Spatially-resolved modeling of electric double layers and surface chemistry for the hydrogen oxidation reaction in water-filled platinum-carbon electrodes

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Supporting Information

Derivation of dual-pathway Hydrogen Oxidation Reaction (HOR)

Similar to Wang et al. [1], we model HOR with the three elementary steps for hydrogen oxidation reaction on Pt surface:

$$\mathrm{H_2{+}2Pt} \rightleftharpoons 2\left(\mathrm{H\text{-}Pt}\right) \text{ Tafel reaction} \tag{A-1}$$

$$\mathrm{H_2{+}Pt} \rightleftharpoons \left(\mathrm{H\text{-}Pt}\right)\mathrm{{+}H^{+}{+}e^{-}} \text{ Heyrovsky reaction} \tag{A-2}$$

$$\left(\mathrm{H\text{-}Pt}\right) \rightleftharpoons \mathrm{Pt{+}H^{+}{+}e^{-}} \text{ Volmer reaction} \tag{A-3}$$

In our derivation, the reactions are modeled at the OHP where hydrogen is consumed and protons are generated. This allows us to account for the diffuse layer charge that otherwise is neglected. While diffuse layer charge might not play big of a role for the Nafion-filled pore due to high proton concentration and very small Debye length, it cannot be ignored for a dilute aqueous electrolyte (e.g., a water-filled pore) with low proton concentration.

For each reaction step, the net reaction rate is equal to the sum of the forward and backward reactions:

$$v_T = k_T\left(1-\theta\right)^2 c_{H2}^{OHP} - k_{-T}\theta^2 \tag{A-4}$$

$$v_H = k_H\left(1-\theta\right)c_{H2}^{OHP}\, exp\left(\frac{\left(1-\alpha\right)F\Delta\psi}{RT}\right) - k_{-H}\theta c_{H+}^{OHP}\, exp\left(\frac{-\alpha F\Delta\psi}{RT}\right) \tag{A-5}$$

$$v_V = k_V\theta\, exp\left(\frac{\left(1-\alpha\right)F\Delta\psi}{RT}\right) - k_{-V}\left(1-\theta\right)c_{H+}^{OHP}\, exp\left(\frac{-\alpha F\Delta\psi}{RT}\right) \tag{A-6}$$

where c_{H2}^{OHP} and c_{H+}^{OHP} are the local hydrogen and proton concentrations at the OHP, θ is the wall coverage by reaction intermediate, (H-Pt), and $1\text{-}\theta$ corresponds to free Pt sites. The *k* terms are the kinetic rate constants for each step. Heyrovsky and Volmer reaction steps involve an electron transfer therefore they have to be adjusted with the exponential term. α is a symmetry factor taken to be 0.5 by Wang et al. We omit a term for the number of electrons transferred per reaction, *n,* by setting it equal to 1, since one electron is transferred in each of the charge transfer steps. $\Delta\psi = \psi_m - \psi_{OHP}$ is the potential difference between the metal and the OHP.

At equilibrium potential, $\Delta\psi_{eq}$, the net current is zero and the rate of forward reaction is equal to that of the backward reaction:

$$\nu_{0T} = k_T \left(1-\theta_0\right)^2 c_{H2}^{OHP} = k_{-T}\theta_0^{\ 2} \tag{A-7}$$

$$\nu_{0H} = k_H \left(1-\theta_0\right) c_{H2}^{OHP}\, exp\left(\frac{\left(1-\alpha\right) F \Delta\psi_{eq}}{RT}\right) = k_{-H}\theta_0 c_{H+}^{OHP}\, exp\left(\frac{-\alpha F \Delta\psi_{eq}}{RT}\right) \tag{A-8}$$

$$\nu_{0V} = k_V \theta_0\, exp\left(\frac{\left(1-\alpha\right) F \Delta\psi_{eq}}{RT}\right) = k_{-V}\left(1-\theta_0\right) c_{H+}^{OHP}\, exp\left(\frac{-\alpha F \Delta\psi_{eq}}{RT}\right) \tag{A-9}$$

where θ_0 is the intermediate coverage at equilibrium potential.

