Polymer electrolyte fuel cells (PEFCs) have attracted a lot of interest as electrochemical energy conversion sources for multiple applications in the automotive, stationary power, portable power, and military sectors due to their high efficiency, modularity and environmental benefits. The commercialization of PEFCs, particularly for the automobile sector, has been hindered by high cost and insufficient component durability. The high cost of component materials, such as platinum (Pt) electrocatalyst and Nafion electrolyte membranes are among the main factors influencing the cost of PEFCs. Recent advances in the design of PEFCs enable high performance with very low total Pt loadings (ca. 0.15 mgPt cm⁻²) and using very thin polymer electrolyte membranes (PEMs; e.g. Nafion 211, ca. 25 μm, or even lower thickness variants). However, the long-term durability of PEFC components still remains a major concern. The key issues affecting PEFC durability include electrode degradation via carbon corrosion, Pt dissolution, catalyst sintering and electrolyte degradation via PEM oxidative degradation. Carbon corrosion and PEM degradation are key degradation modes that need to be mitigated. Carbon corrosion is primarily caused by oxidation of carbon at higher electrode potentials that are encountered during transient conditions or during fuel starvation, whereas PEM degradation is primarily caused by oxidation of the PEM by reactive oxygen species (ROS) generated in-situ during PEFC operation.

Carbon is perhaps the most common catalyst support used in PEFC electrodes because of its low cost, high surface area, high electrical conductivity, and tunable pore structure. However, carbon is electrochemically oxidized to CO₂ in accordance with the following reaction:

\[ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E^0 = 0.207 \text{ V vs. NHE} \]  

This reaction is thermodynamically feasible at the cathode potentials of an operating PEFC, but the reaction kinetics are very sluggish in the normal potential range encountered at the electrode during operation, resulting in carbon exhibiting adequate stability under most common operating conditions. The electrochemical oxidation of carbon can be accelerated at high temperature, during excursions to high potential (which occur due to fuel starvation or due to transient reactant flows during start-up), and high oxygen concentration/water content. Carbon corrosion leads to thinning of the electrode layer, agglomeration of Pt nanoparticles, detachment of Pt nanoparticles from the support, all of which reduce the interaction between Pt and the support, resulting in a loss of electrochemical surface area (ECSA) with a detrimental impact on the overall performance of the PEFC.

To avoid this issue, several researchers have investigated non-carbon, corrosion-resistant materials as alternate catalyst supports for fuel cell electrodes. In addition to being resistant to corrosion under a wide potential window, any viable alternate catalyst supports should possess adequate electron conductivity and surface area. A wide range of non-carbon supports based on metal oxides and metal carbides have been explored with several of them exhibiting good electrochemical stability. However, these oxides and carbide-based supports do not usually have the necessary electron conductivities to obtain electrodes with acceptable performance. Our group has synthesized high-surface-area mixed-metal oxide and doped metal oxide supports that are highly corrosion resistant and possess more than adequate electron conductivity (\( > \sim 5 \text{ S cm}^{-1} \)) to be used in PEFC electrodes. When catalyzed with Pt, these materials show ORR activity approaching that of Pt/C and demonstrated electrochemical stability in a PEFC even upon rigorous potential cycling.

The generation of H₂O₂ during PEFC operation is known to be catalyzed by the carbon present in the electrodes. This is a concern in terms of PEM oxidative degradation, since H₂O₂ can further react in the presence of transition metal ions present as impurities in the membrane electrode assembly (MEA) via the Fenton reaction to form ROS such as the hydroxyl and/or the hydroperoxyl free radicals. These ROS initiate and sustain the chemical degradation of the PEM (via oxidative attack of the polymer chains by ROS). PEM degradation is an autocatalytic reaction with a large induction time, with the ultimate consequence being catastrophic cell and stack failure. The carbon-based support is therefore one of the contributors to PEM degradation. Decreasing the H₂O₂ generation rate and/or...
scavenging the ROS generated during PEFC operation can substantially lower the rate of PEM degradation.\textsuperscript{10,65–68} Several researchers, including our group, have explored the use of free radical scavengers (FRS) within the PEM to scavenge the ROS generated during PEFC operation, with very good results.\textsuperscript{10,60,65,68,69} However, to ensure high durability over the entire lifetime of the fuel cell, it would be best to minimize, to the extent possible, the concentration of H$_2$O$_2$ and other bad actors generated during PEFC operation.

