

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

$$-\sum_{i=1}^{n_X} \frac{c_{X_i,0}}{1 + \frac{\sqrt{K_w}}{K_{X_i}} \exp\left(-\frac{\Delta\phi_D}{V_T}\right)} + \sum_{j=1}^{n_Y} \frac{c_{Y_j,0}}{1 + \frac{K_{Y_j}}{\sqrt{K_w}} \exp\left(\frac{\Delta\phi_D}{V_T}\right)} - 2\sqrt{K_w} \sinh\left(\frac{\Delta\phi_D}{V_T}\right) + \frac{C_m}{F} (V_{ext} - \Delta\phi_D) = 0. \quad (S.3)$$

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 σ_{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

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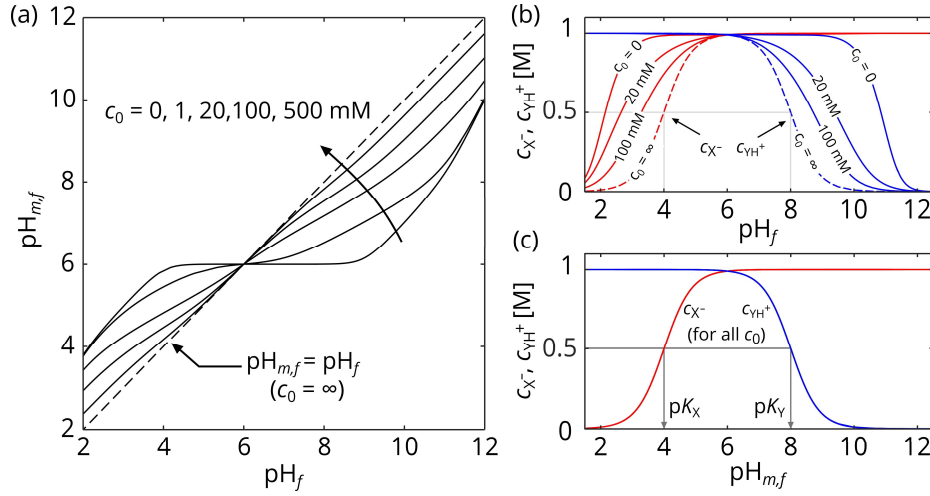


Fig. S.1. Effect of ionic strength on micropore-to-macropore equilibrium for asymmetric carbon. (a) $\text{pH}_{m,f}$ versus pH_f for titration of an asymmetric carbon with $c_{X,0} = c_{Y,0} = 1$ M, $\text{p}K_X = 4$, and $\text{p}K_Y = 8$ at initial concentrations $c_0 = 0, 1, 20, 100$, and 500 mM. $\text{pH}_{m,f}$ is lower (higher) than pH_f above (below) $\text{pH}_{\text{PZC}} = 6$. (b), (c) Concentration of charged acidic and basic groups (c_{X^-} and c_{YH^+}) versus pH_f and versus $\text{pH}_{m,f}$. Similar to symmetric carbon, each c_{X^-} and c_{YH^+} collapses on a single curve when plotted against $\text{pH}_{m,f}$.

(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 $c_{H,0}$, respectively. Assuming the added titrant completely dissociates, electroneutrality requires that

$$c_{+,0} - c_{-,0} + c_{H,0} - K_w/c_{H,0} = 0, \quad (\text{S.5})$$

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

$$c_{+,0} = \frac{c_0 v_{\text{sol}}^0}{v_{\text{sol}}^0 + v_{\text{titrant}}}, \quad (\text{S.6a})$$

$$c_{-,0} = \frac{c_0 v_{\text{sol}}^0 + c_{\text{stock}} v_{\text{titrant}}}{v_{\text{sol}}^0 + v_{\text{titrant}}}, \quad (\text{S.6b})$$

and in case of titration with strong base, as

$$c_{+,0} = \frac{c_0 v_{\text{sol}}^0 + c_{\text{stock}} v_{\text{titrant}}}{v_{\text{sol}}^0 + v_{\text{titrant}}}, \quad (\text{S.7a})$$

$$c_{-,0} = \frac{c_0 v_{\text{sol}}^0}{v_{\text{sol}}^0 + v_{\text{titrant}}}. \quad (\text{S.7b})$$

