Simulating the Electrical Double Layer Capacitance

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Abstract: In this study, a computational model was developed using commercial finite element analysis package COMSOL Multiphysics (Burlington, MA) to simulate the electrical double layer (EDL) structure and quantify the EDL capacitance for the first time. In the modeling the electrochemical process at an EDL structure was considered by solving the Poisson, Nernst-Plank and Butler-Volmer equations without applying electroneutrality and Boltzmann distributions. Moreover, to consider the effect of charge transfer on the EDL capacitance, the cases with and without redox reactions were modeled. To take advantage of the computational equation solving capability, the dielectric constant inside the compact layer was considered as varying smoothly and continuously, rather than as a constant or a set of constants.

Keywords: Electrical double layer, capacitance, electrode, electrolyte, interface.

1. Introduction

When a solid surface makes contact with a liquid medium, an EDL structure will form spontaneously through thermodynamic interaction between electrons and ions. According to the canonical works by Gouy, Chapman, Stern, Frumkin and Grahame,[1-2] the EDL consists of a compact layer (a surface-localized part) and a diffuse layer (a thermally mobile and spatially distributed part). The compact layer is made of solvent molecules and/or specifically adsorbed ions, and the diffuse layer solvated ions (Fig.1).

A close examination revealed that in these classical studies, the ionic species were assumed to follow Boltzmann distributions and remained in electroneutrality. Obeying a Boltzmann distribution requires that the ionic species are in a thermodynamic equilibrium state. But when reactant species enter a redox event, the net dynamic Faraday current generated by the electron transfer at the metal/electrolyte interface will break up the thermodynamic equilibrium. On the other hand, while electroneutrality holds true in the bulk part of the solution, it is impossible to maintain electroneutrality in the vicinity of the electrode surface when the electrode is electrically polarized.[3] Therefore, to overcome these problems, we have developed a computational model[4-5] to simulate the electrochemical processes at an EDL structure by solving the Poisson, Nernst-Plank and Butler-Volmer equations without applying electroneutrality and Boltzmann distributions.
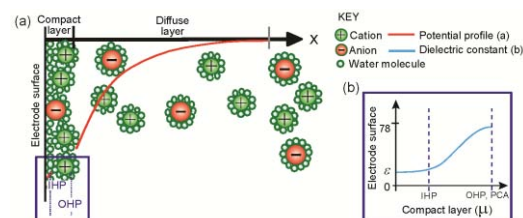

Fig. 1 – (a) Schematic of EDL structure where μ is thickness of compact layer, and ε is dielectric constant at electrode surface; (b) Profile of dielectric constant inside the compact layer.

2. Simulation of the Capacitance of the Electrical Double Layer

As schematically shown in Fig.2, a two-dimensional (2D) quarter-circle geometric model in a cylindrical coordinate system (u, v) is considered to represent a three-dimensional (3D) spherical electrode by taking advantage of the axisymmetery (about the u-axis) and the in-plane symmetry (about the v-axis). In this model, an electrode of radius r_0 is placed at the origin of the coordinate system. The space surrounding the electrode is divided into two domains: the first represents the electronic compact layer of the EDL of the electrolyte located within $r_0 \leq r < r_0 + \mu$ (note $r = \sqrt{(u^2 + v^2)}$), and the second represents the electrolyte located between $r = r_0 + \mu$ and $r = 1000r_0$. Inside the compact layer, there is an inner Helmholtz plane (IHP) and an outer

Helmholtz plane (OHP). In the simulation, it is assumed that the region inside the IHP is mainly filled with localized species, and that the OHP is the plane of closest approach (PCA) for all the ions and the position of electron transfer (PET).
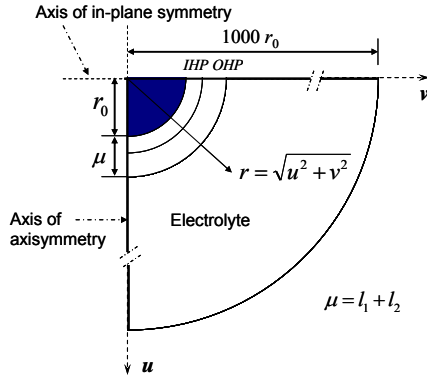

Fig. 2 – A 2D axisymmetric geometric model depicts a spherical nanometer electrode surrounded by an EDL structure in an electrolytic solution. The shaded quarter-circle represents the electrode approach, μ is thickness of compact layer, and ε is dielectric constant at electrode surface.

For the electrode reaction, a one-step single-electron reaction $O^z + e^- \leftrightarrow R^{z-1}$ is considered at the PET, where O^z is the reactant ion in its oxidized form and R^{z-1} is the product ion in its reduced form with z being the charge valence of the oxidized species.