Appropriate selection of operating parameters (such as temperature, relative humidity, cell potential) is one way to reduce H$_2$O$_2$ generation.\textsuperscript{91,92} However, there are constraints in terms of tuning these operating parameters given their influence on PEFC performance. Therefore, it is advantageous to identify the sources and contributors to H$_2$O$_2$ generation during fuel cell operation. H$_2$O$_2$ can be formed through both chemical and electrochemical pathways.\textsuperscript{1,3,4,11,58–64} Since the electrochemical pathway (and perhaps even the chemical pathway) is catalyzed by carbon, a key issue to be considered in identifying a replacement catalyst support is the influence of said support material on the net rate of generation of H$_2$O$_2$ and ROS, and consequently, on the macroscopic rate of PEM degradation. An excellent and stable support may be unviable if it substantially accelerates PEM degradation.

In this study, we evaluated H$_2$O$_2$/ROS generation rates and PEM macroscopic degradation rates on a corrosion-resistant non-carbon catalyst support (RuO$_2$-SiO$_2$: RSO),\textsuperscript{32,47} a benchmark carbon (C) support, and on these same supports when catalyzed with platinum. We have employed an in-situ fluorescence spectroscopy method devised by our group to obtain in-situ ROS generation rates.\textsuperscript{65,71} We have also used rotating disk electrode (RDE) and gas evolution experiments to probe both sets of materials to ascertain whether the RSO support and Pt/RSO catalyst contribute to PEM degradation. We suggest that the methods presented here can serve as a guide to screen any other viable non-carbon support candidates.

**Experimental**

The following methodology was employed to study the effect of different supports and catalysts on the rate of PEM degradation: (i) the in-situ ROS generation rate was evaluated for each support and catalyst using in-situ fluorescence spectroscopy,\textsuperscript{65,71} (ii) the intrinsic electrochemical H$_2$O$_2$ generation rate was determined for each support and catalyst using ex-situ rotating ring disk electrode (RRDE) experiments; and finally, (iii) the H$_2$O$_2$ decomposition rates (estimated as the oxygen gas evolved) were examined on each support and catalyst using ex-situ fluorescence spectroscopy. RSO was used as the model non-carbon support and Vulcan XC 72 (C) was used as the benchmark carbon support. RSO with a 0.5:0.5 molar ratio of Ru:Si was selected because we have shown in our previous work that this formulation possesses the appropriate conductivity (5 S cm$^{-1}$) and BET surface area (290 m$^2$g$^{-1}$) to replace carbon catalyst supports.\textsuperscript{92}

**Measurement of in-situ ROS generation rate and ex-situ macroscopic PEM degradation rate.**—In-situ fluorescence spectroscopy was used to determine ROS generation rates in the presence of C, RSO, Pt/C and Pt/RSO during fuel cell operation. Details of the in-situ fluorescence method and the experimental setup employed have been described in detail in our previous work, and also concisely presented below for ready reference.\textsuperscript{65} 6-carboxyfluorescein (6CFL) was used as the fluorescent molecular probe to monitor the ROS generation rate. The MEAs prepared and evaluated in these experiments employed the following electrode configurations: (i) Carbon gas diffusion layer (GDL) with carbon microporous layer; (ii) Carbon GDL with RSO microporous layer; (iii) Titanium GDL with RSO microporous layer (Ti porous material was plated with Pt prior to its use); (iv) Carbon GDL with Pt supported on C (Pt/C, 57.1 wt%, Tanaka K. K, hereinafter Pt/C); (v) Carbon GDL with Pt supported on RSO (Pt/RSO, 24 wt% - hereinafter Pt/RSO); and (vi) Titanium GDL with Pt/RSO. The titanium GDLs were used in conjunction with the RSO support to eliminate the influence of the carbon present in the GDL on H$_2$O$_2$ formation, disproportionation, and ROS formation. In each case, the macroscopic PEM degradation rate was ascertained ex-situ in an independent experiment under identical operating conditions by monitoring the fluoride ion emission rate (FER) at the exit stream of the fuel cell. The experimental methods to estimate in-situ ROS generation rates and ex-situ fluoride ion concentration are briefly explained below.

**Preparation of 6CFL-infused membrane.**—3 mL of 266 $\mu$M 6CFL solution, 5 mL of 20% Nafion solution (from DuPont) and 1 mL of N,N-dimethylformamide were stirred together for 4 hours. The resulting mixture was cast onto a 3.5 × 3.5 inch glass plate, dried at 50°C overnight and finally annealed at 100°C for 30 minutes. The approximate thickness of the membrane was 100 μm.

