Analysis of Inkjet Printed Catalyst Coated Membranes for Polymer Electrolyte Electrolyzers

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Inkjet printing (IJP) is studied as a novel fabrication method for catalyst coated membranes (CCMs) for polymer electrolyte electrolyzers. IrO\textsubscript{2} and Pt/C inks were deposited by IJP over the membrane to fabricate anode and cathode electrodes, respectively. Optical microscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used for ex-situ surface and thickness characterization of the anode catalyst layer (CL). SEM images show the CL is uniform and well adhered to the membrane. EDX images show even distribution of the catalyst and ionomer in the CL. Hydrogen cross-over, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed to estimate hydrogen cross-over, double layer capacitance ($C_{dl}$) and cell resistances. Cross-over results show that the membrane is not damaged during printing. A kinetic study revealed Tafel slopes similar to those in literature. Electrochemical performance tests showed that inkjet printed electrolyzer CCMs achieved 1 and 2 A/cm\textsuperscript{2} current densities at average potentials of 1609 mV and 1696 mV (NRE211) and average of 1743 mV and 1977 mV (N117) respectively. The electrolyzer performance improved slightly when the printing piezo-voltage decreased but with a cost of higher fabrication time. The stability of the electrode was inline with literature data. The proposed electrodes outperform most of the previously reported electrolyzer data in the literature using commercial IrO\textsubscript{2} catalyst.

The transportation sector consumes nearly 30% of the primary energy in the US, mostly in the form of petroleum (94%).\textsuperscript{1} Hydrogen fuel cell vehicles, powered by hydrogen obtained by water electrolysis from renewable sources of energy, can provide a viable alternative to internal combustion engine vehicles that reduces the transportation sector’s reliance on fossil fuels and minimizes its greenhouse gas emissions. Hydrogen could also be used for large-scale energy storage of intermittent renewable energy, and to offset emissions from some industrial sectors, such as fertilizer production and oil upgrading.\textsuperscript{2,3} The study of more efficient water electrolyzers is paramount to realizing the potential of hydrogen as an energy carrier for the applications above.

Polymer electrolyte electrolyzer cells (PEECs) have been investigated since 1960s when General Electric introduced them for their inherent advantages over alkaline electrolyzers, namely: a) greater safety and reliability as no caustic electrolyte is circulated in the cell stack;\textsuperscript{4} b) higher partial load range;\textsuperscript{5} c) higher current density (up to several Amperes per square centimeter);\textsuperscript{6} and, d) high differential pressure without damage.\textsuperscript{7,8} Since then many research groups have studied this technology. Current challenges for PEEC commercialization are: a) the cost of the bipolar plates, b) the use of precious metal catalyst, e.g., Ir and Pt, and c) low durability.\textsuperscript{9} In order to reduce catalyst loading, novel electrode fabrication methods that achieve better control over the electrode microstructure and minimize catalyst waste are required.

A critical factor determining catalyst utilization of polymer electrolyte fuel cells (PEFC) and PEECs is the membrane electrode assembly (MEA) fabrication method. Over the past two decades, a variety of MEA and catalyst coated membrane (CCM) methods have been explored in the literature including wet and dry spraying, ultrasonic spraying, doctor blade followed by decal transfer, screen printing, magnetron sputtering, electro deposition, electro spraying and electrospinning. The goal of this article is to analyze the use of IJP for the manufacturing of PEECs with low loading and to study the effect of inkjet piezo-electric voltage on the CCM’s electrochemical performance. Given that the anode of a PEEC is commonly based on unsupported iridium, the ink composition and fabrication is substantially different from that of PEFCs.

In the following, the experimental method used for fabrication and characterization of the electrode and PEECs is first described. Then, ex-situ and in-situ results are provided and discussed with respect to previous literature data.

