# Electrical conductivity of PEM fuel cell catalyst layers: Throughplane vs. in-plane (124)

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In this study, new accurate procedures are proposed for measuring in-plane and through-plane electrical conductivities of PEM fuel cell catalyst layers (CLs) to alleviate the previously reported high noise to signal ratio in the literature. CLs are coated on ethylene tetrafluoroethylene (ETFE) substrates for in-plane measurements and aluminum (Al) substrates for through-plane measurements. DC measurements of electrical resistance are performed using an off-the-shelf testbed, connected to custom designed through-plane probes and in-plane sample holder for respective measurements. Through-plane measurements of a CL, performed for the first time in this study, show three orders of magnitude difference compared to in-plane values. Specifically, a value of  $0.11 \pm 0.01 \, \mathrm{S} \cdot \mathrm{m}^{-1}$  was measured for the through-plane direction, while measurements in the in-plane direction on a fresh sample yielded a value of  $173 \pm 20 \, \mathrm{S} \cdot \mathrm{m}^{-1}$ . The measured data along with other observations indicate the existence of a discontinuous thin film of ionomer (or ionomer patches) near the decal side of fresh CLs.

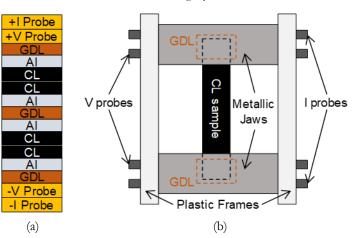
#### Introduction

Power generation in PEM fuel cells (or in short PEMFCs) happens by combining hydrogen and oxygen through two half reactions occurring inside two respective catalyst layers (CLs), which are microporous materials and a part of a membrane electrode assembly (MEA). The final electrochemical reaction between hydrogen and oxygen in a PEMFC is exothermic, directly affecting the performance and degradation of the PEMFCs by affecting local temperature variations inside its MEA. A considerable amount of Joule heating also occurs in the MEA components, including the CLs where all the electron generation happens. Accordingly, knowledge of electrical conductivity of CLs is needed for performance and degradation analysis/optimization of PEMFCs, yet it has not been studied in-depth due to the many challenges in its measurement for thin CLs (~2-8 µm thick). Specifically, the current literature lacks systematic measurement procedures for effective deconvolution of the signal from the bulk of a CL from its substrate/interfaces as well as for effective deconvolution (or separate measurements) of through-plane and in-plane values; the reported values are effective values (combinations of in-plane and through plane values) and have up to two orders of magnitude difference [1-4]. Accordingly, the focus of this work is on developing new procedures for separate measurements of in-plane and through-plane electrical conductivities of CLs.

## Measurement procedures

Measurements are performed by a Micro Junior 2 micro ohmmeter (Raytech, USA). The ohmmeter measures the electrical resistance of a sample in a four-probe configuration by passing a DC current through the sample. As shown in Figure 1 (a), to measure the through-plane electrical resistance of CLs coated on Al substrates, the samples are cut into circular pieces by a punch, and the pieces are stacked and clamped between four custom-made gold-plated probes attached to corresponding current and voltage leads of the ohmmeter. Gas diffusion layers (GDLs) between the stacks compensate for out-of-flatness of the sample and probe surfaces which otherwise cause highly variable electrical contact

resistances (ECRs). For measuring the in-plane electrical resistance of a CL coated on ETFE substrate, the sample is cut into a strip and clamped inside a custom-made in-plane sample holder, shown in Figure 1 (b), and connected to the current and voltage leads of the ohmmeter in a four-probe configuration. For inplane measurements, GDLs are used between the clamps and the sample to reduce the ECRs and to protect the CL surfaces. GDLs have a significantly lower resistance than the CLs in both through-plane and in-plane measurements; therefore, the measured total resistance of a sample can be expressed as a summation of the bulk resistance of the CL in the stack/sample and the ECRs present in measurements. Accordingly, measurements for at least thicknesses (in case of through-plane measurements) or lengths (in case of in-plane



**Figure 1.** Schematics for (a) through-plane and (b) in-plane measurements.

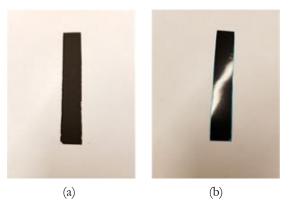
measurements) of the sample should be conducted to effectively deconvolute the signal from the bulk of the CL from the ECRs.

### Results and discussion

Measurements of a CL with ionomer-to-carbon (I/C) weight (wt) ratio of 0.9 and 50 wt% Pt in Pt/C catalyst (carbon-supported platinum) yielded a through-plane value of 0.11 ± 0.01 S·m<sup>-1</sup> and an in-plane value of  $173 \pm 20 \,\mathrm{S} \cdot \mathrm{m}^{-1}$ , showing that there were three orders of magnitude difference between the in-plane and through-plane values of electrical conductivity. Considering that the electrical conductivity in the through-plane direction was low, and considering the much shinier surface of the decal side of the CL than its normal side after peeling off the CL from the ETFE substrate using a tape, as shown in Figure 2, there should be patches of ionomer near the decal side which could hinder the electron conduction in the throughplane direction and result in such a significant difference between the in-plane and through-plane directions, as shown in the schematic of Figure 3. Nonetheless, more proof is still needed using more direct methods like x-ray photoelectron spectroscopy (XPS), which could analyze surface chemistry of the CL. This method is currently under investigation by the authors.

## References

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**Figure 2.** CL surfaces: (a) normal side of the fresh sample, (b) decal side after transferring onto a tape

Pathways for funneling electrons in

lonomer patches

CL

Normal side

Figure 3. Suggested structure for a fresh CL.