



# Asymmetric size of ions and orientational ordering of water dipoles in electric double layer model - an analytical mean-field approach



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## ABSTRACT

Electric double layer is theoretically described within the mean-field approach by taking into account the orientational ordering of water dipoles and asymmetric size of cations and anions. Analytical expressions for the spatial distribution of ions and water dipoles are derived. The effect of asymmetric ionic size on accumulation of counterions and partial depletion of water molecules near the charged surface, on spatial dependence of relative permittivity and on differential capacitance of electric double layer are presented.

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## 1. Introduction

Accumulation of counterions and depletion of coions in the vicinity of a charged surface in contact with an electrolyte solution results in a formation of electric double layer (EDL) [1–15]. Helmholtz initiated the investigation of EDL [16,17] followed by Gouy [18] and Chapman [19] who upgraded the model by considering Boltzmann spatial distribution of the counterions and coions in the Poisson's equation [1,20–22]. Later, Debye and Hückel generalized the Gouy-Chapman model [1,20].

Stern [23] was the first to include the finite size of ions in the EDL model by assuming the distance of closest approach of counterions to the charged surface [24,25]. A more sophisticated approach to take into account the finite size of ions in EDL was introduced by Bikerman [2] and followed by further advance studies [6,8,26–36]. EDL models were further improved by considering the orientational ordering of water dipoles resulting in prediction of local decrease of relative permittivity of electrolyte solution in the saturation regime close to the charged surface [37–39,12,14,15,24,40–44].

Recently, a mean-field model of EDL was developed by Gongadze and Iglič [45] (referred as in this paper as GI model) which encapsulates both, the excluded volume effect (finite size of ions) and orientational ordering of water dipoles, considered as point-like dipoles at the centres of the finite sized spheres with

permittivity equal to the square of optical refractive index of water. In the GI model, the different size of positively and negatively charged ions in EDL was not taken into account [45]. Therefore, in this paper the equations of GI model are generalised in order to incorporate the latter feature. The corresponding analytical expressions for ion spatial distribution functions are derived and included respectively into the Poisson's equation. The influence of different size of ions on the ion and water spatial distribution functions, on spatial dependence of relative permittivity and on differential capacitance for negative and positive voltage are presented and discussed.

## 2. Theory

### 2.1. Equal size of ions

By assuming that coions, counterions and water molecules occupy a single lattice site, the number density of water molecules ( $n_{0w}$ ), counterions ( $n_0$ ) and coions ( $n_0$ ) in the bulk electrolyte solution is constant. Therefore, the probability that a single lattice site in a bulk solution is occupied by one of the three kinds of particles (positive ions, negative ions and water molecules) in the electrolyte solution is:

$$\mathcal{P}_+(x \rightarrow \infty) = \mathcal{P}_-(x \rightarrow \infty) = \frac{n_0}{n_0 + n_0 + n_{0w}}, \quad (1)$$

$$\mathcal{P}_w(x \rightarrow \infty) = \frac{n_{0w}}{n_0 + n_0 + n_{0w}}, \quad (2)$$

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The corresponding number densities in a bulk solution are:

$$n_+(x \rightarrow \infty) = n_-(x \rightarrow \infty) = n_s \frac{n_0}{n_0 + n_0 + n_{0w}}, \quad (3)$$

$$n_w(x \rightarrow \infty) = n_s \frac{n_{0w}}{n_0 + n_0 + n_{0w}}, \quad (4)$$

where  $n_s$  is the number density of lattice sites:

$$n_s = 2n_0 + n_{0w}. \quad (5)$$

In the vicinity of the charged surface, the number density of ions and water molecules is influenced by the charged surface, so the probabilities that a single lattice site is occupied by a particle of one of the three kinds should be corrected by the corresponding Boltzmann factors, leading to ion and water dipole distribution functions in the form [14,45]:

$$n_+(x) = n_s \frac{n_0 e^{-e_0 \phi \beta}}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (6)$$

$$n_-(x) = n_s \frac{n_0 e^{e_0 \phi \beta}}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (7)$$

$$n_w(x) = n_s \frac{n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (8)$$

where  $\beta = 1/kT$ ,  $kT$  is the thermal energy,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $e_0$  is the unit charge and  $\phi$  is the electric potential. Further

$$\begin{aligned} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega &= \frac{2\pi \int_0^\pi d(\cos \omega) e^{-\gamma p_0 E \beta \cos(\omega)}}{4\pi} \\ &= \frac{\sinh(\gamma p_0 E \beta)}{\gamma p_0 E \beta}. \end{aligned} \quad (9)$$