Fabrication and Characterization

Ink fabrication.—Catalyst inks for the anode electrode were prepared by mixing 44.7 mg of IrO\textsubscript{2} (99%, Alfa Aesar, A17849) with a total of 500 mg of 50-50 %wt. mixture of isopropanol (IPA) and propylene glycol (PG). The mixture was ultra-sonicated for 60 minutes and then 47 mg of Nafion solution (Liquion solution LQ-1105 1100EW 5 %wt., Ion Power) was added during sonication, drop-by-drop, to achieve a 5 %wt. Nafion content in the catalyst layer. The mixture was then probe sonicated (QSonica S4000) for 15 minutes (amplitude 20, 2 minutes on, 1 minute off) and degassed for another 60 minutes. The ink was then stored for several days in preparation for use. The cathode ink was fabricated by mixing 37.5 mg of Pt/C (46.7 %wt., Tanaka Kikinzoku International, TTK) in a 48–52 %wt. ratio mixture of IPA and PG following the process discussed in Ref. 12. 321 mg of Nafion solution was added to achieve a 30 %wt. Nafion content in the cathode electrode.

CCM fabrication.—A commercial inkjet material printer (Dimatix DPM-2800 series, Fujifilm) was used to print the electrodes on a Nafion membrane. The cartridge used (DMC-11610) has 16 square nozzles (21×21 μm nozzle) that are spaced 254 μm apart from each other which produce a droplet size of 10 pL. The ink was degassed before being placed in the cartridge. Then, the piezo-electric waveform and voltage were selected as shown in Figure 1. For printing, three...
Table I. Summary of PEEC fabrication methods described in the literature. The numbers in parenthesis indicate the loading in mg/cm². $S =$ sprayed catalyst.

| Ref. | CCM fabrication Method | Anode | Cathode | Membrane | Temp (°C) | E (V) @ 1 A/cm² |
|------|------------------------|-------|---------|----------|-----------|----------------|
| 16   | Decal IrO₂ (3)         | Pt black (3) | PFSA    | 80       | 1.59      |
| 17   | Decal IrO₂ (3)         | Pt black (0.5) | PFSA    | 80       | 1.53      |
| 18   | S-Decal IrO₂ (0.5)     | Pt black (3) | PFSA    | 80       | 1.56      |
| 19   | S-Decal IrO₂ (0.5)     | Pt black (0.5) | N115    | 80       | 1.78      |
| 20   | Spraying IrO₂ (2)      | 40%Pt/CX72 (2) | N115    | -        | 1.68      |
| 21   | S-Membrane IrO₂ (2)    | 10%Pt/C JM (0.4) | N115    | 80       | 1.65      |
| 22   | S-Membrane IrO₂ (2)    | 20%Pt/C Etek (0.4) | N115    | 80       | 1.65      |
| 23   | S-Membrane IrO₂ (2)    | Pt black (2.5) | N115    | 80       | 1.6      |
| 24   | Sputtering IrO₂ (2)    | Pt/C (-) | N117    | 80       | 1.85      |
| 25   | S-Membrane IrO₂ (3)    | 30%Pt/C TTK (0.5) | N112    | 80       | 1.66      |
| 26   | S-Membrane IrO₂ (1.5)  | 30%Pt/C TTK (0.5) | N1035   | 80       | 1.67      |
| 27   | Spraying IrO₂ (3)      | 30%Pt/Val XC72 (0.6) | N115    | 80       | 1.72      |
| 28   | Spraying IrO₂ (0.5)    | Pt/C (0.5) | N212    | 80       | 1.57      |
| 29   | S-Membrane IrO₂ (2.5)  | 30%Pt/C Etek (0.5) | N115    | 80       | 1.7      |
| 30   | Decal IrO₂ (1)         | 40%Pt/C JM (0.2) | N212    | 80       | 1.64      |
| 31   | Electrodeposition IrO₂ (0.1) | 46%Pt/C TTK (0.4) | N112    | 90       | 1.6      |
| 32   | Decal IrO₂ (0.5)       | 46%Pt/C TTK (0.25) | N115    | 80       | 1.72      |
| 33   | Inkjet IrO₂ (1.17)     | 46%Pt/C TTK (0.1) | N117    | 80       | 1.743     |
| 34   | Inkjet IrO₂ (1.17)     | 46%Pt/C TTK (0.1) | N211    | 80       | 1.608     |

Small droplets with minimal tails and satellite droplets were achieved at lower piezo-voltage as shown in Figure 1. A drop spacing of 20 μm was used to print for both anode and cathode electrodes. The catalyst is printed on a 5 cm² area on the surface of either Nafion NRE211 or N117 membrane. The catalyst loading was controlled by varying the number of layers printed on top of the membrane. The vacuum platen in the printer was maintained at 60 °C while printing. After printing, the membrane is dried at 80 °C for 2-3 hours before printing the cathode side of the membrane.

