Synthesis, characterization and hydrogen storage characteristics of ambient pressure dried carbon aerogel


A Hydrogen Energy Centre, Department of Physics, Banaras Hindu University, Varanasi 221005, India
b Department of Chemical Engineering and Technology, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India
c Application Development Division, Vikram Sarabhai Space Centre, Indian Space Research Organization, Trivandrum, Kerala 695022, India

A R T I C L E   I N F O
Article history:
Received 6 October 2015
Received in revised form 12 December 2015
Accepted 26 December 2015
Available online 21 January 2016

Keywords:
Carbon aerogel
Submicropore
Hydrogen storage

A B S T R A C T
The present communication deals with the hydrogen storage performance of ambient pressure dried pristine as well as platinum doped carbon aerogel (CA-0.10 Pt). These carbon aerogels (CAs) have been prepared from resorcinol-formaldehyde (RF) through sol–gel synthesis route with sodium carbonate as a catalyst (C). The synthesis parameters adapted led to the formation of CA having preponderance of submicropores. Structural and microstructural characteristics of these carbon aerogels have been investigated through XRD, SEM, TEM, nitrogen adsorption and Raman spectroscopic techniques. Nitrogen adsorption and TEM studies confirm the large density of micropores with the majority of pores having sizes between 0.30 and 1.46 nm (submicropores). The hydrogen storage characteristics of as synthesized carbon aerogels have been investigated by monitoring the hydrogen ad/desorption curves. At room temperature and at pressure upto 22 atm the CA and CA-0.1 Pt have hydrogen storage capacity of 0.40 wt.% and 0.33 wt.% respectively. However, under the same pressure but at liquid nitrogen temperature CA and CA-0.10 Pt have hydrogen storage capacity of 5.65 wt.% and 5.15 wt.%. Feasible reasons for the high hydrogen storage capacities at liquid nitrogen temperature for the present CAs have been put forward.

I N T R O D U C T I O N
Carbon aerogels are relatively new class of materials associated with a wide variety of applications, including hydrogen storage [1–4]. Hydrogen is considered to be the promising upcoming green fuel. It has the potential to replace the conventional fossil energy sources like coal and petroleum. Hydrogen takes care of the two detrimental effects associated...
with using the fossil fuel, the pollution and the climate-change effects. For specific usage of hydrogen, particularly for fuel cells, its storage is the main concern and has become a challenging topic of contemporary research [5,6]. Several techniques like (a) compression of gaseous hydrogen (b) liquefaction (c) storage in the form of solid hydrides and porous materials have been investigated [7–9]. The porous materials are an attractive option for hydrogen storage as they are light weight, exhibit nearly complete reversibility, possess faster kinetics and manageable pressure of hydrogen ad/desorption [10,11]. A wide range of porous carbon materials have been investigated, including graphene, SWCNT, CA and many others [11]. The hydrogen storage capacity of these materials typically lies between 1.70 wt.% and 5.70 wt.% at liquid nitrogen temperature [12–16] which satisfy the DOE limits of storage (2017: 5.50 wt.%, 40 kgH2/L) [17]. Out of various porous solids, CA shows promising hydrogen storage properties particularly at liquid nitrogen temperature, owing to their continuous porosity, ultrafine pore size and high surface area [3]. Apart from hydrogen storage applications, CAs also have several other attractive applications, such as an active electrode material for supercapacitors, batteries, fuel cells, gas filtration membranes, reinforcing agents for natural rubber, light weight structural composites for space fuel cells, gas filtration membranes, reinforcing agents for an active electrode material for supercapacitors, batteries, CAs also have several other attractive applications, such as surface area [3]. Apart from hydrogen storage applications, CAs also have several other attractive applications, such as an active electrode material for supercapacitors, batteries, fuel cells, gas filtration membranes, reinforcing agents for natural rubber, light weight structural composites for space fuel cells, gas filtration membranes, reinforcing agents for an active electrode material for supercapacitors, batteries, CAs also have several other attractive applications, such as surface area [3].

