

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

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

# First-principles studies concerning optimization of hydrogen storage in nanoporous reduced graphite oxide

C.B. Robledo, M.I. Rojas\*, O. Cámara, E.P.M. Leiva

INFIQC, Departamento de Matemática y Física, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

## ARTICLE INFO

### Article history:

Received 26 September 2013

Received in revised form

5 December 2013

Accepted 30 December 2013

Available online 28 January 2014

### Keywords:

Hydrogen storage

Reduced graphite oxide

Nanoporous material

Density functional theory

## ABSTRACT

By means of Density Functional Theory (DFT) calculations we investigated the optimal pore size for reduced graphite oxide (GOH) to favor hydrogen storage and to prevent oxygen interference. The interlayer distance of GOH is found to increase with oxygen content, given by the number of hydroxyl groups. Four types of GOHs were considered, with O/C ratio within a 0.09–0.38 range. In the case of the highest O/C ratio considered, 0.38, a spontaneous redox-reaction between hydroxyl groups delivering a water molecule and an epoxy group was found. Thus, GOHs with high O/C ratio are not recommended for hydrogen storage. In these materials the absorption energy values of hydrogen is in the range of  $-0.2$  and  $-0.5$  eV/molecule, that is within the values expected to allow an efficient storage. The best GOH for hydrogen storage was found to be that with a 0.09 O/C ratio since it has the largest void space and adequate absorption energy,  $-0.52$  eV/molecule. On the other hand, oxygen absorption energy is lower in absolute value than that of hydrogen, which favors absorption of the latter, thus creating adequate conditions for its storage without oxygen interference.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Hydrogen is the optimal energy carrier to be employed as vehicular fuel in a new energy economy based on renewable resources. Its heating value is three times higher than that of petroleum and it is a clean fuel since its energy conversion does not produce greenhouse gas effect emissions (GEI) [1,2]. Although their lightness, high specific surface area and low cost make carbonaceous compounds good candidates for hydrogen storage, their storage capacity needs further

improvement in order to suit the requirements for vehicular applications. The storage system must be able to safely store the gas at room temperature and at a maximum of  $350 \text{ bar}^1$  quickly and must allow numerous cycles of charge/discharge. Thus, the challenge is to develop a carbonaceous material that allows us to store on board four kilograms of hydrogen. Such a material should have both a reasonable volume and weight, allowing an autonomy of over 500 km for a standard fuel cell vehicle [3].

Depending upon the hybridization state of carbon, these materials can bind hydrogen via various mechanisms,

\* Corresponding author. Tel./fax: +54 (0)351 5353853.

E-mail addresses: [mrojas@fcq.unc.edu.ar](mailto:mrojas@fcq.unc.edu.ar), [marianarojas65@gmail.com](mailto:marianarojas65@gmail.com) (M.I. Rojas).

<sup>1</sup> Pressure used in the storage system of the Honda FCX, fuel cell powered automobile. <http://world.honda.com/FuelCell/FCX/tank/>. 0360-3199/\$ – see front matter Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved. <http://dx.doi.org/10.1016/j.ijhydene.2013.12.206>

including physisorption, Kubas and chemical bonding. It has been established that the energy per hydrogen molecule must be in the order of 0.1 eV–0.5 eV to establish a reversible absorption/desorption process [4,5]. It has been proposed that hybrid carbon materials decorated with metals may have even higher storage capacities [6,7] than pure carbon materials. Graphite intercalation compounds with alkaline metals also improve the hydrogen storage compared to pristine graphite but it does not fulfill the requirements for mobile applications [8,9]. Nevertheless, there is a significant difference between the theoretical predictions and the experimental measurements, since it has not been possible to reproduce experimentally the storage capacities predicted theoretically. Recently, it has been found through calculations that oxygen traces in the gas phase could strongly interfere with hydrogen storage. This is so because oxygen may either oxidize [10] or block the metallic decorations [11,12].

Although neither pure carbon materials nor hybrid ones suits the requirements for on board applications,<sup>2</sup> mainly concerning gravimetric density, there are promising results related to them [9,11,13]. The problem of oxygen interference could be solved by designing nanoporous materials precluding oxygen access by means of pore-size optimization [14].

