

Short communication

Inkjet printing of carbon supported platinum 3-D catalyst layers for use in fuel cells[☆]

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Abstract

We present a method of using inkjet printing (IJP) to deposit catalyst materials onto gas diffusion layers (GDLs) that are made into membrane electrode assemblies (MEAs) for polymer electrolyte fuel cell (PEMFC). Existing ink deposition methods such as spray painting or screen printing are not well suited for ultra low ($<0.5 \text{ mg Pt cm}^{-2}$) loadings. The IJP method can be used to deposit smaller volumes of water based catalyst ink solutions with picoliter precision provided the solution properties are compatible with the cartridge design. By optimizing the dispersion of the ink solution we have shown that this technique can be successfully used with catalysts supported on different carbon black (i.e. XC-72R, Monarch 700, Black Pearls 2000, etc.). Our ink jet printed MEAs with catalyst loadings of $0.020 \text{ mg Pt cm}^{-2}$ have shown Pt utilizations in excess of $16,000 \text{ mW mg}^{-1} \text{ Pt}$ which is higher than our traditional screen printed MEAs ($800 \text{ mW mg}^{-1} \text{ Pt}$). As a further demonstration of IJP versatility, we present results of a graded distribution of Pt/C catalyst structure using standard Johnson Matthey (JM) catalyst. Compared to a continuous catalyst layer of JM Pt/C (20% Pt), the graded catalyst structure showed enhanced performance.

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Keywords: PEM fuel cells; Ink jet technology; Catalysts; Membrane electrode assemblies; Pt loading of carbon black

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are rapidly gaining attention as alternatives to current power sources due to their high efficiencies and ability to operate without greenhouse gas emissions [1,2]. One of the obstacles preventing the commercialization of fuel cells is the utilization of noble metals, most often platinum or platinum based alloys, to catalyze the oxidation and reduction reactions [3]. Methods for producing Pt nanoparticles supported on carbon have helped to lower platinum loadings in PEMFCs [4,5]. Although research reduced catalyst loading levels down from 4 to below $0.4 \text{ mg Pt cm}^{-2}$ [4,6], the Pt utilization of typical commercially offered prototype fuel cells remains very low (20–30%) [7]. Thin film deposition such as sputtering have been investigated for catalyst deposition

at ultra low loadings [1,8]. While this method could allow for large scale production, the expenditure is still substantial due to costs associated with clean rooms, Pt targets, and ultra high vacuum equipment. In addition, the Pt deposited is often unsupported and the electrolyte cannot be deposited simultaneously with the Pt limiting the catalyst layer to only two dimensions. In this work, we present the use of inkjet printing (IJP) as a deposition method for creating 3-D catalyst layers onto a GDL for use in a fuel cell.

IJP has emerged as one of the most popular forms of data imaging for home and small office applications and is quickly gaining recognition in a variety of other fields [9,10]. IJP works by placing tiny droplets of ink solution onto a substrate without dependence on the high-speed operation of mechanical printing elements [10]. Because IJP methods are additive (reducing waste and processing steps) they have been evaluated for several multilayer devices including organic transistors, 3-D MEMs, biopolymer arrays, and photonic crystal microarrays [11,12]. Other useful adaptations of IJP include applications in the following: combinatorial materials research, polymer light emitting diode displays, microcircuitry, life sciences, ceramics, and carbon nanotubes [13–21]. For fuel cell applications, this tech-

