Hydrogen Peroxide Formation Rates in a PEMFC Anode and Cathode

Effect of Humidity and Temperature

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Hydrogen peroxide (H₂O₂) formation rates in a proton exchange membrane fuel cell (PEMFC) anode and cathode were estimated as a function of humidity and temperature by studying the oxygen reduction reaction (ORR) on a rotating ring disk electrode. Fuel cell conditions were replicated by depositing a film of Pt/Vulcan XC-72 catalyst onto the disk and by varying the temperature, dissolved O₂ concentration, and the acidity levels in hydrochloric acid (HClO₄). The HClO₄ acidity was correlated to ionomer water activity and hence fuel cell humidity. The H₂O₂ formation rates showed a linear dependence on oxygen concentration and square dependence on water activity. The H₂O₂ selectivity in ORR was independent of oxygen concentration but increased with the decrease in water activity (i.e., decreased humidity). Potential dependent activation energy for the H₂O₂ formation reaction was estimated from data obtained at different temperatures.

Proton exchange membrane fuel cell (PEMFC) technology, owing to its high efficiency, operational flexibility, and superior modularity, has the capability to be the structural and fundamental unit of an impending hydrogen economy. Two main issues that impede its progress toward commercialization are cost and durability. The U.S. Department of Energy’s (DOE) projected performance requirements for the year 2010 are 5000 h (with 20,000 start/stops) at $45/kW for automotive stacks and upwards of 40,000 h at $400–$750/kW for stationary power plants. In addition, current engineering requirements demand stack operation at higher temperatures ($400–750/°F$) and low relative humidities ($<75/\%$ RH). Elevated temperature operation offers better tolerance to CO, faster oxygen reduction reaction (ORR) kinetics, and better water and thermal management enabling easier system integration. However, elevated temperatures and the desire to operate at ambient pressures means the fuel cell needs to be operated at lower relative humidities. Since much of the ionomer and membrane technologies have evolved around the water dependent perfluorinated systems such as Nafion, both high temperature and low humidity conditions cause severe performance degradation and remain an impediment toward achieving DOE’s performance and durability targets.

One of the mechanisms for catalyst/ionomer chemical degradation in PEMFCs involves the formation of hydroxyl and hydroperoxyl (OH⁻ and OO⁻) radicals caused by hydrogen peroxide (H₂O₂) formation on the catalyst surface via Reaction 1:

\[ \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad E^0 = 0.695 \text{ V vs SHE} \quad [1] \]

and subsequent decomposition via Reactions 2 and 3. Using a novel in situ spin trap electron paramagnetic resonance study, Panchenko et al. reported no evidence of OH⁻ and OO⁻ radicals in the anode. They observed the presence of radicals in the cathode and near the membrane-cathode interface. Therefore, the H₂O₂ diffuses into the membrane and chemically breaks down to hydroxyl radicals and ions on metal ions present in the membrane:

\[ \text{H}_2\text{O}_2 + \text{M}^{3+} \rightarrow \text{M}^{3+} + \text{OH}^- + \text{OH}^- \quad [2] \]

\[ \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{OOH}^- + \text{H}_2\text{O} \quad [3] \]

These radicals react with the perfluorosulfonic acid type ionomer in the electrode and the membrane to produce hydrofluoric acid (HF). The sequence is listed below:

\[ R_p - \text{CF}_2\text{COOH} + \text{OH}^- \rightarrow R_p - \text{CF}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad [4] \]

\[ 2R_p - \text{CF}_2 + 2\text{OH}^- \rightarrow R_p - \text{CF}_2\text{OH} + R_p - \text{COF} + \text{HF} \quad [5] \]

\[ R_p - \text{COF} + \text{H}_2\text{O} \rightarrow R_p - \text{COOH} + \text{HF} \quad [6] \]

The fluoride emission rate is a measure of membrane degradation given in Eq. 5 and 6. Since two-thirds of Nafion is fluorine (on a mass basis), this chemical degradation results in mechanical instability in the membranes causing pinholes and eventual failure. Since this degradation is initiated by the peroxide-radical attack, understanding H₂O₂ kinetics at the electrocatalyst/ionomer interface at low humidities and elevated temperatures from a PEM fuel cell context is vital toward explaining the increased degradation rate observed under such conditions. Though Liu and Zackerbrod have reported a method for in situ detection of H₂O₂ formation, it only served as a qualitative indicator of the existence of peroxide. In situ quantification of peroxide kinetics is very difficult owing to its instability.