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

$$v_{\text{titrant}} = \frac{c_{H,0} - K_w/c_{H,0}}{c_{\text{stock}} - (c_{H,0} - K_w/c_{H,0})} v_{\text{sol}}^0, \quad (\text{S.8a})$$

$$v_{\text{titrant}} = \frac{c_{H,0} - K_w/c_{H,0}}{-c_{\text{stock}} - (c_{H,0} - K_w/c_{H,0})} v_{\text{sol}}^0, \quad (\text{S.8b})$$

for acid and base titration, respectively. Now, for known pH_0 values, we calculate $c_{+,0}$, $c_{-,0}$, and v_{titrant} using Eqs. (S.6) to (S.8). 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 $v_{\text{sol}}^0 + v_{\text{titrant}}$. The final electrolyte and micropore pH (pH_f and $\text{pH}_{m,f}$) 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 $c_{X,0} = c_{Y,0}$ and $\text{pH}_{\text{PZC}} = (\text{p}K_X + \text{p}K_Y)/2 = 7$. We here show an asymmetric case where we set $c_{X,0} = c_{Y,0} = 1$ M (as before), $\text{p}K_X = 4$, and $\text{p}K_Y = 8$. Note, $(\text{p}K_X + \text{p}K_Y)/2 \neq 7$ here. For other parameters, refer to Table 1 of the main text. Fig. S.1 shows $\text{pH}_{m,f}$ (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 $\text{pH}_{m,f} = \text{pH}_f$. Note that all curves coincide at $\text{pH}_{\text{PZC}} = 6$ as expected, however, the plot is not symmetric around pH_{PZC} . Moreover, similar to symmetric case, $\text{pH}_{m,f}$ 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 $\text{pH}_{m,f}$. Results again show that c_{X^-} and c_{YH^+} curves all collapse when plotted versus $\text{pH}_{m,f}$ (i.e. they are not functions of ionic strength). Additionally, note that c_{X^-}

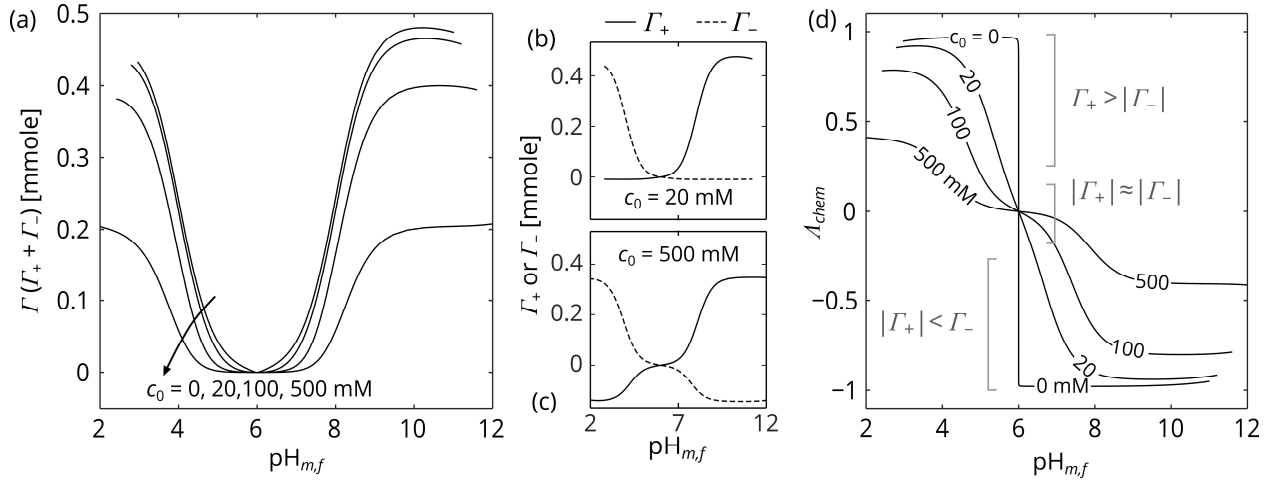


Fig. S.2. Effect of ionic strength and micropore pH environment on salt adsorption dynamics for carbon with asymmetric surface chemistry parameters of $c_{X,0} = c_{Y,0} = 1$ M, $pK_X = 4$, and $pK_Y = 8$. (a) Net adsorbed salt $\Gamma = \Gamma_+ + \Gamma_-$ as a function of $\text{pH}_{m,f}$ for $c_0 = 0, 20, 100$, and 500 mM. Salt adsorption is considerable at $\text{pH}_{m,f} < pK_X$ and $\text{pH}_{m,f} > pK_Y$ and is much lower otherwise. Moreover, Γ decreases with ionic strength (or with c_0). (b), (c) Cationic and anionic salt adsorption (Γ_+ and Γ_-) for $c_0 = 20$ and 500 mM cases. (d) Chemical charge efficiency Δ_{chem} versus $\text{pH}_{m,f}$. General trend of Δ_{chem} is similar to the case discussed in the main text, however, Δ_{chem} is not symmetric about PZC ($\text{pH}_{PZC} = 6$) here.

