Supporting Information

Finite-element simulations of the influence of pore wall adsorption on cyclic voltammetry of ion transfer across a liquid-liquid interface formed in a micropore

Jonathan S. Ellis,[1] Jörg Strutwolf,[1] Damien W. M. Arrigan[2,]*

[1]Tyndall National Institute, Lee Maltings, University College Cork, Cork, Ireland. [2]Nanochemistry Research Institute, Department of Chemistry, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia.

*Corresponding author. Email: d.arrigan@curtin.edu.au; Tel: +61-8-9266-9735; Fax: +61-8-9266-4699.

This supporting information contains 1. modeling equations using dimensionless variables, 2. derivation of the weak form boundary condition used for surface adsorption, 3. table describing the dimensionless variables used in the simulations, 4. CV plots for various adsorption rate constants k_{ads}, 5. CV plots and surface concentration profiles for b_0 and 6. CV plots and surface concentration profile for various scan rates (4 figures).

1. Modeling equations in terms of the dimensionless variables

In terms of the dimensionless variables (see Table S1), Eqs. 1, 3, 9, and 10 become:

$$\frac{\partial C_1(X,R,\tau)}{\partial \tau} = \frac{1}{4}\gamma\nabla^2 C_1(X,R,\tau)$$
$$\frac{\partial C_2(X,R,\tau)}{\partial \tau} = \frac{1}{4}\nabla^2 C_2(X,R,\tau) \quad \text{(S.1)}$$

$$\gamma\frac{\partial C_1(X,R,\tau)}{\partial X}\bigg|_{X=X_s} = K\left[C_1(X_s,R,\tau)e^{-\alpha\Phi} - C_2(X_s,R,\tau)e^{(1-\alpha)\Phi}\right] \quad \text{(S.2)}$$

$$\frac{\partial C_s}{\partial \tau} = \frac{1}{4}\left[\gamma_s\frac{\partial^2 C_s}{\partial R^2} + K_{ads}C_1(B_0 - C_s) - K_{des}C_s\right] \quad \text{(S.3)}$$

$$-N_0 = -\mathbf{n}\cdot(\gamma\nabla C_1) = K_{ads}C_1(B_0 - C_s) - K_{des}C_s \quad \text{(S.4)}$$

The 1/4 term in Eqs. S.1 and S.3 arise from conversion to dimensionless time. Equations S.1 to S.4 are solved using finite-element simulations, described in the article.

2. Weak Boundary Condition for Surface Adsorption

Eq. 9 can also be written as

$$\frac{\partial c_s}{\partial t} - k_{ads} c\left(b_0 - c_s\right) + k_{des} c_s = \nabla \cdot \left(D_s \nabla c_s\right) = \nabla \cdot N = F \tag{S.5}$$

If c_s^{test} is an arbitrary test function of c_s, we can write

$$\int_\Omega \left[c_s^{test} \nabla \cdot \left(D_s \nabla c_s\right)\right] dA = \int_\Omega \left[c_s^{test} \left(\frac{\partial c_s}{\partial t} - k_{ads} c\left(b_0 - c_s\right) + k_{des} c_s \right)\right] dA \tag{S.6}$$

Applying Green's formula,

$$\begin{aligned} &\int_{\partial\Omega} \left[c_s^{test} \left(D_s \nabla c_s\right) \cdot \mathbf{n}\right] ds - \int_\Omega \left[\nabla c_s^{test} \cdot \left(D_s \nabla c_s\right)\right] dA \\ &\qquad = \int_\Omega \left[c_s^{test} \left(\frac{\partial c_s}{\partial t} - k_{ads} c\left(b_0 - c_s\right) + k_{des} c_s \right)\right] dA \end{aligned} \tag{S.7}$$

Noting the boundary condition in Eq. 12, the first integral in Eq. S.7 disappears and we can write

$$0 = \int_\Omega \left[D_s \left(-\nabla c_s^{test} \cdot \nabla c_s\right) + c_s^{test} \left(k_{ads} c\left(b_0 - c_s\right) - k_{des} c_s - \frac{\partial c_s}{\partial t} \right)\right] dA \tag{S.8}$$