**Preparation of modified rhodiumine 6G barrier membrane.**—2 mL of 417 $\mu$M R6G solution, 5 mL of 20% Nafion solution and 2 mL of 2-propanol was stirred together for 4 hours. The resulting mixture was cast onto a 3.5 × 3.5 inch glass plate, dried at 50°C overnight and annealed at 100°C for 30 minutes. The approximate thickness of the membrane was 100 μm. The as-prepared Nafion-R6G membrane was further modified by soaking the Nafion-R6G membrane in Fenton’s reagent (a mixture of 10 mL of 0.1M ammonium iron (III) sulfate and 10 mL of 3% H$_2$O$_2$ solution) under stirring for 60 minutes. The Fenton reaction uses ferrous iron as a catalyst to generate ROS that later oxidize the Nafion-R6G membrane. The treated membrane was washed with DI water, and soaked in 0.5 M sulfuric acid for 1 hour, then washed with DI water prior to use. The barrier membrane does not have any fluorescence properties and prevents the interaction between catalyst and fluorescent molecular probe (i.e. 6CFL) as explained in our previous study.\textsuperscript{65,71}

**Preparation of membrane electrode assembly (MEA) with tri-layered membrane.**—The catalyst ink for making the electrocatalyst layers was prepared as follows: 1) 0.5 grams of Pt/C (57.1 wt% Pt/C, Tanaka K. K, TEC10F50E) was placed in a glass vial and wetted with a few drops DI water; 2) 6 mL of methanol was added to the glass vial and the content stirred for 3 hours; 3) 1.07 g of 20% Nafion dispersion was added and the suspension stirred overnight. The amount of Nafion dispersion used resulted in 30 wt% binder loading in the electrode.

To prepare MEAs, the catalyst ink was directly sprayed onto one side of a Nafion membrane (approx. thickness 30 μm). A heating lamp was placed behind the membrane to evaporate the solvent. After the catalyst layers were deposited on two such thin membranes, the MEA comprising all the layers (the central 6-FL infused membrane, the two barrier membranes, and the two catalyzed membranes) was assembled and hot pressed at 60°C for 30 seconds at 2000 psi. The optical fiber probe was embedded between the two central 6CFL-infused membranes, with the modified Nafion-R6G barrier membranes placed between the central 6CFL membranes and each electrocatalyst layer. All prepared MEAs had an active area of 5 cm$^2$, with a platinum loading of 0.4 mgPt cm$^{-2}$ on the cathode and 0.2 mgPt cm$^{-2}$ on the anode. The bifurcated optical fiber probe was connected to a xenon light source attached to a monochromator, and the emitted fluorescence was monitored using a CCD detector. All fuel cell experiments reported in this study were performed at 80°C, with a relative humidity of the inlet gases of 75% RH. Further details describing the in-situ fluorescence setup are included in our previous work.\textsuperscript{65}

**Measurement of fluoride ion concentration.**—The concentration of fluoride ions in the exit stream of the fuel cell was measured using an ion-selective electrode (ISE). Prior to measuring the fluoride ion concentration, a pH/ISE meter instrument (Model 250, Denver Instruments) with a fluoride ion-selective electrode (obtained from Fisher Scientific) was calibrated using fluoride ion standard solutions (0.1, 1, 10, and 50 ppm). The calibration procedure was performed as follows: 1) For each standard, 10 mL of fluoride standard solution was added to 10 mL of total ionic strength adjustment (TISAB) buffer solution; 2) The fluoride ion selective electrode was immersed in the solution while stirring and the voltage recorded (after stable signal
was reached); 3) A calibration curve was plotted as a linear plot of voltage (mV) versus the logarithm of the fluoride ion-concentration (in ppm), and used to calculate the concentration of fluoride in the unknown samples. The ISE was rinsed thoroughly with abundant DI water before each measurement.

The fluoride ion emission flux was estimated by collecting condensed water samples from the exiting cathode and anode streams of the fuel cell at regular time intervals. The fluoride ion concentration was determined in each sample using the ISE. The fluoride ion selective electrode was immersed in the sample/TISAB buffer mixture (prepared by mixing an equal volume of the collected sample and the TISAB buffer) and the potential measured under continuous stirring (the value was recorded once stable signal was achieved). The fluoride concentration was determined by using the calibration curve previously built. Note: membranes without 6CFL and R6G were used for the experiments to evaluate the fluoride ion emission flux.

Ex-situ measurement of the electrochemical H₂O₂ generation rate.—The rate of generation of H₂O₂ on the C, RSO, Pt/C and Pt/RSO was estimated electrochemically using a rotating ring disk electrode (RRDE). The electrochemical characterization was performed in a three-compartment electrochemical cell in an oxygen saturated 0.1 M perchloric acid electrolyte at room temperature (approx. 23 °C). The RRDE setup comprised a glassy carbon disk (0.1964 cm²) as the primary working electrode and a platinum ring (0.11 cm²) as an auxiliary working electrode. A saturated calomel electrode (SCE) was used as the reference electrode, and a Pt foil was used as the counter electrode. The GC electrode was attached to a rotator (Pine Instruments) to control the rotation rate, and the potential was controlled using a Solarton multichannel potentiostat (model 1480 Multistat).

