Supporting Information

A Molecular Theory for Optimal Blue Energy Extraction by Electrical Double Layer Expansion

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A. Local excess chemical potentials

Classical density functional theory (CDFT) provides an analytical expression for the local excess chemical potentials of ionic species, i.e., μ_i^{ex} in Eq. (1) in the main text. For the primitive model of electrolyte solutions used in this work, μ_i^{ex} includes contributions due to hard-sphere (HS) repulsion and electrostatic correlation (EL)

$$\mu_i^{ex}(\mathbf{r}) = \mu_i^{HS}(\mathbf{r}) + \mu_i^{EL}(\mathbf{r}) \qquad \text{* MERGEFORMAT (S1)}$$

The hard-sphere term accounts for the ionic excluded volume effects, which can be accurately described with the modified fundamental measure theory (MFMT)[1, 2]

$$\beta\mu_i^{HS}(\mathbf{r}) = \sum_{\alpha}\int d\mathbf{r}'\phi_{\alpha}\omega_i^{(\alpha)}(\mathbf{r}-\mathbf{r}') \qquad \text{* MERGEFORMAT (S2)}$$

In Eq.* MERGEFORMAT (S2), the summation applies to six weight functions, $\omega_i^{(\alpha)}(\mathbf{r})$, $\alpha = 0,1,2,3,V1,V2$, that are the same as those in the original fundamental measure theory[3]. Among them, two scalar weight functions are related to the volume and the surface area for a spherical particle of diameter σ_i:

$$\omega_i^{(3)}(\mathbf{r}) = \theta(r - \sigma_i / 2)$$ * MERGEFORMAT (S3)

$$\omega_i^{(2)}(\mathbf{r}) = \delta(r - \sigma_i / 2)$$ * MERGEFORMAT (S4)

where $r = |\mathbf{r}|$, $\delta(r)$ is the Dirac-delta function, and $\theta(r)$ is the Heaviside step function; and one is a surface vector weight function related to the variance across the particle surface

$$\boldsymbol{\omega}_i^{(V2)}(\mathbf{r}) = (\mathbf{r} / q)\delta(r - \sigma_i / 2)$$ * MERGEFORMAT (S5)

Other weight functions are given by

$$\omega_i^{(0)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r}) / (\pi\sigma_i^2),\ \omega_i^{(1)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r}) / (2\pi\sigma_i),\ \boldsymbol{\omega}_i^{(V1)}(\mathbf{r}) = \boldsymbol{\omega}_i^{(V2)}(\mathbf{r}) / (2\pi\sigma_i)$$ * MERGEFORMAT (S6)

The coefficients on the right side of Eq.* MERGEFORMAT (S2) are defined by the functional derivatives of the local excess Helmholtz energy density with respect to the six weighted densities:

$$\phi_0 = -\ln(1 - n_3)$$ * MERGEFORMAT (S7)

$$\phi_1 = \frac{n_2}{1 - n_3}$$ * MERGEFORMAT (S8)

$$\phi_2 = \frac{n_1}{1 - n_3} + \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{12\pi n_3^2 (1 - n_3)^2} n_2^2 (1 - \varsigma^2 - \varsigma^4 + \varsigma^6)$$ * MERGEFORMAT (S9)

$$\phi_3 = \frac{n_0}{1 - n_3} + \frac{n_1 n_2}{(1 - n_3)^2}(1 - \varsigma^2) - \frac{n_2^3 (1 - \varsigma^2)^3}{36\pi}\left[\frac{2 - 5n_3 + n_3^2}{(1 - n_3)^3 n_3^2} + \frac{2\ln(1 - n_3)}{n_3^3}\right]$$ * MERGEFORMAT (S10)

$$\boldsymbol{\phi}_{v1} = -\frac{\mathbf{n}_{v2}}{1 - n_3}$$ * MERGEFORMAT (S11)

$$\boldsymbol{\phi}_{v2} = -\frac{\mathbf{n}_{v1}}{1 - n_3} - \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{6\pi n_3^2 (1 - n_3)^2} n_2 \mathbf{n}_{v2} (1 - \varsigma^2)^2$$ * MERGEFORMAT (S12)

where $\varsigma = \mathbf{n}_{v2} / n_2$, and the weighted densities are

$$n_\alpha(\mathbf{r}) = \sum_i n_{\alpha,i}(\mathbf{r}) = \sum_i \int d\mathbf{r}'\rho_i(\mathbf{r}')\omega_i^{(\alpha)}(\mathbf{r}-\mathbf{r}')$$ * MERGEFORMAT (S13)

