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Simulating the Electrical Double Layer

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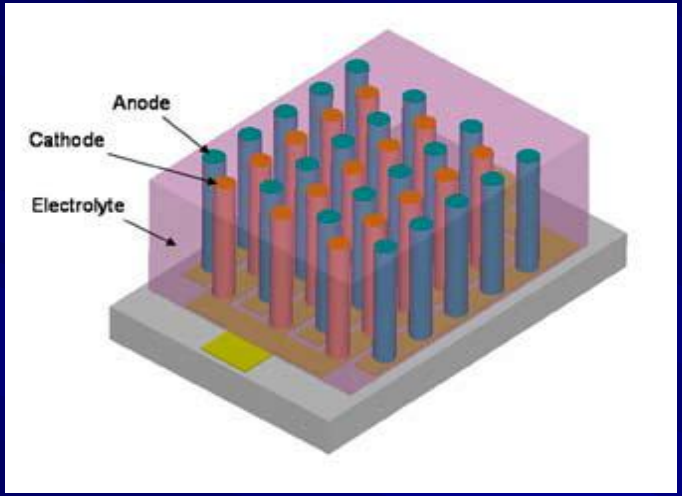
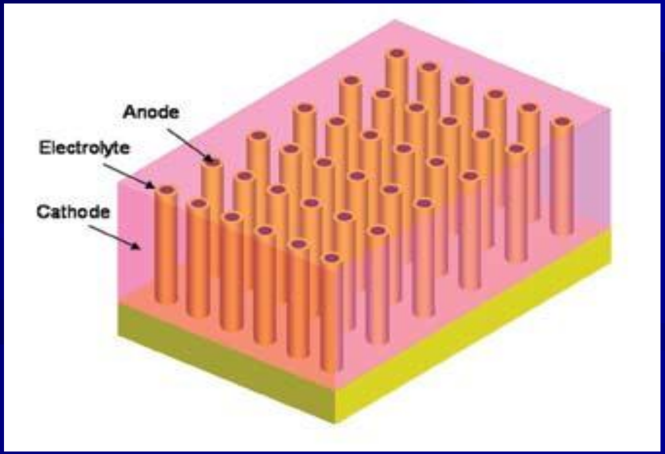
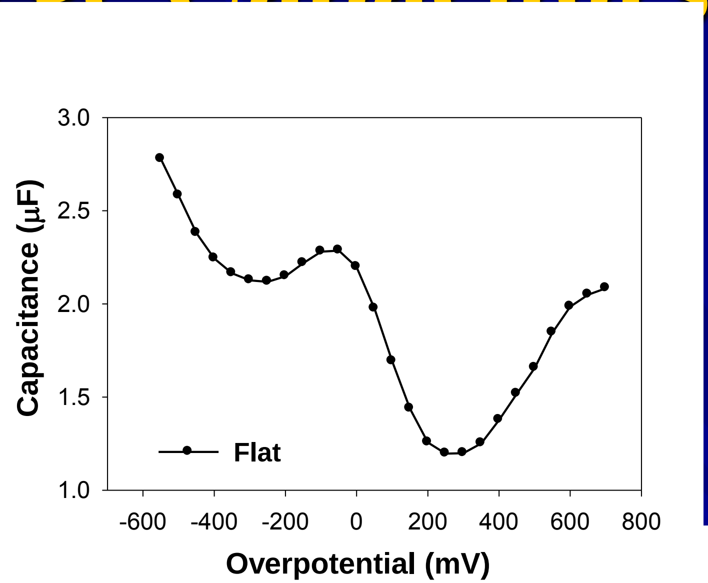
Overview

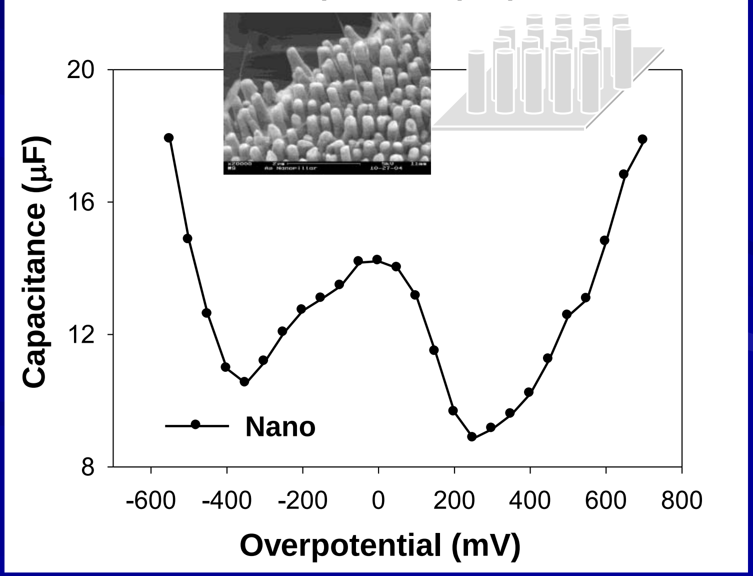
- The drive to make supercharge capacitors
- Electrochemical based capacitor
- The structure of electrical double layer (EDL)
- The effect of EDL structure on electron transfer
- The EDL capacitor
- Conclusions

