EVALUAREA EXPERIMENTALĂ A INFLUENȚEI DOPĂRII MATERIALELOR CARBONICE CU METALE TRANZIȚIONALE ÎN PRIVINȚA CAPACITĂȚII LOR DE STOCARE A HIDROGENULUI

EXPERIMENTAL ASSESSMENT OF THE INFLUENCE OF TRANSITIONAL METAL DOPING ON CARBONIC MATERIALS REGARDING THEIR HYDROGEN STORAGE CAPACITY

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The experimental investigation of hydrogen adsorption capacity in Ruthenium doped nano-structured carbonic materials, by using two methods has been carried out within this paper. It is well known that carbonic materials along with metal hydrides are considered to be one of the most promising materials to be used for hydrogen storage by using adsorption method, specifically based on "spill-over" phenomena. These materials have different applications and one of the most important is considered to be fuel cells technology for mobile applications, namely onboard automotive hydrogen storage. By using transitional metals in order to dope carbonic materials, their adsorption capacity increases, thus approaching "the target" of 4,5% weight ratio of H_2 adsorbed in a substrate, according to US Office Of Energy Efficiency And Renewable Energy [1]. Within this paper carbon based nanomaterials: multi-wall nanotubes (MWNT) and poly-aniline (PANI) have been used as substrates for Ruthenium doping and their hydrogen storage capacity has been determined. PANI has been firstly prepared and after that doped in laboratory, while MWNT have been purchased from the market and afterwards doped in laboratory. The doping procedure consists of a physical-chemical method which involves Ru salts and the use of ultrasounds in order to activate the carbon based substrate for doping.

The adsorption and storage capacity of carbonic materials has been determined by using spill-over phenomena in a PCT Pro-User apparatus, provided by SETARAM and also calculated from cyclic voltametry, by using VoltaLab-40 apparatus. In order to investigate the adsorption capacity of the nano-structured carbonic materials, the experiments have been carried out at different pressures (ranging from 10 to 30 bar). Both substrates have been characterized in order to determine their porosity, BET surface and XRD before and after doping. Lucrarea de față prezintă investigarea experimentală prin două metode a capacității de adsorbție a hidrogenului a unor materiale carbonice nanostructurate dopate cu Ruteniu. Este bine știut că materialele carbonice alături de hidrurile metalice sunt considerate a fi unele dintre cele mai promițătoare materiale care pot fi folosite pentru stocarea hidrogenului prin adsorbție, în special datorită fenomenului de "spill-over". Aceste materiale au diferite aplicații, iar una dintre cele mai importante este considerată a fi tehnologia celulelor de combustibil pentru aplicații mobile, respectiv stocarea hidrogenului la bordul autovehiculelor.

Prin folosirea metalelor tranziționale pentru a dopa materialele carbonice, capacitatea de stocare a acestora din urmă va crește, astfel putând ajunge la "ținta" de 4,5 % procent masic de hidrogen adsorbit în substrat, conform celor declarate de Biroul American pentru Eficiența Energetică și Energii Regenerabile [1]. În cadrul lucrării, nanomateriale pe bază de carbon, respectiv nanotuburi de carbon cu pereți multipli (MWNT) și polianilina (PANI) au fost folosite drept substrat pentru doparea cu Ruteniu, iar apoi le-a fost determinată capacitatea de stocare a hidrogenului. PANI a fost mai întâi preparată în laborator și apoi dopată cu Ru, în timp ce MWNT folosite au fost de tip comercial și au fost doar dopate în laborator. Procedura de dopare constă într-o serie de procese fizico-chimice care implică săruri de Ru și utilizarea ultrasunetelor pentru pregătirea substratului în vederea dopării.

Capacitatea de adsorbție și stocare a hidrogenului a materialelor carbonice a fost determinată într-un aparat PCT Pro User (SETARAM) care folosește fenomenul de "spill-over" dar a fost și calculată din voltamograme prin utilizarea voltametriei ciclice cu ajutorul unui aparat VoltaLab-40. Pentru a studia capacitatea de adsorbție a materialelor carbonice nanostructurate, experimentele au fost efectuate la diferite presiuni: 10, 20 și 30 bar. Ambele tipuri de materiale au fost investigate din punct de vedere structural, respectiv porozitate, suprafața specifică BET și "RD înainte și după dopare.

