Analysis of H2/Air Polarization Losses of Low-Pt-Loading Cathodes with Various I/C Ratios and Carbon Supports

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The role of catalyst layer microstructure and ionomer content is critically important at ultra-low platinum loading due to enhanced mass transport resistance compared to high platinum loading. In the present work, cathode-coated membranes with two types of carbon supports and various I/C ratios are fabricated using reactive spray deposition technology (RSDT) where low Pt loading (cathode 0.1 mg cm\(^{-2}\), anode 0.05 mg cm\(^{-2}\)) cathode layers are directly deposited on Nafion membranes. Similar performance is obtained at optimal I/C ratios for Pt/Ketjen Black (KB) CCMs and Pt/multi-wall carbon nanotube (MWNT) CCMs, with optimal I/C ratio being 1.0 and 0.5, respectively. Six types of polarization overpotentials are analyzed using a six-step method established in our previous work to elucidate the influence of catalyst layer microstructure and ionomer content on fuel cell performance. Since MWNT requires 50% less ionomer and are chemically more stable than KB, MWNT is a preferred support for ultra-low platinum loading electrodes. The six-step method connects catalyst layer properties with specifically targeted overpotentials and is thus a powerful tool in catalyst layer optimization.

In our previous work, we established a systematic six-step method to analyze the polarization sources for low-platinum loaded PEMFC. We demonstrated that the cathode electrode concentration overpotential was reduced with electrodes fabricated by reactive spray deposition technology (RSDT) compared to commercial GORE PRIMEA CCMs at 0.4 and 0.1 mg cm\(^{-2}\) cathode Pt loading. The current limiting method was not used in Ref. 25 and the present work because it utilizes only one data point (the limiting current) to extrapolate oxygen transport resistance. On the other hand, the six-step method accounts for every data point on the polarization curve and provides a comprehensive understanding of mass transport limitation in the entire current region. Moreover, a real fuel cell does not operate near the limiting current condition due to local fuel starvation that causes severe carbon corrosion. Therefore, we resort to Butler-Volmer equation to estimate the limiting current. At the highest current density, the amount of variance in \(\eta_{corr}\) remains as low as 5.7% with different limiting current densities. Thus, the overpotentials are in general not sensitive to the limiting current density. A window of about 100 mA cm\(^{-2}\) is allowed for the estimation of limiting current.

In this work, we investigate the effect of ionomer-to-carbon (I/C) ratio and several types of carbon support using electrodes fabricated with reactive spray deposition technology (RSDT). The RSDT process has been able to optimize the electrode microstructure and to reduce the optimal ionomer content to ~15 wt% for catalyst layer composed of Pt supported on Vulcan XC-72R. The ionomer of this process was found to penetrate the micropores and improve contact with Pt nanoparticles. Herein, the investigation of the effect of I/C ratio on the polarization behavior of an air-breathing fuel cell is continued using the following carbon supports, each with distinctive structural properties, Ketjen Black carbon (KB) and multi-walled carbon nanotube (MWNT).

The six-step analysis method\(^a\) modified for low Pt loading\(^b\) is used to separate and quantify the contributions of different polarization sources as well as to evaluate the oxygen transport limitation in the gas diffusion layer (GDL) and the cathode ionomer/PT interface. The assumptions for this method are: 1) the ORR follows first order reaction with respect to oxygen partial pressure; 2) the ORR kinetics follows Butler-volmer equation, i.e. Tafel kinetics; 3) oxygen...
transport follows Fick’s first diffusion law in the flow field, gas diffusion layer, and macro pores in the cathode catalyst layer where oxygen transport is governed by molecular diffusion; on the other hand, the oxygen transport is governed by Knudsen diffusion in the cathode catalyst layer due to mesopores (10–100 nm) and micropores (less than 10 nm); 4) the effect of anode polarization can be neglected; and 5) no electrical short in the cell. A brief description of each step is provided below:25

1. The non-electrode ohmic overpotential is denoted by:

\[ \eta_{\text{corr1}} = iR_{\text{nonelectrode}} \]  

where \( i \) is the operating current density and \( R_{\text{nonelectrode}} \) is the non-electrode ohmic resistance comprised of membrane and all other contact resistances of the MEA. \( R_{\text{nonelectrode}} \) is measured using current interruption method with the inherent module in the fuel cell test station. The first-step corrected cell potential is defined as:

\[ V_{\text{corr1}} = E + \eta_{\text{corr1}} = E + iR_{\text{nonelectrode}} \]  

where \( E \) is the measured cell potential (V) at current density \( i \).

2. The cathode electrode ohmic overpotential mainly concerns the ionic resistance in the cathode. It is denoted by:

\[ \eta_{\text{corr2}} = iR_{\text{electrode}} \]  

The cathode electrode ohmic resistance, \( R_{\text{electrode}} \), is obtained using an iterative method under the assumption (1) where the current ratio between H\(_2\)/O\(_2\) and H\(_2\)/air I-V curves is 4.8 at the same cell potential. The current ratio of 4.8 stems from the ratio of oxygen concentration in pure oxygen and air (100%/21% = 4.8) when the same total gas flow for air and oxygen is purging the cathode. The corrected cell potential after this step is:

\[ V_{\text{corr2}} = V_{\text{corr1}} + \eta_{\text{corr2}} = E + iR_{\text{nonelectrode}} + iR_{\text{electrode}} \]  

3. The non-electrode concentration overpotential (\( \eta_{\text{corr3}} \)) is associated with the molecular diffusion of oxygen in the flow channel, GDL, and the meso- and macropores in the cathode. The limiting current density (\( i_{\text{lim}} \)) needs to be determined to estimate \( \eta_{\text{corr3}} \). The limiting current density was found using an iterative procedure that employs the Butler-Volmer equation:

\[ \frac{i + i_s}{1 - \frac{i}{i_{\text{lim}}}} = i_s \exp \left[ \frac{V_{\text{eq}} - V_{\text{corr2}}}{b^\dagger} \right] \]  

where \( b^\dagger \) is the modified Tafel slope when the experimentally controlled current is corrected for \( i_{\text{lim}} \) (left hand side), \( i_s \) is the hydrogen crossover current. The correct magnitude of \( i_{\text{lim}} \) makes the plot of \( V_{\text{corr2}} \) vs. \( \log[1 - \frac{i}{i_{\text{lim}}}] \) linear following Equation 5. The resulting straight line represent the cell potential (\( V_{\text{corr}} \)) corrected for \( \eta_{\text{corr3}} \) and the difference between the resulting straight line and \( V_{\text{corr2}} \) is defined as \( \eta_{\text{corr3}} \). Hence, the corrected cell potential is:

\[ V_{\text{corr3}} = V_{\text{corr2}} + \eta_{\text{corr3}} = E + iR_{\text{nonelectrode}} + iR_{\text{electrode}} + \eta_{\text{corr3}} \]  

4. The electrode concentration overpotential (\( \eta_{\text{corr4}} \)) is associated with the Knudsen diffusion of oxygen in the cathode as well as the oxygen transport in the ionomer thin film and at the ionomer/Pt interface. It is determined by the difference between the Tafel slope \( b \) in the kinetic controlled region (10–100 mA cm\(^{-2}\)) of H\(_2\)/O\(_2\) polarization curve and Tafel slope \( b^\dagger \) in H\(_2\)/Air polarization curve:

\[ \eta_{\text{corr4}} = (b^\dagger - b) \log \left[ \frac{i + i_s}{i_s} \right] \]  

where \( i_s \) is called the breaking current density where the Tafel slope starts to deviate from the theoretical value, indicating additional polarization loss due to \( \eta_{\text{corr4}} \). Following our previous work,25 \( i_s \) is set to be 10 mA cm\(^{-2}\) for all samples. The corrected cell potential with electrode concentration overpotential is:

\[ V_{\text{corr4}} = V_{\text{corr3}} + \eta_{\text{corr4}} = E + iR_{\text{nonelectrode}} + iR_{\text{electrode}} + \eta_{\text{corr3}} + (b^\dagger - b) \log \left[ \frac{i + i_s}{i_s} \right] \]  

5. The ORR activation overpotential from Tafel equation, \( \eta_{\text{corr5}} \), is defined as the potential loss due to Tafel kinetics at current density higher than the start of I-V curve (10 mA cm\(^{-2}\)):

\[ \eta_{\text{corr5}} = b \ast \log \left[ \frac{i + i_s}{10 + i_s} \right] \]  

The corresponding corrected cell potential is:

\[ V_{\text{corr5}} = V_{\text{corr4}} + \eta_{\text{corr5}} = E + iR_{\text{nonelectrode}} + iR_{\text{electrode}} + \eta_{\text{corr3}} + (b^\dagger - b) \log \left[ \frac{i + i_s}{i_s} \right] + b \ast \log \left[ \frac{i + i_s}{10 + i_s} \right] \]  

6. The activation overpotential from catalyst activity, \( \eta_{\text{corr6}} \), is defined as the activation potential loss at 10 mA cm\(^{-2}\):

\[ \eta_{\text{corr6}} = V_{\text{eq}} - V_{\text{corr2}} @ 10 \text{ mA cm}^{-2} \]  

The calculation of \( V_{\text{eq}} \) can be found in Ref. 31.

