Supporting Information

Self-Healing Catalysis in Water

Short Title: Self-healing catalysis in water
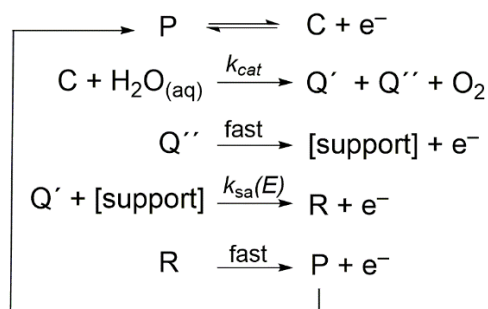
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Formal Kinetics Model for Self-Healing

The chemical steps for self-healing are,

$$
\begin{array}{rcl}
P & \rightleftharpoons & C + e^- \\
C + H_2O_{(aq)} & \xrightarrow{k_{cat}} & Q' + Q'' + O_2 \\
Q'' & \xrightarrow{fast} & [support] + e^- \\
Q' + [support] & \xrightarrow{k_{sa}(E)} & R + e^- \\
R & \xrightarrow{fast} & P + e^-
\end{array}
$$

where the various individual species are defined in terms of alphabetical labels of Figure 3 in the text. The [support] term indicates a Co(III) film with a vacancy for re-insertion of Co ion into the film. The H^+ and P_i concentrations are included in the operand rate constants for k_{sa} and k_{OER} and hence the scheme only accounts for electron equivalency (e^-).

We consider a catalytic system operated at a constant electrode potential E in a solution containing a large concentration of substrate (in this case, H_2O) but initially no Q' (Co^{2+} ion in solution). The initial surface concentration of CoP_i deposited onto the electrode is $\Gamma_{CoP_i}^0$ (which defines the total Co concentration). We assume that self-exchange electron transport in the CoP_i film is sufficiently fast (see text) and thus the CoP_i film behaves as a catalytic monolayer. The electrode surface area is S and the volume of the solution is V. We consider well-defined hydrodynamic conditions (i.e. a constant diffusion layer δ) and linear diffusion of Q' (with diffusion coefficient D). The substrate (i.e., H_2O) is in large excess and its concentration $C_{substrate}^0$ is constant throughout the solution.

The kinetic behavior of Q' is sketched in Scheme S1, representing the concentration profile of Q'
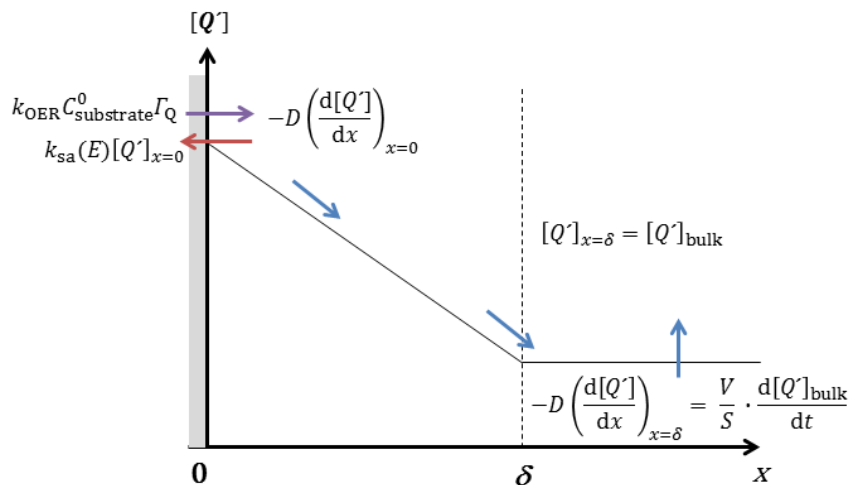
Scheme S1. Rate constant dependence of the concentration of Co^{2+} ions in solution as a function of distance from the electrode surface.

and the various boundary relationships detailed below (the catalytic film on the electrode surface is at $x = 0$).

At diffusion layer/catalytic film interface, $x = 0$:

The flux of Q´ leaching from the catalytic film is equal to difference between the rate of pre-catalyst production and the rate of catalyst assembly,

$$-D\left(\frac{\mathrm{d}[Q']}{\mathrm{d}x}\right)_{x=0} = k_{\mathrm{OER}}C^0_{\mathrm{substrate}}\Gamma_{\mathrm{C}} - k_{\mathrm{sa}}(E)[Q']_{x=0}$$

where Γ_{C} is surface concentration of active catalyst C, $C^0_{\mathrm{substrate}}$ is effectively 1 since it is the solvent, and k_{sa} and k_{OER} are the rate constants defined in Figure 3.

In the diffusion layer, $0 < x < \delta$:

Mass transport of the Q´ occurs only by diffusion:

$$\left(\frac{\mathrm{d}^2[Q']}{\mathrm{d}x^2}\right) = 0,$$

hence

$$D\left(\frac{\mathrm{d}[Q']}{\mathrm{d}x}\right)_{x=0} = D\left(\frac{\mathrm{d}[Q']}{\mathrm{d}x}\right)_{x=\delta}$$

and

$$D\left(\frac{\mathrm{d}[Q']}{\mathrm{d}x}\right)_{x=0} = \frac{D}{\delta}([Q']_{x=\delta} - [Q']_{x=0})$$

At the solution bulk/diffusion layer boundary, $x = \delta$:

The rate of Q´ accumulation in the solution bulk is equal to the flux of Q´ out of the diffusion layer:

$$-D\left(\frac{\mathrm{d}[Q']}{\mathrm{d}x}\right)_{x=\delta} = \frac{V}{S} \cdot \frac{\mathrm{d}[Q']_{\mathrm{bulk}}}{\mathrm{d}t}$$

and

$$[Q']_{x=\delta} = [Q']_{\mathrm{bulk}}$$

We assume a Nernstian behavior for the P/C couple defined by standard potential E^0_{cat}, fast catalysis and fast oxidation of both Q´´ and R. Under these conditions,

$$\Gamma_C \approx \left(\Gamma^0_{CoP_i} - \frac{V}{S} [Q']_{x=\delta} \right) \cdot \exp\left[\frac{F(E - E^0_{cat})}{RT} \right]$$

Thus

$$k_{OER} C^0_{substrate} \Gamma_C = k_{OER} C^0_{substrate} \left\{ \left(\Gamma^0_{CoP_i} - \frac{V}{S} [Q']_{x=\delta} \right) \cdot \exp\left[\frac{F(E - E^0_{cat})}{RT} \right] \right\}$$

$$= k^{app}_{OER}(E) - k'^{app}_{OER}(E)[Q']_{x=\delta}$$

where

$$k^{app}_{OER}(E) = k_{OER} C^0_{substrate} \left\{ \Gamma^0_{CoP_i} \exp\left[-\frac{F(E^0_{cat})}{RT} \right] \right\}$$

$$k'^{app}_{OER}(E) = k_{OER} C^0_{substrate} \left\{ \frac{V}{S} \cdot \exp\left[\frac{F(E - E^0_{cat})}{RT} \right] \right\}$$

Then the flux of Q´ leaching from the catalytic film is,

$$-D \left(\frac{d[Q']}{dx} \right)_{x=0} = k^{app}_{OER}(E) - k'^{app}_{OER}(E)[Q']_{x=\delta} - k_{sa}(E)[Q']_{x=0} = -\frac{D}{\delta} ([Q']_{x=\delta} - [Q']_{x=0})$$

leading to,

$$[Q']_{x=0} = \frac{k^{app}_{OER}(E) + \left[\frac{D}{\delta} - k'^{app}_{OER}(E) \right] [Q']_{x=0}}{\left[\frac{D}{\delta} + k_{sa}(E) \right]}$$

and finally,

$$\frac{d[Q']_{bulk}}{dt} + \frac{S}{V} \cdot \frac{D}{\delta} \left(\frac{k'^{app}_{OER}(E) + k_{sa}(E)}{\frac{D}{\delta} + k_{sa}(E)} \right) [Q']_{bulk} = \frac{S}{V} \cdot \frac{D}{\delta} \left(\frac{k^{app}_{OER}(E)}{\frac{D}{\delta} + k_{sa}(E)} \right)$$

Taking into account that ([Q´]bulk)t=0 = 0 leads to,

$$[Q']_{bulk} = \frac{k^{app}_{OER}(E)}{k'^{app}_{OER}(E) + k_{sa}(E)} \left[1 - \exp\left(-\frac{t}{\tau} \right) \right]$$

with

$$\tau = \frac{V}{S} \cdot \frac{\delta}{D} \left(\frac{\frac{D}{\delta} + k_{sa}(E)}{k'^{app}_{OER}(E) + k_{sa}(E)} \right) = \frac{1 + \frac{k_{sa}(E)}{D/\delta}}{k_{OER}(E) + \frac{k_{sa}(E)}{V/S}}$$

taking into account that $k_{OER}(E)$ introduced in the text corresponds to,

$$k'^{app}_{OER}(E) = \frac{V}{S} k_{OER}(E)$$

The fraction of remaining active film after equilibration of Co^{2+} ion with the bulk solution is,

$$\frac{\Gamma^{active}_{CoP_i}}{\Gamma^0_{CoP_i}} \approx 1 - \frac{\frac{V}{S}}{\Gamma^0_{CoP_i}} [Q']_{bulk} = 1 - \frac{\frac{V}{S}}{\Gamma^0_{CoP_i}} \cdot \frac{k^{app}_{OER}(E)}{k'^{app}_{OER}(E) + k_{sa}(E)} \left[1 - \exp\left(-\frac{t}{\tau}\right) \right]$$

When $t \gg \tau$, a steady-state limit is reached and

$$\frac{\Gamma^{active}_{CoP_i}}{\Gamma^0_{CoP_i}} = 1 - \frac{V}{S} \left(\frac{k_{OER} C^0_{substrate} \cdot \exp\left[\frac{F(E - E^0_{cat})}{RT}\right]}{k_{OER} C^0_{substrate} \frac{V}{S} \cdot \exp\left[\frac{F(E - E^0_{cat})}{RT}\right] + k_{sa}(E)} \right)$$

i.e.

$$\frac{\Gamma^{active}_{CoP_i}}{\Gamma^0_{CoP_i}} = \frac{k_{sa}(E)}{k_{OER} C^0_{substrate} \frac{V}{S} \cdot \exp\left[\frac{F(E - E^0_{cat})}{RT}\right] + k_{sa}(E)}$$

Considering the expressions of $k_{sa}(E)$ and $k_{OER}(E) = k_{OER} C^0_{substrate} \exp\left[\frac{F(E - E^0_{cat})}{RT}\right]$ for CoP$_i$ as given in the text (Eqs. (3) and (5)), and rearranging the above expression, Eq. (6) given in the text is straightforwardly obtained.