

Title: CHARACTERIZATION OF PEM FUEL CELL MEMBRANE-ELECTRODE-ASSEMBLIES BY ELECTROCHEMICAL METHODS AND MICROANALYSIS

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CHARACTERIZATION OF PEM FUEL CELL MEMBRANE-ELECTRODE-ASSEMBLIES BY ELECTROCHEMICAL METHODS AND MICROANALYSIS

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Proton exchange membrane (PEM) fuel cells use platinum catalyzed proton exchange membranes for hydrogen conversion into electrical energy. The hydrogen / oxygen reactions occur in the catalyst layer of the membrane-electrode assembly (MEA). For high fuel cell performance, the MEA must be optimized for high proton transfer, hydrogen oxidation and oxygen reduction kinetics, and catalyst utilization for low cost. Testing of these MEAs is a long and complex process, with many variables to be examined. Characterization of the MEAs is required for a complete understanding of the variables at work for different MEA processing techniques. We have successfully utilized several characterization techniques to evaluate catalyst and ink formulations in three dimensions, including the platinum catalyst activity.

The use of electrochemical techniques such as hydrogen adsorption and desorption, and carbon monoxide oxidation complement microscopic analysis techniques such as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray microfluorescence (XRMF). These techniques can be used for characterization of the MEA to determine the elemental and morphological characteristics of the catalyst layer and membrane interface. This can reduce the time required for fuel cell testing of MEAs, and helps lead to a greater understanding of the MEA production variables. Uniformity of the catalyst layer is important for reduction of the catalyst loading and for the optimization of the fuel cell performance. There are many important process variables which must be examined to optimize the process involved in the assembly and application of the catalyst layer on the MEA. Examination of the catalyst layers (anode and cathode) in all dimensions helps illustrate whether the production process has been successful in producing a catalyst with uniform properties.

Hydrogen adsorption / desorption (HAD) analysis of MEAs is used to determine the active catalyst surface area, to help determine whether the

entire catalyst layer is active, and to determine relative catalyst utilization. Cyclic voltammograms demonstrating HAD evaluation of the catalyst layer is shown in fig. 1. Fig 1a is an MEA before testing in a single cell apparatus. The voltammogram has a high capacitance due to the high surface area of the graphite support, and the porous nature of the catalyst layer. Integration of the hydrogen desorption peak and subtraction of the double layer capacitance provides the active platinum surface area.

HAD measurements indicate that the active Pt surface area is high, on the order of $50 \text{ m}^2/\text{g}$ of Pt, although TEM and XRD techniques have measured surface areas a factor of 2 higher.¹ The weight % of the platinum to graphite support affects the active Pt surface area per unit mass of Pt. Alloying of Pt also affects the Pt utilization. HAD measurements have also been made at elevated temperatures, pressures, and different gas compositions to examine effects upon on hydrogen adsorption. Using HAD and CO oxidation techniques, Pt and Pt/alloyed catalysts have been evaluated for relative tolerance to CO and CO₂ in the feed gas and affects of catalyst ink processing.

Carbon monoxide oxidation has also been used to evaluate the catalyst layer. CO oxidation also is a measure of the relative catalyst surface area, however HAD and CO oxidation are complimentary In Situ techniques. Hydrogen has been seen to adsorb onto platinum surfaces coverage with graphite layers², thus HAD measurements can measure greater amounts of Pt than will be effective in a fuel cell. However, CO oxidation will only evaluate Pt catalyst that larger molecules such as CO and O₂ have access to. By comparing CO oxidation and HAD, processing differences have been monitored that affect the performance of the MEA in the fuel cell.

An alternative use of PEM fuel cells is for operation in a regenerative mode, so that excess energy can be converted back into chemical energy for storage. Regenerative PEM fuel cells require operation of the cell to occur in an electrolysis mode. We operated in reverse biased mode to examine the effect of regenerative operation on our MEAs. Fig. 1b is the voltammogram of an MEA after electrolysis in a single cell test stand. The active platinum surface area has been decreased by nearly a factor of three, and subsequent evaluation by SEM indicated the catalyst layer was no longer intact. These evaluations of the catalyst layers show that degradation of the catalyst layer occurs during electrolysis, which indicates that

these membrane electrode assemblies are not suitable for regenerative operation.