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

Fig. S.2a shows net salt adsorbed Γ as a function of $\text{pH}_{m,f}$ 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 $\text{pH}_{m,f} < pK_X$ and $\text{pH}_{m,f} > pK_Y$ and is much lower otherwise. Moreover, Γ 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 $\text{pH}_{m,f} = \text{pH}_{PZC} = 6$ rather than at $\text{pH}_{m,f} = 7$, and (2) salt adsorption saturates at $\text{pH}_{m,f}$ several units larger than pK_Y (i.e. $\text{pH}_{m,f} > pK_Y + 2$). The latter is because

micropore surface charge saturates at $\text{pH}_{m,f}$ several units higher (lower) than pK_Y (pK_X). Figs. S.2b and S.2c show individual cationic and anionic salt adsorption (Γ_+ and Γ_-) for $c_0 = 20$ and 500 mM cases, respectively. We again see that (1) counter-ion adsorption (i.e. adsorption of cations at high $\text{pH}_{m,f}$ and anions at low $\text{pH}_{m,f}$) 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 Δ_{chem} (see Fig. S.2d) shows the trend similar to symmetric case with the following differences: (1) PZC is moved to $\text{pH}_{PZC} = 6$, and (2) Δ_{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

$$\sum_{i=1}^{n_X} \sigma_{X_i^-} + \sum_{j=1}^{n_Y} \sigma_{Y_j H^+} = - \sum_{i=1}^{n_X} \frac{c_{X_i,0}}{1 + c_H/K_{X_i}} + \sum_{j=1}^{n_Y} \frac{c_{Y_j,0}}{1 + K_{Y_j}/c_H} = 0. \quad (\text{S.9})$$

where $\sigma_{X_i^-}$ and $\sigma_{Y_j H^+}$ 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 $n_X + n_Y$ in c_H . Exact value of PZC in general case then requires finding this root. PZC for $n_X = n_Y = 1$, on the other hand, requires finding the real positive root of the quadratic below and is straightforward.

$$(c_{Y,0}/K_X)c_H^2 + (c_{Y,0} - c_{X,0})c_H - c_{X,0}K_Y = 0. \quad (\text{S.10})$$

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, α_1 and α_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

$$c_H = \begin{cases} K_X \alpha_1 \varepsilon & c_{X,0} > c_{Y,0} \\ K_Y / (\alpha_2 \varepsilon) & c_{X,0} < c_{Y,0} \end{cases} \quad (\text{S.11})$$

where ε is

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

and α is either α_1 or α_2 (they both result in the same ε). Taking logarithm of Eq. (S.11), pH_{PZC} can be written as

$$\text{pH}_{\text{PZC}} = \begin{cases} \text{p}K_X - \log \alpha_1 - \log \varepsilon & c_{X,0} > c_{Y,0} \\ \text{p}K_Y + \log \alpha_2 + \log \varepsilon & c_{X,0} < c_{Y,0} \end{cases} \quad (\text{S.13})$$

Fig. S.3 shows pH_{PZC} versus α_1 and α_2 with $\text{p}K_X = 4$ and $\text{p}K_Y = 10$. The results show that pH_{PZC} decreases with α_1 and increases with α_2 . Taking the limit of Eq. (S.13) as $\alpha_1 \rightarrow 0$ (i.e., $c_{X,0} = c_{Y,0}$), ε approaches $\sqrt{K_X/K_Y} \alpha_1^{-1}$ and we arrive at familiar equation $\text{pH}_{\text{PZC}} = (\text{p}K_X + \text{p}K_Y)/2$. On the other hand, according to Eq. (S.12), ε approaches unity for large enough α (α_1 or α_2) and we have

$$\text{pH}_{\text{PZC}} = \begin{cases} \text{p}K_X - \log \alpha_1 & c_{X,0} > c_{Y,0} \\ \text{p}K_Y + \log \alpha_2 & c_{X,0} < c_{Y,0} \end{cases} \quad (\text{S.14})$$

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

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

So, for $\alpha_1 \gg \alpha_0$, ε approaches unity and pH_{PZC} is independent of $\text{p}K_Y$. For $\alpha_2 \gg \alpha_0$, ε approaches unity and pH_{PZC} becomes independent of $\text{p}K_X$. 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 $\text{p}K$ values and analytical concentrations.

