Ceramic carbon electrodes (CCEs) have demonstrated their ability to function as proton exchange membrane fuel cell electrodes under low relative humidity (RH) conditions. Small quantities of sulfonated silane in the catalyst layer produced electrodes with high surface area, porosity, and water retention, which improved catalytic activity and proton conductivity. The purpose of this work was to investigate the mechanisms that facilitate enhanced performance of CCE electrodes under different RH conditions. Differences in transport phenomena related to membrane, electrode, and reactant concentration components were measured and compared for standard Nafion-based and CCE cathode catalyst layers using oxygen, air, helox (21% O2 in He), and 4% O2 in N2. Membrane electrode assemblies were characterized via cyclic voltammetry and electrochemical impedance spectroscopy. CCE cathodes displayed decreased resistance related protonic and electronic transport when relative humidity was lowered, and both types of electrodes suffered limitations due to oxygen transport losses where the oxygen also undergoes reduction in the catalyst layer. Remarkably, at 20% RH there was no change in performance at lower oxygen concentrations or mass transport loss observed for the CCE cathodes, indicating that the overall oxygen transport (through the gas diffusion layer and ionomer) is enhanced using this type of electrode structure.

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was previously determined to be optimal for fuel cell performance.\(^8,9\)

After several days, the partially gelled CCE was spray deposited onto a Toray gas diffusion layer (TPGH-090, 10% wet proofing) coated with a microporous layer (MPL) using an air brush. Following deposition, the resulting electrode was dried for 30 min at both room temperature and 135 °C. The electrode had a platinum loading of 0.34 mg cm\(^{-2}\) and a total silicate loading of 40 wt%, and will be referred to hereafter as SS-CCE.

**MEA preparation.**— Standard Nafion-based electrodes were prepared in-house to act as the anode and the state-of-the-art cathode for transport testing. A solution of Nafion (5 wt% in alcohols, Ion Power Liquion LQ-1105) was mixed with 20% Pt on Vulcan XC72 carbon black (Premetek Co.). Deionized water and isopropyl alcohol were added to the solution to adjust consistency for spraying. The resulting mixture was stirred for 2 hours, sonicated for 1 hour, and stirred for at least 1 hour before spray-deposition onto carbon fibre paper (CFP) from Toray (TPGH-090, 10% wet proofing). The resulting gas diffusion electrode (GDE) was left to dry at room temperature overnight and then placed in an oven to dry at 135 °C for a minimum of 30 minutes. The final GDE composition was 0.31 mg cm\(^{-2}\) platinum and 30.1 wt% Nafion.

Fuel cell membrane electrode assemblies (MEAs) were fabricated by hot-pressing (150 kg cm\(^{-2}\) for 90s at 130 °C) a 5 cm\(^2\) test electrode (cathode) and a similar-sized commercial anode (preparation detailed above) across a Nafion NRE212 membrane. MEAs were tested in a 5 cm\(^2\) test fuel cell (Fuel Cell Technologies) on a commercial fuel cell test station (Fuel Cell Technologies, 120A unit) controlled using Labview software. External plumbing was configured to allow selection between oxygen (99.99 HFC grade OX4.0, Praxair) and nitrogen (99.988 NI4.0, Praxair) feeds, or between air (21% oxygen A10.0XD, Praxair), helox (21% oxygen in helium HE OXR3, Praxair), and 4% nitrogen in oxygen (NI OXR1, Praxair) feeds. Hydrogen (99.999 HY5.0, Praxair) was used at the anode.

**Electrochemical measurements.**— Cyclic voltammetry (CV) measurements were conducted using a Solartron 1470E multichannel potentiostat controlled using Multistat software (Scribner Associates). CV measurements were performed for a potential range between 0.08 and 1.4 V (vs. reversible hydrogen electrode) with humidified N\(_2\) flowing at the cathode and with the H\(_2\) anode serving as both the reference and the counter electrode. The desired temperature for analysis was allowed to stabilize and a minimum of 20 cycles were performed before collecting CVs.

Electrochemical impedance spectroscopy (EIS) measurements were conducted using a Solartron 1260 frequency response analyzer controlled using Multistat software (Scribner Associates). EIS measurements were collected over a frequency range of 100 kHz to 0.1 Hz at a DC bias potential of 0.425 V (vs. reversible hydrogen electrode). EIS data was analyzed using a finite transmission-line model developed by the Pickup group.\(^{10,11}\) For fuel cell electrodes, EIS measurements were performed with humidified N\(_2\) flowing at the cathode and with the H\(_2\) anode serving as both the reference and the counter electrode.

Fuel cell testing procedures to study transport processes were adapted from Sambandam and Ramani.\(^3\) Firstly, MEAs were tested at 25 °C and 100% relative humidity (RH) to obtain initial CV, EIS, and polarization curves. Once stable measurements were acquired, the remaining experiments were conducted at a cell temperature of 80 °C and with 10 psig (170 kPa) back pressure at the anode and cathode. Both control and SS-CCE samples were measured with 100% RH at the anode and 75% RH at the cathode. Since previous studies of SS-CCE performance indicated significant mass transport issues at high humidity, the SS-CCE MEA was also tested with cathode conditions of 66% RH, 43% RH, and 20% RH. CV and EIS measurements were taken with gas flows of 50 ml min\(^{-1}\) for H\(_2\) and 100 ml min\(^{-1}\) N\(_2\) to mitigate H\(_2\) crossover.

