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Supplementary Information

Towards a Generic Understanding of Oxygen Evolution Reaction Kinetics in Polymer Electrolyte Water Electrolysis

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Oxygen evolution reaction mechanism

The reaction rate as well as equilibrium equations for a considered rds are deduced for quasi equilibrium. A general example is given below.

Reaction

$$vA + B \rightleftharpoons C + n e^{-} \tag{1}$$

Reaction rate for product c

$$\frac{\partial c_c}{\partial t} = \frac{j}{nF} = k_{\pm 1} c_A^{\nu} c_B e^{\frac{F\beta}{RT}E}$$
(2)

Quasi-equilibrium

$$n F k_{+1} c_A^{\nu} c_B e^{\frac{\beta F}{RT}E} = n F k_{-1} c_C e^{\frac{-(1-\beta)F}{RT}E}$$
(3)

$$K c_A^{\nu} c_B e^{\frac{F}{RT}E} = c_c \tag{4}$$

The reaction rates and reaction orders of hydrogen and oxygen were determined for every reaction step of the four proposed mechanism in literature considering present step is the theoretical rate determining step.

Bockris's Oxide Path (BOP)

$$\mathbf{H}_{2}\mathbf{O} \leftrightarrow \mathbf{O}\mathbf{H}^{*} + \mathbf{e}^{-} + \mathbf{H}^{+}$$
(5.1)

$$n F k_{+1} (1 - \theta_{OH}) c_{H_2O} e^{\frac{\beta F}{RT}E} = n F k_{-1} \theta_{OH} c_{H^+} e^{\frac{-(1 - \beta)F}{RT}E}$$
(5.2)

$$K_1 \ \frac{c_{H_2O}}{c_{H^+}} \ e^{\frac{F}{RT}E} = \frac{\theta_{OH}}{(1-\theta_{OH})}$$
(5.3)

$$i = n F k_{+1} (1 - \theta_{0H}) c_{H_2 O} e^{\frac{F\beta}{RT}E}$$
(5.4)

$$20H^* \leftrightarrow 0^* + H_2 0 \tag{6.1}$$

$$n F k_{+2} \theta_{0H}^{2} = n F k_{-2} \theta_{0} c_{H_{2}0}$$
(6.2)

$$K_2 \ \frac{1}{c_{H_2O}} = \frac{\theta_O}{\theta_{OH}^2}$$
(6.3)

$$i = n F k_{+2} \left((1 - \theta_{OH}) K_1 \frac{c_{H_2O}}{c_{H^+}} e^{\frac{F}{RT}E} \right)^2$$
(6.4)

$$i = n F k_{+2} (1 - \theta_{OH})^2 K_1^2 \frac{c_{H_2O}^2}{c_{H^+}^2} e^{\frac{2F}{RT}E}$$
(6.5)

$$\mathbf{20}^* \leftrightarrow \mathbf{0}_2 \tag{7.1}$$

$$i = n F k_{+3} \left(K_2 \frac{1}{c_{H_2O}} * (1 - \theta_{OH})^2 K_1^2 \frac{c_{H_2O}^2}{c_{H^+}^2} e^{\frac{2F}{RT}E} \right)^2$$
(7.2)

$$i = n F k_{+3} K_2^2 K_1^4 (1 - \theta_{OH})^4 \frac{c_{H_2O^2}}{c_{H^+}^4} e^{\frac{4F}{RT}E}$$
(7.3)

Bockris's Electrochemical Oxide Path (BEOP)

$$\mathbf{H}_{2}\mathbf{0} \leftrightarrow \mathbf{O}\mathbf{H}^{*} + \mathbf{e}^{-} + \mathbf{H}^{+}$$

$$(8.1)$$

The reaction rate and equilibrium equations are consistent with Eqs. 5.1 to 5.4

$$\mathbf{OH}^* \leftrightarrow \mathbf{O}^* + \mathbf{e}^- + \mathbf{H}^+ \tag{9.1}$$

$$n F k_{+2} \theta_{OH} e^{\frac{\beta F}{RT}E} = n F k_{-2} \theta_{O} c_{H^{+}} e^{\frac{-(1-\beta)F}{RT}E}$$
(9.11)

$$K_2 \quad \frac{1}{c_{\mathrm{H}^+}} e^{\frac{F}{RT}E} = \frac{\theta_O}{\theta_{OH}} \tag{9.12}$$