Rotating ring disk electrode (RRDE) studies on supported Pt catalysts have been successfully used as a technique to quantify peroxide formation and for screening oxygen reduction catalysts. Paulus et al. reported the use of a thin-film RRDE method for characterizing oxygen reduction reaction (ORR) in supported high surface area catalysts and were able to quantify the amount of H₂O₂ produced during the ORR. They decreased the film thickness and improved the ionomer-catalyst film stability at higher rotation speeds, which resulted in uniform collection efficiencies and better peroxide measurements. Antoine and Durand reported a weak platinum particle size effect on H₂O₂ production during ORR and agreed with previously reported observations that H₂O₂ yields were higher for potentials less than 0.4 V vs the standard hydrogen electrode (SHE). Enayettullah et al. studied ORR electrocatalysis on polycrystalline Pt microelectrodes in various concentrations of trifluoromethane sulfonic acid (TFMSA). They reported higher Tafel slopes and lower activation energies for ORR in higher concentrations of TFMSA, which was attributed to lower water activity. Murthi et al. studied ORR in supported Pt and Pt alloy catalysts in a 1 M and 6 M TFMSA as a way to study the effect of water activity. They reported higher peroxide yields in 6 M TFMSA solution compared to a 1 M solution. However, none of these studies correlate...
the measured peroxide yields and selectivity to peroxide formation rates in a PEM fuel cell as a function of cell operating conditions.

Therefore, the objective of this investigation was to predict H₂O₂ formation rates in a PEM fuel cell. This was accomplished by measuring H₂O₂ formation rates at rotating ring disk electrode (RRDE). Fuel cell conditions were replicated by depositing a film of Pt/ Vulcan XC-72 catalyst onto the disk and by varying the temperature, dissolved O₂ concentration, and the acidity levels in HClO₄. The HClO₄ acidity was correlated to ionomer water activity and hence fuel cell humidity. Peroxide formation rate in the anode was predicted using oxygen permeability measured across Nafion 112 membrane and the fraction of oxygen that reduces the H₂O₂. Peroxide formation rate in the cathode was predicted using the rate constants measured from RRDE experiments and the local concentrations of oxygen and protons.

Experimental

Rotating ring disk electrode (RRDE).— For the RRDE studies, commercially available Pt/Vulcan catalyst (20% Pt on Vulcan XC-72R carbon, Johnson Matthey Inc., West Chester, PA) was used. Catalyst coated glassy carbon electrodes were prepared as described by Schmidt et al.22 Aqueous suspensions of 1 mg catalyst mL⁻¹ were obtained by pulse-sonicating 20 mg Pt/Vulcan catalyst with 20 mL triple-distilled, ultrapure water (Millipore Corp.) in an ice bath (70% duty cycle, 60 W, 15 min). Sonication was done using a Braun-Sonic U type 8530/1 sonicator. A glassy carbon disk served as the substrate for the supported catalyst and was polished to a mirror finish (0.05 μm deagglomerated alumina, Buehler) prior to catalyst coating. An aliquot of 14 μL catalyst suspension was pipetted onto the carbon substrate, which corresponded to a Pt loading of ~14.1 μg Pt cm⁻². After evaporation of water for 30 min in N₂ atmosphere (381 mm Hg, vacuum), 14 μL of diluted Nafion solution (5% aqueous solution, 1100 EW; Solution Technology Inc., Mendenhall, PA) was pipetted on the electrode surface and further evaporated for 30 min in N₂ atmosphere (381 mm Hg, vacuum). Nafion was used to adhere the Pt/Vulcan particles onto the glassy carbon electrode (the ratio of H₂O/Nafion solution used was ~100/1). Previous work by Paulus et al. indicates that this procedure yielded a Nafion film thickness of ~0.1 μm and that the utilization of the Pt/Vulcan catalyst (based on H-adsorption charge) on the electrode with this film was ~100%.