is the water dipole Boltzmann factor after rotational averaging over all possible angles  $\omega$  [14,45,5]. The angle  $\omega$  is the angle between the gradient of the electric potential and the vector of the water dipole moment [14,45]. Here  $p_0$  is the magnitude of the external water dipole moment,  $E$  is the magnitude of electric field strength. In the model, a single water molecule is considered as a finite sized sphere with permittivity  $n^2$  and a point-like rigid (permanent) dipole/quadrupole at the centre of the sphere, where  $n$  is the optical refractive index of water [14,45]. Hence, the cavity field and the electronic polarisability of water molecules are taken into account [46], while the short range interactions between water molecules are neglected. Accordingly, the value of the constant  $\gamma$  is given by [45,14]:

$$\gamma = \frac{3}{2} \left( \frac{2+n^2}{3} \right). \quad (10)$$

## 2.2. Different size of ions

Consider now a case where negative and positively charged ions occupy more than one lattice site, while a single water molecules still occupy just one lattice site. In the following,  $\alpha_+$  and  $\alpha_-$  are the number of lattice sites occupied by a single positive and negative ion, respectively. The probabilities that a single lattice site in the bulk solution is occupied by one of the three kind of particles in electrolyte solution (positive ion, negative ion and water molecule) are then:

$$P_+(x \rightarrow \infty) = \frac{\alpha_+ n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (11)$$

$$P_-(x \rightarrow \infty) = \frac{\alpha_- n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (12)$$

$$P_w(x \rightarrow \infty) = \frac{n_{0w}}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (13)$$

while the corresponding number densities in bulk are

$$n_+(x \rightarrow \infty) = \left( \frac{n_s}{\alpha_+} \right) \frac{\alpha_+ n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (14)$$

$$n_-(x \rightarrow \infty) = \left( \frac{n_s}{\alpha_-} \right) \frac{\alpha_- n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (15)$$

$$n_w(x \rightarrow \infty) = n_s \frac{n_{0w}}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (16)$$

where  $n_s$  is the number density of lattice sites:

$$n_s = \alpha_+ n_0 + \alpha_- n_0 + n_{0w}. \quad (17)$$

Similarly as in [14,45], in the vicinity of the charged surface, the number densities of ions and water molecules are corrected by the corresponding Boltzmann factors:

$$n_+(x) = n_s \frac{n_0 e^{-e_0 \phi \beta}}{\alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (18)$$

$$n_-(x) = n_s \frac{n_0 e^{e_0 \phi \beta}}{\alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (19)$$

$$n_w(x) = n_s \frac{n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}{\alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}. \quad (20)$$

Taking into account Eq. (9), we can rewrite Eqs. (18)–(20) as:

$$n_+(x) = n_0 e^{-e_0 \phi \beta} \frac{n_s}{\mathcal{D}(\phi, E)}, \quad (21)$$

$$n_-(x) = n_0 e^{e_0 \phi \beta} \frac{n_s}{\mathcal{D}(\phi, E)}, \quad (22)$$

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{D}(\phi, E)} \frac{\sinh(\gamma p_0 E \beta)}{\gamma p_0 E \beta}. \quad (23)$$

where:

$$\mathcal{D}(\phi, E) = \alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + \frac{n_{0w}}{\gamma p_0 E \beta} \sinh(\gamma p_0 E \beta). \quad (24)$$

The magnitude of the polarisation in the vicinity of the negatively charged surface is given by [14,43,45]:\*

$$P(x) = n_w(x) \left( \frac{2+n^2}{3} \right) p_0 \mathcal{L}(\gamma p_0 E \beta). \quad (25)$$

Combining Eq. (23) and Eq. (25) gives the polarization in the form:

$$P(x) = p_0 n_{0w} n_s \left( \frac{2+n^2}{3} \right) \frac{\mathcal{F}(\gamma p_0 E \beta)}{\mathcal{D}(\phi, E)}, \quad (26)$$

where the function  $\mathcal{F}(u)$  is defined as:  $\mathcal{F}(u) = \mathcal{L}(u)(\sinh u/u)$ . Combining  $\varepsilon_r(x) = n^2 + P/\varepsilon_0 E$  and Eq. (26) yields the relative (effective) permittivity:

$$\varepsilon_r(x) = n^2 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \left( \frac{2+n^2}{3} \right) \frac{\mathcal{F}(\gamma p_0 E \beta)}{\mathcal{D}(\phi, E) E}. \quad (27)$$

In the limit of vanishing electric field strength ( $E \rightarrow 0$ ) and zero potential ( $\phi \rightarrow 0$ ), the above derived expression for relative permittivity (Eq. (27)) gives the Onsager expression for permittivity [47].