For the electrical field and mass transport, an electrostatic problem governed by the Poisson equation $\nabla(\varepsilon\varepsilon_0\nabla V) = 0$ is solved in the compact layer and a combined Nernst-Plank and electrostatic problem governed by $\partial c_j/\partial t = \nabla(D_j\nabla c_j+z_jFD_jc_j\nabla V/RT)$ and $\nabla(\varepsilon\varepsilon_0\nabla V) = \rho$, where $\rho = \sum z_jc_j$, is solved in the electrolytic domain outside of the compact layer. Here D_j, z_j, and c_j are respectively the diffusivity, the charge valence and the concentration of the ionic species j, t is time, F is the Faraday constant, R is the gas constant, T is the absolute temperature, V is potential, ε is the dielectric constant, ε_0 is the vacuum permittivity, and ρ is charge density. In this simulation, the dielectric constant ε is considered to vary smoothly and continuously[4-5] inside the compact layer of the electrolyte as shown in Fig.1.

For the electrode reactions occurring at the PET, electronic fluxes J_O for O^z and J_R for R^{z-1} are applied: $-J_0=J_R=k_0*\exp[-\alpha F(E_t-V-$ $E^{0'})/RT]*c_0-k_0*\exp[(1-\alpha)F(E_t-V-E^{0'})/RT]*c_R$, in which k_0 is the standard electron transfer rate constant, α is the charge transfer coefficient, E_t is the potential applied at the electrode, V is the potential at PET, and $E^{0'}$ is the standard potential of the redox couple (which is assumed to be 0 in this study). For electrode polarization, a known electrode potential sweep at a rate of 20 mV/s (E_t, in the form of a triangle function) is applied at the electrode surface ($r = r_0$), and a zero potential ($E_t=0$) is applied at $r=1000r_0$. The resulting electrical field (ϕ) surrounding the electrode is determined and the EDL capacitance is calculated using the following formula: $C_{EDL}=\varepsilon\varepsilon_0(\partial^2\phi/\partial r\cdot\partial E)$.[2] For the supporting electrolyte, an excess amount of the cation/anion pair in the form of A^+B^- with a concentration 100 times that of the reactant (species O^z) is considered. To accompany the reactant initially, a counter ion, Ct, with a charge of $-sign(z)$ at a concentration $|z|$ times that of the reactant is also considered.

Commercial finite element analysis package COMSOL Multiphysics (Burlington, MA) was used to solve these equations by running the electrostatics and electrokinetic-flow application modes simultaneously. For this study, the parameters listed in Table 1 were used. Prior to all the analyses, a mesh refinement study was performed to identify a proper mesh for assuring a converged result.

Table 1- Material constants and kinetic and geometric parameters used in the simulation.[6-7]

D_O, D_R	1×10^{-9} (m²/s)	$E^{0'}$	0 (V)
D_A	1.33×10^{-9} (m²/s)	T	298 (K)
D_B	2.03×10^{-9} (m²/s)	ε_0	8.85419×10^{-12} (F/m)
D_{Ct}	2.0×10^{-9} (m²/s)	ε_I	6
c_A^b, c_B^b	500 (mol/m³)	ε_2	78
c_{Ct}^b	$|z|\cdot c_O^b$ (mol/m³)	S₁	3.6
c_O^b	5 (mol/m³)	S₂	3.05
c_R^b	0 (mol/m³)	l_1	0.4 (nm)
α	0.5	$\mu=l_1+l_2$	0.7 (nm)
F	9.64853×10^4 (C/mol)	z	-1
k_0	10 (m/s)	r_0	1~200 (nm)
R	8.31 (J/K)		

Note: c_i^b represents the concentration of species i in the electrolytic solution.

3. Results and Discussions

3.1. Model Validation

For validation, besides the mesh refinement (data not shown), the limiting current density obtained for a nanometer electrode governed by a diffusion-controlled process (i.e., the effect of EDL was ignored) is compared with the theoretical prediction[2]: $i_{dL}=FD_0c_0^b/(r_0+\mu)$, where D_0 is the diffusivity of the reactant and c_0^b is its concentration in the bulk solution. A difference of about 0.1% is found from this comparison, suggesting a very good agreement between the simulated and theoretical results.
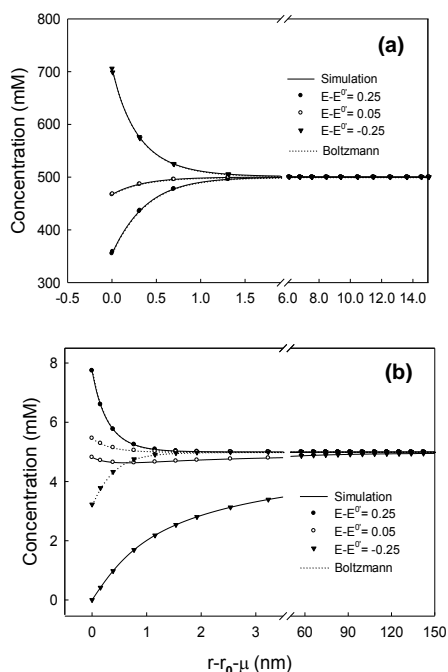