The catalyst ink was prepared as follows: 16 mg of 57.1% Pt/C (Tanaka K. K.) catalyst was weighted and wetted with a few drops of DI water, and suspended in 19 mL of DI water + 6 mL of 2-propanol. To the previous suspension, 100 µL of 5 wt% Nafion dispersion (to give thin-film electrodes with 20 wt% Nafion ionomer once solvents were dried) was added and the mixture was sonicated for 30 min. Finally, 10 µL of the catalyst ink was placed on the glassy carbon disk electrode using a micropipette and dried. The electrode was rotated in an inverted position at 400 rpm during the drying process to get a more uniform thin film. Electrodics with Pt/RSO electrocatalyst and, C and RSO catalyst supports were prepared similarly, by adjusting the amount of material weighed and the volume of 5 wt% Nafion solution added. The electrocatalyst and support loadings were 19 mgPt cm⁻²Disk and 100 mgcm⁻²Disk. All the electrodes had a 20 wt% Nafion loading. This thin-film electrode was employed as the working electrode for the experiments below.

The potential of the working electrode (disk) was sweep from 0.35 V to 1.05 V vs. RHE at a scan rate of 2 mV s⁻¹. The corresponding disk current was measured. This current represents the rate of the oxygen reduction reaction (ORR). Simultaneously, the rate of H₂O₂ produced as an intermediate during the ORR in the disk was measured indirectly by oxidizing it back to water at the ring electrode. A constant potential of 1.314 V vs. RHE (1.0 V vs. SCE) was maintained at the ring electrode to assure complete oxidation of the H₂O₂ reaching the Pt ring. The currents measured at the ring and disk were used to calculate the amounts of H₂O₂ produced in each case.

All the potentials in this work were referenced vs. RHE, however, a SCE reference electrode was used in the experiments. A calibration of the SCE electrode vs. RHE was done prior to the start of the experiments (the potential of the SCE electrode was −0.973V vs. RHE). The applied potentials were IR corrected; background subtraction was also employed to obtain the ORR disk currents.

Catalyst activities (at 0.9 V vs. RHE) were determined in an independent RDE experiment where the electrode was rotated at 1.600 rpm and the working electrode potential was sweep from 0.35 V to 1.05 V vs. RHE at a scan rate of 20 mV s⁻¹. The applied potential was IR corrected, and the background (current obtained by doing the same experiment in N₂-degassed electrolyte) was subtracted from the measured current before calculation of the catalyst activities.

Ex-situ measurement of the catalytic H₂O₂ decomposition rate.—The chemical decomposition rates of H₂O₂ over C, RSO, Pt/C and Pt/RSO were estimated using a two-reactor setup designed to measure the O₂ generated due to disproportionation of H₂O₂, which is shown in Figure S1. The first reactor was filled with 10% H₂O₂ solution. The second reactor was filled with 250 mM of 9,10-dimethylanthracene (DMA - a fluorescent dye solution that is sensitive to oxygen) and was connected to the first reactor using PVC tubing. Both the 10% H₂O₂ solution and 250 mM DMA solution were initially purged with N₂ to remove any dissolved oxygen.

A 5 cm² active area GDL coated with C, RSO, Pt/C or Pt/RSO was then introduced and contacted with the H₂O₂ solution in the first reactor. Since carbon and RSO have a significant difference in their BET surface areas, their corresponding loadings on the GDL were varied to keep a constant total surface area of 0.05 m²support cm⁻²GDL (the BET surface area of C and RSO were 235 m²g⁻¹ and 290 m²g⁻¹, respectively). In the case of Pt/C and Pt/RSO, the total surface area was held constant (ca. 0.05 m²support cm⁻²GDL) after accounting for the percentage of Pt in each case (the Pt percentage in Pt/C and Pt/RSO were 57.1% and 24%).

During the H₂O₂ disproportionation reaction, N₂ was continuously fed into the first reactor at a flow rate of 10 mL min⁻¹ to obviate atmospheric oxygen ingress and to serve as a carrier gas to transport the oxygen produced during catalytic H₂O₂ decomposition in the first reactor to the sensing solution in the second reactor. The product oxygen entering the second reactor oxidized the DMA, decreasing its fluorescence signal. The fluorescence of DMA (in the second reactor) was continuously monitored using a bifurcated optical fiber probe connected to a detector (identical set-up to that used for in-situ fuel cell studies). The rate of decomposition of H₂O₂ was estimated from the fluorescence decay rate, which was sensitive to the rate of oxygen ingress, which in turn was directly related to the H₂O₂ disproportionation rate.

