

Investigation of Dielectric Decrement and Correlation Effects on Electric Double-Layer Capacitance by Self-Consistent Field Model

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Abstract. The differential capacitance of electric double-layer capacitors is studied by developing a generalized model of the self-consistent Gaussian field theory. This model includes many-body effects of particles near the interface such as ionic sizes, the order of water alignment and electrostatic correlations, and thus can present more accurate predictions of the electric double-layer structure and hence the capacitance than traditional continuum theories. Analytical simplification of the model and efficient numerical method are introduced, in particular, the approximation of the self-Green's function which describes the self energy of a mobile ion. We show that, when the applied voltage on interfaces is small the dielectric effect of the electrode materials plays an important role. For large voltage, this effect is screened, but the dielectric saturation due to the alignment of the nearby water is shown to be essential. For 2:1 electrolytes, abnormal enhancement on the capacitance due to the dielectric electrode is observed, which is due to the interplay of the image charge effect and Born solvation energy in the self energy of ions.

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1 introduction

For a charged surface in an electrolyte, counterions are attracted to the surface by the electric field. The structure of the screened ions forms the so-called "electric double layer"

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(EDL) structure. The study of EDLs is of great interest in understanding the electrochemical capacitors (ECs) or supercapacitors because of the rising demand for high power energy storages and the development of blue energy devices [1, 2]. For example, the “capacitive mixing” for harvesting the free energy of solutions has been shown promising for blue energy applications, which are paid great recent theoretical attention such as the effects of different salt concentrations [3], multi-valence [4] and electrode materials [5] to the energy production process. These studies show many-body effects such as short-range size effect and long-range electrostatic correlation play important role in determining the structure of the EDL and the efficiency of energy storages, thus the EDL capacitance can not be accurately described by the classical Poisson-Boltzmann (PB) theory due to the ignorance of these many-body effects.

As a result of the limitations caused by the mean-field treatment, there are many different approaches to extend the PB theory in order to correctly describe the EDL. A simple but widely used extension is the Gouy-Chapman-Stern model [6–8], which considers a charge free layer or the so-called Stern layer near the surface and a diffuse layer beyond that. Another approach is to introduce the ionic steric effects that prevent ions from accumulating near the highly charged surface because of the high ionic densities [9–11] with a local correction of entropic contribution in free energy. Based on this treatment, Kornyshev [12] proposed an analytical formula for EDL capacitance at a metal and ionic liquid interface. Alternately, the density functional theory (DFT) introduces fundamental measure theory [13], which more accurately describes the ion-size effect [14, 15], and thus provides richer phenomena of the EDL capacitance [16].

An important issue for the EDL capacitance is the effect of the inhomogeneity of the dielectric permittivity within the EDL. The dielectric constant of the electrolyte has been shown to depend on both the electric field and ionic concentrations from the experimental results [17, 18]. On one hand, the field dependency of the dielectric function was systematically studied early in the 1950s by Booth [19, 20]. The corresponding Booth model was later introduced into the PB theory [21–23] and the research on the EDL capacitors [24–26]. On the other hand, there will be a decrease of the dielectric constant of solutions when salts are added to them. This is thought as a result of the effective polarizability or solvation of ions when the water molecules around the ions are prevented from orienting against the applied field and hence the dielectric constant of the electrolyte will be reduced. This important property was investigated by Hasted, *et al.* [17], followed by many publications in this field [27–31]. For the related work on the EDL capacitance, the readers are referred to Refs. [32–34]. It is also shown by MD simulations [35–37] that the interfacial dielectric function is closely related to the molecular solvent structure of the surface, and this space-dependent dielectric permittivity can significantly change the ionic distribution surrounding an interface as is observed by primitive-based Monte Carlo calculations [38].

To go beyond the mean field theory such that many-body interactions can be included, a self-consistent field theory by Gaussian variational formulation has been systematically derived [39–41]. The theory presents a better approximation of the potential