Graphite oxide (GO) (stack of several layers of graphene oxide) can be obtained from oxidative-acid treatment of graphite. The most effective experimental synthesis of GO is via the Hummers method [15]. The main reactants used in this method are potassium permanganate, sodium nitrate and sulfuric acid. During the oxidation process, functional groups such as hydroxyl (–OH) and epoxy (–O–) are incorporated into the graphite structure. These groups are responsible for the expansion between graphene planes and for the generation of the split porous structure [16,17]. In experiments, pore dimension in graphite changes from 3.36 to 7.31–7.91 Å depending on the oxidation time [18]. It is possible to control pore size through the oxidation time. On the other hand, Jimenez et al. [14] suggested that hydrogen absorption is improved by functionalization, due to the acid character of the groups, which polarizes the hydrogen molecules. Motivated by these encouraging results, materials derived from graphite oxide were considered in this work as a candidate for hydrogen storage.

In this work we study the properties of reduced graphite oxides (GOH) and their nanoporous structure by means of density functional calculations. The GOH we simulated consisted of pure hydroxyl groups (–OH) defining different oxygen coverage degrees. Hydrogen and oxygen absorption energies are studied in the optimized and expanded geometries (with pores of between 0.6, 0.7 and 0.8 nm). The present work presents essentially two novel results: On one side, we find that the hydrogen binding energy in these systems is between –0.52 and –0.65 eV, that is, very close to the energy window suggested in Refs. [4,5] for optimal hydrogen storage. On the other side, we find that oxygen

is not a meaningful interferent in these systems, something that precludes hydrogen adsorption on other systems.

## 2. Calculation

### 2.1. Computational details

All DFT calculations were performed using the Quantum Espresso package [19] with van der Waals interactions. The Kohn-Sham orbitals and charge density were expanded in plane-waves basis sets up to a kinetic energy cutoff of 35 and 200 Ry for all atoms respectively. Ultra soft pseudopotentials were employed with the Perdew–Wang approximation for exchange and correlation in the PW91 functional [20–22]. The Brillouin zone was sampled with  $2 \times 2 \times 1$  irreducible Monkhorst–Pack k-point grid [23]. The convergence threshold for the total energy at each electronic calculations was set to  $1 \times 10^{-8}$  Ry. Geometry optimizations were performed employing the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm (for stress minimization) and total forces acting on each ion were minimized to reach less than  $1 \times 10^{-3}$  Ry/a.u. by movement of the ionic positions.

### 2.2. The model of GO and GOH

Prior to the investigation of oxidized and reduced structures and with comparative purposes, it was necessary to study graphene sheets and graphite structures. The graphene sheet was simulated with a unit cell with  $z = 2$  nm, so that the plane and its image did not interact; this was done to minimize the C–C distance. In the case of graphite, the structure was composed of stacking sheets of graphene in AB disposition. In order to determine the optimum interlayer distance between graphene sheets, the energy vs. distance was assessed.

The GO and GOH structures were represented by means of a unit cell with two carbon sheets of 32 C atoms each, stacked in an AB arrangement as in the case of graphite. The unit cell was tetragonal ( $0.986 \times 0.854 \times z$ )nm<sup>3</sup> with periodic boundary conditions in the x,y,z coordinates and the z value was equal to twice the interlayer distance ( $d$ ). This distance was a function of the O/C ratio.

For GO structures different amounts of epoxy (–O–) and hydroxyl (–OH) groups were randomly arranged to represent amorphous oxides, as it was proposed by Liu et al. [17]. In this work we considered four different amorphous oxides, with a ratio of 2 between functional groups, which are within the

**Table 1 – Molecular formula, oxygen/carbon ratio and values of layer adhesion energy of the carbon structures simulated. The average value of the angle between carbon atoms and the hydroxyl group are displayed in the last column.**

Substrate	Molecular formula	O/C content	$E_{\text{adhesion}}$ [J/m <sup>2</sup> ]	Angle O–C–C [°]
Graphite	C <sub>64</sub>	0.00	–0.31	–
GOH1	C <sub>64</sub> (OH) <sub>6</sub>	0.09	–0.31	108.2
GOH2	C <sub>64</sub> (OH) <sub>12</sub>	0.19	–0.51	107.3
GOH3	C <sub>64</sub> (OH) <sub>18</sub>	0.28	–0.69	108.2
GOH4	C <sub>64</sub> (OH) <sub>24</sub>	0.38	–1.89	107.9

<sup>2</sup> The 2017 DOE target for a promising Hydrogen Storage Material (HSM) is that it should be able to contain a gravimetric density of about 5.5 wt% hydrogen, volumetric capacity of 0.040 kg H<sub>2</sub> L<sup>–1</sup> and should be able to reversibly absorb/desorb H<sub>2</sub> in the temperature range of –40 to 60 °C and moderate pressures (min. 5 bar max. 12 bar). [http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets\\_onboard\\_hydro\\_storage.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf).

Download English Version:

<https://daneshyari.com/en/article/1270529>

Download Persian Version:

<https://daneshyari.com/article/1270529>

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