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Analysis of Low Platinum Loading Thin Polymer Electrolyte Fuel Cell Electrodes Prepared by Inkjet Printing

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ABSTRACT

Thin, low Platinum loading polymer electrolyte fuel cell (PEFC) electrodes fabricated by inkjet printing are investigated. Catalyst coated membranes (CCMs) with Pt loading of 0.026 mg_{Pt}/cm^2, catalyst layer thickness between 1.5 and 2 μm and varying Nafion loadings (NL) on the cathode electrodes of 10, 20, 30, 40 and 50 wt% are analyzed. Ex-situ scanning electron microscopy (SEM) visualization shows that the layers are porous and composed of Pt/C aggregates binded by ionomer. In-situ electrochemical testing shows that the Tafel slope of these electrodes is relatively large, i.e., 120 mV/dec. Further, at 80 °C and varying relative humidities, the CCMs are not sensitive to Nafion loading changes within the 20 wt% - 40 wt% range. Proton transport limitations are only observed at low NL of 10 wt% while transport losses are only observed at high currents for CCM with 50 wt% NL. Comparing conventional and thin, low loading, inkjet printed electrodes, the inkjet printed electrodes show a much higher sensitivity to oxygen partial pressures. These results suggest that macro-scale oxygen and proton transport are not limiting the electrode at the 20 wt% - 40 wt% Nafion range. Pt mass activity for the inkjet CCM at ambient pressure was observed to be 196 A/mg_{Pt} (12.4 kW g_{Pt}^{-1}), i.e., 10 times higher than a spray coated CCM, due to its reduced CL thickness and thereby reduced transport losses in the macro-scale. The Pt utilization at 2 bar gauge pressure is 47.6 kW g_{Pt}^{-1} and represents one of the highest utilization values reported for low Pt loading electrodes.

1. Introduction

Polymer electrolyte fuel cells are considered an alternative to the internal combustion engine for powering future automobiles owing to their high efficiency, quick start-up capabilities and capacity to operate without producing greenhouse-gas emissions when fueled with hydrogen [1]. Improvements in catalyst and electrode fabrication technologies have resulted in a drop of Pt loading from 28 mg_{Pt}/cm^2 in the 1960s to less than 0.2 mg_{Pt}/cm^2 today [2]. Despite this remarkable progress, Pt electrodes still contribute significantly to the overall cost of the system. A recent study on the cost breakdown of a PEFC stack showed that 34% of its total cost is attributed to the catalyst [3]. Thus, a reduction of Pt loading in the CCMs without any loss in performance and durability is essential to make this technology a viable energy source.

Low loading electrodes have been the subject of several recent studies [4–16]. Greszler et al. [4] fabricated low loading electrodes by using a mixture of catalysed and non-catalysed carbon black particles in order to keep electrode thickness, and thereby transport properties, similar to that of conventional electrodes while reducing the Pt loading. Sputtering of a high-active area substrate is used in nanostructured thin film (NSTF) electrodes to fabricate electrodes with low loading, high active area and a thickness of 0.2 - 0.6 μm [5]. Due to the reduced thickness and lack of ionomer in the CL, Debe [5] reports a higher dependence of cell performance on operating conditions. Further, the layers are prone to flooding during wet operating conditions especially at low temperature [5]. Electrospraying has also been used to fabricate low Pt loading electrodes with loading as low as 0.02 mg/cm^2 [14,15]. In this case, the CL produced are very porous with thickness of 50 μm or greater [14,15]. Millington et al. [16] report using ultrasonic-spray method for fabricating gas diffusion electrodes (GDEs) with Pt loading in the range of 0.4 - 0.05 mg/cm^2. Although an exact value was not reported due to the non-distinguishable boundary between CL and

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micro-porous layer, the coating thickness was estimated to be from 200 nm to 50 μm [16]. Catalyst layer performance is determined by proton and gas transport. Reducing the thickness of the catalyst layer could result in a model electrode that is mainly limited by micro-scale losses at the catalyst/electrolyte interface and the catalyst activity. Studies of thin, low loading electrodes of the order of one micron in thickness, and with Nafion inside the layer, have seldom been reported. The aim of this article is to fabricate and study such electrodes and to assess their sensitivity to proton and oxygen transport.

Catalyst layer performance usually depends on the catalyst layer composition and fabrication method. Nafion ionomer is normally added to the CL to facilitate proton transfer. The effect of ionomer loading in the CL on cell performance has been examined for conventional electrodes, i.e., electrodes with carbon and Nafion and a thickness of 10 - 20 μm [17–29]. In this case, an optimal Nafion loading usually exists such that a good trade-off exists between gas and proton transport. The lack of an optimal value would indicate that neither of these processes are limiting the electrode performance and that the performance is limited by either kinetic or micro-scale losses at catalyst-electrolyte or gas-electrolyte interfaces. For the conventionally fabricated CLs, the optimal NL has been found to be between 30 - 36 wt%. Lee et al.[17] state that the optimal Nafion loading changes with oxygen concentration. Sasikumar et al. [23,24] found that the optimal NL increases with decreasing Pt loading. They reported the optimal NL to be 20, 40 and 50 wt% for CLs with a Pt loading of 0.5, 0.25 and 0.1 mg/cm^2 respectively. In thin, low loading electrodes, macro-scale proton and oxygen transport losses should be minimized and therefore, it is hypothesized that a lower sensitivity to ionomer loading should be observed if the electrodes were kinetically limited. The impact of Nafion loading on the transport and cell performance of CCMs with thin, low loading electrodes has however not been reported.

