Supplementary Information for
Equilibria model for pH variations and ion adsorption in capacitive deionization electrodes

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Abstract
This document contains supplementary information and figures further describing our acid-base equilibria and titration models, point of zero charge approximation, simplified governing equations in the ideal solution (infinite dilution) limit, and details of derivation of a generalized charge efficiency parameter.

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S-1. Ideal solution limit
We here discuss adsorption and surface charge dynamics in the ideal solution limit (infinite dilution where $c_+ = c_- = 0$) with and without external voltage. Electroneutrality condition in the ideal solution limit requires pH of electrolyte after equilibration with carbon to be 7 ($c_H = \sqrt{K_w}$). So, the micropore concentration of hydronium is

$$c_{m,H} = \sqrt{K_w} \exp(-\Delta \phi_D / V_T), \quad (S.1)$$

and ionic charge density in the micropores can be written as

$$\sigma_{ionic} = F(c_{m,H} - K_w/c_{m,H}) = -2F \sqrt{K_w} \sinh(\Delta \phi_D / V_T). \quad (S.2)$$

For the case where external voltage $V_{ext}$ is applied, charge compensation requires $\sigma_{chem} + \sigma_{ionic} + \sigma_{elec} = 0$. So, we substitute Eqs. (S.1) and (S.2) into charge compensation equation and arrive at a single equation below for Donnan potential

$$-\sum_{i=1}^{n_x} \frac{c_{X,i,0}}{1 + c_{m,H} / K_{X_i}} + \sum_{j=1}^{n_y} \frac{c_{Y,j,0}}{1 + K_{Y_j} / c_{m,H}} - 2 \sqrt{K_w} \sinh\left(\frac{\Delta \phi_D}{V_T}\right) + \frac{c_m}{F}(V_{ext} - \Delta \phi_D) = 0. \quad (S.3)$$

Note, the left-hand side of Eq. (S.3) strictly decreases with increasing $\Delta \phi_D$. So, this equation has at most one real solution for any $V_{ext}$. In the absence of applied voltage (floating electrode) electronic charge $\sigma_{elec}$ vanishes and thus micropore ionic charge and surface chemical charge compensate each other (i.e., $\sigma_{chem} + \sigma_{ionic} = 0$). Eq. (S.3) can then be simplified to

$$-\sum_{i=1}^{n_x} \frac{c_{X,i,0}}{1 + c_{m,H} / K_{X_i}} + \sum_{j=1}^{n_y} \frac{c_{Y,j,0}}{1 + K_{Y_j} / c_{m,H}} + c_{m,H} - K_w / c_{m,H} = 0. \quad (S.4)$$

Eq. (S.4) can be recast as a polynomial of degree $n_X + n_Y + 2$. Similarly, note each term in Eq. (S.4) is strictly increasing in $c_{m,H}$ and thus this equation has at most one real solution.

S-2. Titration model
In Section 4.1 of the main text, we showed results of titration model for carbon with acidic and/or basic surface charges. We here discuss titration model in more detail. We assume electrolyte solution has initial volume of $v_{sol}^0$...
Fig. S.1. Effect of ionic strength on micropore-to-macropore equilibrium for asymmetric carbon. (a) pH$_{m,f}$ versus pH$_f$ for titration of an asymmetric carbon with $c_{X,0} = c_{Y,0} = 1$ M, $pK_X = 4$, and $pK_Y = 8$ at initial concentrations $c_0 = 0, 1, 20, 100, and 500$ mM. pH$_{m,f}$ is lower (higher) than pH$_f$ above (below) pH$_{PZC} = 6$. (b), (c) Concentration of charged acidic and basic groups ($c_{X^-}$ and $c_{YH^+}$) versus pH$_f$ and versus pH$_{m,f}$. Similar to symmetric carbon, each $c_{X^-}$ and $c_{YH^+}$ collapses on a single curve when plotted against pH$_{m,f}$.

