# Electrosorption of Ions from Aqueous Solutions

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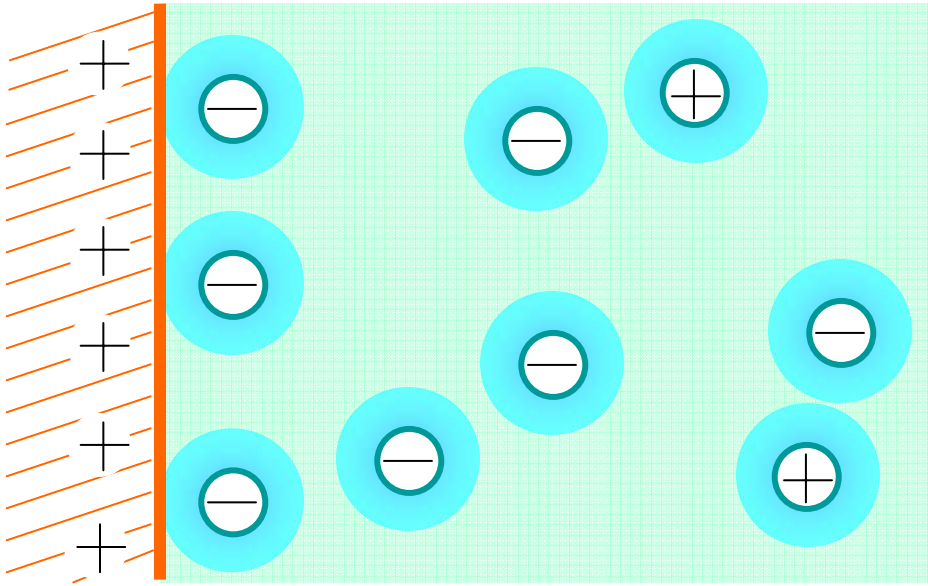
# Research Objective

- Understand the fundamental mechanisms of electrosorption of ions in nanostructured materials, leading to advanced techniques for ion transport and separation.
- Develop guidelines for optimal conditions for electrosorption.

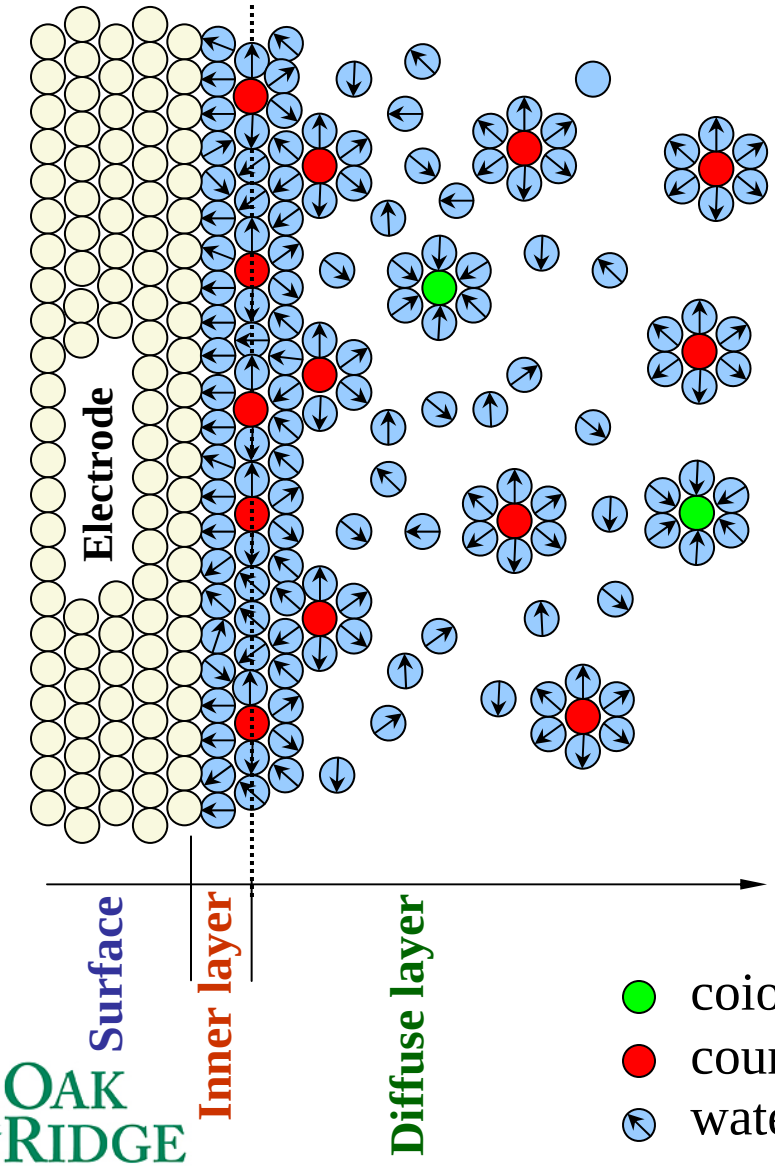
# What is Electrosorption?

- A charged surface in an aqueous environment leads to a potential difference across the solid/electrolyte interface.
  - Neutralizing space charge: counterion accumulation
  - Electrical double layer (EDL) formation



EDL is a very important interfacial phenomenon to many physical, chemical, and biological systems.

# Historical Development of EDL Theory




- **Helmholtz**

  A single ion distribution consists of a plane layer of charge opposite to that at the surface

- **Gouy-Chapman**

  A diffuse model of EDL, in which the potential decreases exponentially due to sorbed counterions from the solution

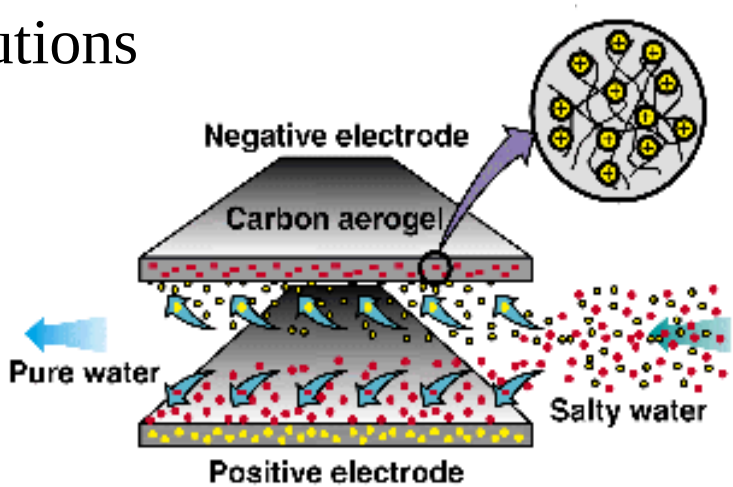
- **Stern**

  Combination of the Helmholtz single sorbed layer and the diffuse layer

- coion
- counterion
- water molecule

# Application of Electrosorption

- Water purification and desalination
  - Removal of ions from aqueous solutions
  - Advantages:
    - ✓ High capacity
    - ✓ Reversibility
    - ✓ Long-term reproducibility
    - ✓ No secondary waste



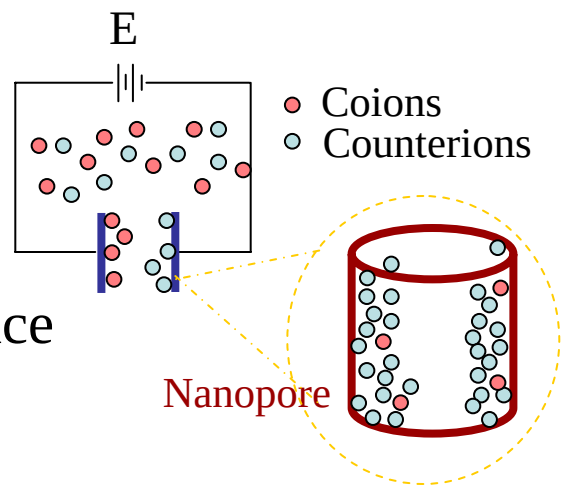

Schematic of the electrosorption process using carbon aerogel

- Energy storage in supercapacitors

- Ion selectivity and transport through biological membranes

# Materials Suitable for Electrosorption

- Carbon materials of nanoporous structure
  - Activated carbon, carbon fiber, carbon aerogels, *etc.*
  - High specific surface area
  - Good electrical conductivity




- EDL capacitors
  - Characterization via a double-layer capacitance at the carbon/electrolyte interface
- Occurrence of EDL overlapping
  - When the pore size is comparable to the EDL thickness, double layers overlapping occurs.