**Experimental**

**Chemicals and materials.**—The detailed process of CCM fabrication by RSDT can be found in our previous publications.03,35 Typically, Pt-2, 4-pentanedione (Colonial Metals, Inc.) was used as Pt precursor and dissolved in a combination of 62.5 wt% xylene (Sige Aldrich, ACS reagent, ≥98.5%), 21 wt% acetone (Sige Aldrich, HPLC ≥99.9%) and 16.5 wt% liquid propane (Air gas, ≥90%) with 10 mM Pt concentration. KB EC-600JD (Akzo Nobel) or MWNT (Ballard power systems, Inc.) was used as catalyst support. The carbon supports were thermally treated at 400°C in nitrogen environment for 4 hours to remove any adsorbed organic contaminants. The carbon slurry was prepared by dispersing carbon in methanol with 2.5 mg mL\(^{-1}\) concentration, followed by adding Nafion dispersion (DuPont D521, 5wt%, 1100 EW) drop-wise. Then, the slurry was sonicated (Misonix S-4000, Qsonica, LLC) in an ice bath for 90 min before use. The I/C ratio in the slurry was set at 0.5, 1.0, 1.5 for KB and 0.3, 0.5, 0.8 for MWNT. Since the BET surface area of MWNT is much lower than KB, the I/C ratios for MWNT were lower than KB. The anode and the cathode both had the same I/C ratio. For both types of carbon, the resulting Pt loading was ~0.1 mg cm\(^{-2}\) for the cathode and ~0.05 mg cm\(^{-2}\) for the anode, confirmed by inductive-coupled plasma (ICP) analysis. The thickness of the cathode and anode were 12–13 μm and 6–7 μm, respectively.

**Physical characterizations.**—The procedure for nitrogen adsorption and mercury porosimetry followed that described in Ref. 30. The surface area was determined from nitrogen adsorption. Freshly-deposited CCMS were cut into small strips and placed in a sample...
tube for degas at 105 °C for 12 hours. Nitrogen adsorption analysis was performed with a Micromeritics 2020 at 77 K with a dose of 3 cm$^{-2}$.

The pore size distribution of the catalyst layer was determined using both nitrogen adsorption and mercury intrusion porosimetry (MIP) methods. The theory of Barrett, Joyner and Halenda (BJH) applied was to results from the desorption branch of the nitrogen adsorption isotherm to calculate pore size distribution below 100 nm. MIP was performed with an AutoPore IV (Micromeritics, Inc.) up to 60,000 psi to measure pore size ranging from 10 nm to 10 μm. The Washburn equation for cylindrical pores was applied to calculate the pore size. To keep a constant electrode area for the porosimetry tests, 20 circular pieces with a diameter of 0.95 cm (3/8 inch) were punch out of the CCMs.

Bright field transmission electron microscopy (TEM) images of freshly deposited Pt particles supported on KB and MWNT were characterized with a FEI Tecnai T12 operated at 120 kV. Catalyst powders were carefully scraped off and dispersed in ethanol. Twenty microliters of the dispersion were deposited onto a Cu TEM grid (Cu 300 CN, Pacific Grid-Tech) and dried overnight.

### Results and Discussion

#### Microstructure of the catalyst layer

- Understanding the catalyst layer microstructure is essential to establish the property-performance relation in fuel cells. The Pt particle size in the catalyst layer was controlled by the RSDT process to be ~2 nm for both KB and MWNT to minimize the effect of particle size. The TEM bright field images of scrapped-off catalyst layer showed well-dispersed Pt on carbon supports (Figure 1). The individual KB particle has a diameter of 30–40 nm, while the MWNT shows a diameter of 20–30 nm.

- The catalyst layer pore structure was characterized using nitrogen adsorption and mercury intrusion porosimetry (MIP). The advantage of combining these methods is that it provides a complete characterization of the pore size distribution from 2 nm to 1000 nm in the catalyst layer. The nitrogen adsorption volume for the isotherms of KB and MWNT CCMs both decreased when the I/C ratio was increased (Figures 2a, 2b). Both the Pt/KB and the Pt/MWNT CCMs show a slight hysteresis at high nitrogen partial pressure due to capillary condensation. Further, the pristine KB powder and the Pt/KB CCMs also show H3 type hysteresis in the medium range of nitrogen partial pressure (Figure 2a). The H3 type hysteresis typically occurs in samples containing a heterogeneous distribution of pores of tapered capillaries or wedge-formed capillaries with closed sides and open ends. The nature of this hysteresis stems from the different equilibrium pressure between adsorption and desorption for the pores. For materials composed by close-packed and equal-sized spherical particles, capillary condensation occurs within the interstices between the particles forming primarily slit-shaped pores. Gregg and Sing and Soboleva et al. showed similar shape of adsorption and desorption isotherm of KB. A BET surface area of 1174.12 m$^2$g$^{-1}$ was measured for pristine KB powder. The BET surface area of Pt/KB catalyst layer decreased from 669 to 223 m$^2$g$^{-1}$ as I/C ratio increased from 0.15 to 1.5. For the MWNT used in this study, the BET surface area was 316 m$^2$g$^{-1}$ for the pristine powder and decreased from 207 m$^2$g$^{-1}$ to 102 m$^2$g$^{-1}$ for Pt/MWNT CCMs as the I/C ratio increased from 0.3 to 0.8. The porosity of the catalyst layer was obtained from MIP measurements (Figure 2d).

The pore size distribution of cathode catalyst layers affects non-electrode ($η_{corr3}$) and electrode concentration overpotential ($η_{corr4}$). For KB support, previous work has shown that high pore volume below 10 nm suggests good ionomer distribution and low magnitude of $η_{corr4}$. On the other hand, high pore volume in the range of 30–100 nm improves the molecular diffusion of oxygen in the cathode and results in low $η_{corr4}$, but the magnitude of $η_{corr4}$ is usually higher than that of $η_{corr3}$, especially at high current density (>1000 mA cm$^{-2}$). Thus, the mesopore volume between 30 and 100 nm has higher impact on the total overpotential than the pores less than 10 nm.

The pore size distribution below 10 nm were calculated based on BJH desorption model using the data in nitrogen adsorption experiments (Figures 3a, 3c). Pristine KB powders showed a sharp peak in the micropore range (3–4 nm). For Pt/KB CCMs, the peak in 3–4 nm range was reduced as the I/C ratio was increased, indicating the coverage of ionomer in the micropores. Since the carbon is covered with ionomer before mixing with Pt particles in the RSDT process, such high coverage could prevent Pt nanoparticles from being trapped in the micropores as would be the case for preparing electrode with commercial Pt/KB catalyst. Pristine MWNT powder also exhibited microporosity in the range of 2–5 nm. But for the Pt/MWNT catalyst layer, the microporosity almost disappeared, leaving only the mesopores (20–80 nm). The microporosity for MWNT is likely from the interstitial volume between the nanotubes, which is filled completely with the incorporation of ionomer.

