

Effect of Water Conductivity on Proton Exchange Membrane (PEM) Catalyst Durability using Thermal Degradation Resistant Polymer Membranes in Combat Applications

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The U.S. Army is taking an increasing interest in fuel cell technology as vehicles require more electrical power to support additional capabilities. One challenge the U.S. Army faces using Proton Exchange Membrane (PEM) fuel cells is reduced air flow for primary heat rejection in combat vehicles (due to a small operating space and the use of ballistic grills). Internal temperatures inside the stack increase to 140°C resulting in decreased performance. Additives to polymer membranes have been used to mitigate stack heat degradation but can contaminate and increase the electrical conductivity of the stack exhaust water. For water examined here which had a 0.7 mA current applied, an increase in electrical conductivity (using a 5vol% acetic acid mixture) promoted the platinum electrocatalyst detachment from the PEM fuel cell polymer membrane. The increased water conductivity resulted in 30-40% of the total platinum being detached within 67 minutes (400 current cycles).

Introduction

As the U.S. Army has shown interest in fuel cell technology next generation vehicles will require additional electrical power to support different combat roles which can include silent watch (long term mounted surveillance), advanced radios/jamming devices and exportable power supporting stationary applications and vehicle-to-grid connectivity. Fuel cells are attractive in these roles as they generate a lower thermal and acoustic signature while having the capability of being more efficient than current internal combustion engines. The goal is to have increased energy savings and decreased fuel transport logistic burdens. Despite these advantages, significant work needs to be completed before fuel cell technology can be integrated into combat vehicles as previous literature studies have demonstrated that temperature (1), electrical bias (2), particle size (3) and solution chemistry (2) can all contribute to stack degradation within the fuel cell in addition to traditional issues such as thermal-cycling and stack sealing found in many fuel cell stacks. The U.S. Army has the unique challenge of engineering fuel cells into vehicles which have reduced heat rejection which can lead to increase internal stack temperatures. These increased internal temperatures are projected to reach or possibly exceed 140°C and can lead to stack performance degradation. One stack performance degradation mechanism that can occur is the thermal degradation of the polymer membrane. Some common membrane materials used are Tetrafluoroethylene based

fluoropolymer-copolymers (such as Nafion), Polybenzimidazole (PBI), Phosphotungstic Acid (PWA) and phosphoric acid. Selecting a membrane material which has increased thermal degradation resistance is one possible approach to limit performance loss at intermediate stack operating temperatures. Another approach the U.S. Army is analyzing to address increased stack internal temperature is the incorporation of silicon (as quartz or silica) into the polymer membrane structure during its formulation, which literature studies have shown can reduce polymer thermal degradation (2). A third possible method to improve performance and mitigate polymer thermal degradation at intermediate stack operating temperatures includes the addition of additives to the polymer formulation, such as perfluorosulfonic acid and acetic acid, which can be added as side chains into the polymer chemistry to enhance their material properties for increased fuel cell power and durability. These acid side chains have the potential to be detached when these polymers are exposed to elevated operating temperatures, and can increase the electrical conductivity of the water produced by the stack. In addition, some literature studies (4, 5, 6) have fabricated polymer samples using both silicon and acid side chains for characterized during stack operation.

Previous literature studies (2, 7, 8), which have subjected PEM fuel cell membranes to acidic exhaust water showed the electrocatalyst material was removed from the membrane surface. Possible explanations for the detachment of the electrocatalyst material from the fuel cell membrane is considered to occur either through the separate or combined interaction of applied heat, electrical current or exhaust water electrical conductivity/chemistry. These literature studies also used strong acids (i.e. sulfuric acid, nitric acid, perchloric acid, etc) to detach their respective electrocatalyst, which this study views as not likely to be a byproduct in a PEM fuel cell, where a weak acid such as acetic acid would be more likely since many of the polymer membranes are formulated using weak acids. Acetic acid would be a possible byproduct from the polymer membrane due to studies showing it can be leached into the exhaust water even close to room temperature and the addition of a weak acid to the exhaust water would change the solution chemistry and electrical conductivity.

The objective of this study was to investigate the effect on electrocatalyst degradation at the polymer/electrocatalyst/exhaust water interface when the exhaust water solution chemistry and electrical conductivity was altered by the introduction of a weak acid, such as acetic acid in different concentrations. The addition of acetic acid in different concentrations to the exhaust water in contact with the electrocatalyst coated polymer membrane simulates leached acetic acid from the polymer membrane due to the stack operating temperature being increased up to the intermediate temperature range (100°C to 140°C). The polymer membrane used in this paper included quartz as an additive (for increased thermal degradation resistance), and was used to simulate fuel cell stacks reported in literature that incorporated both polymers fabricated using acid-functionalized side chains and silicon for intermediate temperature stack operation. The baseline interaction and contribution of quartz, inside the polymer, was not investigated in this paper since the focus of this study was on changes to the exhaust water chemistry/electrical conductivity and their effect on the degradation rate of the electrocatalyst material. The effect of quartz on the electrocatalyst degradation will be analyzed as the topic of another paper in future work.

