PEFC electrodes manufactured using inkjet printing are investigated. Cell performance, Tafel slope, reaction order and local oxygen transport resistance of electrodes with varying Pt loadings of 0.014 to 0.113 mg/cm² are studied in order to understand the nonlinear relationship between loading and performance. The performance increase with Pt loading was substantially reduced above Pt loadings of 0.08 mg/cm². Electrochemical active area of the electrodes decreased from 66.4 to 40.4 m²/g as the Pt loading increased from 0.026 to 0.113 mg/cm². Below the transition voltage of 0.8 V at 1/2 cell, the Tafel slope was found to be a function of the Pt loading and oxygen partial pressure. The kinetic performance dependence on \( P_{O_2} \) was quantified by measuring the total reaction order. Oxygen transport resistance evaluated from limiting current experiments revealed its dependence on the inlet relative humidity of the reactants. The local oxygen transport resistance was found to drop from 5.93 ± 3.16 s/cm to 3.43 ± 1.67 s/cm as the humidity increased from 50% to 90%.

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Hydrogen polymer electrolyte fuel cells (PEFCs) are a zero emission and efficient energy conversion technology for transportation, stationary and electronic applications. The current generation of fuel cell vehicles provide quick start-up, long-range and increased durability. The high and unstable cost of platinum (Pt), which is the commonly used catalyst, however hinders its commercial prospects, especially when compared to the internal combustion engine. The cost of Pt is responsible for over 34% of the fuel cell stack cost. Less than 10–20% of the catalyst is however estimated to be utilized during the operation of a conventional catalyst layer (CL) due to mass and charge transport limitations. Re-designing the CL to improve these transport limitations has the potential to achieve better Pt utilization, i.e., generate more current per gram of catalyst. The CL fabrication process governs its utilization efficiency, microstructure and Pt loading in the electrodes.

The effect of Pt loading on electrodes manufactured by spraying, using film applicators, sputtering as well as inkjet printing has been studied in the literature. Results show that fuel cell performance is severely degraded at low Pt loading and that an optimal value of Pt loading exists above which the performance gains are not very significant. The reason for the reduced performance of low loading electrodes has thus far mainly been attributed to a high oxygen mass transport resistance at the reaction site. The source of this resistance is still under debate. Oxygen dissolution in the ionomer, densification of the ionomer layer near the ionomer/Pt interface, and catalyst/Oxygen interactions at the catalyst site have been proposed as causes for this local mass transport barrier. These results indicate that in order to understand the performance degradation of low loading electrodes, and to compare different manufacturing techniques, limiting current measurements are required to estimate the local transport resistance.

Low loading electrode studies have focused on analyzing the local mass transport resistance and have provided little detail regarding the reaction kinetics of low loading membrane electrode assemblies (MEA). Recently, Shukla et al. measured Tafel slopes of the order of 120 mV/dec for their low loading electrodes. This value is in disagreement with the value of 60 - 70 mV/dec reported at higher loadings. It therefore appears that kinetics might also have an effect on the reduced performance of low loading electrodes. Therefore, both limiting current density and kinetic parameters should be reported when studying low loading electrodes. Further, in order to understand if the kinetic behavior of low and high loading electrodes is different, the kinetic study should be performed for both electrodes fabricated using the same method. Such study has been undertaken in this article.

The sensitivity of low loading electrodes to oxygen partial pressure has also not been studied in detail. Our results have shown that low loading electrodes are remarkably sensitive to changes in absolute cell pressure. This sensitivity to back pressure would explain why most authors report low loading electrode performance at elevated pressures, e.g. Refs. 5,7,8,11,12. Even for conventional electrodes, the oxygen reaction order has usually been reported only at open circuit voltage, e.g. Refs. 27,28. Our analysis of previous solid state data from Ref. 27 in Ref. 28 showed that the oxygen reaction order changed with overpotential and it did not agree with our proposed modified double trap model. Markiewicz et al. on the other hand reported that the reaction order did not change with overpotential over a range of 0.6 V. They measured the oxygen reduction reaction (ORR) kinetics using a floating electrode instead of an MEA. Given the uncertainty regarding the oxygen reaction order, further studies both ex-situ and in-situ are required. However, this study is the first of its kind to understand the oxygen reaction order for low and moderate loading electrodes is reported. Increasing the Pt loading results in a substantial increase in fuel cell performance up to an optimal loading value. Qi and Kaufman report the optimal Pt loading to be dependent on the type of Pt/C catalyst due to changes in the catalyst surface area. The optimal Pt loading was found to be 0.2 ± 0.05 mg/cm² for the case of 20% Pt/C catalyst and 0.35 ± 0.05 mg/cm² for the case of 40% Pt/C catalyst. Kriston reported the relationship between the electrochemical active area and Pt loading from 0.05 mg/cm² to 0.4 mg/cm². The active area decreased with Pt loading due to the decreasing catalyst accessibility. The performance increase was reported to be substantial from 0.05 mg/cm² to 0.2 mg/cm², but minimal thereafter. Similar performance trends can be observed in other literature on low loading PEFCs. The optimal loading might not only be a function of the type of catalyst, but also the manufacturing method. The impact of this parameter on the optimal Pt loading value has not been discussed and it is another goal of this article.