(before addition of any titrant) and initial salt concentration of $c_0$. We then add either strong acid or base titrant of concentration $c_{stock}$ and volume $v_{titrant}$ to the electrolyte solution. We define the pH value and hydronium concentration at this point (after addition of titrant but prior to the addition of carbon to the electrolyte) pH$_0$ and pH$_{H,0}$, respectively. Assuming the added titrant completely dissociates, electroneutrality requires that

$$c_{+,0} - c_{-,0} + c_{H,0} - K_w/c_{H,0} = 0,$$

(S.5)

where $c_{+,0}$ and $c_{-,0}$ are cation and anion concentrations right after addition of titrant and before carbon-electrolyte equilibration. Note, $c_0$ is initial salt concentration with no titrant added. In case of titration with strong acid, $c_{+,0}$ and $c_{-,0}$ can be written as

$$c_{+,0} = \frac{c_0 v_0^{sol} + v_{titrant}}{v_0^{sol} + v_{titrant}},$$

(S.6a)

and in case of titration with strong base, as

$$c_{+,0} = \frac{c_0 v_0^{sol} + c_{stock} v_{titrant}}{v_0^{sol} + v_{titrant}},$$

(S.6b)

Substituting Eqs. (S.6) and (S.7) back into Eq. (S.5), we arrive at

$$v_{titrant} = \frac{c_{H,0} - K_w/c_{H,0}}{c_{stock} - (c_{H,0} - K_w/c_{H,0})} v_0^{sol},$$

(S.8a)

and

$$v_{titrant} = \frac{c_{+,0} - K_w/c_{H,0}}{c_{stock} - (c_{+,0} - K_w/c_{H,0})} v_0^{sol},$$

(S.8b)

for acid and base titration, respectively. Now, for known pH$_0$ values, we calculate $c_{+,0}$, $c_{-,0}$, and $v_{titrant}$ using Eqs. (S6) to (S8). We then use these parameters as inputs to our multi-equilibria surface charge model (see Section 2 of the main text). The electrolyte volume before addition of carbon is $v_0^{sol} + v_{titrant}$. The final electrolyte and micropore pH (pH$_f$ and pH$_{m,f}$) are then determined using the governing equations discussed in Section 2 of the main text.

S-3. Salt adsorption and micro-to-macropore equilibrium for asymmetric carbon

In model results section of the main text (Section 4.1), we discussed micropore and macropore electrostatic environments as well as salt adsorption and surface charge efficiency for symmetric case where $c_{X,0} = c_{Y,0} = 1$ M (as before), pH$_{PZC} = (pK_X + pK_Y)/2 = 7$. We here show an asymmetric case where we set $c_{X,0} = c_{Y,0} = 1$ M (as before), $pK_X = 4$, and $pK_Y = 8$. Note, $(pK_X + pK_Y)/2 \neq 7$ here. For other parameters, refer to Table 1 of the main text. Fig. S.1 shows pH$_{m,f}$ (final pH of micropore) versus pH$_f$ (final pH of solution) for initial salt concentrations in the range of 0 to 500 mM (solid lines). Dashed line shows pH$_{m,f} = pH_f$. Note that all curves coincide at pH$_{PZC} = 6$ as expected, however, the plot is not symmetric around pH$_{PZC}$. Moreover, similar to symmetric case, pH$_{m,f}$ approaches pH$_f$ only at high ionic strengths.

Figs. S.1b and S.1c show concentration of charged acidic and basic groups ($c_{X^-}$ and $c_{YH^+}$) as a function of pH$_f$ and pH$_{m,f}$. Results again show that $c_{X^-}$ and $c_{YH^+}$ curves all collapse when plotted versus pH$_{m,f}$ (i.e. they are not functions of ionic strength). Additionally, note that $c_{X^-}$
Fig. S.2. Effect of ionic strength and micropore pH environment on salt adsorption dynamics for carbon with asymmetric surface chemistry parameters of $c_{X,0} = c_{Y,0} = 1$ M, $pK_X = 4$, and $pK_Y = 8$. (a) Net adsorbed salt $\Gamma = \Gamma_+ + \Gamma_-$ as a function of $pH_{m,f}$ for $c_0 = 0, 20, 100, 500$ mM. Salt adsorption is considerable at $pH_{m,f} < pK_X$ and $pH_{m,f} > pK_Y$ and is much lower otherwise. Moreover, $\Gamma$ decreases with ionic strength (or with $c_0$). (b), (c) Cationic and anionic salt adsorption ($\Gamma_+$ and $\Gamma_-$) for $c_0 = 20$ and $500$ mM cases. (d) Chemical charge efficiency $\lambda_{chem}$ versus $pH_{m,f}$. General trend of $\lambda_{chem}$ is similar to the case discussed in the main text, however, $\lambda_{chem}$ is not symmetric about PZC ($pH_{PZC} = 6$) here.

