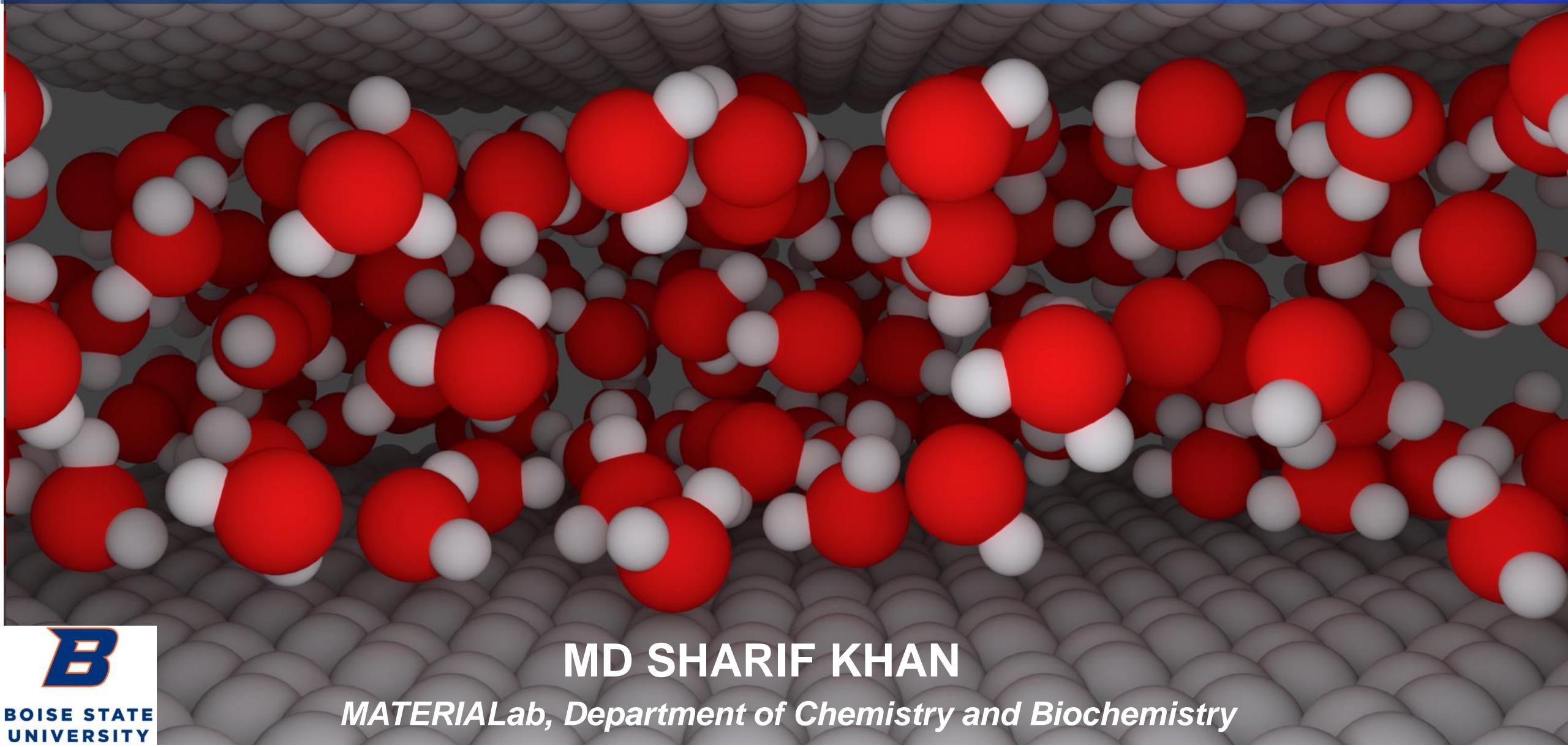


Electrochemical Molecular Dynamics Simulations



B

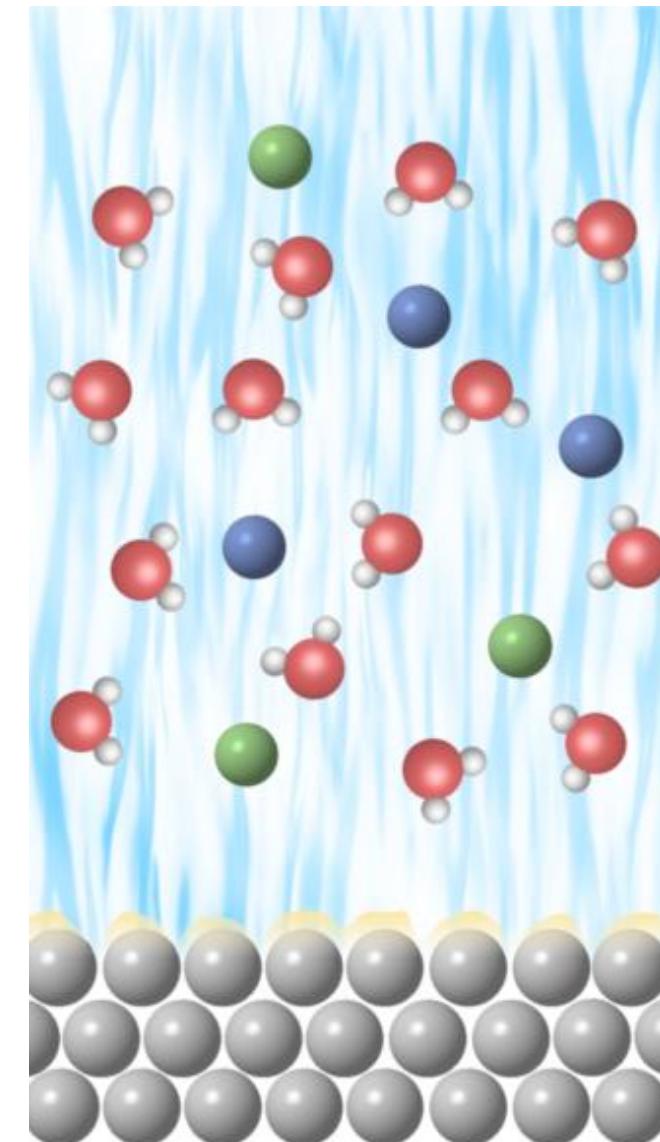
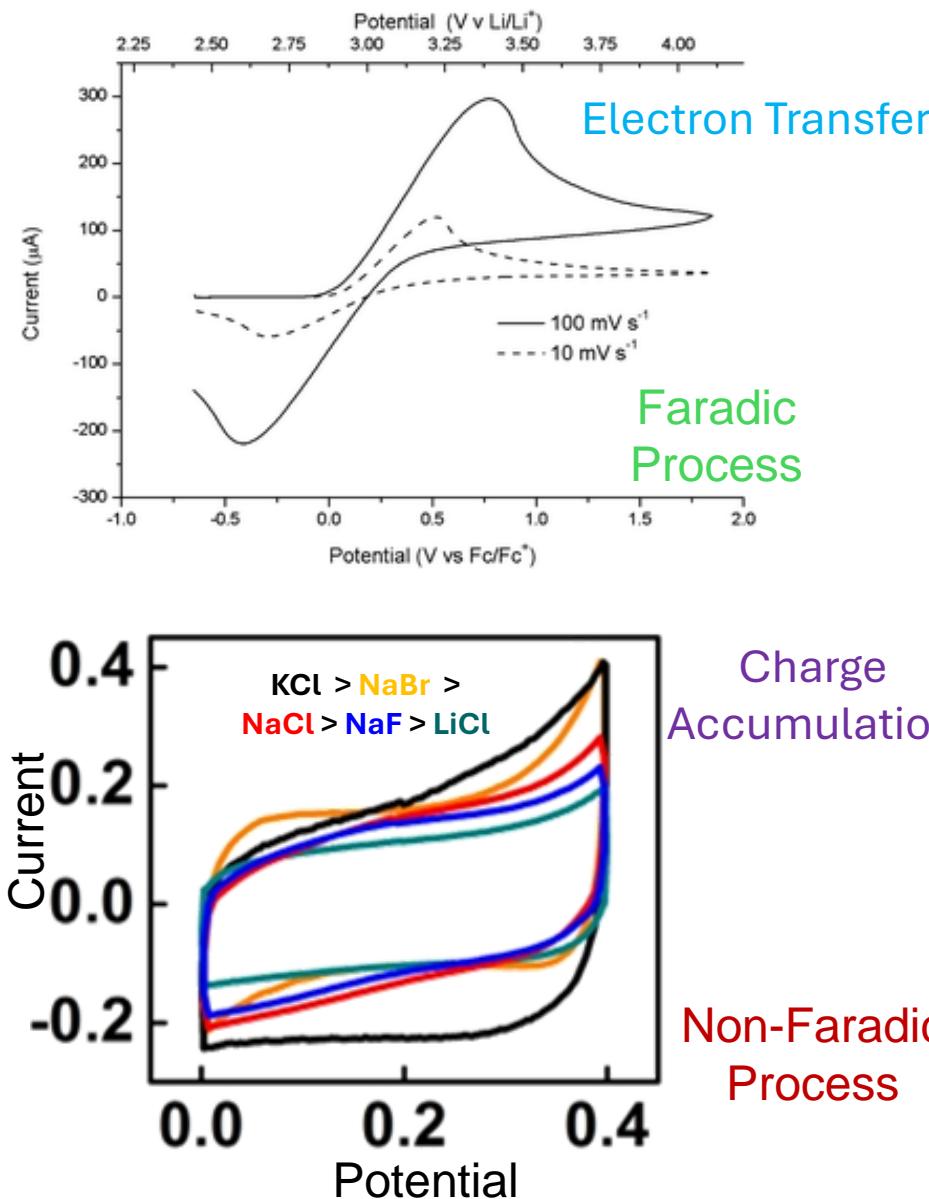
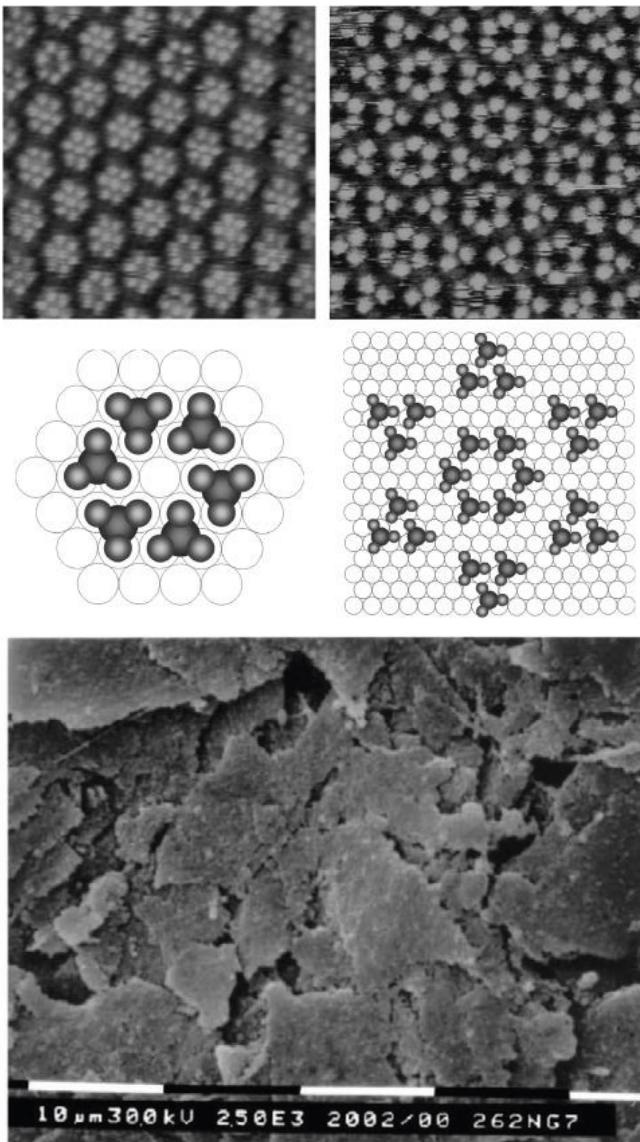
BOISE STATE
UNIVERSITY

MD SHARIF KHAN

MATERIALab, Department of Chemistry and Biochemistry

Electrochemical Interface

Adsorption and sensing

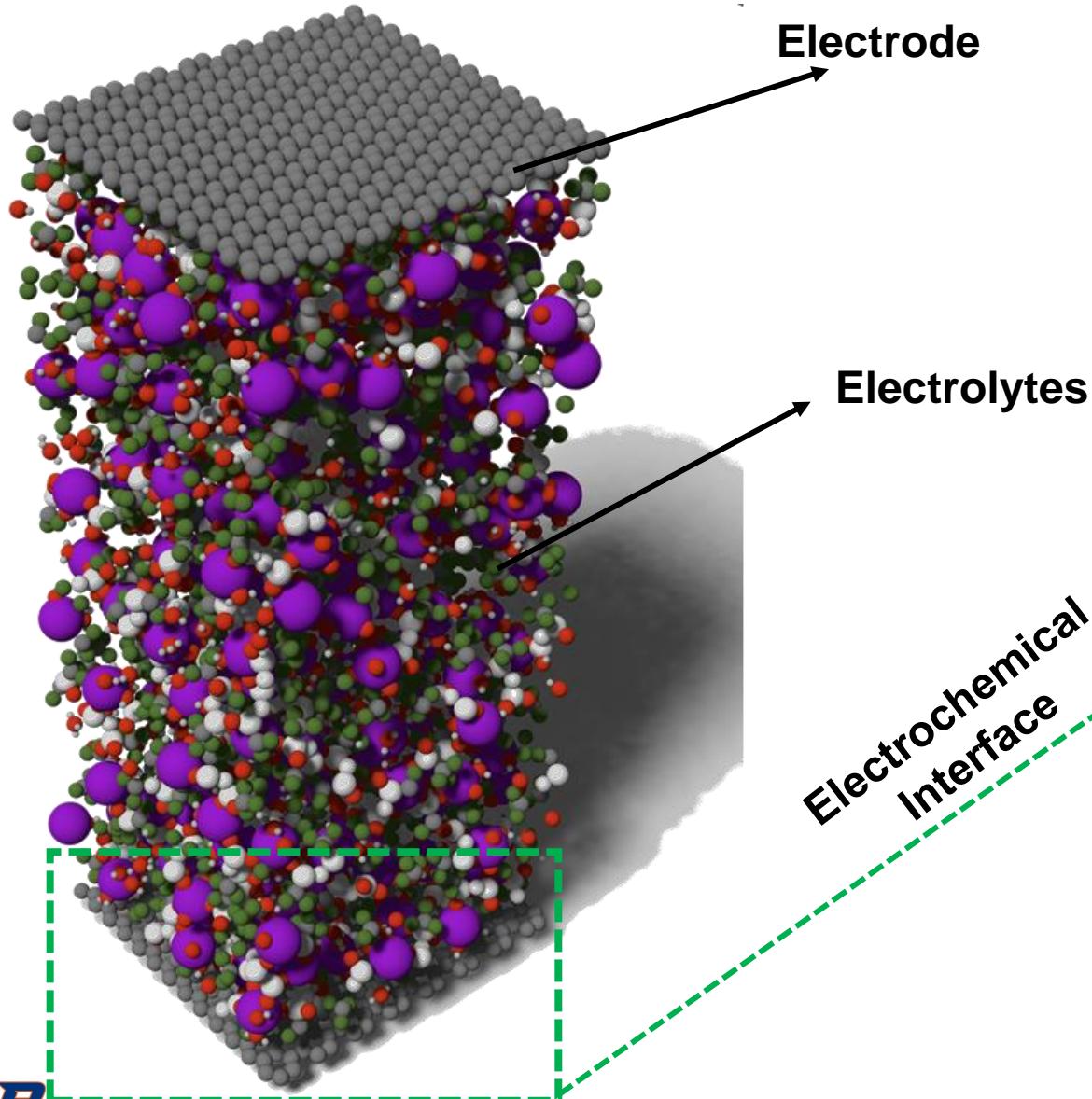


Adv. Sci. 2018, 5, 1700322.