Experimental Methods

Polybenzimidazole (PBI) polymer membrane samples, containing a homogeneous distribution of quartz particles with an average diameter of 6nm. The PBI samples were then sputter-coated with a 6nm thick layer of platinum as the electrocatalyst. These PBI sputter-coated samples were fabricated using the following methods for the water conductivity experiments. First, PBI polymer, containing quartz nanoparticles, was prepared using a proprietary method. The PBI polymer samples with a 1.61 cm² surface area (1.27 cm x 1.27 cm) were cut from sheets of PBI polymer. Next, the 6nm thick layer of platinum catalyst was applied to a single side of each sample using the sputter-coating technique (Quorum; Laughton, East Sussex, United Kingdom). A 99.99% pure platinum target (Electron Microscopy Sciences; Hatfield, PA, USA) with a 57mm diameter and 100μm thickness was used as the platinum source which was applied to each sample. Depending on the characterization test being performed the geometry of the applied platinum coating was different. For samples characterized using heat the platinum sputter-coating layer geometry covered the entire sample face on a single side (1.27 cm x 1.27 cm) shown in Figure 1b below. For samples characterized using an applied electrical current, through the platinum coating, the platinum sputter-coating layer geometry was a strip that was 0.238 cm wide and 0.635 cm in length on a single side, shown in Figure 1a below. The platinum strip for electrical current tests was produced by applying a mask to the polymer surface prior to the sputter-coating process. Creating a strip of platinum (instead of covered the entire polymer surface) allowed the current flow to be directed through the solution being used, which was held within a ceramic solution holder attached onto the polymer surface over the platinum strip. Illustrations of samples used for both characterization experiments, including their respective platinum geometries, are shown in Figure 1.

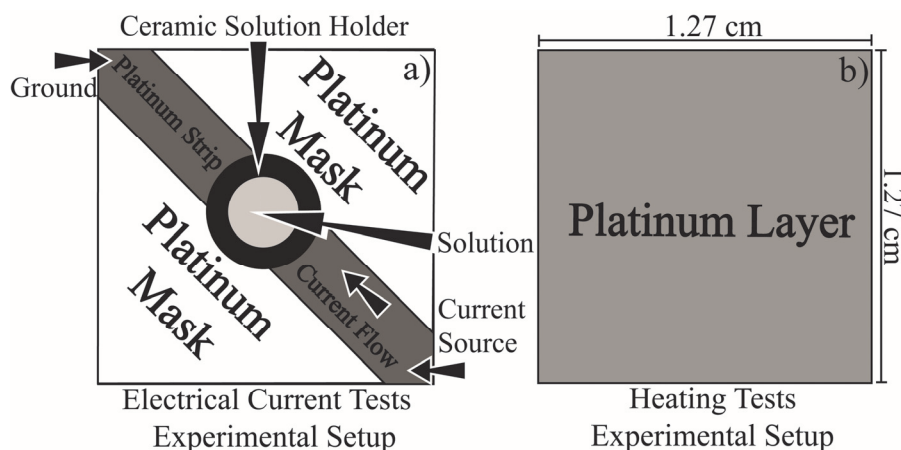


Figure 1. Platinum sputter-coating layer geometries for applied electrical current (a) and heating (b) characterization tests.

Heating and Water Conductivity Experiments

Platinum-coated polymer membrane samples, prepared as shown in Figure 1b, were submerged in 10mL of solution inside glass beakers with the platinum coating facing upwards. Solutions used were: 1. 16 MΩ water (referred as 0 vol% acetic acid for the remainder of this paper), 2. 5 vol% acetic acid (mixture of 99.7% acetic acid and 16 MΩ water) and, 3. 99.7 vol% acetic acid (Fisher Scientific, Waltham, MA, USA). Submerged samples in each solution were heated using set points varying from 65-150°C for a total of 2,280 minutes (38 hours) each, while open to ambient pressure. As solutions evaporated during the heating process an additional 2-3 mL of solution was added, when needed, to maintain the starting volume of 10 mL.