For performance testing, O\(_2\) and auxiliary reactant gases were held at constant flow rates with 10 psig back pressure based on an “ideal” stoichiometry of 2 at 0.2 A cm\(^{-2}\). This resulted in flow rates of 205 ml min\(^{-1}\) and 100 ml min\(^{-1}\) for H\(_2\) and O\(_2\), respectively. Auxiliary reactant gas flows were set at 233 ml min\(^{-1}\) (air and helox) and 1225 ml min\(^{-1}\) (4% O\(_2\) in N\(_2\)) with a constant H\(_2\) flow of 100 ml min\(^{-1}\). Oxidant gases were tested in the order of: O\(_2\), air, helox, and 4% N\(_2\) in O\(_2\). Potentiostatic holds of 0.5–0.7 V were used to aid with conditioning and ensure stable performance before polarization curves were taken. After performance measurements were finished for the MEA, CV and EIS measurements were again taken at 25 °C and 80 °C to examine changes in the electrochemically active surface area (ECSA), conductivity, and resistance. The ECSA was determined by integrating the peak areas on the resulting CVs related to hydrogen desorption from the platinum surface. The area was then divided by the Coulombic charge for the adsorption/desorption of one proton per platinum atom (210 μC cm\(^{-2}\)), followed by division by the mass of platinum present in the sample to reveal the quantity of platinum (in m\(^2\) g\(^{-1}\)) that is accessible for electrochemical reactions.\(^{12}\)

**Results and Discussion**

**CV and EIS.**— The ECSA for platinum was calculated for the Nafion-based and SS-CCE electrodes before and after the transport study was conducted. CV measurements were taken at 25 °C to obtain beginning of life (BOL) and end of life (EOL) values and are displayed in Figure 1 along with the curves collected at BOL (inset). The ECSA for the SS-CCE was slightly higher than for the Nafion-based cathode. This comparison was necessary to conclude that the SS-CCE catalyst layer contained a similar quantity of accessible platinum as the Nafion-based electrode.

EIS experiments were conducted along with the CV tests to track changes in catalyst layer over the course of the study and possibly help explain some of the transport phenomena. Figure 2 compares capacitance plots and Nyquist plots taken at the BOL and EOL for the Nafion-based and SS-CCE cathodes. For both electrodes there is a lengthening of the Warburg region (2b) over experiment duration, indicating an increase in ionic resistance. The SS-CCE cathode catalyst layer at BOL has a lower ionic resistance than the Nafion-based cathode, suggesting the CCE cathode has sufficient construction to facilitate ion transport. These trends are better visualized as capacitance plots (2a) where it is evident that the ability to conduct protons is higher for the SS-CCE cathode than the Nafion-based cathode but that
pressures were calculated for gases at their corresponding anode and cathode temperatures using the Antoine equation:

$$\log P = A - \frac{B}{t + C}$$  \[3\]

where $P$ is the vapor pressure, $t$ is the temperature (in K), and $A$, $B$, and $C$ are constants whose value is dependent on the component under study and the units of pressure to be calculated. For this experiment, $A = 4.6543$, $B = 1435.264$, and $C = -64.845$. The partial pressure calculation took into consideration the fact that anode and cathode gas lines were pressurized to 10 psig (170 kPa).

The total overpotential consists of contributions from multiple sources. Thus, Eq. 1 can be re-written as:

$$V_{cell} = V_{eq} - [\eta_{ohm, membrane} + \eta_{ohm, electrode}$$

$$+ \eta_{conc, nonelectrode} + \eta_{conc, electrode}]$$  \[4\]

where $\eta_{ohm, membrane}$ is the membrane ohmic overpotential, $\eta_{ohm, electrode}$ is the electrode ohmic overpotential, $\eta_{conc, nonelectrode}$ is the non-electrode concentration overpotential, and $\eta_{conc, electrode}$ is the electrode concentration overpotential. Polarization data was collected in triplicate to find the average curve associated with a given set of temperature or RH conditions. The raw data gathered was further analyzed to expose the individual contribution from each of the aforementioned sources to performance loss. A stepwise approach was used to elucidate information about the $\eta_{ohm, membrane}$, $\eta_{ohm, electrode}$, $\eta_{conc, nonelectrode}$, and $\eta_{conc, electrode}$ as per the procedures described by Ramani and Williams’ groups with minimal modification. In the case of membrane ohmic overpotential, the membrane resistance ($R_{mem}$) was estimated using EIS under nitrogen. The value for $R_{mem}$ was taken as the high frequency resistance (HFR) and thus determined as the value at which the impedance profile crosses the x-axis of a Nyquist plot. To gather a more correct approximation of $\eta_{conc, electrode}$, the Tafel data should be corrected for any hydrogen crossover by calculating the hydrogen crossover current and subtracting it from the polarization data at low current density. However, as this value was assumed to be minimal, it was neglected for the purposes of our analysis.

