Hetero Atom Substituted Carbon—Potential Hydrogen Storage Materials

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Nano-materials based on carbon have not shown promise so far for hydrogen storage application. The reason for this situation has been addressed in this presentation. Hetero-atom substituted carbon materials have been shown to exhibit sites responsible for dissociation of molecular hydrogen and its spill—over to carbon surface. Theoretical and experimental results on hetero atom substituted carbon materials have been assembled to verify this postulate. Phosphorus containing carbon materials have been prepared and its hydrogen sorption capacity (~1%) has been evaluated.

Keywords: Hydrogen Sorption, Heteroatom Substituted Carbon, Phosphorous Substituted Carbon, Hydrogen Storage Capacity.

1. INTRODUCTION

The transition to hydrogen based fuel economy critically depends on two major scientific developments for the production of hydrogen and its storage in solid state materials without expanding much energy in these two processes. As it stands today, both these scientific processes can be considered to be a materials issue. The hydrogen production in the photo-electrochemical mode (since this process appears to be energy efficient if suitable materials are to be available) depends on the designing of suitable material which can absorb most of the available solar spectrum as well as can exhibit appropriate redox potentials. This is an exercise in designing and architecting appropriate materials with concern for the operation of both redox reactions at measurable rates.

Variety of solid state hydrogen storage media have been examined in the past decades based on some criteria like storage capacity, reversibility and cost.[1] Hydrogen storage in carbon materials has received considerable attention ever since a storage capacity (though unimaginatively high) of about 67 wt% was reported by Chambers et al.[2] This disclosure has opened up vigorous efforts to realize the dream of storing hydrogen to the extent of DOE standards of storage capacity and other required characteristics for energy storage applications.[3] However, till now, the required storage capacity as per DOE specifications for FY 2005 (4.5 wt%), FY 2010 (6 wt%) and 9 wt% for FY 2015, has not been achieved even though considerable efforts have gone on in realizing this goal. In Table I the

recent data are assembled to assess the current situation. This compilation is not comprehensive but selective.

Hydrogen sorption on carbon materials has been examined from a variety of stand points, like physisorption at low temperatures (usually 77 K),[16] the relationship between surface area of carbon and adsorption capacity,[17,18] the methods of preparation and activation of carbon to increase the surface area and storage capacity,[19,20] designing carbon materials in a variety of dimensional architectures[21–23] as well as by theoretical considerations based on different models.[24,25] None of these attempts could provide appropriate clues for designing and developing carbon materials which will exhibit hydrogen sorption capacity stipulated and required by DOE.

The motivation for this presentation is to examine the other alternatives that can be explored in future among the available possible carbon materials. It is known that carbon can sustain four valancies which indicates that the maximum storage capacity cannot exceed 25 wt%. In the common carbon materials, it is unlikely that all the four valancies of carbon are free to bind with hydrogen. Even if one were to assume that as in graphene materials one residual valency for each carbon atom the storage capacity can be of the order of 6.25 wt%. But as pointed out repeatedly in the literature, the hydrogen storage capacity in carbon materials never reached this figure that is possible from simple arguments (for typical data refer to Table I). This could be due to the incapability of carbon surfaces to dissociate molecular hydrogen as well as to convert the atomically adsorbed hydrogen to molecular form for desorption. This barrier is commonly overcome by supporting metallic particles in carbon materials which

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Table I. Data on hydrogen storage on a variety of carbon materials.

