Characterization of nanocarbon based electrode material derived from anthracite coal

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Abstract

Nanocarbon derivatives (NCD’s) have wide range of scope in the field of sensors, supercapacitors and charge storage application. In the present study, anthracite is used as a precursor to synthesis nanocarbon derivatives. One of the important aspects of this study is to intercalate the synthesized NCD’s with Li-ion to enhance its electrochemical and optical properties. The prepared NCD with Li-ion interface is used as an electrode material to study charge-discharge capacity and cyclic stability. The NCD shows a specific capacitance 65.4 mF g$^{-1}$ and retention of capacitance after 200 cycles. However, adding small amount of supportive electrode material with NCD’s enhances the capacitance after 160 cycles. The drastic increase in electronic conductivity of NCD’s by adding supportive Li-ion permits the electrochemical activity of electrode material to be effectively utilized for practical applications.

1. Introduction

Nano science is the study which includes manipulation, engineering of matter and control of phenomena at nanoscale. It deals with synthesis, characterization and application of nanomaterials. Properties of nanomaterials are significantly different than those of macromaterials having same mass. Main reasons of enhanced properties at nanoscale are; they have large surface area as compared to macro materials with the same mass. Due to this, chemical reactivity and electrical properties of the material increases. At nanoscale, quantum effects become dominant which consequently determines the nature and behaviour of material. Properties such as fluorescence, magnetic permeability, melting point varies with size of the particle. The superior properties of nanomaterial are chemical reactivity, higher strength, higher conductivity, good optical properties, fluorescence, magnetic permeability and light weight etc. Such enhanced properties are utilized by researchers for various applications. Over the past few decades, an innovation in nanotechnology has transformed various areas of our life in advanced ways. Activities and research in this field has gained focus from all across the world [1–3]. Carbon based nanomaterial have been proved to be an ideal additive for electrodes of Li-ion batteries (LIB’s) and supercapacitors, having large storage capacities [4–7].

In present work nanocarbon derivatives (NCD) were synthesized by using anthracite as a precursor. Anthracite has the highest energy and more carbon content among all coals. More carbon content in the source implies more carbon clusters or ions available for NCD formation. However, apart from these factors; microscopic organic components (called as macros) also play a major role. The energy storage applications in portable or remote devices such as batteries and conventional capacitors are acquiring a major concentration of researcher. Carbon materials are considered as one of the most promising electrode material due to high porosity, large specific area and low cost. Electrochemical performance of carbon based electrode materials are affected by the variation of specific surface area [8, 9], structure and functional group [10], pore size distribution [11, 12]. These features suggest that NCD’s are suitable materials for polarizable electrodes. In present study we report the synthesis of composite material by incorporating NCD’s with lithium phosphate (Li$_3$PO$_4$). Different characterization technique helps the study viable to understand the structural, electrochemical and optical properties of NCD’s based composite. Surface area plays an important role for the preparation of electrode...
material. In the present research work, NCD’s were prepared by using anthracite which can be promising material for supercapacitor application due to low surface area, high oxygen group containing functional groups and mesopores in nature. These are some novel characteristics which makes this research more viable for the enhancement of specific capacitance.

2. Experimental procedure

2.1. Synthesis of nanocarbon derivative (NCDs)
The main objective of present study is to synthesis NCD’s by chemical exfoliation of anthracite. Initially 25 ml of nitric acid (M.W. 63.01, Supplier: MOLYCHEM company) and 50 ml of sulphuric acid (M.W. 98.08, Supplier: MOLYCHEM) was mixed and kept under ice bath. Then anthracite (5 gm) was added in the acidic solution. The entire mixture was stirred for 30 min and then 25 gm of KMnO₄ was added which acts as an oxidizing agent. This mixture forms pink colour fumes. The above solution was kept under oil bath at 70 °C for 24 h and subsequently placed in open air for 3 days. The reacted carbon was floating and heavy carbon particles/salts were settled down. Then the floating (reacted carbon) and heavy particle (settled part) were added to 1000 ml and 700 ml of deionised water respectively. Residue and filtrate parts were dried under oven to obtain the powdered form of NCDs.

