



Measurement of Platinum Oxide Coverage in a Proton Exchange Membrane Fuel Cell

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We report results from coulometric measurements of the oxide coverage on dispersed platinum (Pt) as a function of potential in an O₂-free but otherwise normal H₂/air fuel cell cathode environment (0.6–0.9 V_{RHE}, 80°C, 100% relative humidity). The Pt oxide is thus limited to that formed from H₂O and provides a lower bound of the oxide present in an operating fuel cell in which O₂ is present. We found that the oxide coverage does not depend on previous exposure to gas-phase O₂, indicating that the Pt oxide formation reactions are reversible within the experimental parameter space. The results are in excellent agreement with a previously published fundamental model.

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In proton exchange membrane (PEM) fuel cells, the oxygen reduction reaction (ORR) occurs in a potential range where the platinum (Pt) surface is partially oxidized, and ORR kinetic expressions have been developed that are both engineering^{1,2} and mechanistic^{3,4} in form. The latter are characterized by attempts to explicitly consider the impact or role of Pt oxide, which itself can exist in a variety of forms (e.g., OH, O, strongly or weakly bonded). These oxides can form either from water or gas-phase oxygen and affect the ORR rate primarily as intermediates^{3,4} or poisons.^{5,6} Furthermore, the formation and reduction of Pt oxide are known to be very sluggish and perhaps irreversible.^{7,8} Thus, it is not surprising that detailed mechanisms for ORR are still a fertile research area, because the surface state under operation is poorly understood. In situ X-ray absorption spectroscopy^{9,10} and X-ray photoelectron spectroscopy¹¹ allow the study of the oxide as a function of potential, but further work is needed to establish these as species-specific (e.g., O vs OH) and quantitative techniques.

As a limiting case, the system can be simplified by removing the O₂ and studying only the equilibrium associated with H₂O, N₂, and potential. The Pt oxide formation thus requires water as a reactant and depends on the electrode potential



For coverage calculations, we assume in this study with potentials of ≤ 0.9 V_{RHE} [vs reversible hydrogen electrode (RHE)] that PtOH, requiring only one electron transfer and the simplest Pt oxide, is the primary surface species. We use coulometry to determine the amount of charge required to reduce the Pt oxide as a function of electrode potential, as was done in earlier studies at 25°C (Paik et al.¹²) and 100°C (Xu et al.¹³). In those efforts, exposure to O₂ was observed to have a long-lasting impact on the surface oxide coverage of an electrode held at constant potential, persisting even 2.5 h after purging the cathode with N₂. This is an important result because, if true, it implies that accurate ORR kinetics would need to explicitly comprehend Pt oxide kinetics and electrode history, outside the scope of existing kinetics expressions, as discussed by Gottesfeld.¹⁴

In this work, we sought to carefully measure the equilibrium oxide coverage at 80°C from 0.6 to 0.9 V_{RHE}, typical fuel cell electrode operating conditions. Additionally, we maintained the electrode potential at an IR-free value during the O₂ exposures; controlling the measured electrode potential would have lifted the IR-free potential more positive during current passage, driving additional surface oxidation. Whereas this is not a major issue at high potentials (> 0.85 V_{RHE}) when the current is small, it is required to allow accurate measurements at potentials < 0.85 V_{RHE}.

Experimental

The 5 cm² active area membrane electrode assembly was fabricated with 50 wt % Pt dispersed on a Vulcan XC72 (Pt/Vulcan) catalyst (TKK, Japan) and a DE2021 ionomer (DuPont, USA) by hot pressing electrode decals onto a 50 μm thick 1050-EW Nafion membrane (DuPont, USA). The respective cathode/anode Pt loadings were 0.4/0.4 mg_{Pt}/cm², and with ionomer to carbon weight ratios of 1/1. The anode and cathode diffusion media were SGL 25BC.

We used separate mass flow controllers (MFCs) and humidifiers for N₂- and O₂-containing gases, as shown in Fig. 1. Transitioning from a N₂ environment to an O₂ environment required only the switching of a four-way valve and eliminated humidifier purge and manifold dead zone issues from the transition time that were experimental issues in earlier work.^{12,13,15} The experiments were conducted at 80°C, 150 kPa_{abs}, and 100% relative humidity (RH).

The cell was preconditioned for 1 h at open circuit (~ 0.1 V_{RHE}) in 10% H₂ (in N₂) on the anode and N₂ on the cathode with a flow rate of 2000 sccm on both sides. Potentials (0.565–0.865 V_{cell}, 0.6–0.9 V_{RHE}, 50 mV increments) were applied and held for a total of 45 min for each case. The current was then noted, representing the H₂ oxidation current limited by the membrane H₂-permeation rate. The maximum H₂-permeation limiting current under these conditions, ~ 0.15 mA/cm², represented a small baseline correction relative to the Pt oxide reduction current during the subsequent cyclic voltammograms (CVs).