and $c_{YH^+}$ are not symmetric around $pH_{PZC} = 6$ when plotted versus $pH_f$, but are symmetric around $pH_{PZC}$ when plotted versus $pH_{m,f}$.

Fig. S.2a shows net salt adsorbed $\Gamma$ as a function of $pH_{m,f}$ at different initial salt concentrations $c_0$ in the range of 0 to 500 mM. Other parameters are identical to those of Fig. S.1. According to Fig. S.1c, micropore surface charge is more negative (positive) at $pH$ values lower (higher) than $pK_X$ ($pK_Y$). This explains the observation in Fig. S.2a that salt adsorption is considerable at $pH_{m,f} < pK_X$ and $pH_{m,f} > pK_Y$ and is much lower otherwise. Moreover, $\Gamma$ decreases with ionic strength (or with $c_0$).

These trends are similar to the symmetric case discussed in the main text. However, there are the following differences: (1) the minimum adsorption occurs at $pH_{m,f} = pH_{PZC} = 6$ rather than at $pH_{m,f} = 7$, and (2) salt adsorption saturates at $pH_{m,f}$ several units larger than $pK_Y$ (i.e. $pH_{m,f} > pK_Y + 2$). The latter is because micropore surface charge saturates at $pH_{m,f}$ several units higher (lower) than $pK_Y$ ($pK_X$). Figs. S.2b and S.2c show individual cationic and anionic salt adsorption ($\Gamma_+$ and $\Gamma_-$) for $c_0 = 20$ and $500$ mM cases, respectively. We again see that (1) counter-ion adsorption (i.e. adsorption of cations at high $pH_{m,f}$ and anions at low $pH_{m,f}$) dominates co-ion expulsion at low ionic strength, and (2) counter-ion adsorption and co-ion expulsion are of the same order at high ionic strengths. Chemical charge efficiency $\lambda_{chem}$ (see Fig. S.2d) shows the trend similar to symmetric case with the following differences: (1) $PZC$ is moved to $pH_{PZC} = 6$, and (2) $\lambda_{chem}$ is not symmetric around $PZC$.

S-4. Determination of point of zero charge
As discussed in Section 4.1 of the main text, PZC corresponds to $\sigma_{chem} = 0$ and $\Delta\phi_D = 0$. This condition can be written as

$$\sum_{i=1}^{nX} \sigma_{X,i}^- + \sum_{j=1}^{nY} \sigma_{Y,j}^{+*} = -\sum_{i=1}^{nX} \frac{c_{X,i,0}}{1 + c_H/K_{X,i}} + \sum_{j=1}^{nY} \frac{c_{Y,j,0}}{1 + K_{Y,j}/c_H} = 0.$$  \hspace{1cm} (S.9)

where $\sigma_{X,i}^-$ and $\sigma_{Y,j}^{+*}$ are surface charges associated with $i$-th acidic and $j$-th basic functional group. The first term is sum of the (negative) surface charges associated with acidic groups, and the second term is sum of (positive) charges due to basic groups. Note, Eq. (S.9) is strictly increasing (since each term is strictly increasing) and so has at most one real root. Eq. (S.9) can also be recast as a polynomial of degree $nX + nY$ in $c_H$. Exact value of PZC in general case then requires finding this root. PZC for $nX = nY = 1$, on the other hand, requires finding the real positive root of the quadratic below and is straightforward.
\[ (c_{Y,0}/K_X)c^2_H + (c_{Y,0} - c_{X,0})c_H - c_{X,0}K_Y = 0. \] (S.10)