2.2. Fabrication of electrodes
For the preparation of electrode we have used different composition of NCD’s powder is with Li₃PO₄. Based on composition of NCD it can be further categorized in to EMR.2 (NCD:Li₃PO₄::25:75), EMR.4 (NCD:Li₃PO₄::50:50), EMR.6 (NCD:Li₃PO₄::75:25). The prepared fine powders were mixed with PVDF binder. The resultant paste was coated on a glassy carbon working electrode which was kept for drying. Four electrodes were prepared and the electrochemical property of prepared electrode was tested as a working electrode by using CH instrument.

3. Material characterization
The XRD studies was done by using x-ray spectrometer instrument Maker Rigaku, from Japan, 2θ in the range of 10° to 80° with scanning rate and step size of 1° min⁻¹ and 0.01° respectively. The microscopic images of pure NCD and composite were obtained from Scanning electron microscope (Company: Carl Zeiss, Model No: EVO-185H). FTIR studies were carried by using ABB Bomem MB3000 FTIR spectrometer techniques. The FTIR technique is used to understand the chemical composition and was studied in wavenumber range from 500 to 4000 cm⁻¹. UV-absorbance studies were carried out by DH-2000-BAL Ocean Optics in the range of 200–600 nm. Photoluminescence study was done by using Shimadzu fluorescence spectrometer respectively. The electrochemical study was done by using three electrode systems in CH-680 instrument.

4. Result and discussion

4.1. XRD analysis
The structure of Li₃PO₄, synthesised NCD, and their composition (EMR .2, EMR .4, EMR .6) were investigated by powder XRD measurement. XRD spectra analysis was done in the 2θ range 10° to 60°. The x-ray profile of synthesised pure NCD, Li₃PO₄ and electrode material are given in figure 1. The carbon atom present in NCD acts like a three dimensional optical diffraction, which can scatter light in different angles. The x-ray diffraction pattern of synthesized nano–carbon derivatives (NCD) shows non-crystalline nature [13]. NCD shows similar diffraction pattern (002) as graphite sheet due to similar intrinsic properties but not identical [14]. The absence of 001 plane in NCD differ it from other sp² carbon based crystal. Figure 1 shows amorphous peaks at ~25° due to 002 planes and at ~42.3° due to 100 planes with different intensity. The present peaks ensure the existence of an intermediate structure. The 002 planes is responsible for the stacking height (Lc) which is the length along C axis while 100 plane indicates the lateral size (La) which is the crystalline size along the direction of sheet. XRD pattern of commercially available Li₃PO₄ powder matched with COD 901-2501 and the structure is found to be orthorhombic with space group pmm21. Electrode materials which contain NCD and Li₃PO₄ shows peaks correspond to both. The NCD peak corresponds to 002 planes is visible in all compositions. The intercalation of Li₃PO₄ in NCD represents the denomination of Li peaks. The change in crystalline to amorphous nature can be observed. The effect of Li ion in the structure of NCD confirms the intercalation. The crystalline peaks of Li-ion are dominated by amorphous peaks after step wise increment of NCD wt%. Hence the XRD results confirm the effect of Li and NCD in structural formation.
4.2. Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy was performed to identify functional groups present on the NCD is shown in figure 2. FTIR spectra of pure NCD shows dominant peaks at 3363, 2854, 1670, 1617, 1428, 1120, 1068, 880 cm$^{-1}$ represents intermolecular O–H bonding, C–H stretching, C–H stretching in –CH$_2$, C=O stretching, asymmetric C–O–C bridge and C–O stretching respectively. The hydroxyl groups may be due to acids (sulphuric acid, nitric acid) used for the preparation of NCD. Among all functional groups, hydroxyl functional groups are having one of the most dominant peaks in the infrared region. These groups usually do not exist in isolation due to hydrogen bonding with other hydroxyl groups. The hydroxyl groups may be present in the same molecule or in the neighbouring molecules. In the pure Li$_3$PO$_4$ spectra as shown in figure 2, 1040 and 567 cm$^{-1}$ represents vibration of PO$_4$ group [15]. The transmittance peaks at 875, 1420, 1460 cm$^{-1}$ represents presence of CO$_3$ group in figure 3. As the NCD content is increasing in the composites, its signature peak is appearing dominantly. Li$_3$PO$_4$ signature peaks presence at 1000 cm$^{-1}$ show the proper intercalation between Li$_3$PO$_4$ and NCD. A hump at 3000 cm$^{-1}$ shows stretching vibration of groups, such as –OH and –NH and the hydrogen bonds formed by the association of –OH and nitrogen atoms.

