

ON THE USE OF THE UNIQUE RODRIGUEZ-BAKER DATA FOR THE HYDROGEN ON-BOARD STORAGE IN GRAPHITE NANOFIBERS

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Introduction

As is noted, for instance, by Hirscher M, et al. [1], there is the anomalous scattering and non-reproducibility of the known experimental data on the hydrogen gravimetric capability in carbon nanofibers and nanotubes (3 orders of magnitude, if the unique Rodriguez-Baker data [2] are included, and 2 orders, if without them), while there is a 'normal' scattering (within one order of magnitude) – for metallic hydrides (practically, in studies of the same researches).

According to our feeling, the main reasons of such a large difference in the results are related with a larger spectrum of the structure and the sorption process peculiarities for the carbon nanomaterials (in comparison with the metallic hydrides), depending on the regimes of their synthesis, pre-treatment and hydrogenation, and also on their composition (particularly, with respect to metallic catalysts). Some additional aspects can be considered, as well.

In this connection, some new significant results on diffusion, sorption and storage of hydrogen in graphites and novel carbon nanomaterials are discussed, which have been obtained on the basis of the thermodynamic analysis [3-7] of some known experimental data, and their comparison with the theoretical data [8] ('*ab initio*' molecular orbital (MO) studies of chemisorption of hydrogen atoms on graphite).

Results and Discussion

According to analysis [4-7], in many cases the main processes of hydrogen desorption both in an isotropic graphite [9] (TPD peaks I, II, III, IV) and in novel carbon nanomaterials with sp^2 hybridization can be characterized as trapping-with-diffusion rate-controlled processes with the diffusion activation enthalpies of $Q_I \approx 20$ kJ/mol ($H_{2(ads)}$), $Q_{II} = 120$ kJ/mol ($H_{2(ads)}$), $Q_{III} = 250$ kJ/mol ($H_{(abs)}$), $Q_{IV} \approx 365$ kJ/mol ($H_{(abs)}$), corresponding to the related desorption enthalpies (due to the reversible diffusant trapping by carbon chemisorption "sites"). The entropy (frequency) factors of the hydrogen diffusion coefficients in these materials have also been determined [4-7]: $D_{0I} \approx 0,003$ cm²/s, $D_{0II} = 1800$ cm²/s, $D_{0III} \approx 0,007$ cm²/s, $D_{0IV} \approx 600$ cm²/s.

TPD peak III in the isotropic graphite [9] is related with a dissociative chemisorption of H₂ gas molecules on carbon chemisorption sites localized in graphene layers in grains-crystallites, and corresponding to potential "HC- molecules" (within model 'F' [8], sp^3

rehybridization). The total process III is described by an absorption isotherm of the Sieverts-Langmuir type:

$$\left(\frac{X_{III}}{X_{III\text{m}}}\right) = K_{III}(P_{\text{H}_2}/P^0_{\text{H}_2})^{1/2}/[1+K_{III}(P_{\text{H}_2}/P^0_{\text{H}_2})^{1/2}], \quad (1)$$

$$K_{III} = \exp(\Delta S_{III}/R)\exp(-\Delta H_{III}/RT), \quad (2)$$

where $P^0_{\text{H}_2} = 1$ Pa, the absorption enthalpy of $\Delta H_{III} = -19$ kJ/mol ($H_{(\text{abs.})}$); the absorption entropy of $\Delta S_{III} \approx -(14,7-15,4)R$; the largest potentially possible concentration of hydrogen atoms (H/C) in graphene layers of $X_{III\text{m}} = 0,5-1,0$, that is close to the hydrogen content in "a carbohydride-like bulk phase".

The process (III) includes the first stage (1) of hydrogen molecules dissociation to atoms with enthalpy of $\Delta H_{(1)} = 228$ kJ/mol ($H_{(\text{gas})}$), the second stage (2) of hydrogen atoms dissolution between graphene layers with $\Delta H_{(III2)} \approx 0$, and the third stage (3) of hydrogen atoms chemisorption on "HC-sites" with $\Delta H_{(III3)} = -247$ kJ/mol($H_{(\text{abs.})}$); $\Delta H_{III} \approx (\Delta H_{(1)}+\Delta H_{(III3)})$. Thus, TPD peak III in graphite [9] is related with the trapping-with-diffusion of hydrogen atoms in grains-crystallites, with the reversible diffusant trapping (chemisorption) by "HC-sites" in graphene layers; $Q_{III} \approx -\Delta H_{(III3)}$.