Results and Discussion

The rate of in-situ ROS generation at different electrodes.—The in-situ ROS generation rate in the MEAs prepared with the six electrode configurations described earlier were estimated from the in-situ fluorescence response from the 6CFL/R6G/Nafion membrane. The apparent ROS generation rate constant (pseudo-first order kinetics) was calculated using the method described in our previous work. The macroscopic PEM degradation rate was estimated from the FER measured in the effluent streams by using an ion selective electrode. Note: The FER experiments were independently performed on different sets of MEAs. To ensure that all generated ROS contributed to PEM degradation, the FER experiments were performed on layered membranes that did not contain any dye, but were otherwise identical to the membranes used for the in-situ fluorescence experiments. The in-situ fluorescence response obtained with different fuel cell electrode configurations are shown in Figure S2(a) and S3(a) and the corresponding FERs are shown in Figures S2(b) and S3(b).

The apparent in-situ ROS generation rate constant (kₚ, s⁻¹) and fluorode emission flux (Iₙ, ppm/cm².s) were calculated using equations S1 and S2 in the ESI. The details of the calculation can be found in our previous work and also briefly in the ESI section. The apparent in-situ ROS generation rate constant (estimated from the fluorescence response data) was correlated to the macroscopic PEM degradation rate (FER) for all electrode configurations (Figure 1). An excellent correlation was obtained, confirming the underlying relationship between ROS generation and PEM degradation.

The in-situ ROS generation rates on the RSO/carbon GDL and the RSO/Ti GDL electrodes were found to be 29% and 51% less, respectively, than that on the C/carbon GDL electrode. A similar trend was observed in the FER results, wherein the macroscopic PEM
degradation rates in the presence of RSO/carbon GDL and RSO/Ti GDL electrodes were 23% and 52% less, respectively, than in the presence of the C/carbon GDL electrode.

Very similar trends were observed with Pt/C and Pt/RSO. The in-situ ROS generation rates on Pt/RSO/carbon GDL and Pt/RSO/Ti GDL electrodes were 34% and 54% less, than on Pt/C/carbon GDL electrode. The macroscopic PEM degradation rates in the presence of Pt/RSO/carbon GDL and Pt/RSO/Ti GDL electrodes were 7% and 33% less, than in the presence of the Pt/C/carbon GDL electrode. In line with expectations, the fuel cell electrodes with Pt/C and Pt/RSO yielded a lower in-situ ROS generation rate and macroscopic PEM degradation rate when compared to the fuel cell electrodes with C and RSO. This was attributed to the fact that Pt catalyzed the decomposition of H$_2$O$_2$ to water soon after it was generated.

Hence, both in-situ ROS generation rate and macroscopic PEM degradation rate were lowered in an operating fuel cell when the non-carbon support-based electrodes (i.e., RSO/carbon GDL or RSO/Ti GDL) and the corresponding supported electrocatalysts (Pt/RSO/carbon GDL or Pt/RSO/Ti GDL) were employed. Similar fuel cell polarization curves (Figure S4) were obtained for all Pt containing MEAs (Pt/RSO/Ti GDL, Pt/RSO/carbon GDL and Pt/C/carbon GDL) showing that the intrinsic activity of Pt catalyst was not affected by the different catalyst supports. The results further corroborate that in-situ ROS generation rate and macroscopic PEM degradation rate are dictated by differences in H$_2$O$_2$ generation on the catalyst supports.

This is perhaps the first direct (in-situ) confirmation of the contribution of carbon support to the generation of ROS detrimental to PEM stability. As discussed earlier, ROS are formed primarily through the decomposition of H$_2$O$_2$. Fenton’s reaction, while H$_2$O$_2$ is formed both chemically and electrochemically in the operating fuel cell. Since carbon has been reported to be a good catalyst for electrochemical H$_2$O$_2$ generation,\textsuperscript{24} it is intuitive to think that the carbon support promotes PEM degradation as it facilitates the production of H$_2$O$_2$ and hence ROS. The fact that replacing the carbon GDL with a Ti GDL yielded a further reduction in ROS generation and PEM degradation rates, provided further confirmation that carbon actively contributes to PEM degradation in an operating fuel cell. The results above suggested that the RSO support and the derivative catalyst yielded lower ROS generation rates because they were either electrochemically inert toward oxygen reduction, they were more selective toward the 4-electron reduction of oxygen, and/or they were more effective in chemically decomposing the generated H$_2$O$_2$. To test these hypotheses, ex-situ RRDE studies were performed to estimate the H$_2$O$_2$ generation rate on each support and catalyst during the ORR, and ex-situ H$_2$O$_2$ decomposition studies were performed by monitoring the rate of evolution of oxygen.