# Characterization of Carbon Materials

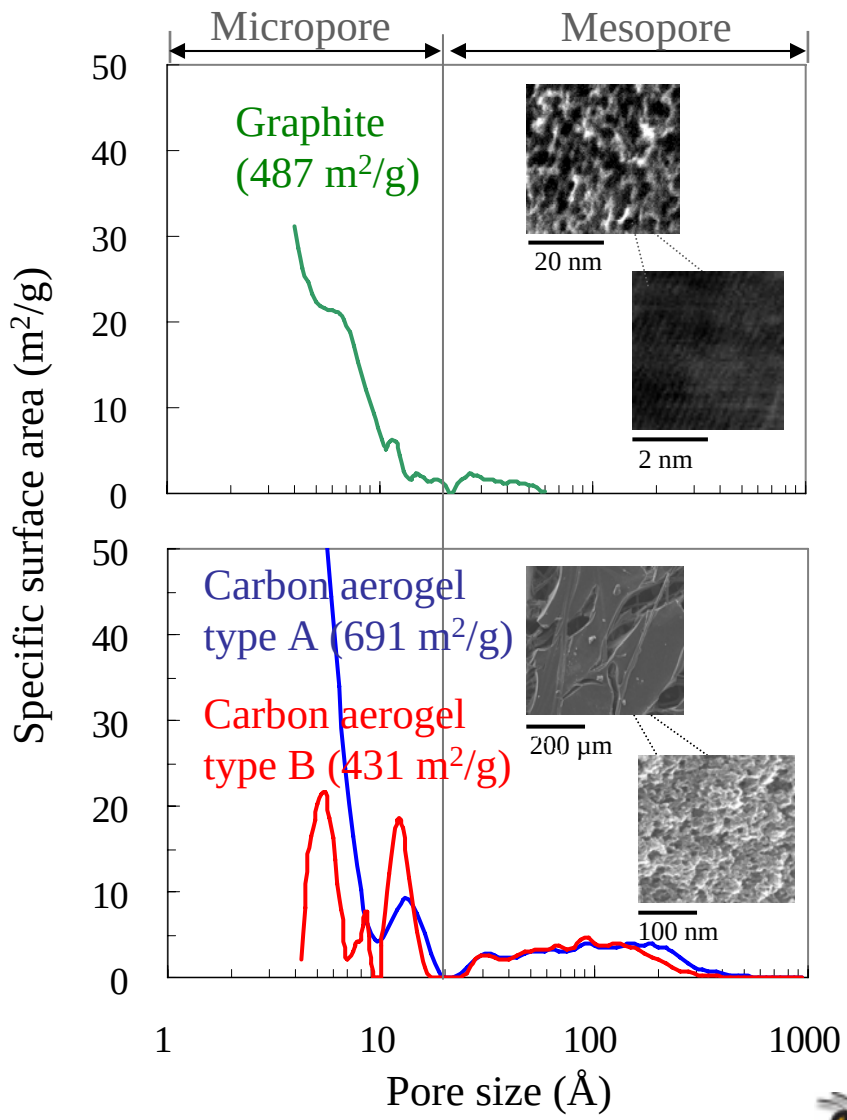
- Nanostructured carbon materials
  - Graphitized carbon
  - Carbon aerogel type A and B

⇨ These nanostructured carbon-based materials exhibit high specific surface area as a result of the contributions of mesopores and micropores.

⇨ Two competing effects are considered:

*(i)* High surface area increases electrosorption capacitance.

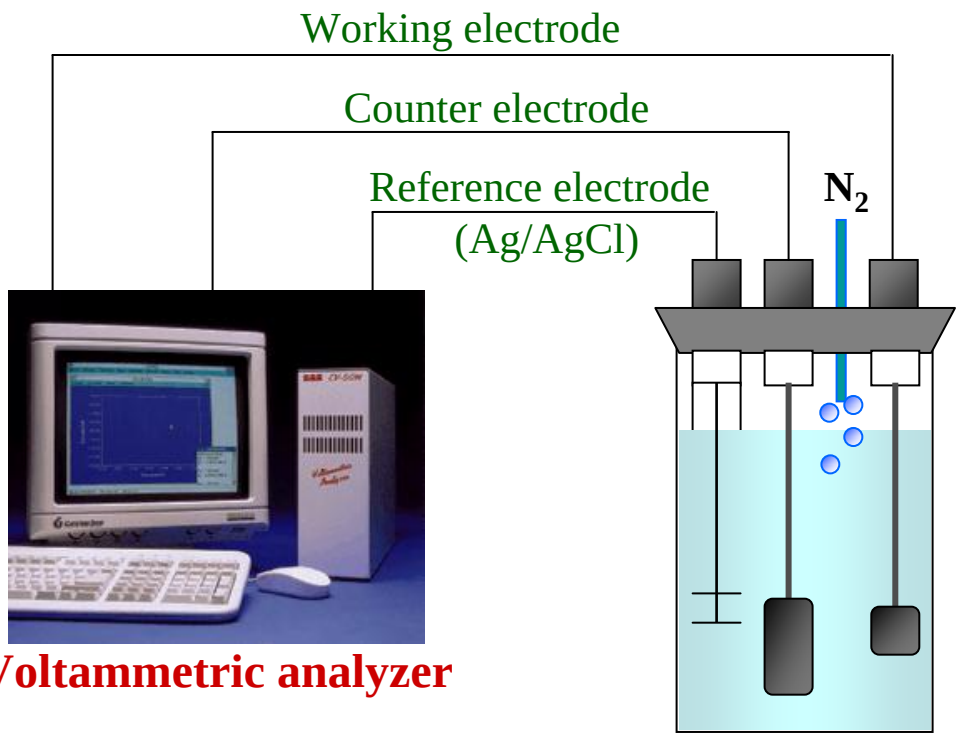
*(ii)* EDL overlapping in micropores decreases capacitance




(Hou *et al.*, JCIS, 302, 54-61, 2006)

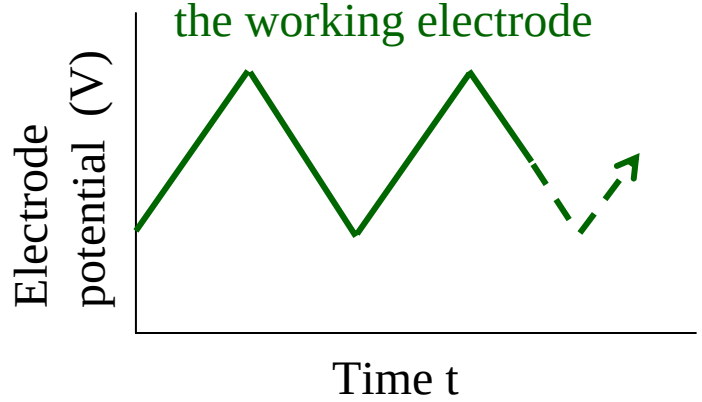
# Cyclic Voltammetry

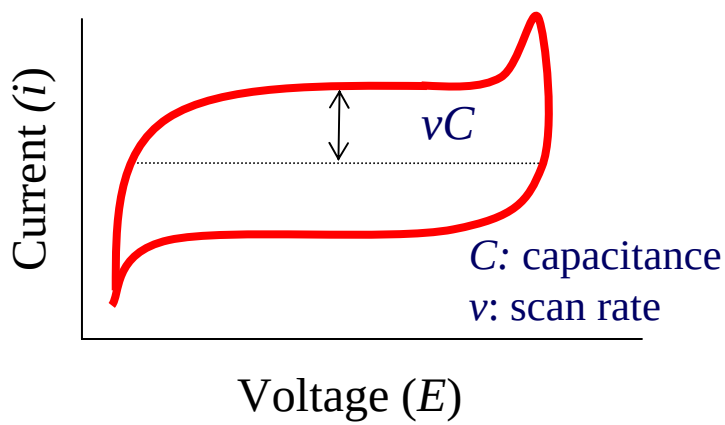
- Study of electrochemical behavior
  - ✓ Surface reaction
  - ✓ EDL capacitance




**Voltammetric analyzer**

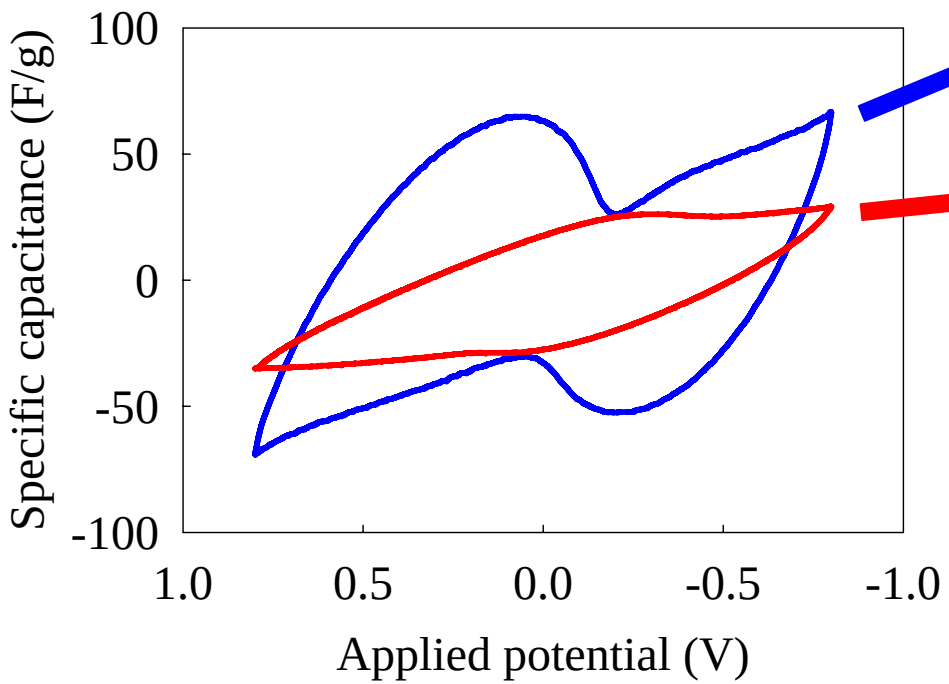
Potential-time behavior at the working electrode




$$C = \frac{d\sigma_0/dt}{dE/dt} = \frac{i}{v}$$

# Experimental Observations




Specific capacitance of graphitized carbon in a 0.01 M NaF solution measured by cyclic voltammetry at fast (1 $mVs^{-1}$) and slow (1 $mVs^{-1}$) scan rates (Hou *et al*., 2006)

**Slow scan rate:**

Mesopore + Micropore capacitances

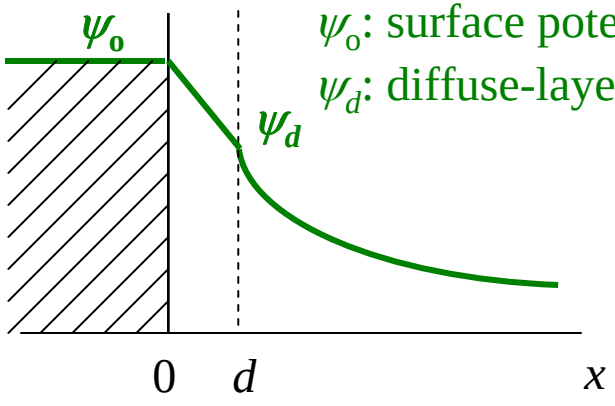
**Fast scan rate:**

Mesopore capacitance only

- ✓ The electrical double layer capacitances have contribution from mesoporous and microporous capacitors.
- ✓ The mass transfer rate of ions is fast inside mesopores, but slow inside micropores.
- ✓ The presence of micropores can become a determining factor in the effectiveness of EDLCs by increasing the surface area.