To eliminate the kinetic rate constants, the reaction rates are divided by their respective equilibrium reaction rates. Although the concentration terms cancel out, they later emerge through the equilibrium potential value:

$$\nu_T = \nu_{0T}\left[\left(\frac{1-\theta}{1-\theta_0}\right)^2 - \left(\frac{\theta}{\theta_0}\right)^2\right] \tag{A-10}$$

$$\nu_H = \nu_{0H}\left[\left(\frac{1-\theta}{1-\theta_0}\right) exp\left(\frac{\left(1-\alpha\right)F\eta}{RT}\right) - \left(\frac{\theta}{\theta_0}\right) exp\left(\frac{-\alpha F\eta}{RT}\right)\right] \tag{A-11}$$

$$\nu_V = \nu_{0V}\left[\left(\frac{\theta}{\theta_0}\right) exp\left(\frac{\left(1-\alpha\right)F\eta}{RT}\right) - \left(\frac{1-\theta}{1-\theta_0}\right) exp\left(\frac{-\alpha F\eta}{RT}\right)\right] \tag{A-12}$$

where the overpotential is defined as the difference between the Pt potential minus the OHP potential less their difference at equilibrium:

$$\eta = \Delta\psi - \Delta\psi_{eq} = \left(\psi_m - \psi_{OHP}\right) - \left(\psi_m - \psi_{OHP}\right)_{eq} \tag{A-13}$$

To find the total current we use steady-state approximation (SSA) theory where it is assumed that the change of the intermediate concentration is zero, $d\theta / dt = 0$.[1] The total current can be expressed as combinations of the Tafel-Volmer, Heyrovsky-Volmer or Tafel-Heyrovsky pathways:

$$j_{HOR} = F\left(\nu_H + \nu_V\right) = 2F\left(\nu_T + \nu_H\right) = 2F\left(\nu_V - \nu_T\right) \tag{A-14}$$

Following the work of Wang et al., we assume the Volmer mechanism is sufficiently faster than the Tafel and Heyrovsky steps that we can develop a model using the second form of Eq. [A-14]. Inserting Eqs. [A-10] and [A-11] in the second form of Eq. [A-14] yields the following total current expression:

$$j_{HOR}=2F\left(\nu_T+\nu_H\right)=2F\nu_{0T}\left[\left(\frac{1-\theta}{1-\theta_0}\right)^2-\left(\frac{\theta}{\theta_0}\right)^2\right]+ \\ +2F\nu_{0H}\left[\left(\frac{1-\theta}{1-\theta_0}\right)exp\left(\frac{(1-\alpha)F\eta}{RT}\right)-\left(\frac{\theta}{\theta_0}\right)exp\left(\frac{-\alpha F\eta}{RT}\right)\right] \tag{A-15}$$

This is the same current as the numerator of Wang et al.'s Eq. [15] except for the equilibrium potential terms in the exponential. Their derivation assumes negligible proton concentration change due to high proton concentration in the acid electrolyte.

To rewrite the kinetic current equation in terms of exchange current densities we multiply the equilibrium rate equations [A-7] and [A-11] by $2F$:

$$2F\nu_{0T}=2Fk_T c_{H2}^{OHP}\left(1-\theta_0\right)^2=j_{0T}S\left(1-\theta_0\right)^2 \tag{A-16}$$

$$2F\nu_{0H}=2Fk_H c_{H2}^{OHP}\,exp\left(\frac{(1-\alpha)F\Delta\psi_{eq}}{RT}\right)\left(1-\theta_0\right)=j_{0H}S\left(1-\theta_0\right) \tag{A-17}$$

where $S\equiv\frac{c_{H2}^{OHP}}{c_{H2}^{ref}}\frac{real\ Pt\ SA}{electrode\ geometric\ SA}=P^rA^r$, c_{H2}^{ref} is the saturated concentration of H_2 under 1 atm- the concentration of hydrogen for which Chen and Kucernak[2] measured exchange current density, P^r is the actual pressure ratio. The exchange current densities obtained by Chen and Kucernak and Wang et al. are defined as:

$$j_{0T}=2Fk_T c_{H2}^{ref} \tag{A-18}$$

$$j_{0H}=2Fk_H c_{H2}^{ref}\,exp\left(\frac{(1-\alpha)F\Delta\psi_{eq}}{RT}\right) \tag{A-19}$$

We rewrite the total current in Eq. [A-15] with the exchange current densities:

$$j_{HOR}=Sj_{0T}\left[(1-\theta)^2-(1-\theta_0)^2\left(\frac{\theta}{\theta_0}\right)^2\right]+ \\ +Sj_{0H}\left[(1-\theta)exp\left(\frac{(1-\alpha)F\eta}{RT}\right)-(1-\theta_0)\left(\frac{\theta}{\theta_0}\right)exp\left(\frac{-\alpha F\eta}{RT}\right)\right] \tag{A-20}$$