Making Supercharge Capacitors







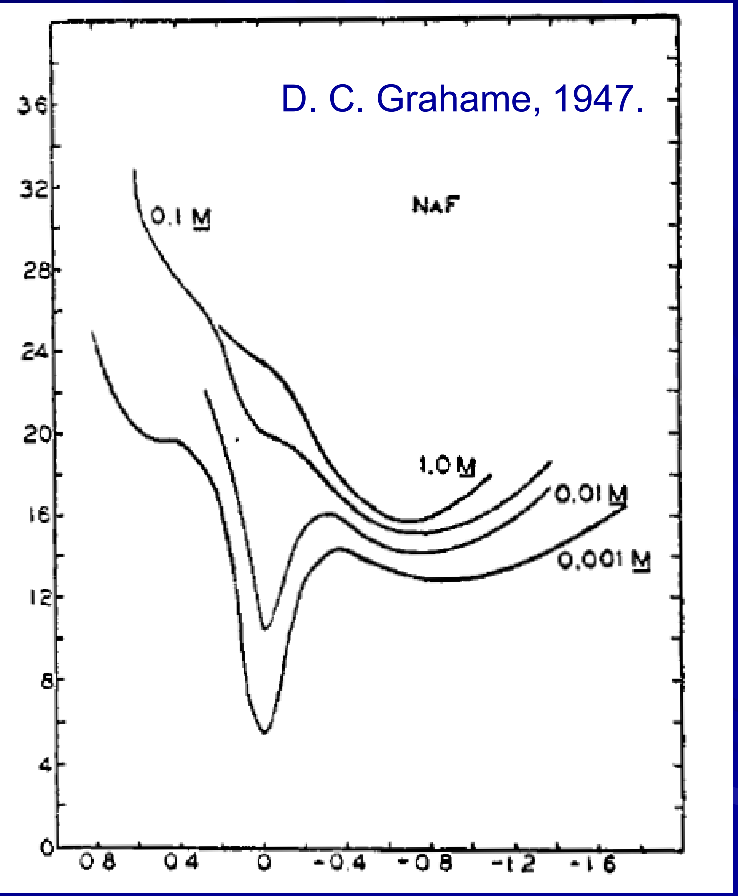


The Electrochemical Society **Interface**, Fall 2008

Electrochemical Based Capacitor

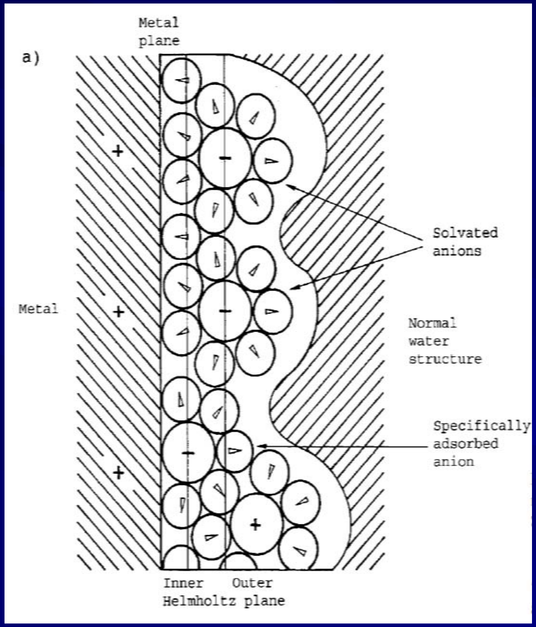
- This topic has been a major interest in electrochemistry for about a century
- In 1997, the Electrochemical Society sponsored a symposium on the double layer to recognize the 50th anniversary of Grahame's seminal work

$$C = \varepsilon\varepsilon_0 A / d$$

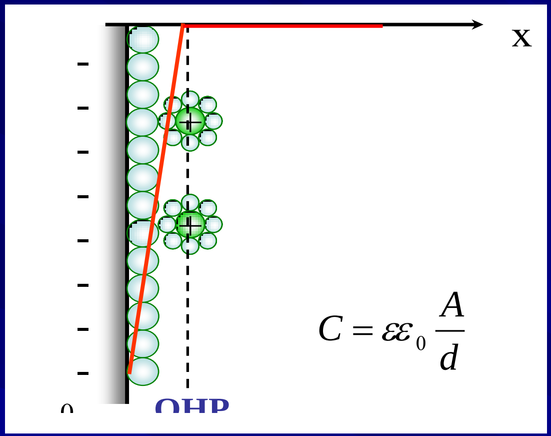


Electrical Double Layer (EDL)

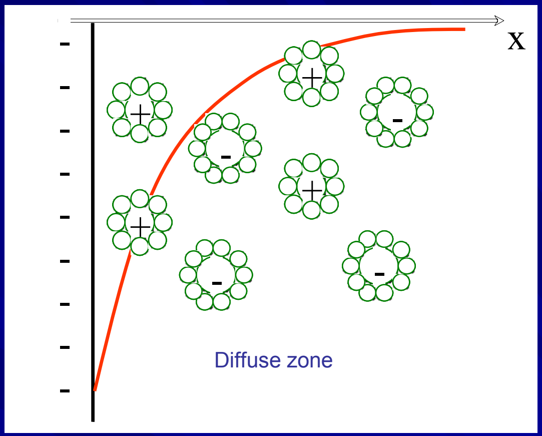
The EDL structure



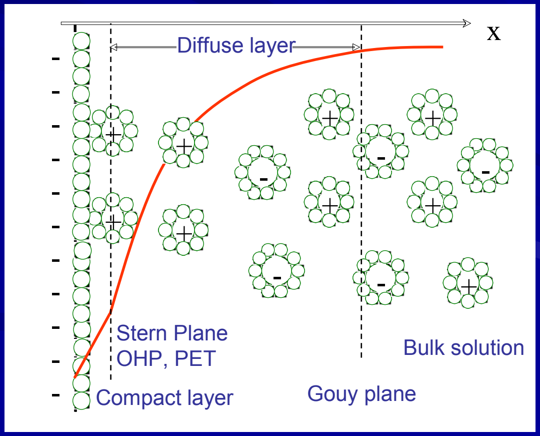
Helmholtz Model



Gouy-Chapman Model



Gouy-Chapman-Stern Model



Problems with the classic theories on electrical double layer (EDL):

1. No electron transfer across the electrode/solution interface
2. Boltzmann distributions for ions in the solution
3. Electro-neutrality

Modeling the EDL

Using COMSOL

- Mass transport by diffusion and electromigration
  - Nernst-Planck equation

$$\frac{\partial c_i}{\partial t} = \nabla\left(D_i \nabla c_i + \frac{z_i F}{RT} D_i c_i \nabla V\right)$$

- Electrostatics
  - Poisson equation

$$\nabla(\varepsilon\varepsilon_0 \nabla V) = -\rho$$

In the compact layer: $\rho = 0$

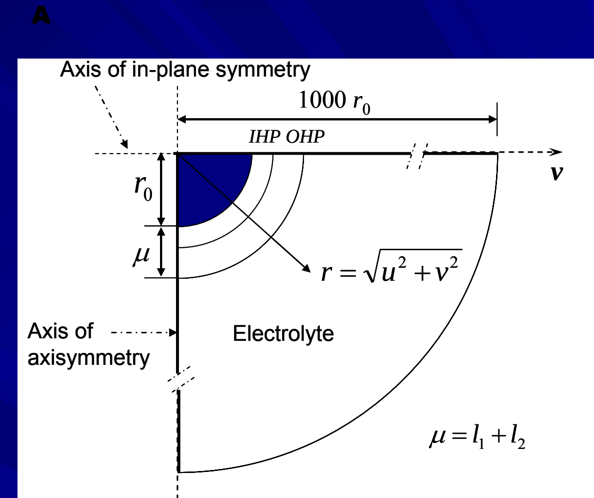
In the solution: $\rho = \sum_i z_i c_i$