Examples of the raw data collected and averaged for the standard Nafion-based and SS-CCE MEAs are shown in Figures 3–5. Figure 3 compares the polarization curves collected for the Nafion cathode at 75% RH under oxygen, air, helox, and 4% $O_2$. A voltage

both electrodes experience some loss in proton conductivity over the course of the experiment. Additionally, the SS-CCE displays a much higher limiting capacitance compared to the Nafion electrode. While the presence of the MPL may contribute to this, our experiments on the MPL show it to have a low contribution to capacitance. There does not appear to be any loss in capacitance, which suggests no significant carbon corrosion or ionomer degradation occurred. The change in ECSA over time is therefore due to Pt dissolution or agglomeration. This conclusion is further supported by the fact that the change in ECSA appears to occur at the same rate for both types of electrodes.

**Polarization data analysis.**— Steady-state polarization curves were collected for test MEAs under $O_2$, air ($21\% O_2$ in $N_2$), helox ($21\% O_2$ in $He$), and $4\% O_2$ in $N_2$. Polarization curves were plotted as cell potential versus current density, and as cell overpotential versus current density on a log scale for subsequent calculations. The overpotential ($\eta$) was calculated from the experimental cell voltage ($V_{cell}$) by subtraction of the theoretical equilibrium cell voltage ($V_{eq}$) using the equation:

$$\eta = V_{eq} - V_{cell}$$  \[1\]

The equilibrium cell voltage was calculated from the Nernst equation in the following form:

$$V_{eq} = V_{eq}^o + \frac{RT}{2F} \ln \left( \frac{P_{O_2}^{1/2} P_{H_2}^{1/2}}{P_{O_2}} \right)$$  \[2\]

In the above equation, $V_{eq}^o$ is the equilibrium cell voltage at the operating cell temperature (1.16–1.21 V) with unit activity of reactants and products, $T$ is the operating cell temperature (353 K), $R$ is the ideal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $F$ is Faraday’s constant (96485 C mol$^{-1}$) and $P_r$ represents the partial pressure of the reactants and products raised to their corresponding stoichiometric coefficients. Partial
Figure 4. Polarization curves taken for SS-CCE catalyst layer at 80°C and 75% RH with different oxidants (10 psig back pressure).

Figure 5. Polarization curves taken for SS-CCE catalyst layer at 80°C and 20% RH with different oxidants (10 psig back pressure).

drop is clearly visible for the air curve compared to O₂ due to the difference in O₂ concentration that results at the catalyst surface even with an identical stoichiometry. The higher potential displayed by the O₂ curve compared to air suggests that mass transport issues are present. The air and helox curves display identical performance at low current densities, but as the current density increases the cathode began to exhibit mass transport issues in air. Ideally, since the O₂ concentration in air and helox are the same, the oxygen will diffuse through water at the same rate, but issues with gas phase diffusion manifest as differences in the two curves. This is because when helox is used as the oxidant, O₂ diffusivity in helium is greater than in nitrogen. The curve where 4% O₂ in N₂ is used at the cathode exhibits poor performance compared to the other oxidants, but this is expected as the low oxidant concentration requires high flow rates to achieve the appropriate stoichiometry and occurs in a similar manner as the voltage drop seen for air, discussed above.

Figures 4 and 5 represent the average polarization curves taken for the SS-CCE cathode taken at relative humidities of 75% and 20%. It is evident in Figure 4 that at 75% RH there were mass transport issues that arise from flooding. The performance under oxygen, air, and helox were similar at low current densities, though at higher current densities the air and helox actually have improved performance. This could be due to the higher flow rates used with air versus oxygen. The increased movement of gas in the catalyst layer may deter liquid water from pooling by drying out the cathode compared to when lower flow rates are used, thus maintaining a better water balance. At 66% RH (not shown) the performance was similar for oxygen, air, and helox, likely due to the decrease in water content in the cathode and for 43% RH (not shown), there were minimal mass transport limitations under any of the oxidant conditions. At 20% RH (Figure 5) the polarization curves for oxygen, air, and helox were essentially identical. The results obtained for the SS-CCE cathodes and the changes observed from Figure 4 to Figure 5 are interesting as an IR drop is expected for air (as observed for the Nafion-based standard), as well as improvement in mass transport for use of helox versus air. However, the polarization curves indicate that oxygen transport is improved when air is used vs. oxygen at high %RH as it removes excess water which may impede gas flow. At low %RH, the identical nature of the polarization response for pure and mixed oxidants suggests that O₂ diffusivity in the gas or liquid phase is not limited in SS-CCE cathodes at lower RH conditions.