SEM and EDS are used to characterize the cross-sectional properties of the catalyst layer. SEM micrographs have demonstrated processing techniques which have produced uniform catalyst layers without large particles present. A backscattered micrograph of a membrane-electrode-assembly is shown in Fig. 2. The membrane (c) is labeled, as are the catalyst layers (b) and the mounting media (a). The membrane has sulfur present, thus is brighter than the background of the sample mounting media, but not as bright as the platinum present in the catalyst layer. The Nafion concentration in the catalyst layer has been monitored by EDS for uniformity. The catalyst layers are made of diffuse catalyst particles, much smaller than the resolution of the image, the actual Pt particles are on the order of 10 nm. TEM has been utilized for examination of the actual Pt particles.

Several characterization techniques, including electrochemical techniques (HAD, CO oxidation) and microscopic techniques (SEM, EDS, TEM and XRMF) have been utilized to increase our understanding of current processing techniques and their effect on catalyst activity. These techniques have decreased required testing time in our fuel cell test stands and have helped to optimize our construction of MEAs.

REFERENCE:

1. Discussions with Bob Allen, E-TEK 1993.
2. D. E. Sauer, Ph.D. Thesis, University of Washington, 1994.

ACKNOWLEDGMENTS:

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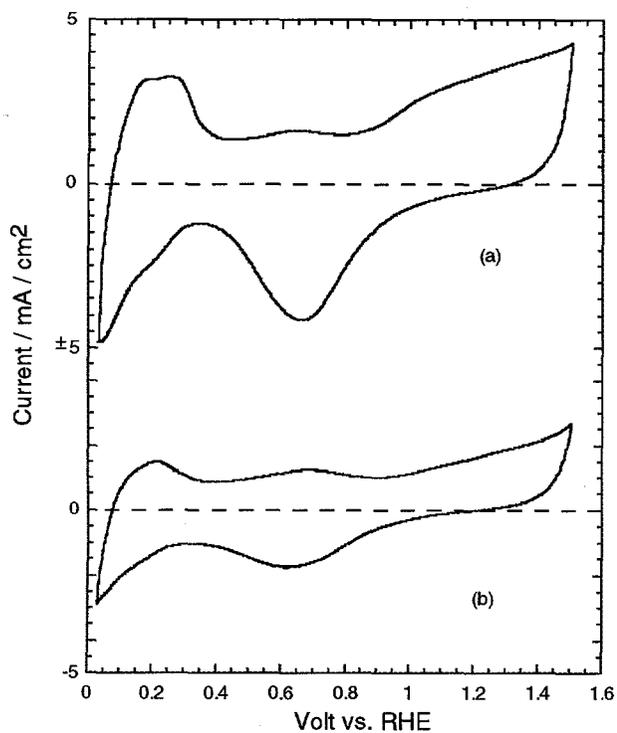


Fig.1: Hydrogen adsorption/desorption cyclic voltammogram of membrane electrode assembly. (a) before electrolysis, (b) after electrolysis reaction. 20 mV/sec sweep rate, T = 25 °C.

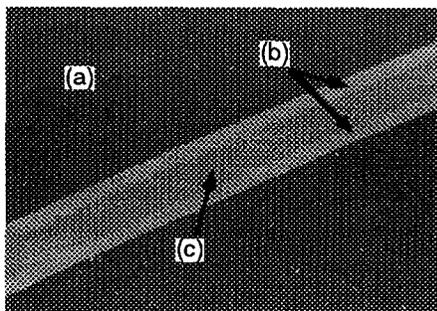


Fig. 2: SEM micrograph (backscattered electrons) of a membrane electrode assembly. (a) mounting epoxy, (b) catalyst layers, and (c) proton-exchange-membrane. Micrograph shows uniform catalyst layer applied to the membrane.

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Hydrogen adsorption / desorption and CO oxidation are used to evaluate the active Pt surface area of fuel cell membrane electrode assemblies. The membrane electrode assemblies are evaluated for useful catalyst life and are examined for relative CO and CO₂ tolerance. The electrochemical measurements combined with microanalysis of membrane electrode assemblies, including SEM and EDS allow a greater understanding and optimization of process variables.