

# Molecular Modeling of Carbon-Based Electrochemical Double Layer Capacitors

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## ABSTRACT

Electrochemical double layer capacitors (EDLCs) are energy storage elements, which are ideally suited for applications that require high power density and a long life cycle. Molecular modeling can be leveraged to gain crucial information of the storage processes in EDLCs for improving and tuning the performance. We present computational studies on carbon-based EDLCs showing how morphologically realistic structures of the carbon electrode can be modeled efficiently. A detailed analysis of the structural properties and a comparison with experimental data will be provided. In addition, the influence of structural modifications and local environment on electrode-electrolyte interactions has been examined. Our findings indicate that the interaction between electrolyte molecules and electrode material can be linked to the performance of carbon-based EDLCs and represents thus a valuable descriptor for virtual screening experiments geared to optimizing EDLC-based energy storage systems.

**Keywords:** Nanoporous material, carbon electrode, electrode-electrolyte interaction, electrochemical double layer capacitor, molecular modeling

## 1 INTRODUCTION

Industrial needs and technological progress in modern everyday life cause an increasing demand in energy. Due to the limited availability of fossil fuels, alternative concepts have to be developed to guarantee energy supply in a sustainable fashion. Renewable energy sources like solar energy or wind power usually require efficient energy storage systems because of natural fluctuations. Depending on the application, various technologies have been developed. Electrochemical double layer capacitors (EDLCs), called supercapacitors, are powerful energy storage devices that offer some distinct advantages: EDLCs possess a high power density and allow highly reversible charging and discharging within seconds up to a million times [1,2]. Typical technical applications of EDLCs are in consumer electronics or in backup power supplies. They are also used to smooth voltage fluctuations in energy grids or in hybrid vehicles as peak-load enhancer. EDLCs consist of two electrodes separated by an ion-permeable membrane immersed in an organic or inorganic electrolyte. The

performance of the EDLCs depends on the combination of electrode material and electrolyte. For the formation of the double layer, it is desirable that the electrode has a high surface area. Carbide-derived carbon (CDC) offers this feature in an exceedingly advantageous way, since the pore size can be tuned through synthesis conditions. This allows adjusting the porosity to the size of the electrolyte ions, which need to penetrate the pores to form the double layer [2]. Much work has been dedicated to study these systems and to gain insights on the charging process [e.g. 1-4 and references therein]. Characterizing such complex processes at the molecular level is, however, still challenging, but essential for improving the performance and overcoming existing limitations of such devices. In order to broaden the understanding and to provide critical insights on the relevant processes at the nanoscale, molecular modeling is ideally suited. In the following sections, we will present a simulation strategy that allows to model morphologically realistic structures of CDC-based electrode materials. Based on this, studies on the electrode-electrolyte interface in the electric field will be presented. In addition, we will demonstrate a systematic approach to investigate electrode-electrolyte interactions and discuss the influence of the local environment and surface functionalization of the electrode material on the interaction between electrolyte and electrode.

## 2 RESULTS AND DISCUSSION

### 2.1 Modeling carbide-derived carbon

In order to model porous carbide, a pseudo-mimetic approach has been pursued inspired by the experimental procedure for creating CDCs. Experimentally, carbides are treated with halogens, e.g.  $\text{Cl}_2$ , to remove the metal or metalloid from the carbon matrix. Therefore, we used the crystal structure of SiC as starting point and built a suitable large supercell. SiC is a commonly used precursor of carbide-derived carbon. As it exists in different polytypes, we have performed simulations for the three most important polytypes 4H-SiC, 6H-SiC, and 3C-SiC. A set of molecular dynamics simulations was performed to model a nanoporous carbon structure as described in the Computational Details section. The final structures have been analyzed with respect to the maximum pore size, hybridization, and ring size distribution.

The diameter of the largest pores ranges between 8.9 and 12.7 Å, which agrees reasonably well with experimental results ranging between 5-20 Å [2]. For evaluating the hybridization, the number of adjacent atoms and the local geometry were analyzed. Based on this, a hybridization of 54-85%  $sp^2$  and 15-49%  $sp^3$  was obtained. The results agree well with literature data [5]. The ring size analysis revealed that the majority of carbon atoms (57-67%) form 6-membered rings, 32-39% is part of 7-membered rings, and only 1-6% belong to 5-membered rings. Rather uniform results were obtained for the different polytypes as well as different simulation setups. Only for one setup (setup D, see Computational Details section) slightly different results were obtained.

