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Supporting Information

New Challenges of Electrokinetic Study in Investigating the Reaction Mechanism of Electrochemical CO_2 Reduction

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Theoretical Tafel slope and reaction order derivation

As mentioned in the main text, derived theoretical Tafel slopes and reaction order could be used to verify the experimentally acquired electrokinetic results and proposed reaction mechanism. Detailed derivations of Tafel slopes and reaction orders respect to possible rate determining steps during electrochemical conversion of CO_2 to CO and $HCOO^-$ are provided. The derivation was accomplished on the basis of previous reports.[1-3]

Tafel slope and reaction order derivation for CO production

Potential rate determining steps for electrochemical CO_2 conversion to CO has been listed below.

(1) $$* + CO_{2\,(aq)} + e^- \rightleftharpoons CO_2^{\cdot -*}$$

(2) $$CO_2^{\cdot -*} + HCO_3^- \rightleftharpoons COOH^* + CO_3^{2-}$$

(3) $$COOH^* + e^- + HCO_3^- \rightleftharpoons CO^* + H_2O + CO_3^{2-}$$

(4) $$CO^* \rightleftharpoons CO + *$$

Except for a specific rate-limiting step, we assume that all other steps are in quasi-equilibrium as below.

$$K_1 = \frac{\theta_{CO_2^{\cdot -*}}}{\theta^* P_{CO_2}}$$

$$K_2 = \frac{\theta_{COOH^*}\left[CO_3^{2-}\right]}{\theta_{CO_2^{\cdot -*}}\left[HCO_3^-\right]}$$

$$K_3 = \frac{\theta_{CO^*}\left[CO_3^{2-}\right]}{\theta_{COOH^*}\left[HCO_3^-\right]}$$

$$K_4 = \frac{P_{CO}\theta^*}{\theta_{CO^*}}$$

Each electrochemical equilibrium constants are defined as below.

$$K_i = \exp\left(\frac{-\Delta G_i^\circ - n_i F\left(E - E_i^\circ\right)}{RT}\right)$$

For steps (1) and (3), n_1 and n_3 = 1 because there is one-electron transfer. For steps (2) and (4), n_2 and n_4 = 0 because electrons are not involved. During the entire derivation, θ^* refers to active site coverage, P_{CO2} is partial pressure of CO_2, k_i is rate constant, R is the gas constant, T is temperature, and F is Faraday's number.

Reaction (1) as rate determining step

Theoretical Tafel slopes could be derived from the rate expression. Tafel slope is defined as shown below.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{CO}}$$

When, assuming Reaction (1) to be rate-determining steps, the partial current density for CO production is written as followed.

$$j_{CO} = 2Fk_1\theta^* P_{CO_2}\exp\left(-\frac{\beta FE}{RT}\right)$$

We begin by taking log of both sides.

$$\log j_{CO} = \log 2Fk_1 + \log\theta^* + \log P_{CO_2} - \frac{\beta FE}{2.3RT}$$

Expressing partial derivative of the rate expression respect to the electrical potential,

$$\frac{\partial \log j_{CO}}{\partial E} = -\frac{\beta F}{2.3RT} + \frac{\partial \log\theta^*}{\partial E}$$

If we assume $\theta^* \cong 1$,

$$\frac{\partial \log\theta^*}{\partial E} = 0$$

$$\frac{\partial \log j_{CO}}{\partial E} = -\frac{\beta F}{2.3RT}$$

If we take inverse of the expression shown above, we can acquire theoretical Tafel slope.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{CO}} = \frac{2.3RT}{\beta F}\ mV/dec$$

Reaction order can be expressed by partial current density respect to $[HCO_3^-]$ concentration. Temperature, CO_2 partial pressure, and electrical potential are assumed to be constant.

$$Reaction\ order = \frac{\partial \log j_{CO}}{\partial \log\left[HCO_3^-\right]} = 0$$

Reaction (2) as rate determining step

When, assuming Reaction (2) to be rate-determining steps, the partial current density for CO production is written as followed.

$$j_{CO} = 2Fk_2\theta_{CO_2^{\cdot -}}^*\left[HCO_3^-\right]$$

Assuming reaction step (1) to be in fast equilibrium, following relationship could be shown.

$$k_1\theta^* P_{CO_2}\exp\left(-\frac{\beta FE}{RT}\right) = k_{-1}\theta_{CO_2^{\cdot -}}^*\exp\left(\frac{(1-\beta)FE}{RT}\right)$$