4.3. Scanning electron microscopy

SEM images of pure NCD and EMR.4 is shown in figure 4. From the micrograph we can observe the formation of NCD from the SEM images. The obtained NCD is almost in the range of 2.56 μm diameter and in cylindrical
shape. However a closer view of image also describes certain more number of small varied shaped NCD's. Whereas the SEM images of EMR.4 represents the interaction of equal amount of NCD and Li-ion. The introduction of Li-ion in NCD drastically changed its shape. The Li-ion ion takes the position at every edge of NCD which introduce the interlinking bonds between NCD and Li-ion. This bonding stretches the shape of NCD from all the sides. The ultimate aim of the intercalation of Li-ion is to disturb the shape of NCD which will help to improve its electrochemical properties.

4.4. UV-visible spectroscopy
Pure NCDs are displaying strong absorbance maxima at 310 nm and 460 nm. In pure NCD's materials, the van Hove transitions occur well into the NIR region. The peaks wavelength can be used to characterize the aggregated NCDs which are tightly bound [16]. Variation can be seen in the pattern of the absorbance spectrum as shown in figure 5, because the peaks emerging from the NCD optical transitions are considerably sharper and more intense with regard to the unspecific absorbance background. Therefore, the position of the peak and relative intensity indicate the extent of debundling in the sample, which is a major decisive factor to assess the quality of the dispersion. The absorbance peak is depending on the amount of NCDs in electrode material. The highest absorbance peak is obtained for EMR.2. The overall UV results suggest that the presence of Li-ion may vary the optical property only at UV-region but remain almost same at near IR-region.
4.5. Photoluminescence spectroscopy
In figure 6 the PL peaks are observed between 400 to 450 nm which are the characteristics peak of NCD. For pure Li$_3$PO$_4$ the peaks are observed between 350 to 400 nm. NCD formation is confirmed by near infrared light emission. Absence of excitonic luminescence shows that metallic tubes are not formed. Quench or increase in PL is due to interaction between NCD’s and other materials or within the NCD’s itself. Drastically increased PL may be due to detachment of carbon molecules. Peaks at shorter excitation wavelengths are attributed to v3 to c3 excitation followed by c1 to v1 emission in the same set of NCD’s. For EMR.4 the non- emissive region is small but it is comparatively large in EMR.6 composite. Several of the features at longer excitation wavelengths region are vibronic bands (electronic transitions with vibration excitation). Hence, composition of Li$_3$PO$_4$ and NCD is showing promising possibilities for photoelectric applications such as biological sensors and optical devices.