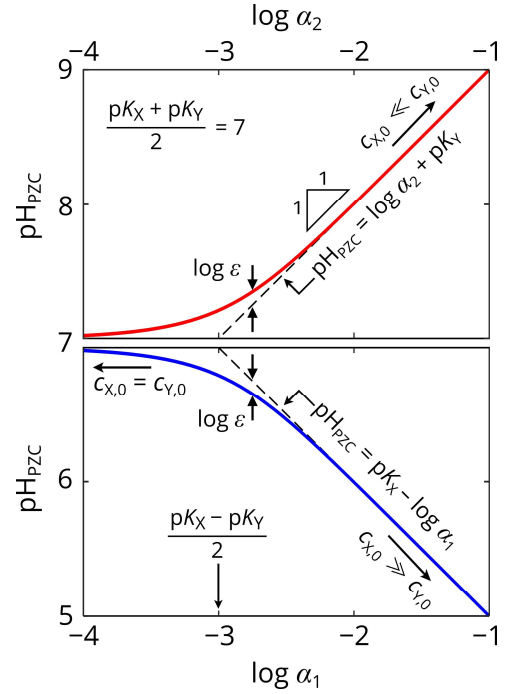


Fig. S.3. pH_{PZC} as a function of α_1 and α_2 for $\text{p}K_X = 4$ and $\text{p}K_Y = 10$ (solid lines). pH_{PZC} decreases with α_1 and increases with α_2 . At small values of α_1 and α_2 (i.e., $c_{X,0} = c_{Y,0}$), pH_{PZC} approaches $(\text{p}K_X + \text{p}K_Y)/2$. At high values of α_1 , on the other hand, pH_{PZC} varies almost linearly with $\log \alpha_1$ as $\text{pH}_{\text{PZC}} = \text{p}K_X - \log \alpha_1$ and so pH_{PZC} is independent of $\text{p}K_Y$. At high values of α_2 , pH_{PZC} is independent of $\text{p}K_X$ and varies linearly with $\log \alpha_2$ as $\text{pH}_{\text{PZC}} = \log \alpha_2 - \text{p}K_Y$. Dashed lines are extrapolation of pH_{PZC} for cases where $\alpha_1 \gg \alpha_0$ and $\alpha_2 \gg \alpha_0$.

S-5. Proposed generalization for charge efficiency of CDI systems

We introduced a generalized charge efficiency for CDI systems with functionalized surface charges in Section 4.4 of the main text. We here present details of derivation. As mentioned in the main text, we assume electrolyte volume is large enough and thus (1) initial and final electrolyte salt ion concentrations are equal to each other and constant ($c_+ = c_{+,0}$ and $c_- = c_{-,0}$), (2) initial and final pH of electrolyte are equal, and (3) pH is moderate such that salt concentration is considerably larger than hydronium or hydroxide. The latter can be justified by the fact that salt concentration in CDI is typically in 10-100 mM range, while even at $\text{pH} = 4$, $c_H = 0.1$ mM. So, c_H is at least two orders of magnitude less than salt concentration. Thus, we can write

$$\sigma_{\text{ionic}} \approx F \left[-2c_0 \sinh \left(\frac{\Delta\phi_D}{V_T} \right) + c_H \exp \left(-\frac{\Delta\phi_D}{V_T} \right) - \frac{K_w}{c_H} \exp \left(\frac{\Delta\phi_D}{V_T} \right) \right], \quad (\text{S.16})$$

$$\sigma_{chem} = F \left[-c_{X,0} \left(1 + \frac{c_H}{K_X} \exp\left(-\frac{\Delta\phi_D}{V_T}\right) \right)^{-1} + c_{Y,0} \left(1 + \frac{K_Y}{c_H} \exp\left(\frac{\Delta\phi_D}{V_T}\right) \right)^{-1} \right], \quad (S.17)$$

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

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

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

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

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

The charge efficiency can then be defined as

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

In this definition, $\Gamma - \Gamma_{PZC}$ is the *extra* salt adsorbed associated with applied potential V_{ext} (note, Γ can be non-zero at potential of zero charge V_{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_{ext} for various values of those parameters. Unless otherwise noted, other parameters used are listed in Table S.1.

