Challenges facing thermal and electrical conductivity measurements in catalyst layers of PEM fuel cells (125)

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This paper presents an overview of an ongoing research project on heat and electron conduction phenomena in catalyst layers (CLs) of PEM fuel cells (PEMFCs). New accurate procedures are proposed for measuring through-plane thermal, in-plane electrical, and through-plane electrical conductivities. CLs were coated on Al for through-plane thermal and electrical conductivity measurements and on ethylene tetrafluoroethylene (ETFE) for in-plane electrical conductivity measurements. Microstructure of the CLs was studied and modeled, and analytical closed-form expressions were derived for the conductivities. Coating a uniform CL thickness, measuring the CL thickness, assessing resemblance of the coated CLs to real-life CLs, removing the systematic errors in the measurements, and accounting for nanoscale effects in the models were some of the challenges tackled and resolved in this project. Recent challenges, which are still under investigation by the authors, are explaining the three orders of magnitude difference between the measured in-plane and through-plane electrical conductivities and including the effects of hydration as well as different CL compositions.

Introduction

Operation of PEMFCs relies on the electrochemical reaction between hydrogen and oxygen producing electricity, water, and heat. This chemical reaction is split into two half-reactions happening inside two microporous CLs that are part of a membrane electrode assembly (MEA). The exothermic nature of the total reaction and conduction of the resultant electricity through the MEA could induce significant local temperature variations which could negatively impact both performance and longevity of the PEMFCs during normal and special operating conditions like freeze-start and warm-up. Accordingly, performance and degradation of PEMFCs are closely linked to thermal and electrical properties of the MEA components. Among the different components, CLs with thicknesses of ~2-8 μm could be regarded as the hotbed of performance and degradation issues due to occurrence of most of the heat and all the electricity generation inside them, yet their thermal and electrical properties have not been studied in-depth due to several challenges in their measurement and modeling. In this work, CL sample preparation, measurement procedures, and new analytical models are developed to obtain an in-depth understanding of heat and electron conduction inside the CLs; further, the underlying microstructure is studied in-depth. The work has been performed collaboratively by Laboratory for Alternative Energy Conversion (LAEC) at Simon Fraser University (SFU) and Automotive Fuel Cell Cooperation (AFCC).

Sample preparation

Three different CL coating methods were evaluated. Two devices for CL printing (Fujifilm and Microfab Inkjet printers) yielded nonuniform thicknesses at a low yield rate and, therefore, were deemed unsuitable. A Mayer bar coater was chosen for CL sample preparation, as it produced highly uniform CLs at a high yield rate.

Thickness measurements

Several methods were examined for measurement of CL thickness, including: i) scanning electron microscopy (SEM) of cross sections of samples embedded in epoxy, ii) SEM imaging of samples freeze-fractured in liquid nitrogen, and iii) using the difference between the weights of CLs in water and air. Overall, the method of epoxy embedding and polishing the cross section using a lapping machine was inferior to the other methods due to smearing the sample cross section.

Study of microstructure

CLs were coated on Al and ETFE substrates using a Mayer bar coater. Effects of substrate type, hot-pressing, and areal Pt loading on different microstructural properties of the CLs were studied to ensure that the measured CLs were true representatives of CLs in real-life fuel cells. The studied microstructural properties are shown in the schematic of Figure 1. A comprehensive investigation established that the studied microstructural properties of the CLs (thickness normalized by the areal Pt loading, porosity, pore size distribution, surface roughness, and crack density) were not altered by hot-pressing, substrate type, and areal Pt loading.

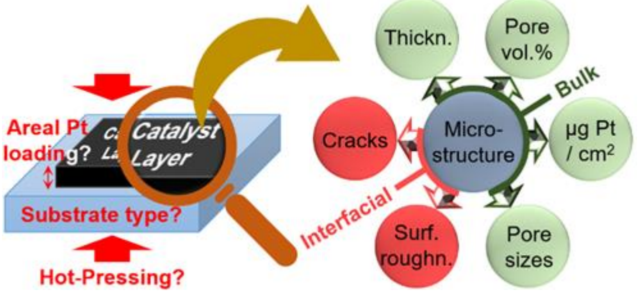

Figure 1. Study of CL microstructure.

