Investigations on Hydrogen Storage Capacity of New Generation Carbon Materials

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TITLE OF THE THESIS

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BRIEF DESCRIPTION ON THE STATE OF THE RESEARCH TOPIC

The concept of environmentally acceptable, renewable and sustainable energy sources worries on the utilization of fossil fuels and their asset imperatives [1]. All the three components of the hydrogen economy, namely, production, storage and application of hydrogen have been posing challenges to the scientific community for the past several decades [2]. Hydrogen storage is an important component for operation of transport sector in green energy mode. Hydrogen storage is particularly challenging as evolving a safe and efficient hydrogen storage medium with the required capacity appears to be difficult. Hence it has evolved as one of the foremost research topics of material research scientists [1]. The US-DOE specifies a hydrogen storage capacity for on board automobile application as required storage capacity for FY 2005 (4.5 wt %), FY 2010 (6 wt %) and 9 wt% for FY 2015, have not been accomplished despite considerable efforts have been expanded in this direction. The question at this time is can one meet this target for the hydrogen energy storage capacity within the time frame available?. There are three possible ways for hydrogen storage namely compression, liquefaction and storage in solids [3]. The first two options compressed gas and liquid hydrogen storage systems are unrealistic to meet the forceful US Department of Energy (DOE) standards which focus for on-board Hydrogen storage systems. Hydrogen transport as compressed gas in high pressure cylinders meets with the restriction of included cost [4]. Safe and financially savvy storage are viewed as important for the predominant use of hydrogen in transport sector as well as in stationary and compact gadgets applications; with the transportation segment representing the most serious challenge. At present, storage of hydrogen in solid matrices appears to be the appropriate option. Solid state hydrogen storage where a host material is utilized as a hydrogen energy carrier, offers necessary volumetric energy densities. Variety of solid state hydrogen storage media has been analyzed in the previous decades in light of criteria like storage capacity, reversibility and cost. Carbon materials have been examined as one of the possible options [5]. In view of the possible promising traits, hydrogen storage using nanostructured carbon materials has quickly gained as one of the hot areas of research in science and technology. The carbon nanostructures also find potential applications in various other areas like super-capacitors, energy conversion systems and fuel cells. The scientific society in their anxiety has examined variety of carbon materials for sufficient hydrogen storage and also focused on realizing reproducible results for hydrogen storage. The minimum storage capacity for commercial application has been estimated to be 6.5 wt% as postulated by DOE [6]. It is necessary to recall that hydrogen storage up to 67 weight % has been reported in exotic carbon materials, though the reproducibility of the result has not been established [6]. Various types of carbon-based adsorbents have been proposed for hydrogen storage, including carbon nanotubes (CNTs), graphite nanofibers (GNFs), activated carbons (ACs), templated carbons (TCs), and graphite. This has opened up a variety of investigations dealing with modification of carbon materials like metal loading [7], preparing carbon materials in various geometrical forms and phase purity and addition of metal oxides[8], but however none of these studies have unambiguously established that carbon nanomaterials can store hydrogen to the extent required by the original DOE standards [9]. The introduction of heteroatom like nitrogen (N), sulphur (S), boron (B) and phosphorus (P) in carbon materials has been shown to produce activation centres for dissociation of molecular hydrogen and thus possibly facilitates hydrogen storage [10-13]. Even though reversible nature of the hydrogen absorption/desorption process on/in carbon-based materials and high surface area sorbents has been realized, they suffer from lower hydrogen storage capacity, especially under desirable operating conditions [14]. However, irrespective of their high surface area, the presence of heteroatom on the surface of carbon materials has been regarded as an attractive feature to increase the hydrogen storage capacity [15].

DEFINITION OF THE CHOSEN PROBLEM

The hydrogen energy economy is "bottle neck" situation for future fuel demands in recent years. The materials for hydrogen storage is emerging research area. For this situation, carbonaceous materials is the most widely used as adsorbent for hydrogen storage because their high porosity and large surface area different morphologies and also enormous hydrogen adsorption capacity. Synthesis of carbon materials from the chemical way and natural sources and also evaluating their potential as adsorbent is the emerging research field for hydrogen storage. However, heteroatoms containing carbon materials shows potential for hydrogen storage on DOE standards. With these backgrounds, an idea has been developed to prepare carbon nanomaterials with heteroatoms using different methods, various precursors, different heteroatom sources and different reaction temperature for utilizing to improve the hydrogen storage capacity for ambient conditions.

OBJECTIVE AND SCOPE OF RESEARCH WORK

Against this background, the need for activators, high surface area, different porous structures, new morphologies is realized. The resultant material should be capable of absorbing hydrogen higher than that by carbon. The activators should facilitate dissociation and migration of the dissociated hydrogen to equipotential carbon surface. While considering these aspects heteroatoms like N, P, S and B seem to be promising due to their property of higher redox potential than that of carbon. This can result in the tuning of the electronic property of the carbon materials. Therefore, the present study is aimed at establishing the role of heteroatom for hydrogen storage in the carbon materials.

