Supporting Information: Tafel-Volmer Electrode Reactions: The Influence of Electron Transfer Kinetics

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I Application of Surface Coverage or Fractional Surface Coverage in Rate Equations

If $\Gamma_{H(ads)}/\Gamma_{max}$ is applied to represent the amount of surface-bonded species, the rate equations (dimensional) for the three reactive species are:

\[ j_{H_2} = -D_{H_2} \frac{\partial c_{H_2}(r, z = 0, t)}{\partial z} = -k_a\left[ c_{H_2}(r, z = 0, t) \right]\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right]^2 + k_d\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right]^2 \] (S1)

\[ \frac{\partial \Gamma_{H(ads)}(r, t)}{\partial t} = 2k_a\left[ c_{H_2}(r, z = 0, t) \right]\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right]^2 - 2k_d\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right]^2 - k_{ox}\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right] + k_{red}\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right]\left[ c_{H^+}(r, z = 0, t) \right] \] (S2)

\[ j_{H^+} = -D_{H^+} \frac{\partial c_{H^+}(r, z = 0, t)}{\partial z} = k_{ox}\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right] - k_{red}\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right]\left[ c_{H_2}(r, z = 0, t) \right] \] (S3)

where $k_a$ (m s$^{-1}$), $k_d$ (mol m$^2$ s$^{-1}$), $k_{ox}$ (mol m$^2$ s$^{-1}$) and $k_{red}$ (m s$^{-1}$) are defined as combined parameters (combined with $\Gamma_{max}$). The rate equations used in the main text are defined in this way and all the parameters mentioned in discussion are combined with $\Gamma_{max}$.

Alternatively, $\Gamma_{H(ads)}/\Gamma_{max}$ is used, the rate equations become:

\[ j_{H_2} = -D_{H_2} \frac{\partial c_{H_2}(r, z = 0, t)}{\partial z} = -k_{a,n}\left[ c_{H_2}(r, z = 0, t) \right]\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right]^2 + k_{d,n}\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right]^2 \] (S4)

\[ \frac{\partial \Gamma_{H(ads)}(r, t)}{\partial t} = 2k_{a,n}\left[ c_{H_2}(r, z = 0, t) \right]\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right]^2 - 2k_{d,n}\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right]^2 - k_{ox,n}\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right] + k_{red,n}\left[ c_{H^+}(r, z = 0, t) \right]\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right] \] (S5)

\[ j_{H^+} = -D_{H^+} \frac{\partial c_{H^+}(r, z = 0, t)}{\partial z} = k_{ox,n}\left[ \frac{\Gamma_{H(ads)}(r, t)}{\Gamma_{max}} \right] - k_{red,n}\left[ c_{H_2}(r, z = 0, t) \right]\left[ \frac{\Gamma_{M}(r, t)}{\Gamma_{max}} \right] \] (S6)
where \( k_{a,n}, k_{d,n}, k_{ox,n}, k_{red,n} \) are defined as non-combined parameters (independent of \( \Gamma_{\text{max}} \)).

The above two definitions have the same dimensionless rate equations as shown in the main text (Eqs. (31), (32) and (33)). However the expressions for the non-combined and combined dimensionless parameters are different, as listed in Table S1. Among the combined parameters, only \( \gamma \) is related to \( \Gamma_{\text{max}} \) and \( \gamma \) cancels out when the true steady-state condition is achieved. But all the non-combined parameters are dependent on \( \Gamma_{\text{max}} \), which makes the steady-state voltammogram change with different \( \Gamma_{\text{max}} \). Under steady-state conditions, the combined parameters allow investigation of the voltammetric responses of the Tafel-Volmer reaction without assumptions regarding the magnitude of \( \Gamma_{\text{max}} \).

