Supporting Information

Unraveling Flow Effect on Capacitive Energy Extraction from Salinity Gradients

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1. Dynamical adsorption-flow (DAF) model

For the one-dimensional system, the dynamical adsorption-flow (DAF) model can be simplified as follows\(^1\):

\[
\begin{align*}
\frac{\partial \rho_i(z;t)}{\partial t} = & \frac{\partial}{\partial z} \left\{ \frac{D_i}{m k_B T} \left[ \rho_i(z;t) \frac{\partial \mu_i(z;t)}{\partial z} + \frac{\partial}{\partial z} \left[ \rho_i(z;t) u_i^2(z;t) \right] \right] \right\} \\
\frac{\partial u_i(z;t)}{\partial t} + u_i(z;t) \frac{\partial}{\partial z} u_i(z;t) = & \frac{\partial}{\partial z} \left[ \rho_i(z;t) \frac{\partial \mu_i(z;t)}{\partial z} m_i \mu_i(z;t) \right]
\end{align*}
\]

(S1)

where \(\rho_i(z;t)\) represents the time-dependent local density of \(i\)-th species with \(i = +, -\) for cationic and anionic particles, \(\mu_i(z;t)\) represents the chemical potential, \(u_i(z;t)\) represents the local velocity, \(D_i\) represents the diffusion coefficient, \(m\) denotes the uniform particle mass of each particle, and \(k_B\) is the Boltzmann constant. The temperature is \(T=298\ K\).

In eq.(S1), the initial velocity of fluid flow is generated with the Hagen–Poiseuille (H–P) equation with no slippery boundary condition\(^2\):

\[
u_i(z;0) = \frac{\Delta \rho_i}{2 \eta L} \left( \frac{H^2}{4} - z^2 \right).
\]

(S2)

The chemical potential \(\mu_i(z;t)\) can be derived from the total Helmholtz free energy functional \(F[\rho_i(z;t)]\):

\[
\mu_i(z;t) = \frac{\delta F[\rho_i(z;t)]}{\delta \rho_i(z;t)}
= \frac{\delta F^{\text{int}}[\rho_i(z;t)]}{\delta \rho_i(z;t)} + \frac{\delta F^{\text{ext}}[\rho_i(z;t)]}{\delta \rho_i(z;t)}
= \mu_i^{\text{int}}(z;t) + V_i^{\text{ext}}(z)
\]

(S3)

Here \(\mu_i^{\text{int}}(z;t)\) is the intrinsic part of local chemical potential of species \(i\). \(V_i^{\text{ext}}\) is the external potential originated from the pore-fluid hard potential:

\[
V_i^{\text{ext}}(z) = \begin{cases} 
\infty, & z \geq H - \frac{\sigma_i}{2} \text{ or } z \leq \frac{\sigma_i}{2} \\
0, & \frac{\sigma_i}{2} < z < H - \frac{\sigma_i}{2} \\
\end{cases}
\]

(S4)
where $H$ is the slit pore width.

The intrinsic Helmholtz free energy, $F_{\text{int}}[\{\rho_i(\mathbf{r})\}]$ in eq.(S3), is decomposed into two contributions: the ideal-gas part and the excess one due to the intermolecular interaction. Namely:

$$F_{\text{int}}[\{\rho_i(\mathbf{r})\}] = F_{\text{id}}[\{\rho_i(\mathbf{r})\}] + F_{\text{ex}}[\rho_i(\mathbf{r})].$$

The ideal-gas term can be formulated exactly as:

$$\beta F_{\text{id}}[\{\rho_i(\mathbf{r})\}] = \sum_i \int d\mathbf{r} \rho_i(\mathbf{r}) \ln \left[ \rho_i(\mathbf{r}) \Lambda_i^3 \right] - 1.$$

Here $\Lambda_i$ is the thermos-wavelength which is immaterial with the final result.