The catalyst-Nafion coated electrode was immersed in deaerated [ultrahigh purity (UHP) nitrogen, Praxair] perchloric acid (HClO₄, 70% ULTREX II ultrapure reagent grade, J. T. Baker) of various concentrations for further synchronized chronoamperometric and potentiodynamic experiments. Though a variety of supporting electrolytes are reported in the literature, anion adsorption on Pt is minimal for only a few electrolytes,23 [e.g., trilfluoromethane sulfonic acid (TFMSA) and HClO₄]. In addition, the ultrapure reagent grade HClO₄ used in this study is free of ionic impurities; especially since Cl⁻ ions, even in trace amounts (i.e., 1 ppm), are shown to drastically change both the activity and the reaction pathway of ORR on Pt catalysts.23,24 All RRDE experiments were performed at atmospheric pressure and all solutions were prepared from ultrapure water (Millipore Inc., 18.2 MΩ cm). The electrochemical measurements were conducted in a standard electrochemical cell (RDE Cell, Pine Instrument Company, Rayleigh, NC) immersed in a custom-made jacketed vessel, the temperature of which was controlled by a refrigerated/heating circulator (Julabo Labortechnik GMBH). A ring-disk electrode setup with a bi-potentiotstat (Bi-Stat, Princeton Applied Research Inc., Oak Ridge, TN) was used in conjunction with rotation-control equipment (Pine Instrument Company, Rayleigh, NC). EC-Lab software (version 8.60, Bio-logic Science Instruments, Claix, France) was used to control the bi-potentiotstat. The Pt ring electrode was held at 1.2 V vs SHE where the oxidation of peroxide is diffusion limited. The catalyst coated glassy carbon disk electrode (5 mm diameter, 0.1966 cm² area, DT21 Series, Pine Instrument Company, Rayleigh, NC) was scanned between 0 and 1.2 V vs SHE to characterize H₂O₂ formation within the potential range relevant to fuel cell operating conditions. Potentials were determined using a mercury-mercurous sulfate (Hg/Hg₂SO₄) reference electrode. All potentials in this study, however, refer to that of the standard hydrogen electrode (SHE). A high-surface area Pt cylindrical mesh (5 mm diameter, 50 mm length) attached to a Pt wire (0.5 mm thick, 5 mm length) was used as the counter electrode.

Effect of oxygen concentration.— The effect of oxygen concentration on ORR and H₂O₂ formation kinetics was studied by varying the concentration of oxygen in the solution. The following three gases were used: oxygen (UHP grade, Praxair), air (Industrial, Praxair) and 10.01% oxygen in nitrogen (Airgas). A gas flow meter (0–500 mL, Dwyer Instruments Inc., Michigan City, IN) was used to control the flow of the gas feed at ~100 mL min⁻¹ into the electrolyte. The electrochemical cell was sealed during the experiments to keep air from affecting the concentration of dissolved oxygen in the electrolyte. The concentration of dissolved oxygen in the electrolyte was estimated using the solubility values for oxygen in pure liquid water at 25°C and 101 kPa.25

Effect of pH.— The effect of proton concentration on ORR and H₂O₂ formation kinetics was studied by varying the acidity of HClO₄ in the 2.0–0.1 M concentration window (~0.301–1 pH, assuming K₅ ≫ 1 for HClO₄). Between solution changes, the electrochemical cell and its components were washed and boiled in deionized water for 5 h to ensure accurate pH levels. The catalyst-Nafion coated electrode was also cleaned in a sonicator before every experiment with triple distilled ultrapure water.

Collection efficiency.— Standard procedure,27 for the determination of collection efficiency of a ring-disk electrode was followed. The electrodes were prepared as described above. The experiment was carried out in an electrochemical cell in deaerated (UHP nitrogen, Praxair) 0.1 M H₂SO₄ (96.5%, J. T. Baker) with 10 mmol L⁻¹ K₂Fe(CN)₆ (99.7%, J. T. Baker). The disk electrode was swept at 1 mV s⁻¹ [vs SHE] while the Pt ring was held at a constant potential of 1.2 V [vs SHE]. At this ring potential, the oxidation of [Fe(CN)₆]⁴⁻, produced at the disk electrode, to [Fe(CN)₅]⁢⁻⁴, proceeds under pure diffusion control. The collection efficiency was determined as N = I_disj / I_disk = 0.20, which was independent of disk potential and consistent with the theoretical collection efficiency provided by the manufacturer of the ring-disk electrode.28

