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CHARGE STORAGE STUDY OF NITROGEN-DOPED ACTIVATED CARBONS

Dr. Dev Prakash
Department of Chemistry, Saraswati (P. G.) College HATHRAS, U. P.

Abstract

Carbons are environmentally friendly materials with natural properties of high electrical conductivity, chemical and thermal stability, and good corrosion resistance as well compatibility with composite materials such as oxides, sulfides and conducting polymers. The surface area and pore size distribution of carbons can be tuned depending on the application (Beguin et al., 2010). Various forms of carbon materials, including activated carbon, carbide derived carbon, graphene, carbon nanotube and carbon aerogel, are well studied especially for energy storage applications in supercapacitors and batteries (Beguin et al., 2010; Gu and Yushin 2014).

Carbon is the primary storage material in EDLC electrodes. The charge storage capacity of the carbon materials largely depends on the surface area, porosity and conductivity. The mesoporosity in carbon materials provides easy access for guest species and facilitates free diffusion throughout the pore channels without blockage. In general, high surface materials with large number of pores show high capacitance, but it is not always factual. In some cases the porosity present in the sample decreases the electrical conductivity thereby fading the capacitance (Hu et al., 2014).

High surface area mesoporous carbon materials are synthesized by sol-gel method, physical and chemical activation of organic precursors at high temperatures, carbonization of aerogels and cryogels, etching of metal carbides, hard template-assisted method followed by carbonization, and template removal, and self-assembly using soft templates through co-condensation and carbonization (Liang et al., 2008). The carbons obtained by these methods show good electrochemical properties suitable for energy storage applications in supercapacitors and batteries.

Keywords: *Super capacitor, Mesoporosity, Nanotube, Graphene.*

Experiment and Results: Nitrogen doping can improve the capacitive behavior of porous carbons, variety of NMC-based materials with different structures, including 1-D N-doped carbon nanotubes and N-doped carbon nanofibers, 2-D N-doped graphene with different dimensions, have been designed for supercapacitor electrode applications (Deng et al., 2016). The nitrogen-doped carbon materials have been synthesized by various methods such as chemical vapor deposition, arc discharge, plasma treatment, electrochemically and thermal annealing method.

Preparation of nitrogen doped activated carbon: In a typical synthesis process, palm flowers were cut into small pieces and washed by deionized water followed by drying in an oven at 80 °C for overnight. After thorough drying, stoichiometric weight ratios of palm flower/melamine were dispersed in 200 ml of 2 M KOH solution in a beaker. The contents of the beaker were stirred for 2 h and the resulting suspensions were sealed in a Teflon-lined autoclave and transferred into an oven at 160 °C. After 12 h, the autoclave was cooled to room temperature and the products were collected by centrifugation and washed with deionized water several times, and dried overnight at 60 °C. The hydrothermally activated samples were carbonized at 800 °C for 2 h under N2 flow with a heating rate of 5 °C min− 1. The resulting carbon samples were soaked in 2 M HCl for 6 h and washed several times by centrifugation using deionized water and finally dried at 60 °C overnight. These activated carbons are designated as NAC-X (nitrogen doped activated carbon), X representing the wt % of nitrogen in the activated carbon.

Textural properties and elemental analysis of NAC samples

Sample	Palm flower/melamine weight ratio	Pore diameter (nm)
NAC-0	1:0	3.9
NAC-2	2:1	1.9
NAC-4	1:1	4.0

Fabrication of electrode and electrochemical measurements: The electrochemical behavior of nitrogen doped activated carbon samples (NAC-0, NAC-2 and NAC-4) from palm flowers were studied with both three- and two-electrode configurations in an aqueous 0.1 M H2SO4 electrolyte using CHI 7081C electrochemical workstation. For the three-electrode system, 5 mm dia of glassy carbon electrode coated by NAC-X samples was used as working electrode, a platinum foil and an Ag/AgCl saturated with KCl was used as a counter electrode and reference electrode, respectively. The working electrode was prepared by dispersing 10 mg of active material in 600 µL H2O, 300 µL isopropanol and 100 µL of 5% Nafion solution followed by sonication for 6 h. A 10 µL of aliquot electrode materials was spread over clean glassy carbon electrode (polished with 0.05 µm γ-alumina micropolish). The solvent of the aliquot was evaporated at 50 °C for 8 h and dipped on aqueous electrolyte for 1 h before starting the experiment. The electrochemical properties of the electrode materials were studied by cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) analysis. The specific capacitance values of all electrodes were calculated by using equation 3.3. For the electrochemical test in the two-electrode system, the working electrode slurry was prepared by mixing 95:5 weight ratio of NAC-X samples and polyvinylidene difluoride (PVdF) binder dissolved in 1-methyl-2-pyrrolidinone. The obtained slurry was coated on carbon cloth and dried in an oven at 60 °C for 8 h. The electrode contained about ~ 2 mg of active material. The two electrodes having similar mass loading of active material were separated by a filter paper, which was fully soaked with 0.1 M H2SO4 electrolyte.

