Comparative Research Concerning Hydrogen Storage by Platinum, Ruthenium and Iridium Doped Multiwall Carbon Nanotubes

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A comparative research related to hydrogen adsorption capacity of multiwall nanotubes (MWNTs) doped with Platinum (Pt), Ruthenium (Ru) and Iridium (Ir) was carried out. Carbonic materials are considered to be one of the most promising materials for hydrogen adsorption and storage; they have different applications and fuel cells technology may be considered the most important of them. By using transitional metals for doping carbonic materials, the adsorption capacity increases, can approach the target of 6.5% weight ratio of $H_2$ adsorbed in a substrate. The doping procedure consists in a physical or chemical method which involves metal for doping of a nano carbon structure. The use of ultrasounds is known in order to activate the substrate by inducing fractures within its internal structure. The adsorption capacity of the carbonic materials, which is a consequence of spill over phenomena, has been determined both by physical adsorption and by cyclic voltammetry. The substrates have been characterized in order to determine their BET and microspores surface and structure. The collected data related to the adsorption capacity have been processed by using a dedicated software. The results have been compared with the available data from literature and a good consistency was found.

Keywords: Hydrogen adsorption, weight ratio, doped carbonic material, carbon nanotubes, platinum doping

The research carried out within the current paper refers to the hydrogen storage using gas-on-solid adsorption method. In more cases solidphase used as substrate for hydrogen storage is multi-wall nanotubes (MWNT). 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. Recently, new carbon nano-structured adsorbents have been produced (graphite nanofibres, single and multi-wall carbon nanotubes) [1]. 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 about 9% weight [10].

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 [2]. The addition of metal alloy (e.g. TiAlO) significantly improves the capacity of hydrogen storage in carbon nanotubes at temperatures 573 - 623 K, could uptake about 69wt. hydrogen [7]. Nowadays, 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 in carbon, for hydrogen storage have been produced by impregnation, precipitation, chemical reduction and hydrothermal or others method [11]. For sorption and storage of other compounds such as carbon organic volatile the metal doped carbon sorbents are successfully used [12 - 14].

There are several paper approaches regarding the surface properties enhancement by using high frequency ultrasounds in order to induce structural fractures within the carbonic material. Also for increasing hydrogen storage capacity, metal doping has been performed [2].

In this paper, the nano-structured carbonic materials have been doped with Pt, Ir and Ru by chemically reducing the metal salts. It is well known that transition metals, also known as platinic metals, are very reactive and can be used for increasing the hydrogen storage capacity of a substrate. Chemical doping was chosen to be used in this paper since, compared with physical doping, the obtained results are identical, and more reproducible. The increased hydrogen storage capacity of metal doped MWNT is attributed to the initial hydrogen adsorption by metal nanoparticles which subsequently dissociate the hydrogen molecules and spill them over to carbon nanotubes [2]. 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 [11].

Generated hydrogen atoms migrate from the metallic catalyst to the support material (MWNT) and then spread within its entire volume. To obtain a notable difference made by the spill over process it is essential that hydrogen atoms to be able to travel away from the metallic catalyst’s vicinity towards the substrate's inner structure. Worldwide research focuses on the understanding the spill over process since until now there are no unanimous opinions related on this subject.

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

Experimental part
Method for obtaining Pt doped MWNTS

In order to obtain and characterize nanostructured carbonic materials as Pt doped MWNT, the procedure described below was used. Thus, equal quantities of MWNT and hexachloroplatinic acid (H$_2$PtCl$_6$) are used in order to obtain Pt doped MWNT using chemical reaction. MWNT are previously functionalized and then treated with H$_2$PtCl$_6$. The necessary quantity of MWNT is mixed with 50
cm$^3$ deionized water and then, by using an ultrasound cannon, their structure was functionalized. Separately, in a Berzelius glass, H$_2$PtCl$_6$ is dissolved in deionized water and heated at 80ºC. The dissolved acid is mixed with the functionalized MWNT and heated for an hour at 80ºC. The mixture of H$_2$PtCl$_6$ and MWNT is ultra sounded for a better contact between MWNT and Pt ions. In a separate glass formic acid is diluted in 25 cm$^3$ of deionized water and then is poured on the mixture for platinum reduction. This final mixture is heated at and vacuum filtered. The obtained solid mixture is then washed until its pH reaches 7. The obtained doped nanotubes are then heated in a vacuum drying chamber.

