Effect of Water Content on Oxygen Reduction Reaction (ORR) Kinetics on Supported Pt Catalyst: A Rotating Disk Electrode Study

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Abstract

The oxidation of water at potentials above 0.7V has been viewed as a potential problem for Pt on the cathode side of a Proton Exchange Membrane Fuel Cell (PEMFC). Pt alloys have shown a minimization or shift to higher potentials the oxide formation due to water oxidation. As a result, an increase in the Oxygen Reduction Reaction (ORR) activity has been observed. Not all of the Pt alloys show the same improvement in ORR activity which raises the question of what role does an alloy play in improving the cathodic overpotential losses. If the minimization of PtOH formation was the primary reason for poor ORR activity, then substantial improvement should be seen for Pt if the water content of the electrolyte was reduced and/or the activity of water and thus its interaction with Pt was also decreased. By looking at how much ORR activity improves for Pt in a more anhydrous environment would help explain the role different alloying metals play with Pt but also suggest new directions for new Pt based alloys, particularly in tailoring the electronic properties of Pt. This is also a chance to get preliminary information on how cathode catalysts will behave in elevated temperature fuel cells where the relative humidity is expected to be lower.

INTRODUCTION

The principle cause of the poor kinetics of the four-electron oxygen reduction reaction (ORR) can be attributed to the low exchange current density. Even with the current state of the art low Pt loading electrocatalysts, there is still a substantial high cathodic overpotential loss of ~ 220mV. This loss which appears even at open circuit potential (OCP) is attributed to a mixed potential at the cathode electrode.

In the late 1970’s and early 80’s, this issue was addressed with the approach of alloying Pt with other transition elements (see following reviews of the early efforts and references their in [1-3]). The early alloy development was targeted for Phosphoric Acid Fuel Cells (PAFCs) which differ from Proton Exchange Membrane Fuel Cells (PEMFCs) in the following ways: PAFCs operate at higher temperatures, the mechanism for proton conduction is different, the water content of the acid electrolyte is much lower than what is required for PEMFC system, oxygen solubility is much higher in the fluorinated PEMFC system, and the overpotential loss due to anion adsorption is substantial in the PAFC system. Mukerjee et. al.[4-6] was the first to show that many of the catalysts originally developed for the enhancement of ORR in the PAFC also showed improved ORR activity in the low temperature, fully hydrated PEMFC system. Watanabe et. al.[7, 8] have also shown that alloys prepared as thin films showed enhanced ORR activity.
Reasons that have been reported for the observed enhancement in ORR activity start with enhanced surface Pt features due to alloy leaching, changes in the surface structure of the Pt skin surface, particle size effect, changes in the short range atomic order (Pt-Pt bond distance), changes in the electronic states, particularly Pt, and the minimization/potential shift of PtOH formation. The more recent works have started to support the shift/minimization of PtOH formation as the rational for the improved ORR activity Pt alloys have shown. But following this rational of developing new Pt alloys to reduce or shift the potential of Pt hydroxyl formation may be a misleading direction for future catalyst development efforts.

In PAFC, the main source of surface poisoning was the phosphate anion. In the fully hydrated PEMFC, the source of Pt poisoning/ORR hindrance on the cathode side is the oxide layer that results from the oxidation of water over Pt.

\[
\text{H}_2\text{O} + \text{Pt} \rightarrow \text{Pt-OH}_{(\text{ads})} + \text{H}^+ + \text{e}^-
\]

Pt alloys have shown the ability to impede this process. The means by which this is achieved still needs to be further investigated. It could be purely the result of increasing the Pt 5d-band vacancy above a certain level or it could be attributed to the alloying metal that may lie below the surface of the Pt skin but yet has surface accessibility which may have a higher affinity for water than Pt (see Anderson's work on water binding energy). Paulus and Ross have also offered a speculation along this line citing solution chemistry and the "common ion" effect to explain that OH formation on the non Pt atoms could hinder the OH formation on Pt.

