Connecting Steady State Voltammetry and Oxygen Reduction Activity

by Venkatasubramanian Viswanathan

Polymer Electrolyte Membrane Fuel Cells (PEMFC) are a desirable power source especially for portable electronics devices and applications in transportation. However, efficiencies of present PEMFC systems range between 35-45%, although the theoretical limits are nearly 80% efficiency for low temperature fuel cells like PEMFC. Even on the best catalysts like Pt, losses due to slow reaction kinetics in the cathode for the oxygen reduction reaction (ORR) lead to an efficiency loss of around 20%.

A simple model to describe the kinetic current of ORR is given by

$$j_k(U) = -j_0^* f(\theta_{ads}) \exp\left(\frac{\alpha F(U^0 - U)}{RT}\right) \quad [1]$$

where U^0 is the reversible potential for the ORR, U is the electrode potential, j_0^* is an intrinsic parameter that is a characteristic of the ORR on a particular electrode surface, $f(\theta_{ads})$ is the number of available sites, α is the charge transfer coefficient, which is usually assigned a value of 1/2. The exponential dependence of j_k on U in reflects that the model considers the first electron-transfer step as the rds.

In the application of the model to hexagonal (111) surface of Pt, we need to compute the available sites by counting the number of sites blocked by the strongly adsorbing species $OH_{(ads)}$ and $O_{(ads)}$. The strongly adsorbing species are mainly produced by the electrochemical discharge of water, which can be characterized by steady state voltammetry. The sites that are blocked from the adsorbates formed from the electrochemical discharge of water are computed based on a blocking model based on observations from the simulations of the adsorbate layer.[2]

We have shown that in the potentials of interest between 0.5 and 1.0 V, $OH_{(ads)}$ is stable only in the environment of H_2O lying parallel to the surface. In addition, DFT calculations show that water in the water bilayer is different from water in the water-OH bilayer. As shown in Fig. 1, water in the water bilayer is ~3.3-3.6 Å away from the surface while the water-OH bilayer is 2.0-2.3 Å from the surface.[3] In addition, $O_{(ads)}$ strongly repels all oxygen containing intermediates in its nearest neighbor environment.[3] Motivated by these observations, we introduce the concept of a triplet site, which consists of a triangular site on hexagonal (111) surface. As shown in Fig. 2, the triplet site is blocked when the site contains OH/H_2O or $O_{(ads)}$ and the site is free otherwise.

Using the computed site-availability function shown in Fig. 3 and an intrinsic current density for ORR of j_0^* = -80 mA/cm^2, we show that this simple model is able to capture the activity for oxygen reduction reaction over the entire potential range. As seen in Fig. 4, the continuously changing Tafel slopes over the potential range of interest can be captured well by this simple model.

This seems to suggest that the number of available sites acts as a single descriptor for activity over a wide potential window.