The next step is relating the ratio of intermediate coverage to its value at equilibrium, θ/θ_0 to the potential. We use the expression derived in Wang et al.'s appendix, which requires the assumption of a fast Volmer step relative to the Tafel and Heyrovsky steps:

$$\frac{\theta}{\theta_0} = \frac{exp\left(-F\eta/\gamma RT\right)}{1-\theta_0+\theta_0\, exp\left(-F\eta/\gamma RT\right)} \qquad \text{[A-21]}$$

where γ is the potential range constant found with the three reaction exchange rates.

Since the values of θ and θ_0 are much smaller than 1, we approximate the $1-\theta$ and $1-\theta$ terms in Eq. [A-20] as 1. By substituting the Eq. [A-21] into the current equation [A-20] we get the following current equation:

$$\begin{aligned} j_{HOR} = Sj_{0T}&\left[1-\left(\frac{exp\left(-F\eta/\gamma RT\right)}{1-\theta_0+\theta_0\, exp\left(-F\eta/\gamma RT\right)}\right)^2\right]+ \\ +Sj_{0H}&\left[exp\left(\frac{(1-\alpha)F\eta}{RT}\right)-exp\left(\frac{-\alpha F\eta}{RT}\right)\frac{exp\left(-F\eta/\gamma RT\right)}{1-\theta_0+\theta_0\, exp\left(-F\eta/\gamma RT\right)}\right] \end{aligned} \qquad \text{[A-22]}$$

Now we develop an expression for the equilibrium potential for evaluating the overpotential. Since the overpotential terms are arrived at through an initial expression for the Heyrovsky reaction step, we consider the equilibrium potential for the Heyrovsky step rather than the overall HOR. At equilibrium, the electrochemical potential, $\bar{\mu}$ for the reactants and products is equal between the reactants and products. In the case of the Heyrovsky step, this equality can be written as:

$$\mu_{H2}+\bar{\mu}_{1-\theta} = \bar{\mu}_{\theta}+\bar{\mu}_{H+}+\bar{\mu}_{e} \qquad \text{[A-23]}$$

where the subscripts indicate the species and μ is the chemical potential (hydrogen is uncharged therefore its electrochemical potential is equal to chemical potential). For charged species *i*, the electrochemical potential can be expressed as: $\bar{\mu}_i = \mu_i + nF\psi$. Where ψ corresponds to potential of a plane where the species are located. Using this property and rearranging Eq. [A-23] yields:

$$\Delta\psi_{eq} = \left(\psi_m - \psi_{OHP}\right) = \frac{1}{nF}\left(\mu_\theta - \mu_{1-\theta} + \mu_{H+} + \mu_e - \mu_{H2}\right) \qquad \text{[A-24]}$$

Next, we relate chemical potentials to standard-state chemical potentials, μ_i^0 and species activities, a_i using the property: $\mu_i = \mu_i^0 + RT\, ln\, a_i$. We substitute this property into Eq. [A-24] to get:

$$\begin{aligned} \Delta\psi_{eq} &= \frac{1}{nF}\left(\mu_\theta^0 - \mu_{1-\theta}^0 + \mu_{H+}^0 + \mu_e^0 - \mu_{H2}^0\right) \\ &+\frac{RT}{nF} ln\, a_{H+} - \frac{RT}{nF} ln\, a_{H2} + \frac{RT}{nF} ln\, a_{\theta,0} + \frac{RT}{nF} ln\, a_{1-\theta,0} \end{aligned} \qquad \text{[A-25]}$$

Using a dilute, ideal solution approximation by assuming the activity of species *i* to be equal to the ratio of actual concentration to that at the standard-state conditions ($a_i = c_i / c_i^0$) we rearrange the Eq. [A-25] to become:

$$\Delta\psi_{eq} = \frac{1}{nF}\left(\mu_\theta^0 - \mu_{1-\theta}^0 + \mu_{H+}^0 + \mu_e^0 - \mu_{H2}^0\right) + \frac{RT}{nF} ln\left(\frac{c_{H+}^{OHP} / c_{H+}^0}{c_{H2}^{OHP} / c_{H2}^0}\right) + \frac{RT}{nF} ln\left(\frac{\theta_0}{1-\theta_0}\right) - \frac{RT}{nF} ln\left(\frac{\theta_{std}}{1-\theta_{std}}\right) \quad \text{[A-26]}$$

