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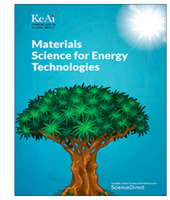

Biomass derived anode for high-electrochemical performance potassium-ion capacitors

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Low cost metal ion storage system with abundant resources and high working voltage is promising candidate for current market demand. Advance energy technologies are focusing on the development of energy storage system via waste management. Here flexible potassium-ion capacitor was developed using waste silk cocoon from textile industry as a carbon source for N-S doped carbon nanofibers. This carbon material used as an anode material for K^+ ion excessive adsorption through potassium alloy on the N-S doped carbon nanofiber as anode and large graphitic layer containing exfoliated graphite cathode. The present anode exhibits high electroactive surface area and hierarchical mesoporous structure. High specific capacitance, cyclic stability and electrochemical rate stability exhibits by this anode due to its excellent mechanical stability and high conductivity. Keeping these features in mind, a potassium-ion capacitor was constructed using N-S doped carbon nanofibers as anode and exfoliated graphite with large graphitic layers as cathode electrodes. The capacitor displays a high specific capacitance 200 mAh g^{-1} and stable cycling life (68% capacity retention over 140 cycles). This will promote application of flexible N-S doped carbon nanofibers as hybrid capacitors. The satisfactory electrochemical results promote the waste management concept for scalable production of eco-friendly energy storage system.

1. Introduction

Worldwide, Lithium ions are used in batteries (LIBs) as energy source is applied in various automotive industries and various electronic gadgets [1–4]. Scare availability of lithium source confined the LIBs development in large scale energy supply and production [5]. Reserve natural resources such as alkali metals (Na^+, K^+) ions for development of energy storage system is now more focused by researchers which exhibits similar electrochemical properties to Lithium [6–11]. Among them, potassium-ion capacitors (PICs) are proven sustainable energy system and better alternative to LIBs. The main challenges with PICs are the very slow electrochemical kinetics and expansion of volume due to the K^+ ion size in comparison to Li^+ ion (~1.39 Å) vs Li (0.71 Å) causes structure instability and poor electrochemical performance. Worldwide, lots of efforts has been put by researchers to develop cheap, highly stable electrode with high specific conductance and cycling stability for PICs [12–17]. Several metals and carbon allotropes anode materials are employed as an electrode material for fabrication of alkali metals-based energy storage system (potassium-ion batteries or capacitors). Highly desired properties such as the low voltage, cheap, feasible fast kinetics and eco-friendliness [18–21], which are found in carbonaceous electrode materials makes it suitable electrode for fabrication of PICs. So far, some of the hybrid PICs use diverse positive and negative carbon materials (carbon foam, carbon microspheres, metal doped activated carbon, graphite) with some exciting achievements [18,22,23]. As per literature survey, large size of K^+ ions in potassium-based energy storage system, exhibits low life cycle and poor K^+ ions storage capacity due to very slow electrochemical transportation at carbon based electrodes [24]. The waste textile

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silk cocoon derived 3D interconnected carbon fibers provide suitable intrinsic properties to enhance metal ions storage with flexibility and mechanical strength. Keeping the concept of sustainable development and green energy in the mind, flexible electrode material derived from waste silk textile could provide new approach of development of self-sustain flexible electrodes [25].

Herein, a novel green approach is successfully used to develop N-S doped carbon fibers with interconnected conductive network using waste silk cocoon derived carbon nanofibers as the electrodematerial. N-S doped carbon fibers (NSCNF) were used as an anode for development of the PICs. Fabricated anode material was characterized via spectroscopic and electrochemical method along-with mechanical stability. The NSCNF electrochemical properties were examined in different electrolytes. The obtained electrochemical results reveal that silk cocoon derived NSCNF based anode applied in PICs open a new avenue for eco-friendly and sustainable energy system.

2. Materials and methods

2.1. Chemicals

Chemicals and solvent used in this paper work were analytical grade and were used without further purification. Triple distill water were used for preparation of solvent.