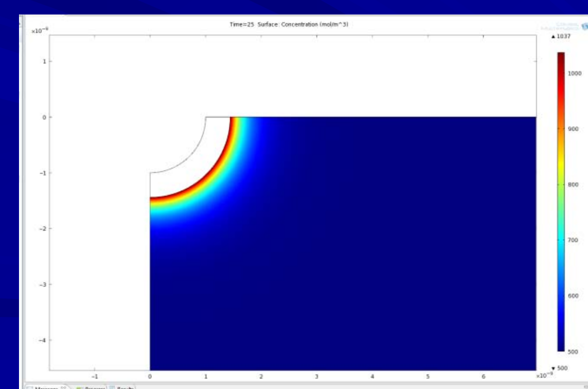
- Reversible/irreversible systems
  - Butler-Volmer kinetics

$$O^z + e^- \underset{k_b}{\overset{k_f}{\longleftrightarrow}} R^{z-1}$$

$$k_f = k_0 \cdot \exp[-\alpha F(E_t - V - E^{0'})/RT]$$

$$k_b = k_0 \cdot \exp[(1-\alpha)F(E_t - V - E^{0'})/RT]$$

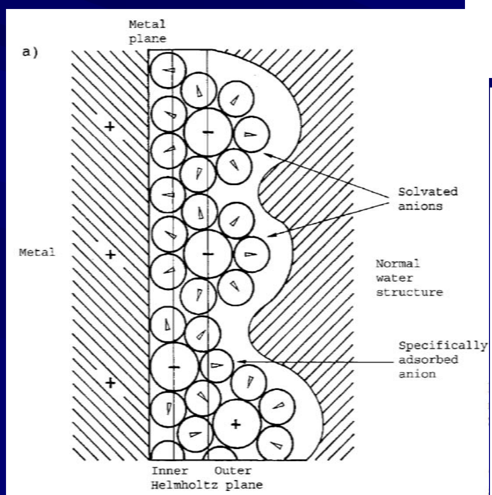


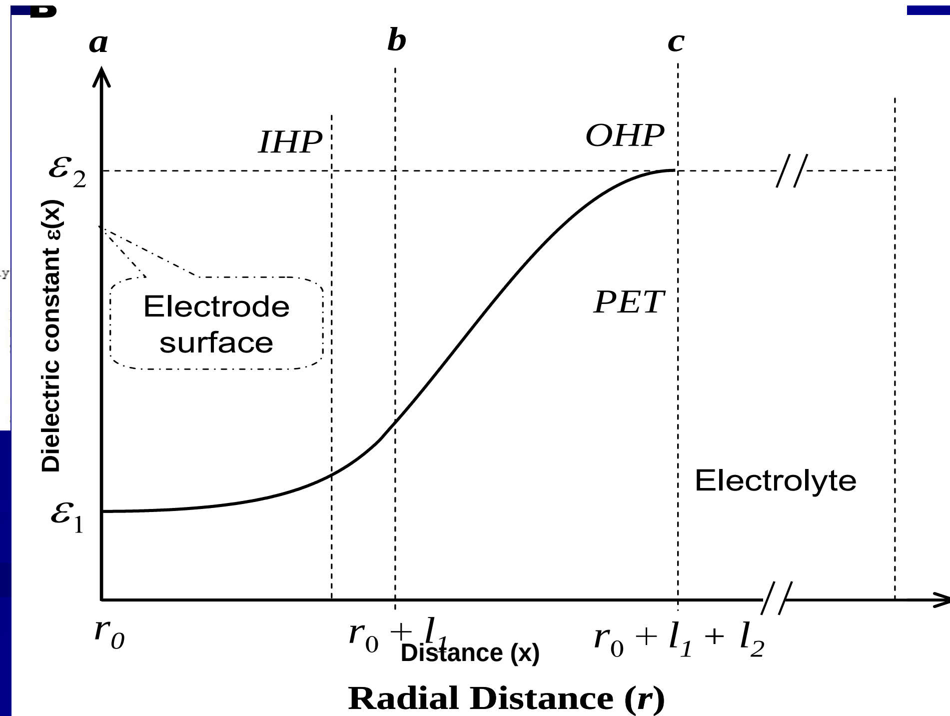


Modeling Using COMSOL

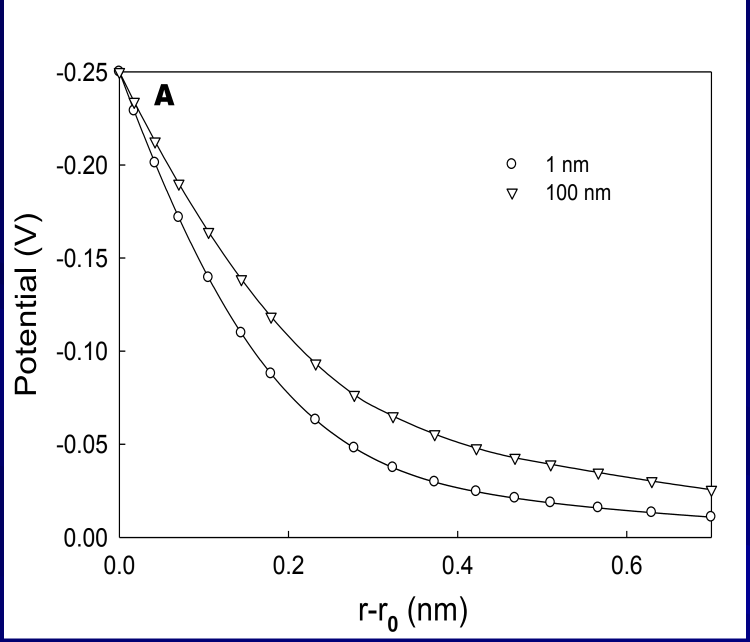
- Dielectric constant inside the compact layer