Fig.3 (a) Concentration distribution of species A^+ at various electrode potentials of $E-E^{0'}= 0.25$V ($i/i_{dL} \approx 0$), $E-E^{0'}= 0.05$V ($i/i_{dL} \approx 0.12$), and $E-E^{0'}= -0.25$V ($i/i_{dL} \approx 1$); (b) Concentration distribution of the reactant (species O^z).

After that, the radial concentration distribution of some selected ions at three different electrode potentials: $E-E^{0'}= 0.25$V (at which $i/i_{dL} = 0$), $E-E^{0'}= 0.05$V ($i/i_{dL} \approx 0.12$), and $E-E^{0'}= -0.25$V ($i/i_{dL} \approx 1$) is examined. For the electroinactive ion A^+ (Fig.3A) its concentration follows closely a Boltzmann distribution in all three cases. For the electroactive reactant (species O^z; Fig.3B), however, the concentration

follows a Boltzmann distribution only when the net current is zero at $E-E^{0'}= 0.25$V, and it deviates significantly from the corresponding Boltzmann distribution when there is a net current flowing at both $E-E^{0'}= 0.05$V and $E-E^{0'}= -0.25$V. These results confirm that in the presence of a net Faraday current, the electron transfer at the electrode will cause redox activities, which in turn will disrupt the thermodynamic equilibrium state of the electroactive ions. Thus in this situation, a Boltzmann distribution for the reactant will not be maintained. These electroinactive ions and the reactant ion under a zero current condition, however, are able to maintain their thermodynamic equilibrium states, thus their concentrations are expected to follow Boltzmann distributions.

3.2. EDL Capacitance

The charged species in the EDL structure make the double layer a capacitor: its capacitance is governed by the thickness of the compact layer as well as its state of dielectric saturation. The layer's thickness is related to the sizes of the surface-localized ions and/or molecules, and the state of dielectric saturation is influenced by the propensity of the ions and/or molecules toward surface localization. By varying the dielectric constant (ε) to reflect the change in the state of dielectric saturation (a lower ε means a higher degree of dielectric saturation) and varying the compact layer thickness (μ) to reflect the difference in size of the localized ions, we observed that the EDL capacitance generally increased as the dielectric constant increased and decreased as the compact layer thickness increased. As shown in Fig.4, an increase in ε from 6 to 24 causes a drastic increase in capacitance (approximately 16 to 38 μF/cm^2, Fig.4a), and an increase in μ from 0.33 to 0.66 nm causes a drastic drop in capacitance (approximately 23 to 9 μF/cm^2, Fig.4b). Usually, the value for ε changes from 6 for an electrode surface highly saturated by the adsorbed ions or molecules to 78 for an electrode surface surrounded by water, and the value for μ varies from 0.3 to 0.7 nm depending on the size of the localized ions or molecules in the EDL.[8] These results indicate the discriminative capability of

the capacitive effect of the EDL in terms of the dielectric state and size of the localized ionic species.
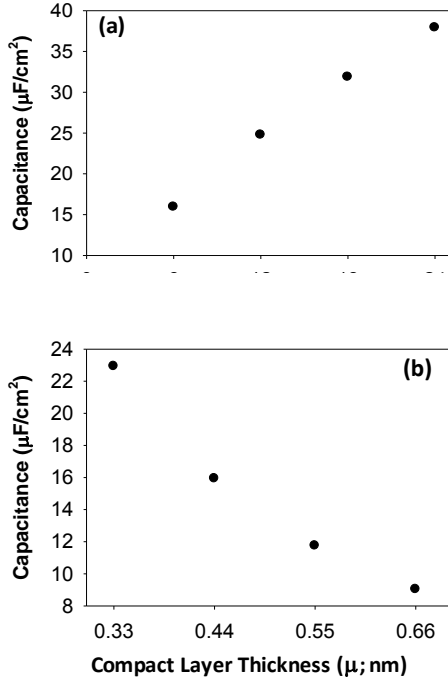