2.2. Synthesis of anode material for PIC

Textile industry silk cocoon waste was collected and used further for resource for carbon. In pre-treatment steps, silk cocoon wastes were washed by hot water and dried at room temperature for 2 days. A typical synthetic procedure of NSCNFs was as follows: 8 g of silkworm cocoon waste was soakedin 50 mL $(NH4)_2HPO_4$ solution (10%, mass fraction).

The waste silk cocoon was washed with ethanol: deionized water (1:1) 100 mL solution and dried at room temperature. It was soaked in ammonium phosphate solution for 1 day. After drying silk cocoon, 250 g of washed cocoon was soaked with methylene blue dye (0.2 $g\,L^{-1}$). Here Methylene blue (MB), contains phenothiazines group, consisting both N and S element. N and S element can incorporate into the carbon nanofibers via carbonization step, and the synergistic effect of N and S both elements facilitate the kinetics reaction of the potassium ion [24]. Though carbonizing carbon along with MB at 950 °C for 2 hrs, the nitrogen, sulphur-co-doped carbon nanofibers (NS-CNF) was obtained. However, compared with other textile based electrodes, the catalytic activity of NS-CNF for the capacitive behaviour is better, after complicated carbonation process and then, acetic acid solution (0.1 mM, 20 mL) and 0.1 g Na_2SO_4 were taken in bath and heated at150 °C for 35 min. Treated silk fibres was carbonized at 950 °C for 1.5 hrs at 1.5 °C min^{-1}in presence of nitrogen gas. The obtained carbonized material is denoted in this paper as NSCNF.

2.3. Characterization

Morphology of the fabricated samples was imaged by using a scanning electron microscope (SEM, HITACHI/TM-1000, Japan). FT-IR spectroscopy (Thermo-Nicolet 6700, range 400–4000 cm^{-1}) used to study the change in structure after stepwise modification of CNFs. Thermal gravimetric analysis (TGA) was done to study thermal stability after stepwise N-S doping in CNFs. The characteristics of the crystalline nature and defects for NSCNF were investigated by Raman spectroscopy with an excitation wavelength of 532 nm (Raman, Lab RAM HR800).

2.4. Electrochemical measurements

All electrochemical measurements were conducted on a CHI 760E electrochemical workstation (CH Company) in 1.0 M KOH aqueous electrolyte solution with a typical three- electrode configuration. The reference electrode was silver-silver chloride, and one platinum wire was used as the counter electrode. The working electrode was immersed into electrolyte with a nominal area of 1 cm^2. The electrochemical performance tests including galvanostatic charge – discharge and cyclic voltammetry (CV).