Table S.1
Parameters used in Fig. S.4

Parameter	Description	Value	Unit
$c_{X,0}$	Analytical concentration of acidic group	1	M
$c_{Y,0}$	Analytical concentration of basic group	1	M
pK_X	Acid dissociation constant	4	-
pK_Y	Base dissociation constant	10	-
C_m	Volumetric micropore capacitance	145	F cm ⁻³
z_+, z_-	Cation and anion valance	1	-
c_0	Initial salt concentration	20	mM

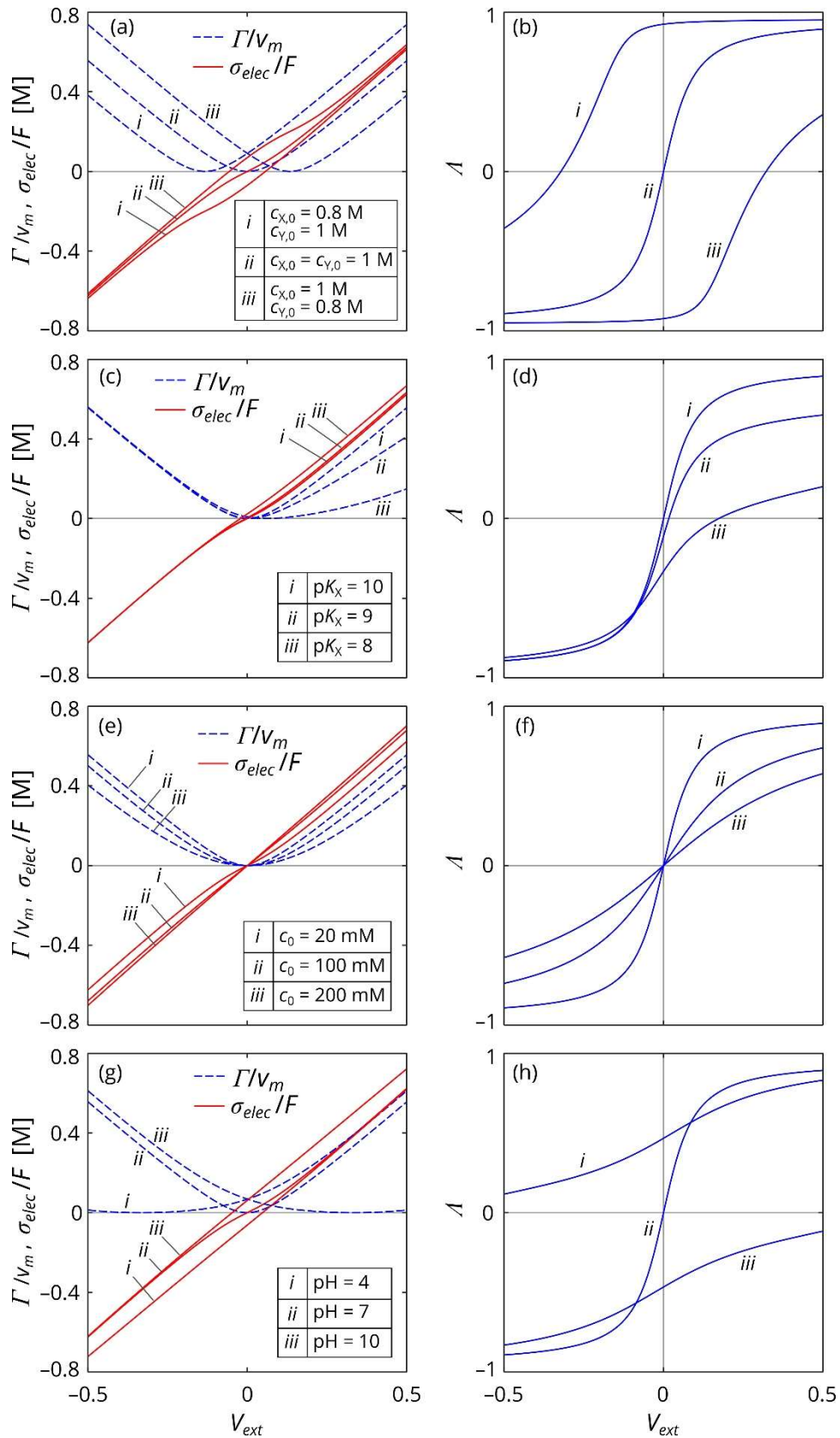


Fig. S.4. Volumetric adsorbed salt and electronic charge (in units of M) vs external voltage V_{ext} at various (a) analytical concentration of acidic and basic surface charges, (c) dissociation constant of acidic functional groups, (e) salt concentrations, and (g) electrolyte pH values. (b), (d), (f), (h) Charge efficiency vs V_{ext} for parameters as in (a), (c), (e), and (g). Other parameters used are listed in Table S.1.