Adv. Energy Mater. 2023, 13, 2203307

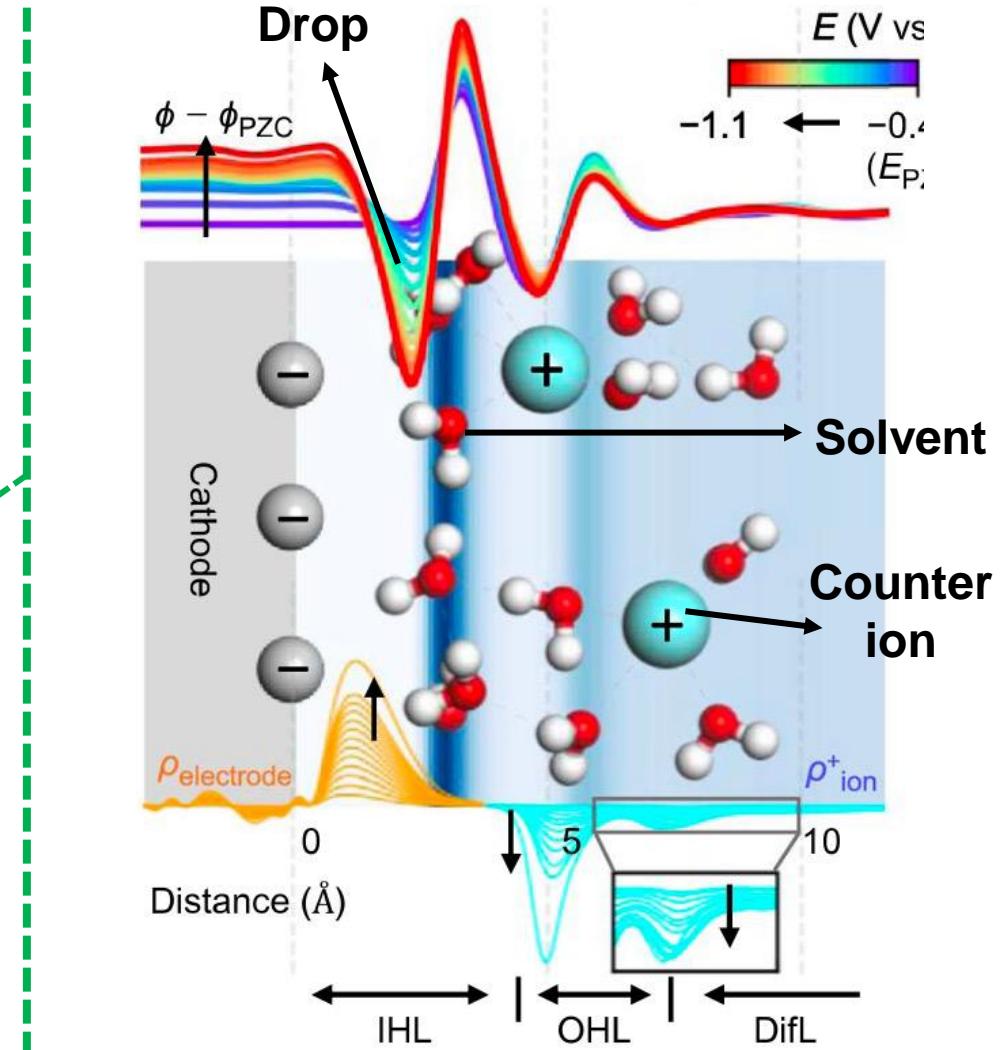
Designing Electrochemical Interface

Supercapacitor



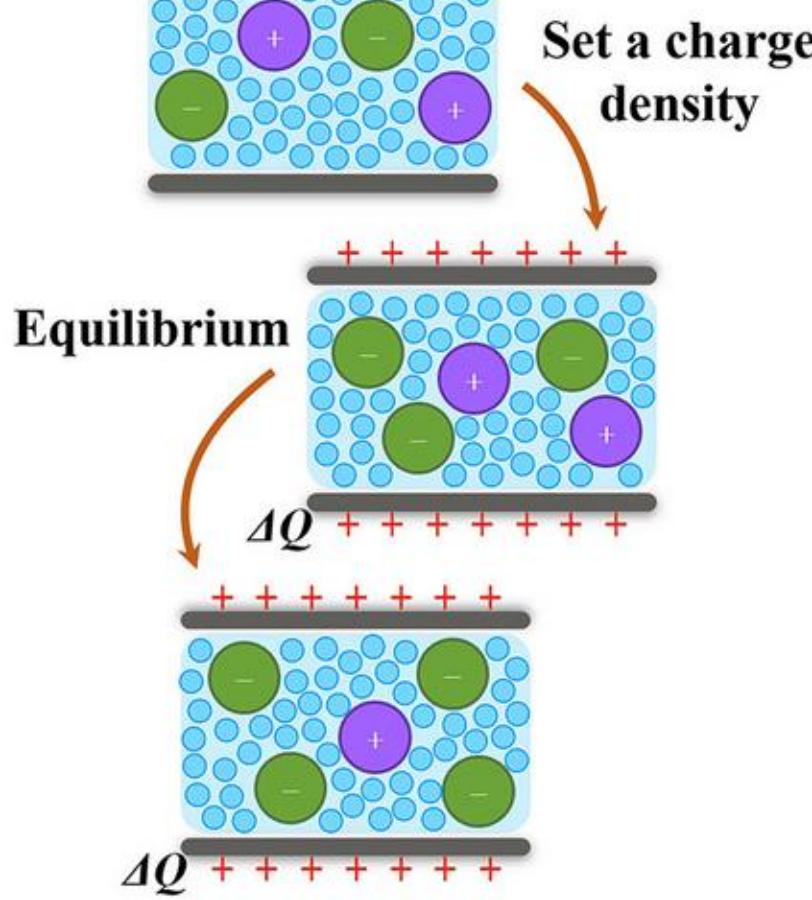
Electrochemical
Interface

Potential Drop

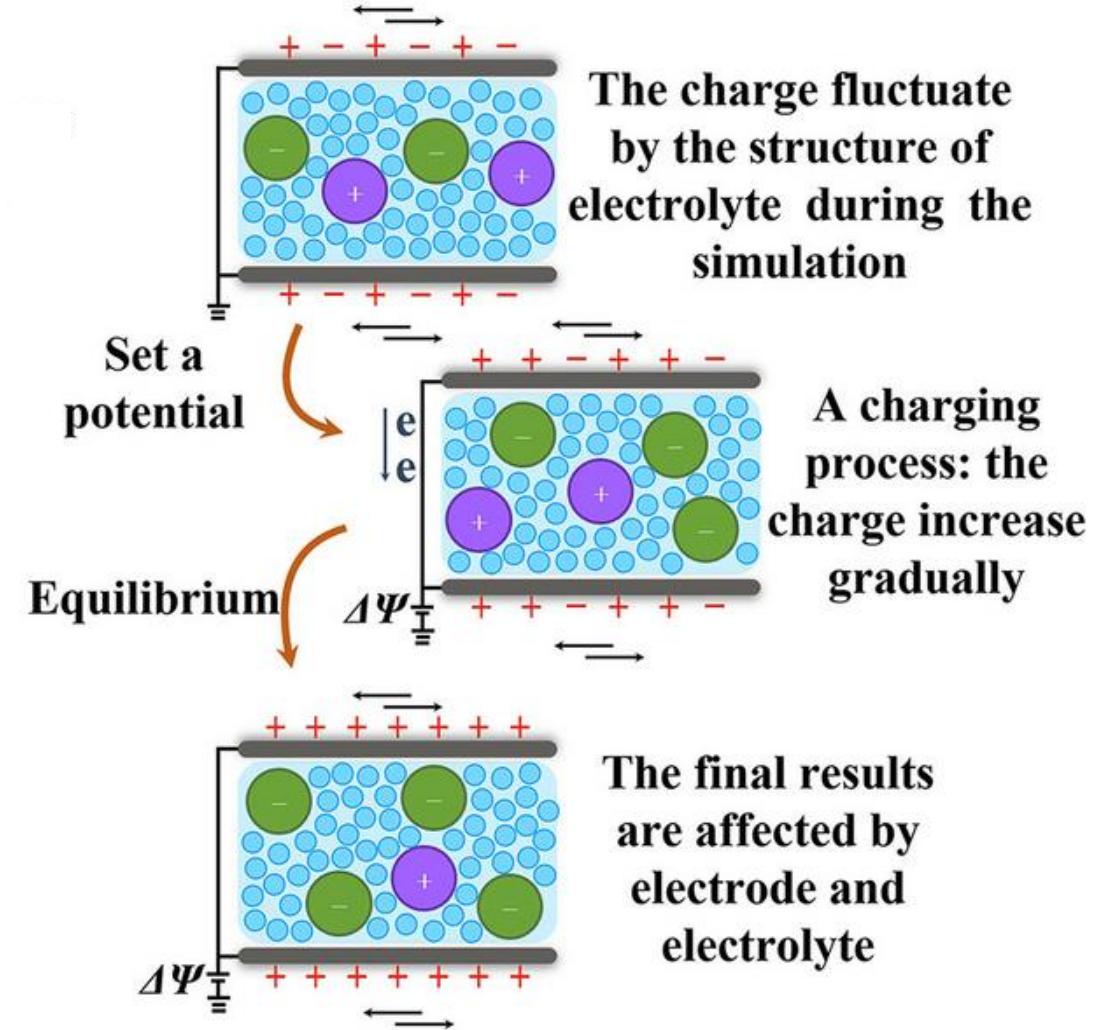


Methods

Constant Charge Method (CCM)



Constant Potential Method (CPM)



Potentially Confusing: Potentials in Electrochemistry



Cite This: *ACS Energy Lett.* 2021, 6, 261–266



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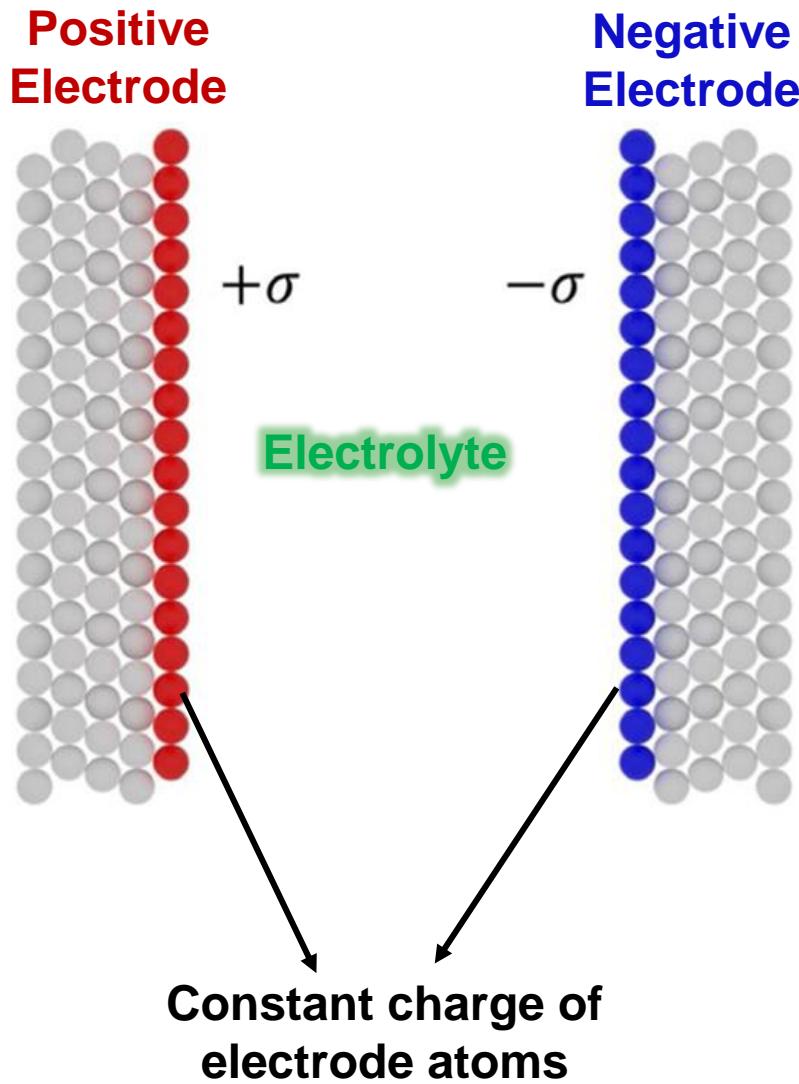


