

Available online at www.sciencedirect.com

ScienceDirect

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

Interaction of hydrogen in carbon matrix with impurities of nickel. Effects of spin fluctuation

J.L. Gervasoni^{a,b}, S. Segui^{a,b,*}

^a Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, 8400 S C de Bariloche, Río Negro, Argentina

^b CONICET, Argentina

ARTICLE INFO

Article history:

Received 21 October 2013

Accepted 17 November 2013

Available online 27 December 2013

Keywords:

Hydrogen storage

Carbon materials

Nickel impurities

ABSTRACT

This work aims to define general criteria to allow theoretical and experimental design of new materials with high hydrogen content, with a view to their potential application as moderators in reactors at high temperatures and hydrogen storage materials.

To this end we study the effects of nickel impurities on the properties of pure carbon (slabs as well as nanoparticles and gels) in order to analyze the thermodynamical characteristics, and improve the behavior of alloys for Ni-metal hydride rechargeable batteries. These elements are chosen because they have a wide range of solubility of hydrogen, which from the technological point of view makes them important candidates in the search for new materials. Our results show that this kind of carbon material could be used as support for hydrogen storage improving the screening charge density and the density of available states, as analyzed by the authors in previous works.

Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

New concepts in energetic implementation tend to greater efficiency and better use of fuel, minimizing negative residuals. In this context, hydrogen is a possible substitute for fossil fuels as an energy carrier with zero emissions. However, its use present some limitations that must be overcome, and considerable effort is being devoted to solve them. One of the most important problems is the storage of hydrogen in adequate systems, due to its extreme mobility within a solid. A promising alternative is the use of porous carbon materials, which have proved to be most suitable for storing hydrogen by adsorption under laboratory conditions. Nevertheless, the storage capacity of such materials worsens at moderate conditions of temperature and pressure [1,2], and must be

modified to improve the interaction of hydrogen with the carbon surface.

Recent studies show that the presence of certain metals in porous carbon systems would increase its hydrogen storage capacity [3]. Such a compound could improve the overall kinetic properties besides combining hydride storage capacity with a total weight reduction of the system, due to the slight carbon matrix. However, the effect of the nature of the carbon material and the type of metal doping needs to be studied in order to optimize the final properties of the doped system [4–6].

In this work, we intend to contribute to the understanding of critical issues related to the storage of hydrogen within stable carbon structures. To this end, we investigate the effects of hydrogen on the physical properties of carbon slabs with nickel impurities, both magnetic and non-magnetic, and compare the results with those obtained for pure carbon slabs.

* Corresponding author. Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, 8400 S C de Bariloche, Río Negro, Argentina. Tel.: +54 2944 445118; fax: +54 2944 445299.

E-mail address: segui@cab.cnea.gov.ar (S. Segui).

0360-3199/\$ – see front matter Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved. <http://dx.doi.org/10.1016/j.ijhydene.2013.11.069>

2. Theoretical description

Given the complexity involved in the study of metal-hydrogen systems, its interactions are studied using different models. One of them, based on the density functional formalism [7,8] is the so called jellium model [9], wherein the metal is replaced by a uniform electron gas plus a background of positive charges with the same average density, maintaining the neutrality of the metal. The most important characteristic parameter of this model is the radius of the volume occupied by an electron in the jellium, r_s [10]. Since each atom contributes Z electrons, the number of electrons per cubic centimeter is given by:

$$n_0 = 0.6022 \times 10^{24} Z \frac{\rho_m}{A} = \frac{N}{V} \quad (1)$$

Then:

$$r_s = \left(\frac{3}{4} \pi n_0 \right)^{-\frac{1}{3}} \quad (2)$$

Moreover, as r_s is a measure of the electronic density, it can be calculated from the bulk modulus (B) of the material, given by the inverse of the electron density compression in the interstitial positions [11].

$$B = \frac{1}{K} = V \frac{\partial P}{\partial V} \quad (3)$$

With r_s obtained in this way, it is possible to calculate one of the most important physical properties of the metal system – hydrogen: the induced charge density $\Delta n(r)$ or equivalently, the integrated charge density, $Q(r)$:

$$\Delta n(r) = -\frac{1}{4\pi r^2} \frac{d}{dr} Q(r) \quad (4)$$

Once the induced charge density is obtained, we can calculate various macroscopic properties of the system, such as: solution volume (V_H), the heat of solution (ΔH) and the induced density of states (IDOS).