From the relationship shown in equilibrium constant K_1, it is possible to express current respect to θ^* and

assuming $\theta^* \cong 1$, partial current can be expressed as followed.

$$j_{CO} = 2Fk_2\frac{k_1}{k_{-1}}P_{CO_2}\left[HCO_3^-\right]\exp\left(-\frac{FE}{RT}\right)$$

Taking log of both sides achieves following term.

$$\log j_{CO} = \log 2Fk_2\frac{k_1}{k_{-1}} + \log P_{CO_2} + \log\left[HCO_3^-\right] - \frac{FE}{2.3RT}$$

With temperature, CO_2 partial pressure, and $[HCO_3^-]$ concentration remaining constant, Tafel slope can be expressed as shown below.

$$\frac{\partial \log j_{CO}}{\partial E} = -\frac{F}{2.3RT}$$

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{CO}} = \frac{2.3RT}{F}\ mV/dec$$

Reaction order could be expressed by partial current density respect to $[HCO_3^-]$ concentration. Since temperature, CO_2 partial pressure, and electrical potential remain constant, reaction order could be derived as shown below.

$$Reaction\ order = \frac{\partial \log j_{CO}}{\partial \log\left[HCO_3^-\right]} = 1$$

Reaction (3) as rate determining step

When assuming Reaction (3) to be rate-determining steps, the partial current density for CO production is written as followed.

$$j_{CO} = 2Fk_3\theta_{COOH}^*\left[HCO_3^-\right]\exp\left(-\frac{\beta FE}{RT}\right)$$

Assuming reaction step (1) and (2) to be in fast equilibrium, and using equilibrium constant K_1 *and* K_2, partial current for CO production could be shown as followed.

$$j_{CO} = 2Fk_3K_2\frac{\left[HCO_3^-\right]^2}{\left[CO_3^{2-}\right]}K_1\theta^* P_{CO_2}\exp\left(-\frac{\beta FE}{RT}\right)$$

In the limiting case where buffer equilibration and/or mass transport are rapid relative to the rate of catalytic turn-over, the following solution equilibrium can be used in order to express the partial current in terms of $[HCO_3^-]$.[1]

$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^- \qquad K_{buffer} = \frac{\left[HCO_3^-\right]^2}{\left[CO_3^{2-}\right]P_{CO_2}}$$

$$j_{CO} = 2Fk_3K_2\left[HCO_3^-\right]^2K_1\theta^* P_{CO_2}\exp\left(-\frac{\beta FE}{RT}\right) * \frac{P_{CO_2}K_{Buffer}}{\left[HCO_3^-\right]^2} = 2Fk_3K_2K_1\theta^* \exp\left(-\frac{\beta FE}{RT}\right) * P_{CO_2}^2K_{Buffer}$$

Taking log of both sides and differentiating respect to potential, it is possible to achieve following term. Noticeably, as shown on given Equilibrium constant of reactions, only K_1 is dependent to potential as it involves electron during the reaction.

$$\frac{\partial \log j_{CO}}{\partial E} = \frac{\partial \log K_1}{\partial E} - \frac{\beta F}{2.3RT} = -\frac{F}{2.3RT} - \frac{\beta F}{2.3RT} = -\frac{F}{2.3RT}(1+\beta)$$

From above equation, Tafel slope could be written as followed.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{CO}} = \frac{2.3RT}{(1+\beta)F}\, mV/dec$$

Reaction order could be expressed by partial current density respect to [HCO_3^-] concentration. Considering temperature, CO_2 partial pressure, and electrical potential to remain constant, reaction order could be shown as below.

$$Reaction\ order = \frac{\partial \log j_{CO}}{\partial \log\left[HCO_3^-\right]} = 0$$

Reaction (4) as rate determining step

When assuming Reaction (4) to be rate-determining steps, the partial current density for CO production is written as followed.

$$j_{CO} = 2Fk_4\theta_{CO^*}$$

Assuming reaction step (1), (2), and (3) to be in fast equilibrium state, and using equilibrium constant for mentioned reactions, surface coverage of CO could be expressed as shown below.

$$\theta_{CO^*} = \frac{K_3\left[HCO_3^-\right]}{\left[CO_3^{2-}\right]} * \frac{K_2\left[HCO_3^-\right]}{\left[CO_3^{2-}\right]} * K_1\theta^* P_{CO_2} = K_3K_2K_1\theta^* P_{CO_2}\frac{P_{CO_2}^2K_{Buffer}^2}{\left[HCO_3^-\right]^2}$$

