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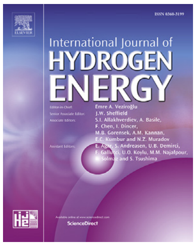

Nitrogen doped porous carbon derived from EDTA: Effect of pores on hydrogen storage properties

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ABSTRACT

N doped carbon samples have been prepared from commonly available precursor EDTA and thoroughly characterised using a variety of techniques. It has been found that with increase in annealing temperature graphitic character increases along with decrease in nitrogen content. During chemical activation by treatment with H_3PO_4, C atoms from the network structure get oxidised preferentially giving rise to larger pores, as confirmed by TEM and SAXS analysis. Possible mechanism of activation has been proposed based on NMR and XPS results. From NMR it is established that the activated samples consist of both orthophosphate (Q^0) and pyrophosphate (Q^1) structural units and are weakly linked to carbon network. Pore size has been correlated with hydrogen storage capacity and it has been found that the presence of large number of pores with lower diameter is preferable for getting better hydrogen storage capacity in porous carbon based materials.

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Introduction

Large surface area amorphous and porous carbons find extensive applications as electrode materials in electrochemical energy storage and as materials for storage of gases like CO_2, SO_2, H_2S, H_2 etc. [1–5]. In many studies, porous carbons are modified by doing with B, N, S, P etc to improve its gas storage properties [6–9]. Such materials exhibit improved storage performance, as presence of these elements at surface can enhance its reactivity. Among the hetero atoms, nitrogen has received more attention due to its high electro negativity and comparable size with carbon atom [10,11]. Moreover, lone pair electrons of nitrogen hybridize with p electrons of carbon thereby modify the electronic structure and properties of carbon based system. Such modifications can introduce more active sites for molecular adsorption and hence influence gas adsorption properties (both physical and chemical adsorption). Nitrogen doped porous carbon can be synthesized by various methods and among them the most frequently used method is carbonization of N-containing precursors such as acetonitrile, melamine, polyaniline, polypyrrole etc. [12,13]. They can also be prepared by co-carbonization of nitrogen containing organic compounds with nitrogen free materials [14,15] and heat treatment of carbon or porous carbon with

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nitrogen containing gases like ammonia, certain amines, pyridines etc. [16,17]. The latter method generally gives low nitrogen incorporation in the carbon frame work. There are also methods based on organic templates, which includes diblock co-polymer micelles [18] and nitrogen rich polymers [19,20] as precursors for making nitrogen doped carbon materials. Less costly and commonly available precursors like coal, coke, pitch or biomass etc., were also extensively used for preparation of nitrogen doped carbon samples [21,22]. Ethylene di-amine tetra acetic acid (EDTA) is one of the very interesting precursors for preparation of N doped porous carbon which can act both as N and carbon source and high nitrogen content could be achieved [23–26]. N doped carbon dots were prepared from EDTA using hot and concentrated H_2SO_4 and the N/C atomic ratio is found to be 8.95%. The value is much higher than most of the N-CD samples reported earlier [25]. Highly nitrogen doped carbon nanosheets (HNCNSs) were also successfully prepared and employed as an efficient electrocatalyst for the oxygen reduction reaction [26].

Pore size of carbon samples also affects the hydrogen absorption capacity tremendously and this feature can be used to optimize the carbon structure for a specific application especially for physisorption of gases on carbon surface [27]. A systematic investigation on carbide derived carbon (CDC) shows smaller pores increase the total hydrogen storage capacity [28]. It is also reported that hydrogen adsorption capacity of porous carbon linearly depends on ultramicropore volume. Highest hydrogen storage is reported for optimized pores with a diameter of 0.59 nm [29]. Properties of N-doped carbon materials, like surface area, pore size and pore volume can be modified by physical and chemical activation methods. Physical activation is generally carried out by carbonization at high temperature (700 °C–900 °C), usually in presence of steam or under CO_2 atmosphere. Chemical activation is done by pre-impregnation of precursor with activating agents, such as, H_3PO_4, KOH and $ZnCl_2$ [22,30–32] and heating at a temperature usually lower than that of the physical activation.