Applied Current and Water Conductivity Experiments

Platinum-coated polymer membrane samples, prepared as shown in Figure 1a, had a ceramic solution holder attached to the polymer surface above the platinum strip and filled with either 0 vol%, 5 vol% or 99.7 vol% acetic acid solution chemistries prior to experimentation. Electrical current leads from a variable voltage/current power supply were connected to each end of the platinum strip while a constant 0.7 mA or 30 mA current was applied across the platinum coating. Voltages across the platinum surface were calculated, using the reported platinum resistivity value from literature (9), and found to be on average 0.06 V for the 0.7 mA current and 2.60 V for the 30 mA current. Electrical currents across the platinum coating strip were applied using a square wave profile with the electrical current applied for 5 seconds and then turned off for 5 seconds. One square wave profile lasted for a total of 10 seconds and will be referred, for the remainder of this paper, as 1 cycle. Samples had either 50, 100, 200 or 400 cycles applied across their respective platinum strip which took ~8 minutes, ~17 minutes, ~33 minutes and ~67 minutes to complete, respectively.

Exhaust Water Solution Electrical Conductivity Experiments

Exhaust water solution electrical conductivity measurements were conducted using an Extech ExStik EC400 conductivity probe (Extech, Nashua, NH, USA). Solution conductivity values were measured from mixtures created by combining 0 vol% and 99.7 vol% acetic acid (Fisher Scientific, Waltham, MA, USA) solutions at room temperature and pressure in different quantities. Each conductivity measurement was obtained by first placing the conductivity probe into the solution so the electrodes were completely submerged and then waiting until a stable reading was obtained. Between each measurement the electrodes were rinsed with 0 vol% acetic acid solution to remove any residual solution left of the electrodes and then the electrodes were air dried.

Electrical conductivity values were also obtained from 0 vol% acetic acid as a function of time. The conductivity probe was placed into the solution which was exposed to room temperature and pressure. Conductivity measurements were recorded every 5 minutes for a total of 70 minutes. The probe electrodes were cleaned in the same manner described above between each measurement to avoid cross contamination.

Energy Dispersive Spectroscopy Experiments

Sputter-coating elemental platinum sample level measurements taken before and after experimentation were performed using a Hitachi Scanning Electron Microscope (SEM) (Hitachi; Krefeld, Germany) with an Oxford Instruments Energy Dispersive Spectroscopy (EDS) detector (Oxford Instruments; Concord, MA, USA). EDS measurements were taken using a beam voltage of 30.0 kV, a 30 μm aperture, a 256 second scan speed, a 10 mm working distance, and a 200x magnification. At least three EDS measurements were taken and averaged for each sample characterized, before and after each experiment, to account for possible variations that may exist throughout the platinum sputter-coating and polymer material. Measurements were taken from the center and sides of each sample to account for platinum degradation changes across the entire sample surface and not just in a single area. Samples characterized by EDS were prepared using two different approaches for heating and electrical current tests. Samples which were heated in different solutions were removed from their respective solution after heating for 38 hours, allowed to air dry and then their platinum sputter-coated surface was analyzed by EDS. Samples which had an electrical current applied through the platinum sputter-coating, while in contact with different solutions had the ceramic solution holder removed, were allowed to air dry, and the platinum which was in contact with the solution was cut away for EDS analysis.

Results

Figure 2 shows the platinum raw EDS peak intensity data from each platinum sputter-coated membrane sample before and after being heated. Overall, heating samples for 38 hours, submerged in different solution chemistries, did not appear to have much effect on the platinum peak intensities for any temperature or solution combination.

Figure 3 shows the platinum peak heights calculated from the heating EDS raw data which were then averaged together for each sample and took into account the standard deviations for each parameter that was changed. Even when statistical sample variations were accounted for each adjusted parameter the platinum loading levels stayed statistically constant, as was observed in Figure 2. Clearly, applied heat when combined with different solution chemistries was not sufficient to remove a statistical amounts of platinum. Next, the effects of applied electrical current will be investigated.