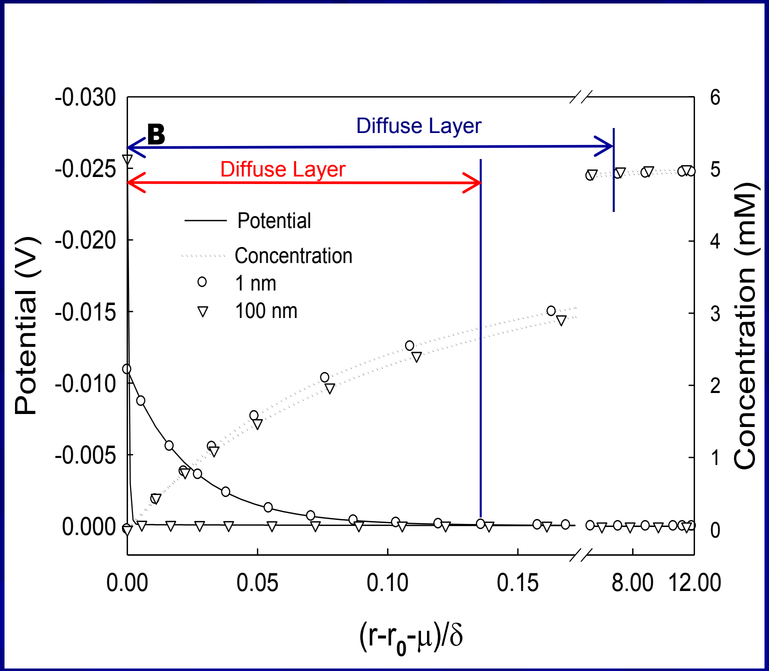
$$
\varepsilon = \begin{cases} \varepsilon_1 \cosh^2[S_1(r - r_0)], & r_0 \le r \le r_0 + l_1 \\ \varepsilon_2 \cos^2[S_2(l_1 + l_2 + r_0 - r)], & r_0 + l_1 \le r \le r_0 + l_1 + l_2 \\ \varepsilon_2, & r_0 + l_1 + l_2 \le r \end{cases}
$$





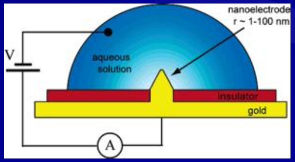
The Size Factor of the EDL





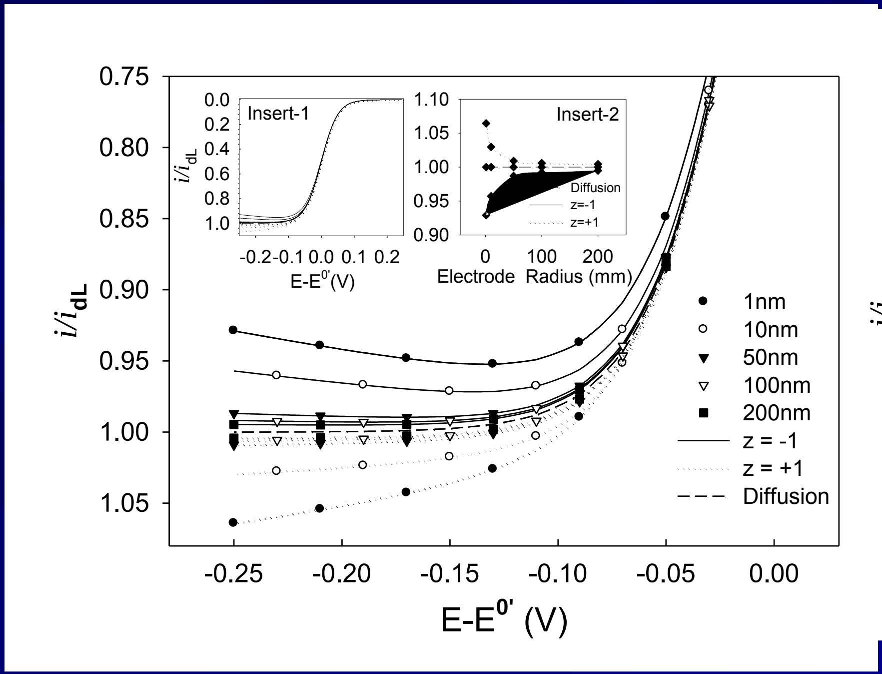
$$\delta_{1nm}^{diffuse} = 1.8\,(\text{nm}),\quad \delta_{100nm}^{diffuse} = 4.5\,(\text{nm})$$

$$\delta_{1nm}^{diffusion} = 14\,(\text{nm}),\quad \delta_{100nm}^{diffusion} = 820\,(\text{nm})$$

