

Understanding the Solvent Effect in Slit-pore Supercapacitor Models using Molecular Modelling

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Supercapacitors have gained increased attention in recent years owing to their high-power density, charge efficiency, and long cycle lifetimes. The performance of supercapacitors has been improving through discovery of novel materials and the understanding of charging/discharging mechanisms [1]. Carbon-based materials have been widely studied as electrodes due to their good electrical conductivity, high surface area, and porosity control [2][3]. Ionic liquids are promising electrolytes with their high energy density and wide electrochemical window. However, their slow transportation properties and low electrical conductivity are drawbacks as pure electrolyte materials. Organic solvents are widely used to increase their conductivity and power density [1]. Molecular dynamic simulations allow to study charging dynamics and structure of supercapacitors with various properties in molecular level.

In this study, molecular dynamic simulations are conducted on supercapacitor systems consisting of carbon electrode, organic solvent acetonitrile (ACN) and ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6). The electrodes are modelled as slit pores with 3-layers of honeycomb lattice model graphene sheets. System model is shown in Figure 1. The systems are built with pore width of 7.78 Å, 11.12 Å and 14.75 Å, ion fractions of 0.77 and 1.00, and solvent dipole moments of 2.06 D, 4.12 D and 6.12 D.

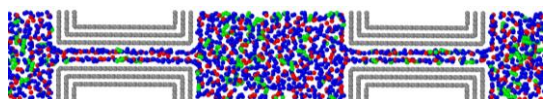


Figure 1. Simulated system. ACN (green), [BMIM⁺] (blue), [PF6⁻] (red)

Initial configurations are obtained with Packmol [4] and molecular dynamic simulations are conducted using the LAMMPS package [5]. Equilibrium simulations are followed

by constant potential simulations with potential difference of 1.0 V. Systems are charged for 15 ns. The charging dynamics of the electrodes, kinetic properties, and molecular structure of the electrolyte at the interface and inside the pores are analyzed to understand solvent effect in slit-pore supercapacitor models. The charging profile of the electrodes, radial distribution functions, number and charge density of the electrolyte, diffusion coefficient, and ionic conductivity are calculated to explain the effect of system parameters on the supercapacitor models. Charging of the electrodes shows that presence of solvent increases the electrode charging under constant potential.

References

- [1] Sampaio, A. M. et al. (2020) "Comparing the performance of sulfonium and phosphonium ionic liquids as electrolytes for supercapacitors by molecular dynamics simulations," *Electrochimica Acta*, 364, p. 137181
- [2] Zhang, Y. and Cummings, P. T. (2019) "Effects of Solvent Concentration on the Performance of Ionic-Liquid/Carbon Supercapacitors," *ACS Applied Materials and Interfaces*.
- [3] Feng, G. and Cummings, P. T. (2011) "Supercapacitor Capacitance Exhibits Oscillatory Behavior as a Function of Nanopore Size", *The Journal of Physical Chemistry Letters*, 2, 2859-2864
- [4] Martínez, L. et al. (2009) "Packmol: A package for building initial configurations for molecular dynamics simulations" *Journal of Computational Chemistry*, 30(13), 2157-2164
- [5] Thompson, A. P. et al. (2022) "LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales", *Comp Phys Comm*, 271,10817



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