Adsorbent	Temperature (K)	Pressure (MPa)	Weight % of hydrogen	Ref
MWNT	300	12	0.3	4, 6
	77		2.27	
SWNT	77	0.1	0.8	5
SWNT acid treated	77		1.8	
ACF	303	3.1	0.26	
CNT	303	11.5	<0.2	7
Wood based carbon	303		<0.3	8
CA800	77	2	3.9	9
CB850	77	2	5.5	
Amorphous carbon	299	1	0.05	
Fishbone CNF	299	1	0.03	10
Platelet CNF	299	1	0.03	
Ribbon CNF	299		0.02	
Nanofibers (Pd/C)		0.1 to 10	0.04–0.33	11
AC	77–303	2–10	0.85–5.5	12
CNF	303	10	0.35	
A-CNF	303	3–10	0.33–1.03	
ZIF templated carbon	77	2	2.6–3.1	13
			3.9–6.2	

MWNT—Multiwall nanotube; SWNT—Single wall nano tube; CNT—carbon nano tube; ACF—activated carbon fiber [for more extensive compilation of data please see the earlier review articles 1, 14, 15].

facilitate the dissociation of molecular hydrogen which could be transported to the carbon surface by spill-over process. The reverse spill-over to recover the fuel possibly depends on the binding strength of atomic hydrogen on carbon and metallic sites respectively. This means that the adsorption sites and binding strength of atomic hydrogen must be of similar magnitude on the activation sites as well as in the transported sites. This situation may or may not be present if metallic particles are supported on carbon surfaces. Instead, if hetero-atoms like N, P, S and B are incorporated in carbon matrices, then these sites can function as hydrogen activating and dissociating centres and the dissociated hydrogen can be easily transported back and forth on to the equipotential carbon surface.[26]

1.1. Hetero Atom Substituted Carbon Materials

Sankaran et al.,[26–32] have employed DFT calculations to understand the effect of heteroatom substitution in carbon materials for hydrogen storage. Typical results of this study on carbon nanotubes are summarized in Table II and the corresponding energy profile for the hydrogenation process for Boron substituted carbon nanotubes is given in Figure 1. Similar calculations have also been carried out on heteroatom substituted fullerenes and the results are summarized in Table III The data given in Tables II and III demonstrate that the dissociation energy of hydrogen molecule is reduced on heteroatom substituted carbon materials and hence it may be possible the atomic hydrogen spill-over to the carbon substrate. Typical energy profile diagram shown in Figure 1 as a function of

Table II. Bond length and dissociation energy of hydrogen on CNT and heteroatom substituted CNTs calculated using B3LYP with 6–31 g (p,d) basis set on the UFF optimized structure.

CNT and substituted hetero atom	Total energy (hartrees)	Bond length $H_1–H_2$ (Å)	Dissociation energy (eV)
Hydrogen	−1.175	0.708	4.76
CNT	−3686.5502	—	—
CNT + H₂	−36687.7161	0.776	4.51
NCNT	−3702.5908	—	—
NCNT + H₂	−3703.5989	0.835	0.22
PCNT	−3989.1694	—	—
PCNT + H₂	−3990.2550	0.815	2.33
SCNT	−4046.0020	—	—
SCNT + H₂	−4047.0067	0.817	0.13
BCNT	−3671.7254	—	—
BCNT + H₂	−3672.9440	0.818	5.95
2BCNT (adjacent)	−3658.6666	—	—
2BCNT (adjacent) + H₂	−3659.8092	0.913	3.88
2BCNT (alternate)	−3659.3491	—	—
2BCNT (alternate) + H₂	−3660.3594	0.928	0.28

reaction coordinate also demonstrates that energy of activation is reduced on boron substituted carbon nano tubes. Similar energy profiles were obtained for other heteroatom substituted carbon nanotubes or fullerenes.

They have also determined the hydrogen uptake capacity on a variety of heteroatom substituted carbon nanotubes and showed that the storage capacity (up to 2 wt%) is dependent on the morphology of the carbon materials generated.

