Electrosorption Capacitance of Nanostructured Carbon-Based Materials

Chia-Hung Hou[†], Chengdu Liang[‡], Sotira Yiacoumi[†], Sheng Dai[‡], and Costas Tsouris[†,‡]

[†]School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA

[‡]Oak Ridge National Laboratory, Nuclear Science and Technology and Environmental Sciences Divisions, Oak Ridge, TN

Abstract

A graphitized-carbon monolithic column and two different types of carbon aerogel are proven to be good electrical double layer (EDL) capacitors that can be applied in the separation of ions from aqueous solutions. The pore size distribution plays a key role in determining the double-layer capacitance in an electrosorption process. Because of the occurrence of double-layer overlapping in narrow pores, mesopores and micropores have significantly different contributions to double-layer capacitance. The effect of the diffuse layer on the electrosorption capacitance can be reduced by increasing the pore size, electrolyte concentration, and applied potential. The results are relevant to the separation of ions from aqueous solutions and energy storage applications.

Objectives

- Provide useful information for synthesis of nanostructured carbon-based materials under various conditions of electrolyte concentration and electric strength.
- Study the roles of mesopores and micropores on the electrosorption processes via experimental investigation and modeling.
- Obtain a better understanding of the formation of the EDL inside nanopores.

Model Development

- Gouy-Chapman theory
  - Poisson-Boltzmann equation

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

B.C.

$$\frac{d\psi}{dx} = 0 \text{ and } \psi = \psi_m \text{ at } x = 0$$

$$\psi = \psi_d \text{ at } x = \pm\frac{w-a}{2}$$

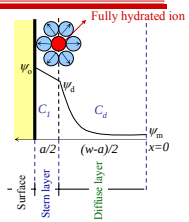
$$\psi = \psi_0 \text{ at } x = \pm\frac{w}{2}$$

  - Diffuse-layer potential

$$\psi_d = \psi_0 - \frac{\sigma_0}{C_1}$$

  - Surface charge density

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

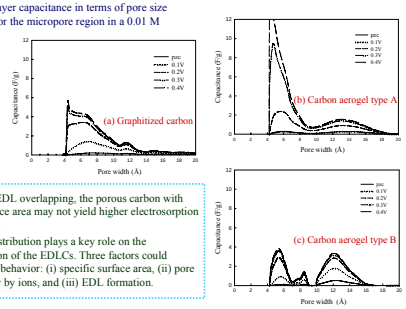


EDL capacitance

$$C_{dl} = \left(\frac{\partial\sigma_0}{\partial\psi_0}\right)_\mu$$

Effect of Pore Size Distribution

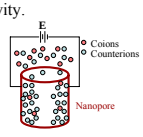
The double-layer capacitance in terms of pore size distribution for the micropore region in a 0.01 M NaF solution:



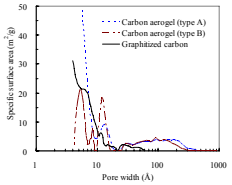
- Due to the EDL overlapping, the porous carbon with higher surface area may not yield higher electrosorption capacitance.
- Pore size distribution plays a key role on the determination of the EDLCs. Three factors could explain this behavior: (i) specific surface area, (ii) pore accessibility by ions, and (iii) EDL formation.

Introduction

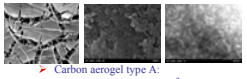
- Carbon materials of porous structure constitute very attractive electrodes for electrosorption because of their high specific surface area and their good electrical conductivity.
- The working principles is that an externally applied electric potential forces charged species toward oppositely charged electrodes, leading to the formation of the EDL.
- When the pore size is comparable to the EDL thickness, the double layers of inner walls of pores overlap. Since nanostructured carbon materials mainly consist of mesopores and micropores, EDL overlapping becomes a key factor for ion transport.



