

***In Situ*, ionic conductivity measurement of ionomer/binder-free Pt catalyst under fuel cell operating condition**

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The high cost of platinum group metal (PGM) catalyst is one of the key barriers to broad commercialization of polymer electrolyte fuel cells (PEFCs). The estimated large scale production cost for transportation fuel cell systems is approximately \$50/kW. The amount of PGM is currently used around 0.17g/kW. Key US DOE targets are \$30/kW for the system and 0.125g/kW for PGM [1]. It is estimated that the most sensitive factors to the system cost are power density and PGM loading. The nanostructured thin film (NSTF) electrode from 3M is a promising electrode for cost reduction and durability. It comprises continuous platinum layers coated on high aspect ratio organic whiskers. Another distinguishing feature is that the NSTF electrode doesn't contain ionomer for proton conduction.[2]. At a loading of 0.15 mgPt/cm<sup>2</sup>, NSTF electrodes generate comparable power to a 0.4 mgPt/cm<sup>2</sup> conventional Pt/C electrode in a fully humidified operating condition at 80°C. Despite of high power with low PGM loading, the charge transport and reaction mechanisms on the NSTF under realistic fuel cell operating conditions are not clearly understood. This uncertainty includes the hydrogen ion transport, which is one of the most important characteristics for PGM utilization with NSTF. The platinum seems to contribute to the transport of both protons and electrons. However, there is a notable lack of proton conductivity measurements for ionomer-free platinum electrodes under real fuel cell operating conditions, including the effects of temperature, relative humidity, and electrode potential. In this work, we present ionic conductivities of ionomer/binder-free porous Pt black cathodes measured *in-situ* using a new direct measurement technique that does not require equivalent circuit analysis.

Figure 1 shows a schematic of the microstructured electrode scaffold (MES) apparatus and a new measurement technique we have used to extract *in-situ* conductivity data during PEFC operation. Hess et al. [3] provides a detailed description of the MES concept for measuring potential distributions across the thickness of an electrode. The MES at the cathode side consists of a stack of alternating 2 μm thick Nafion sensing layers and 7.5 μm thick Kapton insulating layers that surround a 100 μm diameter cavity that is filled with the electrode materials. Here we combine five sensing layers in between six insulating layers, resulting in a total electrode thickness of 55 μm. Using the cylindrical cavity of the MES, we packed Pt black powders without any binder or ionomer to a controlled thickness. By connecting each of the Nafion sensing layers to hydrogen reference electrodes, we can measure the potential, and inject or remove current at discrete points through the electrode.

The conductivity measurement technique is based on introducing a small, periodic perturbation current through the electrode by hydrogen pumping from the anode to the Nafion layer furthest from the membrane (5<sup>th</sup> layer). By measuring the corresponding periodic potential drops close to the membrane (between the 1<sup>st</sup> and 3<sup>rd</sup> Nafion layers), we extracted resistance and conductivity data

using Ohm's law. The perturbation current is kept sufficiently small as not to alter the fuel cell operation. This conductivity measurement technique can be also applied while controlling various operating conditions, such as different relative humidity levels, fuel cell voltage or current, temperature, fuel utilization, etc.

In our initial work, we performed measurements with varying relative humidity at cell temperature of 60°C and OCV while delivering air or nitrogen to the cathode. Figure 2 shows that conductivities of ionomer-free Pt black are high with fully-humidified gases; they are close to published values for Nafion-bound Pt/C electrodes [4]. However, the conductivity drops dramatically with lower relative humidity and is much more sensitive to relative humidity compared to the Nafion-bound Pt/C electrode. Our separate results with air and nitrogen show that the ionic conductivity is not strongly dependent on oxygen concentration while at the OCV state. Ongoing work includes further characterization at other operating conditions, including varying cell potential, different ionomer-free catalysts, and different supports.

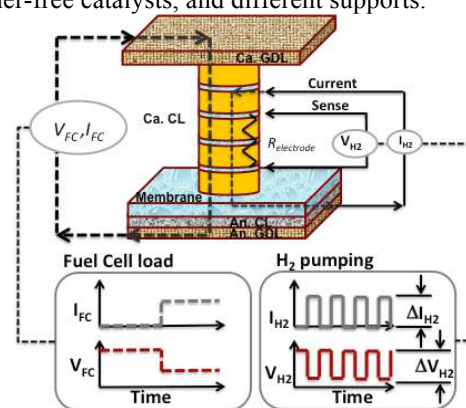


Figure 1: Schematic of a MES and the conductivity measurement technique.

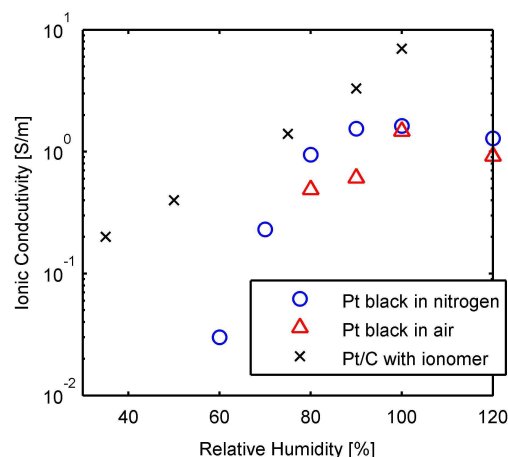


Figure 2: Ionic conductivities at various relative humidity at 60°C for an ionomer-free Pt black electrode in nitrogen and in air and for a conventional Pt/C electrode having ionomer from literature [4].

1. S. Satyapal, Hydrogen and Fuel Cell Technologies FY 2014 Budget Request Rollout, *U.S. Department of Energy*, April 12 (2013).
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4. E. L. Thompson, and D. R. Baker, *ECS Trans.*, **41** (1) 709-720 (2011).