Keywords: Hydrogen adsorption, weight ratio, doped carbonic materials, poly-aniline, and carbon nanotubes.

1. Introduction

Interest of hydrogen as a fuel has grown dramatically since 1990. It can be made available on-board vehicles in containers of compressed or liquefied H₂, in metal hydrides via chemical storage

or by gas-on-solid adsorption. Gas-on-solid adsorption is an inherently safe and potentially high energy density hydrogen storage method that could be extremely energy efficient. Current technologies used for hydrogen storage include high pressure compression at about 70 MPa, liquefaction at

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cryogenic temperatures (20 K) and adsorption into solid state compounds. Among the three types of hydrogen storage technologies, the storage of hydrogen in solid state compounds appears to be the most feasible solution since it is safer and more convenient compared to the other ones [2]. The research carried out within the current paper refers to the hydrogen storage using gas-on-solid adsorption method.

Even though inter-metallic compounds such AB5 (e.g. - LaNi5), AB (e.g. - TiFe), AB2 (e.g. -ZrV₂), A₂B (e.g. - Ti₂Ni), AB₃ (e.g. - LaNi₃) types [2] or AB₄ (e.g. - VH₄) [3] or A₄BC (e.g. - Mg₄NiPd) [5] are heavily designed, obtained and characterized, recently new carbon nano-structured adsorbents have been produced (graphite nanofibres, single and multi-wall carbon nanotubes, graphenes) [4]. In this study [5], the authors are investigating a hybrid molecule by using a combination of molecular dynamics and Grand Canonical Monte Carlo simulation in order to determine the hydrogen storage capacity in carbon nanostructured adsorbents. Pure graphene sheet, N-doped graphene sheet and Pd-doped graphene sheet are used for the investigation, concluding that the insertion of Pd nanoparticles within the graphene sheets could increase the adsorption capacity of adsorbents [6]. The doping procedure by using transitional metals proves to be the most efficient in terms of increasing the hydrogen adsorption capacity of nanostructured carbonic materials. Thus, yttrium doped graphenes were studied within [7] and it was predicted that yttrium attached atoms on graphene surface can absorb up to 9% molecular hydrogen.

Thus, given the relative high price of rare earth metals and/or graphene sheets, cheaper materials are tested as carbon based substrates for hydrogen storage.

Carbon nanotubes possess a unique hollow tubular structure, large surface area and desirable chemical and thermal stability [8]. Generally, activated carbons are ineffective in storing hydrogen because only a small fraction of the pores in the typically wide pore size distribution are small enough to strongly interact with hydrogen molecules at room temperature and moderate pressures. The nanotubes have a great advantage as they are one of the strongest materials known despite being only 1 atomic layer thick. According to the theoretical calculations, carbon nanotubes, in this configuration, should be able to withstand 2 GPa of hydrogen pressure before they start to leak. Even storage at 1 GPa corresponds to a weight storage efficiency of 9% [9].

It has been observed that the hydrogen storage capacity of nano-structured carbon materials can be enhanced by tailoring their surface properties and sample characteristics [10]. The addition of metal alloy (e.g. TiAIO) significantly improve the capacity of hydrogen storage in carbon nanotubes at temperatures 573 - 623 K, could uptake about 6% wt. hydrogen [11].

Now-days, carbon nanotubes are also applied as the support of catalyst due to their special structural morphology and characteristics. Their surface is usually modified to create the functional groups for specific needs before their use as support. Catalysts for hydrogen storage have been produced by: impregnation, precipitation, chemical reduction and hydrothermal methods [12].