In order to study the potential applications of as synthesized nitrogen doped activated carbon in supercapacitors, a device is fabricated in nonaqueous electrolyte (ionic liquid electrolyte), and gel electrolyte (0.1 M H2SO4/PVA). In both the cases, carbon cloth was taken as current collector. A filter paper soaked with ionic liquid was used as separator in the former case, while solid polymer electrolyte (0.1 M H2SO4/PVA) was used as separator for flexible supercapacitor studies. H2SO4/PVA polymer electrolyte was prepared by dissolving 1 g of PVA in 20 ml H2O with continuous stirring at 80 °C. Then 20 ml of 0.1 M H2SO4 was added to the above solution and stirred continuously until to get a homogeneous viscous solution. The above solution was transferred into a petri dish and dry at room temperature to get a thin film.

Physical characterization of nitrogen doped activated carbons: The synthesis procedure of nitrogen doped activated carbon from palm flower is illustrated in Scheme 3.2. It is known that the nitrogen doped carbons obtained from bio-waste materials and different chemical synthesis methods often lack perfection in sp2 -carbon structure of graphene. However, such non-structured carbons can be functionalized for various applications (Abioye and Ani 2015; Subramanian et al., 2007; Ojha et al., 2017; Nanaji et al., 2019; Liu et al., 2018; Li et al., 2018). In the first step, we have used 2 M KOH as an activating agent to introduce micro/meso- porous structures into carbon matrix obtained from palm flower. In the second step, the surface area and porosity of carbons are tuned by varying the temperature of activation at 700, 800 and 900 °C in the flow of nitrogen.

The powder X-ray diffraction pattern and nitrogen sorption isotherms of the activated carbons are shown in Fig. 3.9. The BET surface areas of activated carbon samples are presented in Table 3.4. The table shows that the specific surface area of the activated carbons increased from 610 to 796 m2 g −1, and the carbon synthesized at 800 °C exhibits largest surface area. In order to find out the effect of KOH concentration, we have carried out the activation at three different molar concentrations of KOH (1, 2 and 3 M), while fixing the carbonization temperature at 800 °C. The corresponding powder X-ray diffraction patterns and nitrogen sorption isotherms are given in Fig. 3.10. The activated carbon synthesized by using 2 M KOH solution exhibits clearly high specific surface area (796 m2 g −1). Since double layer capacitor of any carbon sample depends on the surface area of electrode material, we have optimized the concentration of KOH as 2 M and carbonization temperature at 800 °C to achieve the best double layer capacitor performance. During the activation process, the chemical reaction between KOH and carbon material typically consists of following steps.

$4KOH + C \rightarrow K_2CO_3 + K_2O + 2H_2$

$K_2CO_3 + 2C \rightarrow 2K + 3CO$

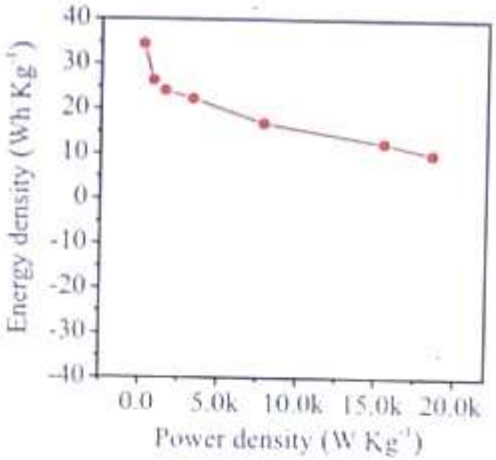
The K2CO3 generated in step 1 causes gasification of amorphous carbon to CO and yields K as shown in step 2, which subsequently intercalates in to the carbon lamella leading to the formation of pores.