Applying instead the dimensionless form, Eq. S.3, the weak form BC is

$$0 = \int_\Omega \left[\frac{1}{4} \gamma_s \left(-\nabla C_s^{test} \cdot \nabla C_s\right) + C_s^{test} \left(\frac{1}{4} K_{ads} C\left(B_0 - C_s\right) - \frac{1}{4} K_{des} C_s - \frac{\partial C_s}{\partial \tau} \right)\right] dA \tag{S.9}$$

This is input in Comsol 3.5a in the Weak Form, Boundary mode as 0.25*gamma_s*(-test(csTr)*csTr-test(csTz)*csTz)+test(cs)*(0.25*react_surf-cst).

3. Table S1. Dimensionless Variables and Equations

System			**Surface**		
Time	$\tau = \frac{4D_2 t}{r_a^2}$	(13a)	*Surface concentration*	$C_s = \frac{c_s}{r_a c_b}$	(14a)
Scan rate	$p = \frac{r_a^2}{4D_2}\frac{F}{RT}v$	(13b)	*Surface adsorption*	$K_{ads} = \frac{k_{ads} c_b r_a^2}{D_2}$	(14b)
Space	$X = \frac{x}{r_a}, R = \frac{r}{r_a}$	(13c)	*Surface desorption*	$K_{des} = \frac{k_{des} r_a^2}{D_2}$	(14c)
Concentration	$C_i(X,R,\tau) = \frac{c_i(x,r,t)}{c_b}$	(13d)	*Binding sites*	$B = \frac{b}{r_a c_b}$, $B_0 = \frac{b_0}{r_a c_b}$	(14d)
Rate constant	$K = \frac{k_0 r_a}{D_2}$	(13e)	*Surface diffusivity*	$\gamma_s = \frac{D_s}{D_2}$	(14e)
Diffusion	$\gamma = \frac{D_1}{D_2}$	(13f)			
Current	$I = \frac{i}{i_{\lim}}$	(13g)			
Potential	$\Phi = \frac{z_i F}{RT}\left(\Delta_o^w\varphi - \Delta_o^w\varphi^{0'}\right)$	(13h)			

4. CV plots for various adsorption rate constants k_{ads}

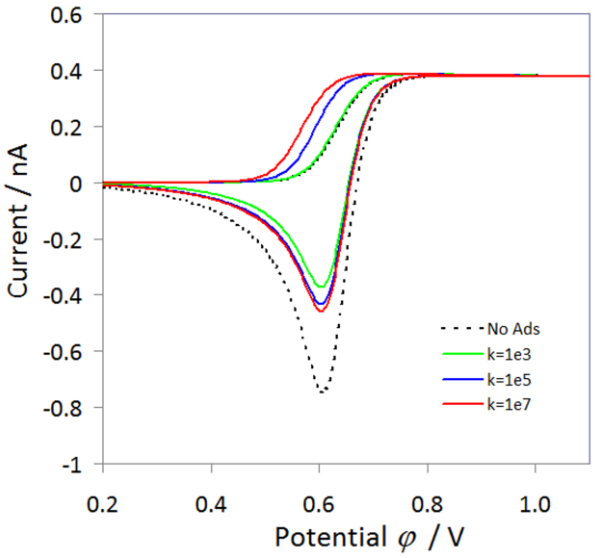

Figure S1. CV plots for various adsorption rate constants k_{ads} ($M^{-1}s^{-1}$).

