Corrugated Pore Model for Design of Non-Precious Oxygen Reduction Cathodes

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Models of gas diffusion electrodes for fuel cells must account for wetting phenomena inherent in formation and operation of the electrode layer. For example, wetting of catalyst active sites by electrolyte is controlled by the meso- and microporosity of catalyst particles via the resulting superhydrophobicity. Similarly, performance of fuel cell electrodes can be effected by quasi-irreversible flooding of catalyst micropores [1]. Taken together, these phenomena can determine the performance of fuel cell electrodes, independent of the inherent turnover rate of active sites, by controlling access and transport to active sites. This issue is particularly acute for non-precious electrodes, where catalyst layer thickness may exceed by an order of magnitude that of platinum-based cathodes.

We report here a model developed to account for the hydrophobic nature of active sites in oxygen reduction electrodes for low temperature fuel cells that employ non-precious electrocatalysts. Based on the random corrugated pore concept (Figure 1, [2]), the model primarily relates the effects of porosity and surface energy at the micro- to mesoscales to catalyst accessibility and water uptake at the scale of catalyst agglomerates.

Measurements of pore size distributions by mercury porosimetry and BET, along with surface energy measurements by water porosimetry are compared over a wide range of pore sizes primarily in the meso- and macropore range (larger than 50 nm) [3,4]. From a more mechanistic perspective, the difference in these adsorption isotherms will be dependent on the surface energy and pore size distributions as evidenced by Washburn's equation [5]:

$$p_C = p_L - p_G = \frac{4\gamma \cos\theta}{r_p}$$

Where p_C is the capillary pressure, with p_L and p_G the liquid and gas pressures respectively, gamma the surface tension, the water contact angle, and r_p the pore radius. Using the more consistent surface properties of mercury and nitrogen a pore size distribution is calculated. This PSD is fitted to water adsorption data to establish hydrophilicity over a range of pore sizes. Pore size and hydrophilicity data are correlated to fuel cell performance of multiple catalyst formulas under varying oxygen and water activities.

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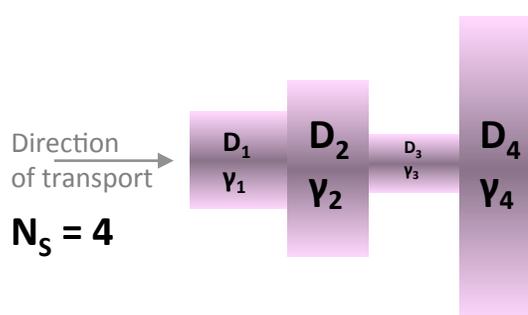5. A. W. Adamson and A. P. Gast, *Physical chemistry of surfaces* (Wiley, New York, 1997).

Figure 1. Schematic of a corrugated pore membrane reactor of N_s cylindrical segments, each having unique diameter and surface energy.