

MODEL SYSTEMS FOR THE STUDY OF ELECTROCATALYSIS AT THE NANOPARTICLE-ELECTROLYTE-GAS REACTANT INTERFACE

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The study of model systems which seek to mimic conditions found at the interface between electrocatalytic particles of nanoscopic dimensions, the electrolyte and a gas phase reactant are expected to provide much needed insight into the nature of the factors that control key aspects of the operation and ultimately the performance of fuel cells. Attempts have been made to explore the electrochemical properties of Pt nanoparticles electrodeposited on a foreign support; however, no surface characterization of the electrode electrolyte interfaces was provided.¹

The approach we have developed and implemented in our research laboratories relies on the use of an ultrasharp Pt tip of the same type employed for scanning tunneling microscopy applications mounted on a piezo driven positioner. This arrangement allows for the tip to approach and eventually contact the surface of, for example, a solid polymer electrolyte film, such as Nafion, placed normal to the translation axis of the tip under highly controlled conditions. Serendipitously, a solid electrolyte would not be expected to form a meniscus that would wet a large area of the tip. A schematic diagram of the set up employed is shown in Fig. A. As indicated this arrangement includes a dynamic hydrogen Pt electrode placed on the underside Nafion surface with the hydrogen evolving component working as a counter reference electrode.

Shown in Fig. B are cyclic voltammograms of two different ultrafine Pt tips in contact with a Nafion membrane acquired using a function generator and electronics available with the Molecular Imaging scanning probe instrument. All the features in these curves are characteristic of clean Pt. Coulometric analysis of the hydrogen adsorption and oxide reduction regions were found to be consistent with the response of ca. 20 million and 400,000 atoms of Pt in contact with the electrolyte, respectively. These correspond to the number of surface sites on spherical Pt clusters of 700 nm and 100 nm diameter, respectively. Unsupported catalysts as those employed in electrodes for direct methanol fuel cells consist of particles with diameters averaging ca. 300 nm.

As evident from these data, the noise level is rather low allowing a quantitative analysis to be carried out with a large degree of reliability. A further increase in sensitivity is expected to be gained by increasing the scan rate, thereby taking advantage of the pseudocapacitive nature of the interface, i.e. the current is proportional to the scan rate.

Particularly intriguing is the possibility of measuring directly the electrocatalytic activity of nanoscopic Pt structures for reactions of relevance to fuel cells, such as hydrogen oxidation and oxygen reduction for which the

currents are expected to be large enough to be detected without special instrumental modifications. Experiments of this type are currently in progress and will be reported in due course.

LITERATURE CITED

[1] A. Kucernak, Abs. 845, 205th Meeting of the Electrochemical Society, San Antonio, TX, U.S.A.

ACKNOWLEDGEMENTS

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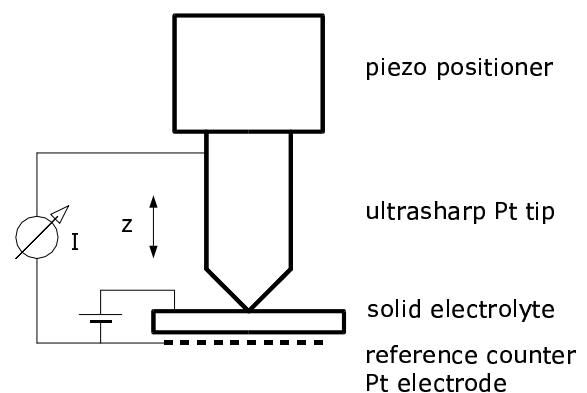


Fig. A: Set up to achieve a variable, nanometer sized contact area of Pt with solid electrolyte

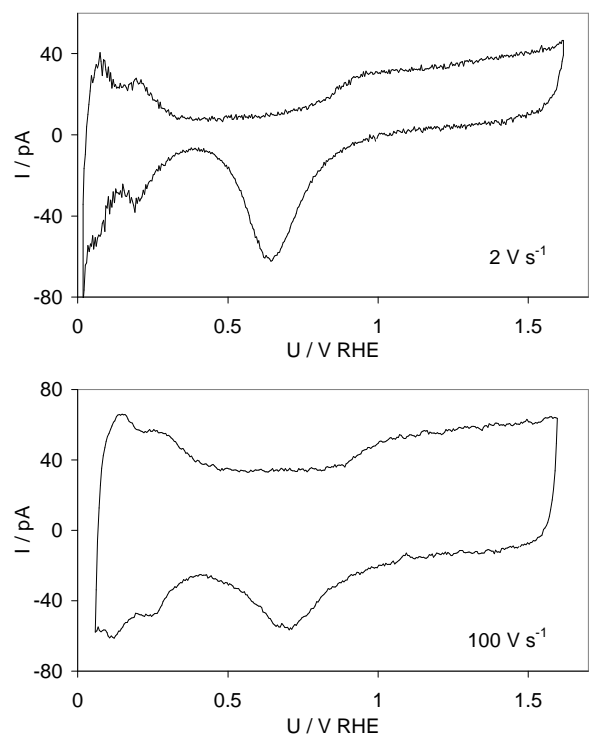


Fig. B: Cyclic voltammograms of the ultrasharp Pt tip / Nafion interface recorded at scan rates of 2 V s⁻¹ (top) and 100 V s⁻¹ (bottom).