θ_{CO^*} has been substituted in the partial current term and partial current j_{CO} can been expressed respect to θ^*, active site coverage.

$$j_{CO} = 2Fk_4K_3K_2K_1\theta^* P_{CO_2}\frac{P_{CO_2}^2K_{Buffer}^2}{\left[HCO_3^-\right]^2}$$

Taking log of both sides and differentiating respect to potential, it is possible to achieve following term.

$$\frac{\partial \log j_{CO}}{\partial E} = \frac{\partial \log K_3}{\partial E} + \frac{\partial \log K_1}{\partial E} = -\frac{F}{2.3RT} - \frac{F}{2.3RT} = -\frac{2F}{2.3RT}$$

From above equation, Tafel slope could be written as followed.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{CO}} = \frac{2.3RT}{2F}\ mV/dec$$

Reaction order could be expressed by partial current density respect to [HCO_3^-] concentration. Considering temperature, CO_2 partial pressure, and electrical potential to remain constant, reaction order could be shown as below.

$$Reaction\ order = \frac{\partial \log j_{CO}}{\partial \log \left[HCO_3^-\right]} = \ -2$$

Tafel slope and reaction order derivation for $HCOO^-$ production

Potential rate determining steps for electrochemical CO_2 conversion to $HCOO^-$ has been listed below.

(5) $$* + CO_{2\,(aq)} + e^- \rightleftharpoons CO^{\cdot -*}_2$$

(6) $$CO^{\cdot -*}_2 + HCO^-_3 \rightleftharpoons OCHO^* + CO^{2-}_3$$

(7) $$OCHO^* + e^- \rightleftharpoons HCOO^{-*}$$

(8) $$HCOO^{-*} \rightleftharpoons HCOO^- + *$$

Except for a specific rate-limiting step, we assume that all other steps are in quasi-equilibrium as below.

$$K_5 = \frac{\theta_{CO^{\cdot -*}_2}}{\theta^* P_{CO_2}}$$

$$K_6 = \frac{\theta_{OCHO^*}\left[CO^{2-}_3\right]}{\theta_{CO^{\cdot -*}_2}\left[HCO^-_3\right]}$$

$$K_7 = \frac{\theta_{HCOO^{-*}}}{\theta_{OCHO^*}}$$

$$K_8 = \frac{[HCOO^-]\theta^*}{\theta_{HCOO^{-*}}}$$

Each electrochemical equilibrium constants are defined as below.

$$K_i = \exp\left(\frac{-\Delta G_i^\circ - n_i F\left(E - E_i^\circ\right)}{RT}\right)$$

For steps (5), (7) and , n_5 and n_7 = 1 because there is one-electron transfer. For steps (2) and (4), n_6 and n_8 = 0 because electrons are not involved. During the entire derivation, θ^* refers to active site coverage, P_{CO2} is partial pressure of CO_2, k_i is rate constant, R is the gas constant, T is temperature, and F is Faraday's number.

Reaction (5) as rate determining step

When assuming Reaction (5) to be a rate-determining step, the partial current density for $HCOO^-$ production is written as followed.

$$j_{HCOO^-} = Fk_5\theta^* P_{CO_2}\exp\left(-\frac{\beta FE}{RT}\right)$$

We begin by taking log of both sides.

$$\log j_{HCOO^-} = \log Fk_5 + \log\theta^* + \log P_{CO_2} - \frac{\beta FE}{2.3RT}$$

Expressing partial derivative of the rate expression respect to the electrical potential,

$$\frac{\partial \log j_{HCOO^-}}{\partial E} = -\frac{\beta F}{2.3RT} + \frac{\partial \log \theta^*}{\partial E}$$

If we assume $\theta^* \cong 1$ during the reaction,

$$\frac{\partial \log \theta^*}{\partial E} = 0$$

$$\frac{\partial \log j_{HCOO^-}}{\partial E} = -\frac{\beta F}{2.3RT}$$

If we take inverse of the expression shown above, we can acquire theoretical Tafel slope.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{HCOO^-}} = \frac{2.3RT}{\beta F}\ mV/dec$$

Reaction order could be expressed by partial current density respect to $[HCO_3^-]$ concentration. Since temperature, CO_2 partial pressure, and electrical potential remain constant, reaction order could be derived as shown below.

$$Reaction\ order = \frac{\partial \log j_{HCOO^-}}{\partial \log \left[HCO_3^-\right]} = 0$$

Reaction (6) as rate determining step

When assuming Reaction (6) to be rate-determining steps, the partial current density for $HCOO^-$ production is written as followed.