In the slab geometry, the ionic density profiles vary only in the direction perpendicular to the surface, *viz*, $\rho_i(\mathbf{r}) = \rho_i(z)$. In that case, the weighted densities are

$$n_{0,i}(z) = \frac{n_{2,i}(z)}{\pi\sigma_i^2}$$ * MERGEFORMAT (S14)

$$n_{1,i}(z) = \frac{n_{2,i}(z)}{2\pi\sigma_i}$$ * MERGEFORMAT (S15)

$$n_{2,i}(z) = \pi\sigma_i \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz'\rho_i(z')$$ * MERGEFORMAT (S16)

$$n_{3,i}(z) = \pi \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz'\rho_i(z')[\sigma_i^2/4-(z'-z)^2]$$ * MERGEFORMAT (S17)

$$\mathbf{n}_{V1,i}(z) = \frac{\mathbf{n}_{V2,i}(z)}{2\pi\sigma_i}$$ * MERGEFORMAT (S18)

$$\mathbf{n}_{V2,i}(z) = -\frac{\mathbf{z}}{z}\pi\sigma \int_{z-\sigma_i/2}^{z+\sigma_i/2} \rho_i(z')(z'-z)dz'$$ * MERGEFORMAT (S19)

Similarly, the local excess chemical potentials are

$$\phi_{0,i}(z) = \frac{\phi_{2,i}(z)}{\pi\sigma_i^2}$$ * MERGEFORMAT (S20)

$$\phi_{1,i}(z) = \frac{\phi_{2,i}(z)}{2\pi\sigma_i}$$ * MERGEFORMAT (S21)

$$\phi_{2,i}(z) = \pi\sigma_i \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz'\phi_2(z')$$ * MERGEFORMAT (S22)

$$\phi_{3,i}(z) = \pi \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz'\phi_3(z')[\sigma_i^2/4-(z'-z)^2]$$ * MERGEFORMAT (S23)

$$\phi_{V1,i}(z) = \frac{\phi_{V2,i}(z)}{2\pi\sigma_i}$$ * MERGEFORMAT (S24)

$$\phi_{V2,i}(z) = \pi\sigma \int_{z-\sigma_i/2}^{z+\sigma_i/2} \phi_{V2}(z')(z'-z)dz'$$ * MERGEFORMAT (S25)

As detailed in our previous work[4, 5], the reduced excess chemical potential due to the electrostatic correlations is given by

$$\beta\mu_i^{EL}(\mathbf{r}) = \beta\mu_i^{EL}[\rho_i(z=R,x)] - \sum_{j=+,-}\int \Delta\rho_j\left(\mathbf{r}'\right)c_{ij}^{EL}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)d\mathbf{r}'$$ * MERGEFORMAT (S26)

According to the mean-spherical approximation (MSA)[6], the direct correlation function (DCF) is

$$c_{ij}^{EL}\left(q\right) = -2l_B\left[-Z_iN_j + X_i\left(N_i+\Gamma X_i\right) - \left(\sigma_i/3\right)\left(N_i+\Gamma X_i\right)^2\right]$$ * MERGEFORMAT (S27)

for the range of $0 \le q \le \left|\sigma_i-\sigma_j\right|/2$

$$c_{ij}^{EL}\left(q\right) = l_B\left[\left(\sigma_i-\sigma_j\right)L_1 - rL_2 + q^2L_3 + q^4L_4\right]$$ * MERGEFORMAT (S28)

and for $\left|\sigma_i-\sigma_j\right|/2 \le q \le \sigma_{ij}$. The MSA parameters are calculated from