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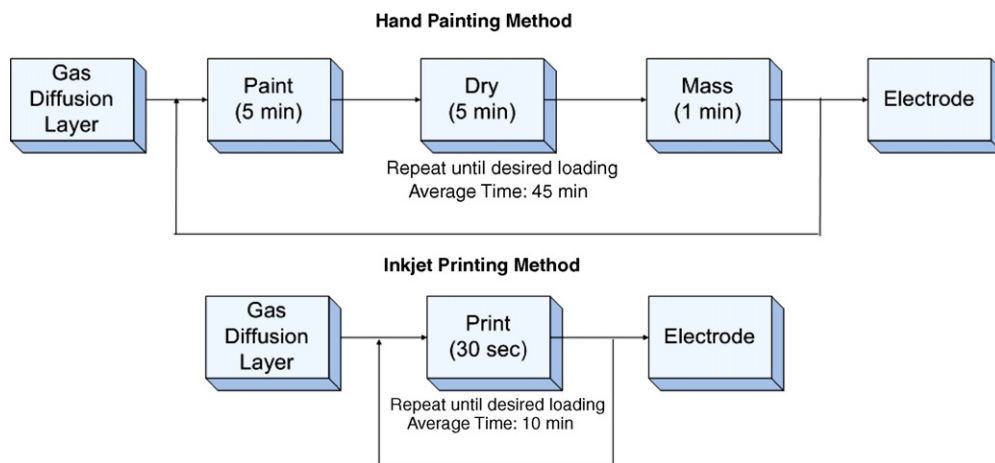


Fig. 1. Time illustration of inkjet printing method compared to hand painting.

nology resolves many of the problems associated with previous methods of catalyst deposition by allowing a uniform distribution of catalyst material onto the surface of the GDL (CCE) or electrolyte CCM (i.e. CCE or CCM catalyst coated electrodes or membranes). With a fixed nozzle volume, each printing delivers precise picoliter control of deposition, which is useful for creating membrane electrode assemblies (MEA) with ultra low ($<0.05 \text{ mg Pt cm}^{-2}$) loadings.

There are several traditional methods of applying the Pt/C electrolyte catalyst layers. Screen printing (similar to brush painting) is a simple and cost effective process involving no apparatus other than a membrane holder (CCM) or paint brush with minimal waste; yet these techniques have several disadvantages. First, the uniformity of catalyst deposited on the electrode is not easily controlled and can vary depending on the person depositing the catalyst material. Second, these processes can be time consuming, requiring iterations of painting, drying, and massing to achieve the desired loading of catalyst. Fig. 1 gives a comparison of how the hand painting process compares to the IJP method. Iterations of the weighing and painting steps, in addition to solvent evaporation or changes in mass uptake of the brush can contribute to poor reproducibility. Spray painting overcomes many of the problems associated with brush painting and allows for a more uniform distribution of catalyst material. It also opens the doors to automation for large scale production; however, a considerable amount of catalyst is often wasted in the feed lines due to periodic clogging which could increase the cost of production.

To produce smooth printings, the ink properties should be taken into account. For example, the ink viscosity must be low enough for each nozzle to expel a droplet of ink. In addition, the size of the particles (usually less than a few hundred nanometers in diameter) and dispersion of the particles should be controlled to prevent clogging of the print nozzles. The ink solution should also have a surface tension large enough to prevent ink from leaking from the nozzles [9]. For fuel cell applications, the controlled blending and deposition of the Pt/C electrolyte catalyst solutions could have a significant impact on the utilization of Pt. This utilization is optimized by allowing the Pt to have simul-

taneous access to the gas, the electron conducting medium, and the proton conducting medium. These interfacial areas, called triple-phase boundaries (gas-electrolyte-electrode), are essential for fuel cell performance [22]. In this article we present a new method of using IJP to deposit 3-D catalyst layer materials for use in PEMFCs. We have evaluated the performance of deposited ultra low loading catalyst layers using standard Johnson Matthey (JM) Pt/C catalyst as well as Pt loaded onto other carbon black materials. To further demonstrate the versatility of using the IJP technique we evaluated the performance of a graded catalyst structure and compared it to a continuous catalyst layer structure.