Using the above expression for  $\varepsilon_r(x)$ , we can rewrite the Poisson's equation into the form of:

$$\frac{d}{dx} \varepsilon_0 \varepsilon_r(x) \frac{d\phi}{dx} = 2 e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{\mathcal{D}(\phi, E)}, \quad (28)$$

\* $\mathcal{L}(u)$  is Langevin function

where the macroscopic (net) volume charge density of co-ions and counterions  $\rho_{free}(x)$  (Eq. (21) and Eq. (22)) [45] was taken into account:

$$\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2 e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{\mathcal{D}(\phi, E)}. \quad (29)$$

The boundary condition at  $x=0$  is:

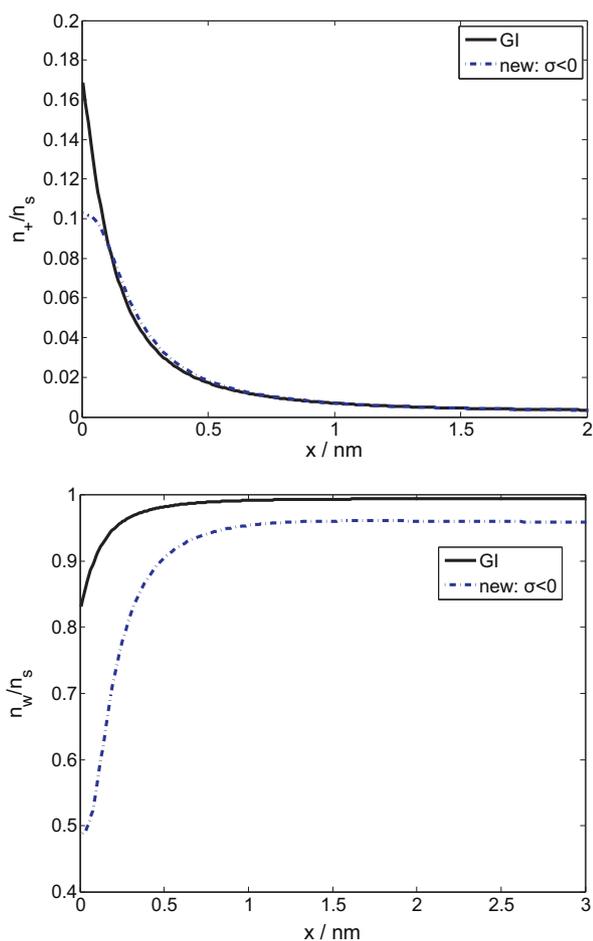
$$\frac{d\phi}{dx}(x=0) = -\frac{\sigma}{\varepsilon_0 \varepsilon_r(x=0)}, \quad (30)$$

where  $\varepsilon_r(x)$  is defined by Eq. (27).