**Characterization of the CCM.**—**Microscopic imaging.**— Electrodes were analyzed for surface defects using transmitting optical (Micromaster, BS200, Fisher Scientific (FS)) and stereoscopic (Leica S8 APO) microscopes before electrochemical experiments were performed.

Scanning electron microscopy (SEM) (Zeiss Sigma 300 VP-FESEM) was used to study CL thickness and microstructure. Energy dispersive X-ray spectroscopy (EDX) (Bruker Xflash Detector 6|60) was used to observe the catalyst and ionomer distribution in the in-plane and through-plane direction of the CL. SEM samples were prepared by freeze fracturing the CCMs using liquid nitrogen. Half CCMs, i.e., membranes with only the anode electrode printed, were imaged before printing the cathode.

**Cyclic voltammetry.**—Cyclic voltammograms were obtained at 30 °C by flowing 0.2 slpm fully humidified H₂ in the Pt/C (reference) electrode and either 0.05 slpm fully humidified N₂ or stagnant water in the IrO₂ electrode. Potential scans were performed at 40 mV/s from 0.05 to 1.2 V. The double layer capacitance ($C_{dl}$) was calculated using:

$$C_{dl} = \frac{(\Delta l/2)}{\nu}$$

where $\Delta l$ is the thickness of the cyclic voltammogram in the double layer region (see Figure 8) and $\nu$ is the scan rate.

**Hydrogen cross-over.**—The measurement of hydrogen crossover is an important method for assessing the safety and Faradaic efficiency of electrolyzers. High H₂ cross-over can result in the formation of an explosive hydrogen-oxygen mixture in the anode channel. It also represents a loss of product hydrogen, thereby decreasing the electrolyzer efficiency.

Chronoamperometry tests were used to measure H₂ cross-over. Experiments were conducted at varying potential from 0.1 V to 0.5 V.
Electrochemical impedance spectroscopy was used to measure the cell resistance for our CCMs. Cell resistances of 0.2 and 0.08 Ω cm² were obtained for CCMs with N117 and NRE211 membranes, respectively. A linear fit of the cell resistance with membrane thickness was used to estimate a membrane resistivity of 7.88 Ω cm which is in line with the value of 6.67 Ω cm used to correct for membrane thickness as discussed above.

**Kinetic parameters.**—Tafel curves were obtained using a potentiostat (VersaSTAT 4, PAR) for current densities in the range of 0.2 to 100 mA/cm². To obtain kinetic parameters, the curves were fitted to a line using MATLAB. The overpotential is calculated as the difference between the cell potential and the theoretical potential (1.18 V) at the operating conditions.

**Electrochemical impedance spectroscopy (EIS).**—Galvanostatic EIS measurements were performed at constant current densities of 0.02, 0.05, 0.1, 0.15 and 0.2 A/cm² using a sinusoidal current of amplitude less than 10% of the total current except at 0.02 A/cm² (30%) and a frequency range between 10 kHz - 1 Hz (50 points per decade). The Pt/C electrode was used as the reference electrode and the IrO₂ electrode (anode) was used as the working electrode. The cells were maintained at 80 °C and the water flowrate was set to 9.1 mL/min. The impedance spectra were fitted to the equivalent circuit shown in Figure 11a using "zfit" MATLAB code³⁸ in order to estimate the ohmic resistance (Rₒ), charge transfer resistance (Rₜ), and double layer capacitance (Cₑ).

**Stability test.**—Stability tests were performed at 0.3 and 1 A/cm² for 24 hours at 80 °C with water flow rate of 9.1 mL/min. The cell was brought to room temperature and deionized water was refilled before starting the test. The data was measured every 10 seconds.

**Results and Discussion**

A summary of all the fabricated CCMs and their loadings are presented in Table II. The loading is calculated using the gravimetric method.³⁹ CCMs that are printed at the same time have the same loading.