There is one trend that can be seen thus far in the list of actively studied alloys, which deserves further attention. This trend emanates from the order of increasing ORR activity reported by Mukerjee et al. (PtNi, PtCo, PtFe, PtCr). The reported order in improved ORR activity follows the reverse order for increasing Pt 5d-band vacancy which will be presented again in this work. Toda and Watanabe has also looked at changes in the electronic state of Pt and has proposed an ORR mechanism where in it is postulated that the Pt-O bond becomes stronger with increasing Pt 5d-band vacancy. As the Pt 5d-band vacancy increases, the ability of that metal to give up an electron also becomes more difficult. So looking back at the trend in ORR enhancement and d-band vacancy, it could be suggested that the reason why PtCr performs the best is: 1) there is minimal PtOH formation in the potential range of 0.7 to 1.0V, thus sufficient Pt sites and 2) the charge transfer process is not significantly impeded, as may be the case with PtNi which shows the least improvement in ORR activity and the large Pt 5d-band vacancy. Thus, the following question is posed: what would happen if the environmental water content or the activity of water around Pt were significantly reduced without causing any other detrimental effects to the electrolyte or any other transport properties which could impact the Oxygen Reduction Reaction?

The objective of this work is to evaluate the role Pt alloys play in a fully hydrated full cell; the specific focus being the minimization of the oxide layer, PtOH formation, that results from the oxidation of water in the 0.8 to 1.0 V range. If the main role of Pt
alloys is to change the electronic state of Pt so as to cause impediment of PtOH formation, then the ORR kinetics for Pt in an acid electrolyte will improve with decreasing the water content and/or water activity so long as the conductivity of the acid is still substantial, and the oxygen permeability (product of solubility and diffusion) is not significantly decreased. Water activity is not a major issue and does not necessarily need to be kept constant. The idea is to minimize the interaction water has with Pt thus decreasing the oxide layer that begins to form at 0.7V. By decreasing this pre-formed oxide layer, the ORR kinetics for Pt are expected to improve substantially.

EXPERIMENTAL

The following supported cathode designated catalysts were synthesized and evaluated for fuel cell performance, kinetics, electrochemical characteristics and electronic and structural properties: Pt, PtCo, PtCr, PtCoCr, PtNi, and PtFe. The catalyst loading on Cabot carbon Vulcan XC-72 was 20%. The cathode electrodes were fabricated using Single-Sided ELAT obtained from DeNora N.A. E-TEK Division at a medal loading of 0.4mg/cm². The anode electrode used was a commercially available 20% Pt/C with 0.4mg/cm² metal loading on Single-Sided ELAT obtained also from DeNora N.A. E-TEK Division. The MEAs with 5 cm² electrodes were fabricated with DuPont Nafion® 1135 membrane using a hot pressing technique.

Fuel cell testing was carried out on a home built multi-channel test station which used an Agilent Technology load bank and modules. Data acquisition was done with a home designed program which utilized LabVIEW™ software. For general screening purposes the fuel cells were run under oxygen or air on the cathode side and hydrogen on the anode side. The cathode/anode backpressures were 60/50 psig respectfully. The cells were operated at 85°C were the gasses were at 100% relative humidity. To ascertain kinetic information such as energy of activation, the temperature of the fuel cell was varied from 40°C to 90°C in 10°C increments. To obtain the reaction order, the fuel cell was kept at 85°C and the backpressure was varied from 5 to 1 atm in increments of 1 atm. After all fuel cell testing had been completed, cyclic voltammetry was performed on the fuel cells to obtain the electrochemical profile of the catalysts in the following manner.

The cathode was purged with N₂ to displace the O₂. Once the OCP had reached a potential of ~ 0.1V, the cathode electrode acted as the working electrode while the anode with H₂ still passing through doubled as the counter and reference electrode. The fuel cells were kept at 85°C with backpressures of 50 psig under 100% relative humidity. The cyclic voltammetry was performed using an Eco Chemie Auto Lab system.

X-ray Adsorption Spectroscopy (XAS) measurements were conducted at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) at the following beam lines: X11A, X18B and X23A2. Measurements were conducted at the Pt L₃ & L₂ edges and the K edge of the alloying elements. All of the experiments were conducted at room temperature in 1M HClO₄ in transmission mode. Details of the spectroelectrochemical cell, data acquisition, monochromator design & resolution and...
electrode preparation are described elsewhere\textsuperscript{4, 5}. Cyclic voltammetry and thus the potential control of the electrodes for the \textit{in-situ} XAS was done with an Eco Chemie Auto Lab system.