Overpotential corrections.— The contribution of each polarization source is relative depending on the current density used for comparison. With this fact in mind, only select current densities are used to compare and quantify the contribution of each loss for the MEAs but the analysis has been performed on the entire data spectrum. Table I compares the overpotential contributions for the catalyst layers when oxygen, air, and 4% oxygen in nitrogen are used as oxidants. Since the performance of the SS-CCE cathode layer was significantly better at

| MEA               | Oxidant | Current Density (mA cm⁻²) | η_{ohm,membrane} | η_{ohm,electrode} | η_{conc,nonelectrode} | η_{conc,electrode} | η_{total} |
|-------------------|---------|---------------------------|------------------|-------------------|-----------------------|--------------------|-----------|
| Nafion Oxygen     | 90      | 16                        | 22               | 15                | 53                    | 106                |
| SS-CCE (75% RH) Oxygen | 90      | 50                        | 59               | 61                | 79                    | 249                |
| SS-CCE (20% RH) Oxygen | 90      | 46                        | 56               | 6                 | 88                    | 196                |
| Nafion Air        | 200     | 34                        | 45               | 115               | 175                   | 369                |
| SS-CCE (75% RH) Air | 200     | 107                       | 126              | 17                | 219                   | 469                |
| SS-CCE (20% RH) Air | 200     | 98                        | 118              | 1.2               | 145                   | 362.2              |
| Nafion 4% O₂      | 100     | 23                        | 30               | 42                | 1.6                   | 96.6               |
| SS-CCE (75% RH) 4% O₂ | 100     | 56                        | 66               | 13                | 14                    | 149                |
| SS-CCE (20% RH) 4% O₂ | 100     | 50                        | 61               | 12                | 89                    | 212                |
20% RH compared to 75% RH, the SS-CCE MEA has been evaluated under both sets of conditions and compared to the Nafion-based MEA.

**Membrane ohmic overpotential.**— It is clear from Table I that contributions from the membrane ohmic overpotential ($\eta_{\text{ohm,membrane}}$) are lower for the Nafion-based catalyst layer than for the SS-CCE catalyst layer. As seen from Table II, which compares different characteristics of the MEAs, the membrane resistance values for the SS-CCE are higher than for the Nafion standard. Since the membranes are identical for the MEAs prepared, the difference in overpotential is likely due to contact resistance between the ionomer in the catalyst layer and in the membrane. The standard MEA includes both a Nafion membrane and Nafion ionomer in the catalyst layer, thus the contact resistance should be minimal. Application of the SS-CCE cathode to the Nafion membrane may introduce increased resistance to proton transport as the sulfonated silane is not as effective at proton conduction as Nafion. Higher contact resistances have been observed for MEAs employing different ionomers in the membrane and catalyst layer.\(^{18,19}\) There is a slight decrease in the membrane ohmic overpotential (due to a decrease in resistance) when the SS-CCE is operated at 20% RH versus 75% RH. Based on the previous research on SS-CCE materials,\(^{20}\) this is due to removal of excess water from the cathode via back diffusion of water from the cathode to the membrane which improves the performance of the MEA at low relative humidity.

**Electrode ohmic overpotential.**— Just as for the membrane ohmic overpotential, the electrode ohmic overpotential ($\eta_{\text{ohm,electrode}}$) is higher for the SS-CCE catalyst layer than for the Nafion-based electrode. Since the electrode ohmic overpotential accounts for both proton and electronic resistance in the electrodes, this is not surprising. As discussed in the previous section, the proton resistance for the sulfonated silane is higher than for Nafion and thus electrode ohmic overpotential would be higher for the SS-CCE materials in the case where the electronic resistance were the same for both electrodes. It is possible that the electronic resistance is slightly higher for the SS-CCE electrodes as well if the morphology of the silane were to impede electron transport through the carbon material. There has been no specific evidence of decreased electronic resistance within this SS-CCE composition, and the relative differences in potential for the membrane and electrode ohmic overpotentials when comparing the SS-CCE and Nafion electrodes is fairly constant. It stands to reason that resistance to proton transport is the culprit in both instances. Comparing the values of the membrane to the electrode ohmic overpotentials, it is clear that for both types of electrodes there is a higher contribution to overpotential from the cathode than from the membrane. Therefore, losses in fuel cell performance are more significantly affected by changes in the electrode than in the membrane.

It was possible in all three analyses to find a value of $R_{\text{electrode}}$ that satisfied the theoretical current ratios ($4.76$ or $5.25$), though for the SS-CCE samples only the ratio between air and 4% oxygen could be evaluated. This is because at 75% RH, the air polarization curves performed better than for oxygen and already the theoretical ratio of oxygen-to-air was not applicable. At 20% RH, the oxygen and air curves were almost identical which was unexpected and indicates that changes in performance due to changes in oxygen concentration within the electrode were not a factor for the SS-CCE under these conditions. Therefore, no value could be found to satisfy the current ratio of 4.76; however the same phenomena was not observed between air and 4% oxygen, thus the ratio between these curves was still able to be evaluated. The successful determination of the theoretical current ratio indicates that there is a first-order dependence on O$_2$ concentration in the absence of transport limitations for both Nafion-based and SS-CCE cathodes. As discussed previously, flooding in the catalyst layer at 75% RH for the SS-CCE will skew the results for determining oxygen concentration, and the high flow of air at low humidity appeared to improve performance of the SS-CCE at low RH as the electrode performs better under drier conditions.