**Method for obtaining Ru doped MWNTs**

The method is basically identical to the one used for obtaining Pt doped MWNTs, but instead of H$_2$PtCl$_6$, Ruthenium Chloride (RuCl$_3$·H$_2$O) is used. All the other parameters and actions were kept as described above. The obtained material is Ru doped MWNTs.

**Method for obtaining Ir doped MWNTs**

The method is basically identical to the one used for obtaining Pt doped MWNTs, but instead of H$_2$PtCl$_6$, Iridium Chloride (IrCl$_3$) is used. All the other parameters and actions were kept as described above. The obtained material is Ir doped MWNTs.

**Results and discussions**

**Materials characterization**

The carbonic materials obtained within the experiments were characterized both structural and functional. The structural characterization was made by X-Ray diffraction and BET analysis. In order to determine the material’s adsorption capacity, the functional characterization was made by cyclic voltammetry and physical adsorption of hydrogen.

**Structural characterization by X-ray diffraction**

The method is based on qualitative analysis of the crystalline phases within a polycrystalline material by using X-Ray diffraction. A D8 Advance diffractometer with Cu anode and X-ray tube was used. The diffractions were made both for the carbonic substrates and for the doped ones. Figure 1 presents the diffraction plots for MWNT and metal doped MWNT.

As it can be seen in figure 1, even tough, initially, only carbon shows a quasi crystalline phase due to its sp$^3$ hybridization (figure 1-a) while forming graphite, after doping it by chemical treatment, a wide metal spread is obtained within the structure of the nanotubes since metallic crystalline phases are formed (figure 1-b, c, d). Platinum appears to have the most well defined crystalline structure and its peak far exceeds the peak of sp$^3$ carbon. Platinum and Iridium have their crystalline structure face-centred cubic and Ruthenium has its crystalline structure simple hexagonal. Crystalline metals were added to the inner structure of the carbonic substrate. According to literature [7], the doping metal is better anchored on the MWNT’s surface after structural fractures appear. In this case, fractures appear due to the ultrasound treatment.

**Structural characterization by BET analysis**

The method is based on measuring the total adsorbed gas quantity on the surface of porous materials. During the analysis, the pressure is modified until equilibrium is reached. Thus, the quantity of adsorbed gas at 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. In figure 2 are presented BET and micro pores' surfaces plots for MWNT and doped MWNT.

As it can be seen in figure 2, after doping, the BET surface of MWNT decreases almost four times from 208.9 m²/g to 45.95 m²/g for Pt, to 51.92 m²/g for Ru and to 52.56 m²/g for Ir. But, in the same time, the micro pores' surface increases almost ten times from 4.98 m²/g to 11.95 m²/g for Pt, 48.57 m²/g for Ru and to 51.41 m²/g for Ir. It results that Ir provides the highest surface of the micro pores while providing the lowest decrease of BET surface.

By doping carbonic materials with transitional metals such Pt, Ru and Ir a decrease of BET surface occur due to the fact that by chemically reducing the metal the pore structure of the substrate drastically changes. Thus, macro and meso pores disappear and micro pores occur. Within these micro pores the spill over process takes place since they are more suitable for hydrogen adsorption.

Functional characterization by cyclic voltammetry

In order to assess the electrochemical activity of the obtained materials - MWNT, MWNT+Pt, MWNT+Ru, MWNT+Ir, their active surface has been determined by cyclic voltammetry measurements which emphasises the electric charges transfer related to hydrogen adsorption/desorption process on the tested materials. Thus, total specific charge transfer (Qₜ) has been determined in hydrogen adsorption/desorption potential area. Table 1 summarizes the results obtained during the cyclic voltammetry testing of the materials.

