitive nature of anion adsorption process within the HUPD region, ECA measurements in the presence of adsorbing anions are normally not indicative of the actual electrochemically active Pt surface area. As observed in Figure 4f, the anion adsorption process can superimpose with the typically observed HUPD current, possibly increasing the apparent ECA, if it is calculated via HUPD. The partial CV scans taken in the presence of DA-3M show the same reversible

adsorption butterfly peaks occurring at 0.3 V observed in the full scan. In the presence of DA-Naf, the partial scans showed a steady decrease in ECA (measured by integration of the HUPD area) as concentration was increased. A pronounced loss in ECA was observed at the highest concentration of 1 mM. The loss in charge in the HUPD region, observed for DA-Naf (Figure 4(a-c)), strongly suggests that additional processes other than carboxylate anion adsorption are occurring. Since it is sterically unlikely that the ether oxygen found in DA-Naf would be able to directly bond to the electrode surface, a different explanation for the loss in HUPD charge involves increases in intermolecular interactions via hydrogen bonding among adjacent model adsorbates.

According to Figure 4, it would appear that hydrogen atoms were able to effectively displace DA-3M from the surface. When DA-Naf was present, however, surface sites previously available for hydrogen adsorption evidently became blocked as concentration increased. Assuming surface coverage increases with concentration, it could be reasonable to suggest that as the proximity of each separate DA-Naf molecule on the surface reaches a threshold, hydrogen bonding among adjacent ether oxygens could occur, resulting in the electrode surface becoming obstructed to a greater extent and preventing hydrogen atoms from reaching the platinum surface.

Figure 3. Voltammograms (a-c) and ORR polarization curves (d-f) of polycrystalline Pt (top row), NSTF (middle row), and Pt/Vu (bottom row) electrodes in the presence of DA-3M at increasing concentrations. Baseline curves (black dash), 0.01 mM (gray dash), 0.1 mM (gray solid), 1 mM (black solid).

Figure 5 shows a correlation between measured ECA and logarithmic concentration dependency with the apparent digression from linearity occurring at 1 mM DA-Naf. This further suggests that additional surface / intermolecular interactions are occurring as concentrations reach higher values.

DA-Naf / DA-3M impact on ORR.— Figures 2 and 3(d-f) show the concentration impact of DA-Naf and DA-3M for polycrystalline Pt, Pt/Vu, and NSTF electrodes for ORR polarization curves. Diffusion limiting currents were not significantly altered in any case. However, a decrease in activity (reported as % loss in transport corrected kinetic current measured at 0.9 V relative to a baseline measurement) was observed for all catalysts, at concentrations starting as low as 0.01 mM, and becoming more severe as concentration of model organic compound increased. Significantly greater ORR activity losses observed at 1 mM for DA-3M (66% loss) compared with DA-Naf (44% loss) may be explained by the less sterically hindered DA-3M molecule allowing for increased molecular ordering at the electrode surface for higher concentrations. In regards to performance loss recoverability, it was found during a complimentary study³¹ in our laboratory that >95% of the baseline activity was achieved for a polycrystalline Pt

electrode after rinsing the contaminated surface with ultra-pure water and testing in a clean, auxiliary cell.

A summary of the overall ORR performance vs. DA-Naf and DA-3M concentration is shown in Figure 6 for all three catalyst surfaces tested (polycrystalline Pt, NSTF, and Pt/Vu). The performance impact of DA-Naf and DA-3M on ORR activity show similar trends for all catalysts, with the overall performance loss for the NSTF catalyst falling in between that of polycrystalline Pt and Pt/Vu. These results seem reasonable since structurally the extended surface of NSTF has characteristics of both the other two catalyst surfaces. A possible explanation for the differences in activity loss observed among the three electrocatalysts may involve surface site availability. Since the total number of available Pt sites on a polycrystalline Pt surface is approximately an order of magnitude less than that of a Pt/Vu surface, and a factor of five less than a NSTF surface, the effective concentration sensed by the polycrystalline Pt electrode is higher than that of the other two. However, the total moles of model compound present in the electrochemical cell, even at 0.1 mM, was still 4.5 orders of magnitude higher than the number of Pt/Vu electrode surface sites, so the relative difference in Pt site abundance among the three surfaces is minimal. Another

Figure 4. Low potential CV scans (after 2.5 minutes continuous cycling upon model compound injection) of polycrystalline Pt (top row), NSTF (middle row), and Pt/Vu (bottom row) electrodes in the presence of increasing concentrations of DA-Naf (a-c) and DA-3M (d-f). Baseline curves (black dash), 0.1 mM (gray solid), 1 mM (black solid).

Figure 5. ECA vs. log of concentration of DA-Naf, obtained at low potential CV scans, for polycrystalline Pt, NSTF, and Pt/Vu electrodes.

explanation for the observed disparities in ORR activity loss involves the actual differences in surface structure among the three electrodes, with either the planar i.e. atomically flat nature of the polycrystalline surface or distribution of Pt (hkl) facets perhaps being more conducive for model compound adsorption and molecular ordering at the surface.

Results in Figure 6 also show linear correlations between kinetic current and log concentration for polycrystalline Pt, NSTF, and Pt/Vu catalysts. Assuming kinetic current is directly related to surface coverage, logarithmic dependency of surface coverage on concentration can be attributed to a Temkin adsorption isotherm model;³² a treatment used when adsorbate-adsorbate interactions are present and accounted for. Similar relationships have been found through studies of acetate adsorption on polycrystalline Pt, which adsorbs through the same carboxylate functional group as present in DA-Naf and DA-3M.^{32,33} The trends observed in Figure 6 in regards to ORR activity are similar to those for ECA correlations in Figure 5. The difference in trend linearity may arise from the inherently different adsorption processes

Figure 6. ORR activity vs log of concentration of DA-Naf (a) and DA-3M (b) for polycrystalline Pt, NSTF, and Pt/Vu electrodes.

competing in the HUPD region at low potential versus Pt oxide formation at higher potentials.

Conclusions

Model compounds representing PEM chemical degradation products, at increasing concentrations, were studied to determine their impact on ECA and ORR activity for polycrystalline Pt, Pt/Vu, and NSTF electrodes. It was found that kinetic current loss for all Pt surfaces studied increased linearly with the log of concentration for both model compounds. The disparity in CV scans between DA-Naf and DA-3M compounds at high concentration (1 mM) was attributed to the ether oxygen found only in DA-Naf, leading to increased intermolecular interactions at the electrode surface. Although severe losses in ORR activity were found at higher concentrations, such concentrations would most likely be rare in an actual fuel cell. Losses in ORR activity found at lower contaminant concentrations likely provide a more realistic picture. Additional experimental techniques such as electrochemical quartz crystal microbalance and surface enhanced infrared electro-spectroscopic methods may provide further insight into the electrode surface adsorption processes and are currently under way. A systematic and fundamental investigation of model compounds with specific acid functional groups as well as differences in perfluoro chain lengths also adds to the understanding of adsorption processes for other membrane degradation products with different chemistries, and is being conducted concurrently with this study. As PFSA membrane technology improves, chemical degradation product concentrations will most likely continue to decrease and thus should not cause major concern for manufacturers, however, different chemical families of membranes

may also pose risks and further investigation for these materials may be required.

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