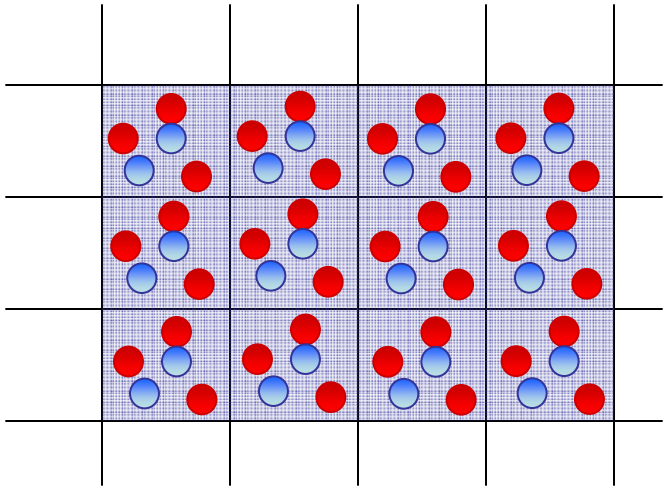
# Modeling Work

- Classical EDL theory
  - ✓ Gouy-Chapman model




$\psi_o$: surface potential
$\psi_d$: diffuse-layer potential

- Molecular modeling method
  - ✓ Monte Carlo simulation



# Classical EDL Theory

- Gouy-Chapman theory
  - ✓ Poisson-Boltzmann (P-B) equation

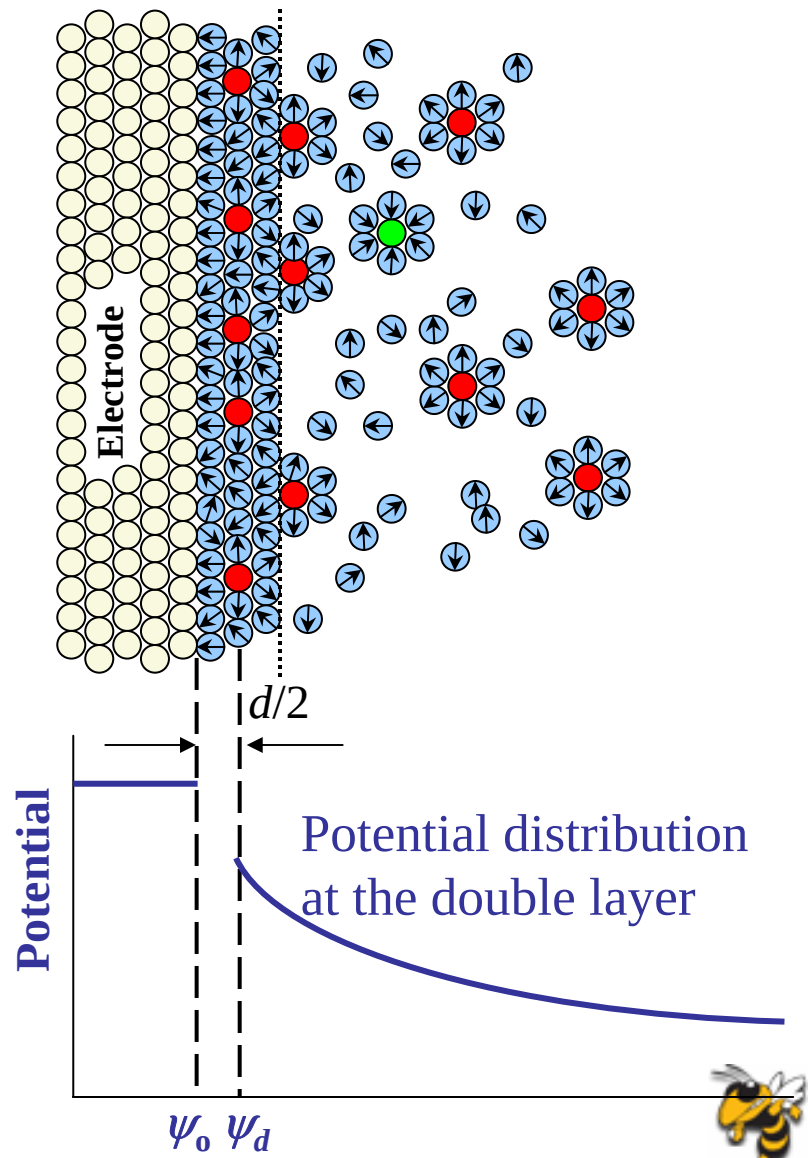
$$\frac{d^2\psi}{dx^2} = \frac{2zeN_0}{\varepsilon}\sinh\left(\frac{ze\psi}{k_B T}\right)$$

$$\psi = 0\Big|_{x\to\infty} \qquad \frac{d\psi}{dx} = 0\Big|_{x\to\infty}$$

  - ✓ Surface charge density, $\sigma_0$

$$\sigma_0 = -\varepsilon_o \varepsilon_r \frac{d\psi}{dx}\Big|_{x=d/2}$$

Ions are considered point charges without size



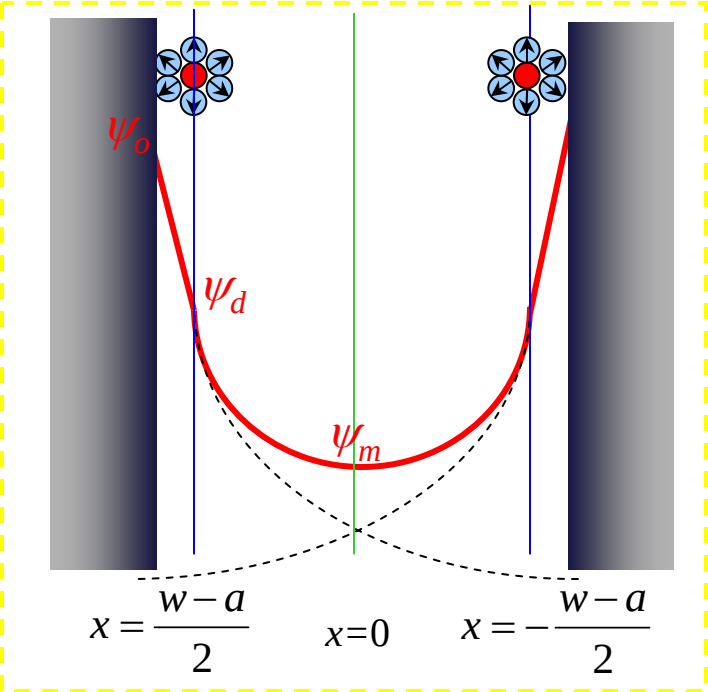
# GC Theory in a Slit Nanopore

- Poisson-Boltzmann (P-B) equation

$$\frac{d^2\psi}{dx^2} = \frac{2zeN_0}{\varepsilon}\sinh\left(\frac{ze\psi}{kT}\right)$$

$$\left.\frac{d\psi}{dx} = 0\right|_{x=0} \qquad \left.\psi = \psi_m\right|_{x=0}$$

$$\left.\psi = \psi_0\right|_{x=\frac{w}{2}} \qquad \left.\psi = \psi_d\right|_{x=\pm\frac{w-a}{2}}$$




✓ Diffuse –layer potential

$$\psi_d = \psi_o - \frac{\sigma_o}{C_1}$$

$$\frac{1}{C_{dl}} = \frac{1}{C_d} + \frac{1}{C_1}$$

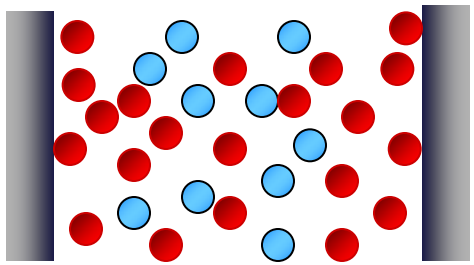
✓ Surface charge density

$$\sigma_0 = (4\varepsilon\varepsilon_0 RTI)^{1/2}\left[\cosh\left(\frac{e\psi_d}{kT}\right) - \cosh\left(\frac{e\psi_m}{kT}\right)\right]^{1/2}$$

$w$: pore width
$a$: diameter of a hydrated ion
$C_{dl}$: double-layer capacitance
$C_1$: inner-layer capacitance
$C_d$: diffuse-layer capacitance

# Potential Distribution inside Mesopores

A mesopore of 100 Å diameter around the pzc ( $\psi_o$ = 0.01 V ) and in a 0.01M electrolyte solution:

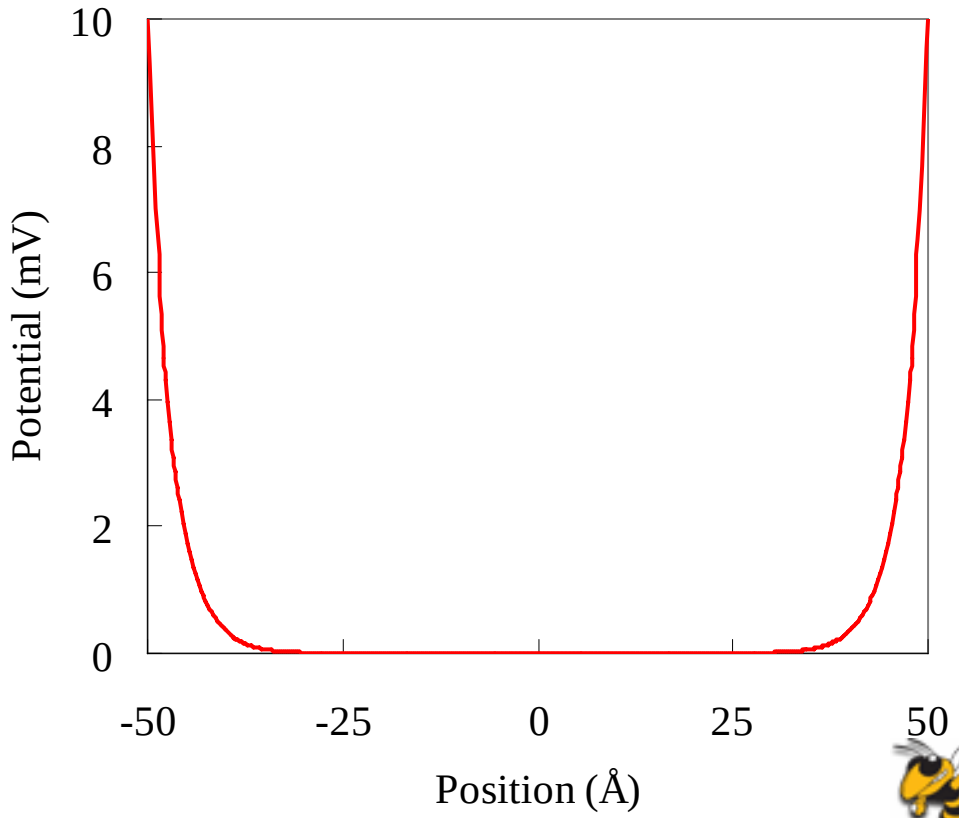


Coion

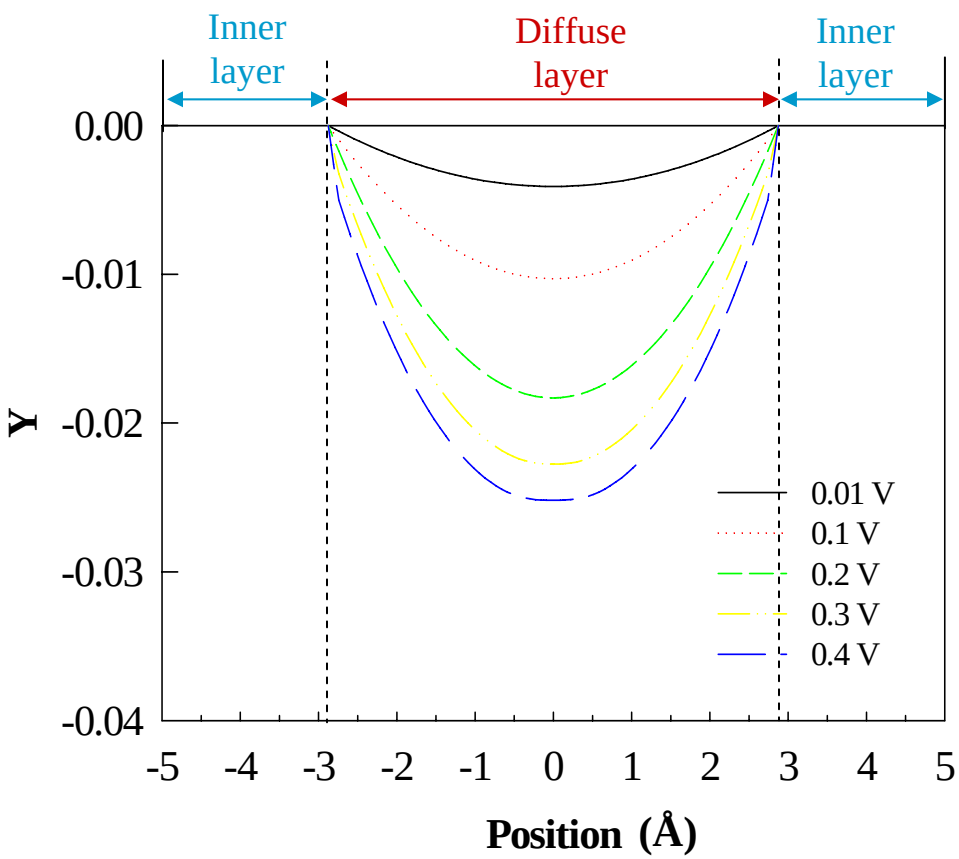
Counterion

No EDL overlapping

- ✓ The double layer can fully develop inside pores.
- ✓ Mesopores exhibit good electrochemical accessibility, but contribute less to the surface area.
- ✓ Both coions and counterions can be transported through the pore.



# Potential Distribution inside Micropores

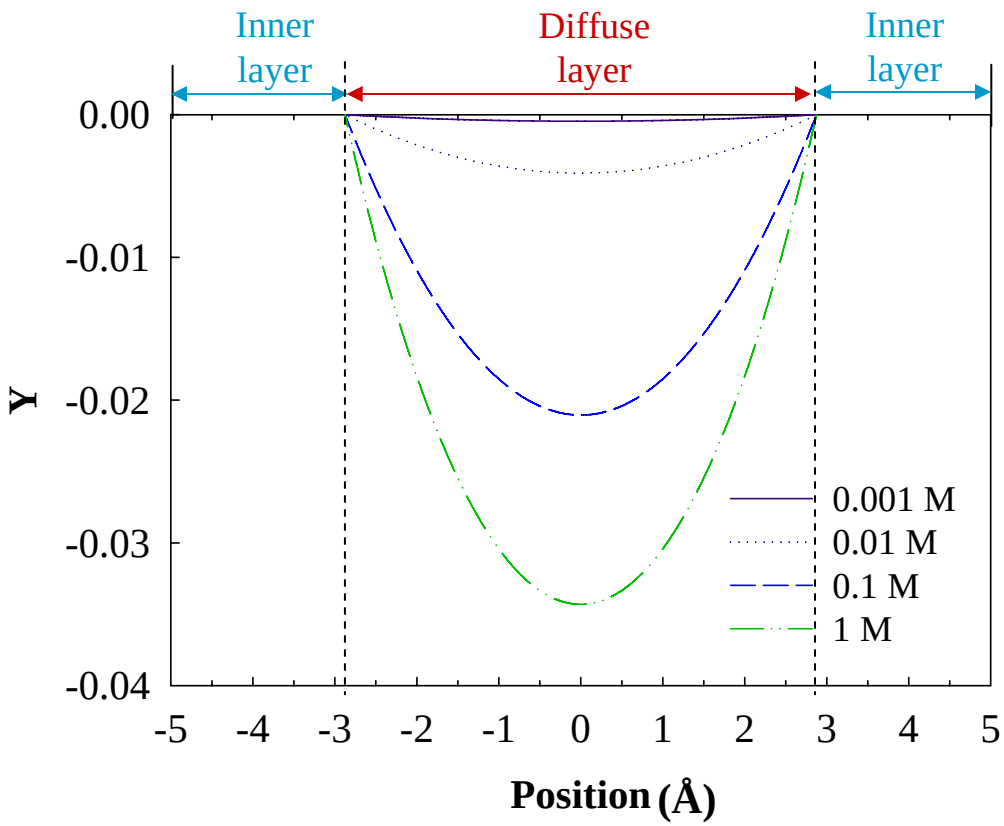


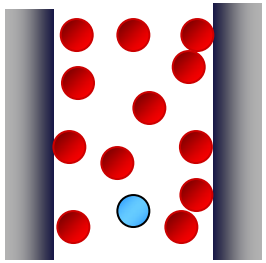

Dimensionless potential $Y = \frac{\psi - \psi_d}{\psi_0}$

A micropore of 10 Å diameter in a 0.01M electrolyte solution and at various applied potentials (Hou *et al.*, 2006) :

- ✓ The electrical potential profile is a function of the applied potential.
- ✓ A micropore has a shallow potential distribution compared to the mesopore.
- ✓ A strong double-layer overlapping effect is predicted for the micropore region.
- ✓ A shallow potential distribution is associated with an ion-exclusion effect.