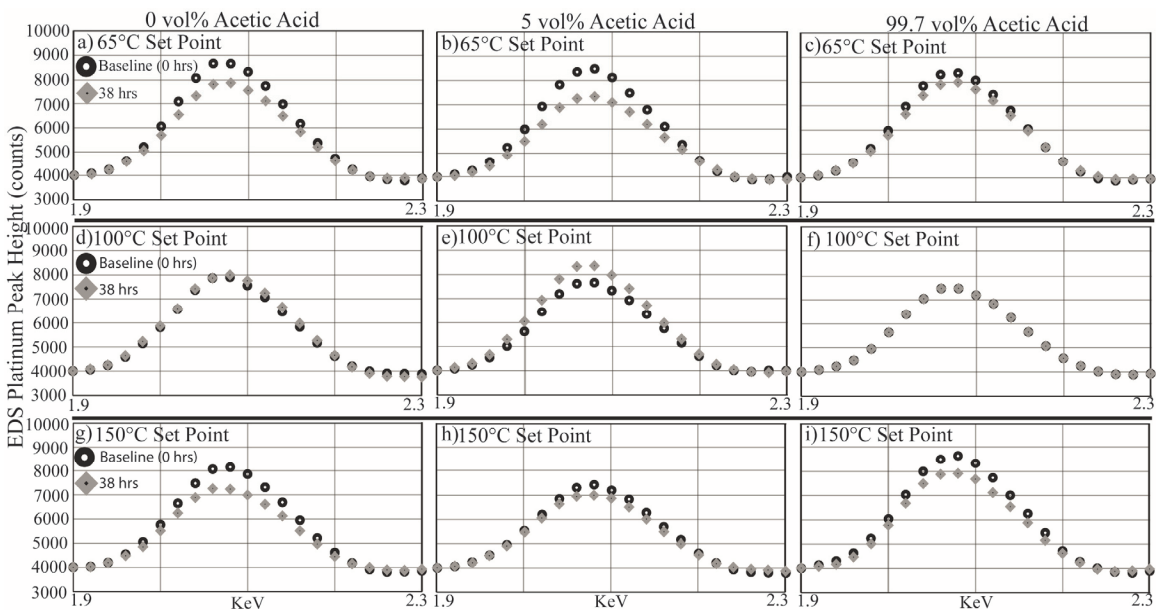


Figure 2. EDS spectrums of platinum sputter-coated polymer membranes heated using a (a-c) 65°C, (d-f) 100°C and (g-i) 150°C set point at atmospheric pressure for 38 hours. Platinum coated polymer membranes were submerged in (a, d, g) 0 vol% acetic acid, (b, e, h) 5 vol% acetic acid and (c, f, i) 99.7 vol% acetic acid for 38 hours. Baseline (before heating occurred) platinum (●) data is shown along with platinum (◆) data after being heated 38 hrs. All data values collected before and after experimentation have been adjusted so they start near the same initial value.

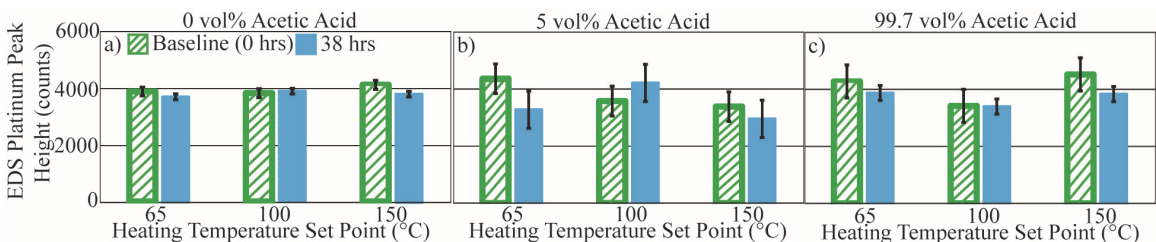


Figure 3. The average EDS values for platinum peaks from polymer membranes submerged in (a) 0 vol% solution, (b) 5 vol% solution and (c) 99.7 vol% solution while being heated at 65°C, 100°C and 150°C set points at atmospheric pressure. Average EDS baseline, including sample variations, (before heating occurred) platinum (▨) data are shown along with average EDS platinum (■) data, including sample variations, after being heated using 65°C, 100°C and 150°C set points for 38 hours.