In order to enhance the understanding of low and moderate loading electrodes, a comprehensive study of the performance, kinetics, reaction order, and local mass transport losses in electrodes with varying loading is performed. To elucidate the effect of reaction order, tests are performed at a variety of oxygen partial pressures. To the knowledge of the authors, such comprehensive study has not yet been reported in the literature. Further, a sensitivity study of local transport resistances with relative humidity is also first reported. In our laboratory, inkjet printing (IJP) has been used as a fabrication tool for depositing catalyst layers over Nafion membrane. We already demonstrated

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Nafion loading was kept constant at 30 wt% (ionomer/carbon (Ion Power) was added drop-wise to the ink during sonication. The suspension prior to its use. Finally, the ink was left on the magnetic stirrer to homogenize the reaction order was evaluated for the electrodes by operating the cells under different $p_{O_2}$ conditions. Oxygen mass transport losses were minimized in the channels by operating the cell using parallel-channel configuration at a constant stoichiometric ratio of 10. The variation of the reaction order with overpotential is discussed.

**Experimenental section** gives details on CCM fabrication, electrode characterization methods and operating conditions used. Results and discussion section discusses the results from the experimental testing, kinetic analysis, evaluation of transport resistance and their comparison to literature values.

**Experimental**

**CCM preparation.**—A similar procedure to the one reported previously was followed to formulate the catalyst inks and fabricate the CCMs, however a lower boiling point solvent was used to aid in the drying process.\(^{25}\) The catalyst, 20% Pt/C on Vulcan XC carbon black (Hi SPEC 3000, Alfa Aesar), was mixed with ethylene glycol and Isopropanol ($\geq 99.5\%$, Fisher Scientific) and bath sonicated for 30 minutes (Branson-1800). 5 wt% of Nafion ionomer solution (Ion Power) was added drop-wise to the ink during sonication. The Nafion loading was kept constant at 30 wt% (ionomer/carbon = 0.54). The ink was then probe sonicated (S-4000, Q-Sonica) for 15 minutes (2 min. ON, 1 min. OFF) to further help in breaking the aggregates. Finally, the ink was left on the magnetic stirrer to homogenize the suspension prior to its use.

CL fabrication was carried out using a commercial inkjet printer (Dimatix-2831, Fujifilm). 5 cm\(^2\) CLs were printed directly on the Nafion membrane as a substrate (NR-211 from Ion Power as received). The Pt loading on the cathodic electrodes was varied by changing the number of printed passes. CLs with 3, 5, 10, 15 and 20 layers (L) were fabricated corresponding to Pt loadings of 0.014, 0.026 $\pm$ 0.005, 0.056 $\pm$ 0.012, 0.080 $\pm$ 0.019 and 0.113 $\pm$ 0.026 mg/cm\(^2\) respectively. The anodic Pt loading was fixed at 0.026 $\pm$ 0.005 mg/cm\(^2\) (5L). Once both anodic and cathodic electrodes were fabricated, the CCMs were dried in the oven at 80 °C for a few hours to evaporate the solvents, boiled in deionized water for around 3 hours and stored for further use. Pt loading of the CCMs was measured using gravimetric analysis, and confirmed by X-ray fluorescence (Thermo Scientific, Niton XL3t) for several samples. The average values and standard deviations are obtained from three independently fabricated samples. For comparison, a spray coated electrode is used. The spray-coated electrode had a cathodic Pt loading of 0.4 mg/cm\(^2\) and used a 46% Pt/C catalyst (TEC10E50E, TKK) over NR-211 membrane.\(^{32}\)

**Ex-situ characterization.**—Microstructure characterization of the electrodes was carried out using field emission scanning electron microscope (SEM) imaging (6301 - F, JEOL). Sample preparation involved freeze-fracturing the CCMs in liquid nitrogen before mounting them on SEM stubs for imaging. A cross-sectional image of the freeze-fractured samples gave an estimate of the CL thickness. A mean value of the thickness with the standard deviation from 15 locations is reported. The density of Vulcan XC-72 carbon black, needed in order to estimate the catalyst layer porosity, was obtained by mercury intrusion porosimetry (Poremaster 33, Quantachrome Instruments). An oven-dried sample of Vulcan XC-72 (Fuel Cell Store) was inserted in a glass penetrometer having a stem volume of 0.5 cm\(^3\). The penetrometer was then filled with mercury and the mercury was pressurized to a maximum pressure of 33,000 psi. The volume of the sample was calculated by subtracting the volume of mercury in the penetrometer without the sample and the volume of mercury after mercury intruded in the sample. Figure 1 shows the pore size distribution (PSD) of the Vulcan carbon from four independent experiments where the logarithmic pore distribution, $\frac{dx}{dx_{max}}$, is plotted vs. the pore radius, where $X$ is the cumulative pore volume fraction.

Assuming the density of mercury to be 13.69 g/cm\(^3\), the averaged density value of Vulcan XC-72 carbon was found to be 1.69 $\pm$ 0.21 g/cm\(^3\). The maximum pressure of 33,000 psi corresponded to a minimum pore diameter of approximately 4 nm. Pores smaller than 4 nm are unlikely to contribute to mass transport. Therefore, this estimate for density is used in our porosity calculations as this porosity might be more representative of the actual available macro-pore network.

