Computational Materials Science 143 (2018) 43–54

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Predicted structural and mechanical properties of activated carbon by molecular simulation

Po-Yu Yang [a], Shin-Pon Ju [a,b,*], Siou-Mei Huang [a]

[a] Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-sen University, 70 Lienhai Rd., Kaohsiung 80424, Taiwan
[b] Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, 100, Shih-Chuan 1st Road, Kaohsiung 80708, Taiwan

ARTICLE INFO

Article history:
Received 24 August 2017
Received in revised form 24 October 2017
Accepted 29 October 2017

Keywords:
Activated carbon
tfMC
Mechanical property
Tensile simulation
Molecular statics

ABSTRACT

Combining the time-stamped force-bias Monte Carlo (tfMC) and simulated-annealing methods, different densities of activated carbon (AC) in different quench rates were constructed. Six AC models were constructed, corresponding to densities of 0.5, 0.7, and 1.3 g/cm^3 and quench rates of 5 K per 30 tfMC steps and 5 K per 6000 tfMC steps, respectively. The structural properties of these models were examined, including porosity, specific surface area (SSA) and pore distribution. In uniaxial tensile simulation, the Young's modulus and the fracture of microstructures were also investigated. The specific surface area and Young's modulus are proportional to the density of AC, but the porosity and the main distribution of pore size are inversely related. The probability distribution of the ring size shows that six-atom rings translate to four- and five- atom ring during tensile simulation. The local shear strain analysis indicates that the fractures appear adjacent to the non-hexagonal ring defects and at the edge of the carbon wall frame in AC and will expand vertically along the tensile axis. This study not only constructs a structural prediction procedure of AC but also provides several detailed information of AC fracture.

1. Introduction

Activated carbon (AC) is an important and unique functional carbon material with a high degree of microporosity and large specific surface area (>3000 m^2/g) [1,2]. AC has been used by humans since very early stages of history due to its extraordinary adsorption property. By 1550 BCE, activated carbon was made from charcoal, char and ash by ancient Egyptians to purify water and for use in the medicinal field [3]. Nowadays, with our increased awareness of environmental issues, AC has been intensively used to remove hazardous species and pollutants such as H_2S [4], CO_2 [5], SO_2 [6], volatile organic compounds [7,8], inorganic S-containing anions [9] heavy metals [10,11], surfactants [12,13], dyes [14], various phenolic [15], anilinic [16] and compounds and aromatic sulfonates [17]. Another advantage of using AC is its lower price, because AC can be prepared from various precursors, including coal, wood, agricultural by-products, lignocellulosic materials, or organic precursors [18]. In addition, due to its high specific surface area, good electron conductivity and easy functional modification, AC is considered as a popular material to act as a chemical reaction catalyst [19,20], an electrode of electric double layer capacitors (EDLC) [21] and fuel cells for hydrogen storage [22].

Because of specific structural properties, the micro structure of AC has been characterized by many methods as reported in previous studies [23–27]. The most common method for pore size distribution analysis is to measure the distribution of gas adsorption–desorption isotherms. Nitrogen gas is the most common probe molecule and the isothermal data can be used to derive the specific surface area, pore volumes and pore size distributions. Moreover, direct observation by X-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM) have clearly pointed out the disordered arrangement of microporous carbons and the heterogeneity of the carbon fragments [1].

Based on these experimental observations, bulk AC is regarded as an aggregation of cross-linked finite graphene sheets in random arrangement [1,28]. In related numerical simulations, Pikunic et al. [24] applied the reverse Monte Carlo (RMC) method to construct the AC structure, obtaining a radial distribution function comparable to that obtained from experimental observations. Palmer and Gubbins [27] conducted a hybrid reverse Monte Carlo (HRMC) simulation to construct the disorder nanoporous AC model, and their model can predict adsorption properties of nitrogen and have good agreement with experimental measurements. Shi used the quench molecular dynamics (QMD) method with the reactive state

* Corresponding author at: Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-sen University, 70 Lienhai Rd., Kaohsiung 80424, Taiwan.
E-mail address: jushin-pon@mail.nsysu.edu.tw (S.-P. Ju).

https://doi.org/10.1016/j.commatsci.2017.10.051
0927-0256/

Table 1
The AC densities at tfMC quench process and after relaxation.

AC Model	Density at tfMC (g/cm^3)	Density after relaxation (g/cm^3)
AC1_30	0.50	0.50
AC1_6000	0.50	0.52
AC2_30	0.70	0.77
AC2_6000	0.70	0.77
AC3_30	1.30	1.40
AC3_6000	1.30	1.41

summation (RSS) potential to predict various AC nanostructures with different quench rates [23]. His simulation results indicated that the porous structural properties of AC, including ring size distributions, pore size distributions, and angle distribution, were significantly influenced by quench rate. For the AC fabrication, the density and porosity can be controlled by using different physical or chemical treatments with reagents. However, the AC growth process which considers the interaction between AC and reagents are too complicated to simulate. Those previous numerical studies have mentioned that a reliable numerical process is still able to construct the realistic AC microstructure even though the reagents are not used in simulation model.

In this study, a new structural prediction method is proposed to improve the efficiency of the QMD method to construct a larger AC model on the atomic scale. The time-stamped force-bias Monte Carlo (tfMC) algorithm [29–31] was used to replace the molecular dynamics element of the quench process in order to predict the structural properties of ACs of different densities which were built from different quench rates. The discussions about the relation between microstructure of AC and mechanical properties are still lacking in previous studies. Thus, the mechanical properties of ACs were also investigated by the uniaxial tensile simulation, and detailed local structural changes during the tensile process were also explored.