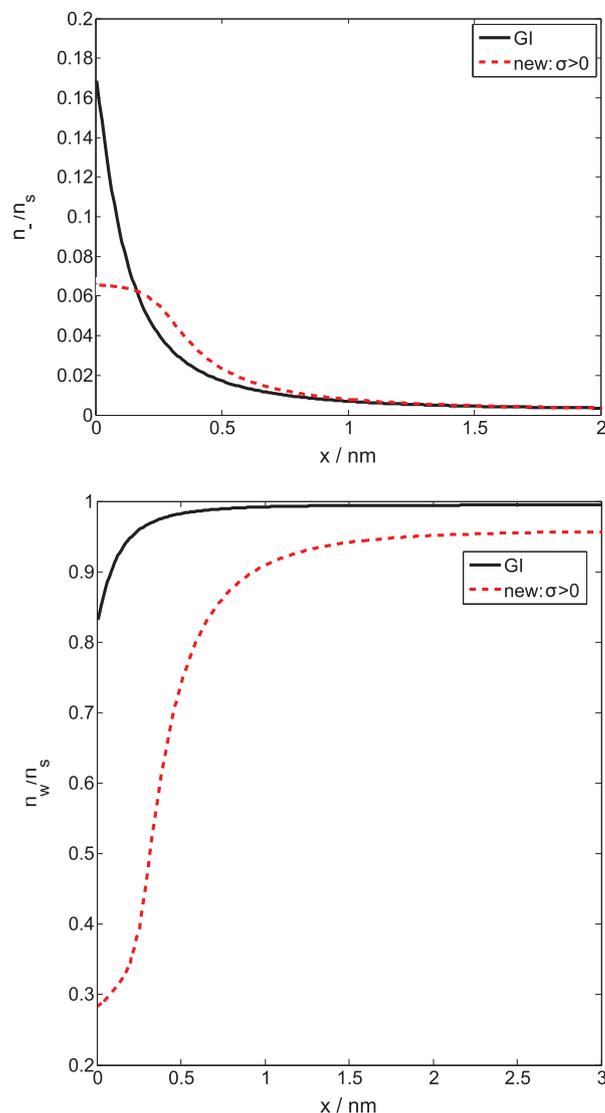
### 3. Results and Discussion

The derived differential equation for spatial distribution of electric potential  $\phi(x)$  (Eq. (28)) was solved numerically using Comsol Multiphysics 5.0 by using the boundary condition Eq. (30) at  $x=0$ .

Fig. 1 shows the spatial dependence of the number density of positive ions ( $n_+$ ) and water dipoles ( $n_w$ ) at a negatively charged surface. It can be seen that due to the negative surface charge density  $\sigma$ , the negative ions of the electrolyte solution are nearly completely depleted from the region near the charged surface, while the positively charged ions are accumulated in this region



**Fig. 1.** The relative number density of positive ions ( $n_+/n_s$ ) (upper panel) and water dipoles ( $n_w/n_s$ ) (lower panel) as a function of the distance from a planar charged surface  $x$  calculated for bulk concentration of ions  $n_0/N_A = 0.1$  mol/l and negative surface charge density  $\sigma = -0.2$  As/m<sup>2</sup> within GI model (full lines) and modified GI model presented in this work (dotted dashed lines). The values of the parameters used are:  $\alpha_- = 11$ ,  $\alpha_+ = 5$ , dipole moment of water  $p_0 = 3.1$  D, optical refractive index  $n = 1.33$ , bulk concentration of water  $n_{ow}/N_A = 55$  mol/l, where  $N_A$  is the Avogadro number.

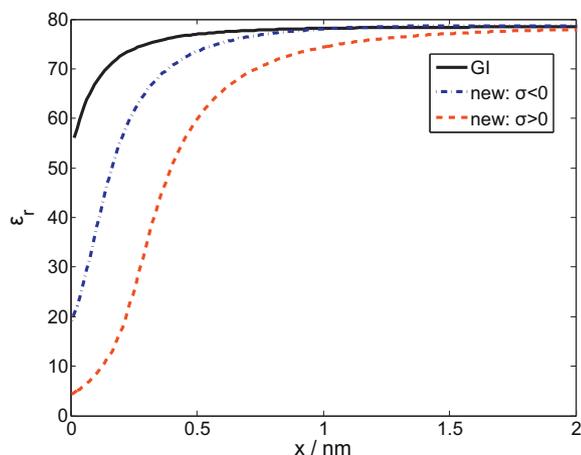


**Fig. 2.** The relative number density of negative ions ( $n_-/n_s$ ) (upper panel) and water dipoles ( $n_w/n_s$ ) (lower panel) as a function of the distance from the planar charged surface ( $x$ ) calculated for the bulk concentration of ions  $n_0/N_A = 0.1$  mol/l and positive surface charge density  $\sigma = 0.2$  As/m<sup>2</sup> within GI model (full lines) and modified GI model (dotted dashed lines). The values of the parameters used here are the same as in Fig. 1.

(Fig. 1). Therefore  $\alpha_+ n_+(x=0) + n_w(x=0) \cong n_s$  as it can be seen in Fig. 1.

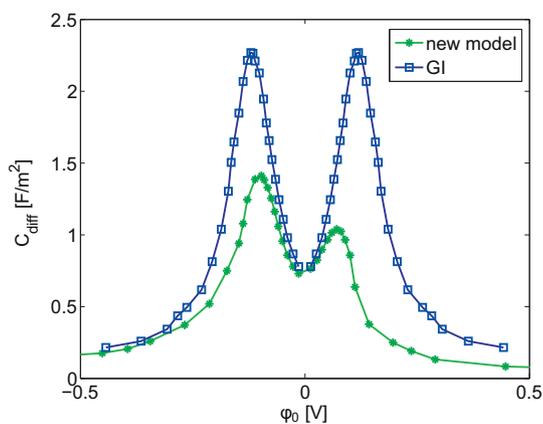
In contrast to the negatively charged surface (Fig. 1), in the vicinity of the positively charged surface, the negative ions are accumulated and positive ions are completely depleted (Fig. 2). Therefore, in this case  $\alpha_- n_-(x=0) + n_w(x=0) \cong n_s$ .