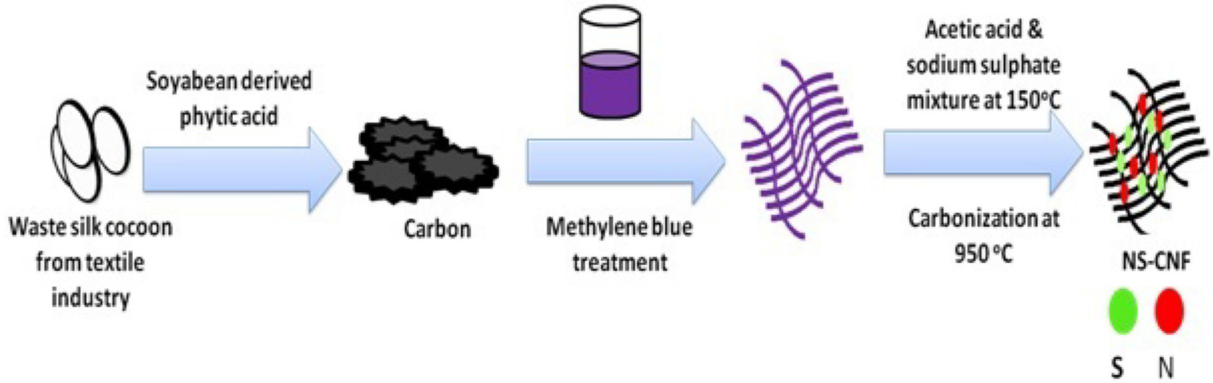
3. Results and discussions

As shown in Scheme 1, the waste silk cocoon was converted into NSCNFs via 3 steps solvents treatment and carbonization process. MB adsorption on the silk cocoon was done via hydrogen bonds present on the surface after chemical treatment of the waste silk cocoon. Secondly, treatment with acetic acid and sodium sulphate at 150 °C results into chemical oxidative polymerization. Lastly, polymerized silk cocoon was carbonized at 950 °C to generate graphitic nature in CNFs which further used as anode material for PICs.

The silk cocoon derived NSCNFs morphology was confirmed by using scanning electron microscopy (SEM) after carbonization of silk cocoon. As shown in Fig. 1a, the MB coated carbon surface was found compact, smooth and homogeneous. SEM image of obtained NSCNFs obtained after the carbonization process revealed the clear 3D interconnected CNFs with shiny N-S nanoparticles at the edge of CNFs. These 3D interconnected NSCNFs facilitate the K^+ ions reversible kinetics which attributes the high electrochemical performance of PICs. Thus, the SEM image investigation approves the simple approach of synthesis of NSCNFs via waste silk cocoon.

Functional group after stepwise modification of silk cocoon derived CNFs was examined by comparative analysis of FT-IR spectrum of CNFs, N-CNFs and NSCNFs (Fig. 2a). As shown in Fig. 2a, the CNFs shows well define characteristic absorption peak at 1600 cm^{-1}, reveals unsaturation arising from the aromatic ring C=C stretching vibrations. In the FT-IR spectrum of NCNFs, broad adsorption peak at 3500 cm^{-1}, this corresponds to amide group at CNFs. The new adsorption peak at 1720 cm^{-1} confirms the carbonyl group of amide groups. The shifting of absorption peak of aromatic unsaturated C=C rings 1600 to 1605 cm^{-1}, confirms the modification of unmodified CNFs to N-CNFs. 1577 to 1604 cm^{-1} after oxidation due to conjugation with carbonyl groups. After cooping of N-S group in silk derived CNFs, the new bands at 1500, 1390, and 1250 cm^{-1} attributed to presence of functional groups C–S, C=O, along with unsaturated C=C aromatic groups. Thus, comparative analysis of FT-IR spectrum of CNFs, N-CNFs and NSCNFs, confirms the synthesis of NSCNFs from silk cocoon waste from industry.

Monitoring the weight loss by thermo gravimetric analysis (TGA) were used to study effect of N-S doping on the silk cocoon derived carbon nanofibers by at inert atmosphere Fig. 2b shows relationship of weight loss as a function of temperature for the various modified CNFs. For non-modified CNFs, total weight loss was 6.2% from 25 to 720 °C, denotes the thermal stability of fibers form of carbon. About 20%weight loss at high temperature range 720 to900°C was observed which can be due to oxidation and combustion of unmodified CNFs. The NCNFs TGA analysis shows two steps of weight loss. The first weight loss at 50–350 °C, indicates the about 20% weight loss due to evaporation of water content in N-CNFs. The second weight loss around 25% due to decomposition of oxygen containing functionalities (formaldehyde, carbonyls, OH) between 360 °C and 800 °C [25]. The N-S CNFs shows steps



Scheme 1. Stepwise synthesis of NSCNFs from waste silk cocoon from textile industry.