In addition to the structural analysis, we have simulated absorption isotherms. Since experimental elemental analysis indicated the presence of oxygen, we have generated partially oxidized structures containing 2 and 5 % oxygen, respectively. The simulated absorption isotherms are compared with experimental data in Figure 1.

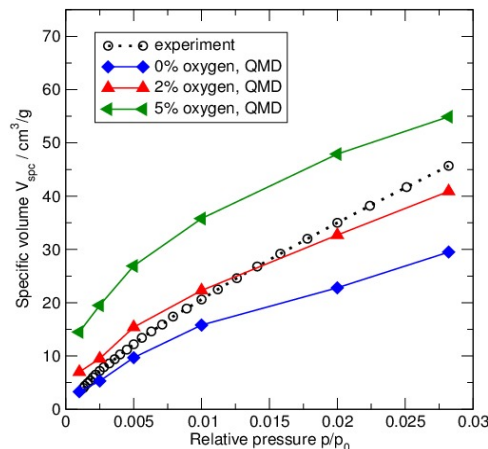


Figure 1: Simulated and experimental  $CO_2$  absorption isotherm. Experimental data were kindly provided by the group of Prof. B. Etzold (TU Darmstadt, Germany).

It should be noted that the experimental isotherm refers to TiC which is expected to behave similar to SiC. The simulated isotherms are in the same range as the experimental one. The best agreement is obtained for the carbon matrix containing 2 % oxygen.

Overall, the analysis of the porous carbon models shows a good agreement with experimental data and can be regarded as a reasonable basis for further simulations.

## 2.2 Modeling electrode-electrolyte interface

In order to analyze the diffusion of electrolyte into the porous electrode, we performed MD simulations of the electrode-electrolyte interface. The interface consisted of the porous carbon and an electrolyte layer containing acetonitrile (ACN) as solvent with tetraethylammonium (TEA) and tetrafluoroborate ( $BF_4$ ) as electrolyte salt. The equilibrated structure is shown in Figure 2. MD simulations

with an external electric field of 0.25 and 0.5 V were performed based on the equilibrated structure. The analysis of the trajectories showed that the diffusion coefficients decrease in the order  $ACN > BF_4 > TEA$  which is consistent with the increasing size of the molecules. For all species, the diffusion coefficients increase with increasing field strength, which is in line with the density profiles showing that more ions diffuse deeper into the porous carbon material with increasing electric field.

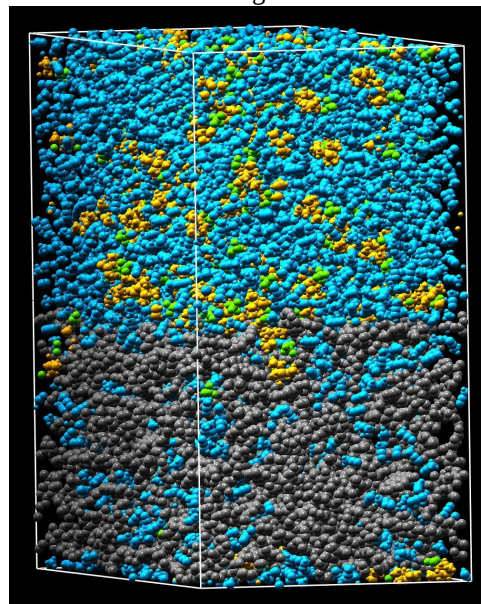


Figure 2: Equilibrated electrode-electrolyte interface. Color code: C – gray, ACN – blue, TEA – yellow,  $BF_4$  – green.

## 2.3 Modeling electrode-electrolyte interaction

For investigating the interaction between electrolyte and electrode, electronic structure simulations were carried out using density functional theory (DFT).

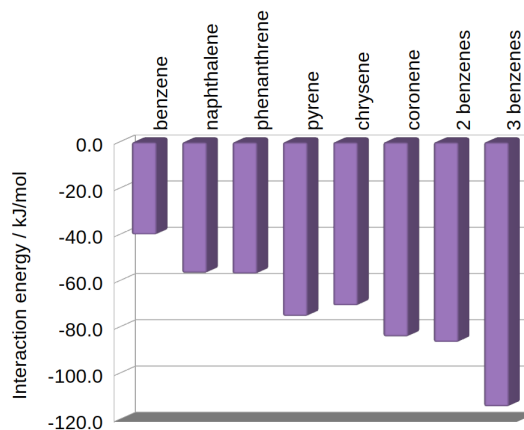


Figure 3: Interaction energies between TEA/ $BF_4$  and hydrocarbons.