Worldwide, researches are focused on inducing fractures within nanotubes structure and then doping them with metals and/or metal alloys. The carbon nanotubes tips have been opened and surface defects have been introduced and then doped with Pd-Ni nano alloys. The Pd-Ni alloy is a catalyst to adsorb and dissociate hydrogen and the defects were sites for atomic hydrogen spill over and hydrogenation. Also, another way to create defects within the nanotube structure is their oxidation at a temperature of 873 k and pulsed into oxygen (each pulse 67µl) to partially oxidize the carbon nanotubes. to create defects and totally open the tube. The Pd-Ni alloy was then doped onto the defective nanotubes by using a traditional wet impregnation method [12].

Surface properties enhancement by using high frequency ultrasounds is sometimes used in order to induce structural fractures within the carbonic material [9].

PANI and MWNT are a unique type of carbon based materials in which, the charge delocalization can, in principle, offer multiple active sites on the substrate backbone for the adsorption and desorption of hydrogen, involving weakening of the H-H bond followed by "spill over" adsorption of hydrogen onto the adjacent nano-fibrous network [13]. Spill over of hydrogen to the carbon nanotubes is one of the unique features that occur during the hydrogen storage in metal or metal oxides doped nanotubes. Transition metal or metal oxide nanoparticle dissociate the hydrogen molecule and spills over the low binding sites, such as, external wall or groove sites of carbon nanotube [12].

The mechanism model of hydrogen storage (number of hydrogen molecules per unit volume) and the internal pressure in the carbon nanotube was set by Brenner et al. (2002) who established the second generation inter atomic potential for carbon [14].

Following the above consideration, there have been prepared various carbonic samples and measured their hydrogen storage capacity using specially designed equipment for nano carbon samples [8].

2. Experimental

In the present paper, the nano-structured carbonic materials MWNT and PANI respectively have been doped with Ruthenium (Ru). It is well known that Ru, as well as Pt, is one of the most R. Mirea, G. Rîmbu, M. Iordoc, A.T. Cucuruz / Experimental assessment of the influence of transitional metal doping on carbonic materials regarding their hydrogen storage capacity

reactive transitional metals that can be used for increasing the hydrogen storage capacity of a substrate. Chemical doping is used in the current paper since, compared with physical doping, the results are identical. and obtained more reproducible. The increased hydrogen storage capacity of metal doped carbonic materials is attributed to the initial hydrogen adsorption by metal nanoparticles which, subsequently, dissociate the hydrogen molecules and spill them over to carbon nanotubes. Pores of molecular dimension can absorb large quantities of gasses, enhanced density of the adsorbed materials inside the pores being a consequence of the attractive potential of the porous walls.

Spill over mechanism proposed within the current paper was chosen because, at a given H_2 pressure, hydrogen molecules suffer dissociative chemisorptions by a sustained interaction with metallic catalyst, in this case Ruthenium nanoparticles.



Fig. 1 - Hydrogen adsorption by "spill-over" phenomena / Adsorbţia hidrogenului prin mecanismul "spill-over".

Generated hydrogen atoms migrate from the metallic catalyst to the support material (MWNT and PANI) and then spread within its entire volume. In order that the spill over process to make a notable difference it is essential for hydrogen atoms to be able to "travel" away from the metallic catalyst's vicinity towards the substrate's inner structure as shown in Figure 1. Researches focuses towards the understanding of spill over process since, until now, there are no unanimous opinions related to this subject in order to fully explain the high storage capacity observed within these materials.

Two types of Ru doped materials have been developed and tested within current research: Ru doped MWNT's and Ru doped PANI. MWNT have been purchased from the market and the doping procedure was performed within the lab. PANI instead, was firstly produced within the lab and then doped. For each of the materials characterizations were performed in term of porosity, BET surface and XRD and also in terms of hydrogen storage capacity, all in order to set the ground values. After doping, same characterizations were performed.

2.1 Method for obtaining Ru doped MWNT

The following experiment refers to the obtaining and characterization of nano-structured carbonic materials as Ru doped MWNT. Thus, Ruthenium Chloride (RuCl₃*H₂O) is used to react with MWNT in order to obtain Ru doped MWNT using chemical reaction.

MWNT are previously functionalized and then treated with $RuCl_3*H_2O$. The necessary quantity (1 g) of MWNT is mixed with 50 cm³ deionised water and then, by using an ultrasound cannon their structure was functionalized. The frequency of the ultrasounds emitted by the cannon is 70 kHz, high enough to fracture the structure of the nanotubes allowing Ru nanoparticles to access these fractures and to form the doped material.