According to analysis [4-7], the concentration of hydrogen absorbed in graphene layers (TPD peak of III type) in nanostructured graphite (S. Orimo et al. (1999-2003), [10]) and in graphite nanofibers (N.M. Rodriguez, R.T.K. Baker et al. (1997-1999), [2]) can be close to the largest possible ("carbohydride-like") values ($X_{III\text{m}}$).

The sorption capability of TPD peak of III type in carbon nanofibers and mechanically prepared nanostructured graphite charged under $P_{\text{H}_2} = 1-10$ MPa and room temperatures can be close to the values ($X_{III} \approx 0.5-0.8$), corresponding to the technical targets for hydrogen storage on-board fuel cell-powered vehicles; however, the near-zero "reversibility" (i.e., a very sluggish diffusion kinetics) of the process is not acceptable.

Ab initio MO calculations [8] (model 'F') give the chemisorption energy of hydrogen atoms in the graphene layers of about -195 kJ/mol (H_{abs}), i.e., the absolute value is considerably less than for $\Delta H_{(III3)}$. It points to the necessity of the further theoretical (as [11, 12]) and experimental studies (in the light of [4-7]) of this contradiction, that has a significant importance in the connection with the graphene structure of carbon nanotubes and nanofibers.

TPD peak IV in isotropic graphite [9] is related with a dissociative chemisorption of H_2 gas molecules on 'armchair' and/or 'zigzag' edge carbon sites localized mainly near the grain boundary regions and corresponding to potential "HC-like molecules" (within model 'C' and/or 'D' [8], sp^2 hybridization). The total process (IV) is described [4-7] by a sorption isotherm of the Sieverts-Langmuir type (1), with $\Delta H_{IV} \approx -140$ kJ/mol ($H_{(\text{abs.})}$); $\Delta H_{(IV3)} \approx (\Delta H_{IV} - \Delta H_{(1)}) \approx -Q_{IV}$. The sorption capacity and the diffusion kinetics ("reversibility") of this peak at room temperatures and technological pressures do not satisfy to the hydrogen vehicles target values.

TPD peaks II and I in isotropic graphite [9] are related with a dissociative-associative chemisorption of H₂ gas molecules on carbon sorption sites localized in the regions of grain-crystallites boundaries and boundaries (interfaces) of graphite filler grains, and corresponding to potential "H₂C-molecules" (within model 'H' [8] of 'zigzag' edge sp³ rehybridization sites (for TPD peak II) and model 'G' [8] of 'armchair' edge sp³ rehybridization sites (for TPD peak I), and also (another variant for peak I) - to potential "H₂C₂-molecules" (within model 'F' [8] of sp³ rehybridization in graphene sites). The total process is described [4-7] by a sorption isotherm of the Henry-Langmuir type:

$$((X/X_m) = K(P_{H_2}/P^0_{H_2})/[1+K(P_{H_2}/P^0_{H_2})], \quad (3)$$

$$K = \exp(\Delta S/R)\exp(-\Delta H/RT), \quad (4)$$

with adsorption enthalpies and entropies values of $\Delta H_{II} \approx -Q_{II}$, $\Delta H_I \approx -Q_I$, $\Delta S_{II} \approx -31R$, $\Delta S_I \approx -23R$, and the largest potentially possible concentrations (H₂/C_{loc}) close to the hydrogen content in "a carbohydride-like adsorbed phase". TPD peaks II and I are related with the trapping-with-grain boundary diffusion of hydrogen molecules, with reversible trapping (chemisorption) of the diffusant by "H₂C(H₂C₂) sites"; the apparent activation enthalpies of the hydrogen diffusion can be close to the desorption enthalpies.

The sorption capabilities (H/C_{tot}) of TPD peaks of II and I types in carbon nanostructures ($2\gamma_{II}X_{II}$ and $2\gamma_I X_I$, with γ_{II} and γ_I being the volume fractions of the sorption regions) can be close to the values (~0.8), corresponding to the technical targets for hydrogen storage on-board fuel cell vehicles; however, the near-zero "reversibility" (the diffusion kinetics) of the II type peak is not acceptable, and moreover, the nature, characteristics and conditions of the manifestation of the I type peak in carbon nanotubes and nanofibers have been insufficiently studied.