It is necessary to examine how the hetero atom substituted carbon materials appear to be suitable for hydrogen storage applications. The essential points in relation to this question are:
(1) Heteroatom substitution provides appropriate centres for the dissociation of molecular hydrogen. (This is manifested in terms of the reduction of the dissociation energy
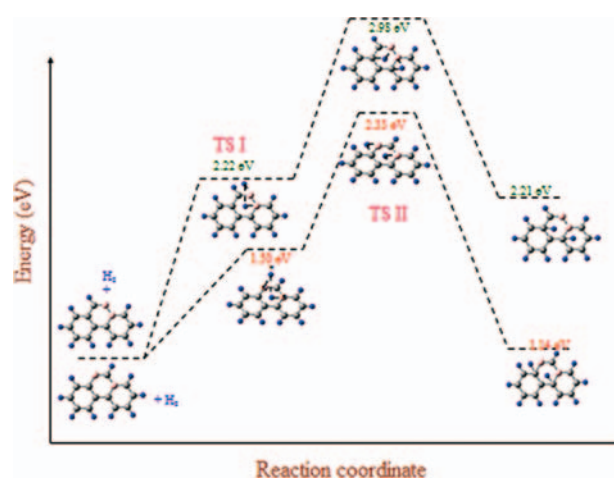

Fig. 1. Energy profile for molecular hydrogen activation and dissociation and adsorption on boron substituted carbon materials data computed by DFT method using (B3LYP) with 6–31 g (p,d) basis set. Balls indicated with arrows are boron atoms.

Table III. Bond length and dissociation energy of hydrogen molecule upon interaction with fullerene—calculated using B3LYP with 6–31 g (p,d) basis set on the UFF optimized structure.

System	Total energy (hartrees)	H_1–H_2 (Å)	Dissociation (eV)
H_2	−1.175	0.708	4.76
C_{60}	−2286.042	—	—
$C_{60} + H_2$	−2287.211	0.707	4.61
NC_{59}	−2302.653	—	—
$NC_{59} + H_2$	−2303.640	0.831	0.36
PC_{59}	−2589.253	—	—
$PC_{59} + H_2$	−2590.276	0.813	0.64
SC_{59}	−2646.036	—	—
$SC_{59} + H_2$	−2647.013	0.815	0.62
BC_{59}	−2272.764	—	—
$BC_{59} + H_2$	−2273.908	0.818	3.92
$2BC_{58}$ (adjacent)	−2259.506	—	—
$2BC_{58} + H_2$ (adjacent)	−2560.567	1.126	1.662
$2BC_{58}$ (alternate)	−2259.487	—	—
$2BC_{58} + H_2$ (alternate)	−2260.477	1.016	0.276

of molecular hydrogen as seen from the data given in Tables II and III).

(2) Since hetero atoms take up substitution positions in the lattice, there is facile transport of hydrogen atoms on to the carbon surface. (This deduction is supported by the energy profile diagram shown in Fig. 1.)

(3) The possibility of generating layered configuration in carbon materials (graphenes) offers additional advantage in terms of appropriate sites in layered configurations. This configuration possibly not only generated residual valency required for hydrogen migration but also provides enough active centres for hydrogen storage.

(4) The heteroatoms may segregate and thus generate a core shell configuration which may be provide sites which are both geometrically and electronically suitable for the hydrogen activation and transport. This type of modified surfaces may not be generated in other materials. (It is known that core shell configurations can alter the electronic properties at the interface and thus is favorable for activation of molecules). In fact that a surface is formed means automatically there is shell around the core bulk and hence surface atoms behave differently with respect to the atoms in the bulk. This configuration may be one of the reasons for the surface atoms to behave differently with respect to the atoms in the bulk.

(5) The substituted heteroatoms in a carbon layer provide nearly equipotential sites facilitating the free transport of hydrogen over the layers.

(6) The possibility of dimensionality in carbon materials especially possibility of generating one or two dimensional architectures may be appropriate for hydrogen sorption behavior.