$$j_{HCOO^-} = 2Fk_6\theta_{CO_2^{\cdot -}}^{*}\left[HCO_3^-\right]$$

Assuming reaction step (5) to be in fast equilibrium, following relationship could be shown.

$$k_5\theta^* P_{CO_2}\exp\left(-\frac{\beta FE}{RT}\right) = k_{-5}\theta_{CO_2^{\cdot -}}^{*}\exp\left(\frac{(1-\beta)FE}{RT}\right)$$

From the relationship shown in equilibrium constant K_5, it is possible to express current respect to θ^* and assuming $\theta^* \cong 1$, partial current can be expressed as followed.

$$j_{HCOO^-} = 2Fk_6\frac{k_5}{k_{-5}}P_{CO_2}\left[HCO_3^-\right]\exp\left(-\frac{FE}{RT}\right)$$

Taking log of both sides achieves following term.

$$\log j_{HCOO^-} = \log 2Fk_6\frac{k_5}{k_{-5}} + \log P_{CO_2} + \log\left[HCO_3^-\right] - \frac{FE}{2.3RT}$$

With temperature, P_{CO_2}, and [HCO_3^-] concentration remaining constant, Tafel slope can be expressed as shown below.

$$\frac{\partial \log j_{HCOO^-}}{\partial E} = -\frac{F}{2.3RT}$$

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{HCOO^-}} = \frac{2.3RT}{F}\ mV/dec$$

Reaction order could be expressed by partial current density respect to [HCO_3^-] concentration. Since temperature, CO_2 partial pressure, and electrical potential remain constant, reaction order could be derived as shown below.

$$Reaction\ order = \frac{\partial \log j_{HCOO^-}}{\partial \log \left[HCO_3^-\right]} = 1$$

Reaction (7) as rate determining step

When assuming Reaction (7) to be rate-determining steps, the partial current density for $HCOO^-$ production is written as followed.

$$j_{HCOO^-} = 2Fk_7\theta_{OCHO^*} \exp\left(-\frac{\beta FE}{RT}\right)$$

Assuming reaction step (5) and (6) to be in fast equilibrium, and using equilibrium constant K_5 *and* K_6, partial current for $HCOO^-$ production could be shown as followed.

$$j_{HCOO^-} = 2Fk_7K_6K_5P_{CO_2}\theta^* \frac{\left[HCO_3^-\right]}{\left[CO_3^{2-}\right]} \exp\left(-\frac{\beta FE}{RT}\right)$$

In the limiting case where buffer equilibration and/or mass transport are rapid relative to the rate of catalytic turn-over, the following solution equilibrium can be used in order to express the partial current in terms of [HCO_3^-].[1]

$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^- \qquad K_{buffer} = \frac{\left[HCO_3^-\right]^2}{\left[CO_3^{2-}\right]P_{CO_2}}$$

$$j_{HCOO^-} = 2Fk_7K_6K_5\theta^* \frac{P_{CO_2}^2 K_{buffer}}{\left[HCO_3^-\right]} \exp\left(-\frac{\beta FE}{RT}\right)$$

Taking log of both sides and differentiating respect to potential, it is possible to achieve following term.

$$\frac{\partial \log j_{HCOO^-}}{\partial E} = \frac{\partial \log K_5}{\partial E} - \frac{\beta F}{2.3RT} = -\frac{F}{2.3RT} - \frac{\beta F}{2.3RT} = -\frac{F}{2.3RT}(1+\beta)$$

From above equation, Tafel slope could be written as followed.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{HCOO^-}} = \frac{2.3RT}{(1+\beta)F} mV/dec$$

Reaction order could be expressed by partial current density respect to [HCO_3^-] concentration. Considering temperature, CO_2 partial pressure, and electrical potential to remain constant, reaction order could be shown as below.

$$Reaction\ order = \frac{\partial \log j_{HCOO^-}}{\partial \log \left[HCO_3^-\right]} = -1$$

Reaction (6+7) as rate determining step

(6+7) $$CO_2^{\cdot -*} + HCO_3^- + e^- \rightleftharpoons HCOO^{-*} + CO_3^{2-}$$

Reaction (6+7) indicates simultaneous involvement of both proton and electron during the rate-determining step, which is combination of reaction (6) and reaction (7). When assuming Reaction (6+7) to be rate-determining steps, the partial current density for $HCOO^-$ production is written as follows.

$$j_{HCOO^-} = 2Fk_{6+7}\theta_{CO_2^{\cdot -*}}\left[HCO_3^-\right]\exp\left(-\frac{\beta FE}{RT}\right)$$