**Experimental**

**Synthesis of carbon aerogel and platinum doped carbon aerogel through ambient pressure drying method**

In the present investigation our objectives were to obtain CAs with negligible shrinkage which was achieved by ambient pressure drying. Moreover, it was envisaged to synthesize such CAs which has a preponderance of micropores with negligible density of mesopores and macropores. The CAs were synthesized from resorcinol (99%) (Merk specialty chemicals India Ltd), formaldehyde (37% in water, Polyformalein Pvt Ltd; Cochin, India) and sodium carbonate (NICE India Ltd.). Several variations of the concentrations of reactant and catalyst were tried. For each of them, microstructure was determined through TEM and SEM. The optimum concentration for achieving highest density of micropores was found to be 1.0 mol of resorcinol to 2.0 mol of formaldehyde i.e. R:F is 1:2 in distilled water with total solids being 30%. Sodium carbonate was used as catalyst and optimum R:C molar ratio was 1500:1 (for the formation of micropores). The precursors were mixed by magnetic stirring for 3 h in a sealed container. After that the mixture was gelled at room temperature for 24 h. The aerogel was then aged in an oven at 50 °C for 24 h and 90 °C for 72 h. In order to promote additional crosslinking of the gel, 2% acetic acid was added to the solvent during the initial water to solvent (acetone) exchange for 24 h. Then the RF wet gel was subjected to acetone exchange at 50 °C for 72 h, where acetone was replaced with fresh acetone once in 24 h. Finally, we have carried out ambient pressure drying of the RF wet gel at three different temperatures i.e. 25 °C, 50 °C and 80 °C. It was found that the optimum microstructure was obtained when drying was done at 50 °C. Therefore, the RF wet gel was allowed to dry at 50 °C (optimum temperature) for 72 h in the acetone medium. The dried RF aerogel samples were then carbonized by heating it under argon atmosphere (Ar flow rate = 2 l/min) by adopting the following heating programme: room temperature to 1050 °C at a heating rate of 1 °C/min and hold the sample at 1050 °C for three hours. Afterwards the samples were cooled from 1050 °C to 300 °C at a heating rate of 0.5 °C/ min and then from 300 °C to room temperature by ambient cooling. Fig. 1 shows the schematic protocol for synthesis of carbon aerogel. Besides the above described pristine CAs, platinum doped CAs (CA-0.10 Pt) were synthesized by gelling the resorcinol-formaldehyde system in the presence of hexachloroplatinic acid solution (0.10 M) followed by the same procedure as adopted for the synthesis of pristine CA.
Characterizations

Structural and microstructural characteristics

Structural characterization of the samples was carried out using X’Pert PRO (PANalytical) X-ray diffractometer equipped with a graphite monochromator employing CuKα radiation (\(\lambda = 1.5402 \text{ Å}\)). Microstructural characterization was done by using FEI Quanta 200 scanning electron microscope (SEM) and FEI Technai-20 G2 (200 kV) high resolution transmission electron microscope (TEM). Raman spectra were obtained using Horiba LabRAM HR800 (Argon LASER light of wavelength 514 nm). The BET surface area and pore size analysis was carried out by nitrogen adsorption/desorption technique using the surface area analyzer (Micrometrics, USA, ASAP 2020 Models).

Hydrogen sorption characteristics of CA and CA-0.10Pt

Hydrogen sorption (ad/desorption) behaviour of pristine and platinum doped carbon aerogels was studied using an automated four-channel Sieverts apparatus (Advanced materials corporation, Pittsburgh USA). All gases used for sorption analysis were of 99.99% purity. Hydrogen ad/desorption curves of carbon aerogel samples were evaluated between the pressure range 0.10 and 22 atm at room temperature as well as at liquid nitrogen temperature (\(-196 \text{ °C}\)). It may be pointed out that our hydrogen ad/desorption evaluation system has been standardized and we have measured hydrogen sorption characteristics of several storage materials [30]. Carbon aerogel (0.50 g) was used for each sorption analysis. The sample was kept in a leak-tight stainless steel hollow cylindrical sample chamber having volume of 25 cc, which was then evacuated to \(10^{-6} \text{ torr}\) for 2 h to clean the surface of the sample. Subsequently doses of hydrogen gas were introduced into the sample chamber and the amount of hydrogen adsorbed at each equilibrium pressure was calculated. The procedure was reversed for desorption studies.