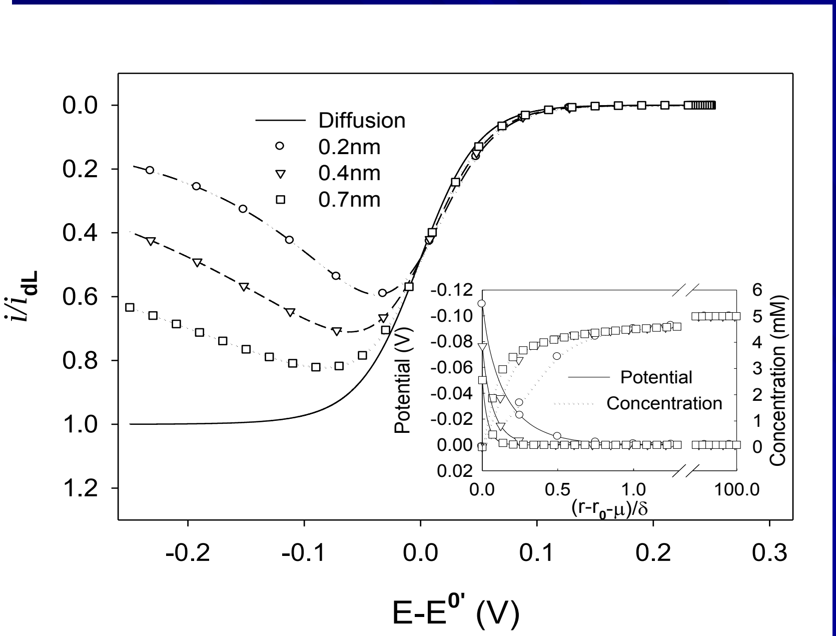


~13% ~0.5%

EDL Effect on Electron Transfer



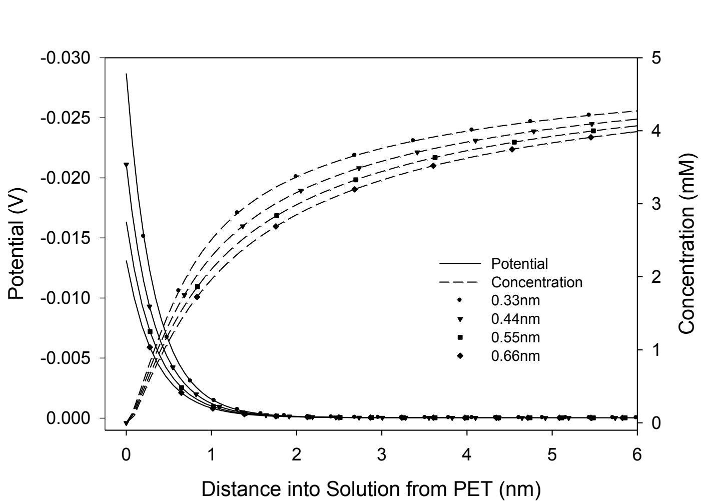
Effect of electrode size

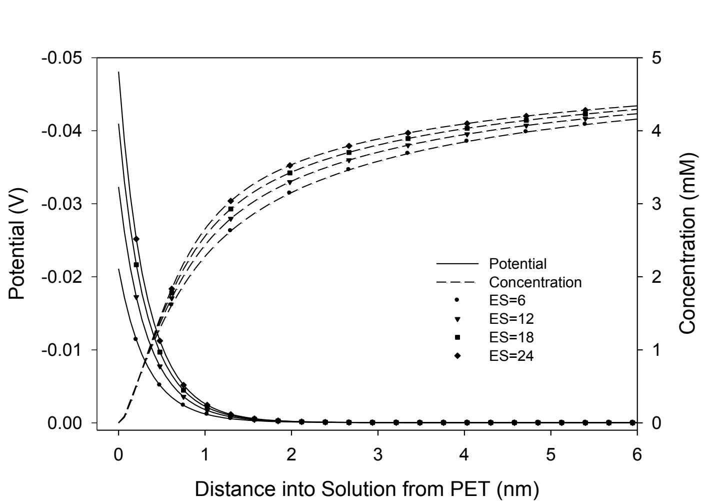


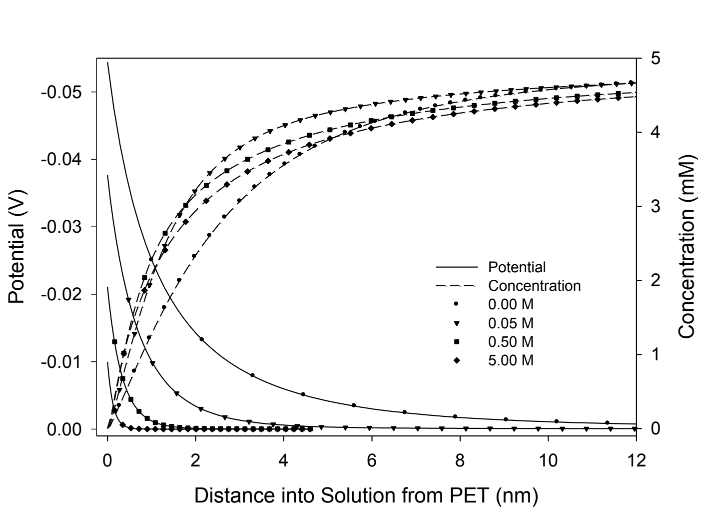
Effect of compact layer thickness

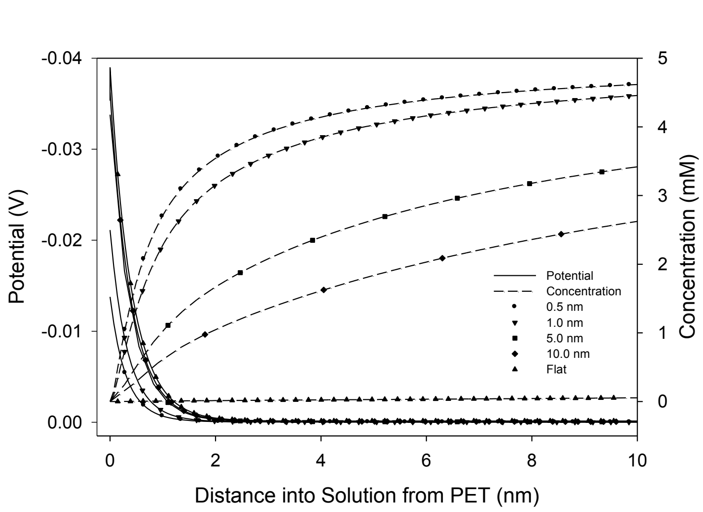
Note: “Diffusion” represents the case in which the EDL effect is not considered.