**CCM characterization.**—Microscopic imaging.—The microscopic images of half CCMs taken using the optical transmission microscope are shown in Figure 3. It can be seen from Figures 3a and 3b and Table II that the IrO₂ electrodes prepared at high piezoelectric voltage require less layers but have many micro-scale cracks. The cracks, however, disappear when the printing piezo-voltage is decreased (Figures 3e and 3f). These cracks appear to play a minor role in the electrochemical performance.

**SEM and EDX imaging.**—Figure 4 shows SEM cross-section and surface images of the anode CL of CCM-1-32V-N117. Figures 4a and 4b show very good attachment between the electrode and the membrane. The measured anode electrode thickness is shown in the Table III along with the literature data. Based on the ink composition, loading and electrode thickness, the porosity of the IrO₂ electrode was calculated, as shown in Table III. The porosity of the inkjet printed electrodes is much lower than the 50–60% usually observed on platinum/carbon electrodes in fuel cells and other values reported in literature for electrolyzer electrodes. It is close to the densest regular packing (rhombohedral packing) of uniform spheres i.e., 25.95%.⁴⁰ As the particles are not uniform, the expected porosity can be lower than that of a rhombohedral packing as in the case of CCM printed at 20 V piezo-voltage. The higher porosity of CCMs printed at 32 V and 26 V is likely due to the cracks in the CCMs.

**Figure 5** shows EDX imaging of the CL cross-section. From the image it can be seen that the catalyst and ionomer are distributed evenly in cross-section of the CL. The estimated %mass of fluorine, iridium and oxygen is 4, 79.7 and 16.3 respectively in cross-section by forcing all other elements to be zero. These are in agreement...
with the expected amounts of F, Ir and O assuming IrO₂ catalyst was used and 5%wt Nafion, i.e., 3, 80.3 and 14.2 taking carbon and sulfur into account. This demonstrates the ink mixing and drop-by-drop deposition do not alter the catalyst morphology and can print Nafion well. The homogeneous Nafion distribution is in agreement with STXM results in literature for fuel cell electrodes fabricated by IJP. A Nafion rich layer near the membrane can also be observed from the F-map (Figure 5b).

**Table II. Summary of fabricated CCMs.**

| Name                  | Piezo-voltage (V) | Membrane | No. of Layers | Loading (mg/cm²) | IrO₂ | Pt |
|-----------------------|-------------------|----------|---------------|------------------|------|--|
| CCM-1-32V-N117        | 32                | N117     | 8             | 1.17             | 0.10 |
| CCM-2-32V-N117        | 32                | N117     | 8             | 1.17             | 0.10 |
| CCM-1-26V-N117        | 26                | N117     | 25            | 1.11             | 0.11 |
| CCM-1-20V-N117        | 20                | N117     | 43            | 1.11             | 0.11 |
| CCM-1-32V-N211        | 32                | NRE211   | 8             | 1.17             | 0.10 |
| CCM-1-20V-N211        | 20                | NRE211   | 43            | 1.11             | 0.11 |

**Table III. Comparison of CL thickness for different fabrication methods.**

| Ref. | Fabrication method | Anode catalyst loading (mg/cm²) | CL thickness (µm) | CL Thickness (µm/(mg/cm²)) | Porosity (%) |
|------|--------------------|---------------------------------|-------------------|-----------------------------|--------------|
| 32   | Decal              | 0.4 (IrO₂)                      | 1.1               | 2.75                        | 49           |
| 41   | Spray Decal        | 1.5 (Ru₃Ir₇O₂)                  | 20–30             | 13.3–20                     | 78–86        |
| 42   | Electrodeposition  | 0.1 (IrO₂)                     | 0.5               | 5                           | 72           |
| CCM-1-32V-N117       | Inkjet             | 1.17 (IrO₂)                    | 1.87 ± 0.15       | 1.6                         | 29           |
| CCM-1-26V-N117       | Inkjet             | 1.11 (IrO₂)                    | 1.69 ± 0.14       | 1.52                        | 26           |
| CCM-1-20V-N117       | Inkjet             | 1.11 (IrO₂)                    | 1.38 ± 0.15       | 1.32                        | 10           |

Figure 3. Optical transmission microscope images at magnification of 4 X (a), (c), (e) and 10 X (b), (d), (f).

Figure 4. SEM images of the anode of CCM-1-32V-N117 CL. Cross-section (10k X) (a) and (b), and top surface at 5k X (c) and 50k X (d).