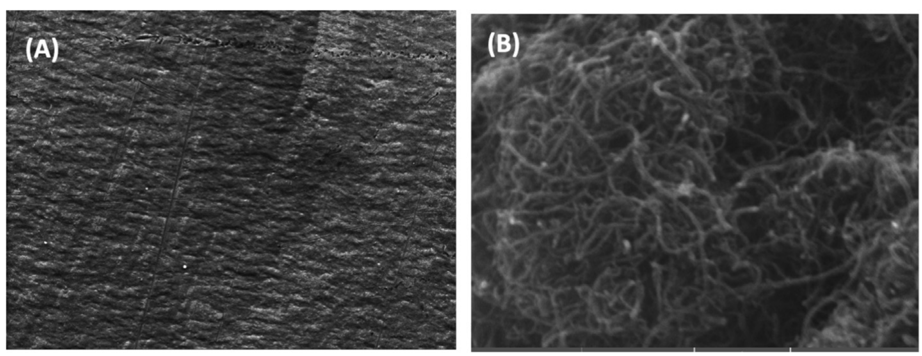


Fig. 1. (A) SEM images of silk derived carbon coated MB and (B) NSCNFs.

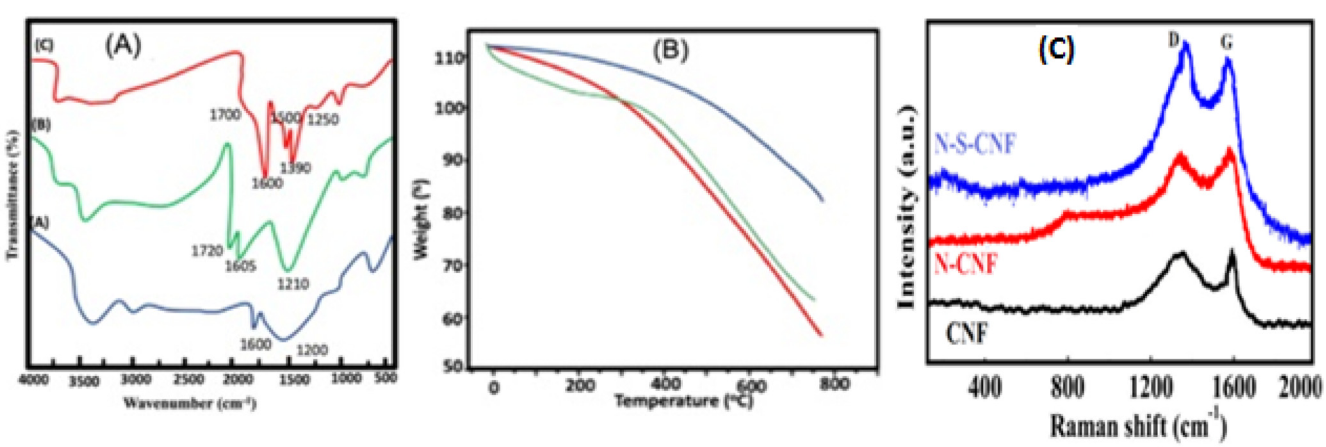


Fig. 2. (A) FT-IR of CNFs, N-CNFs, and NSCNFs, (B) TGA of CNFs (blue curve), N-CNFs (green curve), NSCNFs (red curve) and (C) Raman spectra of the CNF, NCNF and NSCNF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of weight loss in between 25 °C and 800 °C due to decomposition of various complex functionalities (aromatic groups, azo groups, oxygen containing groups), at the surface and combustion at high temperature range. The significant weight loss around 48.5% at high in comparison to CNFs and NCNFs indicates the N-S doping of CNFs derived from silk cocoon provides the thermal stability to the NSCNFs. The excellent thermal of NSCNFs meets the current market demand of the energy storage system.

Furthermore, Raman spectroscopic analysis were performed for different CNF samples (CNF, N-CNF, NSCNF) to elucidate the crystalline behavior of silk cocoon derived CNFs. The effect of doping in CNFs can be evaluated by comparative study of change in graphitic nature and disordered unsaturated structure. The higher D/G peak intensity ratio of CNF (I_D/I_G = 1.23) represents a lower graphitization degree than N-CNF (I_D/I_G = 0.99) and NSCNF (I_D/I_G = 0.95), which results from the introduction of N and S in CNF nanostructure [26]. In NSCNF, N and S atoms embedded in carbon lattice not only enhance the electronic conductivity by increasing unsaturation, but also increase the defects in graphitic structure that promote K^+ ions that results in high capacitance behaviors.