$$\begin{aligned}
L_1 &= \frac{X_i+X_j}{4}\left(S_i-S_j\right) - \frac{\sigma_i-\sigma_j}{16}\left[\left(S_i+S_j\right)^2 - 4N_iN_j\right]\\
L_2 &= \left(X_i-X_j\right)\left(N_i-N_j\right) + \left(X_i^2+X_j^2\right)\Gamma + \left(\sigma_i+\sigma_j\right)N_iN_j\\
&\quad + \left[\sigma_iS_i^2+\sigma_jS_j^2\right]/3\\
L_3 &= \frac{X_i}{\sigma_i}S_i + \frac{X_j}{\sigma_j}S_j + N_iN_j - \left[S_i^2+S_j^2\right]/2\\
L_4 &= \frac{S_i^2}{6\sigma_i^2} + \frac{S_j^2}{6\sigma_j^2}
\end{aligned}$$ * MERGEFORMAT (S29)

and

$$S_i = N_i + \Gamma X_i$$ * MERGEFORMAT (S30)

$$\Gamma = \left(\pi l_B\sum_i \rho_i(z=R,x)X_i^2\right)^{1/2}$$ * MERGEFORMAT (S31)

$$N_i = \frac{X_i-Z_i}{\sigma_i}$$ * MERGEFORMAT (S32)

where X_i is solved from the following non-linear equations

$$\left(1+\Gamma\sigma_i\right)X_i + \alpha\sigma_i^2\sum_j \rho_i(z=R,x)\sigma_jX_j = Z_i$$ * MERGEFORMAT (S33)

$$\alpha \equiv (\pi/2)\left[1-(\pi/6)\sum_i \rho_i(z=R,x)\sigma_i^3\right]^{-1}$$ * MERGEFORMAT (S34)

As shown in our previous work[7], the quadratic expansion is sufficient to capture counter-intuitive electrostatic phenomena such as attraction between like charges and charge inversion in the presence of multivalent ions, which defy the conventional mean-field theories.

