



Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: [www.elsevier.com/locate/jpowsour](http://www.elsevier.com/locate/jpowsour)

## Multi-scale modelling of supercapacitors: From molecular simulations to a transmission line model

C. Pean<sup>a, b, c</sup>, B. Rotenberg<sup>a, c</sup>, P. Simon<sup>b, c</sup>, M. Salanne<sup>a, c, d, \*</sup>

<sup>a</sup> Sorbonne Universités, UPMC Univ. Paris 06, UMR 8234, PHENIX, F-75005 Paris, France

<sup>b</sup> CIRIMAT, UMR CNRS 5085, Université Paul Sabatier, F-31062 Toulouse, France

<sup>c</sup> Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, 80039 Amiens Cedex, France

<sup>d</sup> Maison de la Simulation, USR 3441, CEA – CNRS – INRIA – Université Paris Sud – Université de Versailles, F-91191 Gif-sur-Yvette, France

### HIGHLIGHTS

- Model supercapacitors are simulated under constant applied potential conditions.
- The results are injected in a transmission line model.
- The predicted charging plots agree very well with non-equilibrium MD.

### ARTICLE INFO

#### Article history:

Received 17 February 2016

Received in revised form

23 March 2016

Accepted 28 March 2016

Available online xxx

#### Keywords:

Supercapacitors

Molecular dynamics simulation

Porous materials

Dynamic processes

Transport properties

### ABSTRACT

We perform molecular dynamics simulations of a typical nanoporous-carbon based supercapacitor. The organic electrolyte consists in 1-ethyl-3-methylimidazolium and hexafluorophosphate ions dissolved in acetonitrile. We simulate systems at equilibrium, for various applied voltages. This allows us to determine the relevant thermodynamic (capacitance) and transport (in-pore resistivities) properties. These quantities are then injected in a transmission line model for testing its ability to predict the charging properties of the device. The results from this macroscopic model are in good agreement with non-equilibrium molecular dynamics simulations, which validates its use for interpreting electrochemical impedance experiments.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

Carbon electrodes-based supercapacitors are electrochemical energy storage devices characterized by good power performances. They can be charged/discharged on very short timescales (e.g. a few seconds), so that they are useful in many applications [1]. They also show exceptional cycle lives, since they can sustain millions of cycles whereas batteries survive a few thousand at best. This is due to the molecular mechanism involved in the charge storage. It simply consists in the adsorption of the ions from the electrolyte on high surface area electrodes. Unlike Li-ion batteries, there is no limitation due to faradaic reactions and to the transport of electrons and

ions inside a low conductivity material [2]. The volumetric capacitance, and hence the energy density of the devices, dramatically increases when using nanoporous carbon electrodes [3]. This effect can be optimized by matching the average pore size with the adsorbed ions dimension [4,5], even if the pore size dispersity should be taken into account [6]. However, the power density performances of such devices may be affected. In sub-nanometric pores, the ions become highly confined [7], which has raised the question whether one should expect detrimental transport limitations.

In recent years, several simulation studies have aimed at understanding the dynamics of the ions at the molecular scale. Kondrat et al. have combined molecular dynamics with a phenomenological mean-field type model to study the charging of slit-pores with various wettabilities towards ionic liquids. They have shown that in the generic case (wettable pores), charging is a diffusive process [8,9]. Although the calculated diffusion

\* Corresponding author. Sorbonne Universités, UPMC Univ. Paris 06, UMR 8234, PHENIX, F-75005 Paris, France.

E-mail address: [mathieu.salanne@upmc.fr](mailto:mathieu.salanne@upmc.fr) (M. Salanne).

coefficients for the ions are generally lower than in the bulk ionic liquids, they observed a voltage range in which they eventually became larger, due to the onset of collective modes [9]. More recently, He et al. have also observed such effects in molecular dynamics simulations when the size of the slit-pores match the ionic dimensions [10]. In the case of the adsorption of electrolytes in more complex nanoporous carbons with several types of pores, the enhancement of the diffusivity is not observed [11,12]. However the diffusion coefficient values remain reasonable since they are on average lower than the bulk liquid ones by one order of magnitude only, which explains the fast charging of these supercapacitors.

Injecting the information extracted from molecular-scale simulations into macroscopic models would be very valuable. For supercapacitors, the canonical model used to interpret electrochemical impedance spectra is the transmission line model introduced by de Levie [13,14]. It is an equivalent circuit which consists in an infinite succession of electrode slices composed of a resistance and a capacitor, that are connected together. In a recent work we have shown that it was possible to fit the variation of the total charge on the electrode with respect to time when charging a nanoporous carbon-based supercapacitor using non-equilibrium molecular dynamics simulations [15]. The only fitting parameter was the in-pore resistivity. Here we go further in that direction, by showing that the transmission line model can be fully parameterized without any fitting, simply by including physical quantities determined in equilibrium molecular dynamics simulations. The resulting model shows a very good agreement with non-equilibrium molecular dynamics, which validates its use for the sample sizes we consider. The simulated system consists in a generic electrolyte, i.e. 1-butyl-3-methylimidazolium and hexafluorophosphate ions  $[C_4 \text{ mim}^+][PF_6^-]$  dissolved in acetonitrile at the concentration of  $1.5 \text{ mol L}^{-1}$ , and a realistic model of nanoporous carbide-derived carbons for the electrodes.