Metrics & More



Article Recommendations

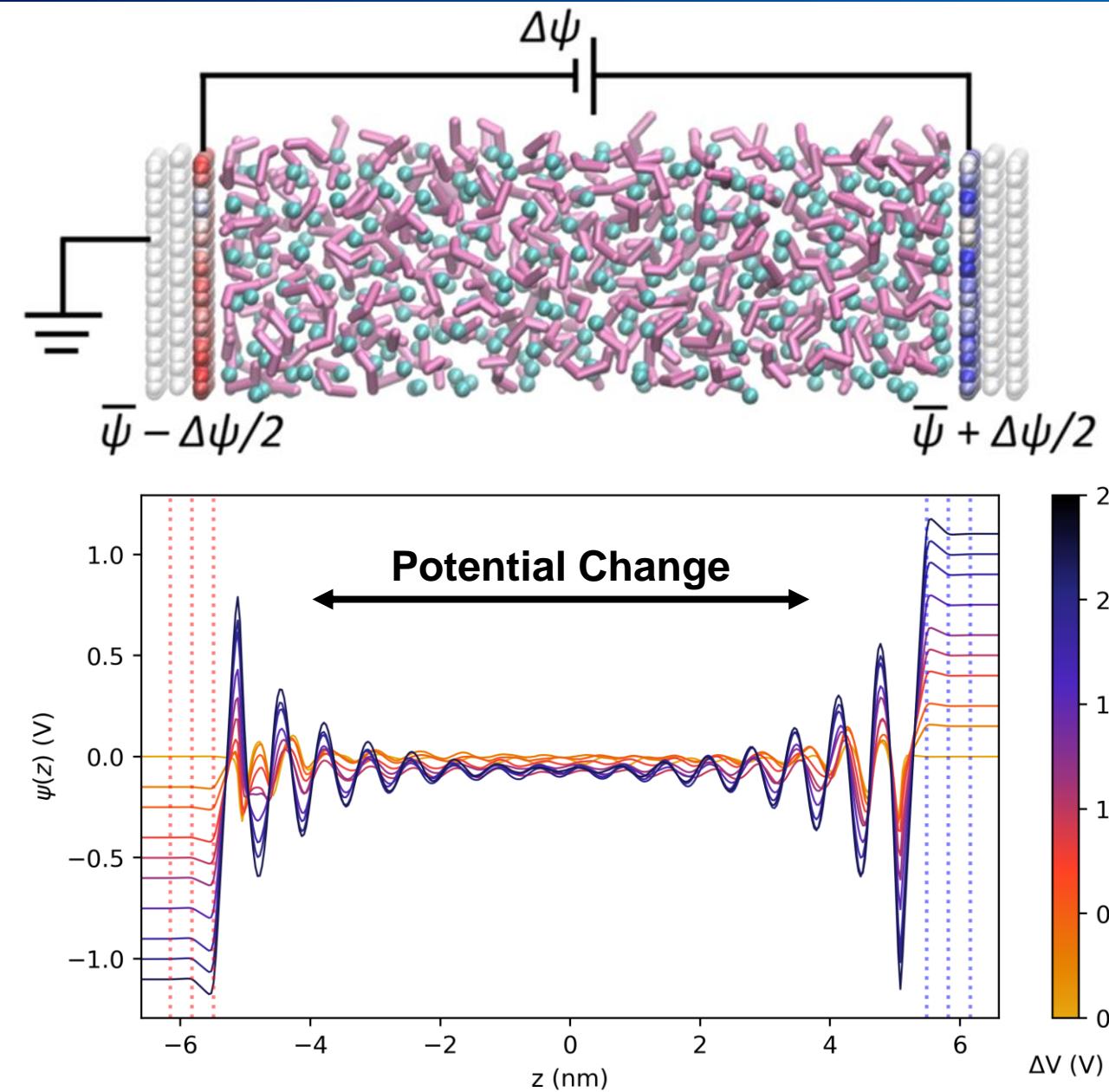
Constant Charge Method (CCM)



- ✓ Most straightforward and computationally inexpensive
- ✓ An electric potential drop can be created across the interfaces
- ✓ Electrolyte rearrangement on the charged electrode surface can be evaluated.

- ✓ Failed to capture the induced polarization of an electrode
- ✓ Post-processing needed to get the potential and sometimes it is complicated
- ✓ Not applicable to complicated morphologies and charging / fluid dynamics

Constant Potential Method (CPM)

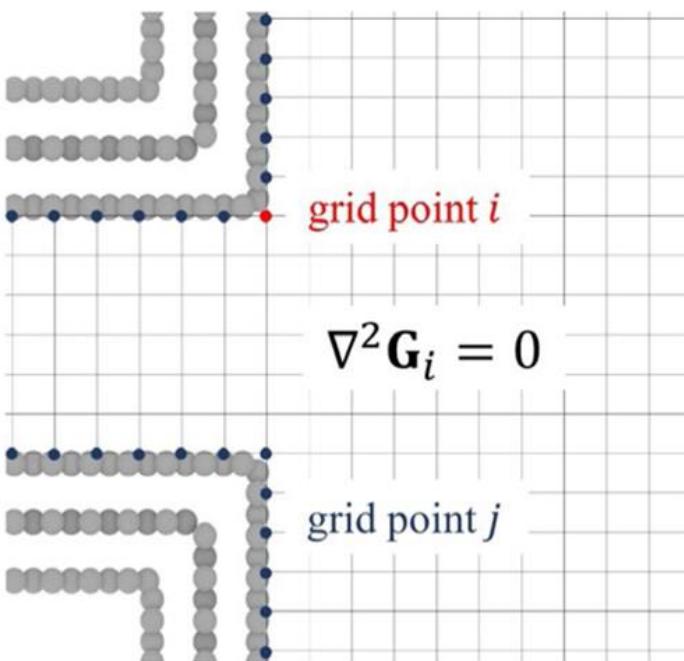


- ✓ A realistic representation of the electrodes
- ✓ Can reproduce the experimental potential
- ✓ Impact on the electrode charges due to counter ion adsorption
- ✓ Capture more complicated morphologies

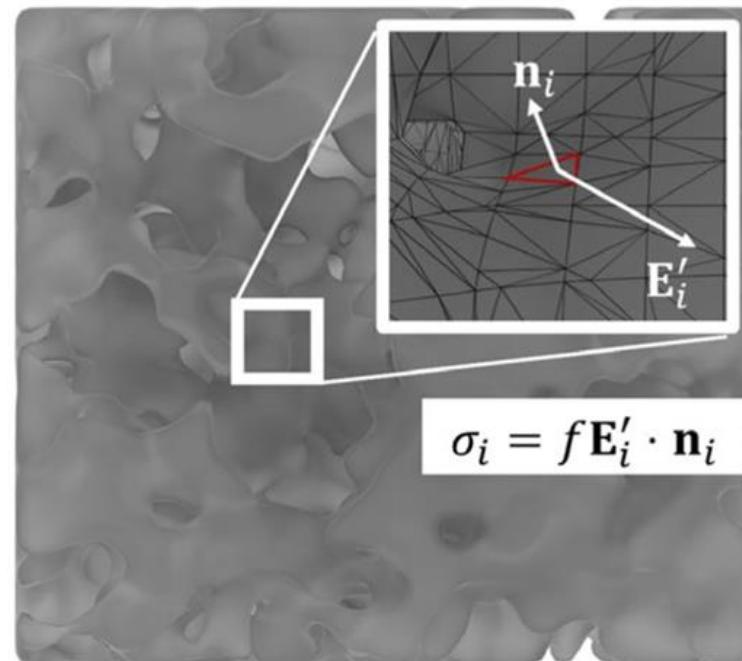
- ✓ Computationally Expensive
- ✓ Complicated to Setting Up
- ✓ Limited for the homogeneous electrodes

Different constant potential methods

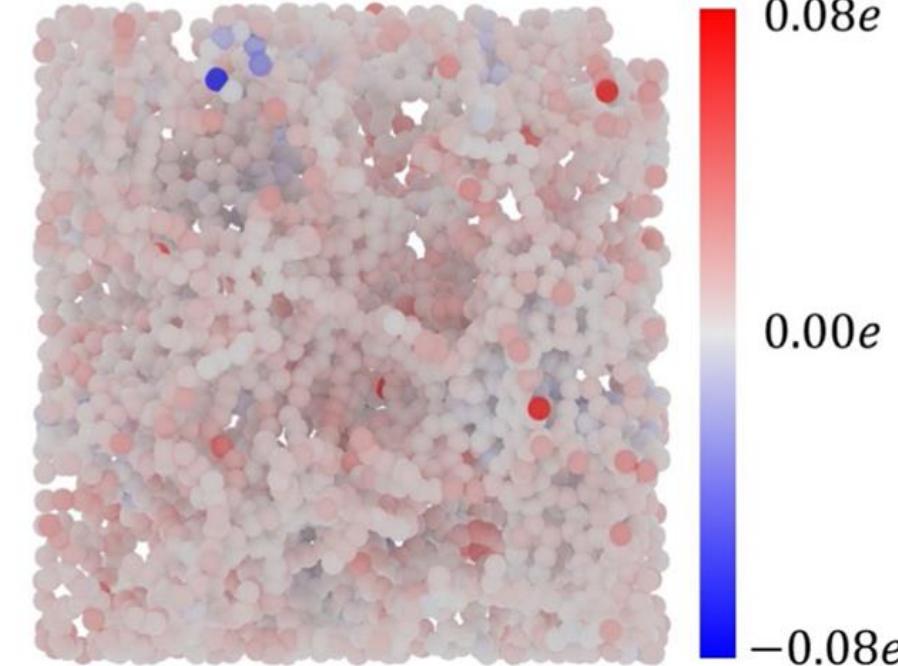
Green's Function Method (GFM)



Induced Charge Computation (ICC)

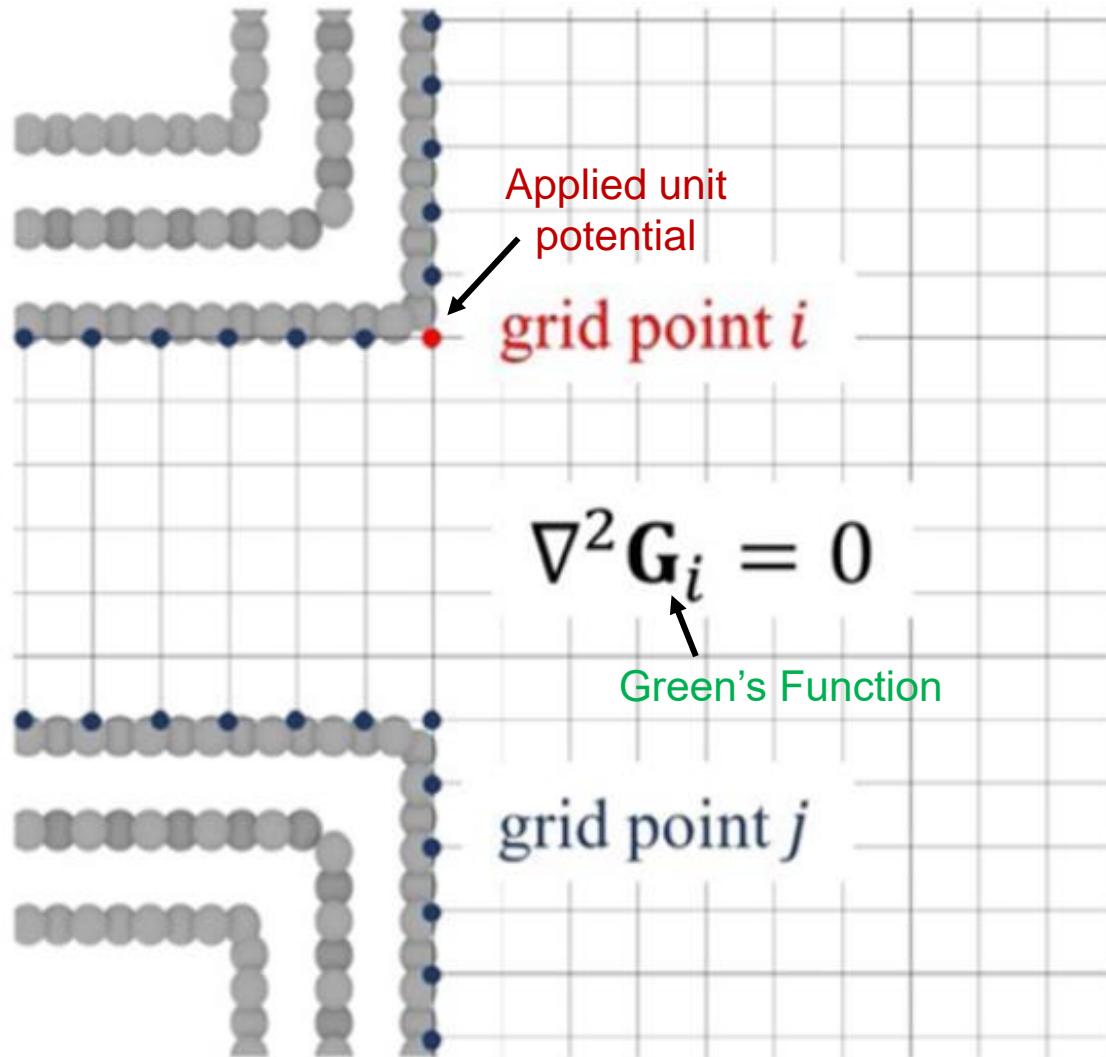


Fluctuating Charge Method (FCM)



Constant Potential Method (CPM)

Green's Function Method (GFM)



Electrical potential divided into two parts

Including electrolytes charges

$$\nabla^2 \phi' = -\frac{\rho_e}{\epsilon_0}, \quad \text{Solved by classical electrostatic method}$$
$$\nabla^2 \phi_c = 0, \quad \text{Using Green's Function}$$