**In-situ characterization.**—Electrochemical characterization was carried out using a potentiostat (VersaStat4 - Princeton Applied Research) and a fuel cell test station (Scribner Associates 850e system with back pressure unit). Cell performance was tested using 5 cm\(^2\) flow-field plates with parallel channel configuration. Cyclic...
voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS) experiments were conducted to measure the active area, hydrogen crossover and CL resistance of the cell (details regarding the experimental parameters used can be found in Ref. 25). Galvanostatic polarization plots (scan rate of 0.1 A per point) were recorded at a cell temperature of 80°C at 50%, 70% and 90% RH. Six plots (three forward and three backward sweeps) were obtained for each of the aforementioned conditions. Ohmic resistance obtained from current interrupt measurements was used for correcting the measured voltage values in order to get the IRFree plots. Tests were performed at a constant stoichiometric ratio of 10 with minimum flow-rates of 0.2 and 0.4 lpm for anode and cathode respectively. The oxygen partial pressure was varied by varying the reactant oxygen concentrations, i.e., 1% oxygen (balance - N₂), 10% oxygen (balance - N₂) and ultra-zero compressed air (Praxair Inc.) and by increasing the gas pressure from 50 to 150 kPa (gauge) when operating with air. Both anodic and cathodic pressures were maintained at the same value.

Limiting current density experiments were carried out using hydrogen and 1% oxygen (bal. N₂) as the anodic and cathodic reactants. A constant stoichiometric ratio of 5 at 1 A was used, corresponding to a cathodic flow-rate of 3.9 slpm at 90% RH. Voltage was scanned from 0.35 V to 0.05 V in steps of 25 mV (15 min./point) and the current was recorded at each point.

For each Pt loading, at least three samples were fabricated and tested for each of the conditions discussed above. An average value with the error bars showing one standard deviation are reported for each case.

**Results and Discussion**

**Microstructure characterization.**—Figure 2 shows the top and cross-sectional SEM images of CLs with varying Pt loadings. Figure 2a shows the top surface of a 5L CCM where the porous structure consisting of catalyst particles can be seen. Figures 2b–2d shows the freeze-fractured side images of the 5L, 10L and 15L electrodes and their corresponding thickness value. Table I reports the measured Pt loadings and CL thicknesses. Even though the catalyst loading doubles with the number of passes, this is not the case for the electrode thickness, and nonlinear increase in thickness is observed with number of deposited layers from 1.90 μm for 5 layers to 5.54 μm for 20 layers. High Pt loading electrodes are therefore more compact and have a reduced porosity. The reduction in porosity with loading is a major drawback of inkjet printing. Future work in needed to improve the electrode pore-distribution and porosity at higher loadings.

CL porosity was estimated based on the ink composition, Pt loading and CL thickness values using the relationships given by Wang et al.35 Densities of Nafion and Pt are taken to be 2 mg/cm² and 21.5 mg/cm², respectively. The density of Vulcan carbon calculated using mercury intrusion porosimetry was found to be 1.69 ± 0.21 g/cm³. Table I gives the values of the calculated CL porosity for the different electrodes. The porosity decreased from 51% to 29% as the number of printed passes increased from 3L to 20L. For an electrode with Pt loading of 0.025 mg/cm², Owejan et al.37 reported a CL thickness value of 11 ± 1.2 μm using 5% Pt/C catalyst. This would correspond to a CL thickness of 2.75 ± 0.3 μm when considering a 20% Pt/C catalyst. For this work, the measured value for a 5L CCM with similar Pt loading is 1.90 ± 0.37 μm. Yu and Carter34 reported a porosity value of 68.1% for their electrodes with ionomer/carbon ratio of 0.5. The higher value may partly be due to the type of fabrication method used and partly due to the higher value of carbon density (2.2 g/cm³) assumed in their case.34 Gode et al.35 reported electrode porosity and thickness values of 52% and 7.6 μm respectively for an electrode with Pt loading of 0.11 mg/cm² using 20% Pt/C catalyst. In our case, a similar Pt loading (0.113 mg/cm²) and catalyst type produced electrodes with porosity and thickness values of 29% and 5.54 μm respectively. The comparison of CL thicknesses and porosities with other reported values may suggest that the type of fabrication method used in this work results in CLs with reduced porosity compared to conventional fabrication techniques.

**Table I. Inkjet printed electrode microstructure parameters.**

| Number of | Platinum loading | CL thickness | CL porosity |
|-----------|------------------|--------------|-------------|
| printed layers | (mg/cm²) | (μm) | |
| 3 | ~0.014 | ~1 | 0.51 |
| 5 | 0.026 ± 0.005 | 1.90 ± 0.37 | 0.51 |
| 10 | 0.056 ± 0.012 | 3.22 ± 0.54 | 0.39 |
| 15 | 0.080 ± 0.019 | 4.71 ± 0.64 | 0.40 |
| 20 | 0.113 ± 0.026 | 5.54 ± 0.88 | 0.29 |

**Performance dependence on Pt loading.**—Figures 3a–3c show the plot of corrected voltage, V<sub>IRfree</sub>, with current density for the different Pt loadings at 50%, 70% and 90% RH, 80°C. In the kinetic region, electrode performance increased with Pt loading. The performance increase was substantially reduced above 0.056 mg/cm² and did not change after 0.08 mg/cm². In the transport limiting region, the performances of the 3L and 5L CCMs were low, whereas they appear to be fairly similar between 15L and 20L CCMs.