A variety of nitrogen and boron containing nanotubes were synthesized (for details of synthesis refer to earlier publications)[26–32] and the hydrogen sorption capacity was measured on them at 1 atm and also at 80–100 bars at
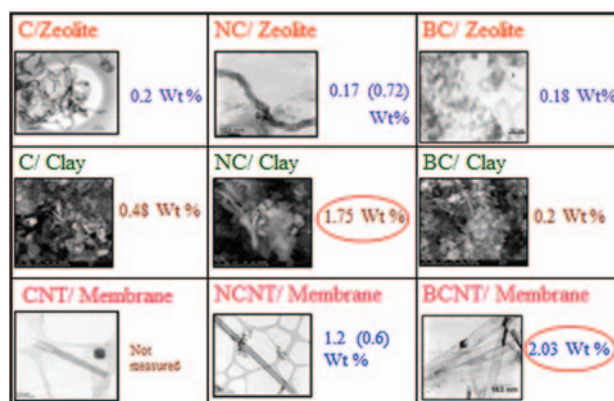
Fig. 2. The morphology and hydrogen sorption capacity at 80–100 bar on carbon nano tubes with and without heteroatoms synthesized using various templates.

300 K. In order to examine the role of morphology of the carbon materials (with or without nitrogen or boron) were synthesized using zeolite, clay and membrane templates and the results are summarized in Figure 2.

In order to test the hypothesis formulated in this presentation, the adsorption capacity of commercial grade carbon (CDX-975) and of the acid and amine treated versions of this carbon was evaluated at 1 atm pressure and at different temperatures and the data generated are given in Table IV. It is seen that at room temperature and above, the adsorption capacity of this carbon material is negligible thus supporting the postulate that carbon by itself may not be able to dissociate molecular hydrogen and hence the storage capacity is also negligible.

To further test the hypothesis that heteroatoms in carbon materials will be able to dissociate and store hydrogen, the adsorption capacity of a variety of nitrogen containing carbon materials at atmosphere pressure was evaluated and the data are given in Table V.

The data given in these tables not only substantiated that hetero atom in substituted configuration is capable of dissociating molecular hydrogen and will also be able to store hydrogen. Incidentally, the data given in these tables show the relationship between specific surface area and adsorption capacity, this relationship is normally claimed in literature.[17, 18]

Table IV. Comparison of specific surface area (SSA) and hydrogen absorption activity of CDX and chemically modified CDX samples.

Sample	CDX-975	T-CDX-975	A-CDX-975	TA-CDX-975
S S A in m^2/g	325	224	129	124
Hydrogen adsorption capacity (cm^3/g) at 1 atm				
77 K	28.1	27.3	8.2	10.4
298 K	0.53	—	—	0.7
373 K	2.83	3.17	3.03	2.97
423 K	4.18	4.25	4.30	—

T-CDX—acid treated, A-CDX—amine treated and TA-CDX—both acid and amine treated.

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Table V. Hydrogen absorption activity of carbon nano-materials at 1 atm and at different temperatures.

Sample	Percentage nitrogen	SSA (m²/g)	Hydrogen absorption at 1 atm (cm²/g)	
			77 K	373 K
PDC	7.6	93	20.4	0.90
MEC	4.3	182	64.5	2.78
CNT1	—	—	—	—
NCNT1	6.4	246	47.5	6.11
CNT2	—	633	28.0	3.42
NCNT2	2.5	646		
CNT3	−1.8	49		3.0
NCNT3		66	7.45	2.4

PDC prepared from polyvinylpyrolidone; MEC from poly acrylonitrile; NCNT1 using poly pyrrole; NCNT2 and NCNT using pyridine.

The results of DFT calculations given in Table II shows that phosphorus substitution in carbon materials is also capable of dissociating molecular hydrogen and hence Phosphorus substituted carbon materials could be one of the suitable materials for hydrogen storage applications.

1.2. Phosphorus Substituted Carbon

It has been shown in the previous section that carbon materials with substitution by heteroatoms like N, S, and B, show hydrogen sorption capacity. However the effect of substitution of phosphorus in carbon materials has not been investigated to the same extent. The theoretical considerations presented in the previous section showed that the effect due to phosphorus substitution in carbon materials will be only marginal as compared to other hetero atom substituted carbon materials. The present investigation is an attempt to formulate a synthesis strategy for preparing phosphorus containing carbon material and examine the hydrogen sorption property of such a synthesized system. In literature various phosphorus containing carbon materials have been prepared using phosphorus sources like phosphoric acid and phosphorus trichloride at high temperatures.[33]

2. EXPERIMENTAL DETAILS

2.1. Materials and Methods

Phenyl acetylene, formaldehyde solution (HCHO), phosphorus trichloride (PCl_3), sodium hydroxide, and orthophosphoric acid were purchased all from Sigma Aldrich and used without further purification.