# Potential Distribution inside Micropores



Coion

Counterion

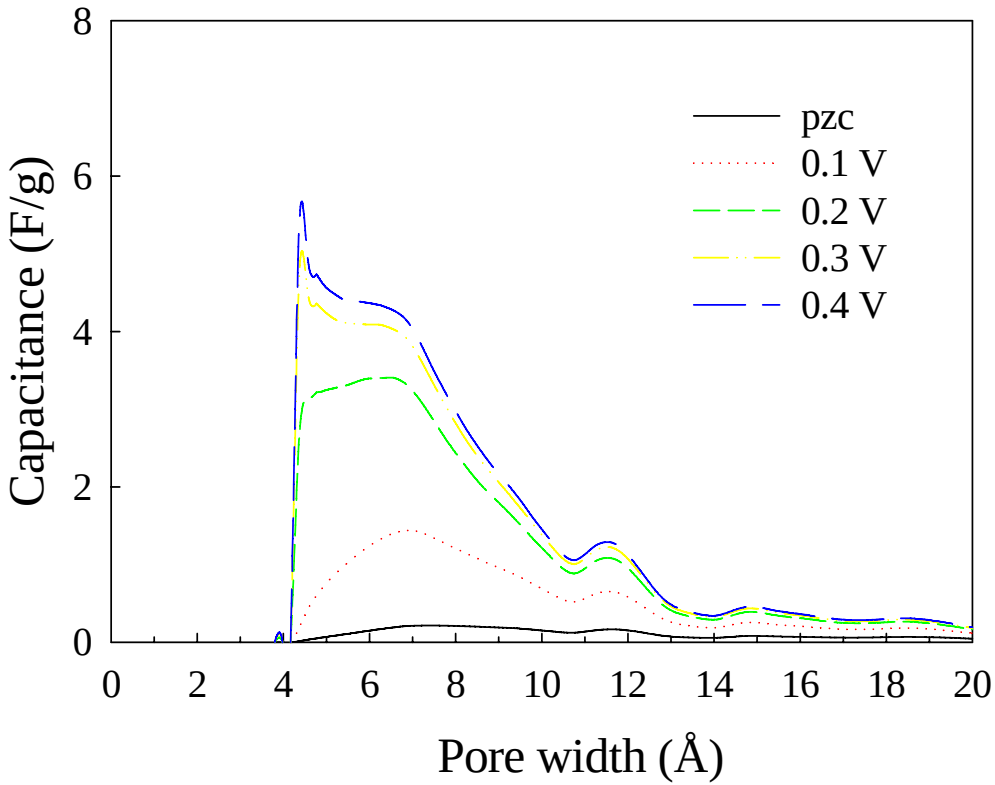
EDL overlapping

A micropore of 10 Å diameter around the pzc ( $\psi_o$ = 0.01 V ) and in various electrolyte solutions (Hou *et al*., 2006) :

- ✓ The electrical potential profile is a function of the electrolyte concentration.
- ✓ More ions penetrate pores at higher electrolyte concentrations or higher applied potential with reducing overlapping effect.
- ✓ EDL overlapping has a negative effect on ion uptake and transport.
- ✓ Counterions are the predominant species as a result of the EDL overlapping.

# Effect of Pore Size Distribution

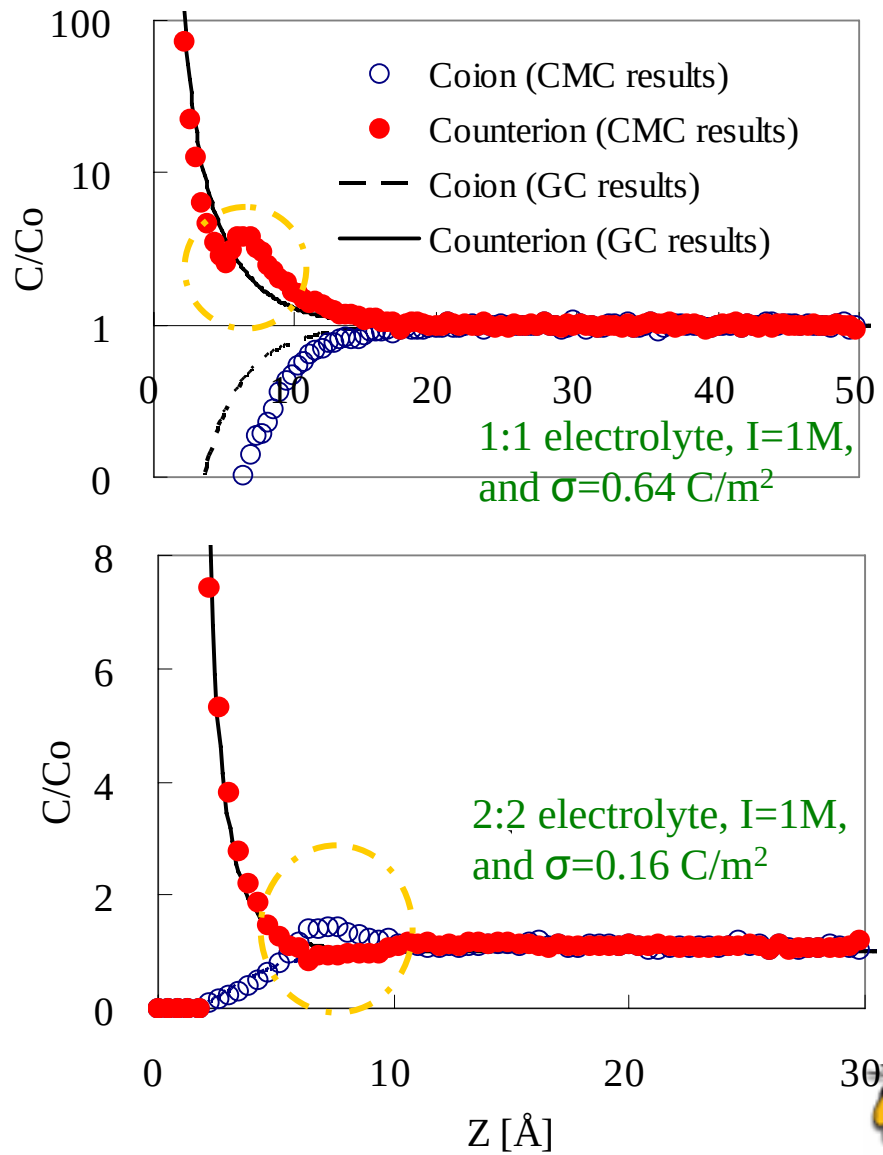
The double-layer capacitance as a function of pore size distribution and applied potential for the micropore region in a 0.01 M electrolyte solution (Hou *et al.*, 2006) **:**




- ✓ The double-layer capacitance of nanostructured materials is strongly correlated to the pore size distribution.
- ✓ Due to the EDL overlapping, porous carbon with higher surface area may not yield a higher electrosorption capacitance.
- ✓ Three factors could explain this behavior:
  - *(i)* specific surface area,
  - *(ii)* pore accessibility by ions,
  - *(iii)* EDL formation.

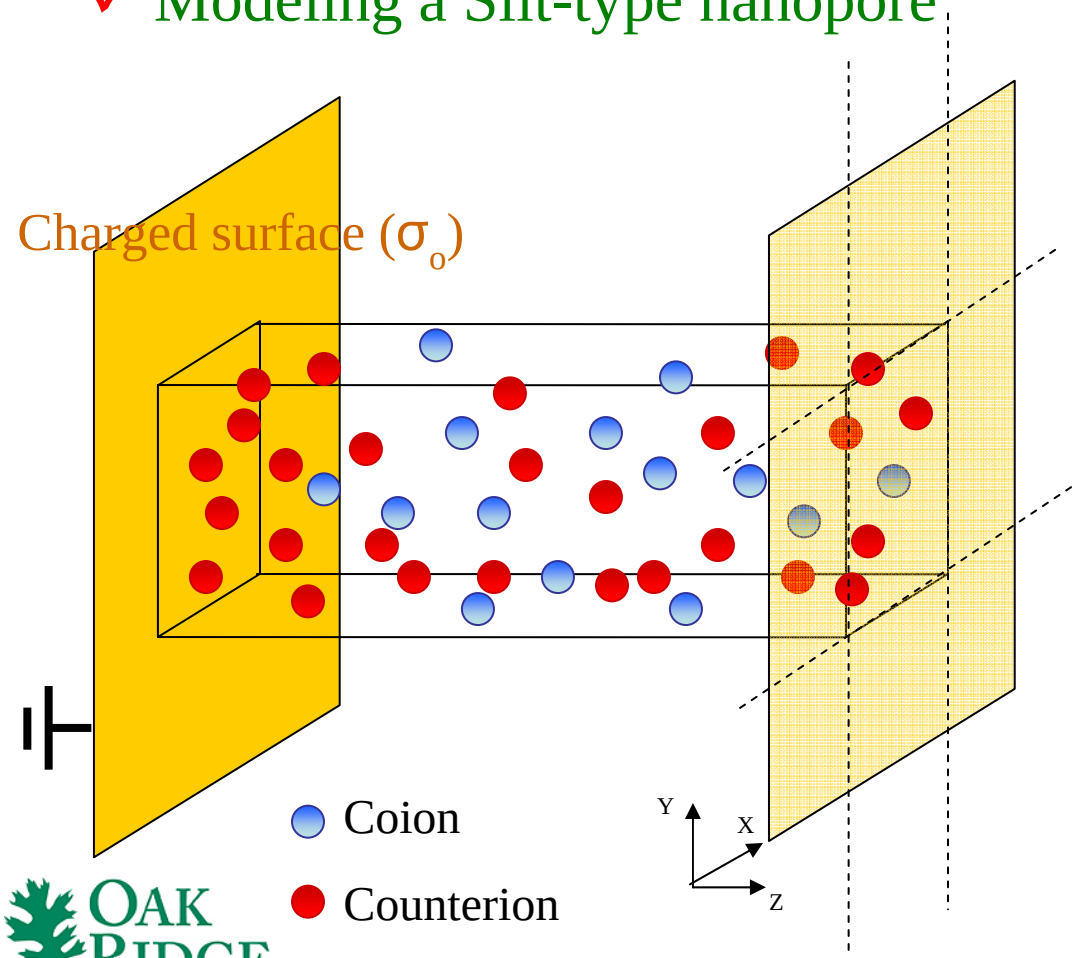
# Limitation of the Classical theory

- The classical GC theory fails in describing the ion behavior under certain conditions:
  - ✓ High concentrations or high surface charge density
  - ✓ Asymmetric electrolyte
  - ✓ Mixtures of symmetric and asymmetric electrolytes
- Monte Carlo simulation considers ion size and ion-ion correlation to overcome the simplification of the classical theory.