Rotating Disk Electrode experiments were conducted using a Pine Instrument Analytical Rotator and Eco Chemie Auto Lab system. A Pt plug electrode (0.283 cm\textsuperscript{2}) polished to a mirror finished with 0.05\mu m alumina acted as the working electrode with a Pt flag as the counter electrode. The reference electrode was a Reversible Hydrogen Electrode. The Trifluoromethane Sulfonic Acid was obtained from 3M Inc. and triply distilled under vacuum. The monohydrate (9.5M) was then prepared. The pure white crystalline material was re-crystallized two more times prior to the preparation of the 6M and 1M solutions used for this investigation. The solutions were first purged with N\textsubscript{2} and the electrode was cycled continuously until a clean reproducible Pt profile was obtained. The solutions were then purged with O\textsubscript{2} were the electrode was rotated at speeds of 400, 625, 900, 1225, 1600, & 2500 rpms. The potential sweep rate was 10mV/s. Oxygen permeability measurements of the electrolytes was also measured using a micro-electrode technique described else where.

RESULTS AND DISCUSSION

Electrocatalyst Specification & Characterization

One of the most powerful aspects of XANES analysis is the ability to determine the Pt 5\textit{d}-band vacancies. The Pt 5\textit{d}-band vacancies were determined by integrating the Pt L\textsubscript{3} and L\textsubscript{2} peak intensities of the XANES spectra which represent the 2p\textsubscript{3/2} and 2p\textsubscript{1/2} to 5d\textsubscript{3/2} transitions. The theoretical aspects and the methodology of this analysis are described else where\textsuperscript{4, 5}. Figure 1 shows that as the electro negativity of the alloying metal to Pt increases, the Pt-Pt bond distance decreases and the Pt 5\textit{d}-band vacancy increases. This is further exemplified in Figure 2 which shows that as the potential of the electrode is changed, the Pt 5\textit{d}-band vacancy does not significantly change for the alloys. The large change observed for Pt is attributed to the charge transfer process for PtOH formation. Thus, one would expect not to see a charge transfer process at 0.84V and possibly higher if the interaction of water with Pt is minimized and the Pt 5\textit{d}-band vacancy for a Pt catalyst would stay constant over a larger potential range and it would be smaller than those shown for the currently studied alloys. The more interesting question to answer would be: what would happen to the Pt 5\textit{d}-band vacancy in an anhydrous electrolyte that was saturated with oxygen? Table I is a summary of the electrocatalyst specifics. In addition to the Pt 5\textit{d}-band vacancies at 0.54V for the different catalysts, and the Pt-Pt bond distances, it can be seen that the particle size for all of the catalyst, determined by both XRD and XAS, are in the 3 nm range.

The catalysts that have been studied have been characterized by XAS to consist predominantly of a Pt skin. Figure 3a & 3b shows the XANES of PtNi taken at the Ni K edge for an acid washed catalyst and a non-washed catalyst. It can be seen for the non-washed sample that the Ni shows changes in the oxidation state as a function of potential. With washing the sample, all of the non-alloyed Ni is removed from the surface and the oxidation state of Ni is stable with change in the potential. To answer the question of...
whether or not the nickel has access to the surface and if a nickel oxide is formed due to the presence of water, XANES should be performed again on the two sets of catalyst in an electrolyte with low water content and that is deprived of oxygen. If the XANES of the Ni K edge does not change with change in water content of the electrolyte then Ni oxide formation due to water is not a factor to consider for ORR on Pt.

For some of the catalysts studied such as an acid washed PtCo, XAS has shown that the Pt and the Co are both stable at 0.9V for prolong periods of time (Figure 4a & 4b). Figure 4c shows the dissolution of Ru from PtRu with increasing potential. Alloy stability may be a function of synthesis methodology. Watanabe et. al.\textsuperscript{[13]} has shown the effects of ordered and disordered phases on supported catalyst stability. Alloy stability may also be a function of the alloying metal itself due to segregation energies\textsuperscript{[14, 15]} and whether it is present on the surface of the catalyst or in the bulk. It was observed in Paffett’s and Gottesfeld’s\textsuperscript{[16]} work which looked at changes in the cyclic voltammetry of bulk PtCr as the Cr is removed from the catalyst that with the removal of the Cr, there was an increase in the PtOH formation in addition to the hydrogen evolution features. This use of cyclic voltammetry applied to fuel cells would be a good means to monitor alloy stability over time. The removal of non-alloyed metals or surface metals may not necessarily show major changes in the cyclic voltammetry, particularly in the PtOH region but, the oxygen/hydrogen polarization curve would improve with the exposure of more Pt sites. This we have seen with other studied Pt alloys and will be the subject of future discussions. Only when the core alloy begins to breakdown, would the cyclic voltammetry of the alloy begin to show PtOH formation.

