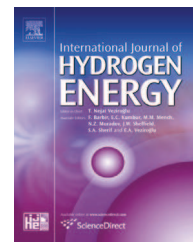Available online at www.sciencedirect.com

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

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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.

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.

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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:

$$n_0 = 0.6022 \text{x} 10^{24} Z \frac{\rho_m}{A} = \frac{N}{V} \qquad (1)$$

Then:

$$r_s = \left(\frac{3}{4} \pi n_o \right)^{\frac{1}{3}} \qquad (2)$$

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].

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

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):

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

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]:

$$v_h = \frac{V_H}{\Omega} = -\frac{1}{B} \sum \frac{1}{3} \frac{R_i}{\Omega} \frac{\partial E}{\partial R_i} \qquad (5)$$

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 $r = 0$:

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

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:

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

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:

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

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_l: the analytical expression for Δg, valid in the range $0 < k < k_F$, can be written as the sum of the partial contributions of:

$$\Delta g \left(\frac{k}{k_l}; l \right) = \Delta g_o + A_s \tanh(\omega x_o) + A_s \tanh[\omega(x - x_o)] \qquad (9)$$

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 ($\Delta E = E_F - E_{system}$) in a ground state, the experimental values were determined in a wide range of

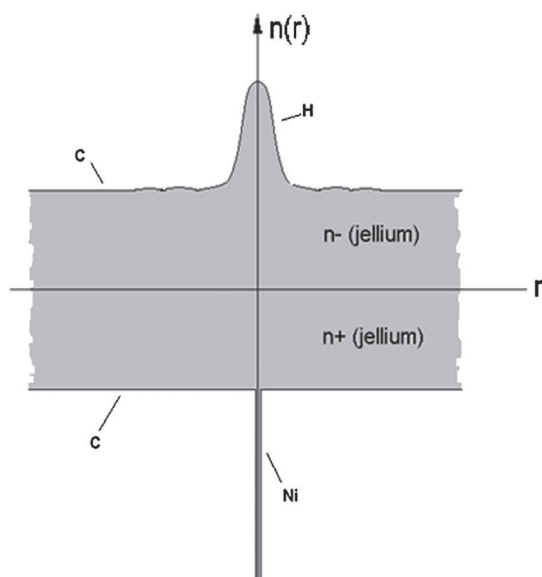Fig. 1 – Scheme of the model.

Fig. 2 – Induced density of states (IDOS) of hydrogen, with and without Ni, at zero spin value.

temperature on liquid phase. Table 1 shows the obtained theoretical values compared with available experimental results.

Using the parameters proposed in [13], we obtained the induced density of states, IDOS, which is shown in Fig. 2. Note that more energy must be given to introduce hydrogen in the jellium carbon plus the impurity of nickel, as obtained from the calculations. On the other hand, the presence of nickel impurity in carbon jellium is energetically more favorable for the presence of hydrogen, as shown in the figure. This number shows that the C–Ni interaction is of ionic character, which is in accordance with more sophisticated models [14].

Finally, we calculate the valence potential taking into account the fluctuations of local order in this system. Maintaining higher order than linear terms (classical approximation) in the screening charge density, and introducing spin–spin interactions via perturbation method, we examine the behavior of the valence potential (due to the jellium fluid), comparing the results obtained with zero spin, and in the framework of the spin assumption. We observe a clear difference between these two systems, as shown in Fig. 3, due to this magnetic jellium presents an intrinsic anisotropy, besides the presence of hydrogen.

4. Conclusions

We have performed density functional calculations to investigate the effect of hydrogen on amorphous carbon diffusion with an impurity of Ni on the surface.

We have obtained thermodynamical (heat of solution and volume of hydrogen) and electronic properties (IDOS) and compared them with those of a pure carbon jellium. Electronic contribution of Ni to the jellium matrix is connected to an increase in the density of electrons in the electron gas, due to the strong electron "donate". We verify that the addition of nickel in the carbon matrix acts as a anchor for the hydrogen, making it more difficult to diffuse.

In addition, we have studied the influence of non-zero spin in this system. The most appropriate techniques in this field are the study of the dielectric properties and NMR (nuclear magnetic resonance) for observing spin-lattice relaxation. However, we were able to highlight the magnetic character of the system using the jellium model, starting from the behavior of valence potential of the total system. From this point, it is necessary to review the basic assumptions of the theory of NMR in order to extend its scope to complex problems such as those of anisotropic fluids.
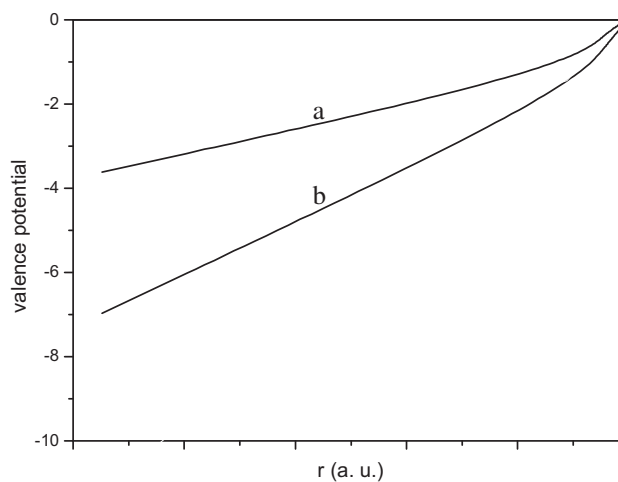

Fig. 3 – Valence potential for the treated system, (a) with spin and (b) without spin value.

Table 1 – Values of thermodynamical properties.		
Sample	V_H [a.u.]	ΔH [kJ/molH]
$C_{jellium}$	7.93	46.52
C + Ni	3.42	12.74

Therefore, the system studied in this work is a potential candidate in intermetallic alloys for technological applications due to the large number of applications that can be done with them (for example in the manufacture of displays, in medicine, biology, etc.).

Acknowledgments

Nomenclature

Avogadro number 0.6022×10^{24}, atom/mol

ρ_m/A	mol per cubic centimeter
Z	electronic number
Ω	atomic volume of the material
B	bulk modulus
∂R_i	strain at the positions (R_i) of metal ions
Z_i	effective charge of the ion at R_i
$x = k/k_F$	k: impulse vector, k_F: Fermi vector
$\Delta g_0, A_s, \omega$	parameters of rational functional forms

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