B. Ionic density profiles in electrodes of various pore size

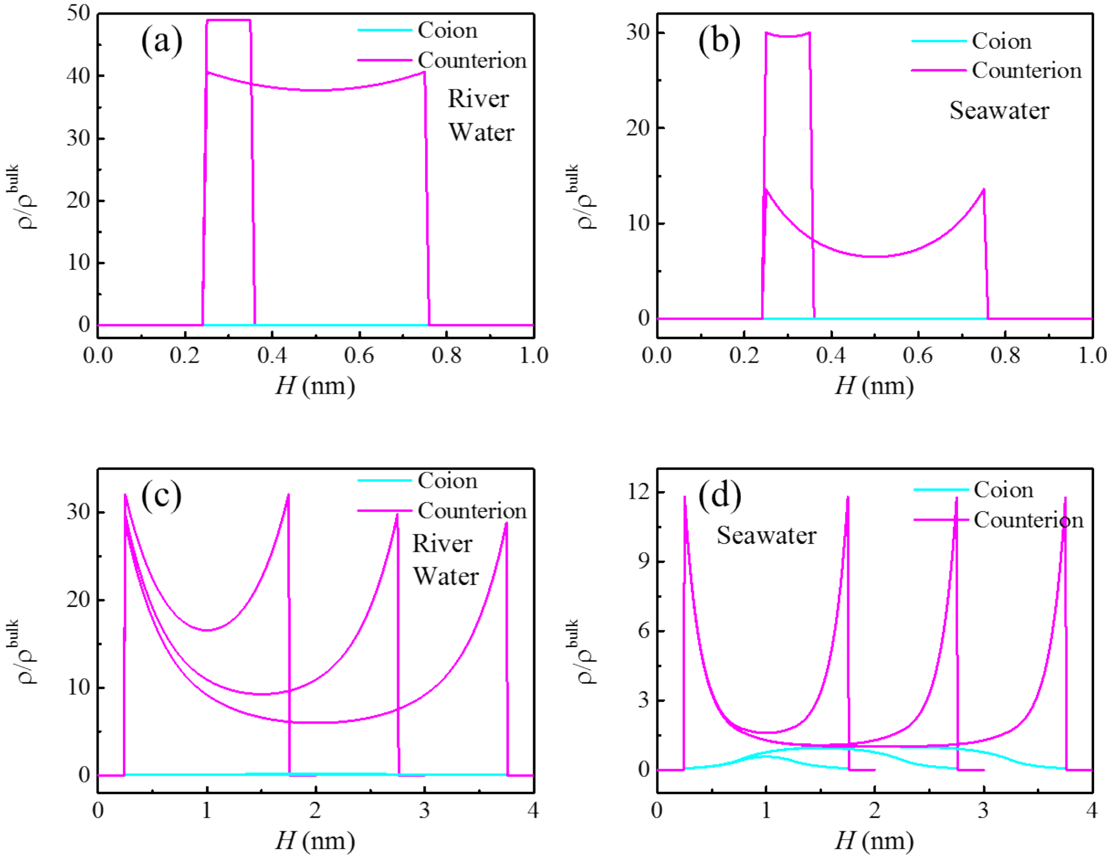

Figure S1 The reduced ionic density profiles in electrodes with slit pores. In all cases, the electrode potential is 0.1 V.

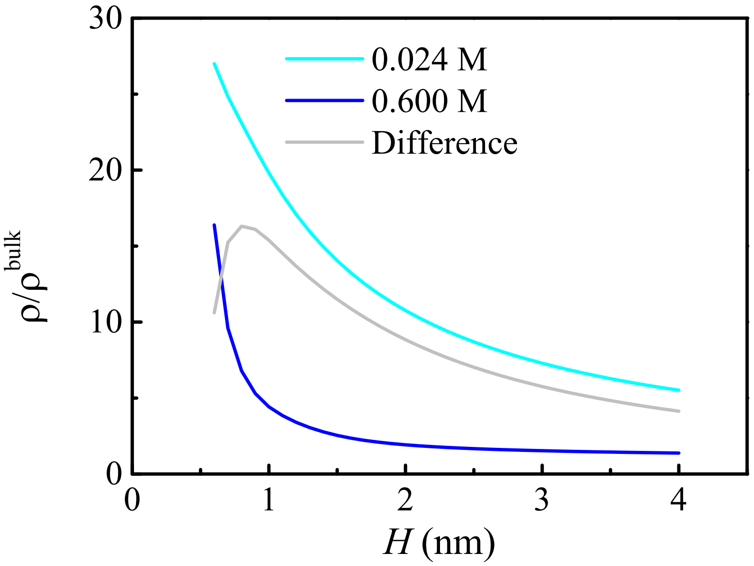

Figure S2 The averaged ion density (ρ/ρ^{bulk}) versus the pore size for an electrode with slit pores in contact with river water (ρ^{bulk} =0.024 M) and seawater (ρ^{bulk} =0.600 M). Here the electrode potential is 1.5 V.

References

1. Yu, Y.-X.; Wu, J., Structures of hard-sphere fluids from a modified fundamental-measure theory. *The Journal of Chemical Physics* **2002,** *117*, (22), 10156-10164.

2. Li, Z. D.; Wu, J. Z., Density-functional theory for the structures and thermodynamic properties of highly asymmetric electrolyte and neutral component mixtures. *Physical Review E* **2004,** *70*, (3), Artn 031109

3. Rosenfeld, Y., Free-energy model for the inhomogeneous hard-sphere fluid mixture and density-functional theory of freezing. *Phys Rev Lett* **1989,** *63*, (9), 980-983.

4. Jiang, J.; Cao, D. P.; Henderson, D.; Wu, J. Z., Revisiting density functionals for the primitive model of electric double layers. *Journal of Chemical Physics* **2014,** *140*, (4), Artn 044714.

5. Jiang, J.; Cao, D. P.; Henderson, D.; Wu, J. Z., A contact-corrected density functional theory for electrolytes at an interface. *Phys Chem Chem Phys* **2014,** *16*, (9), 3934-3938.

6. Ren, F.; Pearton, S. J., *Semiconductor device-based sensors for gas, chemical, and biomedical applications*. CRC: Boca Raton, Fla., 2011; p xii, 312 p.

7. Li, Z. D.; Wu, J. Z., Density functional theory for planar electric double layers: Closing the gap between simple and polyelectrolytes. *Journal of Physical Chemistry B* **2006,** *110*, (14), 7473-7484.