For a better representation of the results, we split the solution of this quadratic to two cases, namely, \(c_{X,0} > c_{Y,0}\) and \(c_{X,0} < c_{Y,0}\). We define \(\alpha_1 = c_{X,0}/c_{Y,0} - 1\) for when \(c_{X,0} > c_{Y,0}\), and \(\alpha_2 = c_{Y,0}/c_{X,0} - 1\) for when \(c_{X,0} < c_{Y,0}\). So, \(\alpha_1\) and \(\alpha_2\) are both positive quantities. These two parameters are a measure of asymmetry in concentration of acidic and basic groups. For example, \(\alpha_1 = 0\) and \(\alpha_2 = 0\) correspond to \(c_{X,0} = c_{Y,0}\); and \(\alpha_1 > 0\) and \(\alpha_2 > 0\) correspond \(c_{X,0} > c_{Y,0}\) and \(c_{X,0} < c_{Y,0}\), respectively. The solution can be written as

\[
c_H = \begin{cases} 
K_X \alpha_1 e^{-\alpha_2} & c_{X,0} > c_{Y,0} \\
K_Y / (\alpha_2 e) & c_{X,0} < c_{Y,0}
\end{cases}
\] (S.11)

where \(\varepsilon\) is

\[ \varepsilon = \frac{1}{2} \left( 1 + \sqrt{1 + 4(\alpha + 1)/\alpha^2 \cdot K_Y/K_X} \right). \] (S.12)

and \(\alpha\) is either \(\alpha_1\) or \(\alpha_2\) (they both result in the same \(\varepsilon\)). Taking logarithm of Eq. (S.11), \(pH_{PZC}\) can be written as

\[
pH_{PZC} = \begin{cases} 
(pK_X - \log \alpha_1 - \log \varepsilon)/c_{X,0} - c_{Y,0} \\
(pK_Y + \log \alpha_2 + \log \varepsilon)/c_{X,0} - c_{Y,0}
\end{cases}.
\] (S.13)

Fig. S.3 shows \(pH_{PZC}\) versus \(\alpha_1\) and \(\alpha_2\) with \(pK_X = 4\) and \(pK_Y = 10\). The results show that \(pH_{PZC}\) decreases with \(\alpha_1\) and increases with \(\alpha_2\). Taking the limit of Eq. (S.13) as \(\alpha_1 \to 0\) (i.e., \(c_{X,0} = c_{Y,0}\)), \(\varepsilon\) approaches \(\sqrt{K_X/K_Y}\) \(\alpha_1^{-1}\) and we arrive at familiar equation \(pH_{PZC} = (pK_X + pK_Y)/2\). On the other hand, according to Eq. (S.12), \(\varepsilon\) approaches unity for large enough \(\alpha\) (\(\alpha_1\) or \(\alpha_2\)) and we have

\[
pH_{PZC} = \begin{cases} 
(pK_X - \log \alpha_1)/c_{X,0} - c_{Y,0} \\
(pK_Y + \log \alpha_2)/c_{X,0} - c_{Y,0}
\end{cases}.
\] (S.14)

For Eq. (S.14) to be valid, we need \((\alpha + 1)/\alpha^2 \cdot K_Y/K_X \ll 1\), or equivalently,

\[ \alpha \gg \alpha_0 = \frac{1}{2} \frac{K_Y}{K_X} \left( 1 + \sqrt{1 + 4K_X/K_Y} \right). \] (S.15)

So, for \(\alpha_1 \gg \alpha_0\), \(\varepsilon\) approaches unity and \(pH_{PZC}\) is independent of \(pK_Y\). For \(\alpha_2 \gg \alpha_0\), \(\varepsilon\) approaches unity and \(pH_{PZC}\) becomes independent of \(pK_X\). The dashed lines in Fig. S.3 show extrapolation of \(pH_{PZC}\) for \(\alpha_1 \gg \alpha_0\) and \(\alpha_2 \gg \alpha_0\) (as described by Eq. (S.14)). These derivations can help in quick estimates of \(pH_{PZC}\) given some knowledge of surface \(pK\) values and analytical concentrations.