From boundary conditions

Boundary Condition

$$\phi_c = \begin{cases} \phi^+ - \phi' & \text{for positive electrode,} \\ \phi^- - \phi' & \text{for negative electrode.} \end{cases}$$

Boundary Condition

$$\mathbf{G}_j^i = \begin{cases} 1, & j = i, \\ 0, & j \neq i, \end{cases}$$

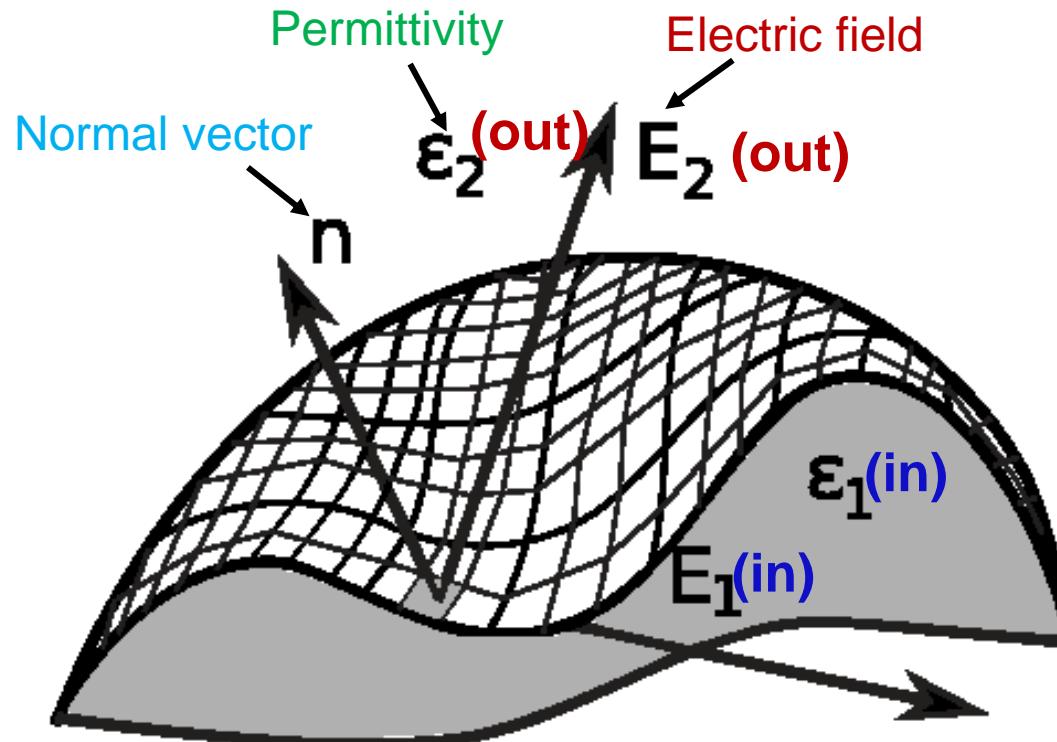
Solution

Total electrode grids

$$\phi_c = \sum_i^{N_e} \mathbf{G}_j^i \phi_i,$$

Constant Potential Method (CPM)

Induced Charge Computation (ICC)



PHYSICAL REVIEW E 2004, 69, 046702

Calculates the induced charge on polarized dielectric electrode – electrolyte boundaries

Polarization along \mathbf{n}

Mutation of \mathbf{E} due to σ

Contribution of induced charge

Electrolytes charge + induced charges on other elements

$$\epsilon_{out} \mathbf{E}^{out} \cdot \mathbf{n} = \epsilon_{in} \mathbf{E}^{in} \cdot \mathbf{n},$$

Induced charge density

$$(\mathbf{E}^{in} - \mathbf{E}^{out}) \cdot \mathbf{n} = \frac{4\pi\sigma}{\epsilon_{out}},$$

Electric field from induced charge

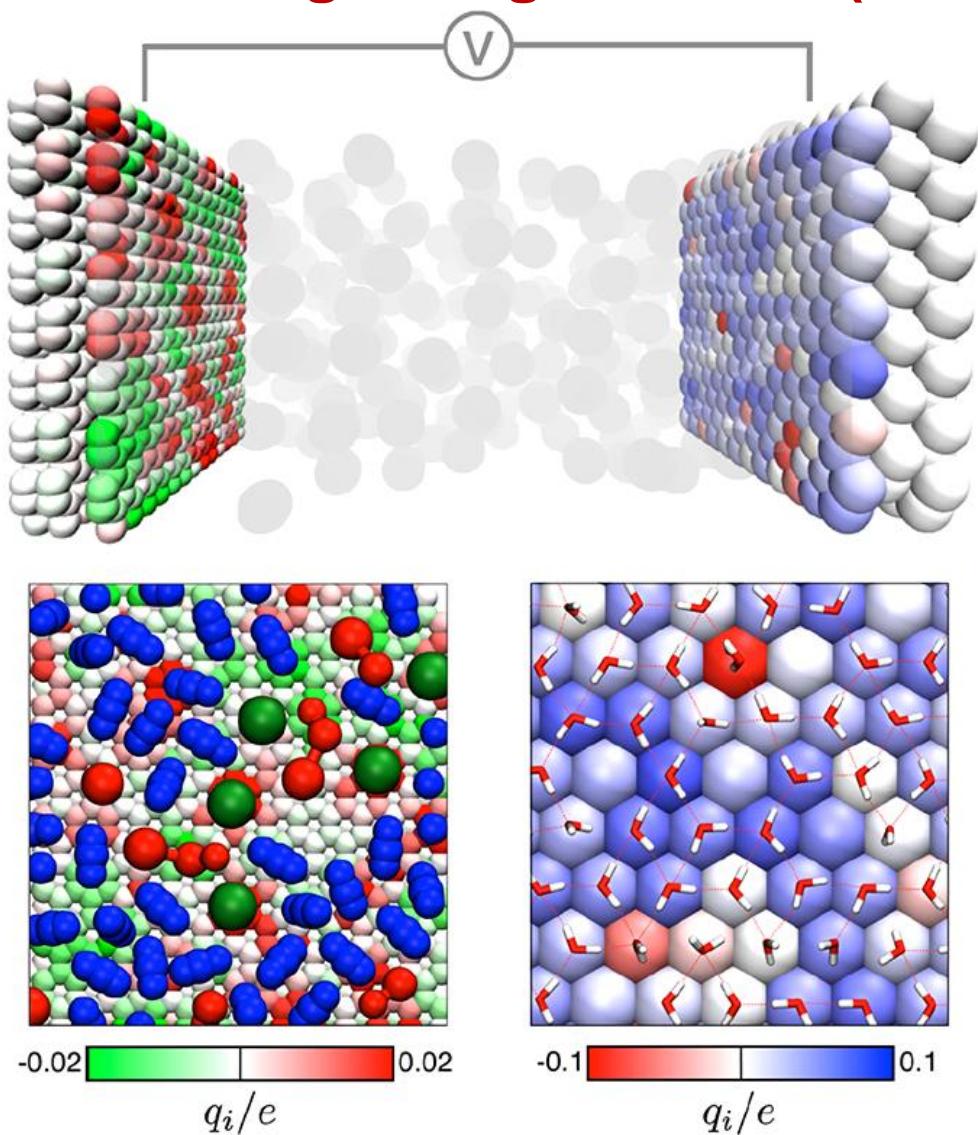
$$\mathbf{E}_i^{in/out} = \mathbf{E}'_i \pm \frac{2\pi\sigma_i \mathbf{n}_i}{\epsilon_{out}},$$

Induced charge of element i

$$\sigma_i = \frac{\epsilon_{out}}{2\pi} \left(\frac{\epsilon_{in} - \epsilon_{out}}{\epsilon_{in} + \epsilon_{out}} \right) \mathbf{E}'_i \cdot \mathbf{n}_i = f \mathbf{E}'_i \cdot \mathbf{n}_i,$$

Constant Potential Method (CPM)

Fluctuating Charge Method (FCM)



Electrode Charge Density

Electrostatic energy as a function of Q

Electrode atom charges

Fluctuating magnitude vector Gaussian width Atomic position

$$\rho_i(\mathbf{r}) = Q_i \left(\frac{\eta^2}{\pi} \right)^{\frac{3}{2}} \exp [-\eta^2 (\mathbf{r} - \mathbf{R}_i)^2]$$

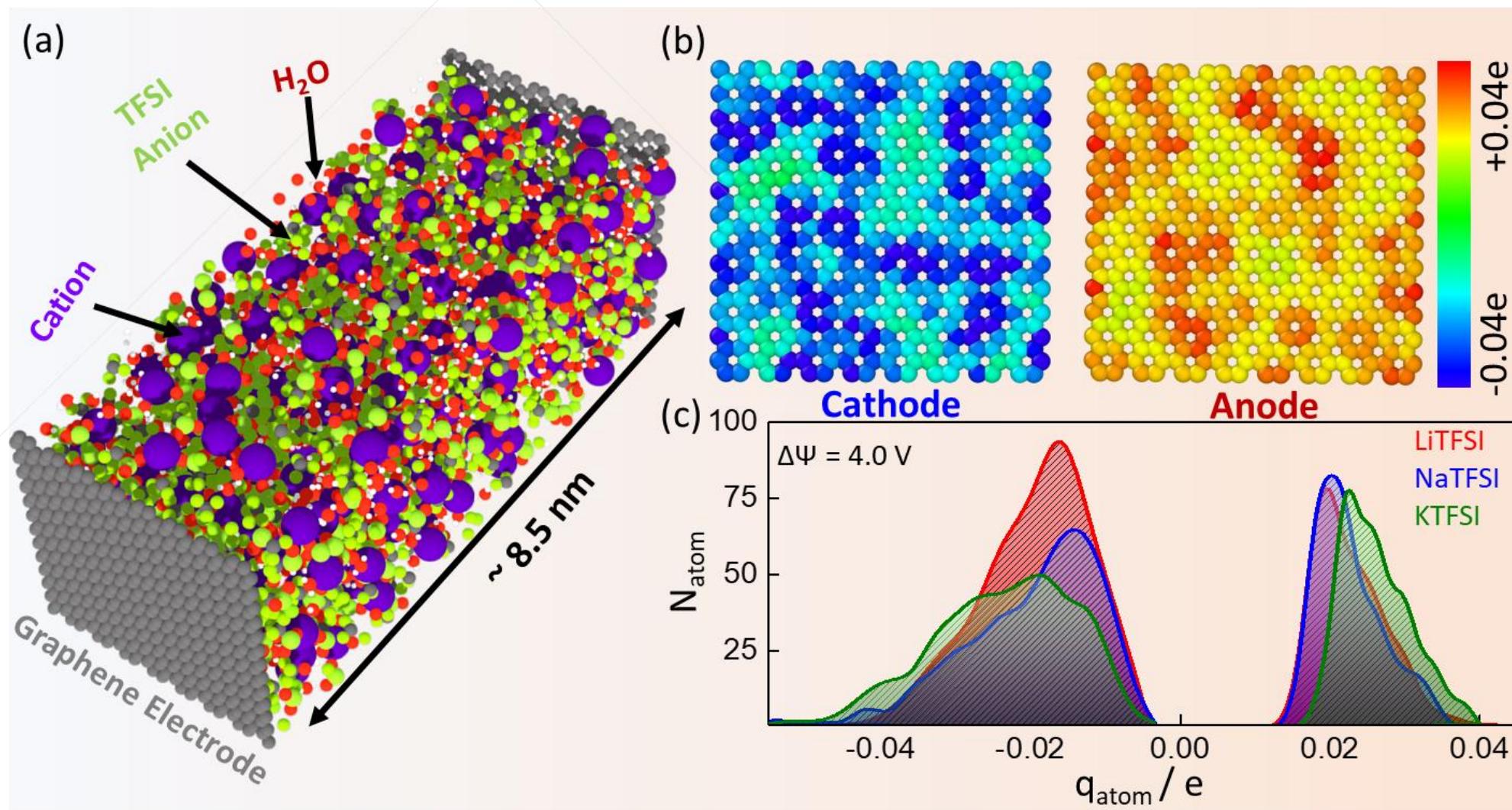
Electrostatic coefficients in electrode atoms Electrostatic coefficients by electrolyte charge Electrostatic energy from electrolytes

$$U_{ele}(Q) = \frac{1}{2} Q^T A Q - Q^T B + C$$

Set potential

$$Q = A^{-1} (B + \phi).$$

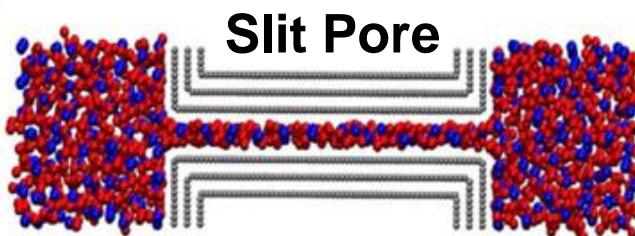
Flat Graphene Electrode Systems



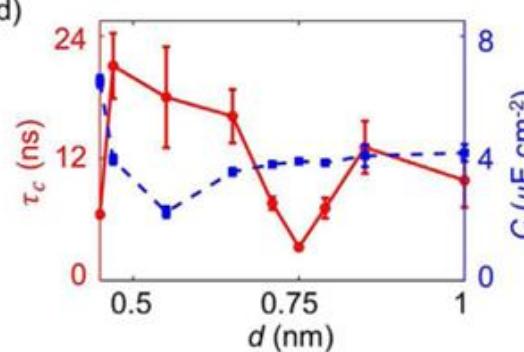
Charge fluctuations of the electrode atoms during the constant potential simulations of a supercapacitor