Separately, in a Berzelius glass, RuCl₃*H₂O is dissolved in deionised water and heated at 80°C. The dissolved substance is mixed with the functionalized MWNT and heated for an hour at 80°C. In the next stage, the mixture of RuCl₃*H₂O and MWNT are ultra sounded using the ultrasound cannon. This intensive mixing ensures a better contact between MWNT and Ru ions.

In a separate glass, 3 cm³ of formic acid is diluted in 25 cm³ of deionised water and then it is poured on the RuCl₃*H₂O and MWNT mixture thus reducing the metallic ion Ru³⁺ to its metal form. This final mixture is heated at 80^oC for an hour and after that is vacuum filtered. The obtained solid mixture is then washed until its pH reaches 7, then the doped nanotubes are heated at 100^oC in a vacuum drying chamber.

2.2 Method for obtaining Ru doped PANI 2.2.1 Method for obtaining PANI

PANI was prepared in the laboratory by chemical oxidation of aniline sulphate $(C_{12}H_{16}N_2O_4S)$ 0.2M with ammonium peroxydisulfate $((NH_4)_2S_2O_8)$ 0.2M according to the literature [15-17].

High purity $C_{12}H_{16}N_2O_4S$ and $((NH_4)_2S_2O_8)$ have been dissolved in sulphuric acid (H_2SO_4). Both solutions, at room temperature, were mixed by using a magnetic stirrer aiming to allow the polymerization process to take place. The solution has been filtered and then washed with H_2SO_4 in order to remove the collateral compounds, the oxidant and the residue. In addition, acetone was used to even deeper wash the precipitate. The resulted poly-aniline salt (C_6H_5 -NH-HSO₄) has been heated for 3 hours at 70°C in a drying chamber.

2.2.2 Method for obtaining doped PANI

0.5 g of obtained poly-aniline has been dispersed in deionised water by using the ultrasound cannon above presented. Then, 1 g of sodium hydrogen carbonate was added and the solution was boiled for 30 minutes in order to neutralise even more the remaining traces of H₂SO₄ previously used for PANI preparation.



а b Fig. 2 - X-Ray diffraction for MWNT a) and MWNT+Ru b) / Difracția de raze X a MWNT a) și MWNT+Ru b).



а Fig. 3 - X-Ray diffraction for PANI a) and PANI+Ru b) / Difracția de raze X a PANI a) și PANI+Ru b).

Meanwhile, RuCl₃*H₂O dissolved in deionised water was added to the boiling solution and ultra sounded for 15 minutes. This final mixture was heated at 80°C for an hour and then vacuum filtered. The obtained solid mixture was washed until its pH reaches 7 and then heated at 100°C in a vacuum drying chamber.

3. Results and discussions

Each carbonic material (un-doped and doped one) was characterized both structural and functional. Structural characterization consisted of: X-Ray diffraction, porosity and BET analysis. Functional characterization was made by cyclic voltametry and physical adsorption of hydrogen in order to determine their adsorption capacity.

3.1. Structural characterization by x-ray diffraction

The method is based on qualitative analysis of the metallic phases within a polycrystalline material by using X-Ray diffraction. A D8Advance diffractometer that uses a Cu anode and X-ray tube was used. The sample vas polished with the smallest size of the polishing powder and then was placed in the diffractometer for analysis.

The diffractions were made for the undoped carbonic substrates and for the Ru doped ones.

In Figure 2 are presented the diffraction plots for MWNT and MWNT+Ru.

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As it can be seen in Figure 2, even tough, initially, only graphite shows a crystalline phase due to its sp³ hybridization, after doping it by using chemical treatment, Ru is spread within the structure of the nanotubes since metallic crystals are formed.

In Figure 3 are presented the diffraction plots for PANI and PANI+Ru.