The two-electron transfer reaction of O₂ reduction to H₂O₂, captured by the Pt ring, was analyzed in this work (see Table I for parameters used in the analysis). At the ring, the H₂O₂ produced at the disk is oxidized via the reverse of Reaction 1. The fraction of H₂O₂ formation, X_H₂O₂, can be determined from the collection efficiency, ring and disk currents by the expression

\[ X_{H_2O_2} = \frac{2I_{disj}/N}{I_{disk} + I_{ring}/N} \]  

The measured current density j corresponding to H₂O₂ formation on a film covered RDE for the first-order ORR kinetics was previously reported to take the following expression,23 in terms of kinetic and mass-transport dependent currents

\[ \frac{1}{j} = \frac{1}{j_{kin}} + \frac{b_1}{nFD_O_2^2} \frac{C_{O_2}}{j} + \frac{1}{jD} \]

where j is

\[ j_{kin} = \frac{I_{disj}}{NA} \]

\[ jD = 0.62nFD_O_2^{2/3}C_{O_2}^{1/6} \alpha^{1/2} \]
The concentration of O$_2$ in the solution was calculated from the partial pressure of O$_2$ in the inlet gas and O$_2$ solubility data for pure liquid water at corresponding temperature and 101 kPa. The difference in O$_2$ solubility in pure liquid water and in HClO$_4$ (up to 2 M) was assumed to be negligible. Combining Eq. 8 and 10 and solving for $j_{\text{kin}}$ gives

$$j_{\text{kin}} = \frac{nF.E^{1/2}}{nFD_O^2C_{O_2}D_{\text{O}_2}^{1/2}C_{O_2}^{1/2}} - \delta_0D_{250}C_{O_2}^{1/2} = 1.6.10^6jD_{250}C_{O_2}^{1/2}$$

The purely kinetic portion of the H$_2$O$_2$ formation rate is

$$R_{H_2O_2} = \frac{j_{\text{kin}}}{2F} = k_f(C_{O_2})^a(C_{H^+})^b$$

where

$$k_f = k_0^{b} \exp\left[\frac{\alpha F n}{RT}\right]$$

In Eq. 12, a and b are reaction orders with respect to O$_2$ and H$^+$, respectively. Only the forward rate term is used in Eq. 12 because at 0.6 V vs SHE and below, the rate of oxidation of H$_2$O$_2$ (the reverse reaction) is negligible. The kinetic rate constant $k_f$ was estimated for different potentials by plotting H$_2$O$_2$ production rate as a function of oxygen concentration for various potentials. Since the electrode reaction rate was shown earlier by Damjanovic and Hudson to be faster on an oxide-free Pt surface than on an oxide-covered surface, both the forward and the reverse scans were used to estimate the reaction rate constant. The potential dependence of this rate constant is given in Eq. 13.

The activation energies for hydrogen peroxide formation reaction were evaluated by using the Arrhenius equation shown below,

$$k_0 = k_0^{b} \exp\left[\frac{\alpha F n}{RT}\right]$$

The activation energies for H$_2$O$_2$ formation on supported Pt catalysts were compared to the computationally estimated activation energies reported in the literature. For example, using density functional theory, Anderson and Albu, Sidik and Anderson, and Wang and Balbuena have reported activation energies for H$_2$O$_2$ formation on Pt$_1$, Pt$_2$, and Pt$_3$ sites, respectively.
of peroxide produced in the ORR at the disk, as captured by the ring and shows no dependence on oxygen concentration.

Figure 2 shows the purely kinetic portion of H$_2$O$_2$ formation rates obtained from Eq. 12 as a function of oxygen concentration in the 2 M HClO$_4$ for different overpotentials. The data show a linear dependence of the oxygen concentration at all potentials i.e., $a = 1$. In this figure, overpotential of 0.670 V represents a potential of 0.025 V vs SHE because the equilibrium potential for H$_2$O$_2$ formation is 0.695 V. Four representative overpotentials were chosen for this plot. The anode experiences the highest overpotential for peroxide formation during fuel cell operation. The cathode potential is above the H$_2$O$_2$ equilibrium potential at open circuit but experiences a significant drop during load conditions, and can go negative of H$_2$O$_2$ equilibrium potential.