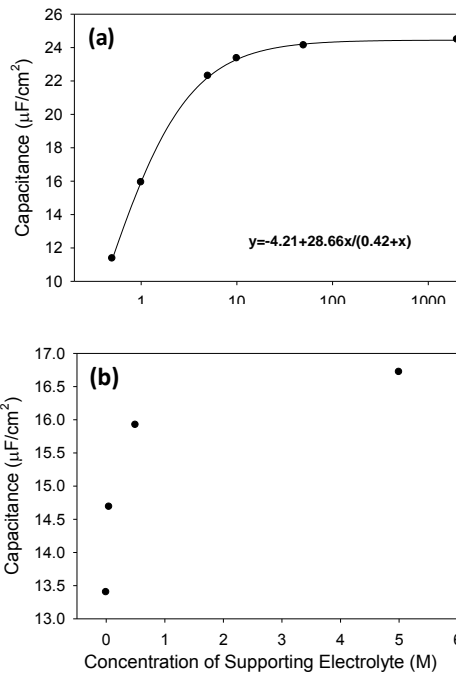Fg.4 Variation of EDL capacitance with (a) dielectric constant ε and (b) compact layer thickness μ.

Fg.5 Variation of EDL capacitance with (a) size of electrode and (b) concentration of electrolyte.

Aside from the effects of dielectric constant and compact layer thickness, we also found that the EDL capacitance also varies with the size of electrodes and the concentration of the supporting electrolyte. As shown in Fig.5, the specific capacitance increases following an asymptotic manner with both the radius of electrode and the concentration of the electrolyte.
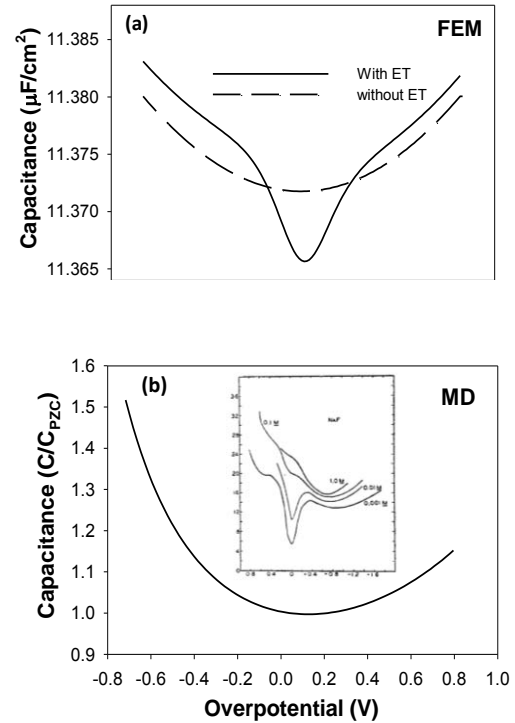

Fig. 6: Variation of EDL capacitance with overpotential obtained from (a) finite element method (FEM) with and without electron transfer (ET) and from (b) molecular dynamics (MD) simulation neglecting ET.

Fig.6(a) shows the EDL capacitance as a function of electrode overpotential. These curves revealed a dip in the EDL capacitance near the potential of zero charge (PZC) when there was electron transfer (ET) caused by redox reactions at the electrode surface. This dip was first reported in Grahame seminal work[9] (shown in the inset in Fig.6(b)), but it could not be accounted for theoretically. Our simulation results suggested that it was due to electron leakage at the electrode surface, which was confirmed independently by molecular dynamics (MD) simulation as presented in Fig.6(b). These results imply that the electrodes in Grahame

work might not be ideally polarized as assumed. This finding shed new insight into a long-standing mystery regarding EDL since the 1940's.

4. Conclusions

In this paper, the capacitive effect of the EDL was simulated for the first time. By taking advantage of the computational partial-differential-equation solving capability of COMSOL Multiphysics, the electrochemical process at an EDL structure was simulated by solving the Poisson, Nernst-Plank and Butler-Volmer equations. In the modeling, the dielectric constant inside the compact layer was considered as varying smoothly and continuously, redox events were allowed at the electrode surface, but electroneutrality and ionic Boltzmann distribution in the vicinity of the electrode surface were not assumed.

The obtained results show that EDL capacitance varies as function of dielectric constant, compact layer thickness, electrode size, and electrolyte concentration. Moreover, when electron transfer redox events were allowed, the capacitance-potential curve showed a dip feature near the potential of zero charge, a phenomenon first reported in Grahame seminal work in 1947 but was never accounted for theoretically.

5. References

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6. Acknowledgements