Effects of EDL

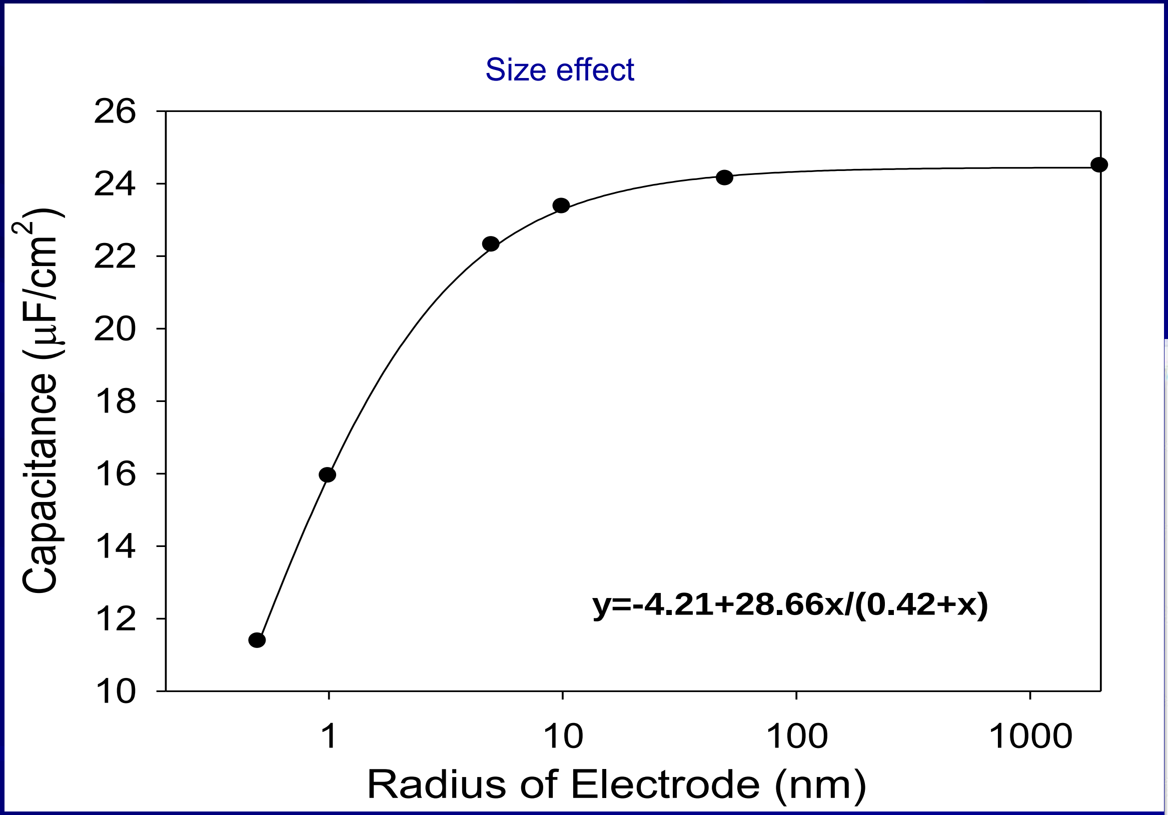




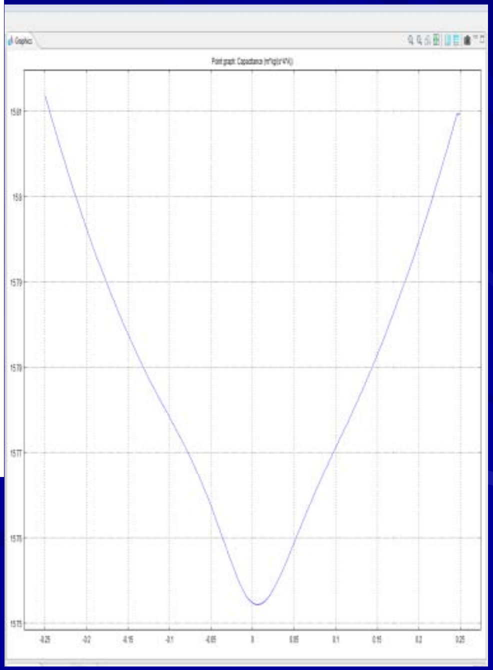




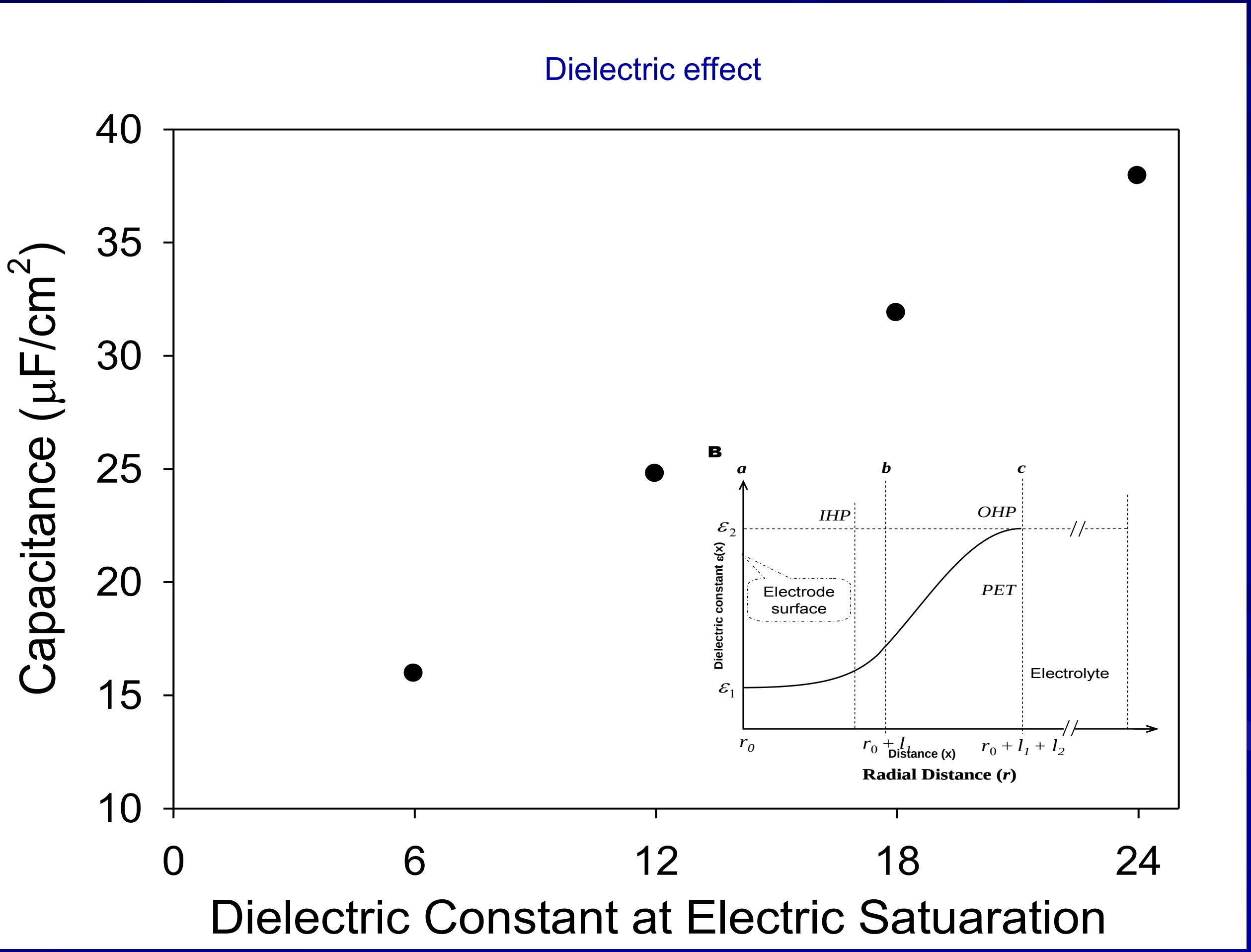