Next we relate $\theta_0 / 1 - \theta_0$ to the free energy change of adsorption following the equilibrium condition for the Tafel elementary step:

$$\mu_{H2} + 2\mu_{1-\theta} = 2\mu_\theta \quad \text{[A-27]}$$

We proceed with the same analysis as was done between Eq. [A-23] and Eq. [A-25] to arrive at the following equation:

$$\frac{1}{nF}\left(\frac{1}{2}\mu_{H2}^0 + \mu_{1-\theta}^0 - \mu_\theta^0\right) = RT\, ln\left(\frac{a_{\theta,0}}{a_{1-\theta,0}}\right) - RT\, ln\, a_{H2,0} \quad \text{[A-28]}$$

We define standard adsorption free energy, $\Delta G_{ad,0}$ as the combination of standard energies for hydrogen dissociative adsorption:

$$\Delta G_{ad,0} = \frac{1}{2}\mu_{H2}^0 + \mu_{1-\theta}^0 - \mu_\theta^0 \quad \text{[A-29]}$$

The standard adsorption potential is then $\Delta\psi_{ad,0} = -\Delta G_{ad,0} / nF$. Inputting Eq. [A-29] into Eq. [A-28], using $a_i = c_i / c_i^0$ and then rearranging results in the expression for equilibrium intermediate isotherm in terms of hydrogen concentration, intermediate isotherm at the standard-state conditions and adsorption free energy:

$$\frac{\theta_0}{1-\theta_0} = exp\left(\frac{-\Delta G_{ad,0}}{RT}\right)\frac{c_{H2}^{OHP}}{c_{H2}^0}\frac{\theta_{std}}{1-\theta_{std}} \quad \text{[A-30]}$$

We now insert Eq. [A-30] and then Eq. [A-29] into Eq. [A-26] for the Heyrovsky step's equilibrium potential.

$$\Delta\psi_{eq} = \frac{1}{nF}\left(\mu_{H+}^0 + \mu_e^0 - \frac{1}{2}\mu_{H2}^0\right) + \frac{RT}{nF} ln\left(\frac{c_{H+}^{OHP}}{c_{H+}^0}\right) \quad \text{[A-31]}$$

Observing that the first term is the standard-state potential for one-step HOR (0 V), we arrive at the following equation for the equilibrium potential for the Heyrovsky step:

$$\Delta\psi_{eq} = \frac{RT}{nF} ln\left(\frac{c_{H+}^{OHP}}{c_{H+}^{0}}\right) \qquad [A-32]$$

Thus the equilibrium potential of the Heyrovsky step depends on proton concentration only. If the concentration of protons remains on the order of magnitude of the standard-state, the equilibrium potential would be 0 V. However, as mentioned before, this is not the case for water-filled pores. Inserting the above equation into the Heyrovsky-Volmer exchange current, Eq. [A-19], we get:

$$j_{0H} = 2Fk_H c_{H2}^{ref}\left(\frac{c_{H+}^{OHP}}{c_{H+}^{0}}\right)^{1-\alpha} \qquad [A-33]$$

To derive the final equation for the HOR current we input exchange current densities – Eq. [A-18] and Eq. [A-33] into Eq. [A-22] for the total current and rearrange to arrive at Eq. [26]:

$$\begin{aligned} j_{HOR} = {} & 2Fk_T c_{H2}^{OHP}\left[1-\left(\frac{exp(-F\eta/\gamma RT)}{1+\theta_0\, exp(-F\eta/\gamma RT)}\right)^2\right]+ \\ & +2Fk_H c_{H2}^{OHP}\left(\frac{c_{H+}^{OHP}}{c_{H+}^{0}}\right)^{1-\alpha}\left[exp\left(\frac{(1-\alpha)F\eta}{RT}\right)-\frac{exp\left(-\left(\alpha+\gamma^{-1}\right)F\eta/RT\right)}{1+\theta_0\, exp(-F\eta/\gamma RT)}\right] \end{aligned} \qquad [A-34]$$

References:

1. Wang, J. X.; Springer, T. E.; Adzic, R. R. *J. Electrochem. Soc.* **2006,** *153,* A1732-A1740.
2. Chen, S. L.; Kucernak, A. *J. Phys. Chem. B* **2004,** *108,* 13984-13994.