# Canonical Monte Carlo (CMC) Simulation

- Monte Carlo (MC) method: Use of random numbers
  - ✓ Modeling a Slit-type nanopore




- Constant *N*, *V*, *T*
- Primitive model
- Periodic boundary conditions in the X, Y directions
- Minimum-image convention
- Two charged surfaces
- Ions as charged hard spheres
- Minimization of the potential energy

# CMC Simulation: System Energy

- The total potential energy:

$$U_T = U_1 + U_2 + U_{LR}$$

*where* $U_1$= single-ion energy

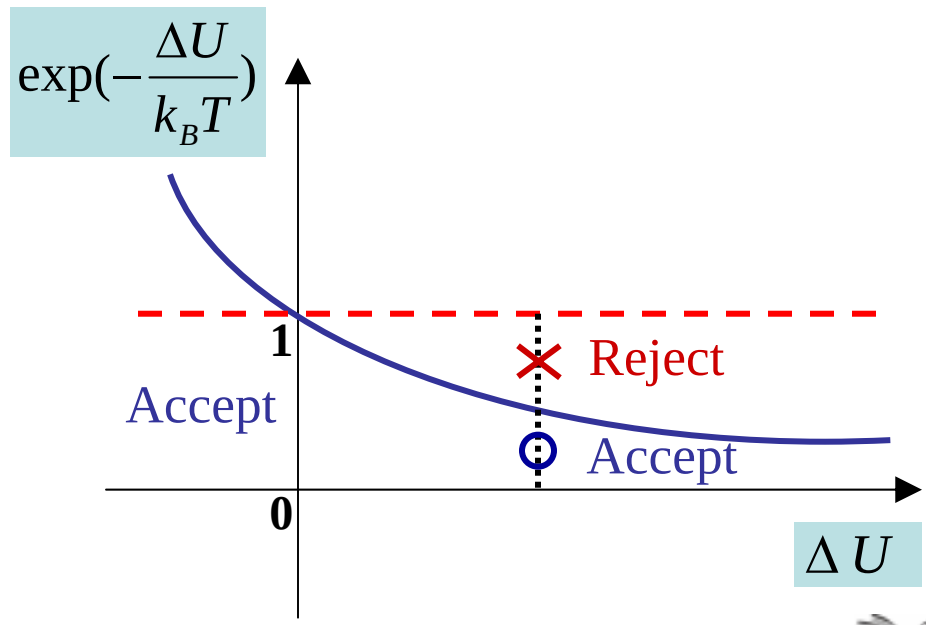
$U_2$= two-ion energy

$U_{LR}$= long-range correction energy

- The movement of ions:

Each ion is randomly moved to determine the minimum energy of the system

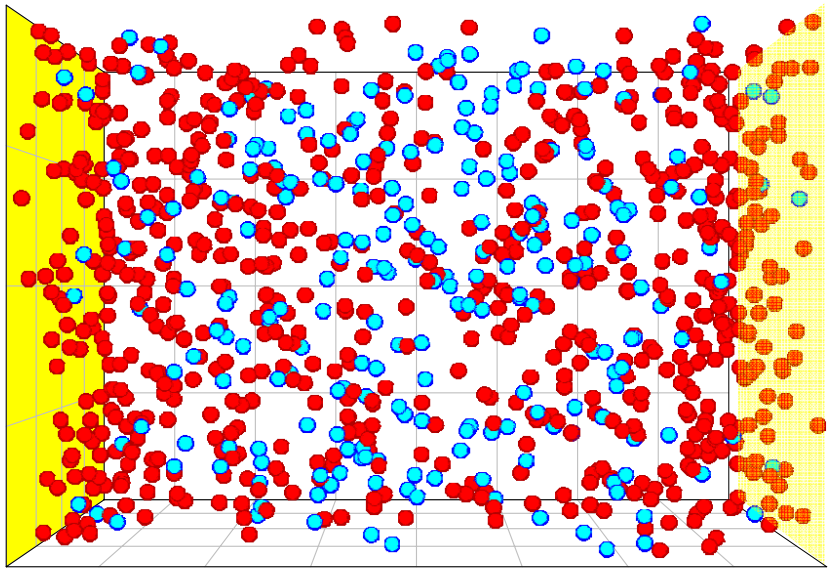
  - Lower energy configuration always accepted
  - Higher energy configuration accepted with the Canonical probability



# CMC Simulation Result

- EDL structure inside a slit nanopore

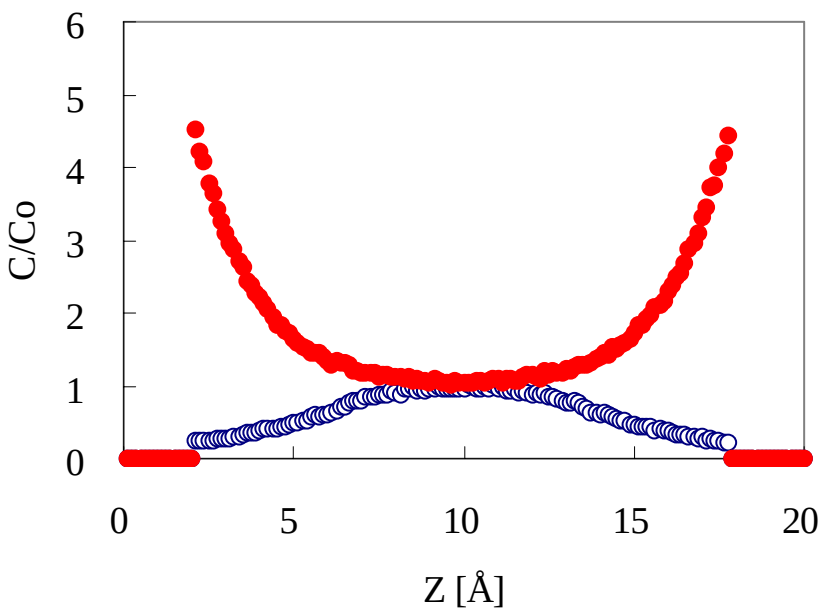
✓ Ion distribution in the simulation box



Coion
Counterion

1:1 electrolyte
Ionic strength, I = 1 M
Surface charge density, $\sigma = 0.1\ C/m^2$