**Ex-situ estimation of the rate of electrochemical H$_2$O$_2$ generation at the different electrodes.**—The ORR was performed on the thin-film electrode deposited on the glassy carbon disk of the RRDE, while the intermediate H$_2$O$_2$ formed during the ORR was monitored at the Pt ring electrode over a wide range of disk-electrode potentials and rotation rates.

The percentage of H$_2$O$_2$ generated at the ring at 0.4 V vs. RHE was calculated using the following equation:\textsuperscript{[25]–[28]}

\[
\%H_2O_2 = \frac{2I_R/N}{I_D + 2I_R/N}
\]  

where N was the collection efficiency, which was determined from an independent RRDE experiment using the ferricyanide/ferrocyanide redox couple. \(I_D\) and \(I_R\) were the disk and ring currents collected at 0.4 V vs. RHE, respectively. The collection efficiency for our RRDE system changed slightly with the rotation rate. It was 27.2% at 100 r.p.m., 27.0% at 400 r.p.m., 26.7% at 900 r.p.m., and 26.6% at 1600 r.p.m. (Refer to Figure S5 and section III of the ESI for the experimental determination of the collection efficiency of the RRDE employed in this study). The collection efficiency accounts for the fact that not all the intermediate generated at the disk is being oxidized at the ring.

Figure 2 shows the percentage of H$_2$O$_2$ generated on C, RSO, Pt/C and Pt/RSO electrodes at a rotation rate of 1600 rpm. The polarization curves for the ORR and the corresponding ring currents at all rotation rates are shown in the ESI (Figures S6 to S9). The comparison of ring currents on all the electrodes is presented in Figure S10. At a disk potential of 0.4 V vs. RHE, the percentage of H$_2$O$_2$ generated during the ORR on the C and RSO electrodes were 32 ± 4% and 26 ± 3%, respectively, while the corresponding values for Pt/C and Pt/RSO were 3.5 ± 0.7% and 1.7 ± 0.5% (see Table I). The percentage of H$_2$O$_2$ generated on Pt/C electrodes has been reported in the literature to be 3–4%, which is in good agreement with the results obtained in this work.\textsuperscript{[24,25]} The H$_2$O$_2$ generation rate on C and Pt/C was higher than that on RSO and Pt/RSO catalysts, which corroborated the trends in ROS generation seen in the in-situ fluorescence spectroscopy measurements.

The ORR data obtained on Pt/C and Pt/RSO was further analyzed and kinetic parameters such as the kinetic current \(i_0\) and Tafel slope...
were estimated. From the ORR data obtained at different rotation rates (See Figures S7 and S8), plots of $i^{-1}$ vs. $\omega^{-1/2}$ (Koutecky–Levich plot or K-L plot) were obtained for each catalyst (See Figures S11 and S12).

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62nFD^{1/2}\alpha^{1/2}v^{-1/2}c_0}$$

[3]

where, $i$ was the measured current density (mA/cm²); $i_k$ was the kinetic current density (mA cm⁻²isc); $n$ was the number of electrons transferred during the electrochemical reduction of oxygen; $F$ is the Faraday constant (96,495 C mol⁻¹ electrons); $D$ was the diffusion coefficient of the oxygen in the electrolyte (1.9 × 10⁻⁵ cm² s⁻¹); $\nu$ was the electrode rotation rate (rpm); $v$ was the kinematic viscosity of the electrolyte (1.0 × 10⁻⁵ cm² s⁻¹); $c_0$ was the bulk concentration of O₂ in the solution (1.1 × 10⁻⁶ mol L⁻¹). 77,78

The $i_k$ on Pt/C and Pt/RSO at 0.9 V vs. NHE (overpotential of 0.33 V) were found to be ca. 4.1 mA cm⁻² and 4.5 mA cm⁻² respectively. The literature value for $i_k$ on Pt/C is 3–5 mA cm⁻² which is in reasonable agreement with the value reported here. 7,72,80 The average number of electrons transferred during the ORR on Pt/C and Pt/RSO (as obtained from Koutecky-Levich analysis) were found to be ca. ~4. In addition, the overpotential corresponding to 4 electrons being transferred was in the range of 0.74 V – 0.84 V for both Pt/C and Pt/RSO, which is consistent with the values reported in the literature. 7,81

From the K-L analysis at different overpotentials ($\eta$), a Tafel plot ($i$ vs. $\eta$) was obtained (See Figure S11c and S12c). The Tafel slopes for Pt/C and Pt/RSO were found to be 68 mV dec⁻¹ and 64 mV dec⁻¹ respectively. The Tafel slope of 68 mV dec⁻¹ was in good agreement with the value reported in the literature for Pt/C. 7,81,82 The ex-situ ORR study demonstrated that both Pt/C and Pt/RSO have a similar ORR activity, however, the H₂O₂ generation on Pt/C was higher than on Pt/RSO.