#### Table I. Test Conditions for CV and I-V performance.

| Test | Anode/Cathode flow rate L min$^{-1}$ | Anode/Cathode %RH | Anode/Cathode stoic | Cell Temperature °C | Scan Window VRHE | Scan Rate mV s$^{-1}$ |
|------|-----------------------------------|------------------|---------------------|----------------------|-------------------|-------------------|
| Cyclic voltammetry | 0.2/0.2 (H$_2$/N$_2$) | 100/100 | - | 80 | 0.05-1.0 | 20 |
| Linear sweep voltammetry | 0.2/0.2 (H$_2$/N$_2$) | 100/100 | - | 80 | 0.05-0.4 | 2 |
| I-V performance | 0.05/0.05 (H$_2$/O$_2$) | 100/75 | 3/20 (H$_2$/O$_2$) | 80 | - | - |
| | 0.05/0.05 (H$_2$/Air) | - | (H$_2$/Air) | - | - | - |
Since the mesopores are not well resolved in nitrogen adsorption method, MIP was used to further elucidate the mesopores distribution of Pt/KB and Pt/MWNT catalyst layers (Figures 3b, 3d). Pt/KB and Pt/MWNT both showed a broad distribution of peaks in the range of 10 to 1000 nm as opposed to Pt/Vulcan which had a sharp peak from 50 to 100 nm. The overall pore volume of Pt/KB CCMs decreased with increasing I/C ratios and the peak pore diameter of the I/C = 0.5 sample was ~20 nm larger than the rest of the three Pt/KB CCMs. Pt/MWNT showed the same trend where lower I/C ratio (0.3) exhibited larger peak pore diameter. The Pt/MWNT CCM with I/C ratio of 0.5 showed the highest pore volume in pores ranging from 10 to 100 nm.

Analysis of polarization losses.—Linear sweep voltammograms (LSV) are shown in Figures 4a and 4b where the hydrogen crossover current, \( i_x \) (mA cm\(^{-2}\)) is measured at 0.4 V vs. RHE. The shape of LSV curves indicates that no electrical short is present for these MEAs. The ECSA is measured using the cyclic voltammetry (CV) in Figures 4c and 4d:\(^{12}\)

\[
\text{ECSA} \left( \text{m}^2 \text{g}^{-1} \right) = \frac{Q_H \left( \text{C} \right)}{210 \mu \text{C cm}^2 \text{Pt} \cdot L \cdot \mu \text{g} \cdot \text{cm}^{-2}} \cdot A \left( \text{cm}^2 \right) \cdot 10^5
\]

The charge of hydrogen adsorption on platinum, \( Q_H \), was integrated from 0.1 V to 0.4 V (vs. RHE). For Pt/KB, the highest ECSA for Pt/KB CCMs is 73 m\(^2\) g\(^{-1}\) measured with an I/C ratio of 1.0. The ECSA decreased slightly to 67 m\(^2\) g\(^{-1}\) with further increase of I/C ratio to 1.5. The ECSA at I/C ratio of 0.5 is the lowest of the three, 57.8 m\(^2\) g\(^{-1}\), suggesting a low catalyst utilization due to insufficient ionomer in the catalyst layer. The highest ECSA for Pt/MWNT is 67 m\(^2\) g\(^{-1}\) measured with an I/C ratio of 0.5. Since the surface area and porosity of KB is much higher than MWNT, the optimal I/C ratio for ECSA was higher for KB because more ionomer is needed to form a thin film on the carbon support to maximize the contact with Pt nanoparticles.

The effect of I/C ratios on the fuel cell performance is qualitatively presented with uncorrected polarization curves of Pt/KB and Pt/MWNT CCMs (Figure 5). The performance of GORE CCMs,\(^{25}\) as an example of the state-of-the-art commercially available CCMs, are compared in parallel with RSDT CCMs. Pt/KB and Pt/MWNT CCMs with optimized I/C ratio show higher performance than the GORE CCM with 0.1 mg cm\(^{-2}\) Pt loading at current density below 1000–1200 mA cm\(^{-2}\). At high current density (>1200 mA cm\(^{-2}\)) the GORE CCM is slightly better than RSDT CCMs. The Pt/KB CCM with I/C ratio of 1.0 out-performed all other Pt/KB CCMs in air-breathing cells at ambient pressure (Figure 5a). At current density above 800 mA cm\(^{-2}\), the slope of polarization curve at I/C ratio of 0.5 is reduced compared to CCMs of higher I/C ratios, indicating lower oxygen transport limitation. (Figure 5a). This is probably due to the high porosity (Figure 2d) and broad pore size distribution (Figure 3b) at I/C = 0.5 that allows better oxygen diffusion in the high current density region. The performance is improved for all Pt/KB CCMs when back pressures are applied (Figures 5b and 5c). At current density below 1200 mA cm\(^{-2}\), the Pt/KB CCM with I/C ratio of 1.5 shows the highest performance. This could be due to the higher ORR activity and lower ORR overpotential loss in the cathode associated with high I/C ratios. Above 1200 mA cm\(^{-2}\), the performance of Pt/KB with I/C ratio of 1.5 decreases faster than other samples, which suggests higher oxygen transport limitation due to low catalyst layer porosity.

The highest performance is measured with I/C ratio of 0.5 for Pt/MWNT CCMs (Figures 5d–5f). Note that at low current densities (< 500 mA cm\(^{-2}\)), the performance of Pt/MWNT CCMs with various I/C ratios are similar. The CCM with I/C ratio of 0.5 is only slightly higher than the other two CCMs. At high current densities (>500 mA cm\(^{-2}\)), the CCM of I/C ratio 0.5 out-performed the other two CCMs, which indicates a significant reduction of oxygen transport limitation. To establish a relationship between the catalyst layer microstructure and the performance, quantitative analysis of polarization...
Figure 2. Nitrogen adsorption isotherm for Pt/KB (a) and Pt/MWNT (b) CCMs. BET surface area (c) and porosity (d) of Pt/C catalyst layer are plotted as a function of I/C ratio. The error bars for BET surface area were obtained from three repeating tests, while the error bars for the porosity were from two identical sample measurements.

overpotentials is needed. Thus, the six-step method is used in the following sections to analyze the effect of I/C ratios on different polarization overpotentials.

The characteristic parameters obtained from the six-step method for all CCMs and operating pressures are summarized in the Appendix (Tables A1–A6). The dash lines in Figures 5a–5f shows the calculated polarization curves where the total potential loss is calculated with the six-step method. Good agreement between the six-step method and experimental data is obtained with error less than 0.1 mV. Three Tafel regions can be distinguished for all CCMs in Tables A1–A6, in agreement with our previous work. Every Tafel region is dominated by one factor. At kinetic current density $> 1000$ mA cm$^{-2}$ ($>800$ mA cm$^{-2}$ for ambient pressure polarization curves), the major contribution of this polarization overpotential is the molecular diffusion of oxygen which is the source of the non-electrode concentration overpotential ($\eta_{\text{corr}3}$). At a kinetic current density of 100–1000 mA cm$^{-2}$, the major contribution of polarization overpotential is the cathode concentration overpotential ($\eta_{\text{corr}4}$) which is attributed to the Knudsen diffusion of oxygen in the cathode and the oxygen transport in the ionomer thin film and at the ionomer/Pt interface. At kinetic current density 10–100 mA cm$^{-2}$, the major contribution of polarization is the ORR kinetics because the current-potential relation is governed by Tafel relation.

The non-electrode and electrode ohmic overpotentials ($\eta_{\text{corr1}}$ and $\eta_{\text{corr2}}$).—The non-electrode ohmic resistance were comparable for all samples tested, ranging from 0.055 to 0.08 Ohm cm$^{2}$ (Tables A1–A6) in agreement with our previous work using the same type of Nafion membrane and test conditions. For Pt/KB CCMs, the highest electrode ohmic resistance ($R_{\text{electrode}}$) is measured at I/C ratio of 0.5 due to insufficient amount of ionomer in the cathode (Figure 6a). Further increase of I/C ratio to 1.0 significantly reduced the $R_{\text{electrode}}$, follow by a slight increase at I/C ratio of 1.5. Although high I/C ratios improved ionic conductivity of cathode, a counter effect occurs with too much ionomer.