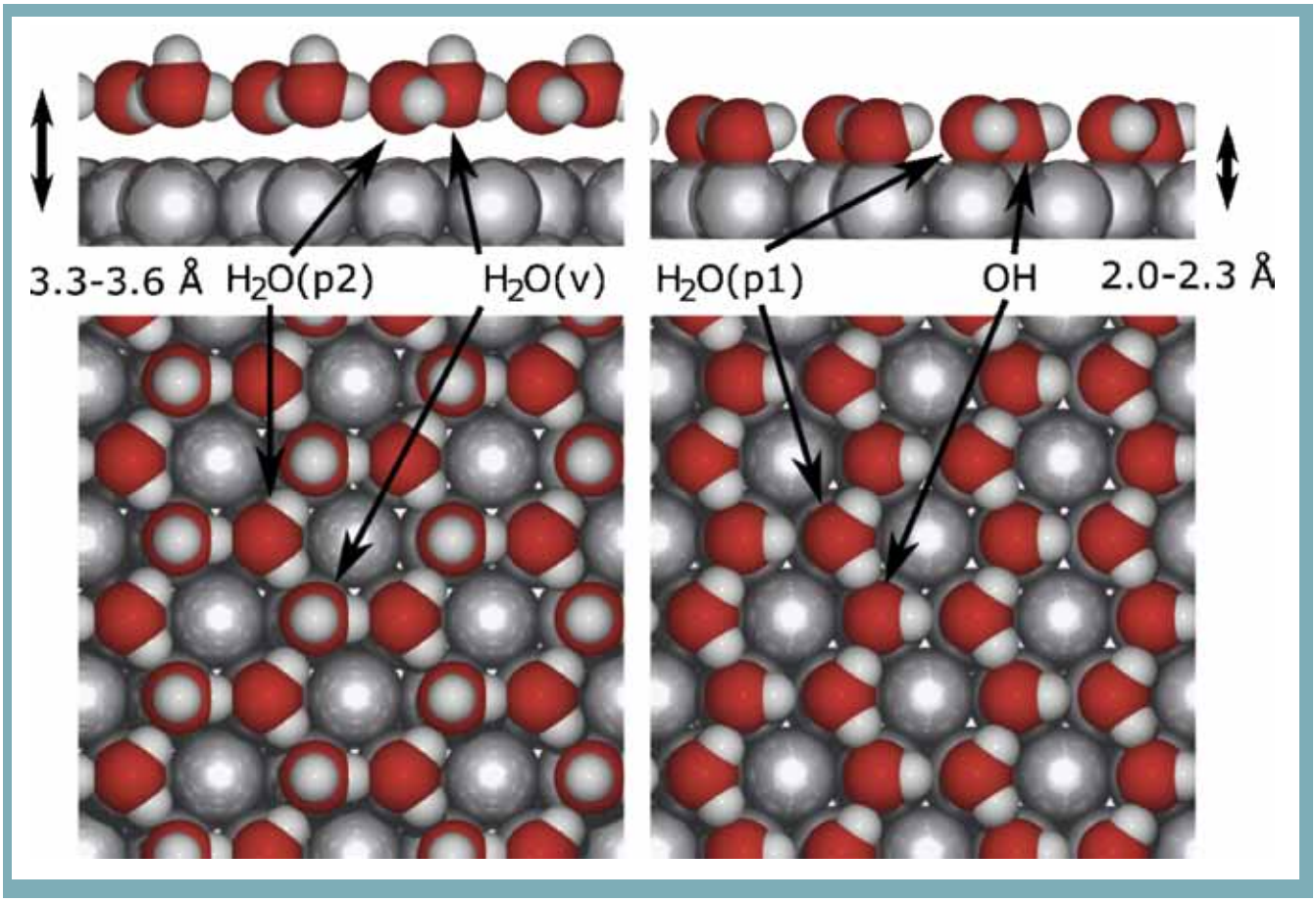

Fig. 1. *Structure of the water bilayer and water-hydroxide bilayer.*

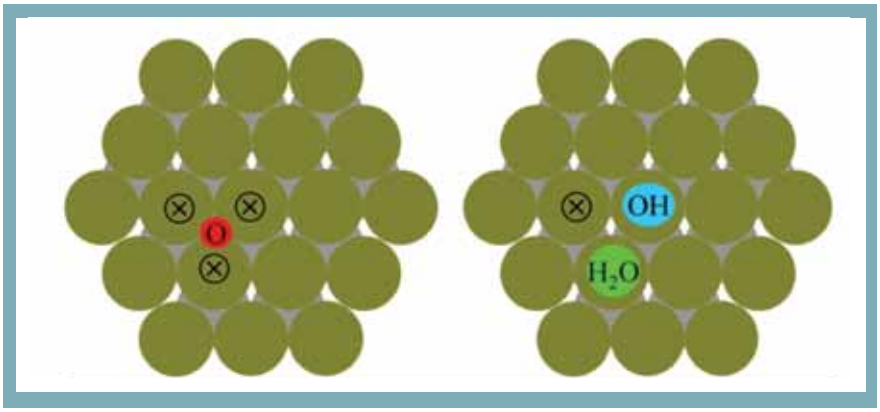

Fig. 2. *Site-blocking model for triplet-site model. Left: site-blocking by O_{ads}; right: site-blocking by OH_{ads}. Crosses represent sites which are blocked. The sites where OH_{ads} and H_2O_{ads} are also blocked.*