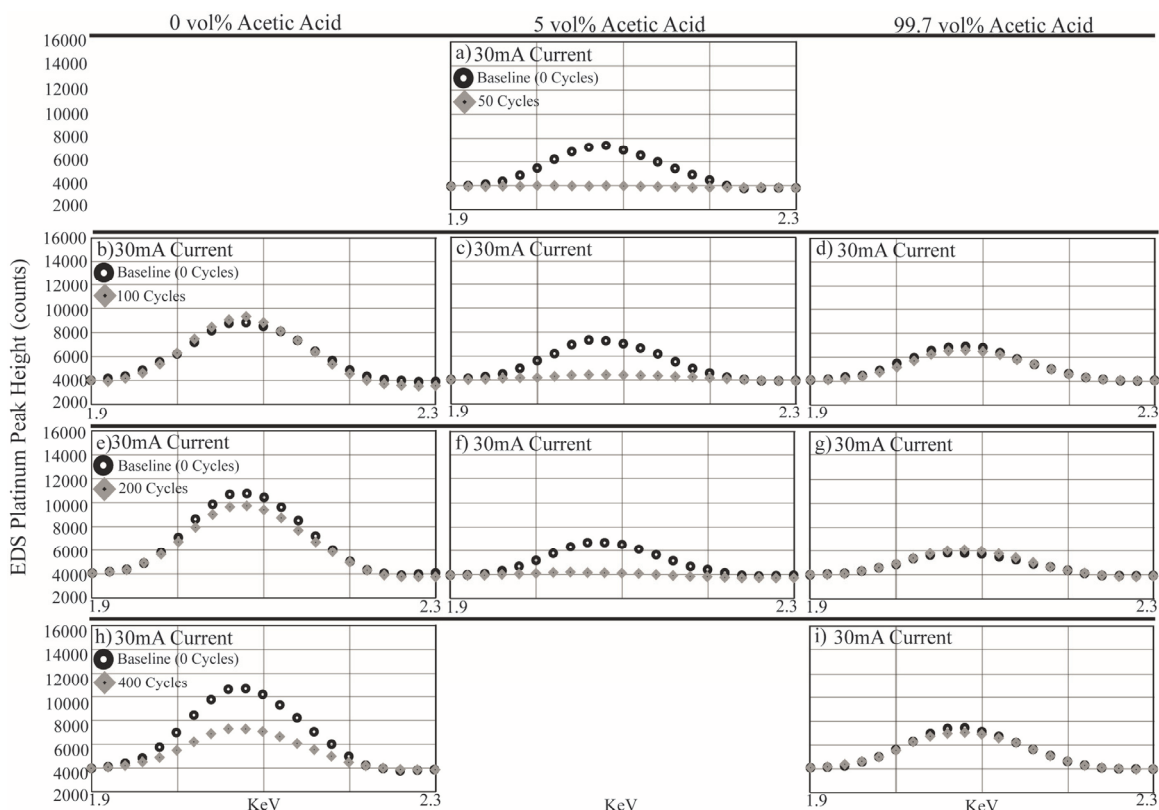


Figure 4. EDS spectrums of platinum sputter-coated polymer membranes applied with a 30 mA current applied (a) 50 cycles, (b-d) 100 cycles, (e-g) 200 cycles and (h-i) 400 cycles at 21°C. Platinum coated polymer membranes were in contacted with (b, e, h) 0 vol% acetic acid, (a, c, f) 5 vol% acetic acid and (d, g, i) 99.7 vol% acetic acid for either 50, 100, 200 or 400 cycles. Baseline (no current) platinum (●) data is shown along with platinum (◆) data after testing. All data collected before and after have been adjusted so they start near the same initial value.

Figure 4 shows platinum EDS peak intensities from the platinum sputter-coated membrane samples before and after having a 30 mA current applied across the platinum strip. Results showed that platinum levels were statistically decreased by ~30-40% after 400 cycles in the presence of the 0 vol% acetic acid solution, platinum showed a near 100% removal when as few as 50 current cycles were used when in the presence of the 5 vol% acetic acid solution and platinum levels showed no changes in intensity when in the presence of the 99.7 vol% acetic acid solution. These results do show that platinum is capable of being removed when in the presence of 0 vol% and 5 vol% acetic acid exhaust water solutions. These findings may be the result of the large current applied through the platinum strip. A lower current value will be used to determine whether these results can be duplicated.