**Non-electrode concentration overpotential.**— Table I highlights the variation in the overpotential due to non-reacting oxygen transport ($\eta_{\text{conc,non electrode}}$). There is no distinct trend between catalyst layers and different oxidants. When pure oxygen is used, the contribution due to oxygen transport in the gas diffusion layer (GDL) is highest for the SS-CCE at 75% RH. This result is reasonable, as the SS-CCE exhibited significant flooding (Figure 4) at 75% RH and thus there is a considerable amount of water in the catalyst layer. The GDL contains a hydrophobic binder whereas the catalyst layer consists of a hydrophilic binder and therefore oxygen transport is restricted by liquid water when it reaches the catalyst layer. No flooding was evident in the oxygen polarization curves for the Nafion catalyst layer at 75% RH or the SS-CCE at 20% RH, thus the contribution of $\eta_{\text{conc,non electrode}}$ is minimal. When air was used as the oxidant, the Nafion-based electrode was more greatly affected by non-reacting oxygen transport than either of the SS-CCE catalyst layers. The higher flow rates for air appear to improve transport through the GDL and binder as the liquid water is forced out of the cathode, but for the Nafion-based cathode the ability of oxygen to be transported is limited. This suggests that the addition of the MPL/GDL system, along with the porous nature of the CCE, may allow for improved oxygen transport to the cathode than can be achieved with direct application of a Nafion-based electrode to a GDL.

For the data obtained for the Nafion-based cathode under air and SS-CCE cathode (75% RH) under air and oxygen, one linear plot could not be made from $\eta_2$ ($R_{\text{mem}} + R_{\text{electrode}}$ corrected overpotential) versus $\log \left[ \frac{I_2}{I_1 (i_{i-L})} \right]$ to account for non-electrode concentration overpotential. In these cases, the data was corrected based on the higher current density data and applied to the entire curve as prescribed by the fitting procedure used by Sambandam and Ramani.\(^{17}\) A deviation from linearity in $\eta_2$ versus $\log \left[ \frac{I_2}{I_1 (i_{i-L})} \right]$ plot indicates that the O$_2$ concentration experiences activation control at low current density, but both activation and diffusion controlled at high current density.\(^{21}\) These deviations occurred near 200 mA cm$^{-2}$ and indicate that at current densities above this value, losses due to hindrance of diffusion were present. Since the low O$_2$ concentrations did not exhibit deviations due to diffusion control, nor did the SS-CCE at 20% RH, it is unlikely that the issue could be attributed to low O$_2$ content in the cathode gas feed. It is more likely that at more humid conditions, there was liquid water at the interface between the cathode and membrane.
between the catalyst layer and GDL that impeded O₂ transport. The high gas flow rates for the low O₂ concentration oxidant would force the water out of the catalyst layer and thus transport is only activation controlled.

Electrode concentration overpotential.— The overpotential that results from both transport and reaction of O₂ in the cathode (η_{conc,electrode}) did not exhibit a clear trend across catalyst layers. For both MEAs, the electrode concentration overpotential had the largest contribution to the total overpotential when oxygen and air were used as oxidants. This indicates that the ability of the cathode to transport and facilitate reactions with oxygen had the greatest effect on the polarization curve. The fact that the values of η_{conc,electrode} were higher for SS-CCE than the Nafion cathode when both were at 75% RH was expected due to the considerable mass transport issues for the SS-CCE. The contribution from η_{conc,electrode} was higher for the SS-CCE at 20% RH than at 75% RH which was unanticipated. It was believed that the reduced water content would improve the transport of O₂ throughout the cathode. Nafion catalyst layers exhibit higher concentration overpotentials as relative humidity decreases due to lower oxygen permeability through the ionomer film at the electrode surface, as well as the lower partial pressure of oxygen at the inlet. The higher contribution of η_{conc,electrode} at 20% RH for the SS-CCE suggests that alleviation of mass transport at low relative humidity is offset by the lower oxygen partial pressure as oxygen transport through ionomer (η_{conc,nonelectrode}) does not appear to be adversely affected by low RH conditions.

MEA characteristics.— Table II summarizes several characteristic parameters that were calculated throughout the process of determining overpotential contributions. Even though identical membranes were used, the membrane resistance for the Nafion-based MEA was lower than for the SS-CCE cathodes due to contact resistance between the cathode and the membrane. There was a slight decrease in membrane resistance when the %RH was lowered for the SS-CCE as the cathode tends to donate excess water to the membrane under dry conditions. The electrode resistance was also lower for the Nafion-based MEA and again was lower for the lower humidity SS-CCE. Since the carbon support and gas diffusion layers tend to have high electronic conductivity, resistance to proton transport tends to be the principal component of R_{electrode}. Fluctuations in the water concentration at high %RH for SS-CCE cathodes may cause variations in proton path-ways and hinder proton transport throughout the experiment as the cathode undergoes repeated flooding and drying.

Sambandam et al. noted that MEAs with a higher limiting current density had a lower contribution from the non-electrode concentration overpotential. This trend was not observed in our data. Figure 6 is an example of the overpotential corrections, as applied to the Nafion-based catalyst layer at 80°C and 75% RH under oxygen (Figure 6a) and to the SS-CCE at 20% RH under oxygen (Figure 6b). For some of the experiments, curves showed limitations that had manifested due to mass transport, which ultimately affects the evaluation of limiting current and thus skews the determination of iₗ. The Tafel slope was used to correct for electrode concentration overpotential and is assumed to be applicable to all oxidants since the Tafel line is theoretically independent of oxygen concentration.