Table S1 Non-combined and combined parameters

<table>
<thead>
<tr>
<th>Non-combined parameters</th>
<th>Combined parameters</th>
<th>Dimensionless non-combined parameters</th>
<th>Dimensionless combined parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{a,n} ) (m(^2) mol(^{-2}) s(^{-1}))</td>
<td>( k_a = k_{a,n} \Gamma_{\text{max}}^2 ) (m s(^{-1}))</td>
<td>( K_{a,n} = \frac{k_{a,n} \Gamma_{\text{max}}^2 \rho}{D_{H_2}} )</td>
<td>( K_a = \frac{k_a \rho}{D_{H_2}} )</td>
</tr>
<tr>
<td>( k_{d,n} ) (m(^2) mol(^{-1}) s(^{-1}))</td>
<td>( k_d = k_{d,n} \Gamma_{\text{max}}^2 ) (mol m(^{-2}) s(^{-1}))</td>
<td>( K_{d,n} = \frac{k_{d,n} \Gamma_{\text{max}}^2 \rho}{D_{H_2} c_{H_2}^*} )</td>
<td>( K_d = \frac{k_d \rho}{D_{H_2} c_{H_2}^*} )</td>
</tr>
<tr>
<td>( k_{ox,n} ) (s(^{-1}))</td>
<td>( k_{ox} = k_{ox,n} \Gamma_{\text{max}} ) (mol m(^{-2}) s(^{-1}))</td>
<td>( K_{ox,n} = \frac{k_{ox,n} \Gamma_{\text{max}} \rho}{D_{H_2} c_{H_2}^*} )</td>
<td>( K_{ox} = \frac{k_{ox} \rho}{D_{H_2} c_{H_2}^*} )</td>
</tr>
<tr>
<td>( k_{red,n} ) (m(^2) mol(^{-1}) s(^{-1}))</td>
<td>( k_{red} = k_{red,n} \Gamma_{\text{max}} ) (m s(^{-1}))</td>
<td>( K_{red,n} = \frac{k_{red,n} \Gamma_{\text{max}} \rho}{D_{H_2} c_{H_2}^*} )</td>
<td>( K_{red} = \frac{k_{red} \rho}{D_{H_2}} )</td>
</tr>
<tr>
<td>( \gamma = \frac{c_{H_2}^* \rho}{\Gamma_{\text{max}}} )</td>
<td>( \gamma = \frac{c_{H_2}^* \rho}{\Gamma_{\text{max}}} )</td>
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</tr>
</tbody>
</table>
II Electron Transfer Rate Constants for the Volmer Reaction

For the Volmer reaction, the reaction rate can be defined as:

\[ j_{\text{H}^-} = k_{\text{ox}} \left( \frac{\Gamma_{\text{H}(\text{ads})}}{\Gamma_{\text{max}}} \right) - k_{\text{red}} c_{\text{H}^+} \left( \frac{\Gamma_{\text{M}}}{\Gamma_{\text{max}}} \right) \]  

(S7)

At equilibrium, the concentration of reactive species should follow the Nernstian relationship:

\[ \exp \left( \frac{F \left( E - E_{\text{H}^+/\text{H}(\text{ads})} \right)}{RT} \right) = \frac{\left( \frac{\Gamma_{\text{M}}}{\Gamma_{\text{max}}} \right) \left( c_{\text{H}^+} / c^0 \right)}{\left( \frac{\Gamma_{\text{H}(\text{ads})}}{\Gamma_{\text{max}}} \right)} \]  

(S8)

and the reaction rate should be zero:

\[ j_{\text{H}^-} = 0 \Leftrightarrow k_{\text{ox}} = \frac{k_{\text{ox}}}{k_{\text{red}}} = \frac{\left( \frac{\Gamma_{\text{M}}}{\Gamma_{\text{max}}} \right) c_{\text{H}^+}}{\left( \frac{\Gamma_{\text{H}(\text{ads})}}{\Gamma_{\text{max}}} \right)} \]  

(S9)

Therefore, from (S8) and (S9), for the Volmer reaction, the oxidative and reductive electron transfer rate constants should follow:

\[ \frac{k_{\text{ox}}}{k_{\text{red}}} = c^0 \exp \left( \frac{F \left( E - E_{\text{H}^+/\text{H}(\text{ads})} \right)}{RT} \right) \]  

(S10)

The above expressions for \( k_{\text{ox}} \) and \( k_{\text{red}} \) reflect the stoichiometry of the reaction and the different standard states defined for solution species and adsorbates. By taking into account the solution non-ideality through the formal potential as well as the variation of the activation energies with the overpotential according to different kinetic models (namely, the Butler-Volmer and Marcus-Hush models), the expressions in the main text are obtained.
III Steady state limiting current for electrochemically reversible Tafel-Volmer reactions and non-reversible reactions following the Butler-Volmer kinetics