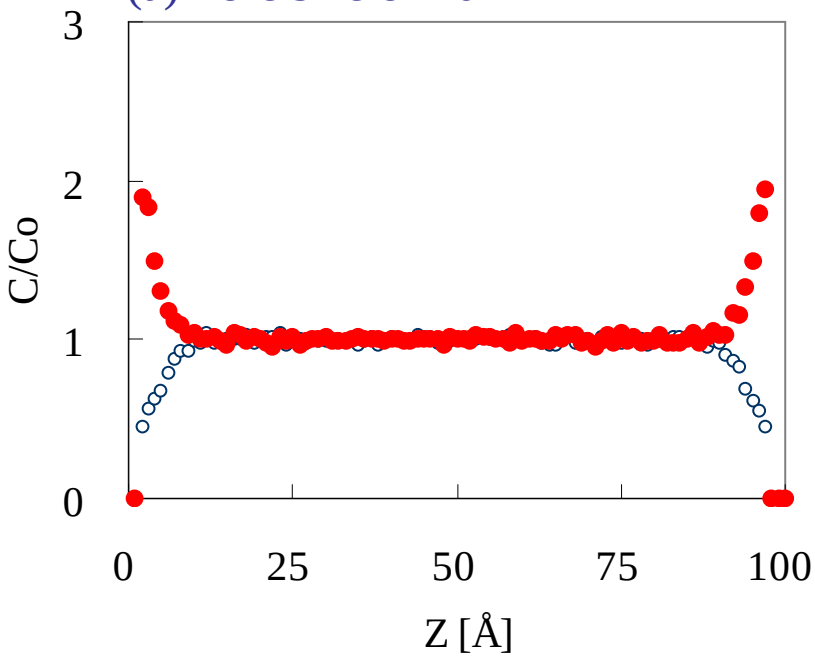
✓ Ion concentration profile



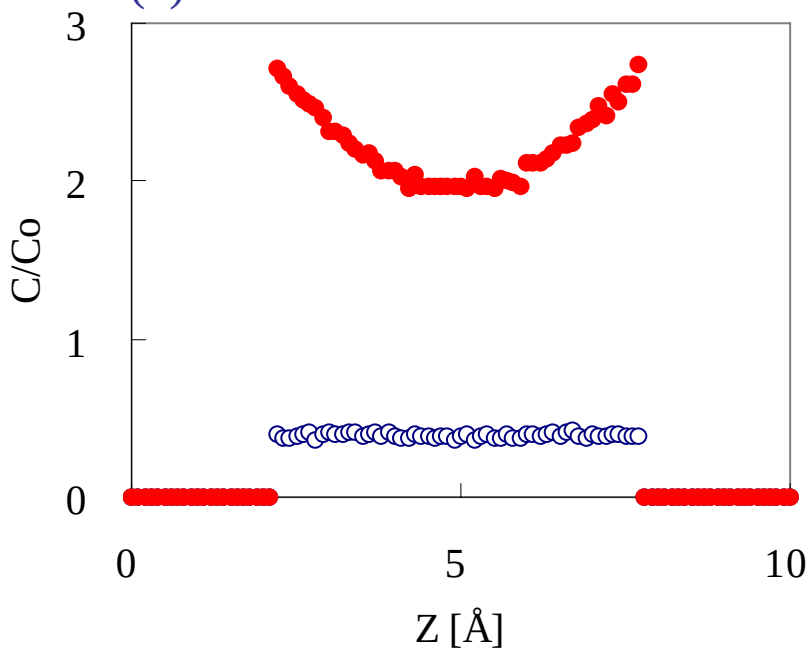
# Effect of Pore Size

1:1 electrolyte
Ionic strength, I = 1 M
Surface charge, $\sigma = 0.05\ C/m^2$

(a) Pore size of 10 nm




(b) Pore size of 1 nm

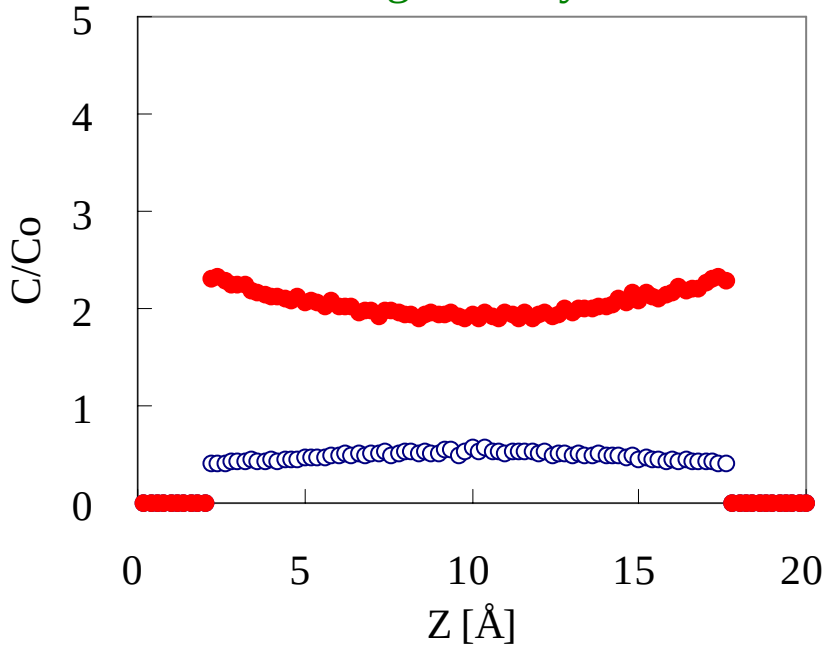



○ Coion (4.25-Å diameter)
● Counterion (4.25-Å diameter)

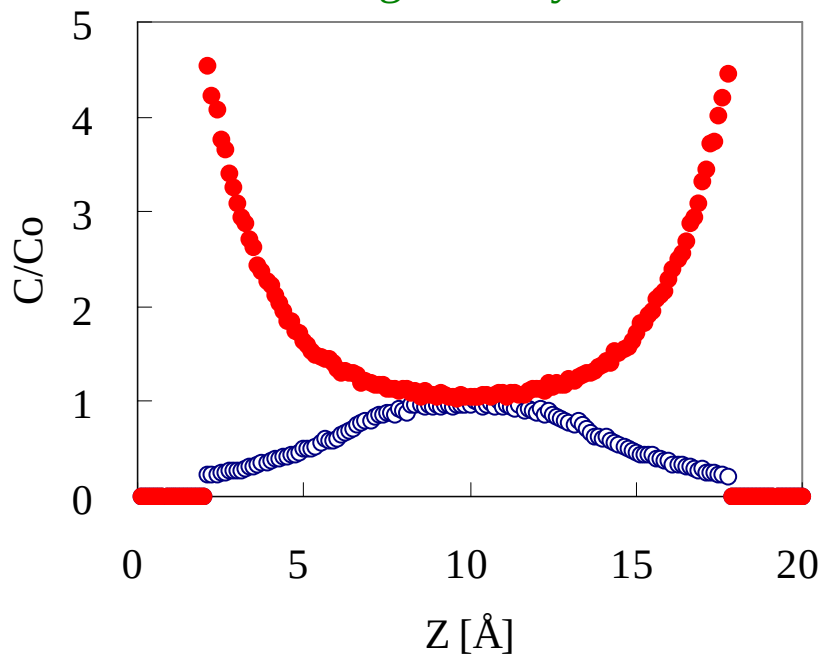
- The behavior of EDL structure inside smaller nanopores:
  - ✓ The occurrence of EDL overlapping
  - ✓ Ion exclusion of coions
  - ✓ Ion selectivity of counterions

# Effect of Ionic Strength/Surface Charge

1:1 electrolyte
Ionic strength = 0.1 M
Surface charge density = 0.012 C/m²




1:1 electrolyte
Ionic strength = 1 M
Surface charge density = 0.1 C/m²



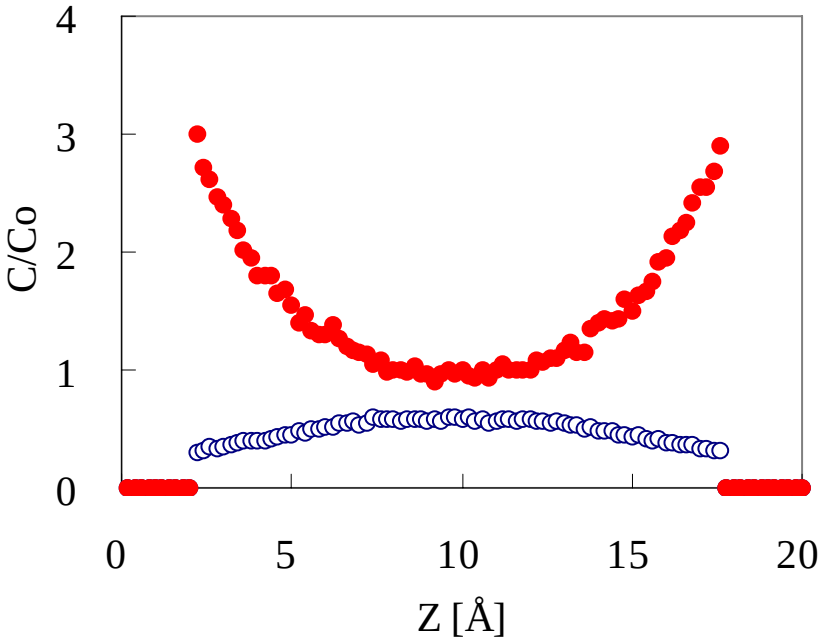

○ Coion (4.25-Å diameter)
● Counterion (4.25-Å diameter)

✓ The distribution of ions in the solution depends on the ionic strength and the surface charge density.

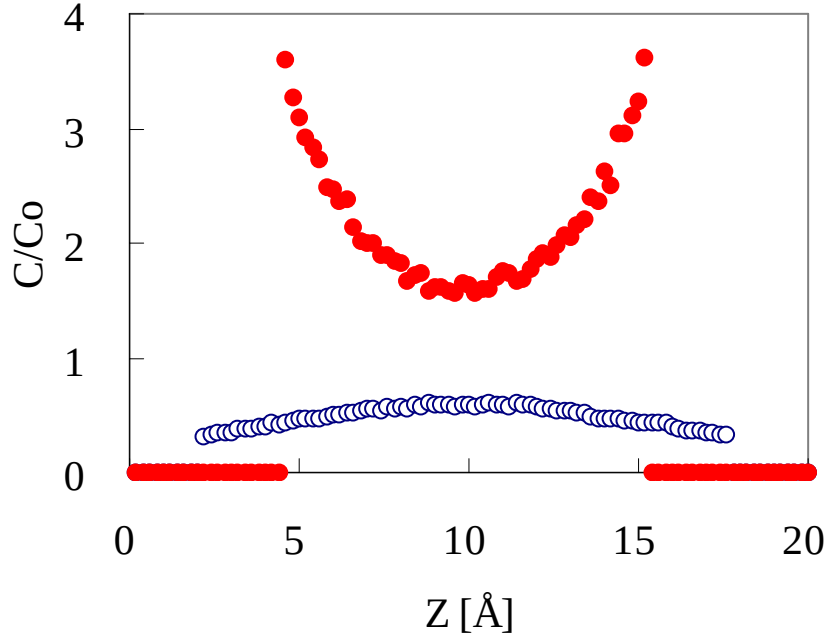
# Effect of Ion-Size

- Asymmetric electrolyte:

1:3 electrolyte, Nanopore with diameter of 2nm
Ionic strength = 1 M , Surface charge = 0.04 C/m$^2$




○ Coion (4.25-Å diameter)
● Trivalent Counterion (4.25-Å diameter)



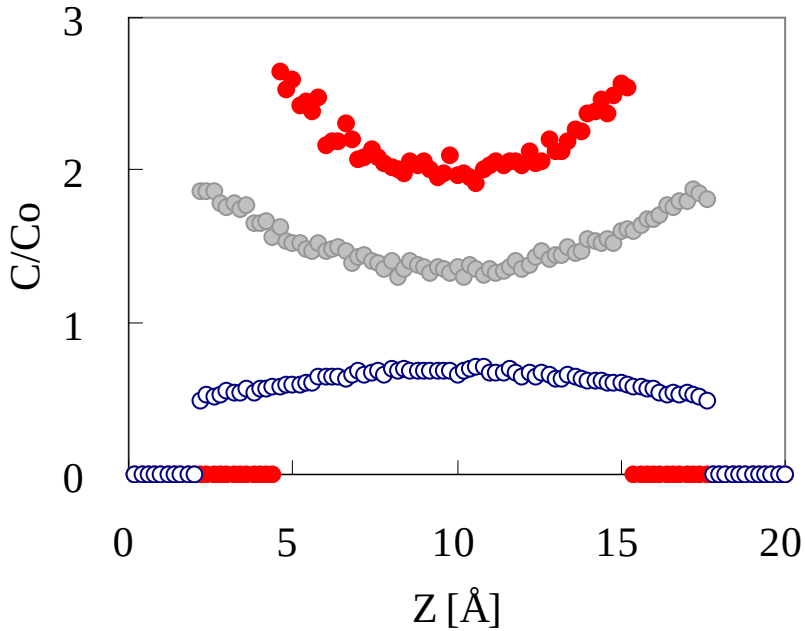

○ Coion (4.25-Å diameter)
● Trivalent Counterion (9-Å diameter)

- ✓ Large size of ions causes the size-exclusion phenomenon, resulting in more overlapping, but more rapid decrease in ion concentration profile.
- ✓ The ion size is an important factor in determining the EDL structure, specially for smaller nanopores.

