Measuring Electrochemically Active Surface Area of PEM Fuel Cell Cathode

Wei Li and Alan M. Lane
Center for Materials for Information Technology (MINT)
Department of Chemical and Biological Engineering
University of Alabama
Tuscaloosa, AL, U.S.A.

Quantitative determination of a hydrogen monolayer, with a 1:1 ratio of H to Pt, is the basis for measuring hydrogen adsorption/desorption in solution by cyclic voltammetry to determine the electrochemically active surface area (ECSA) of Pt. However, this is not straightforward because two types of hydrogen, i.e. underpotential deposited hydrogen (H_{UPD}) and overpotential deposited hydrogen (H_{OPD}), adsorb together (see H_{ads} in Figure 1a) on Pt at different sites in acidic media at low electrode potentials of 0–110 mV vs. SHE. They cannot be resolved by cyclic voltammetry alone.

Differential electrochemical mass spectrometry was demonstrated for the first time to resolve H_{UPD} and H_{UPD} by measuring the H_{2} evolved from water by the hydrogen evolution reaction at the cathode (a Pt electrode) of a proton exchange membrane fuel cell (PEMFC) as shown in Figure 1b. The H_{UPD} at the cathode was thus quantified and determined to form a saturated layer on the Pt surface when the lower potential limit of cyclic voltammetry is below about 70 mV vs. the anode, a dynamic hydrogen electrode. This amount of H_{UPD} can be used to measure the ECSA of a Pt electrode in PEM fuel cells and avoid the error from including H_{OPD}.

Figure 1. CV (a) and H_{2}-DEMS spectrum (b) of the Pt cathode in a PEMFC.

W. Li and A. M. Lane, “Resolving the HUPD and HOPD by DEMS to determine the ECSA of Pt electrodes in PEM fuel cells,” Electrochemistry Communications 13 (2011) 913-916.