2. Experimental

2.1. Catalyst preparation

For most experiments we used was a commercially available (JM) 20 wt% Pt on carbon black (HiSPECTM 3000). The additional materials for the graded catalyst were JM 10 wt% (HiSPECTM 2000) and 50 wt% (HiSPECTM 8000) Pt on carbon black. The flexibility of IJP technology facilitated the investigation of using other carbon supports. The following carbon blacks were functionalized in super critical (SC) methanol using platinum (II) acetylacetonate as a precursor: Vulcan XC-72R (Cabot), Monarch 700 (Cabot), Black Pearls 2000 (Cabot), and an experimental carbon black RC2 (Sid-Richardson). For Pt loading a modified procedure similar to that used by Zhenyu et al. was followed [23]. The pellet form of the RC2 was crushed to a fine powder whereas the other carbon supports were used as received. In a 4.1 ml stainless steel reactor, 35.0 mg of carbon black, 17.6 mg of platinum (II) acetylacetonate, and 3.28 ml of methanol were combined. The contents were sealed and placed into a sand bath at 300 °C for 30 min. Under these conditions the MeOH becomes a supercritical fluid capable of reducing the platinum (II) acetylacetonate. The resulting Pt/C catalyst was dried overnight at room temperature. This procedure results in a stoichiometric loading of 20 wt% platinum.

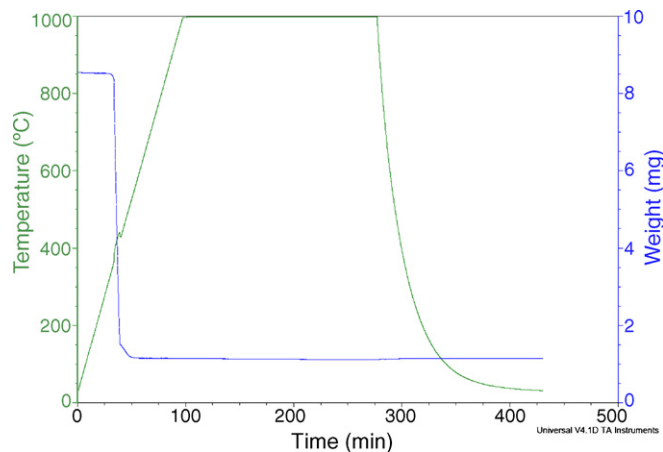


Fig. 2. TGA curves for oxidation of Pt/C composite.

TGA Thermogravimetric Analyzer (Model SDT Q600 Instrument, TA Instruments, Inc.,) analysis was used to determine actual loadings of the prepared catalysts [13]. Experiments were conducted by ramping the sample temperature in air to 1000 °C. Steep reductions in mass were observed around 420 °C where the carbon support was oxidized, leaving the Pt particles behind. At 1000 °C it was assumed that all the carbon support had been removed from the sample and only oxidized Pt particles remained as PtO. Actual catalyst loadings were then calculated based on the beginning mass of the Pt/C nanocomposite and ending mass of the remaining PtO particles [13]. An example of a typical TGA curve is shown in Fig. 2.

Inks for the anode catalyst layers were typically prepared with a ratio of 75 wt% of the Pt/C catalyst and 25 wt% Nafion[®] solution (Aldrich, 5 wt% in lower aliphatic alcohols and water) and dispersed in a suitable solvent mixture with viscosity comparable to HP ink (see Fig. 4). The typical anode solution consisted of 50.3 mg catalyst (JM 20 wt% Pt), 382.9 μ l Nafion[®] solution, and 3.0 ml of methanol. Inks were sonicated for 30 min then stirred with a micro stir bar for an additional 30 min. For all the anode catalyst inks tested, there was no observable settling or agglomeration after several days of observation. For comparison, an anode was fabricated using a hand painting (HP) method, using the standard catalyst dispersed in a mixture of isopropyl alcohol and water. Inks for all cathodes were prepared with 63 wt% Pt/C, 25 wt% Nafion[®], and 12% PTFE (Dupont) dispersed in a 50/50 mixture of isopropyl alcohol and water. The inks were applied by HP at a loading of 0.50 mg Pt cm⁻² for all cathodes.