Figure 4 shows the variation of voltage with Pt loading for the inkjet printed samples at 90% RH and at current density values of 0.1 A/cm² and 1 A/cm². Literature data for varying Pt loading electrodes is also shown for comparison. A direct comparison of performance is difficult because the cell were all operated at different operating conditions, therefore only a qualitative comparison can be made. The operating cell temperature and pressure were 80°C and 150 kPa for the case of Owejan et al.,32 35°C and 101 kPa for the case of Qi et al.,3 and 60°C and 135 kPa for the case of Saha et al.3 As seen in Figure 4, the increase in the measured cell voltage with increasing Pt loading is substantial at loading values below around 0.056 mg/cm² and after which the performance increase slowed down. Similar trends can be observed from the data of Owejan et al. and Saha et al.,3,31 however the threshold Pt loading varied in these cases. Differences may arise from the fact

![Figure 2. SEM images of the IJP CCMs. (a) top surface of the CL (b-d) freeze-fractured side view images of CL samples showing thicknesses for the case of 5L, 10L and 15L samples respectively.](image)
that different catalyst types were used in these works, a factor which is known to affect the optimal Pt loading value.\textsuperscript{3}

\textbf{Analysis of kinetic parameters.}—For the IJP electrodes, a reduced dependence of performance with Pt loading is observed in the kinetic and mass transport region. The plateau obtained in the mass transport region can be rationalized based on increased thickness and reduced porosity of the electrodes. To try and understand the reason for this plateau in performance gain in the kinetic region, analysis of kinetic parameters was carried out.

\textbf{Electrochemical active area.}—Figure 5 shows the CV plots for CLs with 5, 10 and 15 deposited layers. The electrochemical active area was calculated based on the area under the curve with voltage range from 0.4 V to 0.1 V (hydrogen adsorption region) and assuming a charge of 210 $\mu$C/cm$^2$ to remove a mono-layer of protons from a smooth Pt surface.\textsuperscript{25} An average value of the active area is given in Table II for the different Pt loadings. The overall active area increased from 88 cm$^2$ Pt to 228 cm$^2$ Pt as the Pt loading increased from 0.026 to 0.113 mg/cm$^2$. The specific active area per gram of Pt however decreased from 66.38 \pm 7.84 m$^2$/g to 40.40 \pm 3.39 m$^2$/g, suggesting that the catalyst availability dropped with Pt loading. The measured active area values are in agreement with previously reported active area values for inkjet printed electrodes, e.g., 33.9 to 45.7 m$^2$/g.\textsuperscript{3}

Saha, Kriston, and Cho et al.\textsuperscript{5,6,36} also reported a decrease of specific active area with increased loading. Owejan et al.\textsuperscript{12} on the other hand did not observe this decrease when the CL thickness was maintained constant. Therefore, the reduction in the active area might be fabrication specific and in our case, it might be due to the compaction of the layer with increased printer passes that reduces the accessibility of Pt to ionomer. The spray coated CCM exhibited a higher active area as compared to the inkjet printed CCMs. This may be due to the variation in the porosity and pore-distribution of the electrode structure because of the fabrication technique used.

Hydrogen crossover current was found to be between 2 - 4 mA/cm$^2$ at 0.5 V corresponding to a crossover flux between $1.03 \times 10^{-8}$ and $2.07 \times 10^{-8}$ mol/cm$^2$ s$^{-1}$. Variation in Pt loading was not found to affect the crossover value. The protonic electrode resistance obtained...
Table II. Kinetic parameters for the CLs with different Pt loadings operated at a constant stoichiometric ratio of 10 with parallel channel configuration using H2/air at ambient pressure at 90% RH.

| Platinum loading (mg/cm²) | Open cell voltage (V) | Active area (m²/g) | Tafel slope (b, V/dec) | Charge transfer coefficient (α) | Exchange current density (iₒ, A/cm²iₒ) | Total reaction order (m₀.75V,iₒ) |
|---------------------------|-----------------------|--------------------|------------------------|-------------------------------|----------------------------------------|----------------------------------|
| 0.026 ± 0.005             | 0.88 ± 0.02           | 66.3 ± 7.8         | 1.02 ± 0.002           | 0.56 ± 0.01                   | 3.72 ± 0.66 × 10⁻²                   | 1.02 ± 0.18                      |
| 0.080 ± 0.019             | 0.90 ± 0.01           | 52.9 ± 3.3         | 0.97 ± 0.007           | 0.67 ± 0.02                   | 1.46 ± 0.08 × 10⁻²                   | 0.99 ± 0.01                      |
| 0.113 ± 0.026             | 0.92 ± 0.01           | 40.4 ± 3.9         | 0.99 ± 0.001           | 0.70 ± 0.04                   | 9.79 ± 3.60 × 10⁻³                   | 1.03 ± 0.13                      |
| 0.4 (SC)                  | 0.92 ± 0.05           | 49.6 ± 7.7         | 0.068 ± 0.001          | 0.74 ± 0.01                   | 5.97 ± 0.38 × 10⁻⁸                   | 0.99 ± 0.04                      |