A comparison of the results shows that the number density of the positive ions near the negatively charged surface ( $n_+(x=0)$  in Fig. 1) is larger than the number density of the negative ions near the positively charged surface ( $n_-(x=0)$  in Fig. 2) which can be explained by the larger size of the anions (i.e.  $\alpha_- > \alpha_+$ ). Further, since the anions ( $\alpha_- = 11$ ) are larger than cations ( $\alpha_+ = 5$ ), the number density of water  $n_w(x=0)$  at the negatively charged surface (where cations are accumulated) (Fig. 1) is still larger than the number density of water  $n_w(x=0)$  at the positively charged surface with accumulated anions of electrolyte solution (Fig. 2). In consequence, the relative permittivity near the charged surface within the modified GI model (presented in this work) is smaller for  $\sigma > 0$  than for  $\sigma < 0$  as presented in Fig. 3.



**Fig. 3.** Relative permittivity  $\epsilon_r(x)$  as a function of the distance from the charged surfaces at  $x=0$  calculated for GI model ( $\sigma = -0.2 \text{ As/m}^2$ ) (full line) and within modified GI model for  $\sigma = -0.2 \text{ As/m}^2$  (dotted-dashed line) and  $\sigma = 0.2 \text{ As/m}^2$  (dashed line). The values of the other model parameters are the same as in Fig. 1.

It has been shown that the calculated differential capacitance of the EDL within GC model monotonously increases as a function of the increasing surface potential, while in Bikerman [10,12,48] and GI models [14] starts to decrease after reaching a maximal value, as shown in Fig. 4. For higher values of the surface potential, the calculated GI differential capacitance drops below the corresponding Bikerman values to very small values [14] in accordance with the experimental results [49,50]. As presented in Fig. 4, the differential capacitance decreases even more within the modified GI model. As expected, consideration of different sizes of positive and negative ions within modified GI model may describe some characteristics of the experimentally observed asymmetric camel-like dependence of differential capacitance on surface potential/voltage [49–51]. The latter was already studied within an approximate approach for small volume shares of ions everywhere in the electrolyte solution, where the number densities of ions and water molecules were obtained implicitly [52]. In contrast, here the number densities of ions and water molecules are given explicitly by analytic expressions (Eqs. (21)–(23)). Furthermore, the assumption of small volume shares of ions everywhere in the electrolyte solution was not applied here because for larger magnitudes of surface charge density, the volume share of counterions near the charged surface is in general not small.



**Fig. 4.** Differential capacitance as a function of the surface potential  $\phi_0$  calculated within GI and modified GI model for bulk concentration of ions  $n_0/N_A = 0.1 \text{ mol/l}$ . The values of other model parameters are given in Fig. 1.

Further generalisation of the modified GI given in this paper model should include also the Helmholtz/Stern layer taking into account unequal distances of closest approach for cations and anions ions [25,53–55]. This modification would change the relative height for both maxima of the differential capacitance camel-like curve [25] and also move them to higher magnitudes of the potential/voltage [25,56].

#### 4. Conclusion

In this work, the asymmetric size of cations and anions in the electric double layer are described within a mean-field approach and lattice statistics as a generalisation of our previous published GI model [45], which takes into account spatial dependence of relative permittivity due to orientational ordering of water dipoles in saturation regime and partial depletion of water near the charged surface [14]. Within the presented modified GI model, we derived analytical expressions for the spatial distribution of ions and water dipoles in the electric double layer. As illustration, it is shown that the sign of the surface charge of the planar charged surface influences partial depletion of water molecules and local decrease of relative permittivity near the charged surface. The influence of size asymmetry of cations and anions in electrolyte solution on differential capacitance of EDL is also investigated.

For real systems our model can be applied to biological systems where the cell and liposome membranes are in contact with electrolyte solution, usually with predominant sodium cations and chloride anions [3–5,21]. The model can be also used to study the cell membrane interactions with different biomaterials/implants or interaction of cells with inorganic nanoparticles and nanostructured surfaces [14]. In colloid science [22] and electrochemistry [1,24], the presented model can be used in the studies of electrode/ionic liquids interface, as for example in calculation of differential capacitance [24,10,12,48,14,52] (Fig. 4) where the metallic or semiconductor electrodes are in contact with different kind of electrolytes having asymmetric size of ions [51]. Recently, hybrid nanoporous semiconductor electrodes [57], covered by organic materials, are gaining more and more interest, as for example in construction of supercapacitors [58].

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