At the end of the 45 min potential hold, the N₂ flow rate was decreased to 100 sccm to minimize artifacts in the Pt-hydride region of the subsequent CV because of excessive N₂ flow rate on the cathode.^{16,17} After 2 min, CVs (Gamry G750) were collected by cathodically scanning from the holding potential at 20 mV/s down to 0.05 V followed by three cyclic sweeps with potential ranging from 0.05 to 0.6 V_{RHE}. Integration relative to baseline was then done to quantify the charge required to reduce the oxide.

Three additional sets of experiments were also done, each involving exposure to different gas-phase O₂ concentrations. Electrode preconditioning for 1 h at open circuit as described above was followed by potential hold (0.65, 0.7, 0.75, 0.8, 0.85, and 0.9 V_{RHE}) for 5 min for each case. Then N₂ was switched to 2000 sccm air, 50% O₂ in N₂, or 100% O₂ (dry, concentrations before humidification) for 30 min while holding constant the electrode high frequency resistance (HFR) corrected voltage. This was done using a total cell potential control algorithm that relied on current density and 1 kHz HFR measurements; the algorithm was implemented in Labview and updated the electrode potential set point every second. We estimated the potential drop in the cathode electrolyte to be only 11 mV at the highest current density in pure O₂,¹⁸ and no correction was made for this. After 30 min of O₂ exposure, 2000 sccm N₂ was then switched back into the cathode compartment for 10 min of purging while

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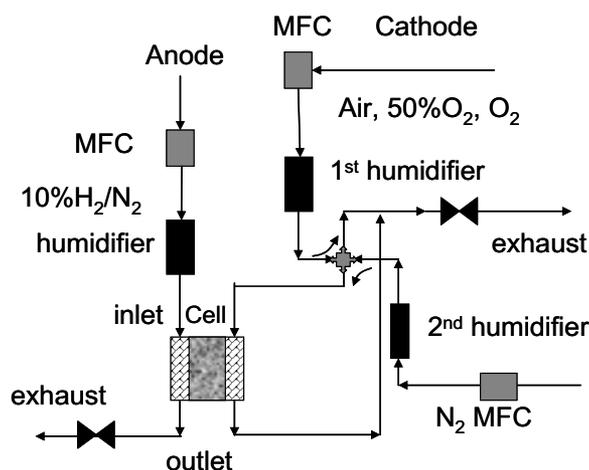


Figure 1. Experimental setup for MFCs and humidifiers. Cathode side was equipped with two separate inlet streams and a four-way valve to minimize $N_2 \rightarrow O_2 \rightarrow N_2$ turnover times.

maintaining the potential hold. Then, the N_2 flow rate was reduced to 100 sccm, and 2 min later the potential was cathodically scanned at 20 mV/s to 0.05 V_{RHE} , yielding the current signal needed to quantify the oxide reduction charge, followed by three CVs (0.05–0.6 V_{RHE}).

The charge required to reduce the oxide for each experiment was converted to surface coverage assuming that the oxide comprised PtOH and required a reduction charge of 210 $\mu C/cm^2_{Pt}$. The Pt surface area, needed to translate the PtOH amount to fractional coverage, was determined as the average of two PtH coverage measurements taken before and after each of the four experimental sets. This was done on the same cell but with a different test apparatus and conditions (30°C, 100% RH with 200/50 sccm H_2/N_2 flow rates, and 210 $\mu C/cm^2_{Pt}$) to minimize experimental artifacts.^{16,17} Measured values varied from 40 to 45 m^2/g_{Pt} .

We reported results from similar experiments in Ref. 15 but in this work we used 10% H_2 in N_2 on the anode and 50 μm membrane vs 100% H_2 and 125 μm membrane in the earlier study. These changes decreased membrane dryout in the low voltage O_2 experiments while also decreasing the H_2 -permeation current, improving the signal-to-baseline ratio. The results reported in this article, within 20% of those reported earlier, are more accurate because of these subsequent experimental improvements.

Results and Discussion

Figure 2 shows the CVs and integration baseline obtained in a H_2/N_2 cell with initial holding potentials ranging from 0.6 to 0.9 V_{RHE} at 80°C, 150 kPa_{abs}, and 100% RH. The charge required to reduce the Pt oxide strongly depends on the potential, decreasing from maximum at 0.9 V_{RHE} down to very little at 0.6 V_{RHE} . The charge passed to reduce the Pt oxide was integrated relative to the integration baseline over the potential range from the initial holding potential down to 0.35 V_{RHE} .