Assuming reaction step (5) to be in fast equilibrium, following relationship could be shown. From equilibrium constant K_5, it is possible to express current respect to θ^*.

$$j_{HCOO^-} = 2Fk_{6+7}K_5P_{CO_2}\theta^*\left[HCO_3^-\right]\exp\left(-\frac{\beta FE}{RT}\right)$$

Taking log of both sides and differentiating respect to potential, it is possible to achieve following term.

$$\frac{\partial \log j_{HCOO^-}}{\partial E} = \frac{\partial \log K_5}{\partial E} - \frac{\beta F}{2.3RT} = -\frac{F}{2.3RT} - \frac{\beta F}{2.3RT} = -\frac{F}{2.3RT}(1+\beta)$$

From above equation, Tafel slope could be written as followed.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{HCOO^-}} = \frac{2.3RT}{(1+\beta)F} mV/dec$$

Reaction order could be expressed by partial current density respect to [HCO_3^-] concentration. Considering temperature, CO_2 partial pressure, and electrical potential to remain constant, reaction order could be shown as below.

$$Reaction\ order = \frac{\partial \log j_{HCOO^-}}{\partial \log \left[HCO_3^-\right]} = 1$$

Reaction (8) as rate determining step

When assuming Reaction (8) to be rate-determining steps, the partial current density for $HCOO^-$ production is

written as followed.

$$j_{HCOO^-} = 2Fk_8\theta_{HCOO^{-*}}$$

Assuming reaction steps (5) and (6+7) to be in fast equilibrium state, and using equilibrium constant for mentioned reactions, surface coverage of $HCOO^-$ could be expressed as shown below.

$$\theta_{CO_2^{\cdot-*}} = K_5 P_{CO_2}\theta^*$$

$$k_{(6+7)}\theta_{CO_2^{\cdot-*}}\left[HCO_3^-\right]\exp\left(-\frac{\beta FE}{RT}\right) = k_{-(6+7)}\theta_{HCOO^{-*}}\left[CO_3^{2-}\right]\exp\left(\frac{(1-\beta)FE}{RT}\right)$$

$$\theta_{HCOO^{-*}} = \frac{K_5 P_{CO_2}\theta^*\left[HCO_3^-\right]}{\left[CO_3^{2-}\right]}\frac{k_{(6+7)}}{k_{-(6+7)}}\exp\left(-\frac{FE}{RT}\right)$$

$\theta_{HCOO^{-*}}$ has been substituted in the partial current term and partial current j_{HCOO^-} can been expressed respect to θ^*, active site coverage.

$$j_{HCOO^-} = 2Fk_8\frac{K_5 P_{CO_2}\theta^*\left[HCO_3^-\right]}{\left[CO_3^{2-}\right]}\frac{k_{(6+7)}}{k_{-(6+7)}}\exp\left(-\frac{FE}{RT}\right)$$

In the limiting case where buffer equilibration and/or mass transport are rapid relative to the rate of catalytic turn-over, the following solution equilibrium can be used in order to express the partial current in terms of $[HCO_3^-]$.[1]

$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^- \qquad K_{buffer} = \frac{\left[HCO_3^-\right]^2}{\left[CO_3^{2-}\right]P_{CO_2}}$$

$$j_{HCOO^-} = 2Fk_8K_5\theta^*\frac{k_{(6+7)}}{k_{-(6+7)}}\exp\left(-\frac{FE}{RT}\right)\frac{P_{CO_2}^2 K_{Buffer}}{\left[HCO_3^-\right]}$$

Taking log of the current term and differentiating respect to potential, it is possible to achieve following term.

$$\frac{\partial \log j_{HCOO^-}}{\partial E} = \frac{\partial \log K_5}{\partial E} - \frac{F}{2.3RT} = -\frac{F}{2.3RT} - \frac{F}{2.3RT} = -\frac{2F}{2.3RT}$$

From above equation, Tafel slope could be written as followed.

$$Tafel\ slope = \frac{\partial(-E)}{\partial \log j_{HCOO^-}} = \frac{2.3RT}{2F}\ mV/dec$$

Reaction order could be expressed by partial current density respect to $[HCO_3^-]$ concentration. Considering temperature, CO_2 partial pressure, and electrical potential to remain constant, reaction order could be shown as below.

$$Reaction\ order = \frac{\partial \log j_{HCOO^-}}{\partial \log \left[HCO_3^-\right]} = -1$$

Supplementary References

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