Nanoporous Electrodes

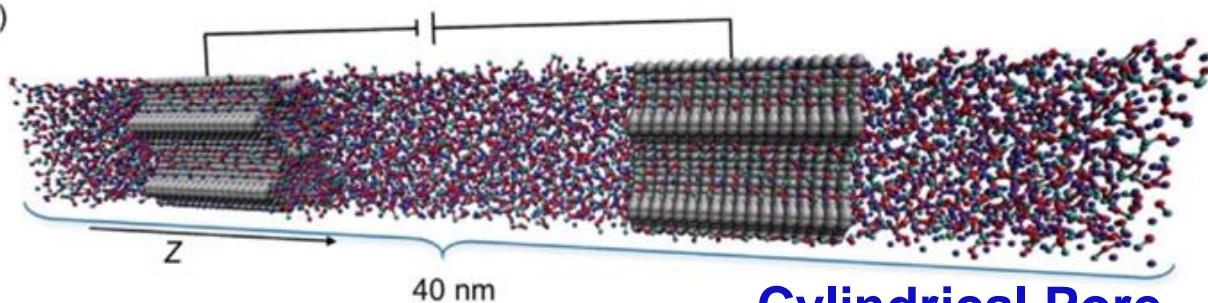
(c)



(d)

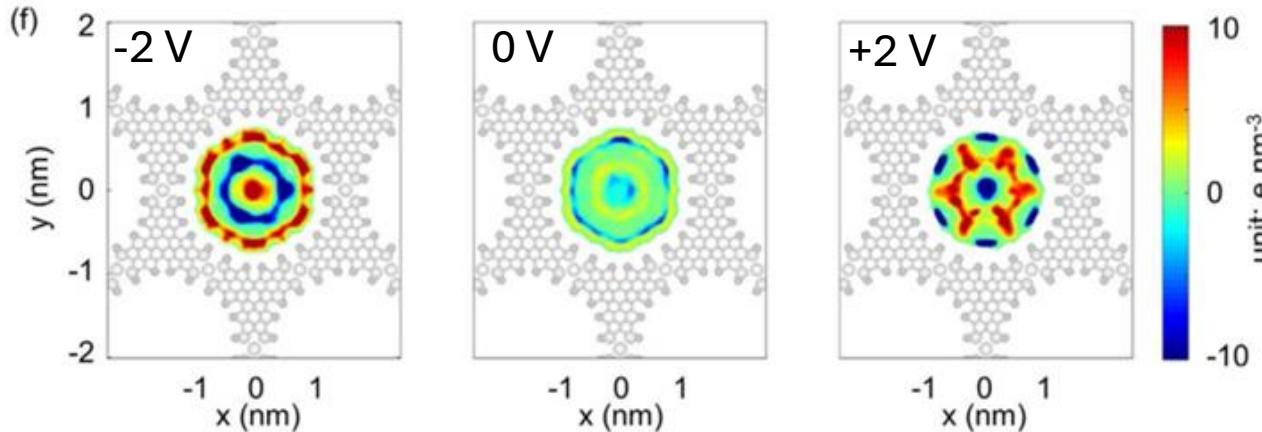


(e)

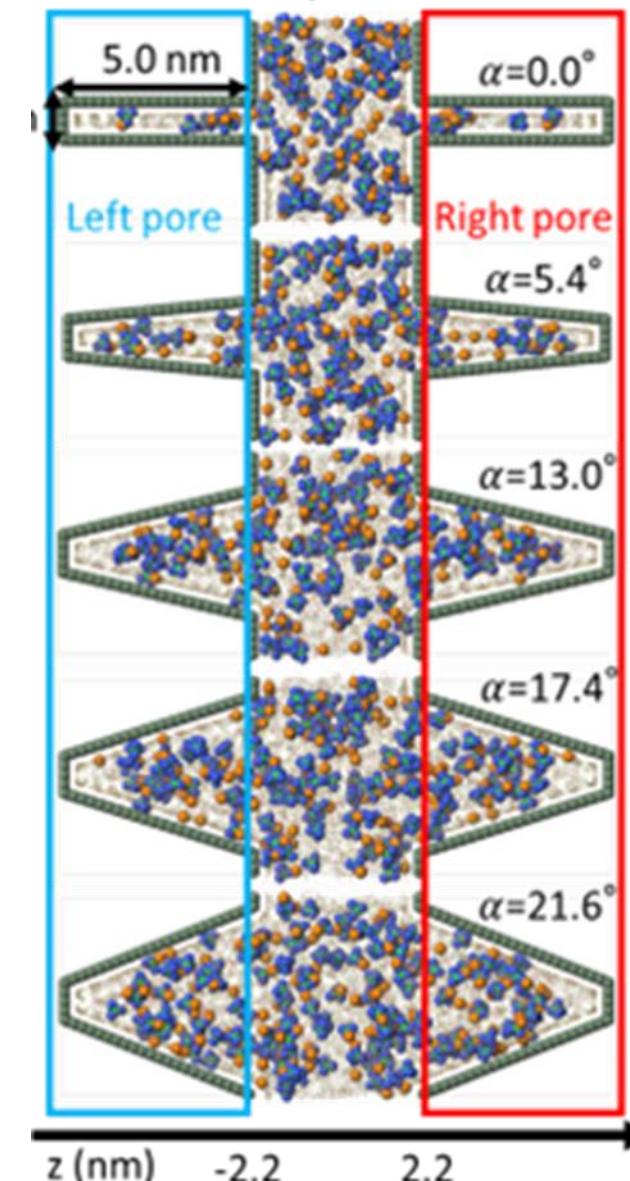


Cylindrical Pore

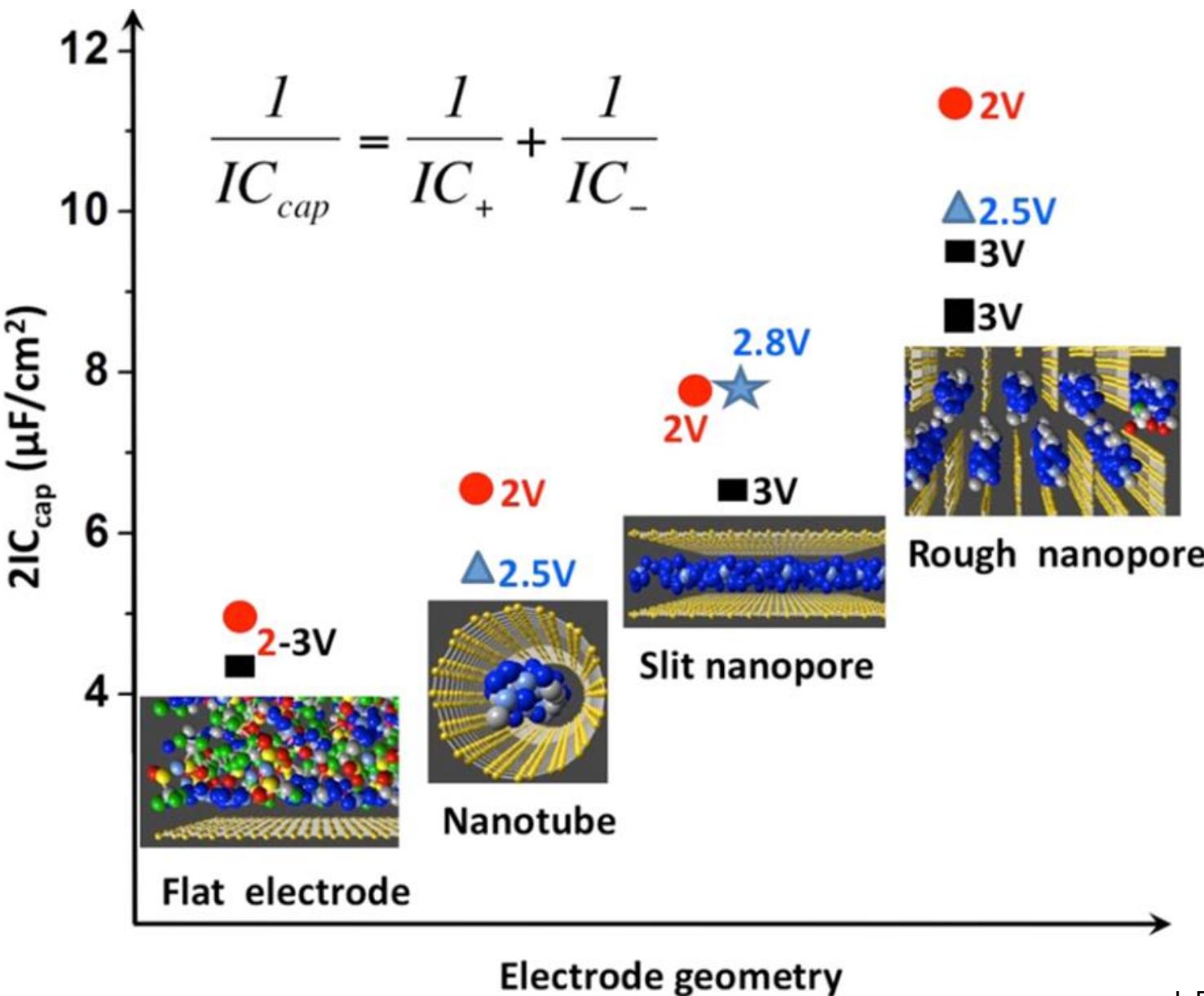
(f)



