

SIMULATION OF AN ELECTROLYTE CONFINED WITHIN A CHARGED POROUS CARBON MEDIA

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Introduction

Supercapacitors are electrochemical capacitors that have an unusually high energy density compared to that of common high-capacity electrolytic ones, with better power performance than batteries, due to the use of porous carbon as material for electrode. We show that a tight-binding description of the charge distribution in the carbon electrode, coupled to a Monte Carlo simulation of its invasion by the electrolyte, allows to determine a criterion for the choice of the better type of carbon material (zeolithe replica versus saccharose cokes) and to understand the processes at the carbon-electrolyte interface such as the location of the charges coming from carbon, the preferential adsorption sites of ions inside the porosity and the repartition of the ionic charges with respect to one another.

Modelling procedure

Two types of porous carbon materials can be considered as possible candidates for electrodes, either presenting well ordered porosities and rather low densities (0.8–0.9 g/cc) as it is the case for zeolithe carbon replicas (C-FAU, C-EMT, see Fig.1) or disordered structures such as those of the saccharose cokes (CS1000, CS400, see Fig.1), involving not only carbon atoms (87% of the structure) but also hydrogen ones (13%), with larger densities (1.25 g/cc for CS1000) except when they are activated (0.9 g/cc for CS1000A). In view of the topological complexity of these structures, any analysis requires to classify the atoms in a finite number of equivalence classes characterizing their local environment. This has been achieved using either the average diameter of the surrounding polyhedra for carbon replica, or more simply the number and nature of the neighboring sites for the cokes.

The electronic structure of the carbon structures is described within the Tight-Binding method in which the sp electrons wave functions are developed as linear combinations of atomic orbitals centered on each site, the probability for the electron to jump from one site to the other being given by hopping integrals which are damped with distance. In this framework, the way to determine the charge distribution in each carbon matrix is to calculate the local electronic density of states (LDOS) on all sites and to get the corresponding charge by integrating it up to the Fermi level. This has been achieved here using the continued fraction techniques within the recursion scheme [1].

Then, once the charge distribution in the electrode has been thus determined, one has to introduce the electrolyte. This has been achieved here in the simple case of a CsCl crystal, melt at 1000K using a Monte Carlo procedure at 1000K, and then introduced and compressed between two rigid carbon

electrodes in order to favor their invasion (still using Monte Carlo simulation, now at 300K) by the Cl⁻ and Cs⁺ ions. Within this procedure, all the electrostatic interactions are accounted for by using Ewald summation while their corresponding chemical counterpart is described within suited Lennard-Jones potentials (except for C-C since the carbon lattice is rigid). All along the procedure, the modifications of the charge distribution on carbon atoms due to their interaction with the electrolyte ions are carried out using a Tight-Binding self-consistent treatment of the charge.

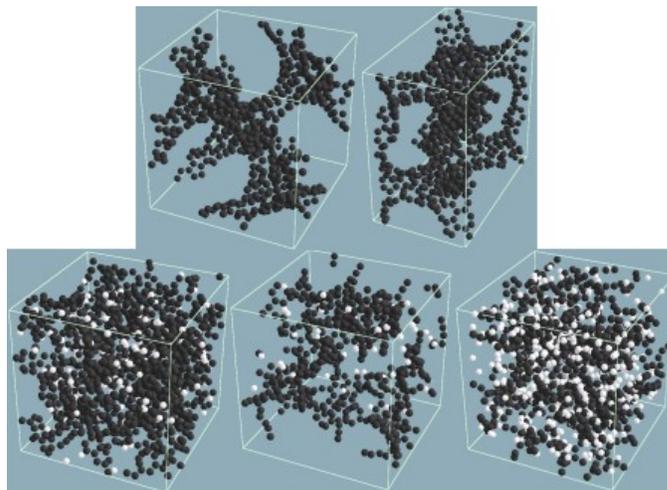


Fig. 1 Unit cells of C-FAU (a), C-EMT (b), CS1000 (c) CS1000A (d) and CS400 (e)