A specific physical (or physicochemical) multilayer hydrogen adsorption, with an anomalous high sorption capacity and adsorbate packing density ("peak V"), seems to be possible in graphite nanofibers (N.M. Rodriguez, R.T.K. Baker, et al. (1997-1999), [2]), which (according to analysis [4-7]) could be "decorated" with "the carbohydride-like phases" (TPD peaks of the II and III types). There are serious reasons [4-7] to suppose that the sorption capacity and "reversibility" (the diffusion kinetics) of this nearly unstudied process ("peak V") can satisfy to the technique requirements for the hydrogen on-board storage in fuel cell-powered vehicles.

On chemiadsorption and chemiabsorption of hydrogen by isotropic graphite, mechanically nanostructured graphite and graphite nanofibers

As is noted by Murata K, et al. [13], one of the main reasons for the negative discussion of the anomalous scattering and non-reproducibility of some known experimental data on the hydrogen gravimetric capability in carbon nanofibers and nanotubes is confusion in the gas storage concepts: physical adsorption, chemisorption, absorption and occlusion. As is also noted by them [13], physical adsorption and chemisorption are

surface phenomena, and in absorption and occlusion, the material taken up is distributed through the body (bulk) of the absorbent.

According to our feeling, some additional aspects (concepts) must be taken into account on evaluating the storage capacity, as follows [4-7, 11].

1. Absorption (in the sense of a true bulk solubility) can be attributed with the thermodynamic characteristics of the gas (adsorbat) interaction with the normal lattice of the absorbent, and it can be of a chemical nature; a situation of a dissociative chemiabsorption has obviously place for hydrogen sorption processes, corresponding to TPD peak of # III type in isotropic graphite, mechanically nanostructured graphite and graphite nanofibers.

2. Adsorption (especially, of a chemical nature) can be attributed with the thermodynamic characteristics of the gas interaction with the free surface regions (nanolayers), both external and internal ones (as pore and cavity surfaces), grain boundary regions (nanolayers) or near dislocation nanoregions in the adsorbent bulk; a situation of a dissociative-associative chemiadsorption has obviously place for processes, corresponding to TPD peaks of # II type in the three materials mentioned above.

3. The sorption process, corresponding to the extremely anomalous 'peak' # V in the Rodriguez-Baker graphite nanofibers, might be related with a specific physico-chemical hydrogen adsorption [4-7], that is a subject of further studies.

On the nature of the catalyst activity of nanostructured graphite, under ball milling in hydrogen molecular gas atmosphere

As has been mentioned above, thermodynamic and diffusion characteristics of two hydrogen desorption processes (similar to the processes of TPD peaks # II and # III) are obtained from the Orimo S, et al. data (1999-2003), [10] on mechanically prepared nanocrystalline graphite charged at $P_{H_2} = 1$ MPa and about 300 K (under the ball milling). It's necessary to emphasize the result [4-7], that the concentrations of both the chemiabsorbed and the chemiadsorbed hydrogen in the mechanically nanostructured graphite are of the same order as the largest possible (carbohydride-like) values and correspond to the extrapolated (equilibrium) values, those are obtained by the use of the isotherms noted above (for TPD peaks # II and # III).

Hence, it follows that the catalyst activity of the ball milling graphite results in the sufficiently fast kinetics of the intermediate step of H_2 dissociation, which occurs over the carbon catalyst. Such a high catalyst activity of the milling graphite is obviously caused by a high stationary concentration of the lattice defects in the material [14]; some of them are attributed with the formation of the dangling C-C sp^2 edge bonds of the zigzag-like or armchair-like types. The nature of the catalyst activity of the ball milling graphite is revealing by the comparison of the absolute values of the H_2 dissociation energy and the adsorption (absorption) energies of atomic hydrogen on the different carbon sites (C-H, C-2H bonds energies), and especially on the sites related with the deformation lattice defects (in the deforming graphite).

On the nature and characteristics of hydrogen apparent diffusivity and solubility in graphites, including neutron- or ion-irradiated ones, and in implant, *a-C:H* and plasma exposed films

According to our feeling with respect to a lot of the corresponding experimental and theoretical data of different researchers (1989-2003), the hydrogen isotopes' apparent and true diffusivity and solubility characteristics and their nature in isotropic, pyrolytic, porous graphitic carbons and different modifications of carbonaceous materials, including neutron- or ion-irradiated and plasma exposed ones, in many cases can be described and interpreted on the basis of using the results [4-7] on thermodynamic and diffusion characteristics of hydrogen behavior in some isotropic and pyrolytic carbon structures.