The volume of the solution is an important property because it determines the changes in the mechanical properties of the material and the best positions for dissolution of hydrogen (vacancy defects or interstitial positions). This is defined as [11]:

$$v_h = \frac{V_H}{Q} = -\frac{1}{B} \sum_i \frac{1}{3} \frac{R_i}{Q} \frac{\partial E}{\partial R_i} \quad (5)$$

According to the Hellmann–Feynman theorem [12], the change of energy ∂E is given by the electrostatic interaction between the electronic density of the material and the impurity of charge Z_0 at $r = 0$:

$$\partial E = \sum_i Z_i \left(\int \frac{\Delta n(r) - Z_0 \delta(r)}{|r - R_i|^3} (R_i - r) d^3r \right) \partial R_i \quad (6)$$

Another fundamental property that results from the induced charge density is the heat of solution ΔH (at infinite dilution, which takes into account the interaction between the electron density of the material and the hydrogen), which is different from the heat of formation, which is a thermodynamic experimental quantity. The latter refers to the stability

of the hydrides, i.e. the energy to be given to the hydrogen atoms to diffuse through the network and as a hydride. Through effective jellium model, we calculate ΔH of the system as the total energy change ΔE (at a temperature of 0 K and pressure of 0 atm) in the dissolution of a hydrogen atom in terms of density functional theory [9,10]. The energy shift is given by:

$$\Delta E_{\text{system}} = \Delta T + \Delta E_e + \Delta E_{\text{exc}} \quad (7)$$

T is the kinetic energy of non-interacting electron gas in the metal host, ΔE_e is the classical electrostatic energy and ΔE_{exc} is the correlation and exchange energy. Once obtained ΔE_{system} it is possible to calculate the value of the heat of solution:

$$\Delta H = [\alpha \Delta E_{\text{system}} + \beta] \text{ [eV]} \quad (8)$$

where: $\alpha = -2.4$ kJ/molH eV y $\beta = -34.92$ kJ/molH [13].

Finally, as a starting point for understanding the electronic properties of the interaction between hydrogen and the host metal, we analyze the IDOS. According to the parameterization made in Refs. [13], its expression can be described by partial contribution of k_i : the analytical expression for Δg , valid in the range $0 < k < k_F$, can be written as the sum of the partial contributions of:

$$\Delta g \left(\frac{k}{k_i}; l \right) = \Delta g_0 + A_s \tanh(\omega x_0) + A_s \tanh[\omega(x - x_0)] \quad (9)$$

where we have defined $x = k/k_F$, with k_F the Fermi wave vector (see the section [Nomenclature](#)).

3. Results

Using the jellium density functional formalism [7,8] we calculate the induced density charge and the charge density integrated at zero temperature and pressure (ground state). These quantities are plotted as a function of the distance of the impurity (H atom) to two systems: the pure carbon and carbon with a nickel impurity. First of all we put a nickel impurity in the carbon jellium (i.e. nickel impurity is part of a new jellium with other charge density or parameter r_s). In this position we introduce a hydrogen atom, but as an external impurity. This is outlined in [Fig. 1](#).

We use this induced charge density in [Eq. \(6\)](#) in order to calculate V_H ([Eq. \(5\)](#)). The calculation of the volume of solution of hydrogen in the matrix using the jellium model was made taking into account the following considerations: the system is in the fundamental state, the hydrogen in the matrix is very dilute, and deformation caused by the dissolution of the hydrogen atom in the crystal lattice is homogeneous and isotropic.

The heat of solution at infinite dilution ΔH , calculated using [equation \(8\)](#), yields a value of 46.52 kJ/molH, which is about three times the value found in the literature [14,15]: 15.33 kJ/molH. Adding an impurity of nickel, this value is close to the experimental one. The persistent difference may be due to the fact that, while the model takes into account the change in energy ($\Delta E = E_F - E_{\text{system}}$) in a ground state, the experimental values were determined in a wide range of

Download English Version:

<https://daneshyari.com/en/article/7719658>

Download Persian Version:

<https://daneshyari.com/article/7719658>

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