This contrasts with the results from Liu et al. where the ionic resistivity decreases monotonically with increasing I/C ratios. Liu et al. extrapolated the ion resistance from EIS measured when the fuel cell is operating in H$_2$/N$_2$ environment. The $R_{\text{cathode}}$ measured in the present work can be considered as the apparent cathode ohmic resistance derived from the H$_2$/Air and H$_2$/O$_2$ polarization curves. Factors such as oxygen reduction reaction, gas transport, water transport, and current distribution etc. are all considered when the fuel cell is operating. On the other hand, the EIS method using transmission-line model focus solely on measuring the through plain ionic resistivity. The factors are minimized as much as possible in the H$_2$/N$_2$ environment where there is no oxygen reduction reaction in the cathode and the mass transport issue is minor. Therefore, although a monotonic trend is observed with the EIS method, it is not necessarily the case with the present work. Moreover, the values reported in Ref. 43 corresponds to $3 \Omega$ cm$^{2}$ to $0.3 \Omega$ cm$^{2}$ of cathode resistance from I/C ratio of 0.2 to 1.2. On the other hand, the $R_{\text{cathode}}$ calculated in the present work is from 0.06 $\Omega$ cm$^{2}$ to 0.015 $\Omega$ cm$^{2}$, approximately an order of magnitude less than the values reported in Ref. 43. Although the ionic resistivity measured with the EIS method is likely reflecting the real values, it cannot be used for overpotential correction. This also suggests that the trend observed with the EIS method may not be applicable to the six-step method in this work.

Non-electrode and electrode ohmic overpotentials ($\eta_{\text{corr1}}$ and $\eta_{\text{corr2}}$). The non-electrode ohmic resistance was comparable for all samples tested, ranging from 0.055 to 0.08 Ohm cm$^{2}$ (Tables A1–A6) in agreement with our previous work using the same type of Nafion membrane and test conditions. For Pt/KB CCMs, the highest electrode ohmic resistance ($R_{\text{electrode}}$) is measured at I/C ratio of 0.5 due to insufficient amount of ionomer in the cathode (Figure 6a). Further increase of I/C ratio to 1.0 significantly reduced the $R_{\text{electrode}}$, follow by a slight increase at I/C ratio of 1.5. Although high I/C ratios improved ionic conductivity of cathode, a counter effect occurs with too much ionomer.

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On the other hand, the $R_{\text{electrode}}$ measured for Pt/MWNT CCMs are close to each other with a deviation less than 0.005 Ohm cm$^{-2}$ in magnitude (Figure 6b). Note that the magnitude of $R_{\text{electrode}}$ measured for Pt/MWNT CCMs is close to the Pt/KB CCMs at high I/C ratios, 1.0 and 1.5. Since MWNT has low surface area and extremely low microporosity, most of the ionomer is distributed at the surface and forms a continuous thin film for ionic transport. In other words, the high-surface-area carbon support has low utilization of ionomer because the micropores need to be filled before a continuous ionomer thin film forms at the surface. Once the ionomer content is enough for a continuous thin film, the magnitude of $R_{\text{electrode}}$ reaches a low magnitude that is similar regardless of the carbon support type. Further increase of ionomer content results in higher $R_{\text{electrode}}$ as is the case with Pt/KB CCM at I/C ratio of 1.5.

For Pt/MWNT CCMs, the influence of I/C ratio at low current density is not significant and reduces with higher operating pressure. Since the surface area and porosity of MWNT is much lower than KB, it is possible that less ionomer is needed to reach the maximum ORR activity. At medium and high current density, the median I/C ratio of 0.5 shows the highest performance. While an I/C ratio of 0.3 is insufficient for optimal performance, I/C ratio of 0.8 is likely too much for MWNT where lumps of ionomer could occur and significantly increases the oxygen transport limitation.

Non-electrode concentration overpotential ($\eta_{\text{corr3}}$)—The influence of I/C ratio on the non-electrode concentration overpotential ($\eta_{\text{corr3}}$) for Pt/KB and Pt/MWNT CCMs are shown in Figure 8. Since the same type of GDL was used for all RSDT-derived CCMs, it can be inferred that the only factor influencing the non-electrode concentration overpotential is the microstructure of the catalyst layer (Figures 2, 3) determined by I/C ratio and carbon support. The $\eta_{\text{corr3}}$ stems from the molecular diffusion of oxygen in the flow channels, GDL, and large pores in the cathode. Based on Fick’s first law, the oxygen partial pressure gradient between the flow channels and the catalyst surfaces increase with current density and decrease with high back pressure. Thus, $\eta_{\text{corr3}}$ increases with current densities and decreases with operating pressure. For Pt/KB CCMs, the $\eta_{\text{corr3}}$ decreased with I/C ratio for all operating pressures. This can be correlated with the pore size distribution (Figure 3) of the catalyst layer in the range of 30–100 nm. As shown in our previous study, higher pore volume in the range of 30–100 nm results in lower $\eta_{\text{corr3}}$. It is noted that the pore range of 30–100 nm suggested combined diffusion of molecular and Knudsen diffusion. However, the Knudsen diffusion coefficient is independent of pressure and is a function of temperature and the pore size, both of which have the same value or range in our discussion here. At I/C ratio of 0.5, the Pt/KB catalyst layer shows the highest porosity and pore volume in the range of 30–100 nm. Hence, $\eta_{\text{corr3}}$
is lower than all other Pt/KB CCMs. As the I/C ratio was increased to 1.0 and 1.5, the porosity and the pore volume decreased (Figure 3) which lead to higher $\eta_{corr3}$ (Figures 8a–8c).

For Pt/MWNT CCMs, the sample at I/C ratio of 0.5 shows the lowest magnitude of $\eta_{corr3}$. The pore size distribution for the I/C ratio 0.5 CCM showed higher pore volume with pore diameter of 30 to 100 nm than the samples with I/C ratios of 0.3 and 0.8, both of which showed similar distribution in the same range (Figure 3d). It is interesting that the sample at I/C ratio of 0.3 shows higher porosity and pore volume in the range of 100 nm to 1000 nm. However, this does not effectively reduce the magnitude of $\eta_{corr3}$. Because the role of small pores outweighs large pores as oxygen must diffuse into the small pores to reach the platinum sites. It is likely that the contribution of larger pores in the overall pore volume is less than that in the range of 30–100 nm. Thus, for both Pt/KB and Pt/MWNT CCMs, high pore volume in the range of 30–100 nm results in lower $\eta_{corr3}$, in agreement with our previous study of commercial GORE CCMs.

Electrode concentration overpotential ($\eta_{corr4}$).—The effect of I/C ratio on electrode concentration overpotential ($\eta_{corr4}$) for Pt/KB and Pt/MWNT CCMs at various operating pressures are shown in Figure 9. The origin of $\eta_{corr4}$ is attributed to the oxygen diffusion limitation in the ionomer thin film and in the small pores cathode catalyst layer where Knudsen diffusion dominates. The linearity of plotting against log current stems from the Butler-volmer equation (Equation 7). The magnitudes of $\eta_{corr4}$ are generally lower than the GORE CCM at 0.1 mg cm$^{-2}$ cathode Pt loading, except for the Pt/KB CCM at I/C ratio of 0.5 which has similar magnitude of $\eta_{corr4}$ with the GORE CCM.

As the magnitude of $\eta_{corr4}$ is small, the effect of operation pressure is less pronounced than that reported in Ref. 25. The change of $\eta_{corr4}$ with different pressures could be due to the variance in determining the Tafel slopes. Although commercial GORE CCMs suggests possible influence of operating pressure in oxygen diffusion through ionomer thin film, the results in Figure 9 do not show a strong dependence of operating pressure. For Pt/KB CCMs (Figures 9a–9c), the lowest magnitude of $\eta_{corr4}$ is found at the optimal I/C ratio of 1.0. At low I/C ratio of 0.5, the $\eta_{corr4}$ shows the highest magnitude at all operating pressures. Further increase of I/C ratio from 1.0 to 1.5 results in higher $\eta_{corr4}$ due to thick ionomer film covering the Pt catalyst. For Pt/MWNT CCMs, the lowest magnitude of $\eta_{corr4}$ is also found for the optimum I/C ratio of 0.5. The highest magnitude of $\eta_{corr4}$ was found at the highest I/C ratio, 0.8, followed by the I/C ratio of 0.3 and 0.5 (Figures 9d–9f).