Wedge Pore

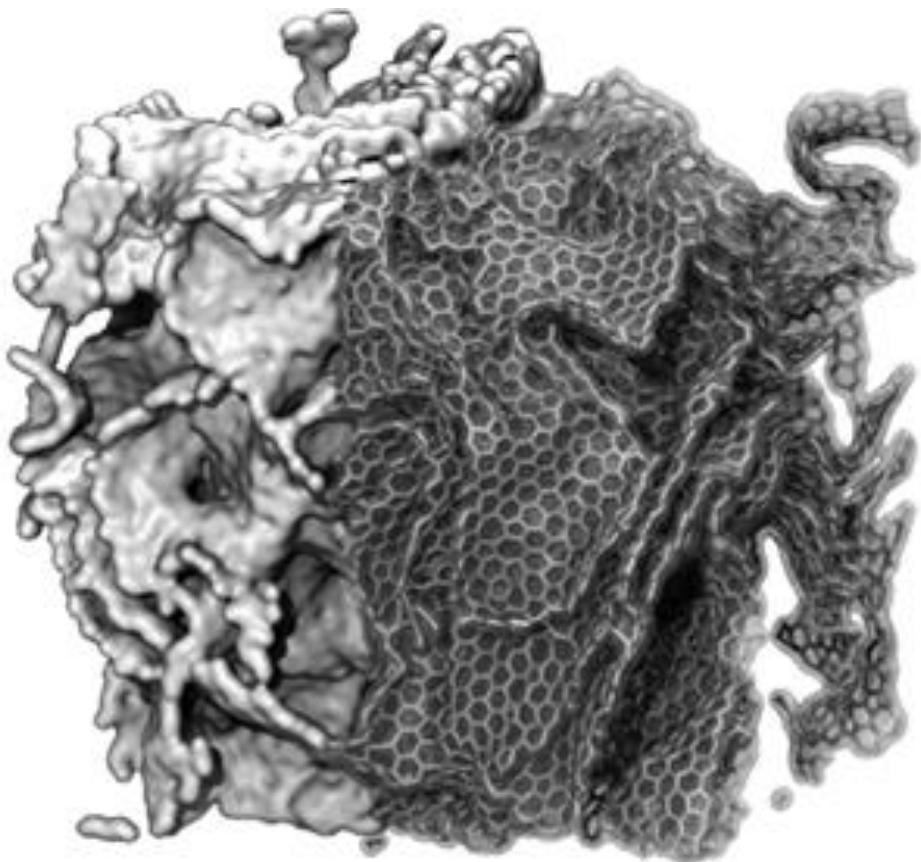


Capacitance in Different Electrode Geometries

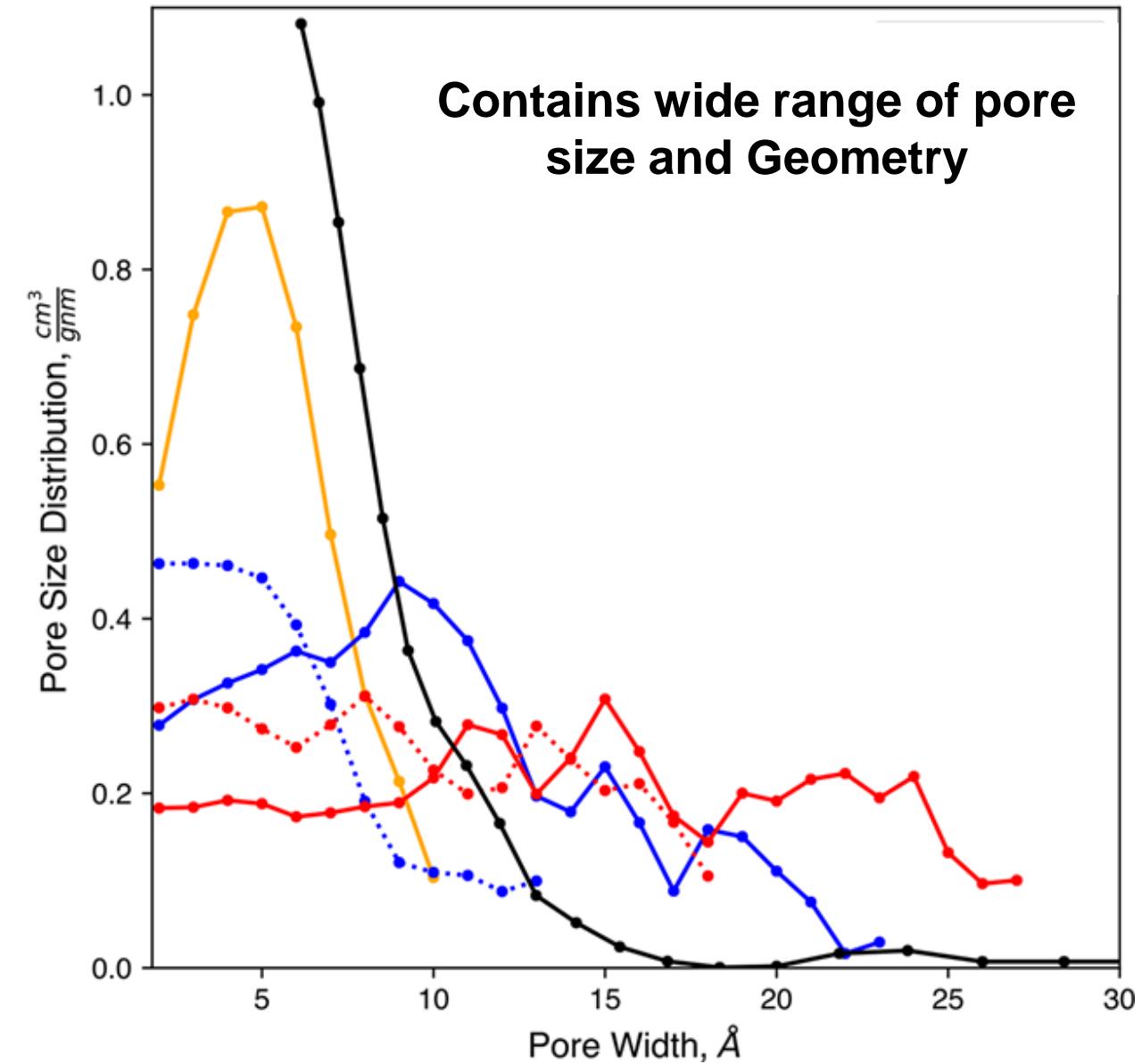


J. Phys. Chem. Lett. 2015, 6, 3594–3609

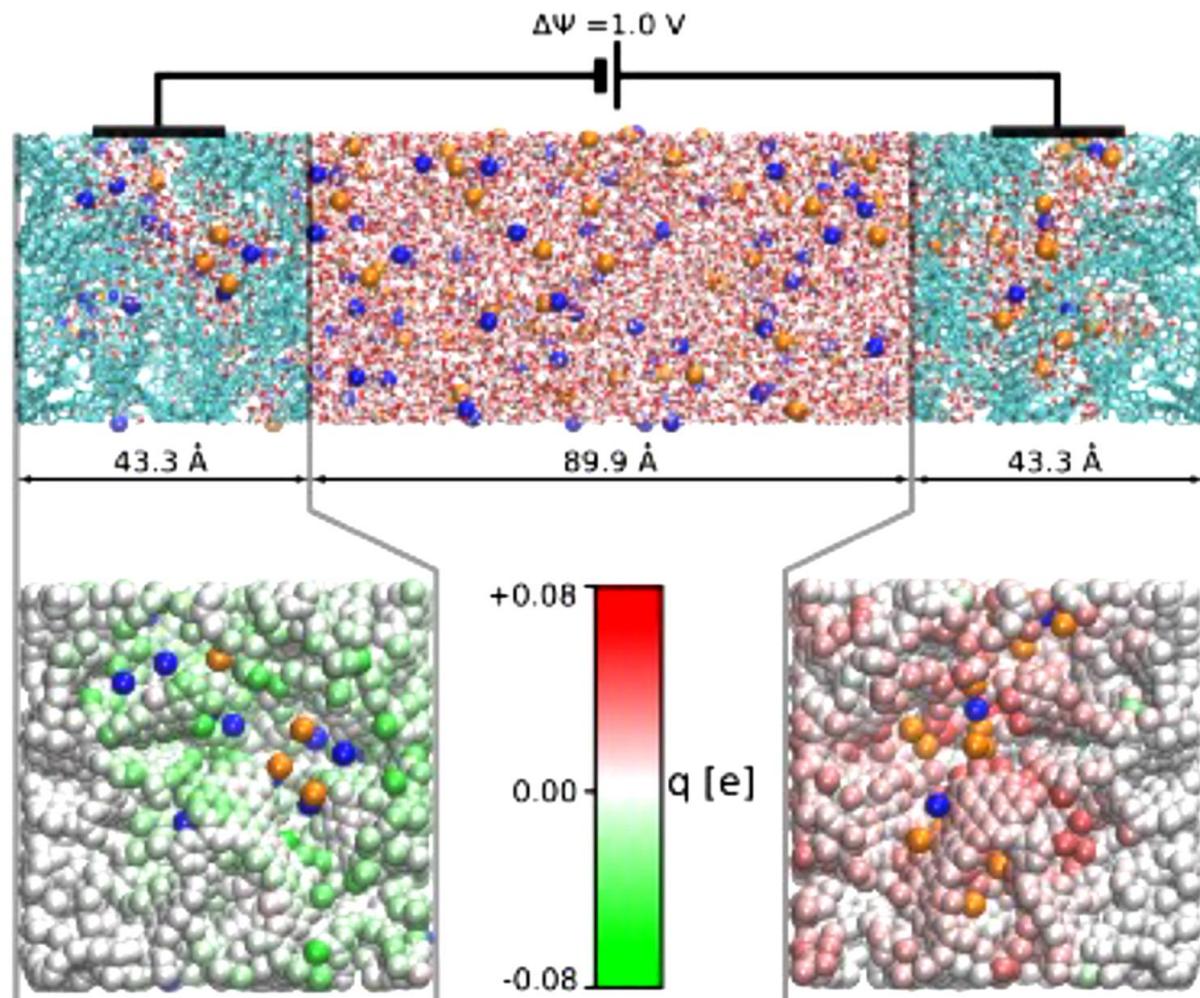
Realistic Nanoporous Electrodes



Activated Carbon



Realistic Nanoporous Electrodes

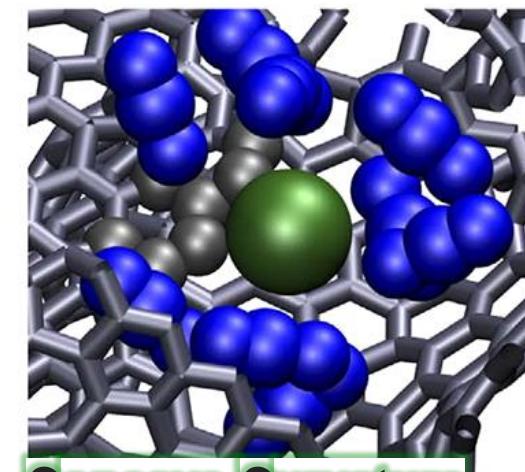


Most of the ion adsorbed in the Edge and Plane sites

Energy Storage Materials 69 (2024) 10341

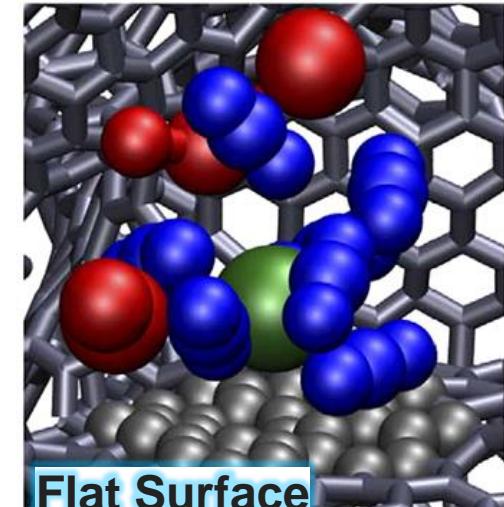
Nat Commun 4, 2701 (2013)

Edge



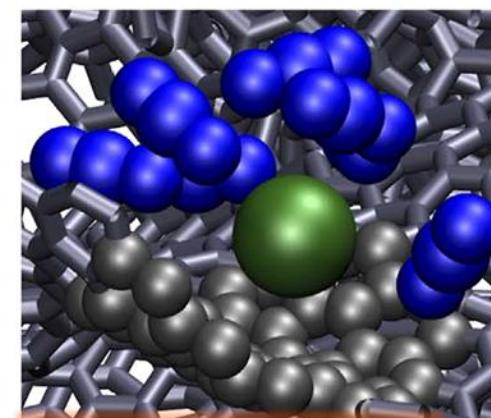
Concave Curvature

Plane



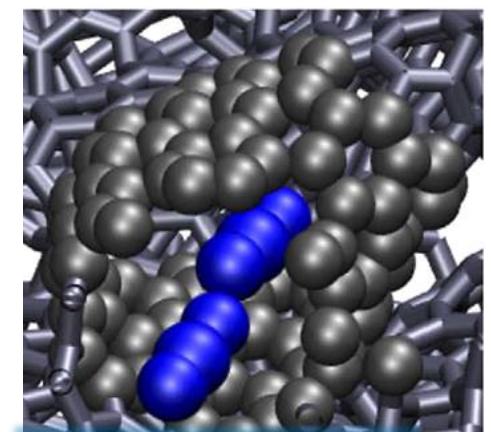
Flat Surface

Hollow



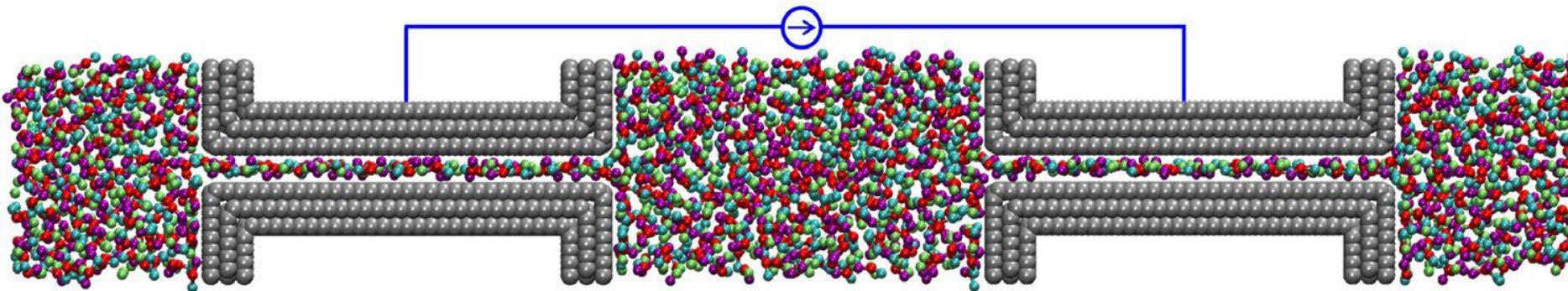
Convex Curvature

Pocket



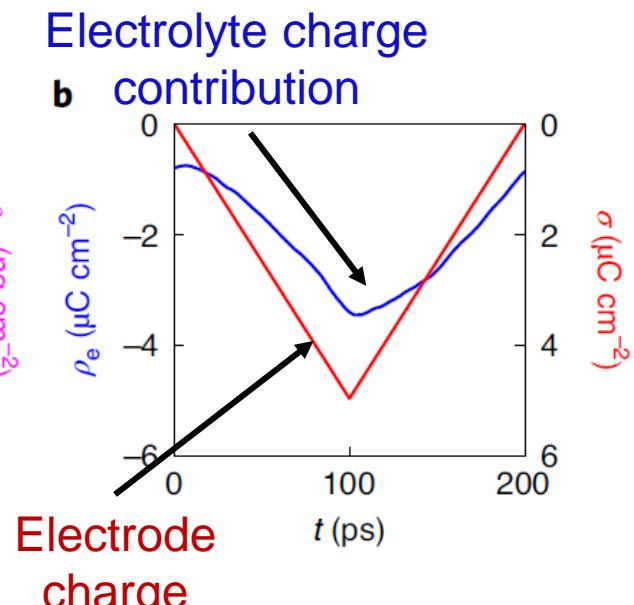
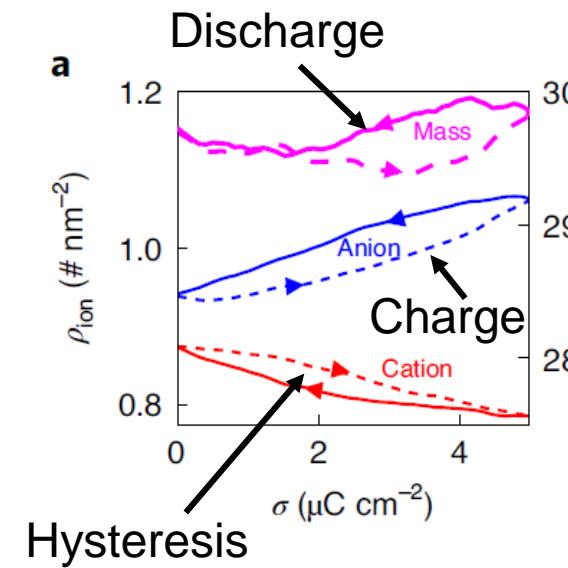
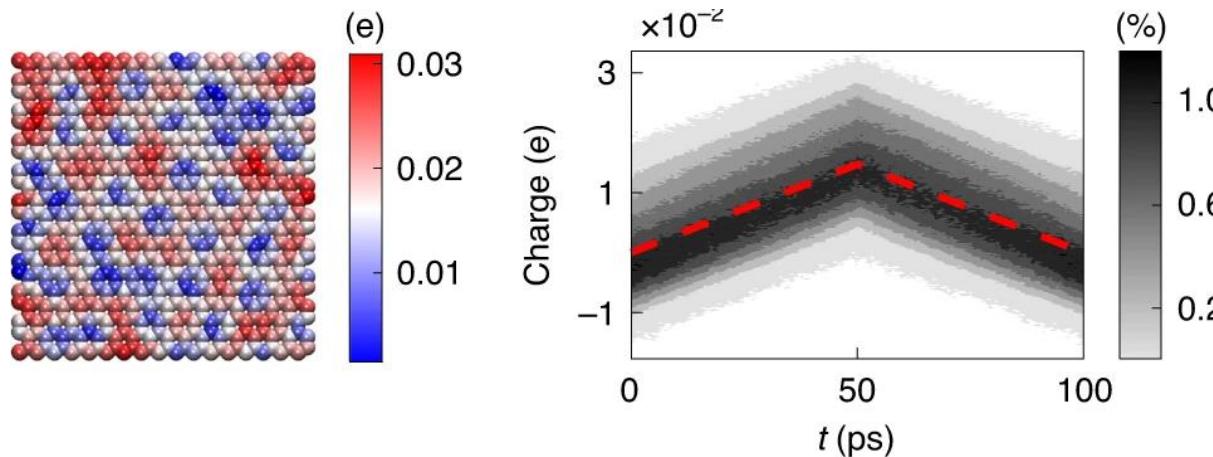
Cylindrical Pores