Figure 5. SEM (a), and EDX fluorine (b), iridium (c) and oxygen (d) maps of the catalyst layer cross-section after the electrochemical tests.
Polarization curves.—Electrolyzer performance was measured on the fabricated CCMs. To estimate the reproducibility of the experiment, two cells printed at 32 V piezo-voltage with N-117 membrane were tested. Figures 6a and 6b show that only a small difference exists between the two printed cells, thereby proving the repeatability of the method.

The effect of printing piezo-voltage on the polarization curve is shown in Figures 6c and 6d. From the figures it can be observed that the performance increases slightly with decreasing piezo-voltage. The increased performance might be associated with the change in morphology and crack density observed in the Microscopic imaging section. The increased performance, however, might not be enough to justify the increase in printing time associated with the increase in number of layers. Figure 6e shows the effect of membrane thickness on the cell polarization curve. The thinner membrane offers less ohmic resistance and hence better performance.

Figure 7 shows the comparison of the obtained iR-corrected potential of IJP CCMs at 1 A/cm² with the published iR-corrected potentials at the same current density. It can be observed that the IJP CCMs outperform most of data in the literature. Ref. 28 and Ref. 30 have similar performance to IJP CCMs at similar operating condition and for similar catalyst loading per square centimeter. Only Ref. 31 has better performance with lower catalyst loading than IJP CCMs due to higher cell operating temperature (90°C).

Cyclic voltammetry.—Estimation of electrochemical surface area (ECSA) of iridium oxide electrodes used in electrolysis is challenging because hydrogen underpotential deposition and carbon monoxide oxidation are ineffective, therefore $C_{dl}$ is used in this article as a relative measure of ECSA by assuming that ECSA will scale proportionally to total surface area, as was proposed in a previous study. The voltammetric charge, $q^*$, obtained by integration of the cyclic voltammogram over the whole potential scan range, i.e., from 0.05 V to 1.2 V, has also been assumed to be proportional to $C_{dl}$. Figure 8 shows the...
values between 6-300 mC/cm² for IrO₂/TiO₂ catalyst. Pathiraja et al. reported 67.93 and 102.8 mC/cm² for Ti/IrO₂-SnO₂ catalyst prepared from different Ir metal concentration precursors. Papaderakis et al. reported 103.95 mC/cm² for IrO₂ catalyst with 1 mg/cm² catalyst loading. Alves et al. reported in the range of 50-250 mC/cm² for Ti/IrO₂-TiO(7-9)CeO₂ catalyst.

**Hydrogen crossover.**—In order to study the membrane damage during fabrication, hydrogen crossover tests were carried out. Table IV also shows hydrogen cross-over flux for all the cells. The hydrogen crossover was observed to be inversely proportional to PEM thickness. Membrane permeability was estimated to be between 1.13 × 10⁻¹⁴ to 1.92 × 10⁻¹⁴ mol/(m·Pa·s)⁻¹, in agreement with literature values which are in the range of 0.987 × 10⁻¹⁴ to 1.97 × 10⁻¹⁴ mol/(m·Pa·s)⁻¹. The hydrogen crossover flux was observed to be higher when experiments were carried out with liquid water than fully humidified nitrogen in the case of Nafion N117 membrane CCMs and similar in the case of Nafion NRE211 membrane CCMs. The hydrogen crossover flux of Nafion membranes is expected to increase with membrane water content. Whereas, the water content of Nafion NRE211 membranes is similar for both fully humidified gas and liquid water. The latter was observed by Schalenbach et al. for Nafion N212 at 80°C. In this case, a small change in H₂ permeability, i.e., ~3.5%, was observed when using a fully humidified gas carrying liquid water and a fully humidified gas.

**Kinetic parameters.**—To understand the activity of the catalyst, kinetic studies were carried out. Figure 9 shows the Tafel plot for CCM-1/2-32V-N117 and CCM-1/2-N211 cells. Table V shows the comparison between obtained kinetic parameter for all the IJP CCMs.