For the charged hard-sphere system in this work, the excess part of the Helmholtz free energy includes the contributions from the hard-sphere repulsion, the electrostatic correlation contribution, and the direct Coulomb interaction:

$$F_{\text{ex}}[\{\rho_i(\mathbf{r})\}] = F_{\text{hr}}[\{\rho_i(\mathbf{r})\}] + F_{\text{el}}[\{\rho_i(\mathbf{r})\}] + F_{\text{c}}[\rho_i(\mathbf{r})].$$

In eq.(S7), the first term is obtained by employing the modified fundamental measure theory (MFMT)$^3$. The second term is obtained by the mean-spherical approximation (MSA)$^4$. The last term is from the direct Coulomb interaction solved by the Poisson equation$^5$.

2. Numerical calculation

In one dimensional case, the density profiles at time $t$ are solved by the equation of:

$$\begin{cases}
\frac{\partial \rho_i(z;\tau)}{\partial \tau} = D_i \frac{\partial}{\partial z} \left[ \rho_i(z;\tau) \frac{\partial \mu_i(z;\tau)}{\partial \rho_i(z;\tau)} + \frac{\partial}{\partial z} \left[ \rho_i(z;\tau) u_i^* (z;\tau^*) \right] \right], \\
\frac{\partial u_i^*(z;\tau^*)}{\partial \tau^*} = -\frac{\partial}{\partial z} \beta \mu_i(z;\tau) - u_i^*(z;\tau^*) \frac{\partial}{\partial z} u_i^*(z;\tau^*) \end{cases}.$$  

(S8)

Here $u_i^*(z;\tau^*) = \sqrt{m/k_BT} u(z;\tau)$, and $\tau^* = \frac{\tau}{\sqrt{m/k_BT}}$. The following boundary condition is adopted:
\[ \rho_i(z;0) = \rho_i^{0}(z), \quad (S9) \]

where \( \rho_i^{0}(z) \) is the density profile at the equilibrium state, which can be obtained by solving the classical density functional theory\(^{5}\).

During the numerical calculation, the mesh grid size in the z direction is set as \( \Delta z=0.02 \sigma \), and the time step size is \( \Delta t=1 \times 10^{-6} \tau_s \). For the convenience, we introduce the symbols of:

\[ M_i[\{\rho_i(z;t)\}] = D_i \frac{\partial}{\partial z} \left\{ \rho_i(z;t) \frac{\partial}{\partial z} \beta_i(z;t) + \frac{\partial}{\partial z} \rho_i(z;t)u_i^2(z;t) \right\}, \quad (S10) \]

and:

\[ \rho_i^{jk} = \rho_i(z_j; t_k), \quad (S11) \]
\[ \mu_i^{jk} = \mu_i(z_j; t_k), \quad (S12) \]
\[ M_i^{jk} = M_i[\{\rho_i(z_j; t_k)\}], \quad (S13) \]
\[ A_i = \rho_i(z_j; t_k)u_i^2(z_j; t_k). \quad (S14) \]

To ensure convergence, we use the Runge-Kutta(RK) method for the iterations. In the RK method, we take:

\[ \alpha_i^k = M_i^k, \quad (S15) \]
\[ \beta_i^k = M_i(\rho_i^k + \frac{\Delta t}{2} \alpha_i^k), \quad (S16) \]
\[ \gamma_i^k = M_i(\rho_i^k + \frac{\Delta t}{2} \beta_i^k), \quad (S17) \]
\[ \sigma_i^k = M_i(\rho_i^k + \Delta t \gamma_i^k), \quad (S18) \]
\[ \rho_i^{k+1} = \rho_i^k + \frac{1}{6}(\alpha_i^k + 2\beta_i^k + 2\gamma_i^k + \sigma_i^k)\Delta t. \quad (S19) \]

Also, we used the RK method for the calculation of the velocity evolution.
3. Additional information

**Figure S1.** Density profiles in SW with and without flow velocity at (a) 20.00 mV, and (b) 60.00 mV. The electrostatic potential distributions in SW with and without flow velocity at (c) 20.00 mV, and (d) 60.00 mV.
Figure S2. The reduction of (a) capacitance and (b) energy density.

Figure S3. The output energy under different operating conditions.
Reference:


