# DFT for designing efficient supercapacitor electrode materials

Josef MacDouall once said "*Chemistry is a game that electrons play*". If one were able to know the roles, they could control the game and uncover the mysteries of materials, which are the backbone of our modern civilization. To this end, energy storage platforms are the bottle-neck hindering the efficient use of electronic devices. However, the reports so far are based on *guess and check* selection of electrode materials and electrolytes, while the use of materials design and material-electrolyte interface design are not widely used. The limited use of computational prediction in designing materials for supercapacitor devices could be due to the wide variety of computational tools that makes it hard to choose the right method for the right material in each case. Herein, a thorough analysis of the available literature is provided and used to propose a road map for researchers to guide them to select the best DFT descriptors to screen materials for use as supercapacitor electrodes.

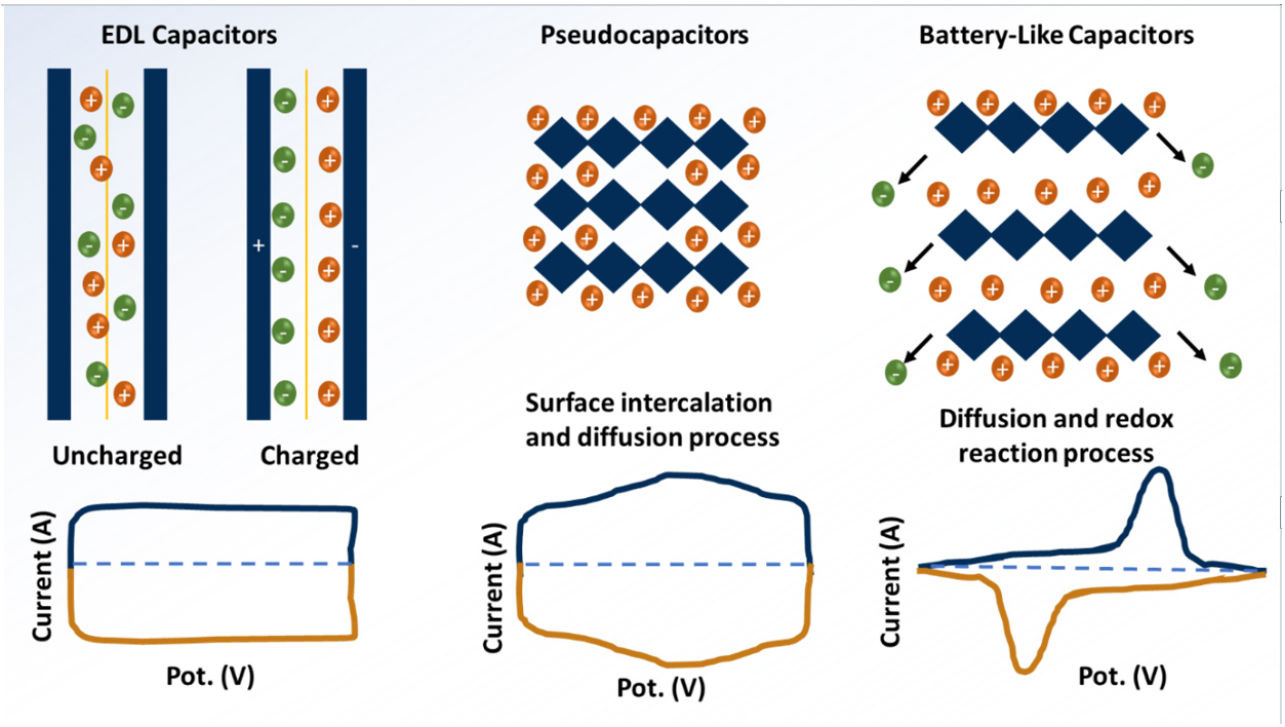


Fig. 1. Various charge storage mechanisms of supercapacitor electrodes.

Materials store electrical charges via different storage mechanisms as illustrated in Figure 1. The electrostatic attraction between the charged surface of a material and the electrolyte ions is called electrical double layer (EDL) capacitance. EDL capacitance depends on the surface area, pore size, the electrolyte ionic size, the mobility of the electrolyte ions and the material/electrolyte

interface resistance. However, if the material exhibits a faradic behavior such as the diffusion of electrolyte ions in/out of the material in terms of fast intercalation or surface redox reaction, this will result in *pseudocapacitance*. The third charge storage mechanism is known as *battery-like* in which the electrode material undergoes a faradic process in terms of redox reaction(s). The reversibility and the nature of the redox reaction in the battery-like materials will give insights on the cycling stability of the electrode material. Moreover, hybrid materials (faradic and non-faradic) have also been investigated to design better electrodes.

Some properties do not need a deep electronic consideration to calculate and it is enough to treat the system classically to obtain accurate results. cDFT is considered an analog to the eDFT and can be successfully applied to classical systems. The cDFT can be used in predicting the characteristics of porous structures. Evans et. al. illustrated a cDFT-based model to predict the porous structure characteristics from theoretical adsorption isotherms, where specific surface area, pore volume, pore size, and pore size distribution can be estimated from adsorption fitting. There are two main approximations used to calculate the theoretical isotherm, the non-local DFT (NLDFT) and the quenched solid DFT (QSDFT). The NLDFT usually overestimates the pore volume and specific surface area in comparison with the QSDFT and the experimental results. Also, the cDFT can be used in predicting the characteristics of electrode/electrolyte interface. Coarse-Grained Classical DFT (CGDFT) is a good model that considers ions in the electrolyte as charged hard spheres and the solvent molecules as hard sphere dimers. The EDL capacitance can be calculated as the derivative of the surface charge density in terms of surface potentials. CGDFT can be used to provide insights on the dependence of EDL capacitance on the pore size.

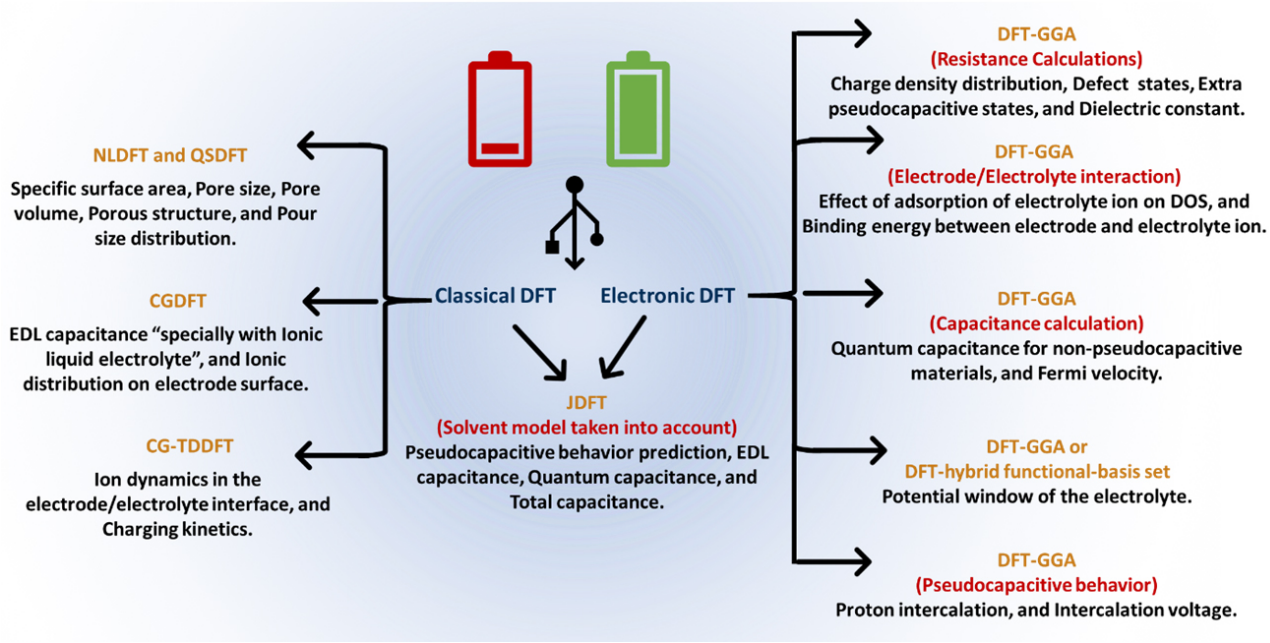


Fig. 2. Roadmap to the use of DFT to choose the supercapacitor electrode material.

The electronic DFT (eDFT) can also give information that helps hosing the best electrode material. eDFT can estimated the bandgap of the material that gives insights on the resistance of the semiconductors. Moreover, the eDFT can predict the binding energy of ions at electrode surface. Besides, DFT can accurately predict the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO represents the anodic limit and the ionization energy of the molecule while the LUMO represents the cathodic limit and the electron affinity of the molecule. One of the most important properties that can be predicted using DFT is the quantum capacitance. Quantum capacitance represents the contribution of the electrode material to the capacitance of the Helmholtz layer at the EDL interface resulting from the electronic response of the electrode. Finally, Joint DFT (JDFT) can combine both classical and electronic DFT to predict the overall performance of the supercapacitor electrode material. Figure 2 presents a roadmap to the use of different DFT routs for prediction of the properties of the electrode materials.

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## Publication

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