Results and discussion

Representative XRD patterns of pristine CA indicates that there are two broad diffraction peaks of CA at 2θ = 24.30° and 2θ = 43.30° (indicated by arrows in Fig. 2(a)). These peaks match with those of CA [31] thereby confirming the formation of CA. The representative XRD peak of CA-0.10 Pt is shown in Fig. 2(b) (inset shows the peak of CA at 2θ = 24.30°). The sharp high intensity XRD peaks obtained at 2θ = 39.85°, 46.80° and 67.40° correspond to crystalline Pt. The presence of sharp intense XRD peaks of Pt suggests that these particles are on the surface of CAs. Characteristic SEM micrographs of pristine CA and CA-0.10 Pt, synthesized in the present investigation are shown in Fig. 3(a) and (b) respectively. It can be clearly seen that Fig. 3(a) exhibits pearl like regions aligned along a string. The pearl like particles are connected through well defined necks. The neck connects two particles making them to exist together rather than getting separate. The existence of necks suggests high mechanical strength of these CAs [31]. Some of these are marked by arrows in Fig. 3(a). Thus, the process of drying at an ambient pressure does not lead to any discernible shrinkage. This is in keeping with our results on synthesis, as described in the previous section. Moreover, the presence of platinum is easily visualized for CA-0.10 Pt in SEM micrographs taken in backscattered mode. It can be noticed that Pt appears in the form of fine particles [one such region is

![Fig. 1 – Synthesis protocol of carbon aerogel.](image-url)
A representative TEM micrograph of pristine CA is shown in Fig. 4(a) (see also Fig 8). As can be clearly seen, the microstructure reveals that the whole area is full of micropores having sizes ranging from 0.30 to 1.46 nm. It can therefore be concluded that the CA synthesized in the present study contains high density of micropores. The Pt doped CAs in addition to micropores (which have broadly the same sizes as in pristine CA), also revealed the presence of

Fig. 2 – X-ray diffraction patterns of (a) pristine CA and (b) CA-0.10 Pt. XRD peaks for CA correspond to disordered carbon matrix (marked by arrows). The sharp XRD peaks in Fig. 1(b) are from Pt which has been doped in CA (inset shows the peak of CA at 2θ = 24.30°).

Fig. 3 – Scanning electron micrograph of (a) pristine CA and (b) CA-0.10Pt. [The white doted contrast represents high density Pt doping (one such region is outlined by a circle)].
comparatively large Pt particles. The sizes of Pt particles have been found to range from 5.0 to 15 nm as shown in Fig. 4(b). Typical Raman spectra of pristine CA are shown in Fig. 5(a). It has strong D (1348 cm\(^{-1}\)) and G (1598 cm\(^{-1}\)) bands, which are similar to the known Raman peaks for CAs [32]. Fig. 5(b) shows the Raman spectra of CA-0.10 Pt. This has strong D (1339.5 cm\(^{-1}\)) and G (1595.50 cm\(^{-1}\)) bands. The I\(_D\)/I\(_G\) ratio is 1.16 for Fig. 5(a) and 1.03 for Fig. 5(b). This suggests disordered structure of carbon. The extent of disorder is lower by ~12% for the Pt doped CA. This may be due to possible local crystallization at regions of contact of CA and Pt particles which are on the surface of CA. These features are in broad agreement with XRD analysis for CA [Fig. 2(a)].

**Hydrogen sorption characteristics**

We now proceed to describe and discuss the hydrogen ad/desorption characteristics of CAs. Fig. 6(a), shows a typical adsorption isotherm of pristine CA and CA-0.10 Pt at room temperature which shows hydrogen uptake of 0.40 wt.% for pristine CA and 0.33 wt.% for CA-0.10 Pt at 22 atm of pressure. Fig. 6(b) shows the adsorption curves of pristine as well as Pt doped CA at liquid nitrogen temperature with hydrogen uptake capacity of 5.65 wt.% and 5.15 wt.% respectively. The Pt doping was done in the hope that it might produce the spillover effect, i.e., hydrogen would dissociate into atoms on the surface of platinum and then spillover and migrate to the interstitial pores of CAs. This would result in additional storage of hydrogen.