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\[ \sigma_{ionic} \approx F \left[ -2c_0 \sinh \left( \frac{\Delta \phi_D}{V_T} \right) + c_H \exp \left( -\frac{\Delta \phi_D}{V_T} \right) - \frac{K_D}{c_H} \exp \left( \frac{\Delta \phi_D}{V_T} \right) \right]. \] (S.16)
\[ \sigma_{\text{chem}} = F \left[ -c_{X,0} \left( 1 + \frac{c_H}{K_X} \exp \left( -\frac{\Delta \phi_D}{V_T} \right) \right)^{-1} + c_{Y,0} \left( 1 + \frac{K_Y}{c_H} \exp \left( \frac{\Delta \phi_D}{V_T} \right) \right)^{-1} \right], \quad (S.17) \]

\[ \sigma_{\text{elec}} = C_m (V_{\text{ext}} - \Delta \phi_D). \quad (S.18) \]

Substituting Eqs. (S.16)-(S.18) into charge compensation equation \( \sigma_{\text{ionic}} + \sigma_{\text{chem}} + \sigma_{\text{elec}} = 0 \), results in a transcendental equation for \( \Delta \phi_D \). We then calculate salt adsorption as

\[ \Gamma = v_m \left[ (c_{m,+} - c_{+0}) + (c_{m,-} - c_{-0}) \right] \approx 2c_0 v_m \left( \cosh \frac{\Delta \phi_D}{V_T} - 1 \right). \quad (S.19) \]

Moreover, we express salt adsorbed at potential of zero charge \( V_{\text{PZC}} \) (i.e. \( V_{\text{ext}} \) at which \( \sigma_{\text{elec}} = 0 \)) as

\[ \Gamma_{\text{PZC}} \approx 2c_0 v_m \left( \cosh \frac{V_{\text{PZC}}}{V_T} - 1 \right). \quad (S.20) \]

The charge efficiency can then be defined as

\[ \Lambda = \frac{\Gamma - \Gamma_{\text{PZC}}}{\Sigma_{\text{chem}} / F}. \quad (S.21) \]

In this definition, \( \Gamma - \Gamma_{\text{PZC}} \) is the extra salt adsorbed associated with applied potential \( V_{\text{ext}} \) (note, \( \Gamma \) can be non-zero at potential of zero charge \( V_{\text{PZC}} \)). Note that charge efficiency here is a function of external voltage, surface properties (i.e. \( c_{X,0}, c_{Y,0}, pK_X, \) and \( pK_Y \) for \( n_X = n_Y = 1 \)), salt concentration \( c_0 \), and initial pH. In Fig. S.4, we show adsorbed salt and electronic charge as well as charge efficiency as a function of \( V_{\text{ext}} \) for various values of those parameters. Unless otherwise noted, other parameters used are listed in Table S.1.

<table>
<thead>
<tr>
<th>Table S.1</th>
<th>Parameters used in Fig. S.4</th>
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<tbody>
<tr>
<td>Parameter</td>
<td>Description</td>
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<tr>
<td>( c_{X,0} )</td>
<td>Analytical concentration of acidic group</td>
</tr>
<tr>
<td>( c_{Y,0} )</td>
<td>Analytical concentration of basic group</td>
</tr>
<tr>
<td>( pK_X )</td>
<td>Acid dissociation constant</td>
</tr>
<tr>
<td>( pK_Y )</td>
<td>Base dissociation constant</td>
</tr>
<tr>
<td>( C_m )</td>
<td>Volumetric micropore capacitance</td>
</tr>
<tr>
<td>( z_+, z_- )</td>
<td>Cation and anion valance</td>
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<tr>
<td>( c_0 )</td>
<td>Initial salt concentration</td>
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Fig. S.4. Volumetric adsorbed salt and electronic charge (in units of M) vs external voltage $V_{ext}$ at various (a) analytical concentration of acidic and basic surface charges, (c) dissociation constant of acidic functional groups, (e) salt concentrations, and (g) electrolyte pH values. (b), (d), (f), (h) Charge efficiency vs $V_{ext}$ for parameters as in (a), (c), (e), and (g). Other parameters used are listed in Table S.1.