To illustrate the oxygen transport mechanism in the ionomer film, Nonoyama et al. 22 and Jomori et al. 45 introduced a concept of effective...
Figure 5. Polarization curves of Pt/KB (a-c) and Pt/MWNT (d-f) CCMs fabricated through RSDT process with various I/C ratios and operating pressures. Performances of GORE CCMs at 0.4 and 0.1 mg cm\(^{-2}\) cathode Pt loading are displayed for comparison. Dash lines are calculated polarizations curves using the six-step method and good agreement with the experimental data is found. Refer to Table I for testing conditions.

ionomer area which is proportional to the ECSA. Jomori et al. proposed a non-linear relation between the oxygen transport resistance in the cathode and the ECSA where the transport resistance decrease with increasing ECSA. For RSDT-derived Pt/KB and Pt/MWNT CCMs, the magnitude of \(\eta_{\text{corr}}\) qualitatively agrees with the magnitude of ECSA at various I/C ratios. Note that Jomori et al. assumed spherical carbon particles and uniform ionomer thickness which are not appropriate in a real cathode. However, the concept of effective ionomer area can be used to interpret the correlation between \(\eta_{\text{corr}}\) and ECSA for Pt/KB and Pt/MWNT CCMs. Further study on the effect of carbon support geometry, such as aspect ratio and curvature, is required to validate the concept of effective ionomer area.

**ORR kinetics and catalyst activity (\(\eta_{\text{corr5}}\) and \(\eta_{\text{corr6}}\)).** Figure 10 shows comparison of activation overpotential (\(\eta_{\text{corr6}}\)) and ORR activity measured in oxygen-breathing cells at 0.9 \(V_{\text{R-faradaic}}\) and 100 kPa. The \(\eta_{\text{corr6}}\) presented in Figures 10a and 10b agree with the ORR activity in Figures 10c and 10d, where high \(\eta_{\text{corr}}\) is associated with low ORR activity. It is noted that the \(\eta_{\text{corr}}\) of Pt/MWNT CCMs is more sensitive to the change of operating pressure than Pt/KB CCMs. On the other hand, the ORR activity is less sensitive to I/C ratios. This is reflected in the H\(_2\)/Air Tafel plot at low current density (Figure 7) where the curves for Pt/MWNT improves with operating pressure but varies less than Pt/KB CCMs.

The relation between mass activity and I/C ratio is different between KB and MWNT. This could be related to different micropore volume and surface area between KB and MWNT. For high-surface-area KB, extended ionomer coverage could be achieved at higher I/C ratio, without increasing the ionomer film thickness. The carbon grains and the ionomer are well percolated forming complete path of electrons and protons from GDL to PEM. Therefore, a continuous decrease of activation overpotential with the increase of I/C ratio was observed, which lead to an increase of ORR activity with the I/C ratio. For MWNT, as the micropores are immediately filled with
ionomer upon mixing (Figure 3c), excessive ionomer could remain on the external surface of the carbon. The maximum ORR activity is obtained at I/C ratio of 0.5, which suggest that further increase of ionomer content in the catalyst no longer enhance the triple-boundary interface between carbon, ionomer and Pt.

The Tafel slopes (Figure 11) for each CCMs are measured in the current range of 10–100 mA cm$^{-2}$ and the results lies between 60 and 70 mV/dec., in agreement with the theoretical value of 70 mV/dec. Based on Equation 9, the magnitude of Tafel slope is a direct measurement of the overpotential due to ORR kinetics ($\eta_{corr}$). Figure 11 shows that the Tafel slopes decreased slightly with the increase of I/C ratio, for both Pt/KB and Pt/MWNT CCMs, which agrees with the fact that higher ORR activity is found at higher I/C ratios (Figures 10c and 10d). A recent work from Ishikawa et al. also shows low overpotential with increasing I/C ratio which is attributed to improved proton transport due to increased ionomer connectivity and reduced ionomer

Figure 7. H$_2$/Air Tafel plots of Pt/KB (a-c) and Pt/MWNT (d-f) CCMs fabricated through RSDT process with various I/C ratios and operating pressures. Non-electrode and electrode resistances are corrected. All plots are corrected with crossover current, $i_x$. 

Figure 8. Non-electrode concentration overpotential of Pt/KB (a-c) and Pt/MWNT (d-f) CCMs at various I/C ratio and operating pressures.
Contribution of six polarization sources in PEMFC performance.—For a comprehensive understanding of PEMFC polarization, Figure 12 summarizes the contribution of six types of polarization overpotentials for RSDT-derived CCMs and GORE CCMs. The analysis of overpotentials for the GORE CCMs can be found in our previous work. The total polarization overpotentials (mV) are similar for all CCMs with 0.1 mg cm$^{-2}$ cathode Pt loading (Tables A7–A9) with variances less than 5 mV, which agrees with Figure 5 where comparable performance can be found at current densities selected in Figure 12.

Overpotentials related to ORR activation and Tafel kinetics are the dominant sources of polarization for all CCMs, including the high Pt loading GORE CCM (Figure 12). Although overpotentials related to ORR is mainly determined by the catalyst material (Pt), high I/C ratio for Pt/KB CCM results in lower ORR activation overpotential than Pt/MWNT and GORE CCMs. However, the Pt/KB CCMs has higher non-electrode concentration overpotential than Pt/MWNT and GORE CCMs. Because the pore volume between 30 to 100 nm is reduced at high I/C ratio. Therefore, the total overpotentials are comparable among all RSDT and GORE CCMs at 0.1 mg cm$^{-2}$ Pt loading. The benefit of reduced activation overpotential due to high I/C ratio is counter-balanced by the reduction of pore volume in the catalyst layer.

The contribution of non-electrode concentration overpotential for both RSDT CCMs in Figure 12 are higher than the GORE CCMs. Since the GDL type are consistent for all CCMs tested, the non-electrode concentration overpotential reflects the microstructure of cathode catalyst layer. It is shown in our previous work that this is because the cathode of RSDT CCMs have lower pore volume in the range of 30–100 nm. Further optimization for RSDT-derived CCMs will focus on increasing the mesopore volume of cathode catalyst layer using carbon support with controlled mesopore distribution. On the other hand, the contribution of cathode electrode concentration overpotential is lower for both RSDT CCMs at optimized I/C ratios. This demonstrates the advantage of RSDT process for improving the ionomer distribution in the cathode catalyst layer.

Lastly, the non-electrode ohmic overpotential for both RSDT CCMs make higher contribution than that for the GORE CCMs. This is because the RSDT CCMs used thicker membrane (50 μm) than the GORE CCMs (18 μm) while the test hardware and GDL type were consistent for all sample tested. Thus, thinner membrane (about 20 μm thickness) is recommended for future studies. In the meantime, RSDT process parameters may require adjustment to reduce the influence of process temperature on the membrane during fabrication to prevent drying/deformation.

In summary, at optimized I/C ratios KB shows lower activation overpotential but higher non-electrode concentration overpotential than those for MWNT. Since the total polarization overpotential is comparable between KB and MWNT, MWNT is preferred for catalyst support in PEMFC as it requires 50% less ionomer in the cathode. Reduction of ionomer use can reduce the fabrication cost for the electrodes. More importantly, MWNT is more resistant to corrosion at high potentials during start/stop and fuel starvation conditions.

The present work demonstrates that the six-step method of polarization analysis is a powerful tool to separate six types of overpotentials and correlate them with catalyst layer properties, fabrication process, and testing parameters/conditions. The six-step method points out a path for future optimization of low Pt-loading electrodes with specifically targeted overpotentials.

Conclusions

In this study, CCMs with two types of carbon supports and various I/C ratios were fabricated in RSDT process where low Pt loading (0.1 mg cm$^{-2}$) catalyst layer were directly deposited on Nafion membranes. The optimal performance in air-breathing cells was achieved at I/C ratio of 1.0 for Pt/KB CCMs and at I/C ratio of 0.5 for Pt/MWNT CCMs. Six types polarization sources were analyzed and the key results from this study are:

1. The non-electrode ohmic resistance ($\eta_{\text{corr1}}$) are comparable for all cells as the MEA materials and hardware are consistent in this work. The cathode electrode ohmic resistance ($\eta_{\text{corr2}}$) depends on I/C ratio for Pt/KB CCMs. Lowest $\eta_{\text{corr2}}$ is measured at the optimal I/C ratio of 1.0. On the other hand, $\eta_{\text{corr2}}$ is less sensitive to the I/C ratio for Pt/MWNT CCMs and thus low I/C ratios can be used to reduce the cost.

