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Predicting ion specific capacitances of supercapacitors due to quantum ionic interactions

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ABSTRACT

A new theoretical framework is now available to help explain ion specific (Hofmeister) effects. All measurements in physical chemistry show ion specificity, inexplicable by classical electrostatic theories. These ignore ionic dispersion forces that change ionic adsorption.

We explored ion specificity in supercapacitors using a modified Poisson–Boltzmann approach that includes ionic dispersion energies. We have applied ab initio quantum chemical methods to determine required ion sizes and ion polarisabilities. Our model represents graphite electrodes through their optical dielectric spectra. The electrolyte was 1.2 M Li salt in propylene carbonate, using the common battery anions, PF_6^-, BF_4^- and ClO_4^-. We also investigated the perhalate series with BrO_4^- and IO_4^-.

The capacitance $C = d\sigma/d\psi$ was calculated from the predicted electrode surface charge σ of each electrode with potential ψ between electrodes. Compared to the purely electrostatic calculation, the capacitance of a positively charged graphite electrode was enhanced by more than 15%, with PF_6^- showing $> 50\%$ increase in capacitance. IO_4^- provided minimal enhancement. The enhancement is due to adsorption of both anions and cations, driven by ionic dispersion forces. The Hofmeister series in the single-electrode capacitance was $PF_6^- > BF_4^- > ClO_4^- > BrO_4^- > IO_4^-$. When the graphite electrode was negatively charged, the perhalates provided almost no enhancement of capacitance, while PF_6^- and BF_4^- decreased capacitance by about 15%.

Due to the asymmetric impact of nonelectrostatic ion interactions, the capacitances of positive and negative electrodes are not equal. The capacitance of a supercapacitor should therefore be reported as two values rather than one, similar to the matrix of mutual capacitances used in multielectrode devices.

1. Introduction

Supercapacitors have found a role in energy storage applications due their high capacitances (a measure of their ability to store energy), particularly in comparison to conventional dielectric capacitors [1,2]. In simple terms, a supercapacitor ("electric double layer" capacitor) is an electrolyte solution with mobile charge located between two electrodes. Mobile charge adsorbs to the electrodes due to physical (not chemical) interactions. The term "supercapacitor" may also extend to the class of so-called pseudocapacitors which involve electron transfer (chemical interaction) between electrode and electrolyte, similar to yet distinct from a battery [1,3], but here we focus on the electric double layer capacitor. A standard dielectric capacitor, by contrast, contains only a dielectric material between electrodes. The operation of the standard capacitor involves the polarization of otherwise immobile molecules, whereas the supercapacitor involves the movement of electrolytic ions to form an electric diffuse layer (adsorption layer) at the electrodes. The theory of supercapacitors therefore falls under the domain of the theory of interfaces and solutions, alongside colloid science.

In colloid and interface science, the nature of the ionic adsorption layer is often studied with the aid of the Poisson–Boltzmann model or through its simpler linearized cousin, the Debye–Hückel model. In this model, the equilibrium distribution profile $c_i(z)$ of the ith ion is taken as a Boltzmann distribution

$$c_i(z) = c_{i0} \exp[-\Delta\mu(z)/kT] \tag{1}$$

where $\Delta\mu(z)$ is the interaction energy pulling an ion toward or away from an electrode. Here c_{i0} is the bulk concentration of the ion, z is the distance from the electrode, k is Boltzmann's constant and T is the temperature. In the classic theory of electrolytes, only the electrostatic interaction of the ion with the electrostatic potential $\psi(z)$ is accounted for, such that $\Delta\mu(z) = q\psi(z)$, q being the electric charge of the ion. In this way, the ionic charge is the sole ionic property involved in the adsorption of the ion to the electrode. The behavior of

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different ions with the same valency, such as phosphorus hexafluoride PF_6^-, boron tetrafluoride BF_4^- or perchlorate ClO_4^-, are therefore indistinguishable at this level of theory. No ion specificity in the capacitance of such a supercapacitor is predicted.

But in other branches of colloid science, ion specific effects are routinely observed at sufficiently high electrolyte concentrations (typically above physiological concentrations exceeding 0.1 M, although low concentration ion specific phenomena have been observed [4]). The original observation of ion specificity was made by Franz Hofmeister in 1885, who studied the efficacy of salt at precipitating protein molecules from solution [5] and after whom ion specific effects have become known as Hofmeister effects. In more recent years ion specific effects have been reported [6] in pH measurement [7] and in the behavior of buffer ions [7,8], in enzyme activity [9,10] and the vitality of bacteria [11], the stability of air bubbles [12], electrophoretic mobilities [13] and surface charges of proteins [14] and, extending Hofmeister's own experiments, in the coagulation of proteins [15]. Ion specificity has been observed in the electrochemical properties of redox proteins [16] and ion selective electrodes [17].

Extensions to colloid and electrolyte theory have been put forward to explain the origin of specific ion effects [18,19]. In the language of the Poisson–Boltzmann model, additional nonelectrostatic ion interactions need to be added to $\Delta\mu(z)$, alongside the electrostatic interaction. The chief nonelectrostatic interaction is typically taken to be the quantum chemical van der Waals or dispersion energy of the ion, although others may also be considered [20]. The general impact of nonelectrostatic interactions is to increase or decrease the degree of ion adsorption beyond that expected from electrostatic interactions. This will always introduce a spread across different ions in the value of properties such as electrode capacitance. In extreme cases it may lead to reversal of the electric field due to superadsorption of anions to positively charged surfaces [21–25], which could result in a switch from attractive to repulsive interactions between the surfaces themselves [26].