Figure 3 shows the potential dependence of the rate constants estimated from Eq. 12. The 25°C data between $\eta$ values 0–0.3 V and 0.3–0.65 V was fit with two separate linear equations in Fig. 3. The respective intercepts represent $k_f^{0}$ (Eq. 13) and are independent of $C_{H^+}$. These values, as a function of $T$, were used to obtain activation energy.

Figure 4 shows the ring currents and the fraction of H$_2$O$_2$ formed with different acidities. Perchloric acid systems in the 0.1 and 2.0 M concentration range equilibrated with pure O$_2$ were used to study the effect of proton concentration. Figure 4 shows an increased rate of H$_2$O$_2$ formation with increasing proton concentration. Since the disk currents were similar for all acid concentrations, the increased ring currents meant that selectivity toward peroxide formation was a function of proton concentration.

Figure 5 shows the dependence of H$_2$O$_2$ formation rate on proton concentration. This is consistent with the RRDE results of Murthi et al. in 1 and 6 M TFMSA. The points are measurements and lines are predictions according to Eq. 12. The reaction order with respect to H$^+$ in the H$_2$O$_2$ formation reaction was found to best fit the data for
The reaction pathway in ORR on Pt catalysts similar to that of Cl− anions as previously reported by Schmidt et al.,23 Stamenkovic et al.,25 and Markovic and Ross.26 However, the bond strength of ClO4− adsorption on Pt is much weaker than Cl− and SO42− and its influence on the reaction pathway of ORR is also very minimal.23,25

The H2O2 formation rates measured as a function of water activity, potential, and temperature using RRDE experiments was used to predict H2O2 formation rates at the anode and cathode of PEM fuel cell. Peroxide formation rate at the anode was predicted using oxygen permeability from the cathode and XH2O. Peroxide formation rate at the cathode was predicted via Eq. 12, i.e., as a product of the rate constant and the local reactant concentrations. Peroxide formation at the cathode occurs only for fuel cells operating under considerable load (i.e., high cell current) such that the local potential goes negative relative to the equilibrium potential for peroxide formation. For estimation of peroxide rates, local potential at the cathode was taken to be 0.6 V (i.e., η = 0.095 V).

Nafion is a super-acid catalyst and hence the local acidity at the catalyst-membrane interfaces was calculated from the local water content and the fixed number of sulfonic acid groups. The water sorption properties of Nafion as a function of temperature and water activity had been studied by several laboratories.32,37

Using a tapered element oscillating microbalance technique, Jalani et al.37 measured water uptake in Nafion as a function of water activity in vapor phase between 30 and 110°C and reported that the water uptake increased with temperature and was highest at 110°C. The difference in water uptake between 30°C and 110°C is negligible for lower water activities.4 For this work, the absorption isotherm of Nafion 117 membranes measured at 30°C by Zawodzinski et al.38,39 was used. Between water activity values of 0 and 1, the experimentally determined O2 permeability from the cathode and Cl− anions as previously reported by Schmidt et al.,23 Stamenkovic et al.,25 and Markovic and Ross.26

It was assumed that all sulfonic acid groups exist in a completely dissociated form. Figure 6 shows the variation of λ and pH of Nafion as a function of water activity. Even at vapor-saturated conditions [λ = 14], the pH of Nafion is below 0. This trend (not shown) is seen for HClO4, also a strong acid. The acid was assumed to be completely dissociated i.e., Ka ≈ 1. This approach in relating membrane electrode assembly acidity to water activity and hence to the humidity of the incoming gases facilitates in computing peroxide rates inside a fuel cell. Quantitatively, the measured peroxide rates via the RRDE experiments at a particular oxygen concentration, pH value, and temperature should equal the peroxide rates inside the fuel cell at the same pH value and temperature. Since rate constants were measured at 25°C using RRDE, they had to be estimated at higher temperatures in order to be used to calculate peroxide formation rates in a fuel cell. Activation energies for H2O2 formation on supported Pt catalysts were estimated from kinetic currents obtained at 15, 25, 35, and 45°C. Figure 7 shows the Arrhenius plot of the logarithmic pre-exponential term kDE vs the inverse of temperature for the two overpotential regions (0–0.3 V and 0.3–0.65 V). The activation energies were obtained from the slope (Ea/R) of a linear fit according to Eq. 14. This procedure is analogous to those described by Neyerlin et al.43 and Bard and Faulkner.44