For this purpose, model systems were created which were systematically modified in order to study different aspects of the electrode-electrolyte interaction. Special emphasis was put on the local environment, the influence of surface functional groups, and on the pore size. Three sets of model systems were created: (a) hydrocarbons with TEA/BF<sub>4</sub>, (b) naphthalene and indole derivatives with TEA/BF<sub>4</sub>, and (c) carbon nanotubes (CNT) with TEA/BF<sub>4</sub>. Interaction energies between -40 and -114 kJ/mol between the ion pair and hydrocarbons were obtained, while interaction energies with functionalized naphthalene and indole derivatives range between -48 and 159 kJ/mol. Results for set (a) and (b) are illustrated in Figure 3 and 4.

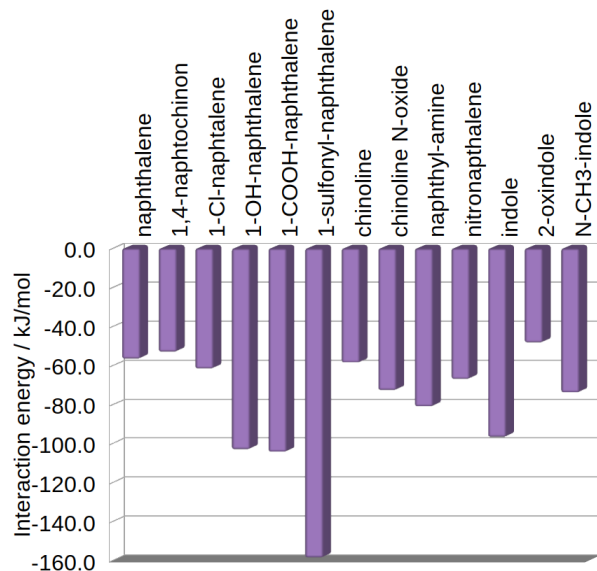


Figure 4: Interaction energies between TEA/BF<sub>4</sub> and naphthalene and indole derivatives.

Functional groups, which allow for hydrogen bonding have the potential to strongly bind the ion pair. This implies that the mobility at the interface can be reduced due to stronger interactions. However, when ions are kept near the surface, the concentration in the bulk electrolyte reduces which in turn increases the mobility through the pore. In addition, we have calculated interaction energies separately for cations and anions. While there is only minor influence of surface functionalization on the interaction with cations, the impact on anions is more pronounced.

For the carbon nanotubes, either the anion or the cation was placed inside the CNT. The diameter of the CNT was systematically varied between 7 and 14 Å. Interaction energies as a function of the pore size are illustrated in Figure 5. The strongest interaction is observed for different diameters, due to the different size of anion and cation. We have compared the interaction energies with experimentally determined capacitances for the cation. The interaction energies show the same trend as the measured capacitances. In addition to pristine CNTs, functional groups (-SOH<sub>3</sub> and

-COOH) were introduced inside the CNT. The interaction energy increased for both cation and anion, but remarkably stronger for the anion.

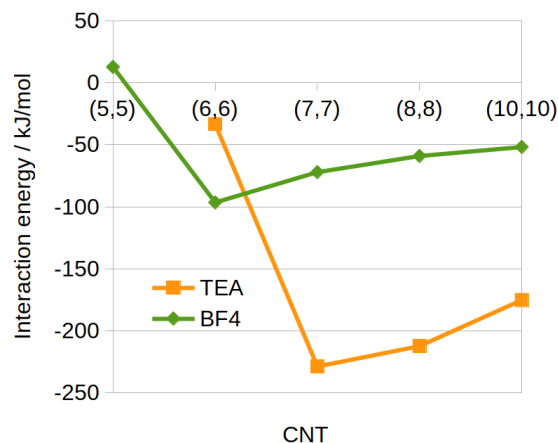


Figure 5: Interaction energy between CNT and TEA or BF<sub>4</sub>, respectively.

### 3 COMPUTATIONAL DETAILS

Scienomics MAPS software platform [6] was used for building models and manipulating model structures as well as for setting up simulations to mimic the process and for analyzing the results of such runs. Additional analysis was performed using Zeo++ [7] and polypy[8].