4.6. Electrochemical studies
Cyclic voltammetry is a method to do electrochemical studies of electrode material. In present study, 1M H$_2$SO$_4$ is used as electrolyte, platinum wire as counter electrode and Ag/AgCl as reference electrode. Electrode materials coated on glassy carbon working electrode acts as working electrode. Electrode characterization was performed for different scan rates 10, 20, 30, 50, 100, 200 and 300 mV s$^{-1}$. Since it’s an electrode material, figure 7 shows no redox peaks except EMR.6. The absence of redox peaks stipulate that supercapacitors rate of charge and discharge is pseudo constant over entire voltammetric cycles [17]. Electrode material is having stable capacitive process as the curve is symmetric [18]. As the scan rate increases the CV curve of prepared electrode also changes. The pseudo-capacitance behavior and the specific capacitance of electrode material at 10 mV s$^{-1}$ scan rate is 65.4, 75.8, 10.4, and 41.9 mF g$^{-1}$ for pure NCD, EMR.2, EMR.4, EMR.6 obtained respectively. Among the prepared materials EMR .2 (NCD: Li$_3$PO$_4$:::25:75) is the best electrode material according to obtained capacitance value.

Chronopotentiometry is a technique to understand the cyclic stability of an electrode material. Figure 8 shows the galvanostatic charge-discharge curve for NCDs and composites. The CP curve represents particular triangular waveform for pure NCD samples. The NCD shows a specific capacitance 65.4 mF g$^{-1}$ and retention of capacitance after 200 cycles. However, adding small amount of supportive electrode material with NCDS enhances the capacitance after 160 cycles. Adding large amount of Li-ion with NCD’s bound the carbon atoms and restrict the enhancement of specific capacitance. The low cyclic stability and poor capacitance for EMR .4 and EMR .6 decreases its practical applications.

4.7. Electrochemical impedance spectroscopy
Electrochemical Impedance Spectroscopy (EIS) is used to study properties of mechanical analysis of the interfacial process, the surface morphology and ion diffusion of electrode or electrolyte material [19]. The Nyquist plot, which is extracted from the Electrochemical Impedance Spectroscopy (EIS) measurement are typical for supercapacitors. Figure 9 shows the nyquist plot obtained for Pure NCD, EMR.6, EMR.4 and EMR.2. The impedance resistance is made up of two components; they are resistance response on x axis and capacitance.
response on y axis. The Equivalent Series Resistance (ESR) and charge transport resistance of two electrode supercapacitor were represented by the x-intercept of Nyquist plot. A typical Nyquist consist of two parts; one is the low frequency region represented by a nearly vertical line and second a high frequency region which is almost 45 degree line. The slope of Nyquist plot is known as Warburg resistance which is due to the frequency dependence of ion diffusion in the electrolyte to electrode interface [20]. From figure 9 it is evident that EMR.6 is best electrode material.

5. Conclusions

In conclusion, the NCD was prepared by using anthracite as a precursor using staudenmaier method. XRD, FTIR and SEM result confirms the structural, chemical, morphological formation of prepared NCD’s. To improve the electrochemical properties of synthesized NCD, a well known electrode material Li3PO4 is mixed with it. By varying mass composition, different sets of electrode materials are prepared. The Cyclic voltammetry and charge discharge studies reveal the good capacitive and stability of prepared electrode material. As the scan rate increases the CV curve of prepared electrode shows the increment in pseudo-capacitance. The results also confirms excellent electrode-electrolyte interface. It is found that the composition- NCD:Li3PO4=25:75 has large specific capacitance. The impedance study reveals the change from resistive to capacitive component by adding

![Photoluminescence Spectrum of Pure NCD, Li3PO4, EMR.2 (NCD:Li3PO4::25:75), EMR.4 (NCD:Li3PO4::50:50), EMR.6 (NCD:Li3PO4::75:25).](image-url)
Figure 7. Cyclic voltammogram (CV) studies of electrodes Pure NCD, EMR.2 (NCD:Li₃PO₄::25:75), EMR.4 (NCD:Li₃PO₄::50:50) and EMR.6 (NCD:Li₃PO₄::75:25).

Figure 8. Chronopotentiometry (CP) studies of electrodes Pure NCD, EMR.2 (NCD:Li₃PO₄::25:75), EMR.4 (NCD:Li₃PO₄::50:50), EMR.6 (NCD:Li₃PO₄::75:25).
Li-ions in NCD’s. The obtained result suggests the promising application of prepared NCD as an electrode material for super capacitor applications.

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