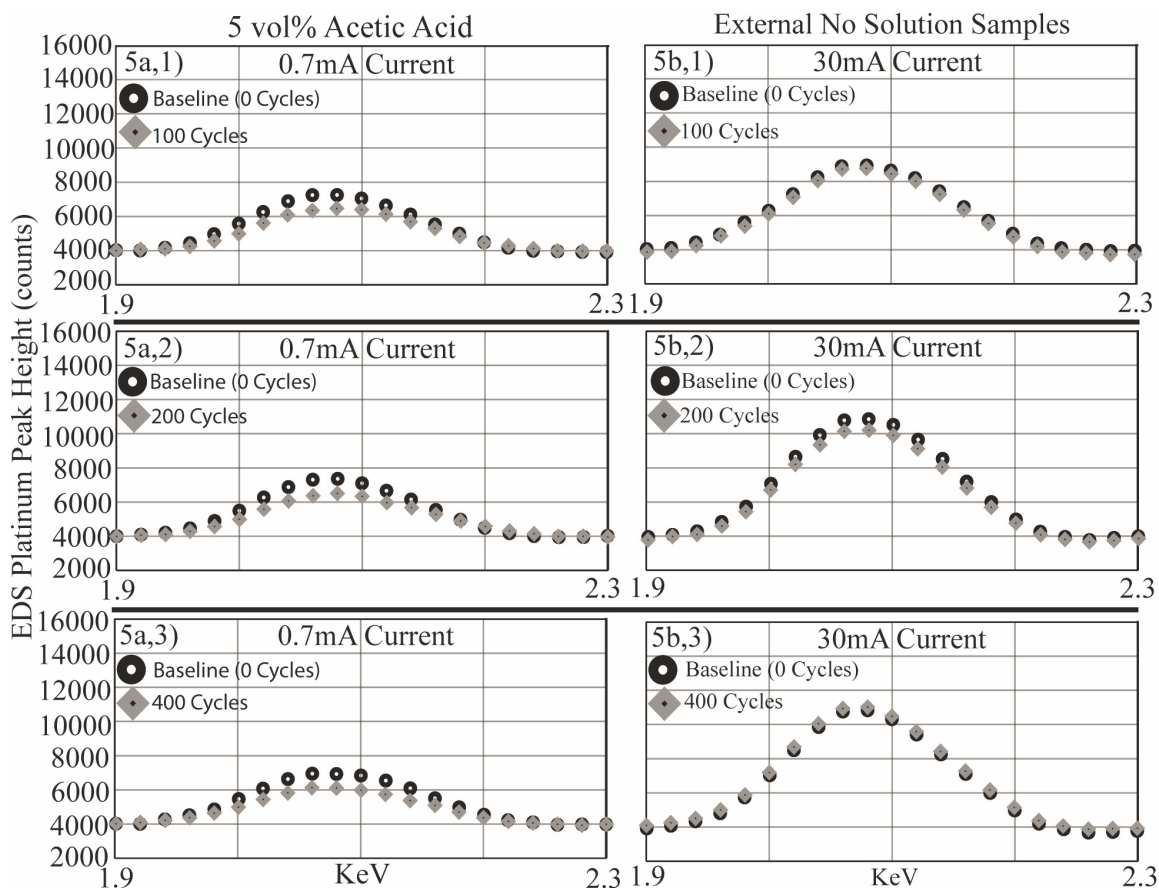


Figure 5. EDS spectrums of platinum sputter-coated polymer membranes applied with either 0.7 mA current (5a, left) or 30 mA current (5b, right). 0.7 mA current was applied for (a,1) 100 cycles, (a,2) 200 cycles and (a,3) 400 cycles at 21°C in contact with 5 vol% acetic acid and 30 mA current was applied for (b,1) 100 cycles, (b,2) 200 Cycles, and (b,3) 400 cycles at 21°C in contact with no solution (outside the ceramic solution holder). Baseline (no current) platinum (●) data is shown along with platinum (◆) data after testing. All data collected before and after have been adjusted so they start near the same initial value.

Figure 5a shows platinum EDS peak intensities from the platinum sputter-coated membrane samples before and after having a 0.7 mA current applied. The 0 vol% and 99.7 vol% acetic acid solutions were not compared using the 0.7 mA current since the 5 vol% solution showed the most dramatic impact when tested using 30 mA, and was considered the most likely to show detectable results when using a significantly lower current. EDS results show the platinum decreased by 36-40% when the 0.7 mA current was cycled for 100, 200 and 400 times in the presence of the 5 vol% acetic acid solution. These results could be the result of the quartz interacting with the platinum while the electrical current is applied. The impact of the electrical current, in the presence of no solution, will be investigated next.

Figure 5b shows the platinum EDS peak intensities from the platinum sputter-coated membrane samples before and after having 30 mA current applied for 100, 200 and 400 cycles, using no solution. Unlike the previous two raw EDS plots, which used different

solution chemistries in contact with the platinum coating, the following samples did not show any changes to the platinum loading levels. This suggests that the quartz inside the polymer samples and/or electrical current are not sufficient, together or alone, to alter the platinum loading levels statistically. This indicates that the solution chemistry is a critical component necessary for the platinum detachment process to occur.