The quantification of ROS generation rates and of FER obtained using in-situ and ex-situ PEM degradation studies, and the ex-situ intrinsic H₂O₂ generation rate obtained from RRDE study suggest that the net ROS formation in Pt/RSO is lower than that in Pt/C, which should enhance PEM lifetime.

**Ex-situ estimation of H₂O₂ chemical decomposition rate.**—Reports in the literature suggest that metal oxides are excellent catalysts for the chemical decomposition of H₂O₂. 8,14 To explore the possibility of a higher rate of chemical decomposition of H₂O₂ on the oxide support, a separate ex-situ fluorescence experiment was performed to monitor H₂O₂ chemical decomposition on C and RSO supports. H₂O₂ chemically decomposes to form water and oxygen via the following chemical reaction. 85

$$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$

[4]

The rate of this reaction was studied using the ex-situ fluorescence experiment described in the Experimental section. The oxygen evolved in reactor 1 was fed into reactor 2, where it oxidized the fluorescent DMA dye, resulting in a fluorescence decay. 86 The rate of H₂O₂ decomposition on any given electrode was thus indirectly estimated by monitoring the fluorescence decay rate of DMA in the second reactor. The results are shown in Figures 3a and 3b.

![Figure 3](https://example.com/figure3.png)

**Table 1. Parameters extracted for the PEM degradation, ORR kinetics and H₂O₂ generation/decomposition performed in this study.**

| Electrodes | Carbon GDL | On Ti GDL | On Carbon GDL | On Ti GDL | %H₂O₂ generated (at 0.4 V vs. RHE) | Number of electrons | Mass and specific activity (at 0.9 V vs. RHE) | Tafel slope (mV dec⁻¹) | H₂O₂ decomposition (x10⁻⁵ s⁻¹) |
|------------|------------|-----------|---------------|-----------|-----------------------------------|--------------------|----------------------------------------|----------------------|-------------------------------|
| C          | 9.9 ± 0.81 | n/a       | 6.0 ± 1.24    | n/a       | 32 ± 4                            | 3.4 ± 0.1          | n/a                                    | 6.59 ± 0.95           | 5.94 ± 0.28                   |
| RSO        | 7.0 ± 0.28 | 4.9 ± 0.21| 4.6 ± 0.48    | 2.9 ± 0.34| 26 ± 3                            | 3.5 ± 0.1          | n/a                                    | 9.65 ± 0.77           | 7.34 ± 0.20                   |
| Pt/C       | 9.0 ± 0.20 | n/a       | 2.7 ± 0.32    | n/a       | 3.5 ± 0.7                         | 3.93 ± 0.03        | n/a                                    | 68 ± 3.6              | 386 ± 6.7                      |
| Pt/RSO     | 5.9 ± 0.19 | 4.1 ± 0.07| 2.5 ± 0.31    | 1.8 ± 0.1 | 1.7 ± 0.5                         | 3.97 ± 0.02        | n/a                                    | 64 ± 3.6              | 547 ± 127.5                   |

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**References:**

1. Literature values for the ORR activity, however, the H₂O₂ generation on Pt/C was higher than on Pt/RSO.
2. The rate of this reaction was studied using the ex-situ fluorescence experiment described in the Experimental section. The oxygen evolved in reactor 1 was fed into reactor 2, where it oxidized the fluorescent DMA dye, resulting in a fluorescence decay. 86 The rate of H₂O₂ decomposition on any given electrode was thus indirectly estimated by monitoring the fluorescence decay rate of DMA in the second reactor. The results are shown in Figures 3a and 3b.

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**Figure 3.** Ex-situ H₂O₂ decomposition rates obtained on (a) C and RSO; and (b) Pt/C (57%, Tanaka K.K.) and Pt/RSO in N₂ purged 10% H₂O₂ solution.
The H$_2$O$_2$ chemical decomposition rate constant on C was estimated from this data to be $6.5 \times 10^{-5}$ s$^{-1}$, which was in reasonable order of magnitude agreement with the values reported in the literature ($1.07 \times 10^{-5}$ s$^{-1}$)$^{87,88}$ The H$_2$O$_2$ chemical decomposition rate on RSO was ca. 30% higher than on C. Likewise, the H$_2$O$_2$ chemical decomposition rate on Pt/RSO was ca. 40% higher than on Pt/C. The parameters obtained experimentally from the above studies are all summarized in Table I.