The nitrogen content is tuned by varying the weight ratio of palm flower/melamine, where melamine is the precursor for nitrogen.. The broad peaks around ~23° and 43° confirm the presence of disordered amorphous carbon. As compared to NAC-0 and NAC-4, the peak intensity of NAC-2 is weaker, indicating a lower degree of graphitization, which is further confirmed by the Raman spectra. Raman scattering measurements are carried out to estimate the degree of functional and structural evolution of NAC. Raman spectra of NAC-0, NAC-2 and NAC-4 are compared in Fig. 3.11b. All samples show two strong peaks at around 1298 and 1600 cm−1, which are indexed to D band and G band vibrations, respectively. The D band corresponds to the vibration of disordered carbon, while G band reflects the bond stretching of ordered sp2 carbon. The relative intensity ratio of D band and G band (ID/IG) reveals the degree of graphitization as well as degree of defects on the carbon network.

Considering all the features carbon samples discussed above, NACs are potential materials for fabricating miniscule devices. As a proof-of-concept, these materials are tested for supercapacitor applications in aqueous, non-aqueous and solid gel electrolytes employing both two and three electrodes setups. The supercapacitive performances are evaluated by CV, GCD and EIS techniques. Initially three electrode configuration has been chosen to carry out electrochemical studies using 0.1 M aqueous H2SO4. Figure 3.16a shows the comparative CV tests of NAC-0, NAC-2 and NAC-4 at a scan rate of 30 mV s−1 . All the curves exhibit a typical rectangular curves from −0.5 to 0.5 V, which implies that the charge stored is essentially by electrochemical double layer mechanism with a small contribution coming from the pseudocapacitance due to oxygen/nitrogen groups present on NACs (Hao et al., 2013; Jha et al., 2012). The integral area under the curve for NAC-2 is much higher than that of NAC-0 and NAC-4 samples, indicating higher capacitance performance of NAC-2 by improved ion diffusion/adsorption processes.

The NAC-2 sample is expected to offer the highest capacitance due to large surface area which is hereby confirmed by CV test. The rate performance of NAC-2 is shown in Fig. 3.16b, which displays good shape preservation of CV curves even at high scan rates, suggesting good charge propagation within the electrode. Again the area of CV curve increases with increasing scan rate, which is related to diffusion of the active ions in micro/meso-porous structures.

However, doping excess hetero atom (N) may decrease the conductivity with more resistive behavior and number of active sites in carbon framework as well. The long term electrochemical stability of NAC-2 is examined by continuous 2000 GCD cycles at a current density of 2 A g−1. The capacitance 79 retention and the coulombic efficiency of NAC-2 sample, respectively, are about 92% and 98% after 2000 GCD cycles. However, NAC-0 and NAC-4 samples retain 77% and 83% of initial capacitance after 2000 GCD cycles, respectively, which indicate excellent pore accessibility and long term electrochemical stability of the nitrogen-doped carbons materials.



CONCLUSIONS: In summary, activated carbons are extracted from palm flower at different temperatures and KOH concentrations. Chemical activation of palm flower with 2 M KOH at 800 °C gives rise to carbons with surface areas ~800 m 2 g −1. Nitrogen doping into carbon produces activated carbons of with surface areas ~1054 m 2 g −1. The palm flower derived N-doped activated carbon electrodes are studied for supercapacitor applications in an aqueous, nonaqueous (ionic liquid) and flexible solid state membrane (0.1 M H2SO4/PVA) by fabricating a symmetric device.

The micro- and meso-porous nature NAC was confirmed by HR-SEM, HR-TEM and BET analysis. Among all the activated carbons, NAC-2 shows highest specific capacitance of 296 F g−1 at 0.5 A g−1. In a laboratory experiment, a red LED was illuminated using three serially connected 3 V supercapacitor stacks. Using [EMIM][ESO4] ionic liquid as electrolyte, the potential window of symmetric device is extended up to 3 V and the device delivered high energy and power densities of 34.4 Wh kg−1 and 155.4 W kg−1, respectively. The most important result is that the device exhibited long term cyclic stability over 50k cycles. The device can be bent without affecting its charge storage performance. T

he porous N-doped activated carbons obtained from palm flower residues are promising materials to fabricate environmental friendly, sustainable and flexible supercapacitors at low cost and good performance.

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