

Electrochemical Reduction of Oxygen on Nanoparticulate Gold Electrodeposited on a Molecular Template

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Supporting Information

A simple derivation of equation (12) considers the following EE reactions mechanism:



Considering the flux of A, the steady state condition (The diffusional flux equals the rate of interfacial electrochemical reaction) is given by:

$$\frac{D_A}{\delta_A} (c_A^b - c_A^\sigma) = k_A c_A^\sigma \quad (S2)$$

where D_A is the diffusion coefficient of A, δ_A is the thickness of the diffusional layer for A, c_A^b is the concentration of A in the bulk, c_A^σ is the concentration of A at the electrode surface and k_A is the potential dependent rate constant for the first step. Similar considerations apply to B and the corresponding surface concentrations derived from the steady state are:

$$c_A^\sigma = \frac{D_A c_A^b}{D_A + \delta_A k_A} \quad (S3)$$

Taking also into account the rate of diffusion of B from the electrode surface to the solution, the surface concentration of B is given by:

$$c_B^\sigma = \frac{k_A c_A^\sigma \delta_B}{D_B + \delta_B k_B} \quad (S4)$$

The observed current density j is the sum of the currents due to the reduction of A and B and is therefore given by:

$$j = -2F(k_A c_A^\sigma + k_B c_B^\sigma) \quad (S5)$$

From (S3), (S4) and S5),

$$j = -\frac{2FD_A k_A c_A^b}{D_A + \delta_A k_A} \left(1 + \frac{k_B \delta_B}{D_B + k_B \delta_B} \right) \quad (S6)$$

Taking the inverse of (S6)

$$j^{-1} = - \left[\frac{1}{2Fk_A c_A^b} + \frac{\delta_A}{2FD_A c_A^b} \right] \left[\frac{(D_B/\delta_B) + k_B}{(D_B/\delta_B) + 2k_B} \right] \quad (S7)$$

The reciprocal limiting current density for the first reduction step is given by:

$$j_D^{-1} = - \frac{\delta_A}{2FD_A c_A^\sigma} \quad (S8)$$

The limiting current corresponding to the second step (Reduction of peroxide at very negative potentials) is given by

$$j_{D,B} = -2Fc_B^\sigma(\lim) \frac{D_B}{\delta_B} \quad (S9)$$

From (S3 and S4),

$$c_B^\sigma(\lim) = \frac{(k_A c_A^\sigma)_{\lim} \delta_2}{D_B + \delta_B k_B} = \frac{D_A \delta_B c_A^b}{\delta_A D_B} \quad (S10)$$

From (S9) and (S10),

$$j_{D,B} = -2Fc_A^b \frac{D_A}{\delta_A} = j_D \quad (S11)$$

Equation (2) in the main text is obtained by replacing the diffusional terms by equations (S8) to (S11). The potential dependent rate constants are considered to have the usual exponential dependence of the current on potential for an electron transfer activated process:

$$k_i = k_i^0 \exp \left(- \frac{\alpha_i F(E - E_A^0)}{RT} \right) \quad (S12)$$

k_i^0 are the electrochemical rate constants for reactions (I) and (II) ($A = O_2$ and $B = HO_2^-$), respectively, calculated at the standard potential of the first reaction, E_A^0 . α_i is the corresponding transfer coefficient. This derivation does not take into account slow peroxide desorption, peroxide disproportionation or the participation of chemical steps in the reaction sequence.