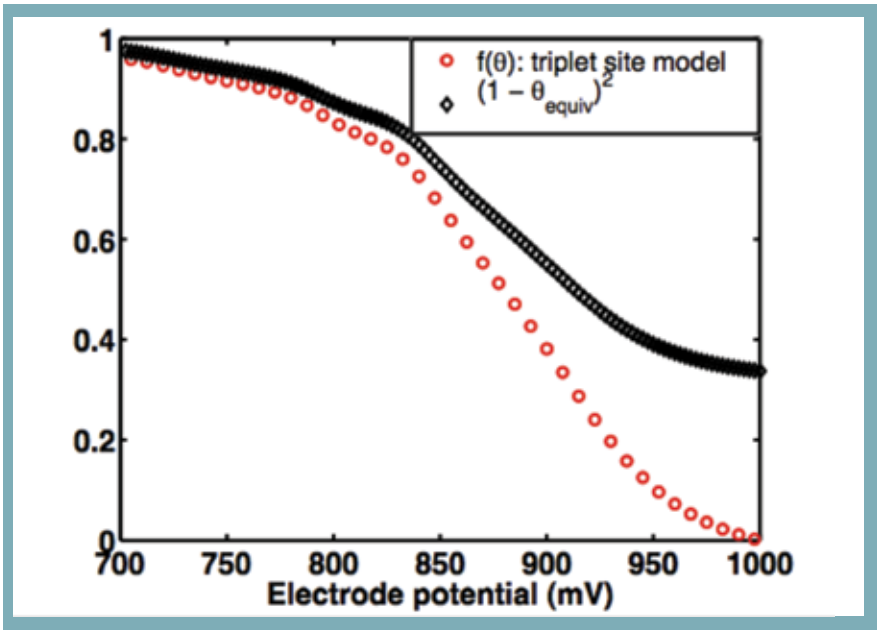

Fig. 3. *Site-availability function $f(\theta_{ads})$ for the triplet-site model from the steady state voltammetry.*

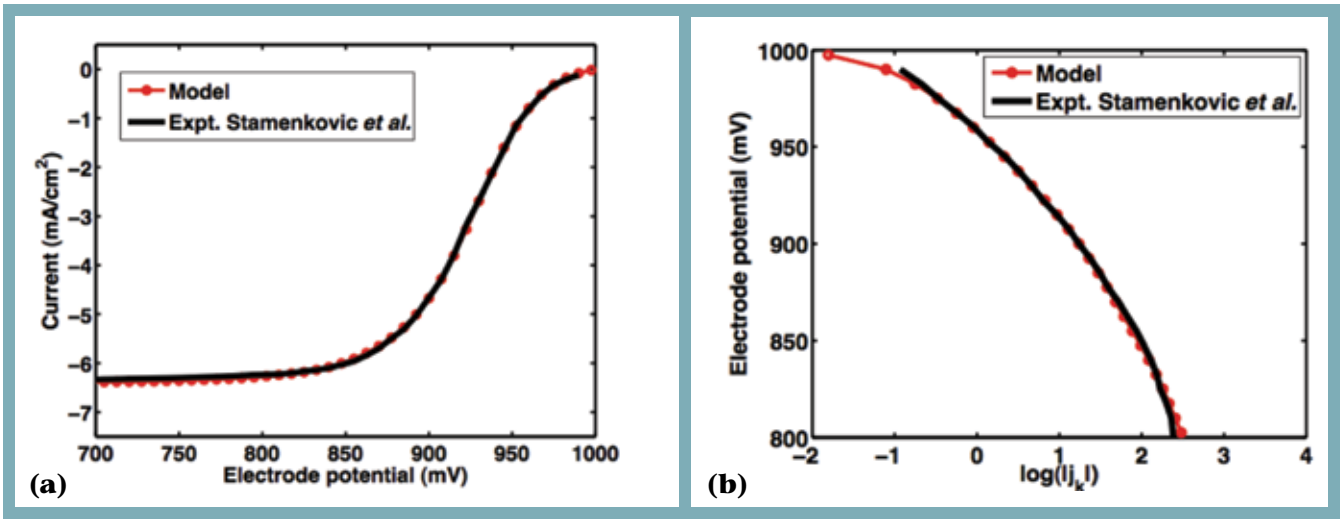

Fig. 4. *Results of the simulations using triplet-site model for (a) total current density and (b) Tafel plot for ORR on $Pt_3Ni(111)$ in 0.1M $HClO_4$. Experimental values are taken from Stamenkovic, et al.[4]*

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