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**Table IV. Double layer capacitance, Charge and H₂ cross-over of all CCMs.**

| Name                  | Cₐl (F/cm²) | Charge (q*) (mC/cm²) | J_H₂ × 10⁻¹⁰ (mol/(cm²·s)) |
|-----------------------|-------------|----------------------|----------------------------|
| CCM-1-32V-N117        | 0.0229      | 77.17                | 8.638                      |
| CCM-2-32V-N117        | 0.0187      | 68.61                | 7.902                      |
| CCM-1-26V-N117        | 0.0254      | 86.72                | 9.61                       |
| CCM-1-20V-N117        | 0.0271      | 92.28                | 10.93                      |
| CCM-1-32V-N211        | 0.0178      | 62.41                | 44.97                      |
| CCM-1-20V-N211        | 0.0205      | 77.69                | 58.71                      |
| CCM-2-32V-N211        | 0.0216      | 75.39                | 6.653                      |
| CCM-2-32V-N211        | 0.0151      | 59.61                | 7.851                      |
| CCM-1-26V-N211        | 0.0231      | 82.16                | 7.34                       |
| CCM-1-20V-N211        | 0.0250      | 88.52                | 7.05                       |
| CCM-1-32V-N211        | 0.0198      | 60.98                | 47.54                      |
| CCM-1-20V-N211        |             |                      |                            |

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**Table V. Comparison of obtained kinetic parameters from Tafel plot with literature data.**

| Name                  | i₀ (A/cm²) | b (mV/dec) | i₀ (A/mgIrO₂ catalyst) |
|-----------------------|------------|------------|------------------------|
| From data in Ref. 21a | 2.304 × 10⁻⁸ | 49        | 1.15 × 10⁻⁸            |
| From data in Ref. 22a | 4.778 × 10⁻⁷ | 38        | 2.39 × 10⁻⁷            |
| From data in Ref. 23a | 4.033 × 10⁻⁶ | 51        | 2.02 × 10⁻⁶            |
| From data in Ref. 24a | 6.743 × 10⁻⁶ | 55        | 1.69 × 10⁻⁵            |
| From data in Ref. 28a | 5.521 × 10⁻⁶ | 48        | 1.84 × 10⁻⁵            |
| CCM-1-32V-N117        | 3.67 × 10⁻⁷ | 46.89      | 3.14 × 10⁻⁷            |
| CCM-2-32V-N117        | 7.15 × 10⁻⁷ | 48.88      | 6.11 × 10⁻⁷            |
| CCM-1-26V-N117        | 6.45 × 10⁻⁷ | 46.24      | 5.86 × 10⁻⁷            |
| CCM-1-32V-N211        | 6.98 × 10⁻⁷ | 45.77      | 6.35 × 10⁻⁷            |
| CCM-1-20V-N211        | 5.10 × 10⁻⁷ | 44.79      | 4.36 × 10⁻⁷            |
| CCM-1-20V-N211        | 3.55 × 10⁻⁷ | 44.11      | 3.23 × 10⁻⁷            |

*CCalculated by fitting a Tafel curve to the extracted data from polarization curves below 100 mA/cm² provided in the articles.*
with kinetic parameters calculated from literature data. The obtained Tafel slopes are similar to those in literature. The exchange current density, once normalized to be per gram of IrO₂, appears to be in line with literature data. It is higher than the values obtained in Ref. 21 and 22 but 2-4 times lower than Refs. 23,24 and 28. The low exchange current density observed highlights that the commercial catalyst used might not be very active, which makes the good performance of the IJP electrodes more remarkable.

**Electrochemical impedance spectroscopy.**—EIS tests were performed to study different voltage loss mechanisms. Figure 10 shows EIS results at different operating pressures and the fitted spectra based on the equivalent circuit in Figure 11a which is used to obtain cell resistance ($R_C$), charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$). The figure shows the model to be appropriate for reproducing the experimental data. The absence of a 45° line at high frequency for all the cells indicates that electrode proton transport losses are small in comparison to charge transfer losses.

Using the model and plotting the different parameters versus current density in Figure 11 shows the charge transfer resistance, $R_{ct}$, decreases with increase in current as expected. It is observed that the $R_{ct}$ remained constant irrespective of membrane thickness at a given current i.e., 0.13 Ωcm² at 1 A for all IJP CCMs. The obtained $R_{ct}$ value is in line with the data reported by Siracusano et al. (0.14 Ωcm² at 1.5 V). The values of the double layer capacitance, $C_{dl}$, obtained by CV and EIS are similar at low current, e.g., for CCM-1-32V-N117 0.0229 and 0.0209 F/cm², respectively. At higher current, the value of the $C_{dl}$ decreases. This decrease might be an indication of liquid water being displaced by oxygen bubbles in the electrode. Tests at lower temperature however, where O₂ solubility is higher, did not change the observed trend. Therefore, the reason for the decrease in the double layer capacitance needs further study.