A 20 x 20 x 6 supercell of the crystal structure of SiC was created based on a SiC unit cell built according to the cell parameters given in Ref. [9]. The structure was equilibrated at room temperature for 50 ps using NVT conditions. Following that step, an NPT simulation at 2500 K was performed for 200 ps. After quenching to room temperature over 1 ns, Si was removed. The resulting carbon matrix was equilibrated at room temperature for 200 ps in an NVT ensemble. The simulation protocol has been varied with respect to different parameters: Simulation length, system size, temperature and quench rate, and the stage at which Si has been removed from the carbon matrix. A schematic overview is provided in Figure 8. In addition, a 2 x 2 x 2 supercell has been subjected to the simulation protocol. Moreover, the final porous structures were allowed to relax in an NPT ensemble up to 30 ns.

For calculating CO<sub>2</sub> absorption isotherms, a CO<sub>2</sub> gas box was equilibrated and the porous carbon matrix was partially oxidized, i.e. 2% and 5% oxygen was added, after removing all non-bonded carbon atoms. Parameters were taken from Refs. [10, 11]. MC simulations consisting of 10<sup>6</sup> steps were performed at 273 K in the Gibbs-NPT ensemble.

For building the electrode-electrolyte interface, the equilibrated carbon matrix was used as structural basis. A slab model was built and relaxed to avoid dangling bonds on the surface.

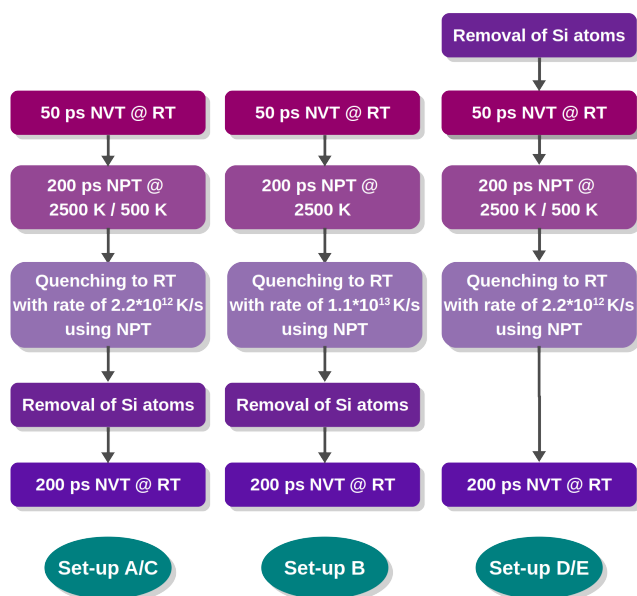


Figure 8: Schematic overview over simulation setups.

On top of the carbon, the electrolyte layer was added containing 2750 solvent molecules (acetonitrile, ACN), molecules, 150 cations (tetraethylammonium, TEA), and 150 anions (tetrafluoroborate, BF<sub>4</sub>). The density was chosen slightly larger than in experiment, because the diffusion of electrolyte into the carbon would otherwise cause a too large drop in the density. OPLS-AA force field parameters were used and missing parameters were taken from Refs. [12-14]. The carbon matrix was kept fixed. The structure was stepwise equilibrated. First, a short optimization was performed to remove bad contacts. Then, an NVT simulation over 10 ps was performed using a time step of 0.1 fs, followed by an NVT simulation of 5 ns using a time step of 1.0 fs. The final structure was used for NVT simulations applying an external electric field using 0.25 and 0.5 V over 1 ns.

Counterpoise corrected interaction energies have been calculated at PBE/def2-SVPD level after full geometry optimization at the same level of theory. CNT structures have been optimized at RI-PBE-MJ/def2-SVP level, while interaction energies have been calculated at PBE/def2-SVPD level.

## 4 CONCLUSION

We have presented a molecular modeling approach, which is capable to create morphologically realistic models of porous carbon-based electrode material as used in EDLCs. Based on this, MD simulations were performed indicating that the diffusivity of electrolyte into the electrode depends on the strength of the external electric field and the molecular size of the ions. In addition, DFT calculations revealed that the interaction between electrode and electrolyte is influenced by the pore size and surface functionalization of the electrode. The effect can be significantly different for cations and anions. This

information is useful for tuning the performances of EDLCs, since the electrode-electrolyte interaction influences ion confinement and mobility, which are both important characteristics of such devices. We have shown that molecular modeling is able to provide useful insights into these complex systems and can be used to guide experiments, thus saving cost and time.

## 5 ACKNOWLEDGMENT

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