It was also observed that the nature of the isotherm and hydrogen storage capacity does not depend upon the number of adsorption cycles. This indicates reversible hydrogen storage in the present CAs. On comparing Fig. 6(a) and (b), it is clear that hydrogen adsorption capacity at room temperature is considerably lower than at liquid nitrogen temperature. This is so since hydrogen adsorption in carbon aerogel as is well known takes place due to binding of hydrogen molecules on carbons through weak bonding. This bonding will be stronger at liquid nitrogen temperature. The hydrogen adsorption (at room temperature and at liquid nitrogen temperature) in the as synthesized CA is proportional to the pressure, and showing near linear behaviour between hydrogen uptake and equilibrium pressure as is also found in other studies [11,12,33]. The saturation limit for hydrogen adsorption curve for physisorption at liquid nitrogen temperature is nearly equal to density of condensed hydrogen in the micropore volume. This does not seem to be attained up to the pressure studied in present investigation. Our Sieverts apparatus had the limitations of working optimally only up to about 25–30 atm. We found that the adsorption upto 22 atm was quite reproducible. Therefore adsorption curves are shown up to ~22 atm (Fig. 6(a) and (b)). However, in few samples when the pressure is raised to 30 atm the storage capacity of ~7.0 wt.% is achieved, although these results are not reproducible. As outlined earlier in the introduction part the properties of the CA depend upon several factors particularly on the concentration and pH of precursors, R:F and R:C, gelation time, mode of drying, carbonization temperature and activation conditions of CA. This is so since the said factors lead to cross linking between precursor’s polymer chain and collapse of pores. The generally adopted method of drying is supercritical drying. However, there have been comparatively sparse studies where ambient pressure dried CA [3,4,28] have been used for hydrogen storage. One advantage of the ambient pressure drying is that under suitable conditions this may lead to CA microstructure containing high density of micropores [3]. As is known this situation is helpful for hydrogen storage [11]. Keeping the above aspects in view, we have prepared carbon aerogel having dominance of micropores through ambient drying. We have found that the aerogel prepared by the above said process and at specific temperature (50 °C) followed by carbonisation at 1050 °C for 3 h leads to CA with microstructure having dominance of micropores. The surface area and pore size analysis was also carried out by nitrogen ad/desorption technique at liquid nitrogen temperature. The nitrogen ad/desorption isotherm curve is shown in [Image 130x62 to 470x214].

**Fig. 4** – TEM micrograph of (a) pristine CA and (b) CA-0.10 Pt.
Fig. 7 which corresponds to type I isotherm on BDDT classification. Such isotherms are observed when adsorptions are limited to at most a few molecular layers. This situation arises with microporous powders whose pore size does not exceed a few adsorbate molecular diameters. A gas molecule inside the micropores experiences overlapping potential from the pore walls which enhances the quantity adsorbed at low relative pressure. Consequently, pores are filled at lower pressures. Since micropores are dominantly present, the exposed surface resides almost exclusively within the micropores. It means that once pores are filled there is little or no external surface available for additional adsorption. The BET surface area was observed to be 379 m$^2$/g. Since, the measurement of surface area is based on BET theory of multilayer absorption, it may not be very accurate for microporous substances where only one or two layers of adsorption of N$_2$ gas are possible. Therefore, the actual surface area of the sample may be greater than the value of 379 m$^2$/g obtained in the present study. The total pore volume was observed to be 0.209 cm$^3$/g. The mesopore volume (pore size > 1.5 nm) was only 0.0254 cm$^3$/g. Macropores were not observed in the sample. The micropore volume calculated by subtracting mesopore volume from total pore volume was 0.1836 cm$^3$/g. The micropore volume was also calculated using the micro pore (MP) method. The micropore volume between pore size 0.42 and 1.50 nm was found to be 0.2064 cm$^3$/g. This value is nearly equal to the above reported value calculated by the difference in total pore volume and mesopore volume. From the values of micropore volume and mesopore volume, it is concluded that the present CA have predominantly micropores. It is to be mentioned that the submicropores less than 0.42 nm would not be detected by nitrogen adsorption technique but the sample still may have a significant density of these pores. Such pores will permit smaller hydrogen molecules to penetrate inside the pores whereas penetration by nitrogen (because of its greater size compared to hydrogen) will be prevented. In such small size micropores (submicropores) hydrogen condensation is expected to take place [34]. Other workers have found indirect evidence of high density of submicropores in ambient dried CA [3,11]. However, we have also shown direct evidence of existence of submicropores having sizes ranging in between 0.30 and 1.46 nm Fig. 4(a–b). Both the results taken together substantiate our conclusion that submicropores are responsible for higher hydrogen capacity of as synthesized CA. The CAs prepared by us invariably exhibited two new features, which are (i) indiscernible shrinkage after drying (which implies that large amount of coherent CA is available for hydrogen storage) (ii) microstructure embodies very high number density of micropores with little evidence of mesopores. It may be pointed out that there has been many studies embodying hydrogen storage in carbons including nanostructured carbon, porous carbons and carbon aerogels [11]. The available literature in CA till date suggests that there are two mechanisms of hydrogen storage in CAs. In one of these, physisorption takes on surface. For many studies, therefore the focus of synthesis and activation process is on
enhancing surface area. These CAs follow Chahine rule [35]. As per Chahine rule the surface area of 500 m²/g should lead to hydrogen storage capacity of 1 wt.%. It should be pointed out that several studies suggest that hydrogen storage in CA may not depend on surface area alone [3]. In other words, these do not follow Chahine rule. The other mechanism of hydrogen storage in CAs is through condensation and pore size filling like assemblage of hydrogen molecules by a surface coverage mechanism. The nature of interaction of hydrogen and carbon in CAs is important. This may lead to methods of improvement in hydrogen storage capacity of CAs. It is known that this interaction is very weak at room temperature. One way to make the interaction strong is to polarize the carbon matrix. The other method is to employ lower temperature and have filling of hydrogen in pores whose size is comparable to the size of hydrogen molecule. In the present study we have adapted the latter method to improve the hydrogen storage property of CA. The broad features of this mode are known but details need to be explored further [34]. We have shown that the dominant pores in our specially synthesized CAs are micropores with size 0.30±1.46 nm (Fig. 4(a–b)). It can therefore be said that in the present case, the pore filling mechanism was operative. It is generally believed that when pore size is in the range of size of the adsorbed molecule several peculiarities which are not well understood arise [34]. The details of hydrogen storage through micropore filling are not well understood. A tentative feasible schematic of the hydrogen adsorption process in CA is shown in Fig. 8. Table 1 shows the comparison of hydrogen storage properties of different carbon materials which reveals that the CAs studied in the present investigation possess comparatively high hydrogen storage capacity of ~5.65 wt.% at 22 atm pressure.