Results and Discussion

To compare the respective conductivities of cokes and carbon replica, we have to characterize which are the sites for which the Fermi level is located in a high part of the LDOS, otherwise they can be considered as insulators, and then to check that the so-determined conducting sites are well connected in the structure. In the case of the carbon replicas, the LDOS are globally similar except in their central part. Whereas the graphene-like neutral sites exhibit two peaks almost symmetric around the Fermi level, the other two classes involve three peaks which are reversed with the sign of the charge transfer. Anyway, in all cases the Fermi level is found in a pseudo-gap revealing a globally insulator character of these replica. The situation is drastically different for the CS1000 and CS400 cokes since in that case the Fermi level is located on a wide and high plateau of the density of states, which indicates that all these atoms are good conductors. This is illustrated in Fig.2 where the conductivity is quantified by the value of the total LDOS at the Fermi level. Let us just mention that a reasonable charge injection ($\sim 0.03e/at$) would not change the results. The question is then: is the better conductivity of the cokes due to their larger density or their disordered structure? The answer is given by the less dense CS1000_A structure (see Fig.2), which definitely demonstrates that disorder is the main factor for a good conduction behavior

The Monte Carlo simulation of the behavior of the CsCl electrolyte initially compressed between two C-FAU electrodes leads to the introduction of 49% of the Cs⁺ and Cl⁻

ions inside the porosity of these electrodes (see Fig.3). This leads to a change in the electronic structure of the carbon atoms which lead on one hand to an overall increase of their conductivity, and on the other hand to a modification of the charge on the sites of the filled porosities, which (as could be expected) becomes either more positive or negative depending on the region. More precisely, a careful analysis of the distance distribution shows that an enhanced positive charge appears in the vicinity of the electrolyte which is compensated by a negative one farther. This is due to a size effect which makes easier for the smaller Cl⁻ to come closer to the pore surface than Cs⁺ cations, inducing a positive charge on this surface. Indeed, the anions can come as close as 2.6Å of the pore surface, whereas the cations can hardly reach 3.25Å. This means that cations can easily invade the pores leading to a modification of the charge of the surface carbon atoms, whereas the anions have more difficulty so that they stay at a distance where the electrostatic interactions are not sufficient to modify the charge of their first carbon neighbors.

References

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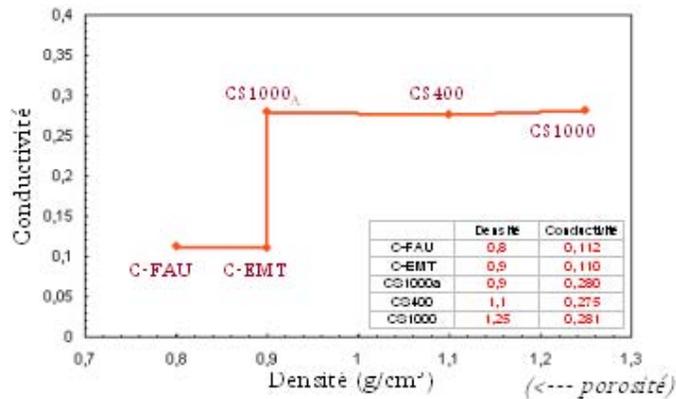


Fig. 2 Schematic variation of conductivity with density and state of disorder.

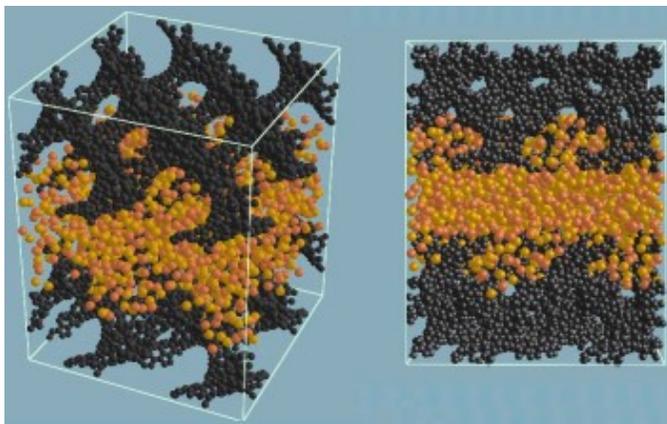


Fig. 3 Snapshot of the invasion of the C-FAU electrode by the CsCl electrolyte.