2. Simulation theory

Molecular dynamics (MD) simulation is a robust and versatile technique and allow tracing the full dynamical path of system through space and time. Some slow processes such as self-assembling or film growth may take place within the temporal range MD simulation is difficult to simulate. Therefore, several acceleration methods have been proposed to extend the simulation temporal domain compared with that used in the MD simulation. Among these methods, Neyts [32] proposed a new method which couples the advantages of MD simulations and stochastic Monte Carlo (MC) simulations. The MD cycle is used to simulate the fast processes, while the subsequent MC cycle is responsible to do the long-time thermal relaxation process. For the MC part, in order to increase the MC acceptance rate, the force-bias MC (fbMC) method [33,34] was developed. Mees [30] proposed a new uniform acceptance force-bias MC method which can still be able to describe dynamical system. Consequently, this method is also called time-stamped force-bias Monte Carlo (tfMC) and it could be a valuable MD alternative for extending the simulation temporal domain. This method has been applied to predicting the nanostructure formation and phase transformation successfully [35,36].

The QMD method adopts a simple thermal quenching protocol by standard MD simulations in the previous study [23]. For our simulation, the time-stamped force-bias Monte Carlo (tfMC) algorithm was used to replace the MD portion of the QMD simulation. In the tfMC simulation, each atom moves along the force direction with a random step size for each tfMC step. For the tfMC method, the system evolves by the random displacement of each atom along the force direction. The displacement of an atom is determined by the multiplication of predefined maximal allowed displacement amplitude and the random number between −1 and 1. Mees stated the system evolution by the tfMC method corresponds to a dynamical simulation using the temporal length at least one order longer than that used in classical MD (∼several femto seconds) [29]. The suggested value for maximal allowed displacement amplitude is about 5–10% of a typical nearest neighbor

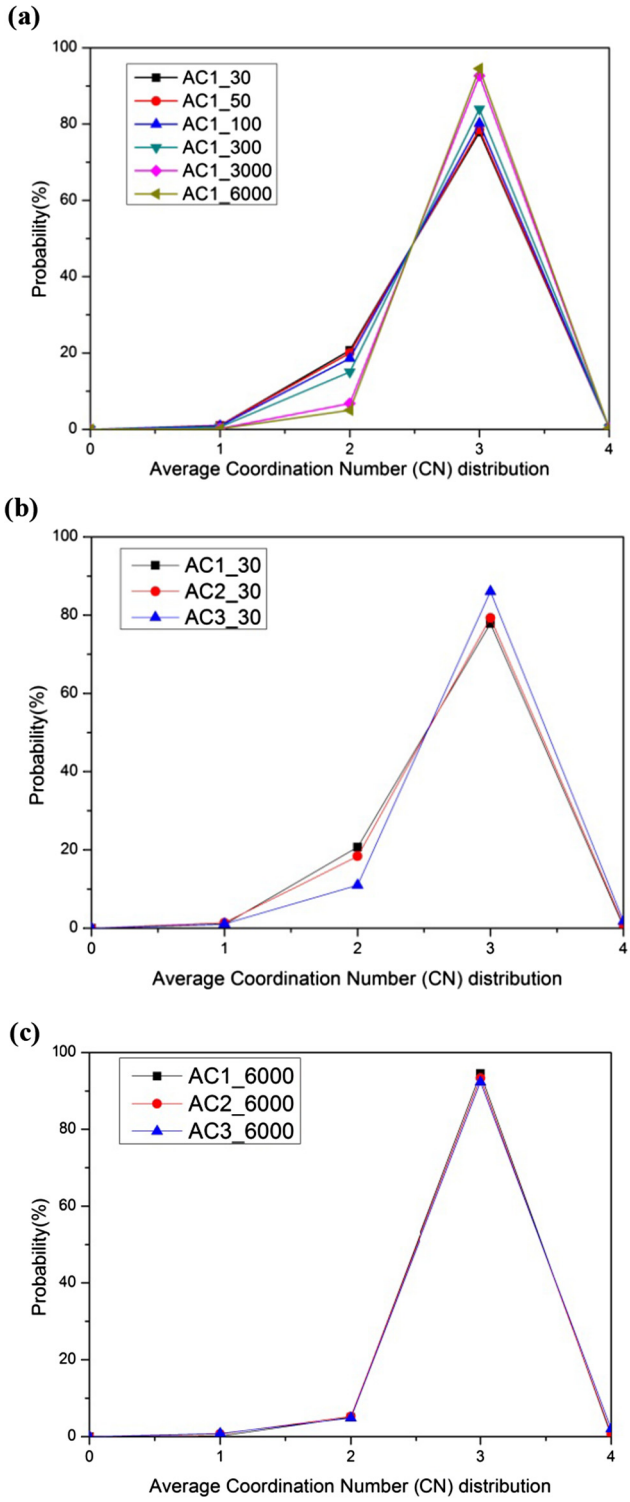

Fig. 1. Average coordination number (CN) of AC for (a) AC1 with different quench rates, (b) AC1, AC2, and AC3 at the fastest quench rate, and (c) AC1, AC2, and AC3 at the slowest quench rate.