Under conditions where the electro-oxidation of H(ads) is so fast that the surface coverage is effectively zero ($\Theta_{\text{H(ads)}} \rightarrow 0$), which is compatible with electrochemically reversible systems and with the Butler-Volmer kinetics at high overpotentials, the electrochemical response is governed by the diffusion of molecular hydrogen and its adsorption on the electrode according to:

$$\frac{\partial C_{\text{H}_2}(R,Z,T)}{\partial T} = d_{\text{H}_2} \left( \frac{\partial^2 C_{\text{H}_2}(R,Z,T)}{\partial R^2} + \frac{1}{R} \frac{\partial C_{\text{H}_2}(R,Z,T)}{\partial R} + \frac{\partial^2 C_{\text{H}_2}(R,Z,T)}{\partial Z^2} \right)$$  \hspace{1cm} (S11)

$$T = 0, \forall R,Z \rightarrow C_{\text{H}_2} = C_{\text{H}_2}^* \hspace{1cm} (S12)$$

$$T > 0, Z = 0, 0 \leq R \leq 1: \quad -d_{\text{H}_2} \left( \frac{\partial C_{\text{H}_2}}{\partial Z} \right)_{Z=0} = -K_s C_{\text{H}_2} \hspace{1cm} (S13)$$

where $d_{\text{H}_2} = 1$ and $C_{\text{H}_2}^* = 1$.

For the steady state conditions considered in this work ($\frac{\partial C_{\text{H}_2}(R,Z,T)}{\partial T} = 0$), the following relationships can be written for the current response$^1$ considering that two electrons are transferred per hydrogen molecule:

$$J_{\text{lim}} = -2 \left( d_{\text{H}_2} \frac{C_{\text{H}_2}^* - C_{\text{H}_2}^{-}}{\delta_{\text{diff}}} \right) = -2K_s C_{\text{H}_2}^{-} \hspace{1cm} (S14)$$

where $C_{\text{H}_2}^{-}$ is the average surface concentration of hydrogen and $\delta_{\text{diff}}^{-}$ is the (average) steady state linear diffusion layer thickness (dimensionless, normalized by the electrode radius) at microdisk electrodes:
\[
\delta_{\text{diff}} = \frac{\pi}{4}
\]  

(S15)

From Eq. (S14), the following expression for \( C_{\text{H}_2}^s \) can be obtained:

\[
C_{\text{H}_2}^s = \frac{1}{1 + \frac{\pi}{4} K_a}
\]  

(S16)

and, by substitution in Eq. (S14), one obtains that the steady state limiting current can be described by:

\[
\frac{J_{\text{lim}}}{J_{\text{diff}}} = \frac{J_{\text{H}_2}}{J_{\text{diff}}} = \frac{\frac{\pi}{4} K_a}{1 + \frac{\pi}{4} K_a}
\]  

(S17)

where \( J_{\text{diff}} \) is the steady state limiting current under diffusion control at microdiscs for a two-electron transfer: \( J_{\text{diff}} = \frac{I_{\text{diff}}}{2\pi \rho F D_{\text{H}_2} c_{\text{H}_2}^*} = \frac{4}{\pi} \). Figure S1 shows the comparison of numerical results with those obtained from Eq. (S17) such that a good agreement (error smaller than 0.3%) is observed in a wide range of adsorption conditions and electron transfer BV kinetics.
Figure S1 Effects of adsorption rate constants on the limiting current. The analytical results are calculated from Eq. (S17). The simulation results are calculated with $K_0 = 10^8$ and $10^{-2}$, $K_d = 10^8$. 
IV Adsorption/Desorption Rate Constants of Figure 6

Table S2 lists the adsorption and desorption rate constants used in the simulation of Figure 6 and Figure 8.

Table S2 Adsorption/desorption rate constants used in Figure 6.

<table>
<thead>
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<th>$K_{\text{ads}}$</th>
<th>$K_a$</th>
<th>$K_d$</th>
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<tbody>
<tr>
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</tr>
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<tr>
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<td>$10^{12}$</td>
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Reference