The thesis work deals with the following aspects.

- Development of appropriate synthesis method for different carbon materials like carbon nanotubes (CNTs), Graphene, carbon materials from polymeric precursors and carbon materials from natural sources with chemical activation.
- Incorporation of different heteroatoms (B, N and P) in these carbon materials.
- The concluding aim is to evolve conditions for the formation of carbon nanomaterials will be characterized using different types of standard analytical methods such as Powder X-ray Diffraction (PXRD), FT-IR spectroscopy, TGA-DTA, RAMAN Spectroscopy, XPS, CHN-elemental analyzer, HRSEM with EDAX, HRTEM with EDAX, SAED pattern, STEM and elemental mapping. BET-N_2 Adsorption isotherms and HPVA (High Pressure Volumetric Analyzer) for using Hydrogen adsorption/desorption measurement. These measurements will provide information on the relationship between the characteristics of these materials namely crystalline nature, functional groups, binding energy, morphology, elements present, surface area, pore volume and Investigation of the hydrogen storage capacity by these materials.

METHODOLOGY

Experimental work has been conducted to prepare the carbon materials at different reaction conditions.

Preparation of Different Types of Carbon Materials

(1) Synthesis Method of Phosphorous Substituted Carbon Material

The typical synthesis procedure is as follows, 5.5 g of resorcinol was taken in a beaker, and 15 mL of formaldehyde solution was added, stirred at room temperature for 1 h and then 31 mL of phosphoric acid (H3PO4) was added stirred for 1 h followed by addition of 1 g of sodium hydroxide (NaOH) The mixture was stirred well at room temperature, then kept in an oven at 373 K for 24 h. The final homogeneous mixture was placed in a quartz boat and subsequently transferred to a tubular furnace for carbonization. The furnace was purged with nitrogen gas at room temperature for 1 h. After 5 min, the temperature was increased at a rate of 5 °C/min to the target temperature (600 and 800 °C). Finally obtained phosphorous containing carbon material was subjected to further characterization.

(2) Synthesis method of Heteroatom Doped Multi-Layered Graphene material

The typical synthesis procedure is as follows, 1.5 g of Graphite oxide was taken in a beaker. GO aqueous dispersion was diluted with 25 mL of distilled water, and then 21 mL of H_3PO_4 solution was added into the GO dispersion under sonication for 2 hours. The hydrothermal reaction carried out and the solution was sealed in a 100 mL Teflon-lined autoclave and maintained at 180˚C for 12 hours. Then, autoclave was naturally cooled to room temperature and the product was taken out. Then again the sample was annealed 500˚C for 2 hours under inert atmosphere heating rate employed is 5˚C/min. Then, the tubular furnace was allowed to cool automatically. The obtained products were filtered and washed with distilled water for three times. Finally, the collected sample was utilized for the characterization. For comparison, RGO was also prepared under the same experimental conditions but without adding the H_3PO_4 into the GO aqueous dispersion.

(3) Synthesis Method of Nitrogen-Doped Carbon Nanotube (NCNTs)

The typical synthesis procedure is as follows, 22 g of polystyrene were taken in a 400mL beaker, and added15 mL of DI water stirred well then added 20mL of benzene stirred well and 15 mL pyrrole was added then stirred well added 2g of ferrocene to the reaction mixture stirred well in an ice bath then added the HCHO and 2g of NaOH now the reaction mixture color is blue then added 2.5 g of Ammonium persulphate (APS) then the color is changed to green this reaction process continued for 24 hours after the reaction mixture is black in color. Viscous product collected and washed with water thoroughly then this product transferred to quartz boat kept in an tubular furnace for carbonization in three different temperatures (500°C, 700°C and 900°C) heating rate employed is 10°C/min. The furnace was cooled to room temperature in the presence of nitrogen. Throughout the procedure, the furnace was continually purged with nitrogen gas. After the carbonization the carbon material again washed with DI water and dried at 90°C for 2h in vacuum oven. The resulting carbon material was ground into a fine powder using a mortar and pestle. Finally, obtained nitrogen doped carbon nanomaterials denoted as (NCNR-500), (NCBCT-700) and (NCNT-900).