Figure 3 shows the CVs collected after holding at a potential of 0.85 V_{RHE} for the various exposure cases, along with the integration baseline. Unlike earlier studies^{12,13} no impact of the O_2 exposure is observed. Figure 4 shows actual time traces for the 100% O_2 exposure experiment at 0.85 V_{RHE} : (i) initial potential hold in N_2 for 5 min, (ii) exposure to O_2 for 30 min, producing a current of 0.13–0.2 A/cm^2 , (iii) return to N_2 , hold for 10 min, and (iv) collection of CVs to reduce the oxide (not shown in this plot). During the O_2 exposure, the electrode voltage was controlled to as low as 0.827 V_{RHE} to compensate for the 0.023 V IR drop. Had this not been done, the electrode potential during the O_2 exposure would have been driven higher than 0.85 V_{RHE} by about 23 mV. The maxi-

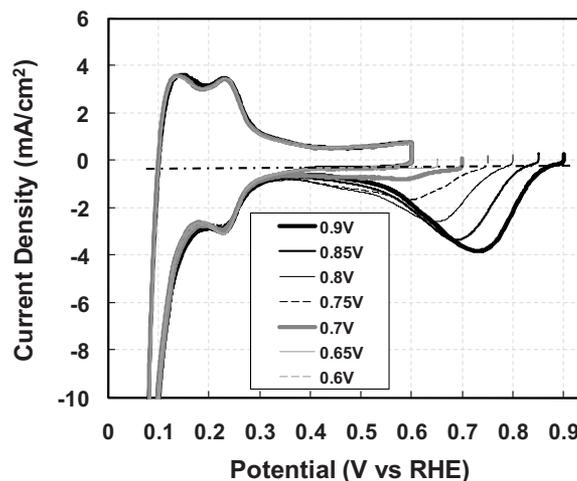


Figure 2. CVs obtained in a cell with 10% H_2 in N_2 on anode and N_2 on cathode at 80°C, 150 kPa_{abs}, and 100% RH with different initial hold potentials for 45 min (0.6–0.9 V vs RHE). The dashed-dotted line represents the charge integration baseline.

mum IR correction in this experimental set, for 0.65 V_{RHE} and pure O_2 , was over 0.250 V. Figure 4 also shows that current density drops during the 30 min hold time; this was presumably due to slowly increasing Pt oxide growth, subsequently removed during the 10 min N_2 hold before coulometry.

To further confirm the oxide reversibility and investigate the sensitivity of the results to IR correction, we also conducted the 100% O_2 exposure, 0.6 and 0.85 V_{RHE} hold experiments without using IR correction. The same results were obtained in these cases, indicating that any formation of oxide due to the exposure of the electrode to the higher IR-free potential was reversibly removed within 10 min when the electrode was returned to the N_2 environment.

Figure 5 shows the calculated PtOH coverages as a function of potential ranging from 0.6 to 0.9 V_{RHE} , with exposure to O_2 at various concentrations. The results indicate that exposure to O_2 had no contribution to the Pt surface oxide coverage after subsequent N_2 exposure. Figure 5 also includes the result of the kinetics model provided by Darling and Meyers¹⁹ assuming PtOH formation rather than PtO formation as used in that work. This equilibrium case of

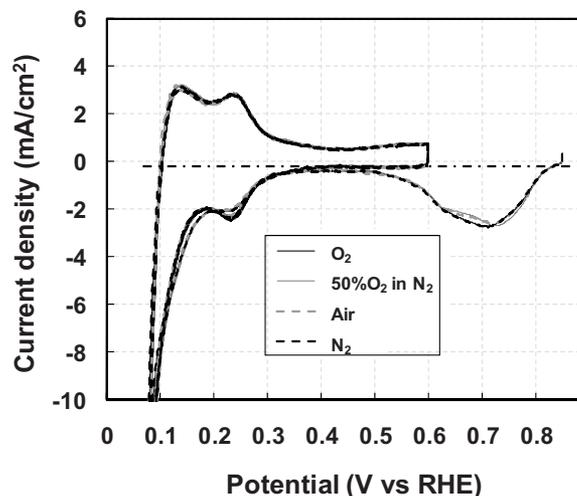


Figure 3. CVs with initial potential hold at an HFR-corrected potential of 0.85 V_{RHE} after exposure to N_2 , air, 50% O_2 , and O_2 for 30 min, respectively, at 80°C, 100% RH, 150 kPa_{abs}. The dashed-dotted line represents the charge integration baseline.