2.2. Printer setup

A commercially available thermal ink-jet printer (Lexmark Z32) was used in this study. The specifications report a maximum resolution of 1200 dpi \times 1200 dpi and a drop size of 28 pl (<http://www.lexmark.com>). Thermal inkjet printers are preferred over piezoelectric inkjet printers as they contain larger nozzle volumes, reducing the chance for clogging. Standard black ink cartridges (Lexmark 17G0050) were used to print the catalyst inks. After emptying, the cartridges were cleaned in a sonication bath for 30 min. The catalyst inks were then placed inside

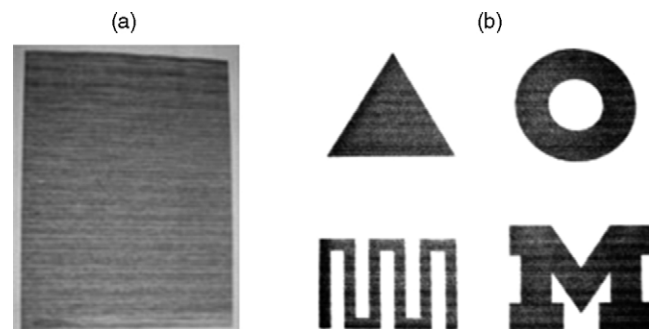


Fig. 3. Illustration of successfully printed catalyst layers using the IJP method (a and b).

the ink well and the cartridge was loaded into the printer. The Pt loading was calculated from the density of the ink, weight percent of platinum Pt supported carbon, the printer resolution, and the volume of each droplet. The loadings were calculated assuming that none of the nozzles were clogged.

Carbon cloth (Toray) was cut into 1" \times 1" squares for use as GDLs. The squares were attached to standard 8.5" \times 11" white paper using double sided tape. A black square of catalyst ink was printed onto the GDL using the "best print quality" feature on the printer settings to achieve the best resolution the printer offers. To ensure that the catalyst ink was printing, a small square was printed elsewhere on the paper. The paper containing the GDL was then reloaded into the paper tray and the printing process was repeated until the desired loading was achieved. Fig. 3a illustrates the successful printing of catalyst onto a full 8.5" \times 11" sheet of paper which could be scaled for larger industrial applications. Fig. 3b illustrates how catalyst deposition can be controlled to specific shapes and areas with an enclosed structure, serpentine channels, and a block letter M. Successful qualitative printings were also performed directly onto Toray carbon paper as well as Nafion[®] 117.

2.3. MEA preparation

All gas diffusion layers used in this study were from E-Tek (ELAT V3.1 double side automated). All electrodes fabricated by IJP or screen printing were placed in an oven for final bake out at 180 °C for 1 h to dry any residual solvent. Nafion[®] 117 (Ion Power) films were cleaned using the following procedure: to remove organic impurities and to obtain the H⁺ form for use in the PEMFC, the membranes were pretreated by boiling in 50 vol% HNO₃ and deionized water for 1 h, rinsing in boiling deionized water for 30 min, boiling in 0.5 M H₂SO₄ solution for 30 min, and boiling twice in DI water for 30 min. The membranes were subsequently stored in DI water until ready for use. The MEAs were made by hot pressing an anode, electrolyte membrane, and cathode in a heated press set at 135 °C for 5 min at a pressure of 10 MPa. The MEAs were conditioned over night until a steady state current was achieved at a potential of 0.6 V. The temperature of the fuel cell was 80 °C and the anode and cathode saturators were set at 90 °C (100% relative humidity). The flow rates of the humidified hydrogen and oxygen were set at 100 sccm.

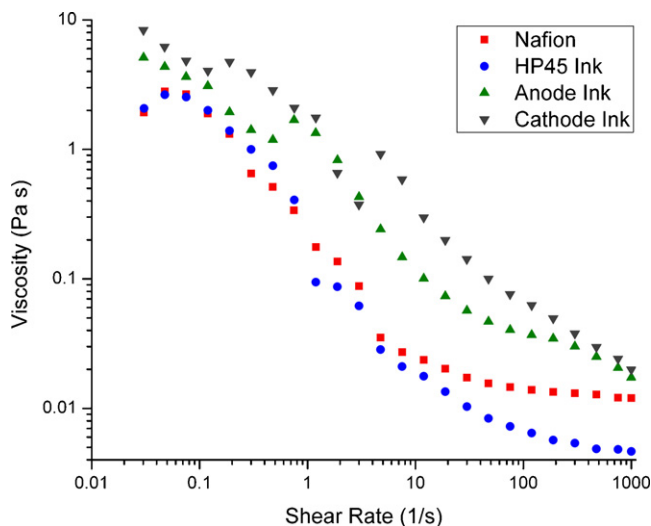


Fig. 4. Viscosity as a function of shear rate for standard catalysts and inkjet solutions.