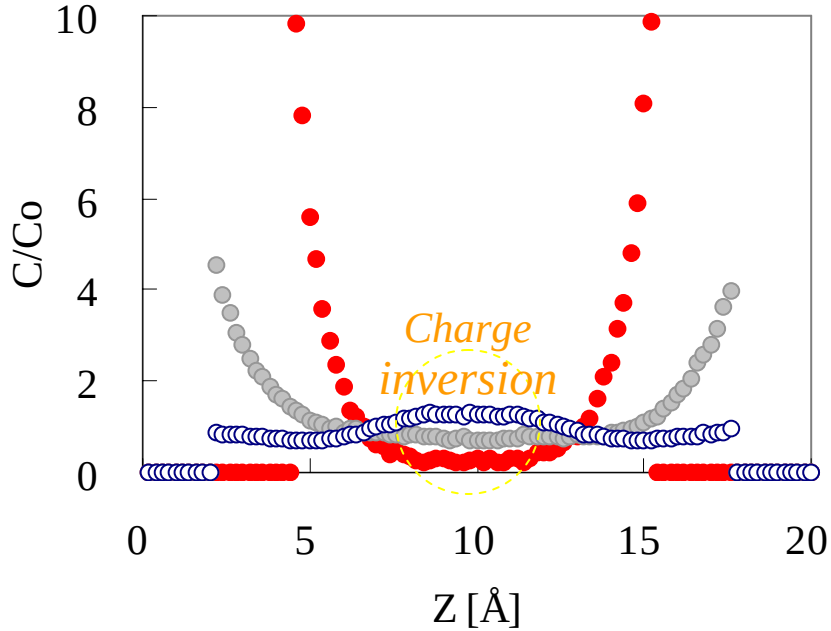
# Mixture of Electrolytes

- Mixture of 1:1 and 1:3 electrolytes :

Ionic strength = 0.5 M
Surface charge density = 0.02 C/m²




Ionic strength = 5 M
Surface charge density = 0.1 C/m²

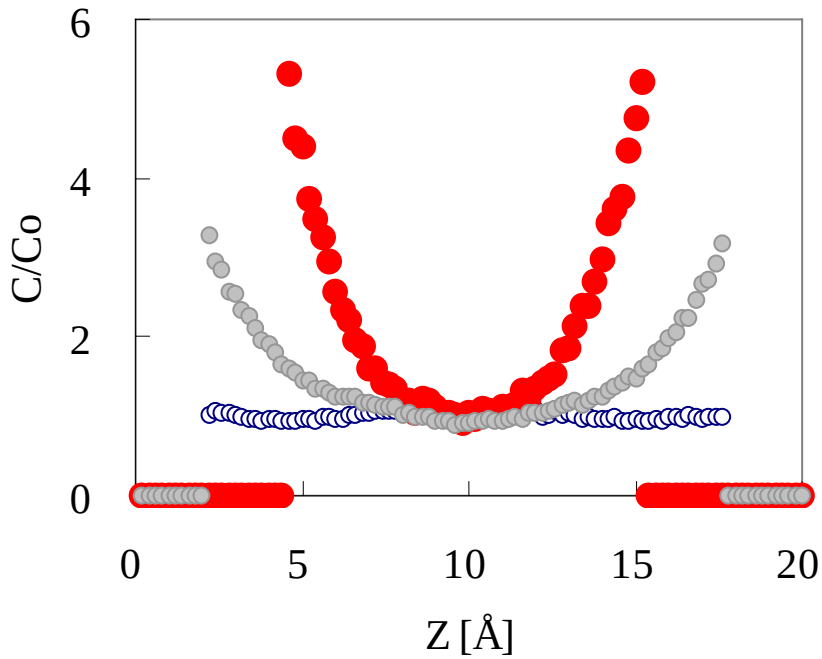



- Trivalent counterion (9-Å diameter)
- Monovalent counterion (4.25-Å diameter)
- Monovalent coion (4.25-Å diameter)

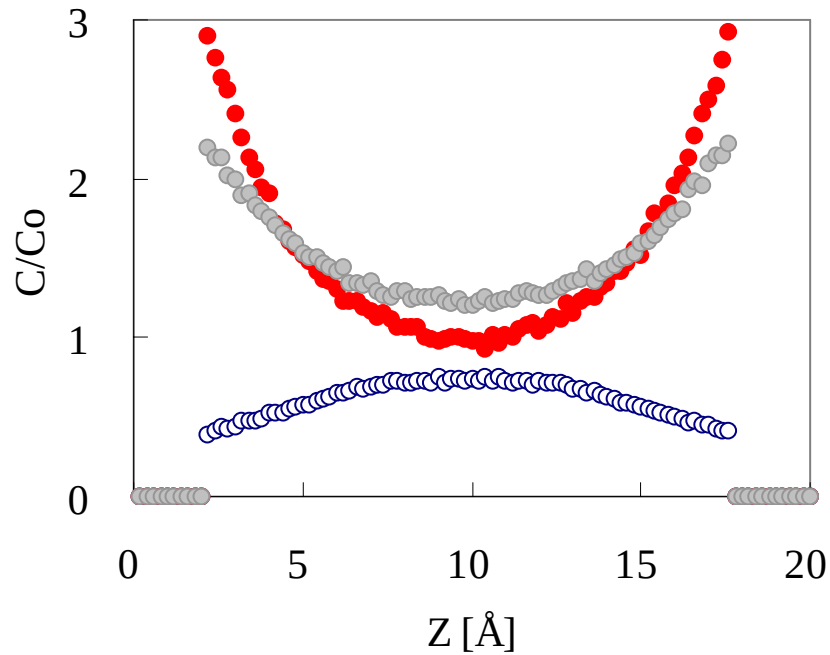
✓ The CMC simulation is applicable to solutions of mixtures symmetric and asymmetric electrolytes and inside nanopores.

# Effect of Ion Size and Ion Valence

- Ion distribution can be effected by two mechanisms: *(i)* ion size (ion-exclusion) and *(ii)* charge asymmetry (energy)




- Monovalent counterion (9-Å diameter)
- Monovalent counterion (4.25-Å diameter)
- Monovalent coion (4.25-Å diameter)

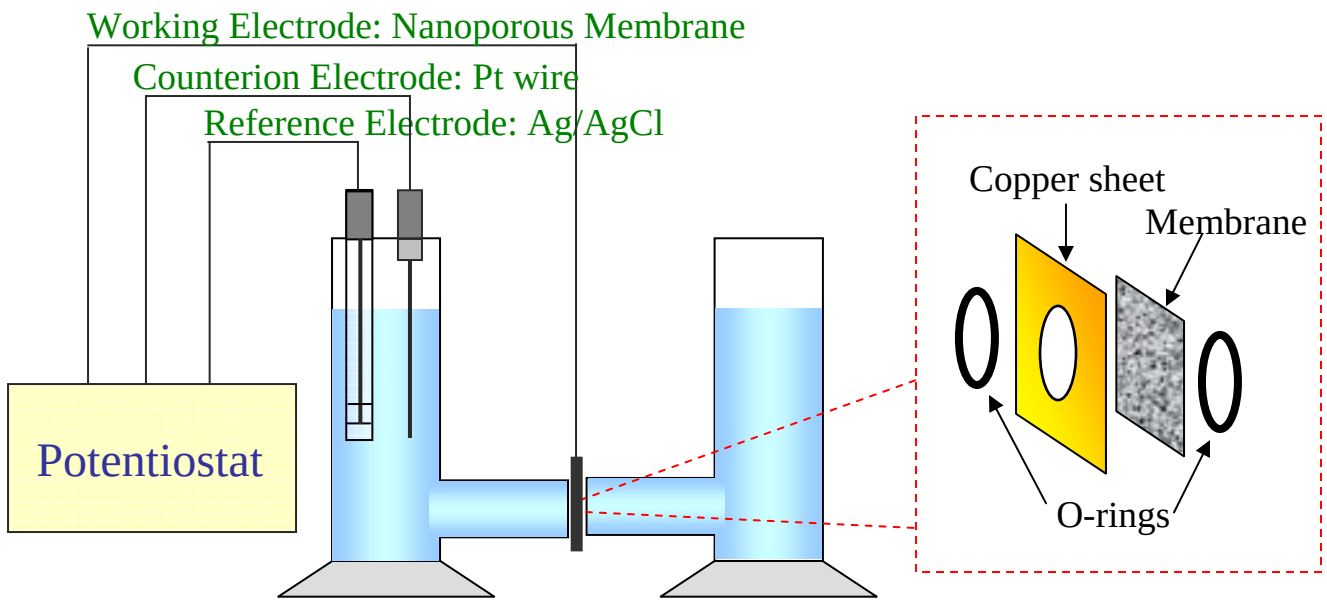



- Trivalent counterion (4.25-Å diameter)
- Monovalent counterion (4.25-Å diameter)
- Monovalent coion (4.25-Å diameter)

Ionic strength = 1 M, Surface charge density = 0.04 C/m$^2$

# Significance in Process Intensification

- The pore size distribution plays a key role in determining the electrosorption capacity of nanostructured materials.
- EDL overlapping has a negative effect on ion uptake and transport.
- Ion selectivity is achievable based on the ion size and charge and the pore size - membrane separation possible.
- For a given solution chemistry, there is an optimal pore size for maximum electrosorption capacity.
- An example of how theory can guide material synthesis for process intensification.

# Future Work

- Experimental work and GCMC simulation will be employed to study the ion sorption and transport in nanoporous materials.
  - EDL structures insides nanopores
  - EDL behavior of mixtures of symmetric and asymmetric electrolytes
  - Investigation of competition of effects resulting from:
    - ✓ The occurrence of double-layer overlapping
    - ✓ The ion-size exclusion
    - ✓ The charge asymmetry of ions