2.2. Physical Measurements

Wide angle powder XRD patterns for the calcined carbon materials were recorded on a Rigaku Miniflex II diffractometer, using Cu Kα irradiation. The XRD patterns were measured in the 2θ range of 10–80° at a scanning rate of 3°
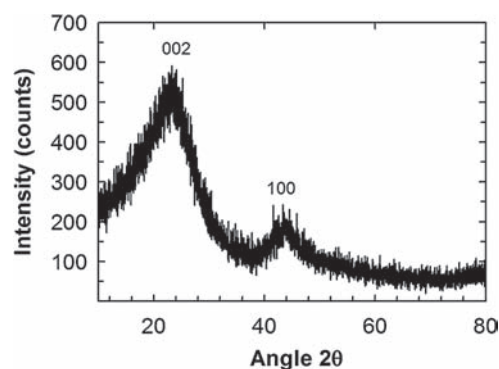

Fig. 3. X-ray diffraction pattern of phosphorus containing carbon material. The two diffraction peaks are attributed to 002 and 100 planes that are similar to those observed for the conventional carbon materials although slight shift in 2 values is observed but it is not perceptible because of the low content of P.

per minute. The Fourier Transform infrared spectrum was recorded using Perkin Elmer spectrometer in the frequency range 4000–450 cm^{-1}, using KBr pellet method. Fourier Transform Raman spectra were recorded by using the standard Bruker pulse instrument. *FEI Quanta FEG 200-High Resolution Scanning Electron Microscope* (HRSEM) was employed for obtaining the micrographs.

2.3. Synthesis

Phosphorus containing carbon materials have been synthesized by the following procedure. 5 ml of Phenyl acetylene is added to 11.5 ml of formaldehyde solution and it was stirred well. The reaction mixture was added to 1.5 ml of NaOH, stirred for 1 h after that the mixture was heated to 200 °C for 1 h. Then 9.5 ml of PCl_3 solution was added and stirred for 2 h and 12.6 ml H_3PO_4 solution was added which resulted in a gel formation. The gel was initially heated to 200 °C for 2 h, kept at room temperature and finally the gel was calcined at 600 °C for 2 h under inert atmosphere. The heating rate employed for calcination was 10°/m. to obtain phosphorus containing carbon material. Either stainless steel container or glassware can be used.
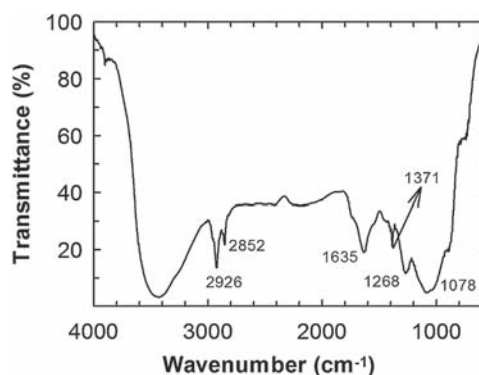

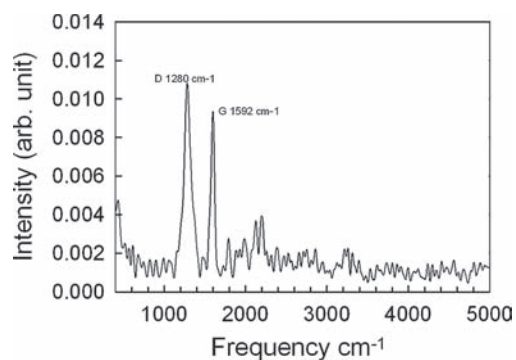**Fig. 4.** FT-IR spectrum of a sample of phosphorus containing carbon.