Oxygen flux across Nafion at higher temperatures.— Oxygen permeability through Nafion depends greatly on the water content of the membrane. It has been shown by Sakai et al.50 that O2 diffusion rates in a completely dry Nafion membrane have values similar to that in polytetrafluoroethylene and approaches the limit of liquid water with increasing water content. Figure 8 shows experimentally measured O2 permeability, corrected for an O2 feed at 101 kPa, across a Nafion 112 membrane as a function of temperature and relative humidity. These permeation rates were estimated using electrochemical monitoring technique and are comparable to those esti-
The potential across the membrane, measured in situ by Liu and Zuckerbrod,13 (Fig. 19) and modeled by Burlatsky et al.,47 at open circuit conditions, indicates that the potential at the anode/membrane interface is \(-0.0 V\). For the purpose of calculating \(H_2O_2\) rates at the anode/membrane interface, a potential of \(-0.0 V\) (i.e., \(\eta = 0.695\) V) was assumed to exist at the interface.

The oxygen flux across the membrane from the cathode to the anode is

\[
F_{O_2} = \frac{D_{O_2}^m}{\delta} (C_{O_2}^a - C_{O_2}^c) \quad [23]
\]

The concentration of oxygen at the anode-membrane interface approaches zero, assuming all of the oxygen crossing over the membrane to the anode side is reduced to water or reacts chemically with hydrogen

\[
R_{H_2O_2}^{an} = \chi_{H_2O_2} \frac{P_{O_2}^m}{\delta} \quad [24]
\]

While the fraction of oxygen that is reduced to peroxide is a strong function of water activity, it is not a function of oxygen concentration (see Fig. 1c). An expression for \(X_{H_2O_2}\) vs \(C_{H_2O_2}\) was obtained from measured values at room temperature

\[
X_{H_2O_2} = 0.2081 - 0.1208(a_w) - 0.072(a_w)^2 - 2.132 \times 10^{-4}(a_w)^3 \quad [25]
\]

Figure 10 shows the \(H_2O_2\) formation rates at the anode/membrane interface. This goes through a peak because oxygen permeability decreases with decreasing water activity, whereas \(H_2O_2\) selectivity increases with decrease in water activity.

These anode and cathode \(H_2O_2\) formation rates cannot be directly correlated with the fluoride emission rates because there are several intermediate reactions between \(H_2O_2\) formation and actual membrane degradation. Though additional mechanisms involving direct radical formation on Pt followed by their chemical attack on the membrane were suggested,47 they need further experimental validation and verification. However, quantification of \(H_2O_2\) formation rates described in this work is important in the mechanistic understanding of membrane degradation. This quantification would help in validating a durability mechanism especially at elevated temperatures and low relative humidities.

**Conclusion**

\(H_2O_2\) formation rates in a PEM fuel cell anode and cathode were estimated by studying the ORR kinetics on a ring disk electrode. Fuel cell conditions were replicated by depositing a film of Pt/...
Vulcan XC-72 catalyst onto the disk and by varying the temperature, dissolved O₂ concentration, and the acidity levels in HClO₄. The HClO₄ acidity was correlated to ionomer water activity and hence fuel cell humidity. H₂O₂ formation rates showed a linear dependence on oxygen concentration and a square law dependence on water activity. The H₂O₂ selectivity in ORR was independent of evidence on oxygen concentration and a square law dependence on oxygen concentration but increased with decrease in water activity dissolved O₂ concentration, and the acidity levels in HClO₄. The Vulcan XC-72 catalyst onto the disk and by varying the temperature, B₅₆ three orders of magnitude lower than cathode formation rates for a setup for oxygen crossover measurements.

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