It is to be mentioned that tests have been made at different potential values: from 5 to 100 mV/s both for doped and un-doped materials. As it can be seen in table 1, in the case of MWNT substrate, the electrical charges storage capacity increases three to six times after doping from 3.89E + 17 to 2.42E + 18 in the case of Pt doping, to 2.06E + 18 in the case of Ru and to 1.23E + 18 in the case of Ir (for testing at 100 mV/s), this increase is noticed also in the case of hydrogen storage capacity, which increases from 0.0162 % to 0.1007% for Pt, to 0.0859% for Ru and to 0.0514% for Ir (for testing at 1000 mV/s).

Functional characterization by physical adsorption of H₂

Carbon nanotubes cannot be good carriers of hydrogen due to their small surface area, but activated carbon is of great potential and a storage capacity over 10% was proven at 77K and 10 MPa [11].

In order to determine the hydrogen adsorption capacity of the doped nano-structured carbonic materials, the material was put in a tight closed recipient and pressurised hydrogen has been inserted. The sample temperature was kept constant at 293 ± 5 K, so, only the pressure influenced the adsorption capacity of the tested materials. The pressure has been kept constant until equilibrium has been reached. The used apparatus was a PCT Pro-user. The experiments were conducted at three different pressures, 10, 20 and 30 bars and were stopped until ΔP between the working and initially set pressure was less than 1 bar. The results were plotted as mass ratio (wt. %) of adsorbed hydrogen vs. pressure.

The following figures show the comparative data between MWNTs and metal doped MWNTs at different pressures.

As it can be seen in figure 3, Pt doped material shows the most increased adsorption capacity. At 9.2 bar, its adsorption capacity is 3.4% wt, unlike Ru and Ir doped ones which have 2.73 and 2.71% wt respectively. This difference
is due to the fact that Pt is the most reactive metal of them having the biggest electro negativity. Its electron affinity energy is 205.3 kJ/mol, Ru has its electron affinity 2.2 and electron affinity energy 101.3 kJ/mol while Ir has electro negativity 2.2 and electron affinity energy 151 kJ/mol.

Figure 4 shows the %wt of hydrogen stored at 20 bars. The general tendency is similar to the one identified in the case of the measurements performed at 10 bars, with Pt having the most increased adsorption capacity, but with higher differences between the three doping metals. Thus, at 19 bars, Pt’s adsorption capacity is 6.68 %wt hydrogen, unlike Ru which has 4.97 %wt and Ir 2.78 %wt.

Figure 5 shows the %wt of hydrogen stored at 30 bars. The general tendency is similar to the one identified in the case of the measurements performed at 10 and 20 bars, with Pt having the most increased adsorption capacity, but again with higher differences between the three doping metals. Thus, at 19 bars, Pt’s adsorption capacity is 6.68 %wt hydrogen, unlike Ru which has 4.97 %wt and Ir 2.78 %wt.
metals. Thus, at 28.8 bars, Pt’s adsorption capacity is 8.73 %wt hydrogen, unlike Ru’s 7.38 %wt and Ir’s 7.95%wt.

Conclusions

The adsorption capacity of the doped MWNT’s is closely related to the nature of the doping metal. Since Pt is the most reactive of them, the storage capacity of the Pt doped MWNTs is bigger than Ru and Ir doped ones.
By doping using transitional metals, the specific area of MWTNs modifies due to the fact that the metal is chemically reduced when used as doping for carbonic material. An increase of almost five times can be noticed for the specific area of the micro pores after doping the carbonic substrate.

By analyzing the data regarding the adsorption degree by using cyclic voltammetry, it was determined that the 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.

After performing the experiments of physical gas-on-solid adsorption of hydrogen, it was determined that the weight ratio of adsorbed hydrogen increases as the pressure increases until values that are in accordance to the ones reported in literature. Thus, at 30 bars, the weight ratio overpasses the target set by the US Department of Energy of 6.5 %wt [1], in the case of MWNTs.

Acknowledgements: The research has been developed within the project no. 220/2014, financed by Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI), Romania, program PNCDI-II - Partnership

References

Manuscript received: 5.12.2018