Table III. Oxygen partial pressure (pO₂, kPa) with varying cathodic reactant and RH at 90°C.

| Cathodic reactant | 50% RH | 70% RH | 90% RH |
|------------------|--------|--------|--------|
| 1% Oxygen (bal. N₂) | 0.78  | 0.69  | 0.60  |
| 10% Oxygen (bal. N₂) | 7.78  | 6.94  | 6.02  |
| Air (ambient)     | 16.35 | 14.57 | 12.64 |
| Air (50 kPaG)     | 26.98 | 25.21 | 23.28 |
| Air (100 kPaG)    | 37.62 | 35.85 | 33.92 |
| Air (150 kPaG)    | 48.27 | 46.48 | 44.56 |

The change in Tafel slope from 120 mV/dec to 80 mV/dec observed in this work is likely due to a transition in the oxygen reaction pathway. Evidence for the existence of a doubling of the Tafel slope has been observed experimentally over several decades, however the transition has usually been observed at high cell current density and, therefore, it has sometimes been attributed to mass transport. Our results show that the transition from 60 mV/dec to 120 mV/dec is not controlled by mass transport but by overpotential. In the case of low loading electrodes, i.e., reduced active area, at low oxygen partial pressures using potentiostatic EIS at 0% cathodic RH was found to increase from 66 mΩ cm² to 210 mΩ cm² for the 5L CCM to around 210 mΩ cm² for the 20L CCM.

**Tafel slope.**—The evaluation of electrode kinetics was carried out by testing CCMs with varying Pt loading at different oxygen partial pressure cases. All the pO₂ cases studied are given in Table III. The Tafel slope, b, was evaluated by taking the first 5 points on the polarization curve (20-100 mA/cm²; except when using 1% O₂ where the range was 5-25 mA/cm²). Resistance corrected voltage, V, obtained from current interrupt method was used for the analysis of the Tafel slopes. The value of resistance from current interrupt method was found to be comparable to that obtained at the high frequency intercept while performing EIS. The exchange current density, iₒ, and charge transfer coefficient, α, was obtained from the intercept and slope of the plot between overpotential, η, and ln(i) respectively. For the evaluation of iₒ, η is defined with respect to the theoretical open cell voltage (OCV) that is based on the Nernst potential.

The kinetic parameters, Tafel slope, exchange current density, charge transfer coefficient and the OCV values for different Pt loading electrodes at 90% RH when operating with air (pO₂ = 12.6 kPa) are given in Table II. The Tafel slope decreased from 0.123 ± 0.002 V/dec for the case of 5L CCM to 0.093 ± 0.001 V/dec for the case of 20L CCM. Figure 6a shows the Tafel plot for the case of a 20L CCM at different oxygen partial pressures. Figure 6b shows the variation in Tafel slope with Pt loading at the four pO₂ cases. Unlike Subramania who report no dependence of Tafel slope on Pt loading or the Pt loading.

![Figure 4](image)

**Figure 4.** Voltage variation for the IJP CCMs at 0.1 and 1 A/cm² at 90% RH, 80°C and ambient pressure. For comparison, literature data from Owejan et al., Qi et al., and Saha et al. is shown at two current densities. The reported values of operating cell temperature and pressure are 80°C, 150 kPa for Owejan et al.; 35°C, 101 kPa for Qi et al., and 60°C, 135 kPa for Saha et al.

![Figure 5](image)

**Figure 5.** Cyclic voltammetry plots for 5L, 10L and 15L electrodes at 30°C using fully humidified H₂/N₂.
pressures, high overpotentials are required in order to achieve current densities of the order of 10 mA/cm², e.g., Figure 6a. In this situation, the Tafel slope is recorded at a cell voltage below the transition overpotential, i.e., 0.7 to 0.9 V, and therefore only the so-called high current region of the Tafel plot is accessible. These results provide further evidence of a changing Tafel slope indicating a transition in the oxygen pathway at a voltage in the range of 0.7 to 0.9 V, further justifying the use of a multi-step reaction model for the ORR as proposed, for example by Wang et al.48 and Moore et al.29

It is interesting to note that previous studies with low loading electrodes, such as Kriston et al.6 and Sahai et al., did not observe a changing Tafel slope. Instead, they observed a Tafel slope of 65 - 75 mV/dec and no change with Pt loadings. The reason for the difference is likely to be that they conducted their experiments at a higher oxygen partial pressure. Based on the reported operating conditions, their $p_{O_2}$ values are 103 kPa for the case of Kriston et al. and 24.5 kPa for the case of Sahai et al. At high oxygen partial pressures, a constant Tafel slope with loading in the range of 70-90 mV/dec is also observed in this work.