In the present study amorphous carbon samples doped with nitrogen were prepared by a simple method by charring commonly available precursor EDTA with conc. H_2SO_4, followed by annealing at different temperatures. Here EDTA acts both as an *in-situ* carbon and nitrogen precursor, facilitating higher extent of nitrogen doping in the sample, compared to post synthesis route. As prepared samples were annealed at three different temperatures namely 500 °C, 600 °C and 700 °C to see the effect of annealing on nitrogen content and pore size. Further, the samples were chemically treated with conc. H_3PO_4 at different temperatures to activate and enhance pore dimensions. Structural/textural changes on both microscopic and macroscopic levels arising due to activation process and nitrogen doping were examined using Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (CPMAS NMR), X-ray Photoelectron Spectroscopy (XPS) and Small angle X-ray Scattering (SAXS) techniques. Impact of annealing and chemical activation on hydrogen absorption properties of the materials have been investigated in detail and presented in this manuscript.

Experimental

Method for preparation of nitrogen doped carbon

20 g EDTA and 30 ml concentrated H_2SO_4 were taken in a beaker and stirred for 30 min, followed by heating at 110 °C so that all EDTA get dissolved, resulting in the formation of a brown coloured solution. Temperature was then raised to 190–200 °C and maintained at this point for 20 min. A black coloured solution was formed which was cooled, diluted with distilled water and neutralized with NaOH solution. The resulting solution was kept overnight so that all the precipitate settled down and the same was filtered and washed for complete removal of sulphate ions. The precipitate was dried in an oven at 100 °C. The as prepared samples were annealed at different temperatures, namely 500, 600 and 700 °C, at a heating rate of 4 °C/min for 5 h in argon flow and cooled at a rate of 5 °C/min in absence of any activating agent. Samples annealed (without chemical activation) are labelled as CN1, CN2 and CN3, respectively. To increase pore dimensions, as prepared nitrogen doped carbon samples (before annealing) were chemically activated using concentrated H_3PO_4 (with carbon:acid = 1:2 by weight) and heated at 400 and 500 °C for 1 h under Ar atmosphere. The activated samples were designated as ACN1 and ACN2. Another set of activated samples were also prepared by taking carbon and acid in the weight ratio of 1:1.5 and heating at 400 (ACN3) and 500 °C (ACN4) for 1 h under Ar atmosphere. The results of ACN3 and ACN4 samples are described in supplementary materials (Fig. S1–S7). The result shows all the samples are stable upto 375 °C and there is no profound effect of annealing and activation on the stability of the samples.

Characterization

Powder X-ray diffraction (XRD) studies were carried out on the samples using a Philips powder X-ray diffractometer (model PW 1071) with Ni filtered CuKα radiation. Morphology and size of representative samples were determined using a Transmission Electron Microscope (Jeol, JEM 2100 F).

To find out the pore dimension of the studied sample, SAXS measurements were carried out using a Rigaku small angle goniometer mounted on rotating anode X-ray generator (CuK_α). Scattered X-ray intensity I(q) (where $q = 4\pi.\sin(\theta)/\lambda$, is the scattering vector, λ is the wavelength of incident x-rays) was recorded using a scintillation counter with pulse height analyzer by varying the scattering angle 2θ. The intensities were corrected for sample absorption and smearing effects of collimating slits [33]. The surface area of nitrogen doped porous carbon were evaluated based on nitrogen adsorption measurements at 77 K after degassing the samples at 100 °C, for 2 h (Surfer Thermofisher Scientific).

^{13}C cross polarization magic angle spinning (CP MAS) NMR and ^{31}P MAS NMR experiments were carried out using a Bruker Avance 400 machine having a standard bore MAS accessory at a basic frequency of 100.5 MHz for ^{13}C nuclei and 161.9 MHz for ^{31}P nuclei. A 90° pulse width of 5 μs, a contact time of 10 ms with a relaxation time of 15 s were employed for recording the

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