Molecular dynamics study of capacitance enhancement of graphene with covalently bonding polypyrrole electrodes in usage of Supercapacitors: effect of chain length of conductive polymer

Tayyebeh Arshi, Sayyed Morteza Mousavi-Khoshdel*, Mohammad-Safi Rahmanifar† and Zahra Khodadadi‡

** Laboratory of Renewable Energies, Department of Chemistry,*
Iran University of Science and Technology, Tehran, Iran
†Faculty of Basic Science, Shahed University, Tehran, Iran
‡Science Faculty, Department of Chemistry, Islamic Azad University, East Tehran Branch, Tehran, Iran
Corresponding author E-mail: mmousavi@iust.ac.ir

Abstract

Supercapacitors (also known as ultracapacitors) are electrochemical structures that are characterized by high power densities and high cycle lifetimes. The simplest supercapacitor is composed of two symmetrical electrodes that are separated by a porous substrate and an electrolyte. Graphene-based electrodes have been widely tested and used in electrochemical double layer capacitors due to their high surface area and electrical conductivity. Recent research efforts have been focused on improving the energy density of supercapacitors by exploring novel electrode materials. Conducting polymers (CPs) can store charges not only in the electrical double layer (EDL) but also through the rapid faradic charge transfer (pseudocapacitance). As a result, the specific capacitance of CP electrodes is higher than that of EDL capacitors based on carbon electrodes. However, one of the drawbacks for CPs as supercapacitor electrodes is their poor cycling stability because CPs is usually brittle and weak in mechanical strengths. The synergistic interaction induced by the growth of p-type polypyrrole on the surface of negatively charged carboxylate functionalized graphene sheets results in higher storage capacity than graphene-only or polymer-only films. The high conductivity of p-doped polypyrrole and high surface area of graphene promotes high charge accumulation in capacitors. In our computational study the microstructure and capacitance of the double layers forming near graphene with covalently bonded polypyrrole electrodes were calculated using classical molecular dynamics. MD simulations were carried out using the Gromacs 4.5 package. In this work, we employed all atoms force field in the frame of OPLS-AA (Optimized Potential for Liquid Simulations/All Atom), and developed it using quantum calculations to parameterize polypyrrole in order to determine the microstructure formed on the graphene electrodes. We employed 34.18×34.53×100 $Å^3$ supercells corresponding to 2 graphene sheets of size 34.18×34.53 $Å^2$ (which is corresponding to 448 C atoms). We first ran MD at 1000 K for 1.2 ns, followed by 3 ns at 300 K to equilibrate the system. Production runs were carried out for 4 ns with atomic positions recorded every 4 ps. All runs were in the NVT ensemble with the temperature controlled by a Nose-Hoover thermostat with a 100 fs damping parameter. Different chain lengths of polypyrrole were attached to graphene sheets in separate simulations and the respective capacitance were calculated in different concentrations of electrolyte and optimal polymer length is obtained.

Keywords: Supercapacitor, Graphene, Polypyrrole, Molecular dynamics

References

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