The obtained cell resistance value is proportional to the membrane thickness which is similar to the value reported by Siracusano et al. (0.18 Ω cm², N115) and Su et al. (0.167 Ω cm², N212) but lower than those reported in Ref. 61 (1.53 Ω cm², N117) and 62 (1 Ω cm², N117).

Comparing the values for the different fabricated CCMs shows that $R_C$ and $R_{ct}$ remain constant with decreasing piezo-voltage. The $C_{dl}$ for cell printed at 32 V piezo-voltage is slightly lower as compared to the cells printed at 26 and 20 V, in agreement with CV data.

**Stability test.**—Figure 12 shows the cell potential over 24 hours for electrode CCM-1-32V-N211 at 0.3 and 1 A/cm² along with the data from Ref. 25 and Ref. 28. The degradation rate obtained for CCM-1-32V-N211 cell at 0.3 A/cm² is 1.413 × 10⁻⁴ mV/sec, half that in Ref. 25 (2.833 × 10⁻⁴ mV/sec). At 1 A/cm² the degradation rate is 3.66 × 10⁻⁴ mV/sec compared to 2.174 × 10⁻⁴ mV/sec in Ref. 28. The cell potential is more stable than the data from Ref. 25 where an N112 membrane and 3 mgIrO₂/cm² catalyst loading on the anode side were used.

**Comparison with literature data.**—In order to evaluate the performance of IJP electrodes, Figure 13 compares the obtained polarization curves with published polarization curves from 2010 to 2012 for all catalysts such as Ir, IrO₂, RuO₂, Pt/Ir, IrO₂/SnO₂, and Ru-IrO₂ and a commercial CCM (Ion Power) tested in our laboratory. It can be observed that the obtained polarization curve lies within the published data. However, due to the low kinetic activity of the commercial catalyst and the low IrO₂ loading of the printed CCMs, the kinetic losses are higher than most of the data in the literature. The activity of the
commercial CCM is much better than the IJP CCMs. However, it seems to suffer from mass transfer losses at higher current density.

In order to provide a more meaningful comparison and remove ohmic resistance effects, the potential obtained at a current density of 1 A/cm² and 80 °C is tabulated in Table VI with data from the literature for electrolyzers with similar IrO₂ loading. The IR corrected potentials are obtained using the PEM resistivity value discussed in the previous section (6.67 Ωcm) for all cases. It can be observed that the IJP CCMs performance is similar or better than most of the CCM in the literature with similar loading and catalyst, even though the catalyst activity was shown to be poor (low exchange current density). Only one CCM has a higher performance, however the catalyst loading is twice as high. These results show that IJP can produce CCMs that are competitive with current fabrication techniques.

Conclusions

Electrolyzer CCMs were fabricated using IJP. The anode catalyst layer morphology was analyzed using optical and electron microscopy for surface and thickness characterization. The CL is uniform and well

![Figure 11](image)

**Figure 11.** Parameters evaluated from EIS data fitting to the equivalent circuit shown in (a).

![Figure 12](image)

**Figure 12.** Comparison of stability test at 1 A/cm², Refs. 25 and 28 have loading of 3 mgIrO₂/cm².

![Figure 13](image)

**Figure 13.** Comparison of polarization curves with published data.
Table VI. Summary of PEM water electrolysis described in the literature. The numbers in parenthesis indicate the loading in mg/cm². All data is at 80°C cell temperature.