Steady State Polarization & Kinetics

Steady state polarization curves have been acquired for many Pt alloy cathode catalysts. Figure 5 represents a selection of iR corrected Tafel plots taken from fuel cell data. Relative to Pt, it can be seen that there is a significant improvement in ORR activity for PtCo and PtCr with the later being the best. This trend has also been observed in other reports\textsuperscript{[4-11]} which include data not shown here. Table II shows a summary of the results presented in Figure 5. All of the results are comparable because the catalyst utilization for all of the studies has been a consistent 50%. The catalyst utilization was determined by the hydrogen desorption and also by the hydrogen adsorption peaks from the fuel cell cyclic voltamgrams. The significant decrease in the energy of activation for all of the Pt alloys is attributed to the decrease in PtOH formation which can be observed via cyclic voltammetry and re-affirmed by XAS as shown in Figures 6a & 6b. Even though the energy of activation for ORR is decreased for all of the Pt alloys, the reaction order does not change because the reduction of oxygen is still taking place on Pt sites and the means by which the reaction occurs has not changed. What has been achieved with Pt alloys is the creation of more Pt sites by the minimization of the oxide layer attributed to PtOH formation and the possibility of the Pt hydroxyl groups from interfering with the ORR process. This may be related to a statement by Yeager et. al.\textsuperscript{[17]} suggesting that O\textsubscript{2} adsorption will increase with a decrease in the dielectric constant of the interface. This statement was in reference to the use of additives and the formation of a self-assembled film in the PAFC system.
The ternary alloy PtCoCr represents a case in which the electronic properties of the Pt would suggest that the performance should be closer to that of PtCr (Figure 2). The performance of the ternary although resembled that of PtCo but was found not to be as good at larger current densities. Part of the reason why the ternary behaved the way it did may be due in part to observations that the Cr was not that well alloyed. The Co was found to be well alloyed. The instability of the Cr was the primary reason why the alloy composition could not be soundly confirmed via XAS and reported in Table II. In addition to what Watanabe et. al. have shown, the ternary alloy may be another example of the role synthesis methodology and composition may play in acquiring top performing Pt alloys. It may also hint at new variables such as new segregation energies that arise from a ternary system that may not otherwise be present in the individual binary systems. The presence and instability of the Cr on/near the surface and possible resulting Cr-oxides may have also increased the dielectric constant of the surface, thus decreasing the adsorption of O₂ to the surface.

In the past a relationship has been demonstrated correlating current density with Pt-Pt bond distance and Pt 5 d-band vacancies. This type of relationship does not separate out principle reasons for why certain Pt alloys perform better than others. This issue is only more complicated by the notion that Pt alloys involving first row transition metals show a minimization/disappearance/shift in PtOH formation in the 0.85V region. The relationship does not afford the room to say that the principle reason for the improved ORR observed from Pt-alloys involving first row transition metals is primarily due to the impingement of PtOH formation in the potential range of 0.7 to 1.0V. Thus it could be inferred that if the environmental water content could be controlled/minimized, or the activity of the surrounding water decreased, with out consequence to other aspects such as proton conduction and resistance as demonstrated by Uribe and Gottesfeld, the Oxygen Reduction Reaction on Pt could show significant improvement. It may even be shown that Pt could out perform any currently studied alloy. This type of result would suggest that the Pt 5 d-band vacancy plays a more significant role in ORR than the Pt-Pt bond distance where the later may be a consequence of the electronic state changes in Pt due to alloying. This would also indicate that the parameter that needs to be controlled for improving cathodic overpotential loss is to minimize the Pt oxide layer that results from the oxidation of water but without increasing the Pt 5 d-band vacancies because of consequence to the electron charge transfer steps.