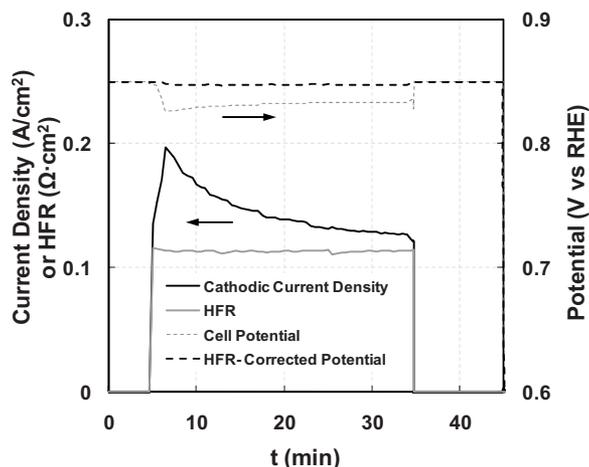


Figure 4. Current density, HFR, cell potential, and HFR-corrected voltage as a function of time at an initial applied potential of $0.85 V_{\text{RHE}}$ with exposure to N_2 for 5 min, then 30 min exposure to 100% O_2 , followed by 10 min N_2 purging at 80°C , 100% RH, and $150 \text{ kPa}_{\text{abs}}$. Dashed curves represent potential, and solid curves represent current density and HFR, respectively.

the model with no adjusted parameters provides an excellent fit to the data. Figure 5 indicates that the PtOH coverage actually exceeds 1 at $>0.85 V_{\text{RHE}}$. In fact, some PtO likely forms in this potential region, requiring two electrons per Pt site, such that the surface coverage remains less than unity. At potentials $>1 V_{\text{RHE}}$, it is well known that place exchange can occur and the Pt oxide coverage can thus exceed one.²⁰

The dependence of the oxide coverage on potential and not on previous O_2 exposure indicates the reversibility of the oxide formed during the gas-phase O_2 exposure, in contrast to earlier results.^{12,13} The difference in setup that most likely explains this is the use of a single manifold and humidifier system in previous studies that may have led to residual O_2 present in the N_2 stream even 2.5 h after the

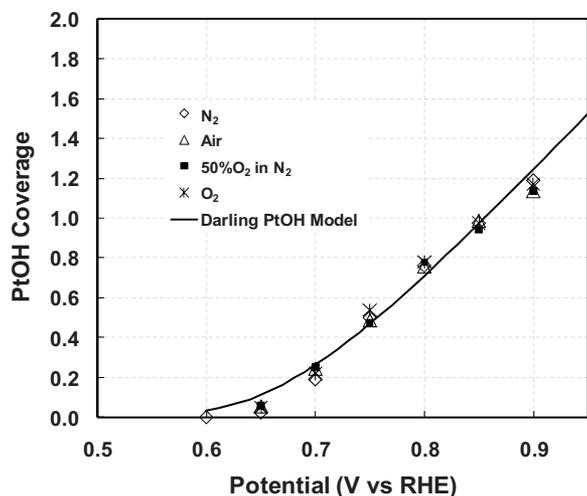


Figure 5. Comparison of PtOH coverage predicted by the Darling–Meyers model¹⁹ with measured PtOH coverage as a function of potential at 80°C , $150 \text{ kPa}_{\text{abs}}$, and 100% RH, for various gas exposures. The anode gas was 10% H_2 in N_2 .

switch over to N_2 . Our previous work also used a setup with a single humidifier¹⁵ and we observed, using open-circuit voltage as a marker, that as much as 4 h were required to eliminate the residual O_2 . The temperature differences may also be a factor; the oxide reduction kinetics may be quite slow at 25°C ,¹² and the oxide formed at 100°C may have been more robust than that formed at 80°C .¹³ The use of IR-free potential control is thought not to be responsible for the variation in results; we showed in this work that this factor made little difference as long as the electrode was returned to N_2 for at least 10 min to allow the system to return to equilibrium.

Conclusion

At 80°C and 100% RH, the equilibrium Pt oxide coverage in a PEM fuel cell grows monotonically from zero at $0.6 V_{\text{RHE}}$, close to the lowest voltage expected in an operating H_2 /air fuel cell, to an amount sufficient to completely cover the Pt with a monolayer of platinum hydroxide at $0.9 V_{\text{RHE}}$, close to the fuel cell open-circuit potential. The amount of Pt oxide did not depend on previous exposure to O_2 , indicating the reversibility of any oxidized species generated in the presence of gas-phase O_2 . The study demonstrates the importance of understanding the role of Pt oxide on the ORR kinetics, and it provides a methodology useful for screening ORR catalysts.

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