Table II also shows the calculated exchange current densities, $i_0$, and charge transfer coefficients, $\alpha$, for all the tested CCMs. $i_0$ decreased from 3.72 ± 0.66 × 10⁻⁷ to 5.97 ± 0.38 × 10⁻⁸ while $\alpha$ increased from 0.56 to 0.74 as Pt loading increased from 0.026 to 0.113 mg/cm² for the IJP CCMs. For the 20L CCM, the value of $i_0$ is in the same order of magnitude to that reported by Neyerlin et al. for their electrode with a loading of 0.2 mg/cm² i.e., 2.47 ± 0.3 × 10⁻⁸ A/cm².

In the previous analysis, the cell voltage was not corrected for the crossover current, even though it can significantly lower the cell voltage. However, it is of interest to study the loss in cell voltage due to crossover in each case. Considering simple Tafel kinetics, the loss in overpotential, $\eta$, related to the hydrogen crossover current, $i_{crosso}$, can be calculated as

$$\eta = \frac{2.303RT}{\alpha F} \log \left( \frac{i + i_c}{mPt_{APt}} \right) \quad [1]$$

where $\alpha$ is the transfer coefficient, $m_{Pt}$ is the Pt loading in mg/cm², $A_{Pt}$ is the electrochemical active area in cm²/mg, $i_c$ is the exchange current density in A/cm², and $F$ is the Faraday constant (96,485 C/mol e⁻). At open cell voltage, the overpotential associated with the crossover current of 3 mA/cm² is calculated to be 0.33 V, 0.29 V, 0.28 V and 0.28 V for 5L, 10L, 15L and 20L CCMs respectively based on the values given in Table II.

**Oxygen reaction order.—** We previously reported that inkjet printed electrodes showed an increased sensitivity to operating pressure as compared to conventional electrodes.25,26 The section above also highlights that low loading electrodes might operate in a different oxygen reaction pathway due to their low initial cell voltage. This might influence the observed MEA reaction order to oxygen. The sensitivity of the cell performance to oxygen partial pressure can be measured at a constant overpotential, $\eta$ (giving a value of kinetic reaction order, $m$) or at a constant $V_{R|F|C}$ voltage (giving a value of total reaction order, $m$).28 In this work, the focus is toward the latter. The total reaction order, $m$, is obtained at a constant cell voltage using

$$m = \left( \frac{\partial \ln i}{\partial \ln p_{O_2}} \right)_{V_{R|F|C}} \quad [2]$$

where $i$ is the current density at a constant voltage and temperature.

The reaction order was extracted from the slope of the line based on the plot of ln(i) vs. ln($p_{O_2}$)25

Figures 7a and 7b show the changes in the average current density values along with standard deviation at each $p_{O_2}$ at 90% RH and voltages of 0.75 and 0.7 $V_{R|F|C}$ respectively. Based on the figure, a linear relationship is observed for both the cases with a slope between 0.8 and 1 for the inkjet printed electrodes.

In order to determine the kinetic reaction order, the overpotential at the electrode must be estimated. This estimation is however challenging due to the effect of crossover. In this work, the overpotential is calculated using,

$$\eta = E_{ib} - E_{cell} - \eta_{crossover} \quad [3]$$

where $\eta_{crossover}$ is the overpotential due to hydrogen crossover calculated using equation 1 while $E_{ib}$ and $E_{cell}$ are the theoretical and measured cell voltages. $E_{ib}$ was calculated from the Nernst equation for each value of $p_{O_2}$. At a constant overpotential of 0.15 $V_{R|F|C}$, the kinetic reaction order, $\gamma$ was thus evaluated at the respective $E_{ib}$. The value of $\gamma$ was found to be 0.68 ± 0.14, 0.78 ± 0.03, 0.80 ± 0.08 and 0.84 ± 0.08 for the case of 5L, 10L, 15L and 20L inkjet printed electrodes respectively at 90% RH. The kinetic reaction order can also be obtained using thermodynamic arguments as discussed in

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**Figure 6.** Tafel slope analysis at 90% RH, 80°C (a) CL with 0.113 mg/cm² Pt loading (20L) (b) variation of b with Pt loading for $p_{O_2}$ values of 0.6 kPa, 6 kPa, 12.6 kPa and 44.5 kPa.
Ref. 28, using the relationship between $m$ and $\gamma$ as $m = \gamma + \alpha/4$. Based on this relation, $\gamma$ for the IJP electrodes appear to be between 0.6 and 0.85. Given that the overpotential has been estimated based on crossover, the total reaction order results are more accurate.