Rotating Disk Electrode

Novak and Conway have looked at the oxide formation on Pt as a function of water content. They showed that as the water content in trifluoroacetic acid was decreased the oxide film growth due to the oxidation of water also decreased. Even with increasing the time held at the anodic end potential, the oxide film still decreased with less water present in the electrolyte. The anhydrous electrolyte showed no PtOH formation or oxide reduction features attributable to an oxide layer. This result was analogous to what has been observed for Pt alloys in a fully hydrated full cell and in 1M HClO₄ using cyclic voltammetry and XAS (Figures 6a & 6b).
To the best of our knowledge, no one has published results specifically looking at the water content effect on ORR for Pt in the absence of Nafion® and without attributing ORR enhancement to the addition of surfactants to the electrolyte or catalyst. Inferences have been made but never specifically shown. Groups such as Yeager's²⁰ have used the term “dry cave” but this normally referred to the use of perfluorinated additives in phosphoric acid to increased O₂ solubility in the electrolyte and at the electrode surface because of the physical adsorption seen by the additive to the catalyst. As a consequence one can also infer the impingement of water to the reaction site because of the hydrophobicity of the additives but also because the adsorbed layer could lead to size restrictions for water and other acid anions as demonstrated by Collman, Durant, Anson et. al.²¹,²² in their porphyrin work. Other works which look at the use of surfactants²³,²⁴ allude to the creation of a hydrophobic shell and increased O₂ solubility to the catalyst surface but show more evidence for decreased anion adsorption.

Figure 7a shows the current density / cell potential results for a Pt plug electrode in 1M and 6M TFMSA. In the potential range of 0.6 to 0.8V, it can be seen that the currents increase faster for the 6M TFMSA case compared to the 1M TFMSA case. This type of trend has also been observed in fuel cell polarization curves when comparing Pt to Pt alloys in the low current density region and this is also clearly shown in the iR corrected Tafel plots of Figure 5. The reason why the diffusion limiting currents for 6M TFMSA are not larger is attributed to the low oxygen permeability which is the product of oxygen solubility and diffusion. Oxygen permeability results were obtain via micro-electrode technique and are reported in Table III.

Figure 7b shows the Tafel plots that were generated from the initial RDE data. The 1M TFMSA case showed a classic two Tafel slope behavior (59 mV/dec & 112 mV/dec). The 6M TFMSA case showed only one Tafel slope. This 110 mV/dec slope which spans both the high over potential and low over potential ranges is analogous to a Pt surface that is free of adsorbed species, mainly the oxide layer which are formed in the low over potential range because of the oxidation of water over Pt. These results coincide with the cyclic voltamograms shown by Novak and Conway¹⁹ which showed that as the water content of the acid electrolyte is decreased, and/or as the activity of water is decreased, so is the adsorbed oxide layer due to the oxidation of water on Pt to PtOH.

Table III summarizes the kinetic information found for the RDE experiment of a Pt plug in 1M and 6M TFMSA. In addition to Tafel slopes and oxygen permeability results, it can be seen that the kinetic current at given potentials is much higher for the 6M TFMSA case than the 1M TFMSA case. Also the exchange current density is at least a factor of 1000 greater in 6M TFMSA than in 1M TFMSA.

Based on the earlier discussion that revolved around the strong influence the Pt 5 d-band vacancies could play in the Oxygen Reduction Reaction, particularly when trying to understand why some Pt alloys perform better than others, the improvement seen in the ORR for the Pt plug going from 1M to 6M TFMSA suggests that as the water content of the electrolyte media is decreased and the more filled the Pt 5 d-band vacancy is the
CONCLUSION

We have focused on the shift/minimization of PtOH formation that has been observed with Pt alloys in a fully hydrated fuel cell and mimicked this phenomenon for Pt in an acid electrolyte by decreasing the water content. The result of decreasing the water content on the oxygen reduction kinetics for Pt was significant. Only one Tafel slope of 110mV/dec could be found, the kinetic currents at 0.8V and 0.7V were nearly doubled, and the exchange current density was a factor of 1000 higher for the 6M TFMSA compared to the 1M TFMSA. In observing the improved ORR activity for Pt in electrolytes with different water contents suggests that the primary achievement gained with the current Pt alloys is the minimization/shift in oxide formation due to the oxidation of water over Pt. This is achieved by increasing the Pt 5 d-band vacancy above a certain level. By decreasing the ability of Pt to oxidize water a penalty is incurred. This sacrifice is a decrease in the charge transfer process necessary for greater enhancement in ORR activity. The results of this work suggest the following new directions for fuel cell research.

The development of new membranes and/or fuel cell operating systems should focus on decreasing either the relative humidity and/or the amount of water necessary for proton conduction or the activity of water. With the achievement of this Pt may surpass the best Pt alloy currently available. The new direction for catalyst development would then be to develop Pt alloys with a lower Pt 5 d-band vacancy.