2. Non-electrode concentration overpotential ($\eta_{\text{corr3}}$) is controlled by the molecular diffusion of oxygen in the GDL and in the mesopores of the catalyst layer. It is reduced with higher back
Figure 10. Comparison of activation overpotential for Pt/KB (a) and Pt/MWNT (b) CCMs with various I/C ratios and operating pressures. Comparison of mass activity measured in oxygen-breathing cells at 0.9 V o.r.r. free, 100 kPa back pressure for Pt/KB (c) and Pt/MWNT CCMs (d). The mass activity is calculated using the Tafel plots in (e) and (f).

Figure 11. Comparison of Tafel slope measured from H2/O2 polarization curves (10–100 mA cm$^{-2}$) for Pt/KB (a) and Pt/MWNT (b) CCMs with various I/C ratios and operating pressures.
pressure or higher pore volume in the pore range of 30 nm-100 nm. At optimized I/C ratio, the \( \eta_{corr} \) for Pt/KB CCM is higher than Pt/MWNT CCM due to lower pore volumes between 30 nm and 100 nm.

3. The cathode electrode concentration overpotential (\( \eta_{corr4} \)) is related to the oxygen transport in the micropores (Knudsen diffusion) and ionomer thin film. For both carbon supports, \( \eta_{corr4} \) was found to be proportional to the ECSA. The I/C ratio with highest ECSA suggests a maximum of effective ionomer area, which results in minimal oxygen diffusion resistance in the ionomer thin film and thus gives the lowest \( \eta_{corr4} \).

4. The ORR overpotentials (\( \eta_{corr5} \) and \( \eta_{corr6} \)) decreased with increasing I/C ratios for Pt/KB suggesting improved triple-phase boundary between Pt, carbon and ionomer and enhanced ionomer coverage on the carbon. Since MWNT has lower surface area and microporosity than KB, the ideal ionomer coverage requires less ionomer and the ORR overpotentials of Pt/MWNT does not vary significantly with the I/C ratio.

The present work demonstrates that the six-step method is a powerful tool to separate polarization overpotentials and to provide a clear path for optimization with specifically targeted overpotentials. Comparing with GORE CCMs, the RSDT-derived CCMs shows low \( \eta_{corr3} \) due to improved ionomer distribution but high \( \eta_{corr3} \) due to insufficient pore volume in the range of 30–100 nm. Using carbon supports with controlled mesopore distribution will allow for a better balance between the pore volume and the ionomer content that can help reduce \( \eta_{corr1} \). In addition, using a thinner membrane can help reduce \( \eta_{corr1} \) for RSDT-derived CCMs. Since the performance of RSDT-derived Pt/KB and Pt/MWNT CCMs at optimized I/C ratio is comparable, it is beneficial to use MWNT for low Pt-loading electrode due to lower ionomer usage in the cathode and better chemical stability against corrosion.

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Appendix

Characteristic parameters used for calculating six sources of polarization overpotentials.

Figure A1. Comparison of Pt/KB CCM with different anode I/C ratios and duplicated cathodes. Test performed at 80 °C, ambient pressure, 100/75%RH, H2/air stoic 3/4, H2/O2 stoic 3/20. Anode loading: 0.05 mg cm\(^{-2}\); cathode loading 0.1 mg cm\(^{-2}\), I/C ratio 1.0.

Figure A2. Comparison of Pt/MWNT CCMs from two duplicated samples. Test performed at 80 °C, 100 kPa backpressure, 100/75%RH, H2/air stoic 3/4, H2/O2 stoic 3/20. Anode loading: 0.05 mg cm\(^{-2}\); cathode loading 0.1 mg cm\(^{-2}\), I/C ratio 0.5.
Table A1. Characteristic parameters of RSDT-derived MEA tested at ambient pressure with different I/C ratio using KB as supports. These parameters are used to calculate all six sources of polarization sources.

| Related Overpotential | Characteristics                          | Unit                  | Pt/KB I/C = 0.5          | Pt/KB I/C = 1.0          | Pt/KB I/C = 1.5          |
|-----------------------|------------------------------------------|-----------------------|--------------------------|--------------------------|--------------------------|
|                       | Equilibrium cell voltage, air, $V_{eq}$   | V                     | 1.1537                   | 1.1537                   | 1.1537                   |
|                       | Electrode ohmic resistance, $R_{ electrode}$ | ohm-cm$^2$        | 0.065–0.08               | 0.060–0.064              | 0.058–0.065              |
|                       | Limiting current, air, $i_{lim}$         | mA/cm$^2$             | 1310                     | 1450                     | 1130                     |
| Concentration, electrode | Slope of $i_{lim}$ plot, air, $b'(i>i_b)$ | mV/dec.              | 91.5                     | 72.21                    | 67.92                    |
| Concentration, electrode | 10–100 mA cm$^{-2}$                       | mV/dec.              | 81.72                    | 70.21                    | 65.21                    |
| Concentration, electrode | 100–800 mA cm$^{-2}$                      | mV/dec.              | 117.05                   | 105.78                   | 102.05                   |
| Concentration, electrode | >800 mA cm$^{-2}$                        | mV/dec.              | 208.89                   | 219.05                   | 191.21                   |
| Activation, Tafel    | Breaking current density, air, $i_b$      | mA/cm$^2$             | 10                       | 10                       | 10                       |
|                       | Kinetic Tafel slope, B (10–100 mA/cm$^2$ | mV/dec.              | 75.25                    | 71.49                    | 63.98                    |

Table A2. Characteristic parameters of RSDT-derived MEA tested at 100 kPa back pressure with different I/C ratio using KB as supports. These parameters are used to calculate all six sources of polarization sources.

| Related Overpotential | Characteristics                          | Unit                  | Pt/KB I/C = 0.5          | Pt/KB I/C = 1.0          | Pt/KB I/C = 1.5          |
|-----------------------|------------------------------------------|-----------------------|--------------------------|--------------------------|--------------------------|
|                       | Equilibrium cell voltage, air, $V_{eq}$   | V                     | 1.1724                   | 1.1724                   | 1.1724                   |
|                       | Electrode ohmic resistance, $R_{ electrode}$ | ohm-cm$^2$        | 0.057–0.065              | 0.062–0.065              | 0.055–0.065              |
|                       | Limiting current, air, $i_{lim}$         | mA/cm$^2$             | 1815                     | 1860                     | 1735                     |
| Concentration, electrode | Slope of $i_{lim}$ plot, air, $b'(i>i_b)$ | mV/dec.              | 87.61                    | 76.19                    | 66.96                    |
| Concentration, electrode | 10–100 mA cm$^{-2}$                       | mV/dec.              | 114.76                   | 82.28                    | 81.24                    |
| Concentration, electrode | 100–1000 mA cm$^{-2}$                     | mV/dec.              | 154.49                   | 127.43                   | 169.67                   |
| Activation, Tafel    | Breaking current density, air, $i_b$      | mA/cm$^2$             | 10                       | 10                       | 10                       |
|                       | Kinetic Tafel slope, B (10–100 mA/cm$^2$ | mV/dec.              | 73.24                    | 75.75                    | 60.3                     |

Table A3. Characteristic parameters of RSDT-derived MEA tested at 180 kPa back pressure with different I/C ratio using KB as supports. These parameters are used to calculate all six sources of polarization sources.

| Related Overpotential | Characteristics                          | Unit                  | Pt/KB I/C = 0.5          | Pt/KB I/C = 1.0          | Pt/KB I/C = 1.5          |
|-----------------------|------------------------------------------|-----------------------|--------------------------|--------------------------|--------------------------|
|                       | Equilibrium cell voltage, air, $V_{eq}$   | V                     | 1.1790                   | 1.1790                   | 1.1790                   |
|                       | Electrode ohmic resistance, $R_{ electrode}$ | ohm-cm$^2$        | 0.065–0.08               | 0.060–0.065              | 0.058–0.065              |
|                       | Limiting current, air, $i_{lim}$         | mA/cm$^2$             | 2075                     | 1955                     | 1840                     |
| Concentration, electrode | Slope of $i_{lim}$ plot, air, $b'(i>i_b)$ | mV/dec.              | 73.99                    | 74.77                    | 64.69                    |
| Concentration, electrode | 10–100 mA cm$^{-2}$                       | mV/dec.              | 105.38                   | 80.48                    | 86.53                    |
| Concentration, electrode | 100–1200 mA cm$^{-2}$                     | mV/dec.              | 148.75                   | 97.27                    | 140.55                   |
| Concentration, electrode | >1200 mA cm$^{-2}$                       | mV/dec.              | 10                       | 10                       | 10                       |
| Activation, Tafel    | Breaking current density, air, $i_b$      | mA/cm$^2$             | 71.8                     | 71.16                    | 61.49                    |
Table A4. Characteristic parameters of RSDT-derived MEA tested at ambient pressure with different I/C ratio using MWNT as supports. These parameters are used to calculate all six sources of polarization sources.

