Effects of lithium doping on hydrogen storage properties of heat welded random CNT network structures

Cengiz Baykasoglu [a,*], Zeynel Ozturk [b], Mesut Kirca [c], Alper T. Celebi [d], Ata Mugan [c], Albert C. To [e,**]

[a] Hitit University, Faculty of Engineering, Department of Mechanical Engineering, Cevre Yolu Avenue, 19030, Corum, Turkey
[b] Hitit University, Faculty of Engineering, Department of Chemical Engineering, Cevre Yolu Avenue, 19030, Corum, Turkey
[c] Istanbul Technical University, Faculty of Mechanical Engineering, Inonu Street, Gumussuyu, 34437, Istanbul, Turkey
[d] Southern Methodist University, Lyle School of Engineering, Department of Mechanical Engineering, 3101 Dyer Street, Dallas, TX 75205, USA
[e] University of Pittsburgh, Department of Mechanical Engineering and Materials Science, 508 Benedum Hall, PA 15261, USA

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ABSTRACT

This paper presents the effects of lithium doping on the hydrogen storage capability of heat welded random carbon nanotube (CNT) network structures having different cross-link densities at room temperature. Cluster based and atom based doping strategies are taken into consideration in the current simulations. Moreover, different doping ratios are used in our calculations to clarify the effect of doping ratio on hydrogen uptake behavior of CNT networks. The network structures are generated by using a cyclic stochastic algorithm and covalently bonded couplings are created by applying the heat welding method via molecular dynamic simulations. Hydrogen storage capacity of the Li-doped CNT networks is investigated using Grand Canonical Monte Carlo (GCMC) simulations. The simulation results show that hydrogen storage capacity is appreciably enhanced with the presence of lithium atoms and increases as the doping ratio increases. Besides, atom based doping method is found to be more efficient in hydrogen uptake than cluster based doping method under the same doping ratio. Furthermore, our results also show that the cross-link density is a critical parameter and hydrogen storage capability of Li-doped CNT network material can be improved with the appropriate choice of cross-link density.

* Corresponding author. Tel.: +90 364 227 45 33; fax: +90 364 227 45 35.
** Corresponding author. Tel.: +1 412 624 2052.
E-mail addresses: cengizbaykasoglu@hitit.edu.tr (C. Baykasoglu), zeynelozturk@hitit.edu.tr (Z. Ozturk), kircam@itu.edu.tr (M. Kirca), acelebi@smu.edu (A.T. Celebi), mugan@itu.edu.tr (A. Mugan), albertto@pitt.edu (A.C. To).

Introduction

Hydrogen is a renewable and environmentally friendly energy source and considered to be one of the most promising alternative candidates to fossil fuels [1–5]. However, the lack of an efficient storage system is one of the major obstacles in front of the practical usage of hydrogen in energy systems [6–9]. This has led to an extensive search for appropriate hosting materials, which can store hydrogen within a reasonable volume without a considerable increase in weight.

Since the discovery of carbon nanotubes (CNTs) in 1991 [10], extensive studies have been carried out to investigate its extraordinary properties including their hydrogen storage capability. Dillon et al. [11] and Liu et al. [12] studied the hydrogen storage behavior of CNTs. These preliminary studies showed that pristine CNTs can be considered as a good candidate for hydrogen storage applications [13]. However, later studies showed that pristine CNTs are not efficient at ambient conditions [14,15]. This fact motivated the scientists to explore the idea of doping metal atoms such as lithium, magnesium, titanium and platinum on pristine CNTs. Several theoretical and experimental studies have shown that metal doping appreciably increased the hydrogen storage capacity of CNTs [16–26]. The hydrogen stored in the metal doped CNTs can be released at higher temperatures and the adsorption–desorption cycle repeats with little reduction in the hydrogen storage performance [18]. In addition, lithium is the lightest member among the alkali metals and generally selected as a dopand in literature. A brief literature review about the hydrogen storage capability of CNTs can be found in Refs. [24–26].