EDL Capacitance



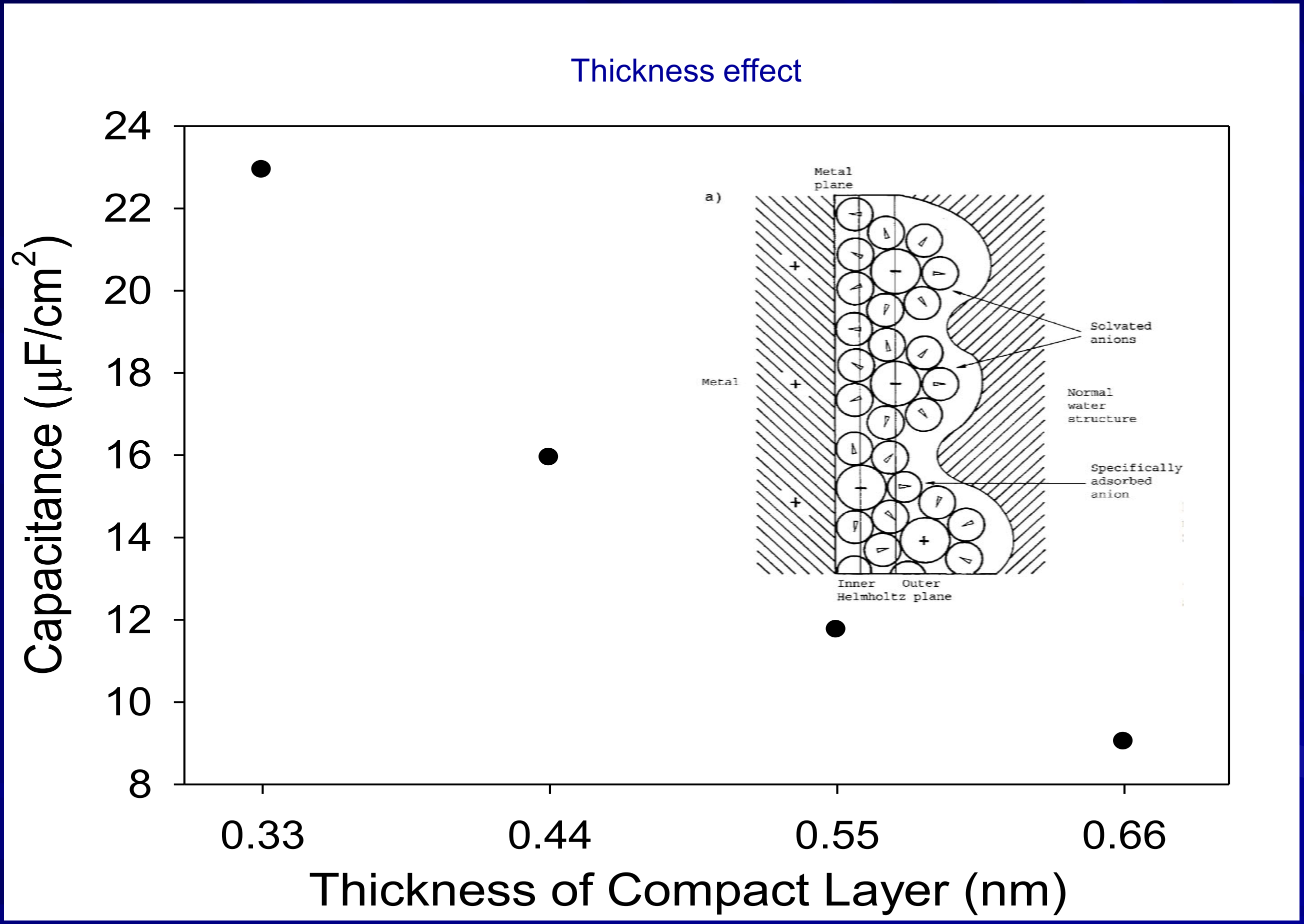
$$C = \varepsilon\varepsilon_0 \frac{\partial^2 \phi}{\partial r \partial E}$$