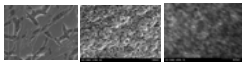
Characterization of Carbon Materials



- Graphite: BET surface area = 487 m²/g



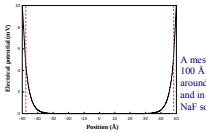
- Carbon aerogel type A: BET surface area = 691 m²/g



- Carbon aerogel type B: BET surface area = 431 m²/g

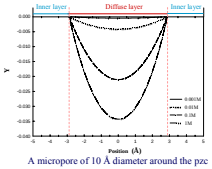
- These nanostructured carbon-based materials exhibit high specific surface areas as the result of the contributions of mesopores and micropores.
- The micropore region has a large contribution to the total specific surface area, and thus, double-layer overlapping will have a pronounced effect on electrosorption capacitance.

Electrical Potential Distribution Inside Nanopores

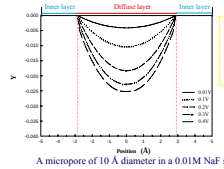


A mesopore of 100 Å diameter around the pzc and in a 0.01M NaF solution

- Because the double layer can fully develop inside pores, mesopores exhibit good electrochemical accessibility.
- In micropores, a shallow potential distribution is observed due to double-layer overlapping. This behavior causes ion exclusion and leads to a slow mass transfer rate of ions.



A micropore of 10 Å diameter around the pzc

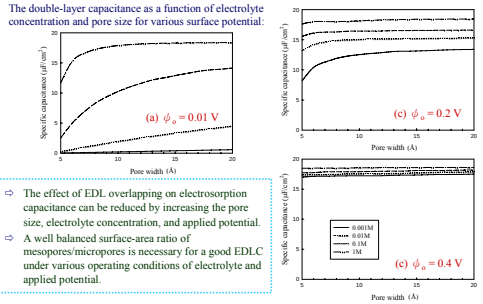


A micropore of 10 Å diameter in a 0.01M NaF solution

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

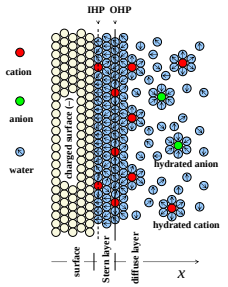
Materials Needed for Electrosorption

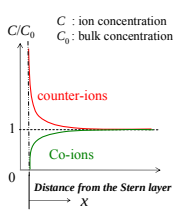
The double-layer capacitance as a function of electrolyte concentration and pore size for various surface potential:



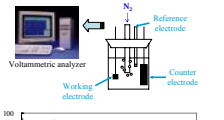
- The effect of EDL overlapping on electrosorption capacitance can be reduced by increasing the pore size, electrolyte concentration, and applied potential.
- A well balanced surface-area ratio of mesopores/micropores is necessary for a good EDLC under various operating conditions of electrolyte and applied potential.

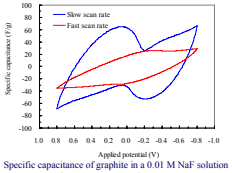
Formation of Electrical Double Layer



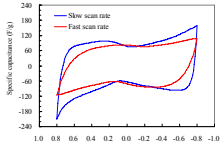


Cyclic Voltammetry





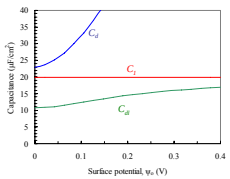
Specific capacitance of graphite in a 0.01 M NaF solution at fast (1 mVs⁻¹) and slow (1 mVs⁻¹) scan rates



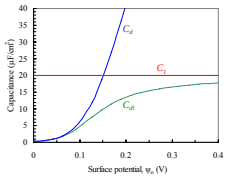
Specific capacitance of graphite in a 1 M NaF solution

- The EDLCs can be classified into 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 under certain conditions.

Effect of Diffuse and Inner Layers



A mesopore of 100 Å diameter in a 0.01M NaF solution



A micropore of 10 Å diameter in a 0.01M NaF solution

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

C_d: double-layer capacitance
C_1: inner-layer capacitance
C_{dl}: diffuse-layer capacitance

- Mesopores and micropores represent significantly different behaviors in the electrosorption process..
- The diffuse layer inside micropores plays a more important role than the diffuse layer inside mesopores during electrosorption.
- Under certain conditions, the diffuse layer dominates the EDL formation and a considerable loss of the double-layer capacitance takes place..

Acknowledgments

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