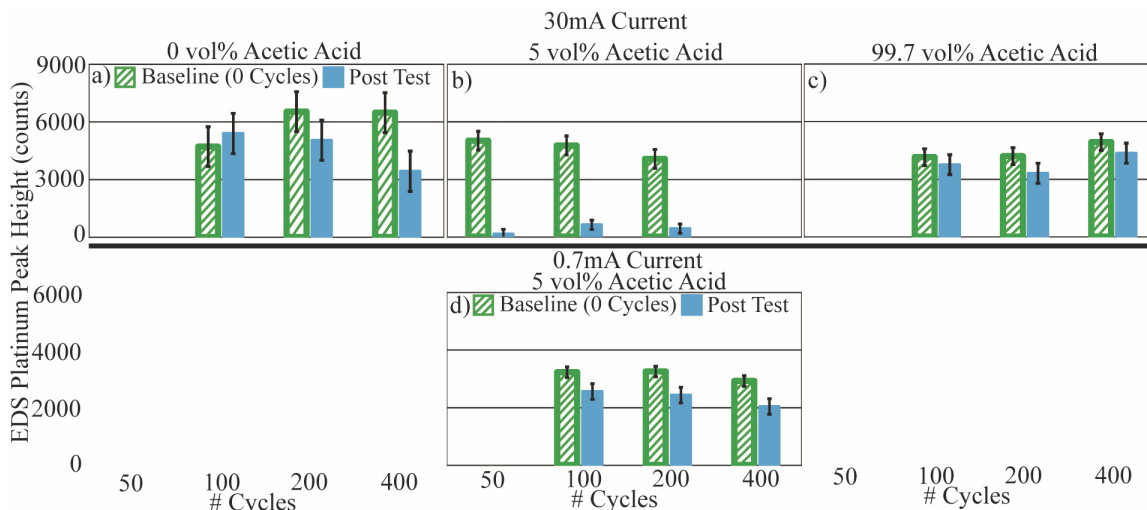


Figure 6. The average EDS values for platinum peaks from polymer membranes in contact with (a) 0 vol% solution, (b) 5 vol% solution and (c) 99.7 vol% solution while being applied with a 30 mA current. Polymer membranes in contact with (d) 5 vol% acetic acid also had a 0.7 mA current applied. All samples were cycled for 50, 100, 200 and/or 400 times at 21°C. Average EDS baseline (no current) platinum (▨), including sample variations, data is shown along with average platinum (■), including sample variations, EDS data after testing.

Figure 6 shows the platinum peak heights calculated from the both the 30 mA and 0.7 mA experimental EDS raw data which were then averaged together for each sample and took into account the standard deviations for each parameter that was changed. Overall all the 5 vol% acetic acid data in Figure 4 was found to be statistically significant, but 400 cycles were required to remove a statistical amount of platinum when using the 0 vol% acetic acid solution. The results in Figure 5a for the 5 vol% acetic showed platinum loss for all results were statistically significant, but the loading level losses were smaller. These results show that two dissimilar solutions, were able to remove platinum while an electrical current was applied, but still removed platinum in different time scales. One common property between these different solutions that possibly could explain these results is solution conductivity.

Figure 7 shows the electrical conductivity of exhaust water solutions containing different amounts of acetic acid ranging from 0 vol% to 99.7 vol% acetic acid. Conductivity values show that only the 5 vol% acetic acid solution is electrically conductive, which literature studies confirm as well (10), (11). Literature studies have however also shown that 0 vol% acetic acid solution can become electrically conductive with time (12), which can explain the similarities in platinum loss between the 0 vol% and 5 vol% acetic acid solutions.

Figure 8 shows the electrical conductivity of 0 vol% acetic acid as a function of time after the solution was exposed to air at room temperature and pressure. The solution remained non-conductive for ~15 minutes before the measurement probe was able to detect conductivity. This amount of time is certainly within the timeframe experienced by the 100, 200, and 400 cycle, 30 mA, 0 vol% acetic acid experiments and supports the literature findings (12).