(4) Synthesis Method of Phosphorous-Doped Porous Carbon

The typical synthesis procedure is as follows: The paste of newly growing (Ficus Benghalensis, Family: Moraceae) was collected and cut into small pieces then thoroughly washed and dried in an oven at 90 °C. The crushed pastes were impregnated with 35 mL of H_3PO_4 for 24 h and dried in sunlight for 6 h to remove the moisture. For the activation process, the preferred amount of preheated crushed paste was transferred in a quartz boat kept at center of the tubular furnace. To optimize the activation temperature, the furnace was initially heated at 200°C and then the heating was continued at 800°C under N_2 atmosphere at the heating rate of 5°C/min. After the calcination, the tubular furnace was cooled to room temperature. The calcined material was washed with distilled water thoroughly. Finally, the synthesized phosphorous-doped porous carbon (PDPC) material was utilized for further characterization.

(5) Synthesis method of boron substituted carbon material

The typical synthesis procedure is as follows, 11.2 g of resorcinol was taken in a beaker, 30 ml of formaldehyde solution was added stirred at room temperature for 1 h, 20 ml of triethylborate (TEB) solution was added stirred well, kept in an oven at 373 K for 24 h. The as-synthesized materials were placed in an alumina crucible and subsequently transferred to a tube furnace for carbonization. The furnace was purged with nitrogen gas at room temperature for 1 h. Then the temperature was increased at a rate of 5°C/min up to 200°C and maintained at 200°C for 5min to remove trace adsorbed contaminants. After 5min, the temperature was increased at a rate of 10°C/min to the target temperature (600°C and 800°C) for 6h. Finally obtained boron containing carbon materials denoted as BC-600 and BC-800 was subjected to further characterization.

ORIGINAL CONTRIBUTION

1. Hydrogen sorption in phosphorous substituted carbon material

The hydrogen storage capacity of phosphorous substituted carbon material with spherical morphology is reported. The phosphorous substituted carbons are synthesized by pyrolyzing a resorcinol formaldehyde resin, chemically bonded with phosphorous. The synthesis is a polycondensation reaction by phosphoric acid with sodium hydroxide as catalyst. Herein resorcinol-formaldehyde resin and phosphoric acid act as carbon and phosphorous sources respectively. The hydrogen adsorption capacity has been studied by high pressure volumetric analyzer and shows high sorption capacity of 2.6 and 2 wt% at 298 K and 100 bar pressure for the phosphorous substituted carbon materials prepared by calcining at 600^0 and 800°C respectively. This value is higher than the hydrogen sorption capacity of pure carbon under comparable preparation conditions 0.18 and 0.16 wt% at 298 K and 100 bar pressure, calcined at 600 and 800^oC respectively.

2. **Heteroatom Doped Multi-Layered Graphene Material for Hydrogen Storage Application**

A variety of distinctive techniques have been developed to produce graphene sheets and their functionalized subsidiaries or composites. The production of graphene sheets by oxidative exfoliation of graphite can be a suitable route for the preparation of high volumes of graphene derivatives. P-substituted graphene material is developed for its application in hydrogen sorption at room temperature. Phosphorous doped graphene material with multi-layers of graphene shows a nearly ~2.2 wt% hydrogen sorption capacity at 298 K and 100 bar. This value is higher than that for reduced graphene oxide (RGO without phosphorous).

3. **Nitrogen-incorporated carbon nanotube derived from polystyrene and poly pyrrole for use as hydrogen storage material**

A facile method for the synthesis of nitrogen enriched carbon nanotubes derived from polystyrene and polypyrrole by the poly-condensation followed by carbonization processes has been developed. The nitrogen-doped carbon nanotubes have specific surface area (870 m^2/g).

The nitrogen-doped carbon nanotube (NCNT-900) exhibited hydrogen storage capacity of 1.9 wt% at 298 K and 100 bar (high pressure). The variation of carbonization temperature leads to prepare carbon materials with different morphologies. Carbonization temperature was varied, namely 500°C, 700°C and 900°C. It is denoted as nitrogen doped carbon nanorods (NCNR-500), nitrogen doped compiled beads like carbon tubes (NCBCT-700) and nitrogen doped carbon nanotube (NCNT-900) respectively. The fabricated nitrogen doped carbon nanotubes show an interesting structural and textural properties and may serve as potential hydrogen storage material.

4. Phosphorous-doped porous carbon derived from paste of newly grown Ficus Benghalensis for use as hydrogen storage material

The synthesis of heteroatom (P)-doped porous carbon derived from the paste of newly growing Indian banyan tree (*Ficus Benghalensis*) is described. The synthesis involves activation, carbonization and phosphorous doping processes using H_3PO_4 as activating agent and as phosphorous source. The phosphorous-doped porous carbon material shows a wafer-like morphology with specific surface area of 1406 m^2/g. This material exhibits hydrogen storage capacity of ~1.2wt% at 298 K and 100 bar. The prepared carbon material is promising for realistic hydrogen storage.