To test this assumption, kinetic Tafel lines were constructed for each oxidant from low current density data. The resulting Tafel slopes are compared in Table II. The typical Tafel slope for a hydrogen/oxygen fuel cell is ca. 60 mV and this value was achieved for the SS-CCE (75%RH and 20%RH) under air and for the SS-CCE at 75% RH under 4% oxygen. Tafel slopes were lower than 60 mV for the Nafion and SS-CCE (20% RH) MEAs, but higher for the 75% RH SS-CCE. Clearly the incidence of flooding limits reaction kinetics for the CCE electrode when pure oxygen and air are used as oxidants. Additionally, the Tafel slope was higher for the SS-CCE at low humidity versus high humidity when the low O₂ concentration oxidant was used. The kinetics are sensitive to differing relative humidities and gas flow rates which results in performance changes at low current density as well as high current density where mass transport limitations are expected.

Total overpotential contributions were calculated for the electrodes by summing the individual overpotentials and are listed in Table I, as well as visualized for values calculated with air as an oxidant in Figure 7. When air is used as an oxidant, it leads to the largest total overpotential for all electrodes. The total values for overpotential are almost identical for the Nafion electrode at 75% RH and the SS-CCE electrode at 20% RH. Clearly, the incidence of high relative humidity in the cathode has a significant impact on SS-CCE overpotentials. While a reduction in relative humidity offers some improvement for ohmic resistance values (Figure 7a), it is not enough to lower values to the level of Nafion-based electrodes. It is evident that SS-CCE cathodes do not suffer significant performance loss due to non-electrode concentration overpotential which is a substantial factor in Nafion electrode performance. Electrode concentration overpotentials are the largest contributors to the total
overpotential, but reduction in the relative humidity at the cathode makes the SS-CCE less susceptible to performance loss as a result of O₂ reaction and transport than the Nafion-based catalyst layer (Figure 7b).

This indicates that SS-CCE materials have different transport dynamics than Nafion-based catalyst layers. Membrane ohmic resistance values are higher for the SS-CCE electrode than the Nafion cathode, but this value decreased for the SS-CCE when operation conditions were adjusted to lower %RH due to back-diffusion of water from the cathode to the membrane. Contributions from electrode ohmic overpotential are slightly higher than for membrane ohmic overpotential. The higher values calculated for the SS-CCE versus Nafion-based catalyst layers was a result of the increased proton conductivity of Nafion. For the non-electrode concentration overpotential, when pure oxygen was used the SS-CCE at 75% RH displayed the largest value. This is expected as the most significant flooding occurs under these conditions, which restricts oxygen transport. The use of air as an oxidant, along with low %RH at the cathode, resulted in lower overpotential contributions in most cases than when other oxidants were used. Higher flow rates used for air aid in forcing water out of the cathode and improved O₂ transport in the catalyst layer and GDL.

Addition of the MPL to the cathode layer construction appeared to improve oxygen transport compared to the Nafion-based catalyst layer without an MPL. While the electrode concentration overpotential did not exhibit a clear trend across catalyst layers, it contributed most to overpotential for both catalyst layers when air and oxygen were used as oxidants. Mass transport issues limited O₂ transport through the cathode when high humidity conditions were used but the contribution was larger at 20% RH, likely a result of slower reaction kinetics due to the temperature differential experienced by the cell to maintain cathode humidity at lower values. As long as the SS-CCE cathodes were kept at low humidity, their performance was not limited by O₂ transport. This can have wide-reaching implications as, while their performance is not as high as for Nafion at 75% RH, their ability to perform reasonably under low RH conditions means they can be used in different environments when Nafion cannot. Furthermore, these electrodes can tolerate transient RH fluctuations.

The experimental methods employed in this study were used to aid in determining sources of polarization and transport losses within the novel CCE catalyst layer structure compared to traditional Nafion-containing electrodes. The MEAs and experimental conditions used in this study are summarized alongside those of comparative literature in Table III. Qualitatively, the polarization curves for each type of catalyst layer and humidity condition studied showed that for SS-CCE cathodes, lower relative humidity improves performance and O₂ transport. This reflected our previous results where performance was improved at lower relative humidity. The reduction in oxygen transport is a large contributing factor to lower performance. Quantitatively, our results can be compared to literature for Nafion-based catalyst layers as well as those prepared with sulfonated poly(ether ether ketone) (SPEEK). The value of each overpotential calculated was highly dependent on the current density used for comparison. The overpotential values for the Nafion-based catalyst layer with air as the oxidant found by Williams et al. 3 were tabulated for 400 and 600 mA cm⁻². The values in this paper were compared at 200 mA cm⁻² as some of the Nafion-based electrode polarization curves did not reach those current densities and thus are not directly comparable to the Williams data. Despite this, the membrane ohmic overpotential was in the same range for both studies, as it should be since Nafion membranes were employed in both studies. The remaining overpotential values were higher for our electrodes compared to the ones studied by Williams et al., though it is important to note that the electrode fabrication processes were different between studies. While this work used gas diffusion electrodes, Williams et al. constructed catalyst-coated membranes and then applied a MPL/GDL after catalyst layer deposition. Since the analysis method is diagnostic as opposed to quantitative, it is more useful to compare trends. The highest component to overpotential for Nafion-based electrodes in both this work and Williams’ studies was from the electrode concentration overpotential, related to oxygen transport and reaction in the catalyst layer. The Tafel slope calculated for oxygen data was smaller for our Nafion-based electrode than for the electrodes found by Williams et al., though they were similar to our SS-CCE electrodes indicating that kinetic parameters are comparable between the two studies.