Galvanostatic Charge Discharge

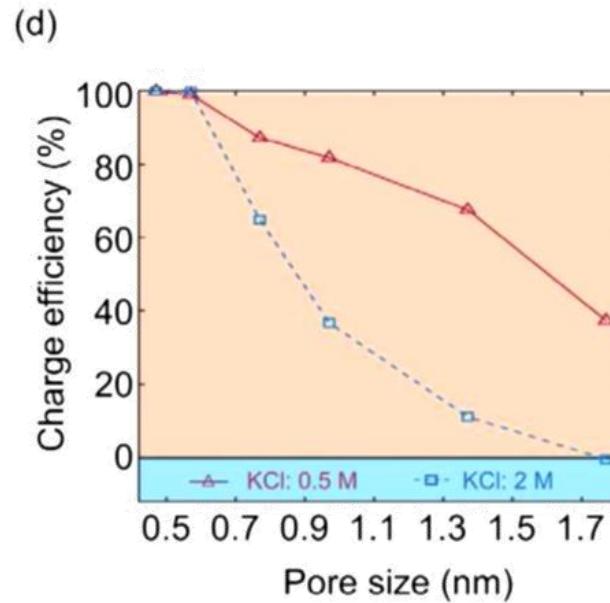
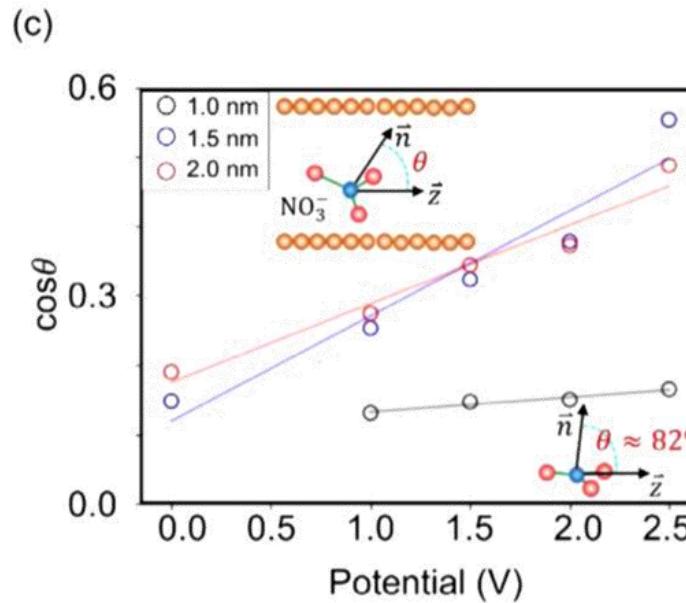
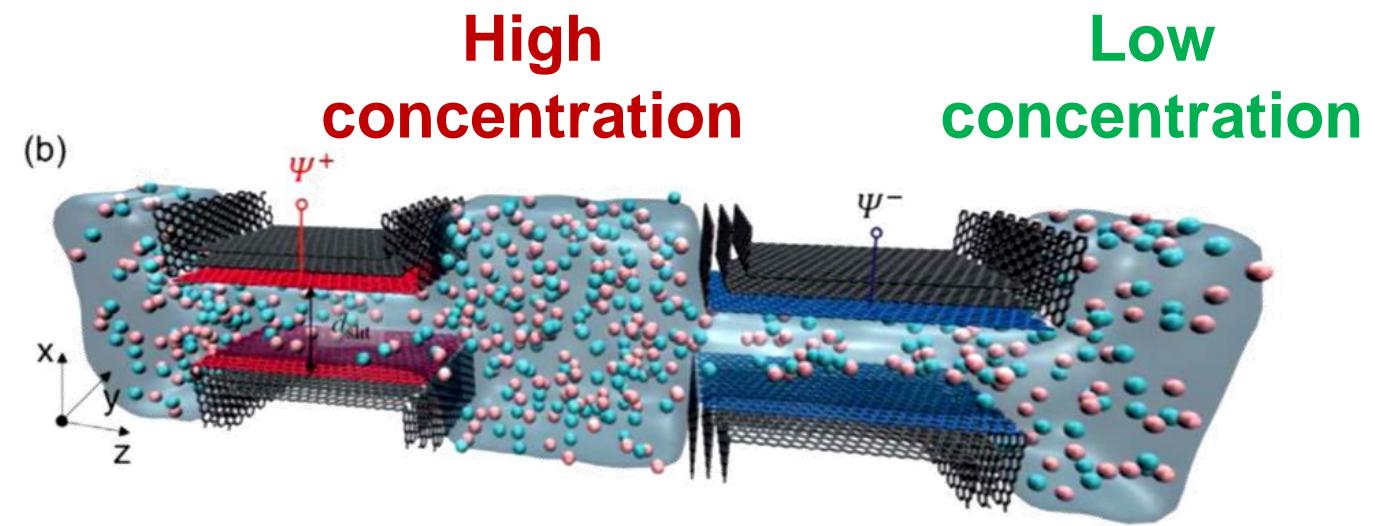
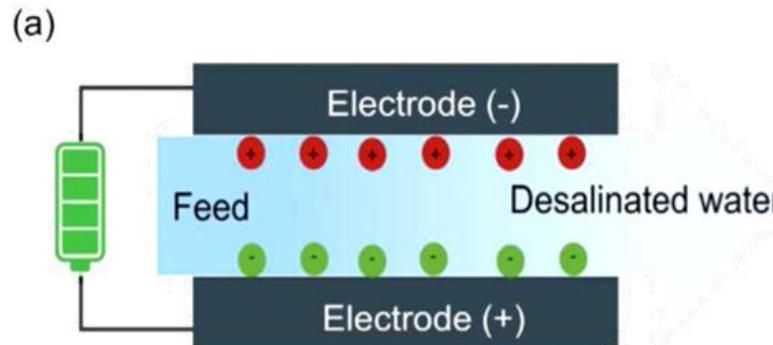


- ✓ Specific Capacitance
- ✓ Power Density
- ✓ Cyclic Stability
- ✓ Materials Performance

Positive Electrode



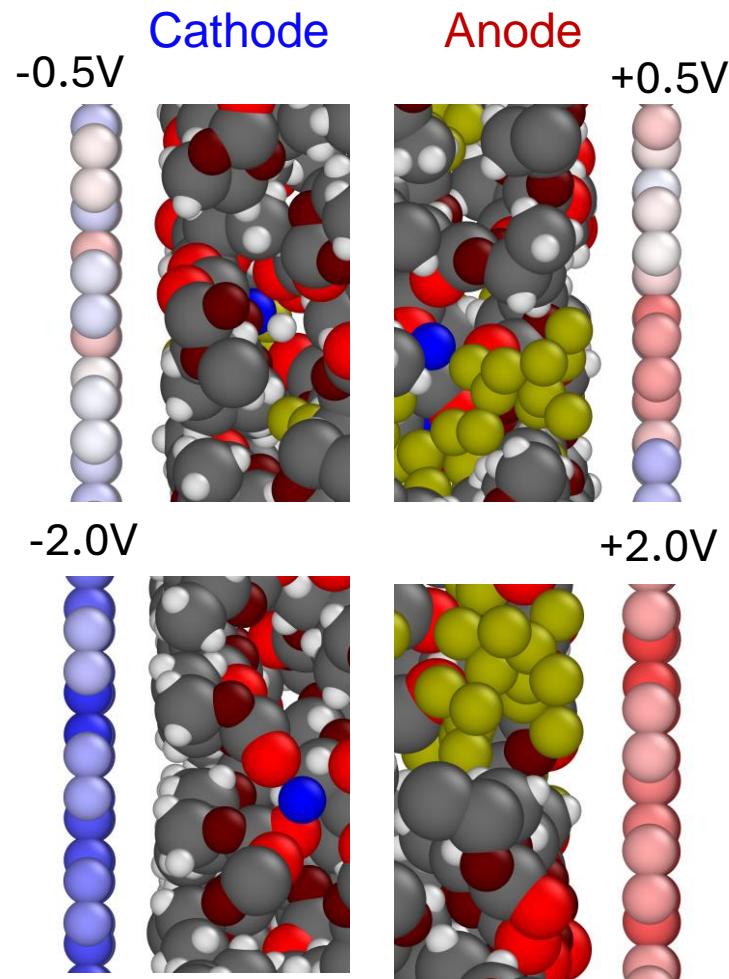
Water Desalination



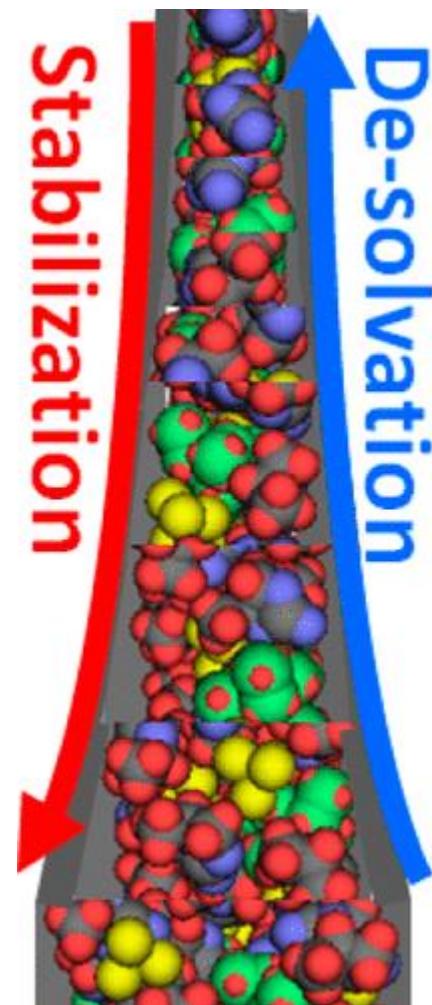
Can elucidate the microscopic mechanism of desalination