5. Hydrogen storage on boron substituted carbon materials

Hydrogen storage capacity of boron substituted carbon materials synthesized by the carbonization of resorcinol and triethylborate as carbon and boron sources respectively is reported. The effects of the boron-doping and carbonization temperature and the role of functional groups have been investigated. The hydrogen adsorption capacity has been studied with a high pressure volumetric analyzer (HPVA) and a maximum of 5.9 wt% hydrogen storage capacity was observed at 298 K and 100 bar pressure. At 77 K in both carbon samples (namely BC-600 or BC-800) show only fractional weight percent of hydrogen sorption (1.1 and 0.5 wt%). The nearly 5 weight % hydrogen storage was obtained by loading heteroatom (B) to carbon sample at 298 K and 100 bar.

CONCLUSION (SUMMARY AND SUGGESTIONS FOR FUTURE WORK)

- Phosphorous containing carbon materials produced by using polymer as the carbon precursor exhibited different chemical environments for phosphorous. The phosphorus substituted carbon materials calcined at 600 and 800°C showed respectively 2.6 wt% and 2 wt% of hydrogen storage capacity at 298 K and 100 bar pressure. This value is higher compared to pure carbon (without P) materials. Sorption materials such as heteroatom (P) substituted carbon are likely to motivate the search for increasing the extent of heteroatom substitution in carbon materials for improving hydrogen storage capacities.

- Nitrogen containing CNTs are amenable for hydrogen absorption than other carbon materials. However, these active sites should be made catalytic in nature by various preparation methods and surface engineering so that necessary hydrogen storage may be achieved. This as-prepared nitrogen doped carbon nanotube (NCNT) material showed hydrogen storage capacity of ~1.9 wt% at room temperature and 100 bar.
- Boron substituted carbon materials have been shown that the boron content, surface area and hydrogen storage capacity can be controlled by carbonization temperature. For effective hydrogen storage these boron atoms should be incorporated chemically into the carbon network. For boron atoms two different environments in the carbon materials have been prepared and the maximum hydrogen storage capacity of 5.9 Wt % has been realized at 298 K and 100 bar pressure.
- A facile route for the preparation of phosphorous containing graphene material has been proposed. The heteroatom substituted graphene material showed a hydrogen sorption capacity of ~2.2 wt% at 298 K and 100 bar. The proposed synthesis can be an alternative method for P-doped graphene with developed specific phosphorous species for hydrogen adsorption as well as green energy exploitation and sustainable environmental preservation.
- The utilization of biomass or biomass wastes as precursors has been used for synthesizing porous carbon for hydrogen storage. This as-prepared porous phosphorous doped carbon material showed hydrogen storage capacity of ~1.2wt% at 298 K and 100 bar. Thus, the proposed synthesis can be alternative resource for P-doped porous carbon material for hydrogen adsorption.
- The heteroatom substitution in the carbon materials opens up another avenue in the hydrogen storage materials research. The results provide insights into how to promote hydrogen storage capacity in heteroatom doped carbon materials and improving the reversibility. Furthermore, this method offers a concerned approach for the synthesis of heteroatoms doped

carbon materials which may be potentially utilized as reversible hydrogen storage medium at room temperature.

LIST OF PAPER PUBLICATIONS

1. **Arjunan Ariharan, Balasubramanian Viswanathan* & Vaiyapuri Nandhakumar**, Hydrogen storage on boron substituted carbon materials, International journal of hydrogen energy, 41 (2016) 3527-3536, Elsevier Publisher (Published). Impact factor (3.9)
2. **Arjunan Ariharan**, **Balasubramanian Viswanathan* & Vaiyapuri Nandhakumar**, Phosphorous substituted multilayered graphene material for hydrogen energy storage application, Graphene, Vol.5 No.2, April 2016, Scientific research publisher (Published). Google based Impact factor (1.6).
3. **Arjunan Ariharan, Balasubramanian Viswanathan* & Vaiyapuri Nandhakumar**, Phosphorous-doped porous carbon derived from paste of newly growing Ficus Benghalensis as hydrogen storage material, Indian Journal of Chemistry Sec A, Vol. 55A, June 2016, pp. 649-656 (Published). Impact factor (0.79).
4. **Arjunan Ariharan, Balasubramanian Viswanathan* & Vaiyapuri Nandhakumar**, Hydrogen sorption in phosphorous substituted carbon materials, Indian journal of chemistry Sec A, Vol. 54A, December 2015, pp. 1423-1433 (Published). Impact factor (0.79).
5. **Arjunan Ariharan, Balasubramanian Viswanathan* & Vaiyapuri Nandhakumar**, Synthesis of nitrogen-doped carbon nanotube from polymeric precursors for application as hydrogen storage material, International journal of hydrogen energy, Elsevier Publisher (Under Review) Impact factor (3.9)

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