

Exploring kinetic and thermodynamic aspects of four-electron electrochemical reactions: electrocatalysis of oxygen evolution by metal oxides and biological systems

Vincent C.-C. Wang^{1,2}

¹ *Shouxing Street, Yancheng, Kaohsiung 803, Taiwan (R.O.C)*

² *Institute of Chemistry, Academia Sinica, Nangang, Taipei 115, Taiwan
(R.O.C)*

Summary

In this part of supporting materials, we demonstrate how to obtain the equation 1 in the main manuscript, which describes the relation between the electrode potential and electrocatalytic current for the four-electron oxidation reaction.

1 The derivation of the equation 1 for four-electron oxidation reaction

According to the Butler-Volmer equation, the forward and backward electron transfer rate constant in a one-electron reaction can be described as follows:

$$k_f = k_0 \exp[-\alpha f(E - E_{eq})] \quad (\text{Reduction}) \quad (1.1)$$

$$k_b = k_0 \exp[(1 - \alpha)f(E - E_{eq})] \quad (\text{Oxidation}) \quad (1.2)$$

$$f = \frac{F}{RT} \quad (1.3)$$

where k_0 , standard electron exchange rate constant; α , transfer coefficient; E , electrode potential; E_{eq} , equilibrium potential; F , Faraday constant; R , ideal gas constant and T , absolute temperature. The transfer coefficient value, 0.5 is applied here.

Dividing 1.1 by 1.2, we can obtain the following relation:

$$g = \frac{k_f}{k_b} = \exp[-f(E - E_{eq})] \quad (1.4)$$

The net rate of all species on the electrode in the scheme S1 can be described as follows:

$$\frac{d\Gamma_{S_0}}{dt} = k_c\Gamma_{S_4}[R] + k_{b1}\Gamma_{S_1} - k_{f1}\Gamma_{S_0} \quad (1.5)$$

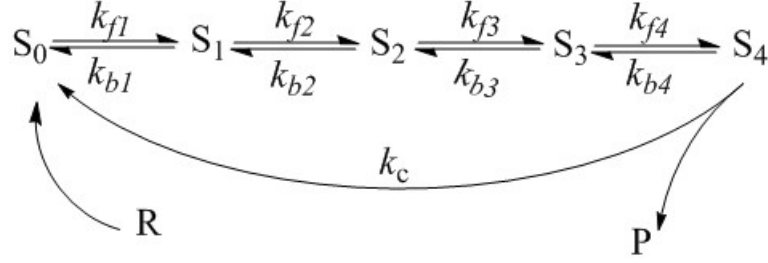
$$\frac{d\Gamma_{S_1}}{dt} = k_{f1}\Gamma_{S_0} + k_{b2}\Gamma_{S_2} - (k_{b1} + k_{f2})\Gamma_{S_1} \quad (1.6)$$

$$\frac{d\Gamma_{S_2}}{dt} = k_{f2}\Gamma_{S_1} + k_{b3}\Gamma_{S_3} - (k_{b2} + k_{f3})\Gamma_{S_2} \quad (1.7)$$

$$\frac{d\Gamma_{S_3}}{dt} = k_{f3}\Gamma_{S_2} + k_{b4}\Gamma_{S_4} - (k_{b3} + k_{f4})\Gamma_{S_3} \quad (1.8)$$

$$\frac{d\Gamma_{S_4}}{dt} = k_{f4}\Gamma_{S_3} - (k_{b4} + k_c[R])\Gamma_{S_4} \quad (1.9)$$

Γ_n represents the surface coverage of the electroactive species S_n



Scheme S1 A scheme for a four-electron oxidation reaction. The definition of symbols can be found in the main manuscript.

The electroactive site is assumed to be saturated with reactants and the mass transport of reactants is not rate-limiting. Therefore, the concentration of R can be treated as a constant. The total surface coverage is given by

$$\Gamma_{Total} = \Gamma_{S_0} + \Gamma_{S_1} + \Gamma_{S_2} + \Gamma_{S_3} + \Gamma_{S_4} \quad (1.10)$$