Despite the improvement in the hydrogen storage capability of CNTs with alkali metal doping, their performance does not still meet the expectations. At this point, many novel lightweight nanoporous materials with adjustable pore structures have been proposed for solving the problems related to hydrogen storage capability [27]. Among them, carbon-based nanostructured materials are particularly accepted as a very promising candidate for hydrogen storage applications due to their high surface/weight ratios combined with their superior structural and thermal properties [9,28–37].

Carbon based nanostructured materials absorb the molecular hydrogen by weak Van der Waals forces at their surfaces. Thus, high surface area and appropriate pore size are the key parameters for improving the hydrogen storage performance of these materials. At this point, many novel carbon based nanostructured materials have been proposed for solving the problems related to hydrogen storage. Kuc et al. [28] studied the hydrogen storage capability of fullerene (C60) intercalated graphite structures. Singh et al. [29] investigated the hydrogen storage in the three-dimensional (3-D) carbon-foams using grand canonical Monte Carlo simulations. Wu et al. [30] examined the adsorption of molecular hydrogen on a 3-D pillared graphene structure under various environments using MD simulations. In another study, Wu et al. [32] studied the hydrogen storage capability of few-layer graphene structures using MD simulations. Besides, Tylianakis et al. [33] investigated the hydrogen storage in a novel 3-D diamond-

like nanoporous architecture composed by interconnected CNTs. On the other hand, some recent studies show that doping carbon-based nanoporous materials with lithium atoms can considerably increase their hydrogen storage capacity. Mpourmpakis et al. [38] examined the hydrogen storage behavior of carbon nanoscrolls (CNSs) and pointed out that CNSs are promising materials for hydrogen storage especially when doped properly with lithium. Dimitrakakis et al. [35] investigated the hydrogen adsorption properties of pristine and lithium-doped 3-D carbon-based nanostructure named pillared graphene. Their results show considerable enhancements on the hydrogen adsorption in case of Li-doping under ambient temperatures. In another study, Tylianakis et al. [36] presented the results of hydrogen storage capacity of pillared graphene oxide for various pore size and doping ratio, and it is shown that Li-doped pillared graphene oxide have higher gravimetric and volumetric hydrogen storage capacities in comparison with the pristine graphitic substrate. Tylianakis et al. [37] also proposed novel carbon-based nanostructures named porous nanotube networks that originated from 3-D junctions between CNTs and investigated the effect of lithium doping on hydrogen storage capacity of these structures. Their results show considerable enhancements on the hydrogen adsorption in case of Li-doping at room temperature.

Carbon-based 3-D porous networks can be produced from 1-D nanostructures using atomic welder during heat treatment or electron irradiation at high temperatures [33,38,39]. At this point, 3-D carbon-based porous networks can generally be classified as ordered and random networks [40]. It is noteworthy that the majority of studies in literature focused on the hydrogen storage capability of ordered carbon-based networks due to their simple and predictable nanostructures. However, the ordered carbon based 3-D porous networks are commonly assumed as ideal structures, which suggest that they do not display topological irregularities and highly possible imperfections [41]. Moreover, CNT networks generated for experimental studies may include intricately distributed tubes in space [42]. In this regard, in our previous studies, we introduced a 3-D novel carbon-based porous material called "heat welded random CNT networks" [41] and investigated the tensile behavior of these materials using MD simulations [40]. The proposed novel random CNT network structure in Ref. [40] has arbitrarily natural morphology, large free volume and surface area. On the other hand, underlying the fact that no published work exists in literature about the hydrogen storage behavior of heat welded random CNT networks, we also investigated the hydrogen storage capability of pure heat welded random CNT network structures by using GCMC calculations [43]. Our simulation results show that random CNT networks could uptake about 2 wt.% at room temperature due to weak interactions between hydrogen molecules and CNT networks. Hence, to enhance the hydrogen adsorption in a CNT network at room temperature, we proposed different Li-doping strategies such as cluster based and atom based lithium doping schemes. The atom based doping scheme are generally used in literature and there is no published work focusing on hydrogen adsorption of lithium nanoclusters doped CNT networks. However, this scheme resembles real systems. Motivated by these facts, we