Fig. 5. Raman spectrum of the phosphorus containing carbon material showing the G and D bands respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization

The phosphorus containing carbon materials thus synthesized were characterized by a variety of techniques. The X-ray diffraction pattern obtained for the synthesized phosphorus containing carbon material is shown in Figure 3. Two broad diffraction peaks centered around 27 and 44 corresponding to (002) (100) planes are seen showing the material prepared is carbon lattice and the FWHM of the reflections are broad and this indicates the possible crystalline of the material prepared. Since the amount of phosphorus is small, changes in 2θ values are not easily perceptible although the peaks are slightly shifted in 2θ values. It is deduced that this carbon material is probably less crystalline in nature.

The FT IR spectrum of the phosphorus substituted carbon material is shown in Figure 4. The spectrum shows a broad absorption band in the region 3200–3600 cm^{-1} with the maximum around 3450 cm^{-1}. This band can be assigned to the O–H stretching mode of some adsorbed water. The position of this band and also the apparent asymmetry on the lower wave number side indicates hydrogen bonds. The absorption band at 2926 and 2852 cm^{-1} can be due to aliphatic character of the C–H bonds. The band at 1636 cm^{-1} may be due to aromatic ring stretching vibrations of the carbon moiety. The features at 1371, 1268 and 1078 cm^{-1} which can be considered as a band with shoulders are associated C–P bonds and similar observations have been recorded by Puziy et al.[33] Kurita et al[34] have also shown by quantum chemical analysis that the bands at 1250, 980 and 700 cm^{-1} are associated with intrinsic C$\equiv$P, C$=$P and C–P stretching vibrations respectively.

In order to ascertain the nano state of the material, the Raman spectrum of the phosphorus substituted carbon material was recorded (Fig. 5). The conventional two finger prints, namely the G and D bands appear at 1592 and 1280 cm^{-1} respectively thus ascertaining the integrity of the carbon material synthesized in this work.
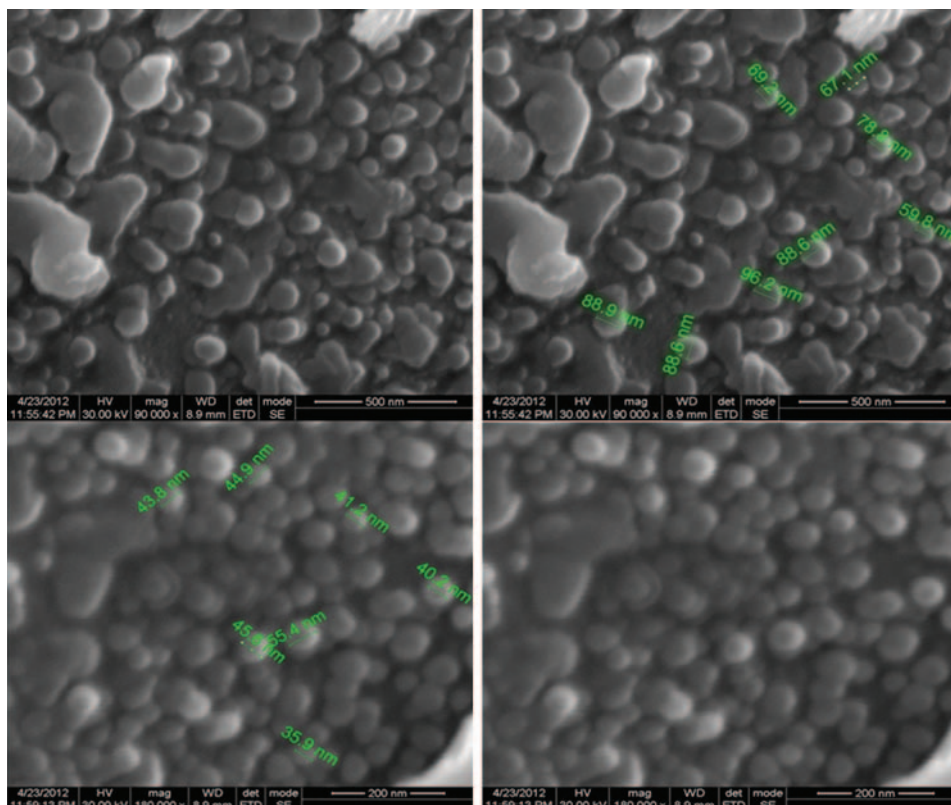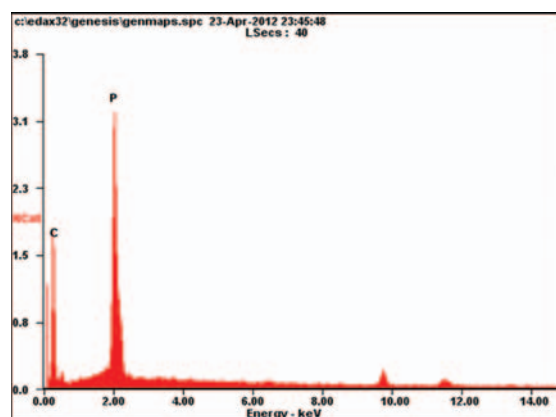