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Change in d-band vacancy with electrode potentials

Figure 1. Pt d-band vacancy vs. Pt-Pt bond distance

Figure 2. Pt d-band vacancy vs. Cell potential

| Electro catalyst | Pt d-band vacancy/atom @ 0.54 V (XANES) | Atomic Ratio (a/o) (XANES) | Pt-Pt bond distance (Å) | CN (Pt) (from EXAFS) @ 0.54 V (first shell) | Particle Size (Å) | XRD (line broadening) | EXAFS @ 0.54 V |
|------------------|----------------------------------------|----------------------------|------------------------|---------------------------------------------|------------------|-------------------------|----------------|
| Pt/C             | 0.329                                  |                            | 2.77                   | 10.05                                       | 25               | 27                      |                |
| PtCr/C           | 0.360                                  | 74/26                      | 2.74                   | 10.48                                       | 32               | 33                      |                |
| PtCo/C           | 0.401                                  | 72/28                      | 2.72                   | 10.67                                       | 36               | 35                      |                |
| PtCoCr/C         | 0.372                                  |                            | 2.72                   | 10.85                                       | 35               | 42                      |                |
Figure 3a. XANES of acid washed PtNi/C at Ni K edge

Figure 3b. XANES of non acid washed PtNi/C at Ni K edge

Figure 4a. XANES of PtCo at Pt L3 edge polarized at 0.9V

Figure 4b. XANES of PtCo at Co K edge polarized at 0.9V

Figure 4c. XANES of PtRu at Ru K edge

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Figure 6a. Cyclic voltammograms of Pt and PtCo in fully hydrated fuel cells

Figure 6b. Fourier transforms of Pt @ 0.54V & 0.84V showing PtOH formation and PtCo @ 0.54V & 0.84V showing no change and no Pt oxide formation

Table II. Summary of kinetic data from fuel cell polarization curves

| Material   | $E_0$ (V) | b (mV/dec) | R ($\Omega \text{ cm}^2$) | $i_0$ ($10^9$ A cm$^{-2}$) | $i_{100 \text{mA/cm}^2}$ (mA cm$^{-2}$) | Roughness Factor (cm$^2$/cm$^2$) | Utilization (%) | $E_{ \Delta} \text{ f} \text{ u} \text{l} $ (kJ/mol) | Reaction Order |
|------------|-----------|----------|-----------------|----------------------------|-----------------------------------|--------------------------------|----------------|-----------------|----------------|
| Pt         | 1.064     | 72.85    | 0.2             | 26.39                      | 182                               | 0.918                          | 182            | 45.45%          | 62.17          | 0.96       |
| PtCoCr     | 1.06      | 65.87    | 0.2             | 15.61                      | 270                               | 0.93                           | 136            | 48.70%          | 20.14          | 1.04       |
| PtCo       | 1.071     | 68.97    | 0.2             | 27.17                      | 300                               | 0.635                          | 180            | 51.43%          | 29.59          | 0.785      |
| PtCr/C     | 1.095     | 65.45    | 0.18            | 34.5                       | 680                               | 0.953                          | 180            | 51.40%          | 29.18          | 1.028      |
Figure 7a. I-V curves of Pt plug in oxygen saturated 1M & 6M TFMSA @ different rotational speeds

Figure 7b. Tafel plots of Pt plug in oxygen saturated 1M & 6M TFMSA @ 1225 rpm

|        | $I_k$ @ 0.8V (mA/cm²) | $I_k$ @ 0.7V (mA/cm²) | $b_{f.o.p.}$ (mV/dec) | $b_{h.o.p.}$ (mV/dec) | $I_p \times 10^{-6}$ (mol/cc) | $C \times 10^{-6}$ (mol/cc) | $D \times 10^{-6}$ (cm²/s) | $CD \times 10^{-12}$ (mol/cm s) |
|--------|-----------------------|-----------------------|-----------------------|-----------------------|-------------------------------|-------------------------------|-----------------------------|---------------------------------|
| 1M TFMSA | 0.076                 | 0.425                 | 59                    | 112                   | 0.056                         | 0.63                          | 9.68                        | 6.09                            |
| 6M TFMSA | 0.114                 | 0.884                 | 110                   | 26                    | 6.88                          | 0.29                          | 2.00                        |                                 |

Table III. Summary of kinetic data for Pt plug in 1M & 6M TFMSA. Oxygen permeability also included.