## 2. Molecular dynamics simulations

The simulation cells consists of  $[C_4 \text{ mim}^+][PF_6^-]$  dissolved in acetonitrile (at the concentration of  $1.5 \text{ mol L}^{-1}$ , which is classically used in experiments [16,17]), surrounded by two identical nanoporous carbon electrodes placed symmetrically. The position of the carbon atoms inside the electrodes, which are held fixed, were obtained by quenched molecular dynamics by Palmer et al. [18]. They have an average pore size of 0.9 nm, and the structural characteristics of the electrodes match well with the experimental data for a carbide-derived carbon synthesized at  $1200^\circ \text{C}$ . We will therefore label it CDC-1200 in the following. The distances between the two electrodes along the  $z$  direction are chosen in order to reproduce the experimental density of the bulk electrolyte. The lengths of the box are provided in Table 1 together with the number of molecules, and a representative snapshot is shown in Fig. 1.

Molecular dynamics simulations are conducted with a timestep of 2 fs. The simulations are performed in the NVE ensemble at room temperature (298 K). Following our previous works [19,20], we use

**Table 1**

Lengths of the box and number of molecules for each kind of simulation. The chosen carbide-derived carbon (CDC) is in both cases the CDC-1200 in contact with the ionic liquid  $[C_4 \text{ mim}^+][PF_6^-]$  dissolved in acetonitrile at a concentration of  $1.5 \text{ mol L}^{-1}$ . Two dimensional periodic boundary conditions are used, i.e. there is no periodicity in the  $z$  direction.  $N_{\text{ions}}$  corresponds to the number of ion pairs and  $N_{\text{ACN}}$  to the number of acetonitrile molecules.

Simulations	$L_x = L_y$ (nm)	$L_z$ (nm)	$N_C$	$N_{\text{ions}}$	$N_{\text{ACN}}$
Non-equilibrium	4,37	19,44	3649	230	2146
Equilibrium	4,37	32,46	3649	384	3584

the coarse-grained model of Roy and Maroncelli [21,22] for the ionic liquid  $[C_4 \text{ mim}^+][PF_6^-]$  and the one of Edwards et al. [23] for acetonitrile. Three interaction sites describe the cation and the acetonitrile molecules, while a single site describes the anion. The Coulombic interactions are calculated through a two-dimensional Ewald summation [24,25] because two dimensional periodic boundary conditions are used (there is no periodicity in the  $z$  direction).

Two series of simulations were performed. The first one involves non-equilibrium simulations, which aim at simulating the charging process, and proceeds via the following steps. The system is first equilibrated for a few nanoseconds with a constant charge of 0 e on all carbon atoms and then with a 0 V potential difference between the two electrodes. Then at  $t = 0$ , this potential difference  $\Delta\Psi^0$  is suddenly set to 1 V (on each electrode we have  $\Psi^+ = \Delta\Psi^0/2$  and  $\Psi^- = -\Delta\Psi^0/2$ ) and maintained constant using a method developed by Reed et al. [24] from the model of metallic carbon electrodes proposed by Siepmann and Sprik [26]. In this approach, the charge distribution on each electrode is obtained by requiring that the potential experienced by each atom is equal to the preset electrode potential value at each molecular dynamics time step. It is computationally expensive compared to constant charge simulations but is compulsory for a realistic description of the charge repartition, which is rather broadly distributed [19,27], and of dynamic processes. In particular we have shown that simulations in which the electrode charge distribution is held fixed yields unphysically high temperature increases during transient regimes [28]. Simulations are continued long enough for the total charge accumulated on the electrode to reach a plateau. Discharge simulations are also performed, by suddenly setting the potential difference to 0 V. In this work we perform a charge-discharge-charge cycle, for a total simulation time of 16 ns.

The second series deals with equilibrium simulations. In that case, the system is first equilibrated with a constant charge of 0 e,  $\pm 0.005$  e, or  $\pm 0.01$  e, which is equally distributed among electrode atoms. We previously showed that these charges are good starting values to initialize constant potential simulations at respectively 0, 1 or 2 V potential differences. Constant-potential production runs of 13 ns are then performed at these values.

## 3. Results and discussion

### 3.1. Electrosorption observation

It is well established that fluids have different transport properties when they are confined in porous media compared to the bulk [29–33]. In the case of electrolytes, the diffusion coefficients of the ions are particularly impacted [34,35]. In addition, when a liquid is adsorbed inside a porous electrode with applied voltage, its composition changes, sometimes leading to an unexpected enhancement of the diffusivity with respect to the bulk [8–10]. In-pore resistivities, mean-square displacements, diffusion coefficients, as well as adsorption lifetimes are complementary quantities which can be extracted from computer simulations to characterize the singular transport in the pores of the material.

In the case of complex porous carbons such as the CDC we study here, there are numerous confinement sites that cannot be represented by simple slit pores. In a previous work, we have identified four different types of sites, which are respectively labelled edge, plane, hollow or pocket, from the less confined to the more confined. The ranking of the sites is based on the degree of confinement, which is defined by the percentage of the solid angle around the ion which is occupied by the carbon atoms [7]. These sites are relatively homogeneously distributed inside the CDC-1200 electrode, as shown in Fig. 2.

Download English Version:

<https://daneshyari.com/en/article/7727273>

Download Persian Version:

<https://daneshyari.com/article/7727273>

[Daneshyari.com](https://daneshyari.com)