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## Preface

# Two tributaries of the electrical double layer

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This special issue of *Journal of Physics: Condensed Matter* focuses on physical aspects of capacitive energy storage and harvesting devices based on electrical double layers. An electrical double layer (EDL) is an interfacial structure in which charges are separated between two neighboring phases or layers. Originally introduced by Helmholtz in 1850, the concept of EDLs has found numerous applications in various areas. Perhaps two of the fastest growing areas are the capacitive energy storage and energy harvesting. This special issue covers a wide range of topics in these areas, ranging from solving fundamental problems to proposing specific working devices.

**Electrical double layer capacitors** (i.e., capacitive energy storage systems based on EDLs) were first developed in the labs of General Electric (late 1950s) and Standard Oil of Ohio (1960s). However unusual it may sound, they were abandoned as unusable, but luckily reborn by the NEC Corporation who marketed them as 'supercapacitors' in 1978. Supercapacitors consist of porous electrodes immersed in an electrolyte medium and store energy in the EDLs at the electrode/electrolyte interfaces [1, 2]. As a result of this simple setup that typically involves no chemical reaction, supercapacitors are distinguished by high power densities and unusual cyclability (reaching more than 1000 000 cycles), but have only moderate energy densities. Largely for the latter reason, supercapacitors did not play an important role in the mainstream energy storage applications historically. However, recent breakthroughs [3, 4] in developing novel electrode materials and room-temperature ionic liquids (ILs) have given a new life to supercapacitors, which now complement and in some cases even compete with the conventional energy storage devices such as batteries. Indeed, the market of then-abandoned supercapacitors was worth about $1.8 billion in 2014 and was estimated to show a year-on-year growth rate of about 9.2% according to some sources [5].

Works on supercapacitors appear now in a wide spectrum of journals covering chemical, material, energy, nanotechnology and applied physics sciences (for the latest review see e.g. [6]). In this special issue we attempted to collect papers focusing specifically on the physical aspects of the supercapacitor research, in all their complexity and depth, highlighting new challenges and yet unresolved problems. A distinct focus is however on electrolytes and electrolyte-electrode interactions. Why is this important? The energy stored in a supercapacitor is roughly $CV^2/2$, where $C$ is capacitance and $V$ the applied voltage. Now, by increasing the voltage from 1V (electrochemical window of a typical aqueous electrolyte) to 3V or more (room-temperature ionic liquids), we increase the stored energy almost by an order of magnitude! On the other hand, it has recently become clear that adding an aqueous or organic component to room-temperature ILs reduces their viscosity and can dramatically accelerate charging [7]. However, this comes at a cost of the decreased stored energy because solvent can narrow the electrochemical window of an electrolyte. A sound understanding of the fundamental mechanisms of electrode-electrolyte interactions is thus needed to enable a significant leap in the performance of supercapacitors. This is where the physics can help improve supercapacitors as is the goal of many works including this special issue.

A brief read-map is provided below to navigate the readers through this special issue. We start from the works by Docampo-Álvarez *et al* [8] and Vatamanu *et al* [9] who approach the discussed problems by using atomistic molecular dynamics simulations. Docampo-Álvarez *et al* deals specifically with the behaviour of water-IL mixtures in charged nanopores, while Vatamanu *et al* focus on the effects due to polar organic solvents (*viz.* acetonitrile). Both studies conclude that the presence of solvent can have a profound and sometimes unexpected effect on charging. For instance, confinement increases the amount of water in the positively charged electrode, but a decrease is observed on neutral and negatively charge surfaces [8]. Such effects must be accounted for when designing supercapacitors and choosing an optimal voltage regime.

The experimental study of Ohkubo *et al* [10] deals with the hydration structures of calcium ions in non-polarized nanopores. They find that calcium ion-assisted adsorption of water falls off significantly when the pores become narrow (0.63 nm). This finding therefore

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supports an earlier idea of using ultranarrow pores, which are known to give anomalously high capacitances [11, 12].

The work of Zhan and Jiang [13] is based on a novel density functional method and investigates what happens when redox reactions are allowed between aqueous electrolytes and electrode surfaces. An interesting aspect of this work is that it determines when the pseudocapacitance (that is the capacitance due to adsorption of hydrogen) is higher than the capacitance of the EDL.

The simulation work of Li *et al* [14] focuses on the asymmetry of divalent cations (*viz*. having different charge head groups) and studies how it influences the properties of the EDLs. This work is motivated by the idea of using divalent ionic liquids to increase the energy storage ability of EDLs. The work concludes that despite some significant differences in the molecular structure, the EDL capacitance is practically unaltered. This result may help design electrolytes that provide high ion diffusivity and hence power density, without compromising the energy storage.

To be able to effectively model supercapacitors, efficient and fast numerical approaches must be developed. The work by Wang *et al* [15] adds to the methods for modeling polarizable electrodes. These authors propose a 'probe-and-average' technique for calculating the electrostatic potential from molecular dynamics simulations, and stress anew [16] the importance of using the constant-potential rather than constant-charge approach to model electrodes in molecular simulations.

Finally, Dudka *et al* [17] develop an exactly solvable model of ILs in metallic slit nanopores. They predict ordered and disordered states of ILs, depending on the pore ionophobicity, and elaborate on the structure an IL can adopt in a strong nano-confinement. This is important to understand in order to be able to prepare an IL in the disordered state, which can potentially increase ion diffusivity and thus accelerate charging [18]. Although the work by Dudka *et al* [17] does not describe the system's response to the applied voltage, it presents a sophisticated analysis of the phase diagram in the non-polarized state and sets the basis for future studies of the capacitive behaviour within their model.

**Capacitive energy harvesting devices** do not store energy but convert mechanical work into electrical energy. The mechanism is again based on the EDL. Such devices typically contain flexible, expandable electrodes so that by applying a mechanical force we can physically push the counterions into the EDLs, thus creating an electrical current to or from the electrode, which can be harvested and stored or used. For instance, Brogioli's device makes use of water with different salinities, whereby the current between two porous EDL electrodes is generated by mechanically replacing the salty sea water with the fresh water (little salt) [19], while Krupenkin's device utilizes the mechanical pressure oscillations in the sole of a shoe caused by walking and converts them into AC currents [20, 21].

This special issue only touches on these ideas. Thus, Lian *et al* [22] study the capacitive mixing technique for energy extraction, which is based on the cyclic expansion of EDLs to harvest dissipative energy due to the salinity differences between fresh and seawater. The authors establish optimal operation parameters for capacitive energy extraction with porous electrodes of different surface hydrophobicity.

The theoretical work of Kolomeisky and Kornyshev [23] explores an idea similar to Krupenkin's device and proposes a novel scenario for mechanical energy harvesting in an 'electrical shoe' with a porous sole. The energy generated by such a shoe when walking can be continuously fed to electronic devices, such as mobile phones, resolving the 'I forgot to charge my phone' and similar problems once and for good.

Last but not least, we would like to thank all scientists who have kindly agreed to contribute and presented their latest results in this special issue. We also thank the staff of *Journal of Physics: Condensed Matter* for their help and professionalism. The literature in this rapidly developing area is vast and grows with an average of a few papers appearing in material and electrochemical, nano and applied sciences journals daily. This modest collection of papers should give a flavour of some of the physics-related directions of the research. As such it may be useful for readers who are experienced researchers in the field and interesting for those who just started being fascinated by the multiple worlds of the electrical double layers.

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