Fig. 6 – Hydrogen adsorption isotherms of (a) pristine CA and CA-0.10 Pt at room temperature and (b) pristine CA and CA-0.10 Pt at liquid nitrogen temperature.
Conclusion

CAs (pristine and doped with Pt) have been synthesized using resorcinol and formaldehyde (1:2 M) via sol–gel technique. Ambient pressure drying has been used to dry the RF aerogel followed by carbonization. The optimum synthesis conditions used ensured the dominance of submicropore (0.30–1.46 nm) which has proven to be beneficial for hydrogen storage. The present investigation suggests that hydrogen storage capacity (~5.65 wt.%) at liquid nitrogen temperature (~196 °C) can be obtained for CAs which have dominant presence of submicropores. This is a new feature emerging from the present study. Hydrogen ad/desorption studies show complete reversibility at room and liquid nitrogen temperature. The hydrogen storage in submicropores takes place by a volume
filing mechanism which may lead to condensation rather than by a surface coverage mechanism. The Pt doped CAs have not shown enhanced storage capacity due to anticipated spillover effect. The present studies suggest that further research on synthesis of CAs with dominant presence of submicropores is required. Also, details of hydrogen storage in CAs through filling of submicropores leading to condensation like assemblage of hydrogen needs to be investigated.

Acknowledgements

Support from the Ministry of New and Renewable Energy (Mission mode project on Hydrogen Storage), Department of Science and Technology and the University Grants Commission, HWB (DAE), ISRO are thankfully acknowledged.

REFERENCES


Table 1 – Hydrogen storage capacity of different carbon materials.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Materials</th>
<th>Hydrogen adsorbed (at – 196 °C)</th>
<th>Reference no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thermally reduced GO</td>
<td>2.07 wt.%, upto 50 atm H2 pressure</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>Fe doped Graphene</td>
<td>2.16 wt.%, upto 50 atm H2 pressure</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Purified SWCNT</td>
<td>2.40 wt.% upto 70 atm H2 pressure</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>CA</td>
<td>5.70 wt.% upto 45 atm H2 pressure</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>Co doped CA</td>
<td>2.50 wt.% upto 45 atm H2 pressure</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>Pd doped CA</td>
<td>1.40 wt.% upto 25 atm H2 pressure</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>CA and Pt doped CA</td>
<td>5.65 and 5.15 wt% respectively upto 22 atm H2 pressure</td>
<td>Present study</td>
</tr>
</tbody>
</table>


[34] Beguin F, Frackowiak E. Carbons for electrochemical energy storage and conversion systems. CRC Press; 2010.