$$i = n F k_{+2} K_1 (1 - \theta_{OH}) \frac{c_{H_2O}}{c_{H^+}} e^{\frac{(1 + \beta)F}{RT}E}$$
(9.13)

$$\mathbf{20}^* \leftrightarrow \mathbf{0}_{\mathbf{2}} \tag{10.1}$$

$$i = n F k_{+3} \left(K_2 \frac{1}{c_{H^+}} e^{\frac{F}{RT}E} * K_1 \frac{c_{H_2O}}{c_{H^+}} e^{\frac{F}{RT}E} * (1 - \theta_{OH}) \right)^2$$
(10.11)

$$i = n F k_{+3} K_2^2 K_1^2 (1 - \theta_{OH})^2 \frac{c_{H_2 O}^2}{c_{H^+}^4} e^{\frac{4F}{RT}E}$$
(10.12)

Krasil`shchkov's Path (KP)

$$\mathbf{H}_{2}\mathbf{0} \leftrightarrow \mathbf{0}\mathbf{H}^{*} + \mathbf{e}^{-} + \mathbf{H}^{+}$$
(11.1)

The reaction rate and equilibrium equations are consistent with Eqs. 5.1 to 5.4

$$\mathbf{OH}^* \leftrightarrow \mathbf{O}^{-*} + \mathbf{H}^+ \tag{12.1}$$

$$n F k_{+2} \theta_{OH} e^{\frac{\beta F}{RT}E} = n F k_{-2} \theta_{O^-} c_{H^+} e^{\frac{-(1-\beta)F}{RT}E}$$
(12.11)

$$K_2 \quad \frac{1}{c_{H^+}} e^{\frac{F}{RT}E} = \frac{\theta_{O^-}}{\theta_{OH}}$$
(12.12)

$$i = n F k_{+2} K_1 (1 - \theta_{OH}) \frac{c_{H_2O}}{c_{H^+}} e^{\frac{(1 + \beta)F}{RT}E}$$
(12.13)

$$\mathbf{0}^{-*} \leftrightarrow \mathbf{0}^{*} + \mathbf{e}^{-} \tag{13.1}$$

$$n F k_{+3} \theta_{0^{-}} e^{\frac{\beta F}{RT}E} = n F k_{-3} \theta_{0^{*}} e^{\frac{-(1-\beta)F}{RT}E}$$
(13.11)

$$K_3 \quad e^{\frac{F}{RT}E} = \frac{\theta_{O^*}}{\theta_{O^-}} \tag{13.12}$$

$$i = n F k_{+3} e^{\frac{\beta F}{RT}E} K_2 \frac{1}{c_{H^+}} e^{\frac{F}{RT}E} K_1 (1 - \theta_{OH}) \frac{c_{H_2O}}{c_{H^+}} e^{\frac{F}{RT}E}$$
(13.13)

$$i = n F k_{+3} K_2 K_1 (1 - \theta_{OH}) \frac{c_{H_2O}}{c_{H^+}^2} e^{\frac{(2 + \beta)F}{RT}E}$$
(13.14)

$$\mathbf{20}^* \leftrightarrow \mathbf{0}_{\mathbf{2}} \tag{14.1}$$

$$i = n F k_{+4} \left(K_3 \ e^{\frac{F}{RT}E} * K_2 \ \frac{1}{c_{H^+}} \ e^{\frac{F}{RT}E} * K_1 \ \frac{c_{H_2O}}{c_{H^+}} \ e^{\frac{F}{RT}E} (1 - \theta_{OH}) \right)^2$$
(14.11)

$$i = n F k_{+4} K_3^2 K_2^2 K_1^2 (1 - \theta_{OH})^2 \frac{c_{H_2O}^2}{c_{H^+}^4} e^{\frac{6F}{RT}E}$$
(14.12)

