

Porous Ring Disk Electrode Model for Oxygen Reduction by Non-precious Electrocatalysts

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A key challenge in the development of non-precious electrocatalysts for oxygen reduction (ORR) is the generation of significant hydrogen peroxide as a stable intermediate. Whereas significant peroxide production does not occur on platinum above 0.5 V/RHE, we observe approximately 1-4% peroxide generation near 0.6 V/RHE under typical RRDE conditions. As described in a companion talk, the degree of peroxide generation is strongly dependent on catalyst loading. Peroxide itself is a powerful oxidizing agent that may have significant impact on fuel cell durability. Therefore it is essential to understand the mechanism of peroxide generation in order to minimize its impact.

We have developed a quantitative model to simulate the ORR on a rotating ring disk electrode, in order to study the mechanism of peroxide generation by MNC electrocatalysts. We start with a simple model for oxygen reduction [1,2] as given in Figure 1, which includes absorption equilibria for all species, a four-electron and a 2+2 electron pathway for oxygen reduction, and the option for disproportionation of peroxide to oxygen and water. This kinetic model is implemented in the context of a porous RDE framework [3] which accounts for transport of reactants and intermediates through catalyst films at high loading.

Some preliminary results are shown in Figure 2, where the model is fit to experimentally disk and ring polarization curves. Here, the rate constants k_2 , k_3 , and k_5 , Tafel slopes b_2 and b_3 , and the electrode permeability were adjusted. The model accurately captures the potential dependence of the ring current, which displays a maximum near 0.7 V. Analysis of current from individual reaction steps is shown in Figure 3, where the four electron step (I_5) dominates the current, and the second two electron step (I_3) is almost negligible. The first electron step (I_2) shadows I_5 at high potential but fades due to adsorption limitations at low potentials.

Additional dependencies are on electrode thickness and disk rotation speed are considered. This model will be applied for prediction of polarization of non-precious oxygen reduction electrodes in both aqueous RDE and gas diffusion electrode environments.

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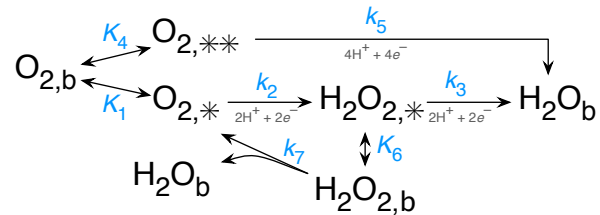


Figure 1. Simplified kinetic model of ORR as implemented in PRDE.

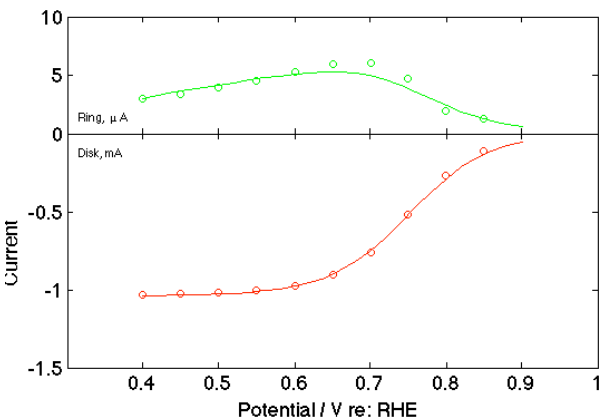


Figure 2. Fit of PRDE model to RRDE data. 0.5 mg cm⁻² loading in 0.5 M H₂SO₄, room temperature, O₂-saturated, ring poised at 1.2 V vs. RHE at 1600 rpm with 5 mm diameter disk. Markers: experimental; Curves: Model fit.

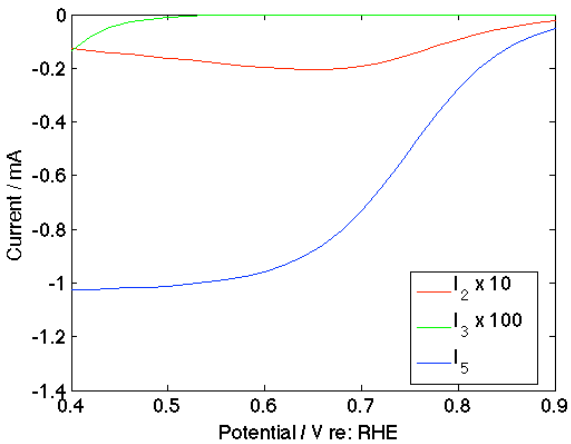


Figure 3. Deconvolution of ORR currents from Fig. 2 into 4e⁻ pathway (I_5) and 2+2 pathway (I_2 and I_3).