Since no literature data on reaction order values for low Pt loading MEAs was found, the values of $m$ obtained in this work were compared to the ones reported by Neyerlin et al.28 and Subramanian et al.37 for MEAs with higher Pt loadings. Table II provides values of $m$ for the inkjet printed electrodes at a constant voltage of 0.75 $V_{IRFree}$. For an MEA with a conventional electrode with a Pt loading of 0.2 mg/cm², Neyerlin28 reported a total reaction order of 0.79 ± 0.02 for an MEA. Subramanian et al.37 did not report individual reaction orders for their low Pt loading (0.06 mg/cm²) and high Pt loading (0.4 mg/cm²) samples, and an average value for $m$ is given as 0.81 ± 0.03 considering simple Tafel kinetics. The values of $m$ measured for conventionally fabricated MEAs in the literature are in reasonable agreement with the observed values for $m$ in this work. Discrepancies may arise from the variation in the type of catalyst, Pt loading and operating conditions used. The IJP electrodes show a similar reaction order to conventional spray coated electrodes. This value shows that the reason for our previous observations showing that low loaded electrodes were more sensitive to an increase in the total cell pressure25,26 were not the result of a changing reaction order. It therefore appears that the reason for the observed increased performance with total pressure when compared to spray coated samples was the change in Tafel slope with increased oxygen partial pressure observed in Figure 6.

Figure 8 shows the variation of $m$ with the overpotential (between 0.85 and 0.65 $V_{IRFree}$). An average value of $m$ with a standard deviation from three tested samples for each Pt loading is given. To avoid regions with mass-transport losses, the oxygen reaction order for cell voltages below 0.7 $V_{IRFree}$ was not measured for the case of 10L, 15L and 20L CCMs. The 5L CCM could not reach higher potentials of 0.8 and 0.85 $V_{IRFree}$ due to its reduced loading and thus, it was computed between 0.65 and 0.75 $V_{IRFree}$ where the current density is below 0.5 A/cm². Figure 8 shows that, considering the error bars, $m$ is nearly one for the electrodes except for the 10L electrode at a higher cell voltage. There have been contradicting trends reported in the literature for the variation of the reaction order with overpotential.27,29,30,37 Data from Markiewicz30 and Parthasarathy,27 who used ex-situ techniques for determination of the reaction order, show that its value is either invariant or increases with cell voltage, respectively. In-situ measurement techniques used by Subramanian37 and Uchimura49 show that $\gamma$ decreases with increasing cell voltage ($V_{IRFree}$). The apparent kinetic reaction order was reported to increase from 0.55 to 0.7 as the potential decreased from 0.875 to 0.65 $V_{IRFree}$.

**Evaluation of oxygen transport resistance.**—Local mass transport losses have been considered responsible for the low performance of low loading electrodes, therefore this local transport resistance was measured for the inkjet printed electrodes with varying loading.
Figure 9. Evaluation of limiting current density for the inkjet printed CCMs at 50, 70 and 90% RH, 80°C using 1% O₂. Error bars show the standard deviation from three tested samples (a) 5L CCM (b) 10L CCM (c) 15L CCM (d) 20L CCM.

at different relative humidity conditions. The total oxygen transport resistance, \( R_{\text{total}} \), at limiting current, \( i_{\text{lim}} \), i.e., when the oxygen concentration at the catalyst surface approaches zero, is given as\(^{17,18}\)

\[
R_{\text{total}} = \frac{4Fc_{\text{O}_2}}{i_{\text{lim}}} = \frac{4F}{i_{\text{lim}}} \frac{P_{\text{O}_2}}{RT} \tag{4}
\]

where \( c_{\text{O}_2} \) is the gas channel oxygen concentration and \( i_{\text{lim}} \) is the measured limiting current density as discussed below. The limiting current was obtained using 1% oxygen as the cathodic reactant. Average limiting current with error bars showing the standard deviation obtained by testing three samples for the 5L, 10L, 15L and 20L electrodes at 50, 70 and 90% RH are shown in Figure 9. Between 0.2 and 0.1 V, the current density appears to decrease. This phenomenon has been observed in literature for conventionally fabricated electrodes and is believed to be the result of transition from a four electron process to a two electron process due to the formation of peroxide instead of water.\(^{18,50,51}\) The transition in the electron transfer mechanism is not only a modification of the kinetics but also of the amount of current produced for the same oxygen flux. Assuming a limiting oxygen flux, \( N_{\text{lim}} \), if the number of electrons produced at the Pt site is 4, then the amount of current produced per mole of oxygen would be \( i_{\text{lim}} = 4F N_{\text{lim}} \). But if part of the reaction proceeds through a 2 electron pathway, the current produced will be reduced to \( 2F N_{\text{lim}} \). Therefore, even though the kinetics are not important because they are fast enough to consume all the oxygen that reaches the reaction site, the number of electrons produced will have an impact on the current. Below 0.1 V, the current density increases due to hydrogen evolution reaction.\(^{18}\) For this study, the limiting current was specified to be the maximum current that was obtained above 0.1 V. A similar procedure has also been followed by Greszler et al.\(^{18}\) for the measurement of their limiting currents.