As for alternative ionomer materials, electrodes prepared with different formulations and concentrations of SPEEK have been examined and compared. Sambandam and Ramani 2 calculated Tafel slopes for SPEEK-based electrodes in the range of 70–83 mV/decade whereas our SS-CCE electrodes were found to have Tafel slopes of

Table III. Comparison of samples and experimental conditions for MEAs studied in literature to determine transport properties.

| Membrane tested | Electrode composition | Cathode Pt loading (mg cm⁻²) | Temperature conditions (°C) | Cathode relative humidity (%) |
|-----------------|-----------------------|-----------------------------|-----------------------------|-------------------------------|
| Aciplex-S       | 20% Pt/C, 0.6 mg cm⁻² Nafion | 0.4                         | 50-90                       | 100                           | 6                             |
| Nafion          | 46% Pt/C, 35 wt% Nafion | 0.46                        | 80, 100, 120                | 100, 70, 35                   | 3                             |
| SPEEK-5         | 40% Pt/C, 30 wt% Nafion or SPEEK | 0.4                         | 80                           | 75                            | 7                             |
| PFSA 750, PFSA 1050, Nafion | 40% Pt/C, 15–31% binder (PFSA, SPEEK, SPSU) | 0.4 ± 0.02                  | 80                           | 75                            | 17                            |
| Nafion          | 20% Pt/C, 30 wt% Nafion or 40 wt% silane | 0.31-0.34                   | 80                           | 75, 20                        | This work                     |

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53 mV/decade (low RH) and 81 mV/decade (high RH). Overpotential values calculated for Nafion-based electrodes (air, 200 mA cm$^{-2}$) combined with SPEEK membranes were lower than when SPEEK-based electrodes were used. The SPEEK-based electrodes had much lower membrane ohmic overpotential values than our SS-CCE electrodes, though the remaining overpotential values were similar in magnitude. Electrode concentration overpotential values are in the same range for both SPEEK (150 and 225 mV) and SS-CCE electrodes (145 and 219 mV), indicating similar limitations due to oxygen reaction and transport are characteristic of electrodes with alternative ionomers. SS-CCE electrodes had much lower contributions from the non-electrode concentration overpotential, suggesting better O$_2$ transport properties in the GDL and ionomer. This may be due to high flow rates of air which aid with drying out the cathode and facilitate the movement of O$_2$ toward reaction sites. All of the SPEEK electrodes tested in comparative literature,$^{17}$ were exposed to 80°C and 75% RH, so the performance of these alternative ionomers at low %RH is left to speculation. For alternative SPEEK/SPSU ionomers,$^{17}$ current ratios could not be found to satisfy the theoretical values during determination of electrode ohmic overpotential which suggested a less than first-order dependence on oxygen concentration, the source of which was not determined but was suspected to be a result of low O$_2$ permeability in SPEEK compared to Nafion.$^{18}$ Theoretical current ratios could be achieved for SS-CCE electrodes, which indicate that the assumption of a first-order dependence on O$_2$ concentration and diffusion based on Fick’s law are valid for these catalyst layers and that the use of a sulfonated silane ionomer does not limit oxygen transport.

Conclusions

Fuel cell cathode catalyst layers prepared using SS-CCE materials were evaluated electrochemically to identify sources of performance loss and compared to a Nafion-based catalyst layer. Cyclic voltammetry revealed that the ECSA was similar for the two electrodes. Impedance results suggested that while the SS-CCE had slightly better proton conductivity and lower ionic resistance than the Nafion-based electrode, both catalyst layers suffered degradation over the course of study. Limiting capacitance did not change for either catalyst layer over time, indicating that carbon corrosion was not an issue.

Four different oxidants were used elucidate differences in transport phenomena due to oxygen concentration and gas diffusion. The Nafion-based cathode was examined at 80°C and 75% RH whereby it exhibited a typical response, with the best performance achieved under pure oxygen. Use of helium as an oxidant diluted resulted in improved oxygen diffusion and mitigated mass transport losses. The SS-CCE catalyst layer examined under identical conditions exhibited significant mass transport limitations. As SS-CCE cathodes display optimal performance under dry conditions, the relative humidity at the cathode was varied and performance monitored. As the %RH decreased, performance of the SS-CCE improved. At 20% RH the SS-CCE performed optimally, and the similarity between the oxygen, air, and helox curves indicates that oxygen diffusivity in both the gas and liquid phases is not an issue at low relative humidity.