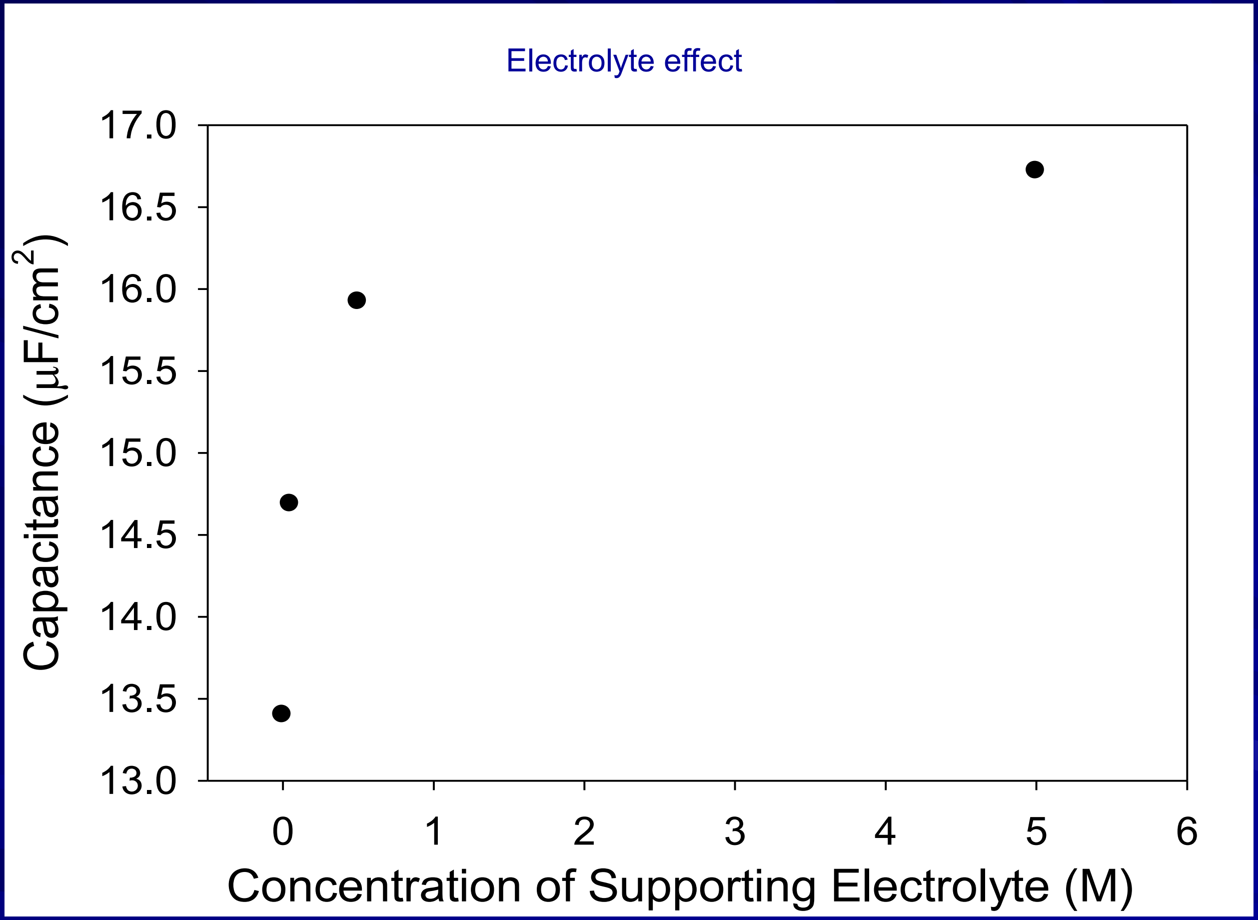
EDL Capacitance



EDL Capacitance

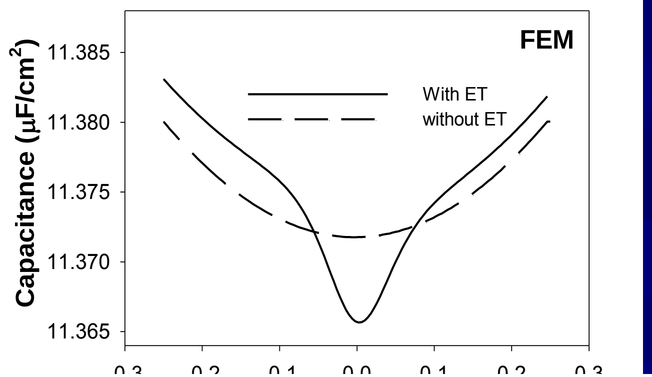


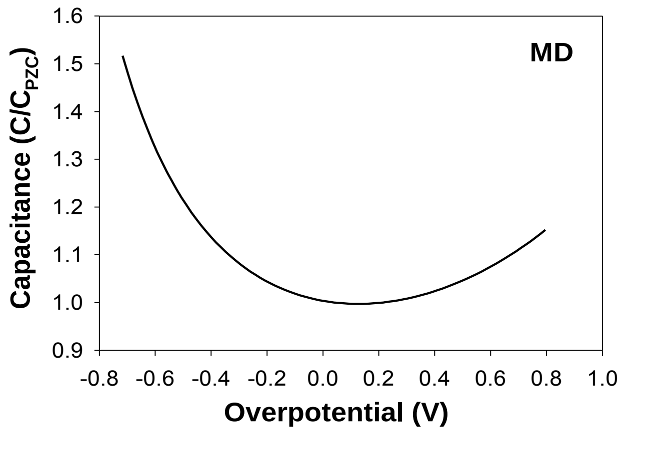
EDL Capacitance

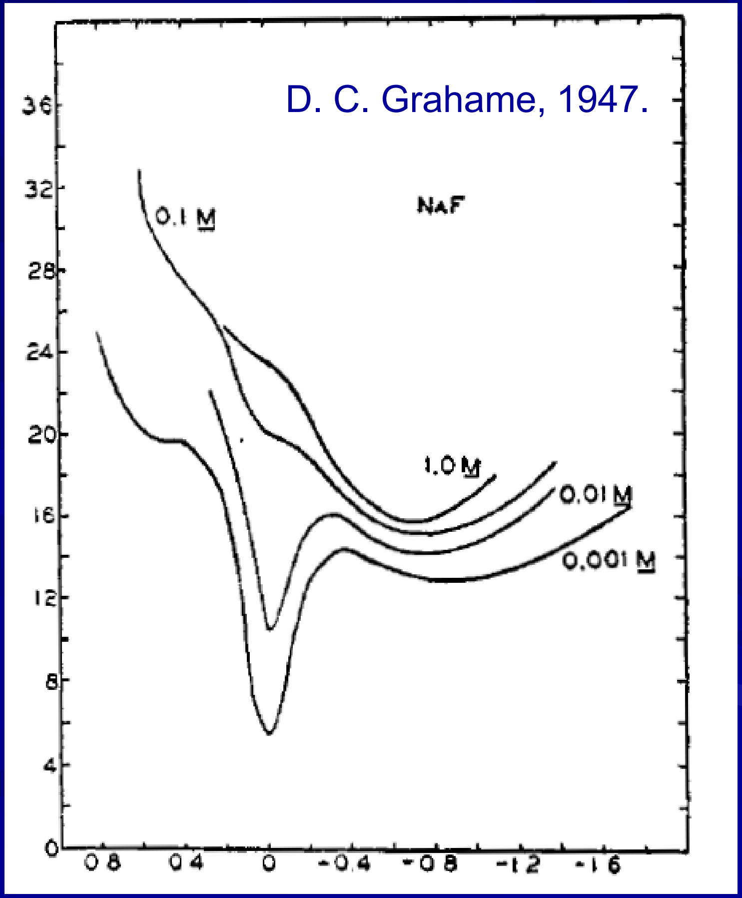


EDL Capacitance: A Surprise

$$C = \varepsilon\varepsilon_0 A / d$$







Conclusions

- EDL capacitance varies as a function of
  - Dielectric constant
  - Compact layer thickness
  - Electrode size
  - Electrolyte concentration
- When redox is allowed, the capacitance-potential curve exhibits a dip feature near the potential of zero charge
- This study shed some new light into enhancing the supercharge capacitors

Acknowledgement

- National Science Foundation
- Bill & Melinda Gates Foundation

Thank You!