As it can be seen in Figure 3, PANI does not initially present a well defined crystalline phase before doping since its internal hybridisation is mainly sp² and only few sp³ (Fig. 3a), but after chemical treatment, Ru creates some changes within the inner structure of PANI, since even the small amount of sp³ hybridization (present at 2theta = 25°) disappear and the plot "flattens" (fig. 3b). These inner changes will be further discussed within the paper.

For both MWNT and PANI, Ru was added to their inner structure. According to literature [6, 11], the doping metal is better anchored on the MWNT's surface after structural fractures appear.







Fig. 5 - Micropores surface for MWNT a) and MWNT+Ru b) / Suprafata microporilor pentru MWNT a) și MWNT+Ru b).



b

Fig. 6 - BET surface for PANI a) and PANI+Ru b) / Suprafața BET a n MWNT a) și MWNT+Ru b).

The ultrasound treatment, as stated before, was used for surface preparation of the carbon based materials aiming to ease the penetration of nanostructured Ru within their structure. It is well known that sp² (PANI in this case) and especially sp³ (MWNT) hybridized carbon materials are virtually impossible to dope until their surface is functionalized.

3.2 Structural characterization by BET analysis

The method is based on the measuring the total adsorbed gas quantity on the surface of porous materials. The material is held at a temperature below the critical temperature of the gas. During the analysis, the pressure is modified until equilibrium is reached. Thus, the adsorbed gas quantity at the equilibrium is given by the difference between the admitted gas quantity and the one necessary for filling the material's pores. The used apparatus was Autosorb-1 having a pressure range between 0.001 and 1 bar. Data acquisition system allows us to determine BET surface and pore distribution.

In Figures 4 and 5 is presented the BET surface and micro pores' surface for MWNT and MWNT+Ru.

As it can be seen in Figures 4 and 5, after doping, the BET surface of MWNT increases almost four times from 51.92 m²/g to $208.9m^2/g$. But, in the same time, the micro pores' surface increases almost ten times from 4.98 m²/g to 48.57 m²/g.

In Figures 6 and 7 is presented the BET surface and micro pores' surface for PANI and PANI+Ru.



Fig. 7 - Micropores surface for PANI a) and PANI+Ru b) / Suprafața microporilor pentru PANI a) și PANI+Ru b).



Fig. 8 - Example of how is calculated the total ions transfer Q_T / Exemplu de calcul al transferului ionic total Q_T .



Fig. 9 - Cyclic voltamograms for MWNT and MWNT+Ru / Voltamograme ale nanotuburilor de carbon nedopate și dopate.



Fig. 10 - Cyclic voltamograms for PANI and PANI+Ru / Voltamograme ale polianilinei nedopată și dopată.

R. Mirea, G. Rîmbu, M. Iordoc, A.T. Cucuruz / Experimental assessment of the influence of transitional metal doping on carbonic materials regarding their hydrogen storage capacity

Sample	Qt, mC/cm ²	Electrical charges	H ₂ ads, g/cm ²	H ₂ ads, % wt
LMWNT 100mV/s	62.3	3.89E+17	6.46E-07	0.0162
LMWNT 50mV/s	65.1	4.06E+17	6.75E-07	0.0169
LMWNT 20mV/s	68.4	4.27E+17	7.09E-07	0.0177
LMWNT 10mV/s	70.7	4.41E+17	7.33E-07	0.0183
LMWNT + Ru 100mV/s	331	2.06E+18	3.43E-06	0.0859
LMWNT + Ru 50mV/s	401	2.50E+18	4.16E-06	0.1040
LMWNT + Ru 20mV/s	695	4.34E+18	7.21E-06	0.1803
LMWNT + Ru 10mV/s	1180	7.37E+18	1.22E-05	0.3061
PANI 100mV/s	17.9	1.11E+17	1.85E-07	0.0046
PANI 50mV/s	25.2	1.57E+17	2.61E-07	0.0065
PANI 20mV/s	40.1	2.50E+17	4.16E-07	0.0104
PANI 10mV/s	58	3.62E+17	6.01E-07	0.0150
PANI + Ru 100mV/s	38.9	2.43E+17	4.03E-07	0.0101
PANI + Ru 50mV/s	59.7	3.73E+17	6.19E-07	0.0155
PANI + Ru 20mV/s	78.7	4.91E+17	8.16E-07	0.0204
PANI + Ru 10mV/s	272	1.70E+18	2.82E-06	0.0706