The contribution of four different overpotentials to MEA performance were calculated and compared across the two different catalyst layers, and for the SS-CCE at high and low relative humidity. For the most part, the electrode concentration overpotential had the largest contribution which suggests oxygen diffusion and reaction in the catalyst layer has the greatest impact on performance loss. Both ohmic overpotentials (and thus resistance values) were lower for the MEA with the Nafion-based cathode relative to the SS-CCE due to lower contact resistance between the electrode and membrane ionomers. In most cases, the SS-CCE cathode at 20% RH had lower overpotentials than at 75% RH. Reduction of ohmic overpotentials was achieved by back diffusion of water from the cathode to the drier membrane at 20% RH. The Nafion-based catalyst layer had lower values for the electrode concentration overpotential than the SS-CCE cathode, which actually performed poorly at low %RH due to the difference in oxygen partial pressure at low relative humidity. Tafel slopes were lower for the Nafion-containing cathode, indicating reaction kinetics were better than with the SS-CCE cathode.

Overall, it the SS-CCE cathodes experience fewer transport-related losses at low relative humidity than high relative humidity. Concentration overpotentials were lower for the SS-CCE at 20% RH than either catalyst layer at 75% RH when air was used as the oxidant. Additionally, at 20% RH, the SS-CCE did not exhibit any reduction in performance when air was the oxidant which is quite remarkable. This suggests that the higher flow rates used with air at the cathode have a positive effect on electrode performance as it helps to alleviate issues from water accumulation in the pores, but oxygen diffusion through the catalyst layer was not affected. While contact resistance and ion transport may be limited when combined with a Nafion membrane, the results suggest these overpotential values could be improved by using alternate fabrication methods such as catalyst-coated membranes.

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References

1. F. Barbir, PEM fuel cells: theory and practice, Elsevier Academic Press, Amsterdam (2005).
2. S. Sambandam, J. Parrondo, and V. Ramani, Physical Chemistry Chemical Physics, 15, 14994 (2013).
3. M. V. Williams, H. R. Kunz, and J. M. Fenton, Journal of the Electrochemical Society, 152, 1635 (2005).
4. Y. Liu, M. W. Murphy, D. R. Baker, W. Gu, C. Ji, J. Jorne, and H. A. Gasteiger, Journal of the Electrochemical Society, 156, B970 (2009).
5. M. Mench, E. C. Kumbur, and T. N. Veazoglou, Polymer electrolyte fuel cell degradation, Academic Press, Amsterdam (2012).
6. Y. W. Rho, O. A. Velev, S. Srinivasan, and Y. T. Kho, Journal of the Electrochemical Society, 141, 2084 (1994).
7. S. Sambandam and V. Ramani, Journal of Power Sources, 170, 259 (2007).
8. J. I. Eastcott, J. A. Powell, A. J. Vreugdenhil, and E. B. Easton, ECS Transactions, 41, 853 (2011).
9. J. I. Eastcott, K. M. Yarrow, A. W. Pedersen, and E. B. Easton, Journal of Power Sources, 197, 102 (2012).
10. M. C. Lelehrve, R. B. Martin, and P. G. Pickup, Electrochemical and Solid State Letters, 2, 259 (1999).
11. E. B. Easton and P. G. Pickup, Electrochimica Acta, 50, 2469 (2005).
12. J. Zhang, PEM fuel cell electrocatalysts and catalyst layers fundamentals and applications, Springer, London (2008).
13. F. S. Saleh and E. B. Easton, Journal of Power Sources, 246, 392 (2014).
14. F. S. Saleh and E. B. Easton, Journal of the Electrochemical Society, 159, B546 (2012).
15. G. W. Thomson, Chemical reviews, 38, 1 (1946).
16. P. J. Linstrom and W. G. Mallard, NIST Chemistry webbook; NIST standard reference database No. 69, National Institute of Standards and Technology, Gaithersburg, MD (2005).
17. S. Sambandam and V. Ramani, Physical Chemistry Chemical Physics, 12, 6140 (2010).
18. E. B. Easton, T. D. Astill, and S. Holdcroft, Journal of the Electrochemical Society, 152, A752 (2005).
19. B. S. Pivovar and Y. S. Kim, Journal of the Electrochemical Society, 154, B739 (2007).
20. J. I. Eastcott and E. B. Easton, Journal of Power Sources, 245, 487 (2014).
21. H. R. Kunz and G. A. Greuer, Journal of the Electrochemical Society, 122, 1279 (1975).
22. R. Anderson, M. Blanco, X. Bi, and D. P. Wilkinson, International Journal of Hydrogen Energy, 37, 16093 (2012).
23. R. Anderson, M. Blanco, D. P. Wilkinson, and X. Bi, The use of the Anode Water Removal Method to Understand Cathode Gas Diffusion Layer Flooding, p. 203, AMER SOC MECHANICAL ENGINEERS, NEW YORK; THREE PARK AVENUE, NEW YORK, NY 10016 USA (2012).
24. H. H. Voss, D. P. Wilkinson, P. G. Pickup, M. C. Johnson, and Y. Basura, Electrochimica Acta, 40, 321 (1995).