| Related Overpotential | Characteristics                                      | Unit       | Pt/MWNT I/C = 0.3 | Pt/MWNT I/C = 0.5 | Pt/MWNT I/C = 0.8 |
|-----------------------|------------------------------------------------------|------------|-------------------|-------------------|-------------------|
| N/A                   | Equilibrium cell voltage, air, $V_{eq}$              | V          | 1.1537            | 1.1537            | 1.1537            |
| ohmic, nonelectrode   | Nonelectrode                                         | ohm-cm$^2$| 0.06–0.072        | 0.06–0.07         | 0.065–0.075       |
| Concentration, non-electrode | Electrode ohmic resistance, $R_{electrode}$         | ohm-cm$^2$| 0.020             | 0.015             | 0.022             |
| Concentration, electrode | Limiting current, air, $i_{lim}$                   | mA/cm$^2$ | 1150              | 1450              | 1200              |
| Slope of $i_{lim}$ plot, air, $b^*(i_{lim}>ib)$ | 10–100 mA cm$^{-2}$     | mV/dec.   | 79.1              | 72.31             | 71.6              |
| Concentration, electrode | 100–800 mA cm$^{-2}$    | mV/dec.   | 90.8              | 76.72             | 91.2              |
| Concentration, electrode | >800 mA cm$^{-2}$    | mV/dec.   | 201.2             | 258.82            | 198.4             |
| Activation, Tafel     | Kinetic Tafel slope, B (10–100 mA/cm$^2$ H$_2$/O$_2$ curve) | mV/dec.   | 68.64             | 62.4              | 61.99             |

Table A5. Characteristic parameters of RSDT-derived MEA tested at 100 kPa back pressure with different I/C ratio using MWNT as supports. These parameters are used to calculate all six sources of polarization sources.

| Related Overpotential | Characteristics                                      | Unit       | Pt/MWNT I/C = 0.3 | Pt/MWNT I/C = 0.5 | Pt/MWNT I/C = 0.8 |
|-----------------------|------------------------------------------------------|------------|-------------------|-------------------|-------------------|
| N/A                   | Equilibrium cell voltage, air, $V_{eq}$              | V          | 1.1724            | 1.1724            | 1.1724            |
| ohmic, nonelectrode   | Nonelectrode                                         | ohm-cm$^2$| 0.06–0.07         | 0.055–0.065       | 0.07–0.075        |
| Concentration, non-electrode | Electrode ohmic resistance, $R_{electrode}$         | ohm-cm$^2$| 0.025             | 0.021             | 0.02              |
| Concentration, electrode | Limiting current, air, $i_{lim}$                   | mA/cm$^2$ | 1560              | 1775              | 1625              |
| Slope of $i_{lim}$ plot, air, $b^*(i_{lim}>ib)$ | 10–100 mA cm$^{-2}$     | mV/dec.   | 71.77             | 65.33             | 67.8              |
| Concentration, electrode | 100–1000 mA cm$^{-2}$    | mV/dec.   | 79.1              | 64.92             | 84.77             |
| Concentration, electrode | >1000 mA cm$^{-2}$   | mV/dec.   | 227.77            | 153.96            | 189.39            |
| Activation, Tafel     | Kinetic Tafel slope, B (10–100 mA/cm$^2$ H$_2$/O$_2$ curve) | mV/dec.   | 64.98             | 62.21             | 61.18             |

Table A6. Characteristic parameters of RSDT-derived MEA tested at 180 kPa back pressure with different I/C ratio using MWNT as supports. These parameters are used to calculate all six sources of polarization sources.

| Related Overpotential | Characteristics                                      | Unit       | Pt/MWNT I/C = 0.3 | Pt/MWNT I/C = 0.5 | Pt/MWNT I/C = 0.8 |
|-----------------------|------------------------------------------------------|------------|-------------------|-------------------|-------------------|
| N/A                   | Equilibrium cell voltage, air, $V_{eq}$              | V          | 1.1790            | 1.1790            | 1.1790            |
| ohmic, nonelectrode   | Nonelectrode                                         | ohm-cm$^2$| 0.052–0.066       | 0.06–0.07         | 0.065–0.075       |
| Concentration, non-electrode | Electrode ohmic resistance, $R_{electrode}$         | ohm-cm$^2$| 0.023             | 0.025             | 0.025             |
| Concentration, electrode | Limiting current, air, $i_{lim}$                   | mA/cm$^2$ | 1875              | 1925              | 1860              |
| Slope of $i_{lim}$ plot, air, $b^*(i_{lim}>ib)$ | 10–100 mA cm$^{-2}$     | mV/dec.   | 68.86             | 64.52             | 65.21             |
| Concentration, electrode | 100–1200 mA cm$^{-2}$    | mV/dec.   | 80.66             | 70.47             | 79.04             |
| Concentration, electrode | >1200 mA cm$^{-2}$   | mV/dec.   | 260.34            | 118.64            | 183.95            |
| Activation, Tafel     | Kinetic Tafel slope, B (10–100 mA/cm$^2$ H$_2$/O$_2$ curve) | mV/dec.   | 64                | 60.28             | 59.18             |
### Table A7. Contribution of different polarization sources for Pt/KB CCM at I/C ratio of 1.0.

| Related Overpotential | Characteristics | Pt/KB I/C = 1.0 ambient | Pt/KB I/C = 1.0 100kPa | Pt/KB I/C = 1.0 180kPa |
|-----------------------|----------------|-------------------------|------------------------|------------------------|
| η_{corr1}            | Non-electrode ohmic (mV) | 31.4 | 6.4 | 64.8 | 9.9 | 42.9 | 8.7 | 88.2 | 14.0 |
| η_{corr2}            | Electrode ohmic (mV) | 7.5 | 1.5 | 15.0 | 2.3 | 10.5 | 2.1 | 21.0 | 3.3 |
| η_{corr3}            | Non-electrode concentration (mV) | 39.2 | 8.0 | 128.0 | 19.6 | 14.2 | 2.9 | 61.3 | 9.8 |
| η_{corr4}            | Electrode concentration (mV) | 8.6 | 1.8 | 18.2 | 2.8 | 5.9 | 1.2 | 12.6 | 2.0 |
| η_{corr5}            | Tafel kinetics: b log(i/10) | 119.0 | 24.2 | 140.0 | 21.5 | 137.0 | 27.7 | 160.0 | 25.5 |
| η_{corr6}            | Activation at 10 mA cm^{-2} | 285.5 | 58.1 | 285.5 | 43.8 | 284.9 | 57.5 | 284.9 | 45.4 |
| η_{Total}            | Total polarization loss (mV) | 491.2 | 651.5 | 495.4 | 628.0 | 488.3 | 594.5 |

### Table A8. Contribution of different polarization sources for Pt/MWNT CCM at I/C ratio of 0.5.

| Related Overpotential | Characteristics | Pt/MWNT I/C = 0.5 ambient | Pt/MWNT I/C = 0.5 100kPa | Pt/MWNT I/C = 0.5 180kPa |
|-----------------------|----------------|-------------------------|------------------------|------------------------|
| η_{corr1}            | Non-electrode ohmic (mV) | 34.6 | 7.1 | 72.7 | 11.2 | 48.0 | 9.9 | 98.5 | 15.6 |
| η_{corr2}            | Electrode ohmic (mV) | 7.5 | 1.5 | 15.0 | 2.3 | 14.7 | 3.0 | 29.4 | 4.7 |
| η_{corr3}            | Non-electrode concentration (mV) | 11.6 | 2.4 | 89.0 | 13.7 | 12.7 | 2.6 | 64.5 | 10.2 |
| η_{corr4}            | Electrode concentration (mV) | 19.5 | 4.0 | 41.5 | 6.4 | 8.8 | 1.8 | 19.5 | 3.1 |
| η_{corr5}            | Tafel kinetics: b log(i/10) | 104.0 | 21.4 | 122.0 | 18.8 | 109.0 | 22.5 | 127.0 | 20.1 |
| η_{corr6}            | Activation at 10 mA cm^{-2} | 309.5 | 63.6 | 309.5 | 47.6 | 292.0 | 60.2 | 292.0 | 46.3 |
| η_{Total}            | Total polarization loss (mV) | 486.7 | 649.7 | 485.2 | 630.9 | 474.3 | 593.8 |
### Table A9. Contribution of different polarization sources for GORE CCM with 0.1 mg cm\(^{-2}\) cathode Pt loading.