3. Results and discussion

3.1. Inkjet printed anode using standard JM catalysts

To confirm that the ink properties of the catalyst ink were suitable for use in IJP, viscosities of catalyst inks were compared to standard black printer ink (HP45) manufactured by Hewlett Packard. A constant stress rheometer (TA Instruments AR1000) was used to measure the viscosity at a give shear rate. As Fig. 4 shows, the viscosity of the standard anode and cathode inks follow a similar trend as the HP45 and Nafion[®] (5%) solution. At the highest shear rate, the viscosity of the HP45 ink was approximately an order of magnitude less than the anode, cathode, and Nafion[®] solution. The shear rate for the printer used is $1.4 \times 10^5 \text{ s}^{-1}$. Although the shear cell could only measure viscosities at a shear rate of 1000 s^{-1} the results were encouraging that suitable dispersions containing the right compounds can be successfully used for IJP.

Two anode catalyst layers were prepared from standard JM Pt/C (20 wt% Pt) using HP and IJP deposition methods. The loading for both electrodes was $0.51 \text{ mg Pt cm}^{-2}$ and both MEAs were tested in a fuel cell test station. Fig. 5 shows the resulting polarization curves. The HP MEA had a peak power density of 387 mW cm^{-2} which is slightly less than the IJP MEA which was 426 mW cm^{-2} . Based upon the loadings, catalyst utilizations for the HP and IJP were 774 and $852 \text{ mW mg}^{-1} \text{ Pt}$, respectively. The difference between these values is within 10%, hence we do not claim that using IJP printing improves a given catalyst layer.

Fig. 6 illustrates how the Pt utilization changes as the loading of the catalyst layer decreases. At a loading of $0.138 \text{ mg Pt cm}^{-2}$ the HP method gave a slightly better Pt utilization with an average Pt utilization of $2500 \text{ mW mg}^{-1} \text{ Pt}$. The clear advantage of IJP is shown at an ultra low catalyst loading of $0.021 \text{ mg Pt cm}^{-2}$. Using HP for such a low loading was not practical (using a standard catalyst solution), as achieving uniformity of catalyst deposition was very difficult as was reaching the correct catalyst

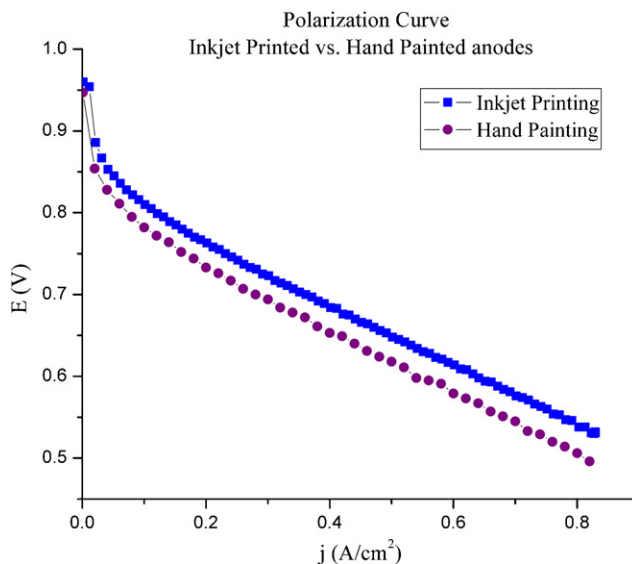


Fig. 5. Illustration of IJP vs. HP both anode loading of $0.51 \text{ mg Pt cm}^{-2}$.

loading without over loading. The IJP technique at this loading gave a reproducible Pt utilization of $17,600 \text{ mW mg}^{-1} \text{ Pt}$. To the best of our knowledge, this is one of the highest values reported in the literature. The dispersion of this ink was made to give this final loading after four complete passes. Hence, it is conceivable that this ultra low loading can be reduced even lower. One possible explanation for the higher platinum utilizations at lower loadings is the higher probability of regions where catalyst, carbon support, and electrolyte come in contact. Known as the triple phase boundary, only the platinum that lies in this region can be utilized. As the thickness of the catalyst layer decreases, typical discontinuities in the catalyst region statistically diminish. This leaves a larger amount of platinum within the triple phase boundary available for reaction.