Obtained charges and storage capacity at different electrical potentials

As in the case of MWNT, the BET surface for PANI also increases after doping with Ru, but at a smaller rate. Thus, the initial value of BET surface is $39.58 \text{ m}^2/\text{g}$ and increases until $46 \text{ m}^2/\text{g}$. Also, like MWNT, the micro pores' surface increases many times after doping. So, the initial value of micro pores surface was $4.1 \text{ m}^2/\text{g}$ and became $37.27 \text{ m}^2/\text{g}$.

By doping carbonic materials with Ru, an increase of BET surface occur due to the fact that chemical and thermal treatment applied to the carbon based materials is acting similar to activation treatment for carbonic materials by using heated steam [11]. By chemically reducing the metal ion from Ru³⁺ to its metal form in order to be used for doping the substrate, the overall pore structure of the substrate drastically changes. Thus, macro and meso pores disappear and more micro pores occur. It is within these micro pores the spill over process take place and they are more suitable for adsorbing hydrogen. Basically, the metal dissociates hydrogen molecule and the micro pores retain it until desorption, as shown in Figure 1.

3.3 Functional characterization by cyclic voltametry

In order to determine the electrochemical activity of the materials, the active electrochemical surface has been determined by cyclic voltametry measurements which higlights the ions transfer necessary to adsorb and desorbs hydrogen on the tested materials. Thus, the *total ions transfer* (Q_T) has been determined in the region of the adsorption/desorption potential, as it can be seen in Figure 8. The method consists of applying a certain potential and monitoring the system's

response in time. The apparatus used was an "allin-one" radiometer analytical model VoltaLab-40 connected to an electrochemical cell type X51V00 having three electrodes. Q_T can be evaluated by using the following equation:

$$Q_T = \frac{1}{2\nu} \int_{E_1}^{E_2} (I_d - I_a) dE \,, \, [C/cm^2] \quad (1)$$

Figures 9 and 10 are showing the voltamograms drafted for doped and un-doped materials.

Where: v – sweeping speed [mV/s],

 I_d – desorption specific current [mA],

I_a – adsorption specific current [mA],

E – Potential [mV].

Table 1 summarize the results obtained during the cyclic voltametry testing of the materials.

It is to be mentioned that tests have been made at different potential values: 10, 20, 50, and 100 mV/s, for both doped and un-doped materials. As it can be seen in Table 1, in the case of MWNT substrate, the electrical charges storage capacity increase eight to ten times after doping from 3.89E+17 to 2.06E+18 (for testing at 100mV/s), as well as hydrogen storage capacity from 0.0162 %, wt to 0.0859 (for testing at 1000mV/s). Unlike MWNT, PANI does not present such a major increase in its adsorption capacity. After doping with Ru, PANI just doubles its storage capacity for electrical charges as well for hydrogen. Thus, if initially, PANI's storage capacity was 1.1E+17 for electric charges and 0.0046 %, wt for hydrogen (tested at 100 mV/s), after doping this capacity becomes 2.43E+17 for electrical charges and 0.0101 %, wt.

3.4 Functional characterization by physical adsorption of hydrogen

Table 1



Fig. 11 - Wt% of hydrogen adsorption at 10 bar for MWNT+Ru a) and PANI+Ru b) / Procentul masic de hidrogen adsorbit la 10 bari pentru MWNT+Ru a) și PANI+Ru b).



a Fig. 12 - Wt% of hydrogen adsorption at 20 bar for MWNT+Ru a) and PANI+Ru b) / Procentul masic de hidrogen adsorbit la 20 bari pentru MWNT+Ru a) și PANI+Ru b).



Fig. 13 - Wt% of hydrogen adsorption at 30 bar for MWNT+Ru a) and PANI+Ru b)/ Procentul masic de hidrogen adsorbit la 30 bari pentru MWNT+Ru a) și PANI+Ru b).