5. CV plots and pore wall surface concentration profiles for different values of b_0

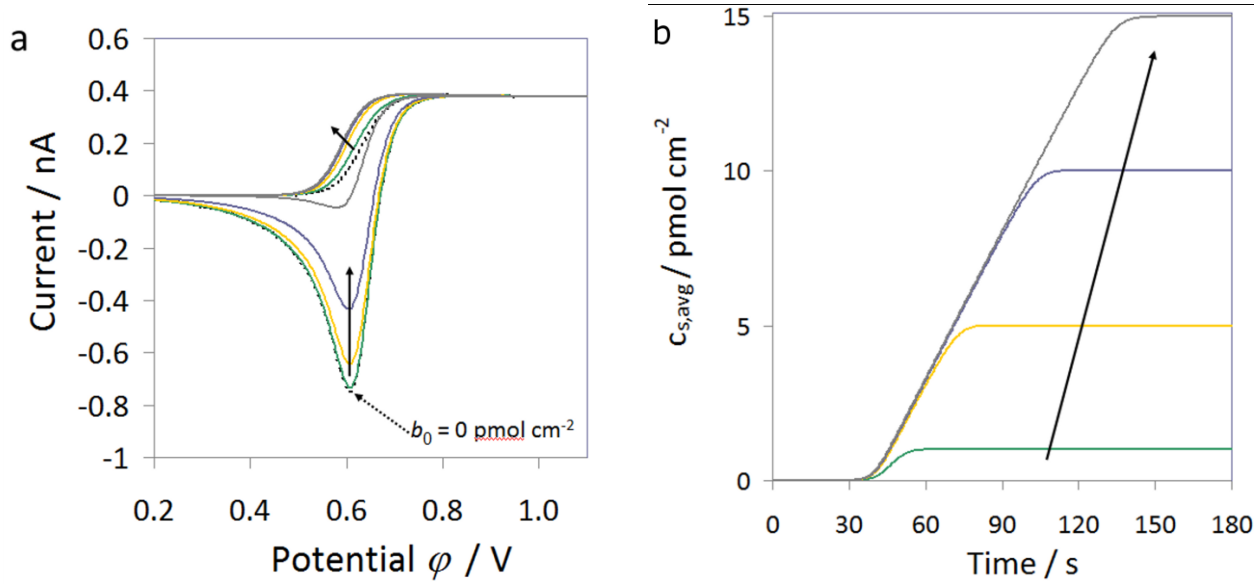

Figure S2. CV plots (a) and surface concentration profiles (b) for b_0 varied between 1 and 15 pmol·cm^{-2}). The arrows show increasing b_0.

6. CV plots and surface concentration profile for various scan rates

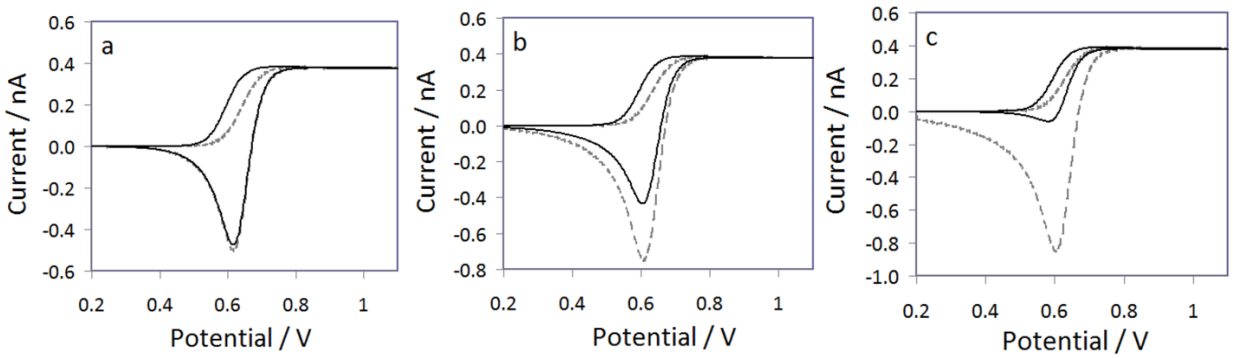

Figure S3. CV plots for (a) 5, (b) 10, and (c) 15 mV s^{-1} without (solid) and with (dashed) adsorption.