Table IV shows the limiting current densities obtained for the different Pt loading cases at 50%, 70% and 90% RH. \( i_{\text{lim}} \) appears to increase with RH even though \( P_{\text{O}_2} \) decreases from 0.78 kPa to 0.6 kPa (from 50% to 90% RH).
Table IV. Limiting current density (mA/cm²) variation with Pt loading and RH.

| Pt Loading (mg/cm²) | 50% RH | 70% RH | 90% RH |
|---------------------|--------|--------|--------|
| 0.026               | 90.8 ± 7.6 | 94.6 ± 5.7 | 97.4 ± 5.7 |
| 0.056               | 105.9 ± 4.9 | 108.0 ± 6.0 | 109.4 ± 4.4 |
| 0.080               | 106.9 ± 1.0 | 108.3 ± 1.8 | 110.7 ± 2.2 |
| 0.113               | 112.5 ± 2.7 | 113.9 ± 1.6 | 115.8 ± 1.3 |

Figure 10 shows the total transport resistance evaluated from Equation 4 vs. inlet humidity for the cases with varying Pt loading. For comparison, data from Nonoyama et al. is also shown in the figure. Even though the electrode type and operating conditions are different, the same trend is observed. The total transport resistance for the inkjet printed electrodes decreased with increasing RH. From 50% to 90% RH, $R_{\text{total}}$ decreased from 1.13 to 0.81 s/cm for 5L CCM, 0.97 to 0.72 s/cm for 10L CCM, 0.96 to 0.71 s/cm for 15L and 0.9 to 0.68 s/cm for the case of 20L CCM. In comparison, $R_{\text{total}}$ decreased from 0.89 to 0.79 s/cm as RH increased from 61% to 106% based on the data from Nonoyama et al.

The transport resistance near the Pt surface, i.e., local oxygen transport resistance, $R_{O_2}^{Pt}$, is related to $R_{\text{total}}$ by the following relationship based on the analysis of Greszler et al.

\[
R_{\text{total}} = R_{Ch} + R_{DM} + \frac{R_{O_2}^{Pt}}{f_{Pt}} \frac{h}{\psi} \coth \left( \frac{h}{\psi} \right) \tag{5}
\]

where $R_{Ch}$ and $R_{DM}$ are the transport resistances through the flow-channels and gas diffusion media, $f_{Pt}$ is the roughness factor which is given as the product of the Pt loading and electrochemical active area, $h$ is the electrode thickness and $\psi$ is a quantity with units of length represented as

\[
\psi = \sqrt{D_{O_2}^{eff} R_{O_2}^{Pt} f_{Pt}} \tag{6}
\]

For the various IJP electrodes, Figure 11 shows the variation of the dimensionless term $(h/\psi)\coth(h/\psi)$ with the local oxygen transport losses $R_{O_2}^{Pt}$, assuming the effective diffusivity ($D_{O_2}^{eff}$) to be 0.0241 cm²/s. It can be seen that $(h/\psi)\coth(h/\psi)$ approaches unity as $R_{O_2}^{Pt}$ increases and can be neglected from the Equation 5, thus reducing it to

\[
R_{\text{total}} = R_{Ch} + R_{DM} + \frac{R_{O_2}^{Pt}}{f_{Pt}} \tag{7}
\]

$R_{O_2}^{Pt}$ was obtained from the slope of the line based on the plot of $R_{\text{total}}$ vs. $1/f_{Pt}$, as shown in Figure 12. Table V shows the average local...
transport resistance from three tested samples for the inkjet printed electrodes and local transport resistances reported in the literature for comparison along with the operating conditions for the cell. For the inkjet printed electrodes, the value of $R_{op}^t$ was found to decrease from 5.93 ± 3.16 s/cm to 3.43 ± 1.67 s/cm as RH increased from 50% to 90%. The values are in agreement with those reported by Greszler et al.18 and Owejan et al.12 who have reported $R_{op}^t$ to be 9.2 s/cm and 4.2 s/cm at 62% RH and 80% RH respectively. Therefore, the local mass transport resistances of inkjet printed electrode are similar to those of conventional electrodes. Regarding the drop in the local mass transport resistances of inkjet printed electrode are of the IJP electrodes at high relative humidity was also in agreement with water content. The measured reduced local resistance at high RH in this work appears to contradict the simulation results. Further study in this area is therefore necessary.

### Conclusions

Inkjet printed electrodes with varying Pt loadings from 0.014 mg/cm² to 0.113 mg/cm² were fabricated and analyzed. Ex-situ characterization showed that the CL thickness increased from 1 μm to 5.5 μm with varying loading. Electrode porosity was found to drop from 51% to 29% with increasing Pt loading as the number of printed passes increased from 3 to 20 layers. The electrode active area decreased from 66.38 ± 7.84 m²/g to 40.4 ± 3.39 m²/g as the Pt loading increased from 0.026 to 0.113 mg/cm². The reduced porosity and active area with increased number of passes lead to a threshold on Pt loading above which gains in cell performance are substantially reduced.

A kinetic study showed that the Tafel slope increased with decreasing Pt loading and oxygen partial pressure. At high loading and oxygen partial pressures, the expected Tafel slope of 60–80 mV/dec. At these conditions, the Tafel slope was obtained by fitting kinetic data at low current densities, but at cell voltages below 0.7–0.8 V. At these cell voltages, the oxygen reduction reaction is known to change mechanism. In low loading electrodes compared to conventional electrodes – Owejan et al. reported 60 to 80 mV/dec in Fig. 3a in Ref. 12; and, iii) very low porosity of inkjet printed electrodes at higher Pt loadings (as low as 29% for moderate loadings). All these effects contribute to the 100–300 mV difference compared to conventionally fabricated electrodes as shown in Figure 4.

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