3.2. Inkjet printed anodes using various carbon supported catalysts

Fig. 7 illustrates results for carbon supported catalysts that were functionalized with Pt using SC MeOH and IJP as anode catalyst layers: XC-72 R (Cabot), Monarch 700 (Cabot), RC2

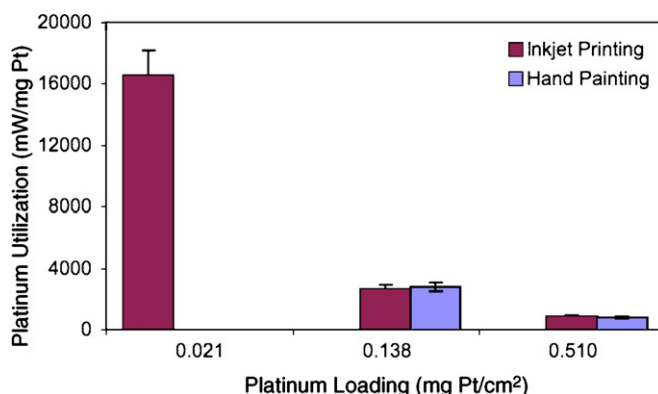


Fig. 6. JM standard IJP catalyst loading vs. Pt utilization.

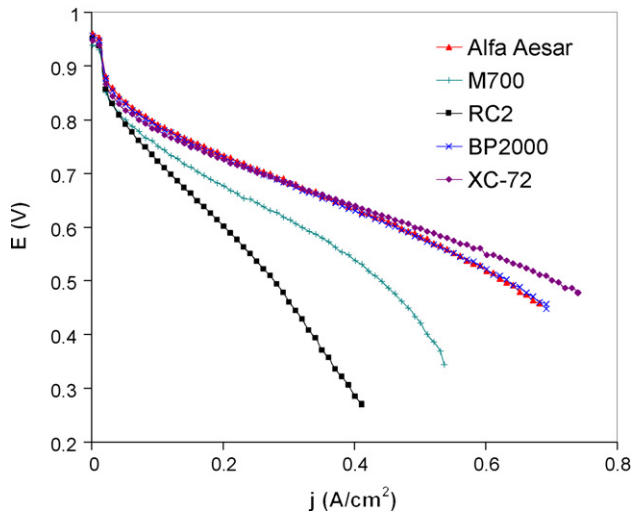


Fig. 7. Illustration of various IJP Pt supported carbons.

Table 1

Carbon support	Particle size (nm)	Surface area (m ² g ⁻¹)
Johnson Matthey	30	254
XC-72	30	254
M700	18	200
Ketjenblack	36	1400
RC2	Pellets	115
Black Pearls 2000	12	1500

(Sid Richardson), and Black Pearls 2000 (Cabot). Table 1 lists the material properties of some typical carbon supports as reported in literature or by the supplier [2]. A range of Pt loadings (10–50 wt%) was used to illustrate the flexibility of IJP. Table 2 illustrates the loading and Pt utilizations of the various supports in comparison to the JM (Alfa Aesar) standard catalyst. From these early results, it appears that BP 2000 is a promising support worthy of further investigation. More solid conclusions regarding the support are beyond the scope of this paper, however significant work has previously been reported by Uchida et al. [24]. Here they claim that Pt must be supported on the outer side of the agglomerate and that the primary pore volume should be increased to allow sufficient contact with the ionomer. From this effort we demonstrate that IJP can be used to deposit a variety of different carbon supports with different material properties (i.e. particle size, surface area, conductivity, etc.).