Electrolyte Structure

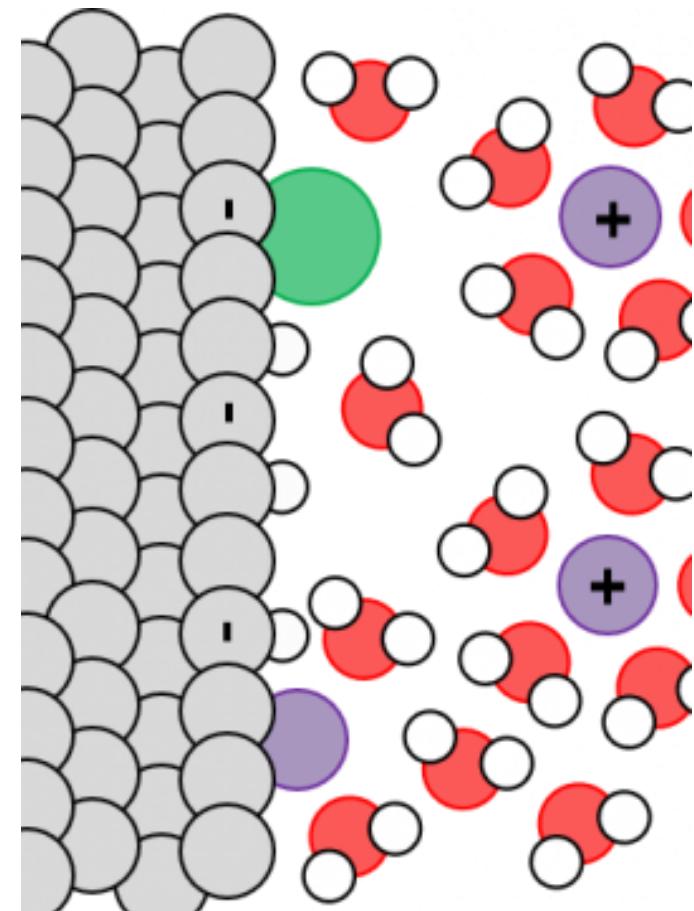
Solvent Orientation



Under Confinement



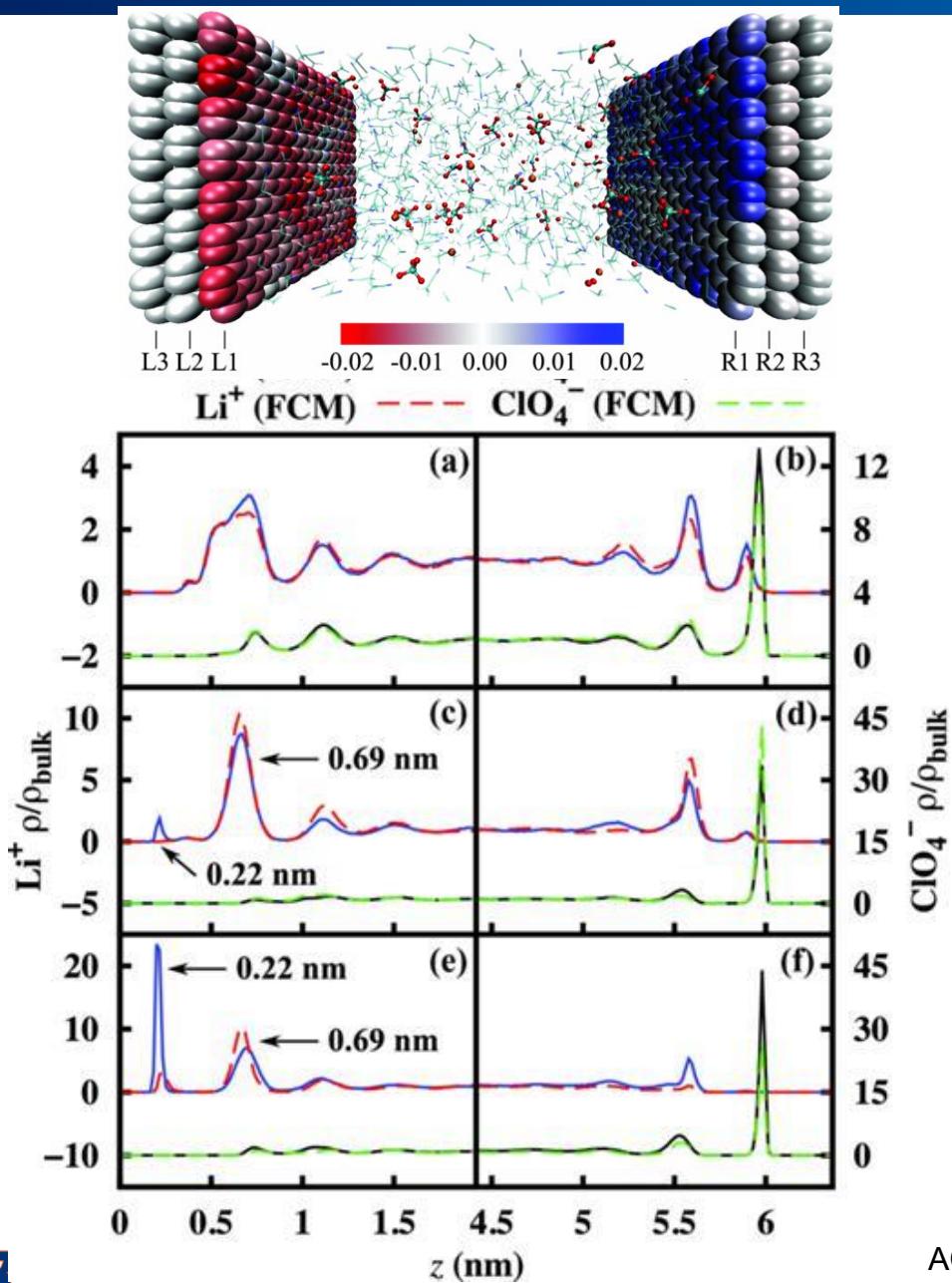
Desolvation



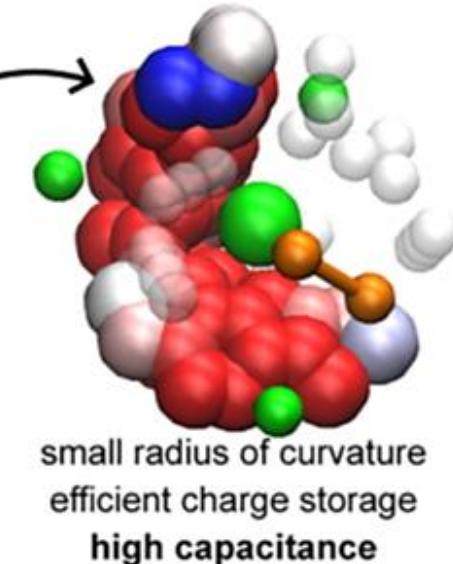
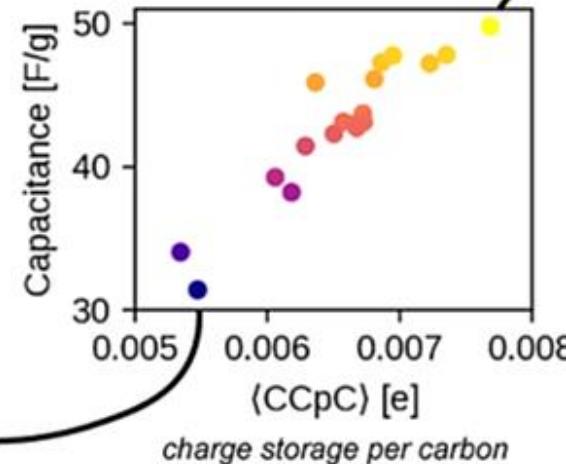
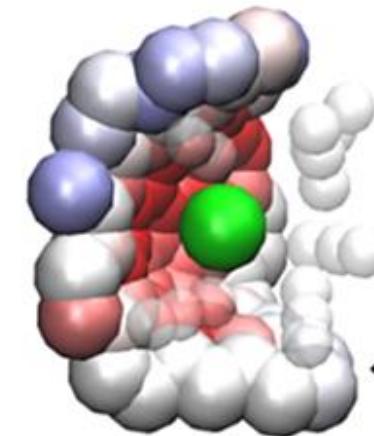
J. Phys. Chem. C 2013, 117, 33, 17092–17098

Ind. Eng. Chem. Res. 2020, 59, 13, 5768–5774

Which Method Should be Selected?



large radius of curvature
inefficient charge storage
low capacitance

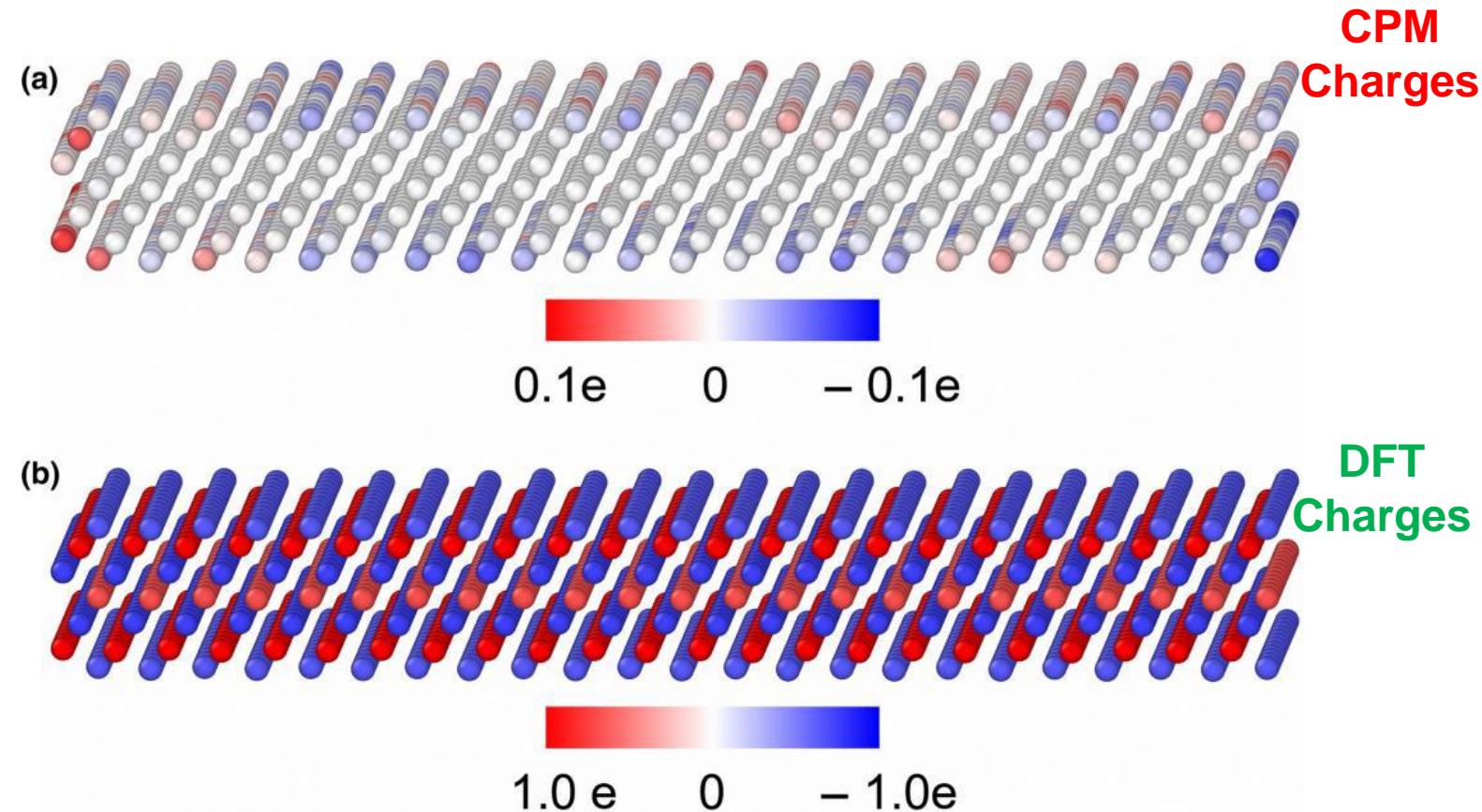


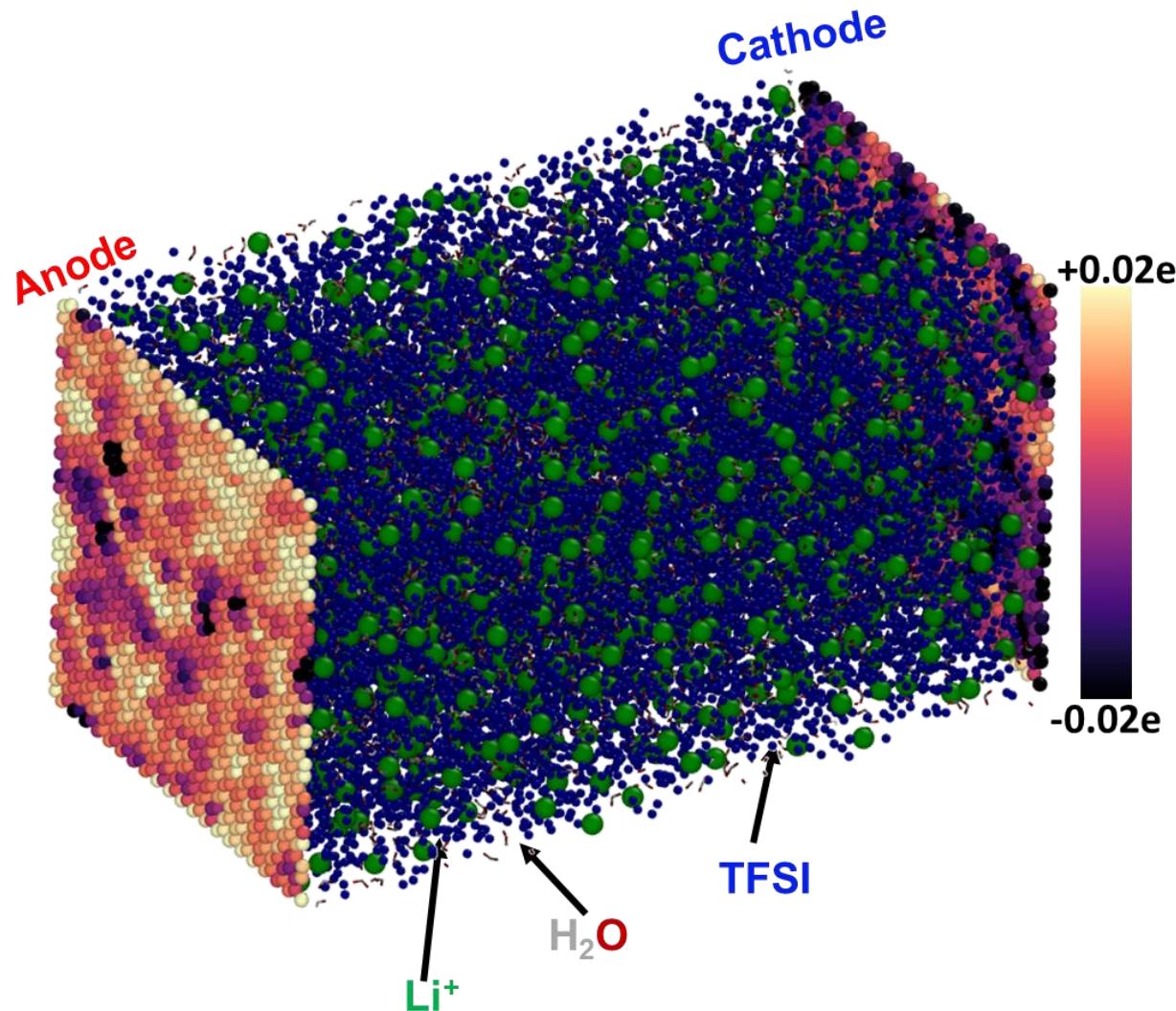
small radius of curvature
efficient charge storage
high capacitance

- ✓ **Nature of the electrodes and electrolytes**
- ✓ **Working potential window**
- ✓ **Properties to evaluate**

Constant potential method for
heteroatomic conductors(doped
graphene, MOFs, MXenes, TMDs
...)

Atomic charges on Mxeneelectrodes ($Ti_3C_2O_2$) in contact with EMIM-Otf:

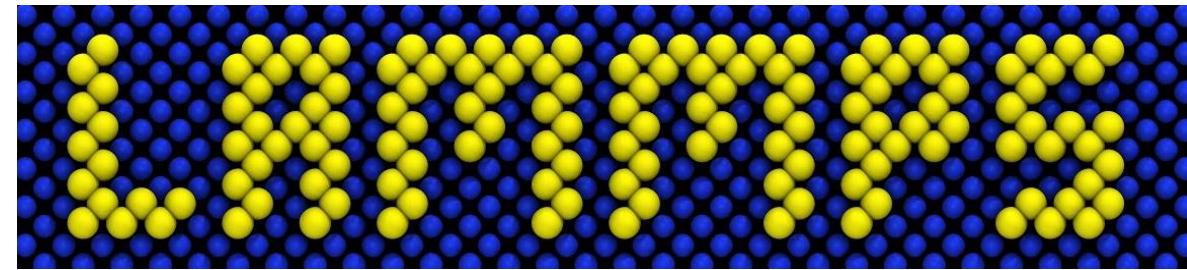




- ✓ Design reasonable initial topologies
- ✓ Decent **force fields** for electrode and electrolytes
- ✓ Find experimental potential window
- ✓ Keep at least **6nm** distance between electrodes
- ✓ Keep the electrode position **fixed**
- ✓ Equilibrate the system before calling CPM



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MetalWalls

Constant Potential Method in LAMMPS

```
# Get solvent and electrode groups
group sol molecule 1:200
group eleleft molecule 201
group eleright molecule 202

# Call constant potential fix
fix comp eleleft comp 1 eleright 1.979 1.0 log_comp

# Compute right electrode charge
# Electroneutrality guarantees qleft = -qright
compute qright reduce eleright q

# Print out charge in thermo
thermo_style custom step ... c_qright

# Run NVT integration
fix nvt sol nvt ${temp} ${temp} ${tdamp}
```

Comp-aware PPPM for even faster runtimes

- kspace_style pppm/comp instead of pppm
- fix ... comp ... pppm

ELECTRODE
+
LAMMPS

J. Chem. Phys. 157, 084801 (2022)