The measurement of in-situ H$_2$O$_2$ and ROS generation and H$_2$O$_2$ decomposition clearly demonstrated the lower generation of H$_2$O$_2$ and ROS on Pt/RSO catalyst compared to Pt/C catalyst. The schematic representation of different modes of ORR pathways and subsequent generation of H$_2$O$_2$/ROS in RSO was presented in Figure 4. It was observed that the apparent in-situ ROS generation rate and ex-situ PEM degradation rate was 1.4 and 3 times lower on RSO and Pt/RSO compared to C and Pt/C catalysts respectively. Ex-situ RRDE experiments confirmed that the intrinsic H$_2$O$_2$ generation on RSO based catalyst support was 50% lower than the C based catalyst supports, which corroborate the observations derived from the in-situ ROS generation rate and ex-situ PEM degradation experiments. At this point, we learned that the intrinsic H$_2$O$_2$ generation is lower on RSO based catalyst support compared to C based catalyst supports. Our additional experiments to measure the intrinsic H$_2$O$_2$ chemical decomposition rate on catalyst supports confirmed that the chemical decomposition rate of H$_2$O$_2$ is 46% and 73% higher on RSO and Pt/RSO respectively. The higher chemical decomposition of H$_2$O$_2$ on RSO and higher generation of H$_2$O$_2$ on C supports plays an significant role in the net generation of H$_2$O$_2$ on these catalyst supports. Furthermore, we results support the hypothesis that the superior H$_2$O$_2$ decomposition rate on RSO was partly responsible for the lower ROS generation on this support and subsequently increase in the lifetime of PEM.

### Conclusions

The influence of catalyst support on PEM degradation during PEFC operation was studied. Carbon-based support was used as a benchmark carbon support and RSO was used as a model non-carbon support.

In-situ fluorescence spectroscopy was used to estimate the ROS generation rate during fuel cell operation, and ex-situ FER measurements (at the fuel cell exit stream) provided an estimate of the macroscopic PEM degradation rate. The in-situ ROS generation/PEM degradation rate of RSO based electrodes with carbon GDL and Ti GDL was 1.4 and 2 times lower than those of C based electrodes with carbon GDL respectively. A similar trend was observed on the Pt/C and Pt/RSO based electrodes.

Ex-situ experiments were conducted using an RRDE setup to estimate the fraction of H$_2$O$_2$ generated during the ORR on the supports and catalysts. The percentage of H$_2$O$_2$ generated on the carbon based electrodes (C and Pt/C) was 50% higher than that on RSO based electrodes (RSO and Pt/RSO). The kinetic current ($i_k$) at 0.9 V vs. NHE and average number of electrons transferred were calculated for Pt/C and was found to be 4.1 mA cm$^{-2}$ and 3.93 respectively and, for Pt/RSO, 4.5 mA cm$^{-2}$ and 3.97 respectively. Tafel slopes of ca. 68 mV dec$^{-1}$ and 64 mV dec$^{-1}$ were observed on Pt/C and Pt/RSO, suggesting that the chemical step after the initial fast charge-transfer step was the rate determining step (RDS) on both electrodes. Additionally, ex-situ fluorescence spectroscopy experiments using DMA (a fluorescent O$_2$ sensor) revealed that the RSO and Pt/RSO electrodes had 46% and 73% higher chemical H$_2$O$_2$ decomposition rates than C and Pt/C electrodes respectively. The combined experimental results obtained using fluorescence spectroscopy, FER and electrochemical measurements demonstrated the lower generation rates of H$_2$O$_2$ and ROS and the higher H$_2$O$_2$ chemical decomposition rates on RSO-based catalysts when compared to C-based supports and catalysts.

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### References

1. M. K. Debe, *Nature*, 486, 43 (2012).
2. F. A. de Bruijn, V. A. T. Dam, and G. J. M. Janssen, *Fuel Cells*, 8, 3 (2008).
3. R. L. Borup and R. Mukundan, *ECS Trans.*, 33, 17, Electrochemical Society (2010).
4. C. Houchins et al., *Membranes (Basel)*, 2, 855 (2012).
5. H. R. Colón-Mercado and B. N. Popov, *J. Power Sources*, 155, 253 (2006).
6. U. a. Paulus, T. J. Schmidt, H. a. Gasteiger, and R. J. Behm, *J. Electroanal. Chem.*, 495, 134 (2001).