Table 2

Catalyst	Pt%	Loading (mg Pt cm ⁻²)	Pt utilization (mW mg ⁻¹ Pt)
JM	20	0.121	2608
M700	35	0.073	3017
RC2	11.7	0.07	1990
BP2000	15.4	0.093	3418
XC-72	47	0.133	2673

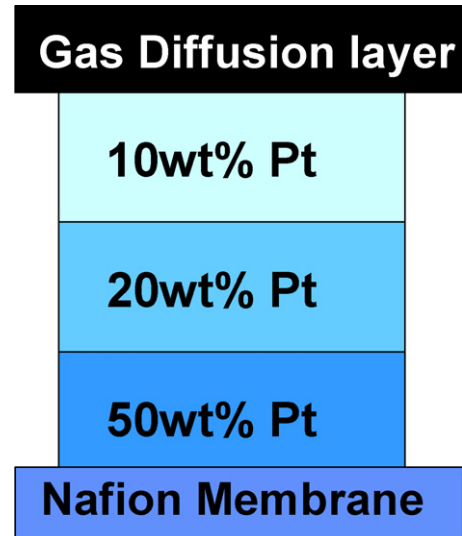


Fig. 8. Illustration of catalyst layer graded structure.

3.3. Graded catalyst deposition

Previous research on thin film catalysts suggests that platinum is better utilized when it is concentrated near either the electrode catalyst layer or electrolyte catalyst layer interface [2]. Using IJP, we were able to deposit catalysts of different Pt concentrations layer by layer such that the region closest to the electrolyte membrane had the highest concentration of Pt while the region furthest away had the lowest concentration, as shown in Fig. 8. Standard JM catalysts (10, 20, and 50% Pt on carbon black) were used in these experiments. The uniform catalyst structure contained 20% Pt on carbon black. As illustrated in Fig. 9, the graded catalyst structure performed better than the uniformly distributed catalyst at nearly the same overall platinum loading. Other gradients in the catalyst layer have been shown to improve performance. For example, a graded Nafion[®] structure was demonstrated by Wang et al. [25,26]. From this work, a Nafion[®] wt% gradient of 20–40% of the subcatalyst layers was shown to perform better than a standard 30% uniform distribution.

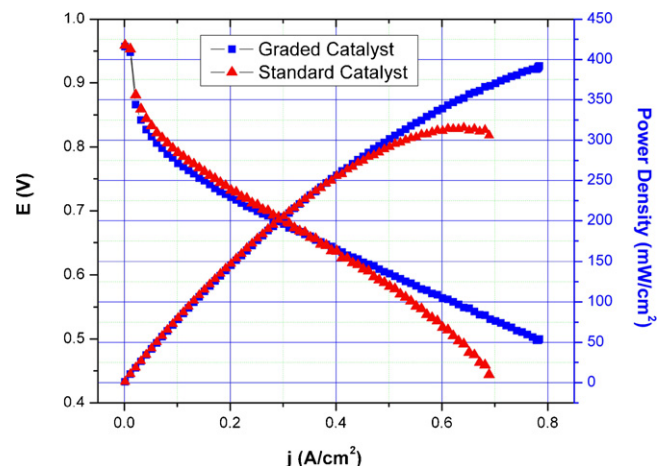


Fig. 9. Performance comparison of a standard uniform catalyst to a graded catalyst.

Significantly increasing the Nafion[®] content of the catalyst layer using IJP is not a trivial task. Although the radius of gyration of Nafion[®] is significantly small [27] compared to the nozzle opening, the presence of the polyelectrolyte in the dispersion can increase particle agglomeration. We have also investigated printing solutions similar to our conventional cathode ink solution. Dispersions with Teflon did not print very well. Investigations into printing Teflon solutions or other hydrophobic materials suitable for the cathode are presently being explored.

4. Conclusion

Inkjet printing has successfully been demonstrated as a catalyst application method for PEMFCs. To the best of our knowledge this is the first time a study such as this has been reported in the literature. The resulting anodes gave comparable, if not better performance than those fabricated using conventional screen printing or hand painting methods. The high precision of IJP allows for controlled catalyst deposition, especially for ultra low platinum loadings. These low loadings, which are not easily attained using conventional methods, give some of the highest platinum utilizations reported in the literature.

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