| Ref. | Fabrication | Method | Anode | Cathode | Membrane | E [V] | E_{IR} [V] |
|------|-------------|--------|-------|---------|----------|-------|-----------|
| 19   | S-Decal     | IrO2 (0.5) | Pt black (0.5) | N115 | 1.78 | 1.695 |
| 20   | S           | IrO2 (2)  | 40%/Pt/CXC72 (2) | N115 | 1.68 | 1.595 |
| 21   | S-Mem       | IrO2 (2)  | 10%/Pt/CXM (0.4) | N115 | 1.65 | 1.565 |
| 22   | S-Mem       | IrO2 (2)  | 20%/Pt/CXKG (0.4) | N115 | 1.65 | 1.565 |
| 23   | S-Mem       | IrO2 (2)  | Pt black (2.5) | N115 | 1.6 | 1.515 |
| 24   | Sputtering  | IrO2 (0.2)| Pt/C | N117 | 1.85 | 1.731 |
| 25   | S-Mem       | IrO2 (3)  | 30%/Pt/CXKG (0.5) | N112 | 1.66 | 1.626 |
| 26   | S-Mem       | IrO2 (1.5)| 30%/Pt/CXKG (0.5) | N1035 | 1.67 | 1.619 |
| 27   | Spray coating| IrO2 (3)  | 30%/Pt/CXKG72 (0.6) | N115 | 1.72 | 1.635 |
| 28   | Spraying    | IrO2 (1)  | Pt/C (0.5) | N212 | 1.625 | 1.591 |
| 29   | S-Mem       | IrO2 (2.5)| 30%/Pt/CXKG (0.5) | N115 | 1.7 | 1.615 |
| 30   | Decal       | IrO2 (1)  | 40%/Pt/CXM (0.2) | N212 | 1.64 | 1.606 |
| 31   | E           | IrO2 (0.1)| 46%/Pt/CXKG (0.4) | N112 | 1.6 | 1.566 |
| 32   | Decal       | IrO2 (0.5)| 46%/Pt/CXKG (0.25) | N115 | 1.72 | 1.635 |
| 62   | Brushing    | Ir (1.5)  | Pt (1) | N112 | 1.69 | 1.656 |
| 63   | S-Mem       | IrO2-Spectrum (5) | 30%/Pt/CXKG (0.8) | N115 | 1.9 | 1.815 |
| 64   | CCM-1/2-32V-N117 | Inkjet | IrO2 (1.17) | 46%/Pt/CXKG (0.1) | N117 | 1.743 | 1.624 |
|      | CCM-1-26V-N117 | Inkjet | IrO2 (1.11) | 46%/Pt/CXKG (0.1) | N117 | 1.73 | 1.611 |
|      | CCM-1-20V-N117 | Inkjet | IrO2 (1.11) | 46%/Pt/CXKG (0.1) | N117 | 1.716 | 1.597 |
|      | CCM-1-32V-N211 | Inkjet | IrO2 (1.17) | 46%/Pt/CXKG (0.1) | N211 | 1.608 | 1.591 |
|      | CCM-1-20V-N211 | Inkjet | IrO2 (1.11) | 46%/Pt/CXKG (0.1) | N211 | 1.615 | 1.598 |

Abbreviations: TKK = Tanaka Corp; JM = Johnson & Matthey; Etek = BASF; S = sprayed catalyst; Mem = membrane; E = Electrodeposition.

adhered to the membrane. EDX imaging showed even distribution of ionomer and catalyst in the CL. Hydrogen crossover, CV, and electrochemical performance tests were also performed. The hydrogen crossover, in line with Nafion membrane permeability measurements, showed that the PEM was not damaged during the CCM fabrication. C_0 obtained from CV and EIS tests are similar at low current densities, but the double layer capacitance measured by EIS appears to decrease with increasing current density. The Tafel slope is similar to literature data while the exchange current density appears to be lower, most likely due to use of the commercial IrO_2 catalyst. The electrolyzer CCMs fabricated with JIP method could generate 1 and 2 A/cm² at potentials of 1609 mV and 1696 mV respectively using a NRE211 membrane. Using Nafion 117 membrane, the same current densities were obtained at 1743 mV and 1977 mV. These results outperform most of the previously reported results in the literature using similar loading and more active catalysts. The CCMs also showed stable performance when tested for 24 hours. These results suggest that inkjet printing can be used to fabricate electrolyzer electrodes with low loading and good performance. JIP might also be an excellent choice for screening new catalysts under MEA conditions. In this study, only 44 mg IrO_2 were needed to produce three 5 cm² CCMs, thereby showing that JIP can be used to produce CCMs with very small amounts of catalyst and with minimal wastage.

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