Fig. 6. Electron micrographs of the phosphorus containing carbon materials.

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Fig. 7. EDAX analysis for phosphorus containing carbon materials.

The morphological aspects of the synthesized carbon materials have been examined from the scanning micrographs and these are shown in Figure 6. The globular morphology of the carbon material is seen and thus the morphology accounts for large inter granular area which may be favorable for gas adsorption. Secondly it is possible that most of the heteroatom (P) may be segregating to the surface thus facilitating hydrogen dissociation. The nano size of the carbon materials and the almost spherical morphology of the carbon material are seen from the micrographs. EDAX analysis was resorted to for ascertaining the amount of phosphorus in this material namely 5 atomic percent (Fig. 7). This is probably indicative of the core shell model is applicable to these materials and the globular morphology may also support this contention.

3.2. Hydrogen Sorption Behavior

The hydrogen absorption capacity of this material was evaluated in the temperature range 300–373 K up to 40 bars in a typical Sivert's apparatus by volumetric method in order to avoid any possible contamination by water absorption. This simultaneous absorption of water and the measurements by gravimetric method have been attributed
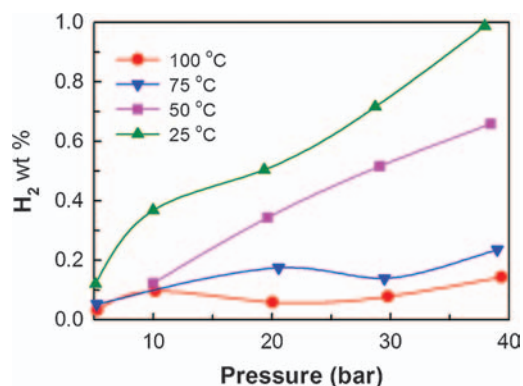
as the reasons for the non-reproducibility and excess of hydrogen absorption data reported on carbon materials, especially on carbons in nano state. The hydrogen uptake isotherms on this material are given in Figure 8. It is seen that a storage capacity of 1% is achieved on this material at 300 K and it decreases with increase in temperature and goes to 0.1% storage capacity at 100 K. These results can be considered from two points of view namely the hydrogen storage in these materials is by a process of adsorption and possibly nearly almost all the adsorbed amount can be reversed with slight increase in temperature which is a desirable characteristic expected for hydrogen storage materials.

4. CONCLUSION

This presentation attempts to substantiate that heteroatom substituted carbon nano state materials can be possible candidates for hydrogen application from both points of view namely required storage capacity and also the desired nearly complete reversibility.

Fig. 8. Adsorption isotherms of hydrogen on phosphorus containing carbon materials as a function of temperature in °C.

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