But ion specific behavior in the context of energy storage (supercapacitors or batteries) has not been systematically studied by theory, although it has garnered some attention experimentally [27,28]. We consider the theoretical case here, using the tools recently developed, applying ion dispersion energies with dynamic polarisabilities and ion sizes calculated by ab initio quantum chemical methods [29,30].

We apply the theory to the calculation of the capacitance of single electrodes, leaving the study of coupled two-electrode systems for consideration elsewhere [31]. Calculations are conceptually performed for an open circuit with no current flow, where ion adsorption is permitted to follow the equilibrium Boltzmann profiles of Eq. (1). The calculations presented here model a supercapacitor in the sense that no charge transfer is considered between electrode and electrolyte solution. Similar ideas could be applied to the study of ion specificity in batteries or pseudocapacitors, but in that case the relationship between ion specific physisorption and energy of charge transfer would need to be carefully accounted for [32].

2. Modified Poisson–Boltzmann model with ion dispersion energies

Under the Poisson–Boltzmann description of the electrolyte, the electrostatic potential $\psi(z)$ may be governed by the Poisson equation for a flat surface,

$$\varepsilon_0\varepsilon_s\frac{d^2\psi}{dz^2} = -\sum_i q_i c_i(z) \tag{2}$$

ε_0 is the permittivity of a vacuum, ε_s is the permittivity (dielectric constant) of the electrolyte solvent. The equation in general is nonlinear due to the presence of the electrostatic potential in the ion profile $c_i(z)$, via Eq. (1).

Under Debye–Hückel linearization the electrolyte is characterized by the Debye length κ^{-1}, where $\kappa^2 = (q_e^2/\varepsilon_0\varepsilon_s kT)\sum_i n_i q_i^2$. The potential then takes the form $\psi(z) = \psi_0\exp(-\kappa z)$, where ψ_0 is the electrode potential, that is the potential difference, taking ground (zero) to be the potential in the electrolyte infinitely far from the electrode. The surface charge σ_0 (the number of electrons pushed away from the electrode due to the potential difference) is given by the electric field $E_0 = -d\psi/dz$ at the surface $(z = 0)$, $\sigma = -\varepsilon_0\varepsilon_s E_0 = \varepsilon_0\varepsilon_s\kappa\psi_0$.

The capacitance C is the ratio of electrode charge to electrode potential, or more precisely the rate of change of electrode surface charge as surface potential varies,

$$C = \frac{d\sigma_0}{d\psi_0} \tag{3}$$

It follows that the Debye–Hückel capacitance is predicted to be $C = \varepsilon_0\varepsilon_s\kappa$. Note, as discussed above, that no ion specificity enters into this estimate of the capacitance, beyond the electrolyte charges which contribute to the Debye length κ^{-1}.

We introduce ion specificity by adding the ionic dispersion energy $\mu_i^{disp}(z)$ alongside the electrostatic energy $\mu_i^{el}(z) = q_i\psi(z)$, and placing the total ion interaction energy

$$\Delta\mu(z) = \mu_i^{el}(z) + \mu_i^{disp}(z) \tag{4}$$

into the Boltzmann profile, Eq. (1). We adopt the dipolar dispersion energy of an polarisable ion [33,34] embedded in the solvent with finite size characterized by a Gaussian radius a_i, used in previous studies [35]. This model neglects the effect of higher order (quadrupole, octupole) dispersion energies [36] or the effect of the ion cavity separating ion from solvent [36,20]. The dispersion energy, then, is

$$\mu_i^{disp}(z) = \frac{B_i}{z^3}g(z) \tag{5}$$

where $g(z) = 1 + (2z/\sqrt{\pi}a_i)(2z^2/a_i^2 - 1)\exp\left[-z^2/a_i^2\right] - (1 + 4z^4/a_i^4)\mathrm{erfc}[z/a_i]$. The dispersion coefficient B_i is determined from the excess dynamic polarisability $\alpha_i^*(i\omega)$ of the ion in the electrolyte, modulated by the dielectric difference between electrode and solvent,

$$B = \frac{\mathrm{kT}}{2}{\sum_n}' \frac{\alpha_i^*(i\omega_n)\Delta(i\omega_n)}{\varepsilon_s(i\omega_n)} \tag{6}$$

with

$$\Delta(i\omega) = \frac{\varepsilon_s(i\omega) - \varepsilon_e(i\omega)}{\varepsilon_s(i\omega) + \varepsilon_e(i\omega)} \tag{7}$$

Summation is taken over the so-called Matsubara frequencies, $\omega_n = 2\pi nkT/\hbar$. The prime ($'$) next to the summation symbol ($\sum'$) in Eq. (6) means that the $n = 0$ term is taken with a factor 1/2. $\varepsilon_s(i\omega)$ and $\varepsilon_e(i\omega)$ are the dielectric functions of electrolyte solvent and electrode, respectively. The excess polarisability of the ion in solution is taken from the theory of a dielectric sphere with permittivity ε_i in a medium [29,37,38],

$$\alpha_i^*(i\omega) = \frac{3V_i}{4\pi}\frac{[\varepsilon_i(i\omega) - \varepsilon_s(i\omega)]}{[\varepsilon_i(i\omega) + 2\varepsilon_s(i\omega)]} \tag{8}$$

where $V_i = a_i^3\pi\sqrt{\pi}$ is the ionic volume [30]. For simplicity we describe the ionic permittivity via the simple relation $\varepsilon_i = 1 + 4\pi n_i\alpha_i = 1 + 4\pi\alpha_i(i\omega)/V_i$, where α_i is the polarisability of the ion in vacuum.

We apply this model to materials used in real supercapacitors and batteries [39,27,1,28], commonly graphite electrodes with lithium electrolytes at 1.2 M concentration in propylene carbonate