Thermal conductivity measurements

Measurements of through-plane thermal conductivity were performed using a custom-made guarded heat flow (GHF) device, as per ASTM Standard E1530-11 [1], and 2) transient method using a modified transient plane source (TPS) method for thin films on a hot disk TPS2500S Thermal Constants Analyser (Hot Disk AB, Gothenburg, Sweden and ThermTest Inc., Fredericton, Canada) [2]. CLs coated on ETFE showed high noise to signal ratio, especially for measurements by the GHF testbed, as opposed to the CLs coated on Al. Moreover, simply clamping a sample in the testbeds turned out to be detrimental to the fragile CLs. Accordingly, samples were coated on Al for the measurements, and a special stacking method was used for mounting the samples inside the testbeds which could protect the fragile CLs and could also enhance the signal to noise ratio. For a specific CL, through-plane values of 0.214 ± 0.005 and 0.218 ± 0.005 $W \cdot m^{-1} \cdot K^{-1}$ were measured by GHF and TPS, respectively. Moreover, despite increasing mechanical pressure whose effect was insignificant, increasing temperature showed a significant increasing effect on the thermal conductivity.

Electrical conductivity measurements

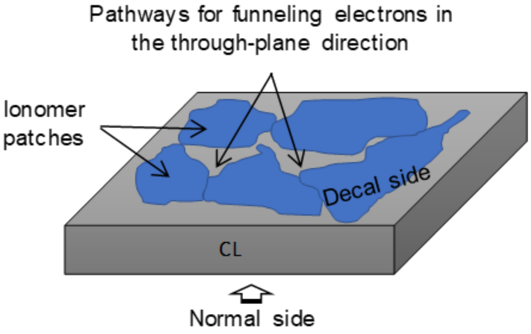

Figure 2. Suggested structure for a fresh CL.

Electrical conductivity measurements were performed using a Micro Junior 2 micro ohmmeter (Raytech, USA). Difficulty arose when through-plane electrical conductivity measurements of a CL (on Al) were performed using the stacking method developed for through-plane thermal conductivity measurements; results were not repeatable, not even for bare Al samples, due to poor conformance of the contacting surfaces. This difficulty was resolved using gas diffusion layers (GDLs) between the stacks. Electrical resistance of the GDLs were found to be orders of magnitude smaller than the CLs, and the GDLs easily deformed under clamping pressure to enhance conformance between the contacting surfaces. Measurements of a CL showed a significant increase in the through-plane electrical conductivity with increasing the mechanical pressure. However, no significant effect on the through-plane electrical conductivity was measured by increasing the temperature. Furthermore, in-plane measurements of the same CL showed three orders of magnitude difference compared to the through-plane value, indicating anisotropic electrical properties and perhaps morphology, which was not consistent with other reports in the literature. Specifically, the through-plane and in-plane values of 0.11 ± 0.01 $S \cdot m^{-1}$ and 173 ± 20 $S \cdot m^{-1}$ were measured, respectively. One potential justification for this anisotropic behavior is that there may be ionomer patches on the decal side of fresh CLs, as shown in Figure 2, which could hinder the flow of electrons in the through-plane direction. This assumption was backed up by observing that the decal side of a CL peeled off from an ETFE substrate, by a tape, was much shinier than its normal side. To determine if there is a greater concentration of ionomer on the decal side surface, further investigation is underway, e.g. using more direct methods like x-ray photoelectron spectroscopy (XPS) to compare the ionomer contents of the normal side and the decal side.

Modeling the geometry and conductivities

Modeling was performed using fundamental laws of heat and electron transfer (diffusion) and contact mechanics. Geometry of the CLs was modeled by building upon the agglomerate models in literature to address some of the shortcomings of those models, and the geometrical model was analytically solved for thermal and electrical conductivities using a multi-scale unit cell approach (effective medium theory), considering four scales for: i) agglomerate clusters, ii) agglomerates, iii) set of carbon particles inside the agglomerates, and iv) structure of a single carbon particle. Challenges arose for dealing with Pt particles supported on carbon particles and for considering nanoscale effects for modeling a single carbon particle due to failure of simple macroscale models in nanoscale. It was found that Pt particles could be neglected in all aspects of modeling except for finding the porosity of the geometrical model. Further, surface forces between the carbon particles were considered to account for finite contact between the particles at zero contact pressure, and a mixed diffusion-ballistic transport model was considered to account for ballistic transport of phonons and electrons in nanoscale, which turned out to be the dominant effect compared to diffusion.

References

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