Wade and Hackerman's Path (WHP)

$$2H_2O \leftrightarrow O^* + H_2O^* + 2e^- + 2H^+$$
(15.1)

$$n F k_{+1} \left(1 - \theta_0 - \theta_{H_2 0}\right) c_{H_2 0}^2 e^{\frac{\beta F}{RT} E} = n F k_{-1} \theta_0 \theta_{H_2 0} c_{H^+}^2 e^{\frac{-(1 - \beta) F}{RT} E}$$
(15.11)

$$K_1 \ \frac{c_{H_2O}^2}{c_{H^+}^2} \ e^{\frac{F}{RT}E} = \frac{\theta_0 \ \theta_{H_2O}}{(1 - \theta_0 - \theta_{H_2O})}$$
(15.12)

$$i = n F k_{+1} \left(1 - \theta_0 - \theta_{H_2 0}\right) c_{H_2 0}^2 e^{\frac{\beta F}{RT} E}$$
(15.13)

$$\mathbf{0}^* + \mathbf{20H}^{-*} \leftrightarrow \mathbf{H}_2\mathbf{0}^* + \mathbf{0}_2 + \mathbf{2e}^- \tag{16.1}$$

$$i = n F k_{+2} \theta_{0H^{-2}} K_1 \frac{(1 - \theta_0 - \theta_{H_20})}{\theta_{H_20}} \frac{c_{H_20^2}}{c_{H^{+2}}} e^{\frac{(1 + \beta)F}{RT}E}$$
(16.11)

Rossmeisl's peroxide path (RPP)

$$2H_2O \leftrightarrow H_2O + HO^* + e^- + H^+$$
(17.1)

The reaction rate and equilibrium equations are consistent with Eqs. 5.1 to 5.4

$$H_2O + HO^* + e^- + H^+ \leftrightarrow H_2O + O^* + 2e^- + 2H^+$$
 (18.1)

The reaction rate and equilibrium equations are consistent with Eqs. 9.1 to 9.13.

$$H_2O + O^* + 2e^- + 2H^+ \leftrightarrow HOO^* + 3e^- + 3H^+$$
 (19.1)

$$n F k_{+3} \theta_0 c_{H_2 0} e^{\frac{\beta F}{RT}E} = n F k_{-3} \theta_{\text{OOH}} c_{H^+} e^{\frac{-(1-\beta)F}{RT}E}$$
(19.11)

$$K_3 \frac{c_{H_2O}}{c_{H^+}} e^{\frac{F}{R_T}E} = \frac{\theta_{\text{OOH}}}{\theta_O}$$
(19.12)

$$i = n F k_{+3} c_{H_{20}} e^{\frac{\beta F}{RT}E} K_2 \frac{1}{c_{H^+}} e^{\frac{F}{RT}E} K_1 \frac{c_{H_{20}}}{c_{H^+}} e^{\frac{F}{RT}E} (1 - \theta_{OH})$$
(19.13)

$$i = n F k_{+3} K_2 K_1 (1 - \theta_{OH}) \frac{c_{H_2 O^2}}{c_{H^+}^2} e^{\frac{(2 + \beta)F}{RT}E}$$
(19.14)

$$HOO^* + 3e^- + 3H^+ \leftrightarrow O_2 + 4e^- + 4H^+$$
 (20.1)

$$i = n F k_{+4} e^{\frac{\beta F}{RT}E} K_3 \frac{c_{H_2O}}{c_{H^+}} e^{\frac{F}{RT}E} K_2 \frac{1}{c_{H^+}} e^{\frac{F}{RT}E} K_1 \frac{c_{H_2O}}{c_{H^+}} e^{\frac{F}{RT}E} (1 - \theta_{OH})$$
(20.11)

$$i = n F k_{+4} K_3 K_2 K_1 (1 - \theta_{OH}) \frac{c_{H_2 O^2}}{c_{H^+}{}^3} e^{\frac{(3 + \beta)F}{RT}E}$$
(20.12)

Temperature dependence of Tafel slope b

The experimentally determined Tafel slopes in dependence of temperature and loading are shown in Figure S1.



Figure S1. Tafel slope as function of loading and temperature.

Loading dependence of the kinetic regime

The iR-free cell voltages are plotted in a semi-logarithmic plot in the kinetic governed regime for loading between 1.0 to 3.0 mg cm⁻². A decrease of kinetic overpvoltages for higher loadings can be observed which is related to higher apparent exchange current densities scaling proportionally with kinetic active sites. Decreasing the cell temperature from 80°C (Figure a) to 70°C (Figure b) an increase in iR-free cell voltages is observed due to a shift in Nernst voltage as well as increased kinetic losses.



Figure S2. iR-free cell voltage curves in dependence of loading at 80 °C and 70 °C are shown in Figure a) and b) respectively.