| Related Overpotential | Characteristics                  | GORE 0.1 Ambient |
|-----------------------|----------------------------------|------------------|
|                       |                                  | \(i = 500\)     | \(i = 1000\) | \(i = 1000\) |
| \(\eta_{corr1}\)     | Non-electrode ohmic (mV)         | 28.2             | 5.5          | 59.0         | 9.0          |
| \(\eta_{corr2}\)     | Electrode ohmic (mV)             | 8.5              | 1.7          | 17.0         | 2.6          |
| \(\eta_{corr3}\)     | Non-electrode concentration (mV)| 15.7             | 3.1          | 72.6         | 11.1         |
| \(\eta_{corr4}\)     | Electrode concentration (mV)     | 35.6             | 6.9          | 57.2         | 8.7          |
| \(\eta_{corr5}\)     | Tafel kinetics: \(b^*\log(i/10)\)| 119.0            | 23.2         | 142.0        | 21.7         |
| \(\eta_{corr6}\)     | Activation at 10 mA cm\(^{-2}\) | 306.9            | 59.7         | 306.9        | 46.9         |
| \(\eta_{Total}\)     | Total polarization loss (mV)     | 513.9            | 654.7        | 505.5        | 620.6        |

| Related Overpotential | Characteristics                  | GORE 0.1 100kPa |
|-----------------------|----------------------------------|-----------------|
|                       |                                  | \(i = 700\)     | \(i = 1000\) | \(i = 1400\) |
| \(\eta_{corr1}\)     | Non-electrode ohmic (mV)         | 34.8            | 6.9          | 69.8         | 11.2         |
| \(\eta_{corr2}\)     | Electrode ohmic (mV)             | 7.0             | 1.4          | 14.0         | 2.3          |
| \(\eta_{corr3}\)     | Non-electrode concentration (mV)| 14.5            | 2.9          | 56.5         | 9.1          |
| \(\eta_{corr4}\)     | Electrode concentration (mV)     | 34.2            | 6.8          | 44.3         | 7.1          |
| \(\eta_{corr5}\)     | Tafel kinetics: \(b^*\log(i/10)\)| 120.0            | 23.7         | 141.0        | 22.7         |
| \(\eta_{corr6}\)     | Activation at 10 mA cm\(^{-2}\) | 295.0            | 58.4         | 295.0        | 47.5         |
| \(\eta_{Total}\)     | Total polarization loss (mV)     | 505.5            | 620.6        | 480.8        | 575.7        |

| Related Overpotential | Characteristics                  | GORE 0.1 180kPa |
|-----------------------|----------------------------------|-----------------|
|                       |                                  | \(i = 700\)     | \(i = 1000\) | \(i = 1400\) |
| \(\eta_{corr1}\)     | Non-electrode ohmic (mV)         | 33.2            | 6.9          | 67.2         | 11.7         |
| \(\eta_{corr2}\)     | Electrode ohmic (mV)             | 10.5            | 2.2          | 21.0         | 3.6          |
| \(\eta_{corr3}\)     | Non-electrode concentration (mV)| 12.9            | 2.7          | 38.0         | 6.6          |
| \(\eta_{corr4}\)     | Electrode concentration (mV)     | 23.2            | 4.8          | 29.5         | 5.1          |
| \(\eta_{corr5}\)     | Tafel kinetics: \(b^*\log(i/10)\)| 110.0            | 22.9         | 129.0        | 22.4         |
| \(\eta_{corr6}\)     | Activation at 10 mA cm\(^{-2}\) | 291.0            | 60.5         | 291.0        | 50.5         |
| \(\eta_{Total}\)     | Total polarization loss (mV)     | 480.8            | 575.7        |              |              |

### Table A10. Contribution of different polarization sources for GORE CCM with 0.4 mg cm\(^{-2}\) cathode Pt loading.

| Related Overpotential | Characteristics                  | GORE 0.4 Ambient |
|-----------------------|----------------------------------|------------------|
|                       |                                  | \(i = 500\)     | \(i = 1000\) | \(i = 1000\) |
| \(\eta_{corr1}\)     | Non-electrode ohmic (mV)         | 28.4             | 6.5          | 60.8         | 11.5         |
| \(\eta_{corr2}\)     | Electrode ohmic (mV)             | 5.0              | 1.1          | 10.0         | 1.9          |
| \(\eta_{corr3}\)     | Non-electrode concentration (mV)| 4.8              | 1.1          | 24.2         | 4.6          |
| \(\eta_{corr4}\)     | Electrode concentration (mV)     | 37.0             | 8.4          | 48.9         | 9.3          |
| \(\eta_{corr5}\)     | Tafel kinetics: \(b^*\log(i/10)\)| 105.0            | 24.0         | 125.0        | 23.7         |
| \(\eta_{corr6}\)     | Activation at 10 mA cm\(^{-2}\) | 257.9            | 58.9         | 257.9        | 49.0         |
| \(\eta_{Total}\)     | Total polarization loss (mV)     | 438.1            | 526.8        | 445.7        | 545.8        |

| Related Overpotential | Characteristics                  | GORE 0.4 100kPa |
|-----------------------|----------------------------------|-----------------|
|                       |                                  | \(i = 700\)     | \(i = 1000\) | \(i = 1400\) |
| \(\eta_{corr1}\)     | Non-electrode ohmic (mV)         | 35.4             | 7.9          | 73.0         | 13.4         |
| \(\eta_{corr2}\)     | Electrode ohmic (mV)             | 9.1              | 2.0          | 18.2         | 3.3          |
| \(\eta_{corr3}\)     | Non-electrode concentration (mV)| 8.5              | 1.9          | 34.7         | 6.4          |
| \(\eta_{corr4}\)     | Electrode concentration (mV)     | 32.5             | 7.3          | 41.7         | 7.6          |
| \(\eta_{corr5}\)     | Tafel kinetics: \(b^*\log(i/10)\)| 106.0            | 23.8         | 124.0        | 22.7         |
| \(\eta_{corr6}\)     | Activation at 10 mA cm\(^{-2}\) | 254.2            | 57.0         | 254.2        | 46.6         |
| \(\eta_{Total}\)     | Total polarization loss (mV)     | 445.7            | 545.8        | 422.5        | 517.2        |

| Related Overpotential | Characteristics                  | GORE 0.4 180kPa |
|-----------------------|----------------------------------|-----------------|
|                       |                                  | \(i = 700\)     | \(i = 1000\) | \(i = 1400\) |
| \(\eta_{corr1}\)     | Non-electrode ohmic (mV)         | 34.3             | 8.1          | 70.7         | 13.7         |
| \(\eta_{corr2}\)     | Electrode ohmic (mV)             | 8.4              | 2.0          | 16.8         | 3.2          |
| \(\eta_{corr3}\)     | Non-electrode concentration (mV)| 6.3              | 1.5          | 30.3         | 5.9          |
| \(\eta_{corr4}\)     | Electrode concentration (mV)     | 23.0             | 5.4          | 30.9         | 6.0          |
| \(\eta_{corr5}\)     | Tafel kinetics: \(b^*\log(i/10)\)| 102.0            | 24.1         | 120.0        | 23.2         |
| \(\eta_{corr6}\)     | Activation at 10 mA cm\(^{-2}\) | 248.5            | 58.8         | 248.5        | 48.0         |
| \(\eta_{Total}\)     | Total polarization loss (mV)     | 422.5            | 517.2        |  |  |