Carbon nanotubes cannot be good carriers of hydrogen due to the small surface area, but activated carbon is of great potential and a storage capacity over 10% was proven at 77k and 10 MPa [12]. Physical adsorption of hydrogen on undoped materials has not been performed since, according to [12], undoped carbonaceous materials are no suitable for hydrogen storage, because they cannot retain more than 0.5 wt.% at room temperature and moderate pressures.

In order to determine the hydrogen adsorption capacity of the Ru doped carbonic materials (MWNT+Ru and PANI+Ru), the following method was used: -the material was put in a tight closed recipient and pressurised hydrogen has been inserted. The sample temperature was kept constant at 293 \pm 5 K, so, only the pressure

influenced the adsorption capacity of the tested materials. The pressure has been kept constant until the equilibrium has been reached. Then, a new increase of the pressure took place, and so on until the final pressure and equilibrium were reached. The used apparatus was a PCT Pro-user delivered by Setaram and the experiments have been conducted at three different pressures, 10, 20 and 30 bars and stopped until Δp between the working and initially set pressure was less than 1 bar. The results have been plotted as mass ratio (wt. %) of adsorbed hydrogen vs. pressure.

The following figures show the comparative data between MWNT+Ru and PANI+Ru at similar pressures. Thus, Figure 11 presents the registered data at 10 bars.

As it can be seen in the comparative plots



Fig. 14 - Comparison between Ru doped MWNT's and PANI's adsorption capacity / Comparație intre capacitatea de adsorbție a nanotuburilor și polianilinei dopate cu Ruteniu

within Figure 11, the amount of hydrogen stored in MWNT+Ru at 9.3 bars is 2.73%, wt and for PANI+Ru is 1.53%, wt, at the same pressure.

Figure 12 presents the registered data at 20 bars.

As in can be observed in Figure 12, at 19.1 bars, the adsorption capacity of MWNT+Ru is 4.97%, wt and of PANI+Ru is 3.1%, wt

Figure 13 presents the registered data at 30 bars.

The plots within Figure 13 show a

comparative adsorption capacity at 30 bars for both MWNT+Ru and PANI+Ru. Thus, the adsorption capacity at 29.2 bars is of 7.38%, wt for MWNT+Ru and 4.53%, wt for PANI+Ru

While MWNT had a BET surface of 50 m^2/g and a quasi crystalline structure due to sp^3 hybridization, PANI had only 3

8 m²/g and an amorphous structure due to its sp² hybridization. Their micro pores surface was initially very small but both materials suffered heavy transformations after doping. And even their micro pores surfaces are similar, 48.57 m²/g for MWNT and 40.27 m²/g for PANI, the fact that MWNT had sp³ hybridization and kept it after doping ensured a proper substrate for hydrogen atoms to be adsorbed and retained.

Figure 14 shows a comparative analysis of the adsorption capacity of MWNT and PANI at different pressures which highlights once more that the adsorption capacities are influenced by the inner structure of the substrate rather than their porosity.

4. Conclusions

• By applying the Ru doping procedure to the functionalized carbon based materials, BET area increases due to the similitude with activation procedure. In the same time, the micro pores' area increases. Thus an increase of almost ten times (for MWNT) and seven times (for PANI) can be observed for the specific area of the pores after the doping procedure.

• After analyzing the data regarding the adsorption capacity by using cyclic voltametry, it was determined that doping increases the material's action on the adsorption phenomena. Thus, the average adsorption degree of the doped material increases more than four times comparing with the un-doped one in the case of both materials.

The adsorption capacity may be correlated with the developed micro porosity, thus, the main influencing factor is the substrate's nature sp^3 hybridisation for MWNT vs., sp^2 for PANI which allows an easier transfer of Hydrogen to the substrate even though the doping metal was the same.

• After performing the experiments of physical gas-on-solid adsorption of hydrogen, it was determined the weight ratio of adsorbed hydrogen increases as the pressure increases until values that are accordingly to the ones reported in literature [12]. Thus, at 30 bar, the weight ratio overpasses the set target by the US Department of Energy of 4.5 wt% [1], in the case of MWNT and approaches this target in the case of PANI.

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