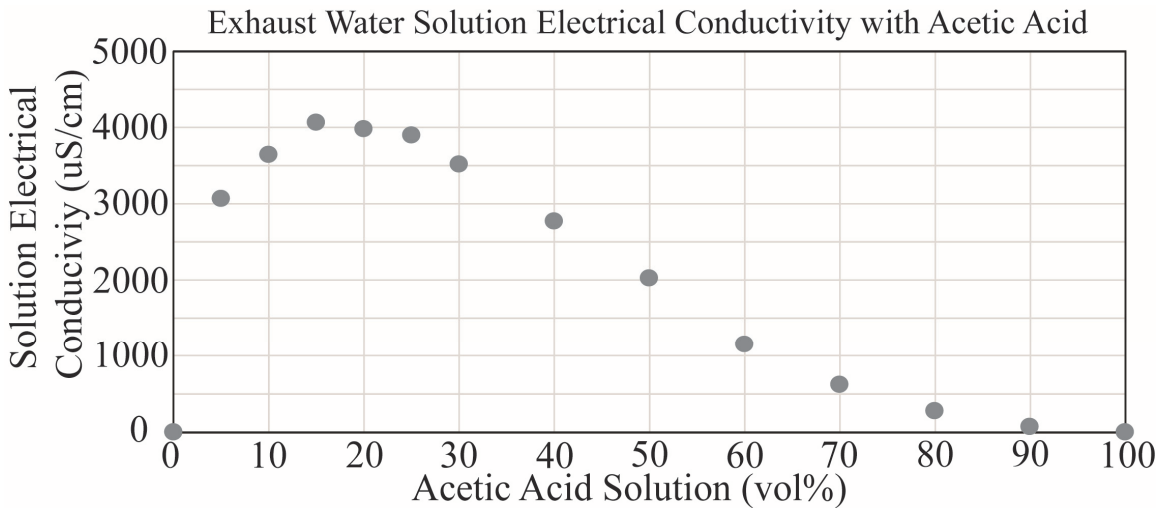


Figure 7. Electrical conductivity measurements from exhaust water solutions containing different amounts of acetic acid (ranging from 0 to 99.7 vol%) using an electrical conductivity probe at room temperature and pressure.

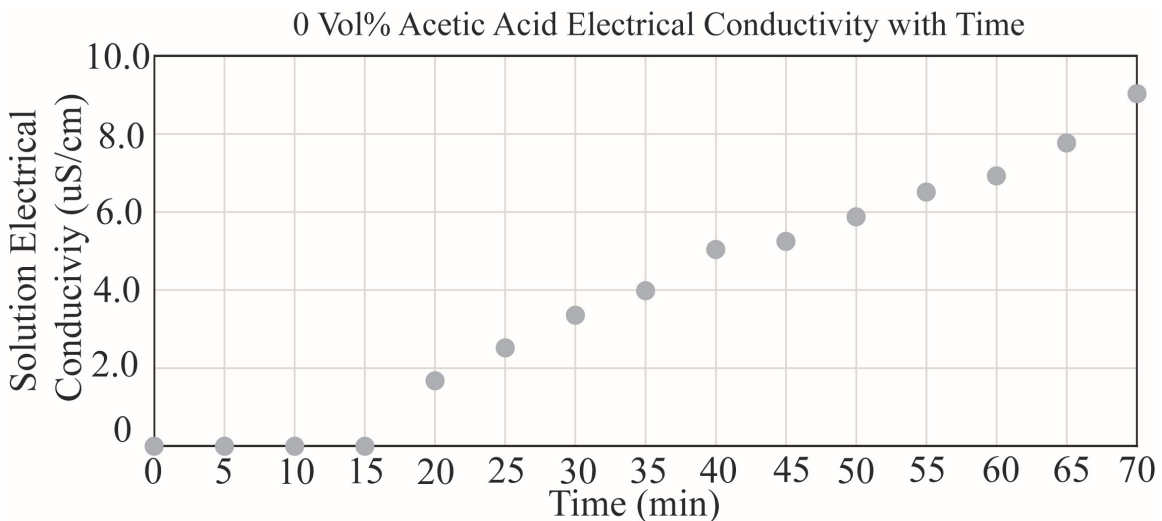


Figure 8. Electrical conductivity measurements from 0 vol% acetic acid solution exposed to air as a function of time at room temperature and pressure.

Conclusions

Exhaust water from PEM fuel cells which has been become electrically conductive through the addition of acetic acid has been shown to promote the detachment of platinum electrocatalyst when an electrical current was passed through the platinum sputter-coated layer. Two electrical current magnitudes, 30 mA and 0.7 mA, were

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applied across the platinum layer and both resulted in statistical amounts of platinum loss when compared to baseline results (no current applied) in 5 vol% acetic acid exhaust water solutions. Results showed the 30 mA current removed nearly 100% of the platinum in areas within 50 cycles (~8 min) while the 0.7 mA current removed between 36-40% of the platinum within 400 cycles (~67 min).

These results also demonstrate the electrocatalyst susceptibility to degradation via increased exhaust water electrical conductivity. Due to polymer membranes being formulated using acid side chains there is potential for this weak acids, such as acetic acid, to leach into the exhaust water produced by the PEM fuel cell and increase the water electrical conductivity. As the U.S. Army operates combat vehicles with reduced heat rejection precautions should be looked at in the future to reduce or eliminate sources within the PEM fuel cell, at intermediate temperatures, that potentially could increase the exhaust water conductivity.

Acknowledgments

The authors thank both Demetrios Tzelepis and Ian Toppler for technical assistance operating the SEM, EDS and XRD equipment. In addition, the authors would also like to thank Dr. Yi Ding for providing helpful discussions and comments.

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