Supporting Information

Light-intensity dependence analysis to uncover multielectron oxygen-reduction mechanism by platinum-loaded tungsten oxide

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Derivation of rate equations

Based on the assumed rate equations (3)-(9), the overall-rate equation (10) was derived assuming steady-state approximation for the short-lived intermediates as follows:

<PC>(1e$^-$): $$I_L\psi_0\Phi - I_L\psi_1\Phi[<PC>(1e^-)] - k_d[<PC>(1e^-)] = 0 \quad \text{(a)}$$

<PC>(2e$^-$): $$I_L\psi_1\Phi[<PC>(1e^-)] - k_r[<PC>(2e^-)][RH] = 0 \quad \text{(b)}$$

R•: $$k_r[<PC>(2e^-)][RH] - k_i[R\bullet][O_2] + k_p[RO_2\bullet][RH] = 0 \quad \text{(c)}$$

RO_2•: $$k_i[R\bullet][O_2] - k_p[RO_2\bullet][RH] - k_t[RO_2\bullet]^2 = 0 \quad \text{(d)}$$

Then, these equations could be converted to:

(a): $$[<PC(1e^-)>] = I_L\psi_0\Phi\,/\,(I_L\psi_1\Phi + k_d) \quad \text{(e)}$$

(b): $$[<PC(2e^-)>] = (I_L\psi_1\Phi\,/\,k_r[RH])\,I_L\psi_0\Phi\,/\,(I_L\psi_1\Phi + k_d) \quad \text{(f)}$$

(c): $$k_i[R\bullet][O_2] = k_r[<PC>(2e^-)][RH] + k_p[RO_2\bullet][RH]$$

$$= \frac{I_L^2\psi_0\psi_1\Phi^2}{(I_L\psi_1\Phi + k_d)} + k_p[RO_2\bullet][RH] \quad \text{(g)}$$

(d): $$k_i[R\bullet][O_2] - k_p[RO_2\bullet][RH] = k_t[RO_2\bullet]^2$$

$$[RO_2\bullet] = \left\{\frac{I_L^2\psi_0\psi_1\Phi^2}{k_t(I\psi_1\Phi + k_d)}\right\}^{0.5} \quad \text{(h)}$$

The overall rate (r) of [RH] consumption is:

$$r = k_r[<PC>(2e^-)][RH] + k_p[RO_2\bullet][RH] = \frac{I_L^2\psi_0\psi_1\Phi^2}{k_t(I_L\psi_1\Phi + k_d)} + k_p[RH]\left\{\frac{I_L^2\psi_0\psi_1\Phi^2}{k_t(I\psi_1\Phi + k_d)}\right\}^{0.5} \quad (10)$$

The reason why a rate constant k_r is not included in the overall rate is that <PC>(2e$^-$) is consumed immediately after creation, i.e., the rate of creation is the same as the rate of consumption to produce R• without depending on k_r and [RH] as described in eq. (b). In other words, assuming the complete consumption of <PC>(2e$^-$) means eq. (c) is shown as eq (c') without application of steady-state approximation to [<PC>(2e$^-$)]:

R•: $$I_L\psi_1\Phi[<PC>(1e^-)] - k_i[R\bullet][O_2] + k_p[RO_2\bullet][RH] = 0 \quad \text{(c')}$$