Such new results could be also important "for optimizing and understanding the interaction between hydrogen and carbon materials" (formulated by A.C. Dillon, M.J. Heben et al. (2001-2002), [15]).

Conclusions

Thermodynamic analysis [4-7] of some known data on hydrogen sorption in by novel carbon nanomaterials allows us to suppose that the anomalous large scattering (up to three orders of the magnitude) in the experimental values of the hydrogen capacity at room temperatures and the technological pressures in the studies of different authors is mostly related with faintly studied physicochemical aspects (processes).

The presented results [4-7] are mainly of the conceptual and methodological significance, and they can serve as an effective basis both for the further fundamental and technological developments on using novel carbon nanomaterials in the field of hydrogen energy for vehicles.

There is a real possibility of revealing the true Rodriguez-Baker regimes of hydrogenation and/or synthesis of graphite nanofibers, providing the manifestation of the anomalous 'peak V', and their use for a radical solution of the urgent problem of the hydrogen on-board storage – a bottle neck in constructing fuel cell-powered non-pollution vehicles.

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References

[1] Hirscher M, Becher M, Haluska M, Chen X, Dettlaff-Weglikowska U, Roth S. Hydrogen storage in carbon nanostructures. Abstracts, MH2002 (International Symposium on Metal-Hydrogen Systems), Annensi, France; 2002, 29.

- [2] Park C, Anderson PE, Chambers A, Tan CD, Hidalgo R, Rodriguez NM. Further studies of the interaction of hydrogen with graphite nanofibers. *J. Phys. Chem. B* 1999; 103:10572-10581.
- [3] Nechaev YuS. Characteristics of the hydride-like segregation of hydrogen at dislocations in palladium. *Physics Uspekhi (Progresses of Physical Sciences)* 2001;171: 1251-1261.
- [4] Nechaev YuS, Alexeeva OK. On the nature, capability and reversibility of hydrogen storage in novel carbon nanomaterials for mobile power units. *Int. J. Hydrogen Energy* 2003;28:1433-1443.
- [5] Nechaev YuS, Alexeeva OK. Characteristics of five desorption peaks for hydrogen in graphite and novel carbon nanostructured materials, in the connection with the on-board storage problem. *Transactions of EHEC-2003, Grenoble, France; 2003, (CO2-43)*.
- [6] Nechaev YuS, Alexeeva OK, Hirschberg JG, Veziroglu TN. On the physico-chemical foundations and perspectives of using novel carbon-based nanomaterials for the hydrogen on-board storage. *Transactions of the HYPOTHESIS V, Porto Conte, Italy; 2003*.
- [7] Nechaev YuS, Alexeeva OK. Thermodynamic analysis of hydrogen sorption by carbon-based materials. *Chemistry Uspekhi (Progresses in Chemistry); 2004*.
- [8] Yang FH, Yang RT. Ab initio molecular orbital study of absorption of atomic hydrogen on graphite: insight into hydrogen storage in carbon nanotubes. *Carbon* 2002; 40:437-444.
- [9] Atsumi H, Tokura S, Miyake M. Absorption and desorption of deuterium on graphite at elevated temperatures. *J. Nucl. Mater.* 1988;155-157:241-245.
- [10] Orimo S, Matsushima T, Fujii H, Fukunaga T, Maier G. Hydrogen desorption property of mechanically prepared nanostructured graphite. *J. Appl. Phys.* 2001;90: 1545-1549.
- [11] Stojkovic D, Zhang P, Lammert PE, Crespi VH. Collective stabilization of hydrogen chemisorption on graphenic surfaces. *Physical Review B* 2003;68:195406-1-195406-5.
- [12] Volpe M, Cleri F. Chemisorption of atomic hydrogen in graphite and carbon nanotubes. *Surface Science* 2003;544:24-34.
- [13] Murata K, Kaneko K, Kanoh H, Kasuya D, Takahashi K, Kokai F, Yudasaka M, Iijima S. Adsorption mechanism of supercritical hydrogen in internal and interstitial nanospaces of single-wall carbon nanohorn assembly. *J. Phys. Chem. B* 2002;106: 11132-11138.
- [14] Nechaev YuS. On the micromechanisms of amorphization of metallic materials. *Transactions (Izvestija) of the Russian Academy of Sciences, Physical Series* 2001;65: 1399-1406.
- [15] Dillon AC, Heben MJ. Hydrogen storage using carbon adsorbents: past, present and future. *Appl. Phys. A* 2001;72:133-142.
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