Recent studies on low Pt loading electrodes have found a surprisingly high local oxygen transport resistance whose source is still unknown [11,4,30]. It is speculated that this resistance may arise from the thin ionomer film around the catalyst particles and there may be a non-linear relationship between the film thickness and its resistance [30,4]. A study of the effect of ionomer loading on thin, low Pt loading electrodes could help in assessing the impact of micro-scale proton and oxygen transport by reducing macro-scale transport losses associated with the length scales of conventional electrodes thereby highlighting the effect of the thin ionomer films.

Conventional fabrication methods make use of a dispersion of carbon supported catalyst and ionomer that is applied over the substrate by means of brush painting, doctor blade deposition, or spraying; whereas the ultra-thin deposition methods such as sputtering or ion-beam assisted deposition directly deposit the catalyst metal over the substrate [6]. While the operating cost and equipment for conventional fabrication methods are cheaper than the ultra-thin deposition method, CL thickness and Pt loading is relatively greater. Conventional ink-based fabrication methods do not provide sufficient control regarding CL uniformity and spatial deposition of catalyst to accurately fabricate thin, low platinum loading electrodes and high resolution functionally graded layers.

In this article, inkjet printing is used to fabricate the thin, low loading electrodes under study. Application of inkjet printers for CCM fabrication has seen a slow progress since its initiation in 2007 [6,31–36]. This type of fabrication method does not have the usual drawbacks of conventional or ultra-thin deposition methods. Drop-on-demand technology means that the transfer losses are significantly reduced with respect to spraying; and the flexibility of controlling the Nafion and Pt loading distribution in the CL is much higher than that with other methods. Further, the controlled deposition provided by inkjet printing readily permits the fabrication of thin, low-loading electrodes and functionally-graded layers. Also, because of its higher reproducibility and ability to use multiple cartridges with different ink compositions, this technology can be easily applied to perform ink composition studies such as the one reported in this article for different Nafion loadings and can be used for large scale commercial fabrication processes as it does not lose its adaptability and versatility when scaled up [32,6]. In our previous work [33], we have shown that under ideal conditions, these low Pt loading inkjet printed electrodes can reach a current density of upto 5 A/cm^2 without any observable transport losses at high overpotentials. Recently, Saha et al. [34] showed that inkjet printed CLs had a more homogeneous distribution of carbon support and ionomer as compared to decal-transferred CLs. Therefore, inkjet printing has the potential to provide a reliable method for fabricating ultra-thin and functionally-graded catalyst layers.

In this article, thin, low-Platinum loading electrodes fabricated by inkjet printing are investigated ex-situ via SEM and then, in-situ using cyclic voltammetry, impedance spectroscopy and performance data at different operating conditions in order to elucidate the sensitivity of these electrodes to operating conditions and ionomer loading. These results are used to investigate the limiting process for this type of electrodes, i.e., transport or kinetic processes.

2. Experimental setup

2.1. Ink formulation

The catalyst ink preparation was done using a similar procedure to that presented by Saha et al. [6]. 37.5 mg of 20 wt% Pt on Vulcan XC carbon black (Alfa-Aesar) was mixed with 1.8 to 2.5 g of isopropanol (IPA), 0.5 g of glycerol (Fisher Scientific) and desired amounts of 5 wt% Nafion ionomer (Ion Power Inc.) depending upon the required NL in the CCM. The amount of ionomer to be added was calculated using the following relation

$$Y_{el} = \frac{m_N}{m_N + m_{Pt/C}} \quad (1)$$

where Y_{el} is the NL in the electrodes, m_N is the amount of solid Nafion to be added and $m_{Pt/C}$ is the amount of catalyst added. Addition of glycerol to the ink helps to increase its viscosity and facilitate proper jetting during the fabrication process. In order to maintain a fixed ink volume irrespective of the NL, the IPA volume was altered to account for the changing amounts of ionomer solution required to achieve different Nafion loadings. The Nafion ionomer was added drop-wise to the ink while it was being sonicated in a water bath (Branson 1800) having an output frequency of 40 kHz, at room temperature since such a technique has been known to improve the cell performance [37]. Once Pt/C, ionomer and dispersion media were mixed, the ink was placed in a water-bath and treated using a probe sonicator (QSonica S-4000) at frequency of 20 kHz for 15 minutes at an amplitude of 20% to break up the aggregates and homogenize the suspension. A water-bath helped to maintain the ink temperature constant during the ultrasonic treatment since a temperature rise in the catalyst ink may reduce the process efficiency as reported by Pollet [38].

2.2. Electrode fabrication

A commercially available piezo-electric printer (Dimatix 2800, Fujifilm Inc.) consisting of programmable piezo-voltages for individual nozzles was used for CCM fabrication of both the anode and cathode electrodes. A pressure pulse is induced inside the ink-cavity by means of a mechanical actuator made of piezoelectric material. A rapid change in volume inside the cavity forces the ink to jet through the nozzle and draw more ink from the reservoir [39].