3.1. Electrochemical investigation at NSCNF

The electrochemical property of the NSCF anode in PICs was evaluated by using cyclic voltammetry (CV) methods. Fig. 3a shows that the CVs at potential window in an interval of − 1.0 to 0.0 V at

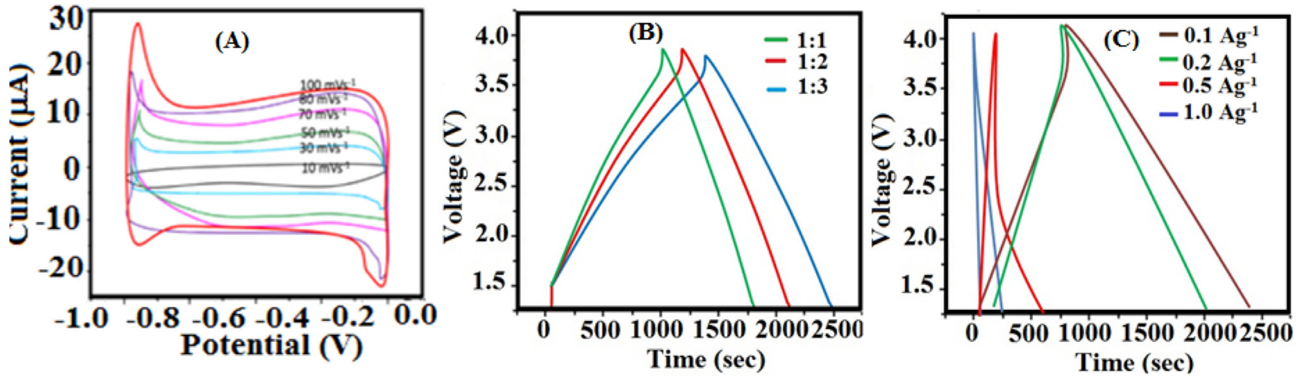


Fig. 3. (A) Cyclic voltammogram of the NSCNF at different scan rates, (B) Galvanostatic charge and discharge profiles for different mass ratios of anode to cathode at 100 mA g^{-1}, and (C) Charge-discharge profiles at different current rates.

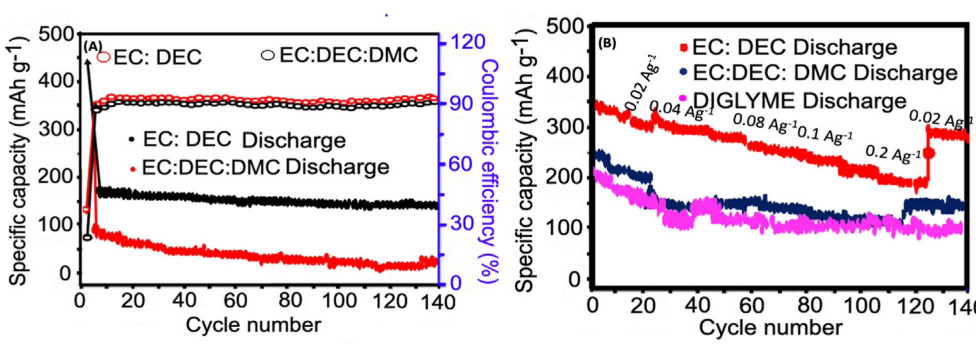


Fig. 4. (A) Investigation of cycling stability of PIC in different electrolyte at 100 mA g^{-1} and (B) PIC rate performance at different current densities.

10–100 mV s^{-1} (scan rates), unchanged the rectangular shaped at high scan rate 100 mV s^{-1}confirms that charging-discharging process exhibits double layer capacitive behavior.