The turnover frequency for an electrocatalyst is proportional to Γ_{S_4} . Therefore, the turnover frequency is given by

$$\text{turnover frequency} = k_c \frac{\Gamma_{S_4}}{\Gamma_{Total}}$$

The electrocatalytic current, I is equal to

$$I = nFA\Gamma_{Total} \times \text{turnover frequency} \quad (1.11)$$

The limiting current is given by

$$I_{lim} = nFAk_c\Gamma_{Total} \quad (1.12)$$

Under the steady-state approximation, the net rate of equation (1.5)-(1.9) is equal to zero. Therefore, the solution of Γ_{S_4} can be solved by Cramer's Rule as follows:

$$\Gamma_{S_4} = \frac{D_1}{D_2}$$

$$D_1 = \begin{pmatrix} k_{f1} & -(k_{b1} + k_{f2}) & k_{b2} & 0 & 0 \\ 0 & k_{f2} & -(k_{b2} + k_{f3}) & k_{b3} & 0 \\ 0 & 0 & k_{f3} & -(k_{b3} + k_{f4}) & 0 \\ 0 & 0 & 0 & k_{f4} & 0 \\ 1 & 1 & 1 & 1 & \Gamma_{Total} \end{pmatrix} \quad (1.13)$$

$$D_2 = \begin{pmatrix} k_{f1} & -(k_{b1} + k_{f2}) & k_{b2} & 0 & 0 \\ 0 & k_{f2} & -(k_{b2} + k_{f3}) & k_{b3} & 0 \\ 0 & 0 & k_{f3} & -(k_{b3} + k_{f4}) & k_{b4} \\ 0 & 0 & 0 & k_{f4} & -(k_{b4} + k_c) \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \quad (1.14)$$

After solving the matrix D_1 and D_2 , we can obtain

$$D_1 = k_{f1}k_{f2}k_{f3}k_{f4}\Gamma_{Total} \quad (1.15)$$

$$D_2 = k_{f1}k_{f2}k_{f3}k_{f4} + k_{f1}k_{f2}k_{f3}k_{b4} + k_{f1}k_{f2}k_{f3}k_c + k_{f1}k_{f2}k_{b3}k_{b4} \\ + k_{f1}k_{f2}k_{b3}k_c + k_{f1}k_{f2}k_{f4}k_c + k_{f1}k_{b2}k_{b3}k_{b4} + k_{f1}k_{b2}k_{b3}k_c \\ + k_{f1}k_{b2}k_{f4}k_c + k_{f1}k_{f3}k_{f4}k_c + k_{b1}k_{b2}k_{b3}k_{b4} + k_{b1}k_{b2}k_{b3}k_c \\ + k_{b1}k_{b2}k_{f4}k_c + k_{b1}k_{f3}k_{f4}k_c + k_{f2}k_{f3}k_{f4}k_c \quad (1.16)$$

Therefore,

$$\frac{\Gamma_{Total}}{\Gamma_{S_4}} = 1 + \frac{k_{b4}}{k_{f4}} + \frac{k_c}{k_{f4}} + \frac{k_{b3}k_{b4}}{k_{f3}k_{f4}} + \frac{k_{b3}k_c}{k_{f3}k_{f4}} + \frac{k_c}{k_{f3}} + \frac{k_{b2}k_{b3}k_{b4}}{k_{f2}k_{f3}k_{f4}} \\ + \frac{k_{b2}k_{b3}k_c}{k_{f2}k_{f3}k_{f4}} + \frac{k_{b2}k_c}{k_{f2}k_{f3}} + \frac{k_c}{k_{f2}} + \frac{k_{b1}k_{b2}k_{b3}k_{b4}}{k_{f1}k_{f2}k_{f3}k_{f4}} + \frac{k_{b1}k_{b2}k_{b3}k_c}{k_{f1}k_{f2}k_{f3}k_{f4}} \\ + \frac{k_{b1}k_{b2}k_c}{k_{f1}k_{f2}k_{f3}} + \frac{k_{b1}k_c}{k_{f1}k_{f2}} + \frac{k_c}{k_{f1}} \quad (1.17)$$

According to the equation (1.4), the equation (1.17) can be simplified to

$$\frac{\Gamma_{Total}}{\Gamma_{S_4}} = 1 + g_1g_2g_3g_4 + g_2g_3g_4 + g_3g_4 + g_4 + \\ k_c \left(\frac{1 + g_3g_2g_1 + g_3g_2 + g_3}{k_{f4}} + \frac{1 + g_2g_1 + g_2}{k_{f3}} + \frac{1 + g_1}{k_{f2}} + \frac{1}{k_{f1}} \right) \quad (1.18)$$

Taking the equation (1.18) into the equation(1.11) , the "equation 1" in the manuscript can be obtained.