In addition, the specific capacity of exfoliated graphite based cathode is quite lower than that of the NSCNF modified anode at the same current density. Thus, at 0.1 Ag^{-1} here optimization of the mass ratio of the NSCNF in the anode and the cathode between 1:1 and 1:4 was performed. From Fig. 3b, it can be seen that KICs with a mass ratio of 1:2 exhibit the best electrochemical performance.

Under different current densities, the galvanostatic charge–discharge curves of KICs are shown in Fig. 3c. The results show that KICs has a linear triangular charge–discharge curve. At the current density of 0.1, 0.2, 0.5, 1.0 Ag^{-1}, the specific capacitance is 79.5, 70.5, 42.4, 19.5F g^{-1}, respectively. The deviation from the symmetrical triangular charge–discharge curve clarify that the energy storage mechanism in proposed KICs follows a hybrid mechanism, which combines both adsorption/desorption with redox reaction during charge–discharge process [27].

The three different electrolytes including 1.0 mol L^{-1} KPF_6 in EC: DEC 1:1 vol%, 1.5 M KPF_6 in EC: DEC: DMC 1:1:1 vol% with 1.0% FEC, and 1.5 M KPF_6 in DIGLYME were used to examine the NSCF electrochemistry. As shown in Fig. 4a, significant good discharge capacity at a current density 100 mAg^{-1} in 1.0 mol L^{-1} KPF_6 was recorded in EC: DEC 1:1 vol%, at NSCNF electrode. The initial discharge capacity is 196.5 mAh g^{-1}, and capacity retention of 68.7% was foundat140 cycles. The good capacity retention approx. 70% is due to the porous carbon nanostructure assembled by interconnected graphitic carbon fibers was obtained after carbonization and doping of N and S elements. Benefiting from their carbon nanofibers framework, large electroactive surface area, and abundant graphitic nanocrystalline structure, these features boost the potassium storage performance. Different kinetics of K^+ ions has been investigated at NSCNF anode what one can expect in conventional tends. In conventional view, due to large size of K ions, electrochemical kinetics may be slower and results into larger impedance. Here, NSCNF in EC:DEC (1:1), electrolyte with no additives shows better electrochemical kinetics because it forms a stable solid electrolyte interphase (SEI) layer, increases affinity towards carbon and facilitates the reversible of K^+ ions diffusion at NSCNF. Moreover, in EC:DE:DMC the DMC will form very thick SEI layers at the surface of NSCNF, thus results into very slow K ions kinetics and negatively affects performance of PICs [28]. Furthermore, the PICs rate performance in 1.0 mol L^{-1} KPF_6 in EC: DEC was better in comparison to EC: DEC: DMC and Diglyme (Fig. 4b). The obtained specific capacities at various current densities were found much higher than the EC: DEC: DMC and Diglyme electrolytes.

4. Conclusions

In conclusion, a flexible anode material based on NSCNFs for PICs was successfully developed via eco-friendly and simple approach. Developed PICs consists of flexible and mechanical stable NSCNFs anode synthesized by using waste silk cocoon and exfoliated graphite cathode. Due to excellent thermal stability, mechanical stability and conductivity of 3D interconnected NSCNFs shows excellent specific capacity and stable life cycle with more 60% capacity retention. The significant electrochemical performance of PICs indicates the fast kinetics of K^+ ions at the NSCNFs. This fast kinetics of K + ions is mainly due to 3D interconnected dense carbon fibers which contains excess functionalities and large graphitic interlayer distance and faradic contributions of N-S groups. The current low cost and eco-friendly approach of developed flexible high conductive carbon electrode material via waste management and green methodology pave a new avenue to develop a sustainable energy storage system.

CRediT authorship contribution statement

Indu Pandey: Conceptualization, Methodology, Formal analysis, Resources, Supervision, Writing - review & editing. **Jai Deo Tiwari:** Conceptualization, Writing - review & editing, Resources, Software, Validation, Investigation. **Ashish Shukla:** Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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