Holey Graphitic Carbon Nano-flakes with Enhanced Storage Characteristics Scaled to a Pouch Cell Supercapacitor

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Abstract: Supercapacitors with holey graphitic carbon nano-flakes (HGCNF) capable of demonstrating large specific capacitance (SC) have been developed for the first time. The unique approach of applying an additional conducting layer of carbon fabric (CF) coated with HGCNF at both half-cells provides a significant enhancement in SC, from 323 to 1142 F g^{-1}, for the half cell and from 8 to 487 F g^{-1} for the symmetric supercapacitor, when the architecture is modified from Ni/HGCNF//HGCNF/Ni to Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni. HGCNF is composed of macro- and meso- pores enabling facile and deep penetration of electrolyte ions across the cross-section, ensuring maximum utilization at high current densities. Peak energy and power densities of 68 Wh kg^{-1} and 2.5 kW kg^{-1}, achieved for the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell, are superior to many reported nano-carbons, including HGCNF/Ni or HGCNF/CF symmetric cells. The corresponding 3 V pouch cell, showed an excellent SC of 80 F g^{-1}.

Keywords: Graphitic carbon; capacitance; supercapacitor; energy storage; pouch cell

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1. Introduction

Carbon nanomaterials, in view of their applicability to high power density and long-lived supercapacitors, have attracted significant research interest in the last two decades. Long lifetimes in excess of a million charge-discharge cycles, low maintenance costs, a near zero toxicity of activated carbon (AC) type materials derived from bio-sources [1,2] and the fact that they are safer than batteries, are the reasons for their use in diverse applications like hybrid vehicles, power tools, regenerative braking and aircrafts. Furthermore, AC type materials are typically manufactured by chemical or physical activation of waste bio-mass such as: rice husk, coconut fibers, peanut shells, dead leaves etc and their processing generally does not involve the use of any harmful reagents thereby ensuring that the final products are non-toxic[3]. The carbon electrode materials are electrically conductive, and when placed in an electrolyte, can accumulate positively and negatively charged ions upon polarization under an external electric field, thus forming an electrical double layer (EDL) and storing charge. For this mechanism of charge storage to be efficient, the carbon electrode should fulfil the following criteria: (1) It should have an electronic conductivity preferably greater than 10^{-2} S cm^{-1}, to enable facile transport of electrons across the electrode, so as to attain power densities as high as 10 kW kg^{-1}. (2) It should have a porous and low tortuosity microstructure, so as to permit easy and deep penetration of the ions in the electrolyte. (3) It should have a high effective surface area for maximum adsorption of ions. This ensures maximum utilization of active material and will result in a high specific capacitance (SC).

AC[4], carbon nanotubes (CNTs)[5], templated carbons[6] and reduced graphene oxide (RGO) nanosheets[7] are the most exhaustively studied materials for EDL based supercapacitor devices. With AC, SCs in the range of 60-150 F g^{-1} are achieved in common organic electrolytes[8] and with aqueous electrolytes, enhanced SCs in the range of 100-350

Besides ACs, graphene or RGO has also been used extensively at the lab-level, primarily due to (i) the nanosheets like morphology that endows them with a high surface area (~1000 m^2 g^{-1}), and (ii) the unobstructed electron conduction pathways available along the two-dimensional (2D) sheets. High SCs (~270 F g^{-1}) have been reported with graphene, with current densities of 0.1 A g^{-1}[10,11]. Among reports of note, a starch/RGO based gel-type supercapacitor possessing a high specific surface area of 1519 m^2 g^{-1}, delivered a SC of 183 F g^{-1} (at 2 mV s^{-1}), and a high energy density of 19.8 Wh kg^{-1} at a power density of 0.5 kW kg^{-1}, with a SC retention of 80% after 8000 cycles at 10 A g^{-1}[12]. In another study, lightweight and highly conducting 3D-printed graphene composite aerogel (3D-GCA) based supercapacitors showed a SC of ~73 F g^{-1} at 0.5 A g^{-1}, an exceptional rate capability with 90% SC retention over 0.5 to 10 A g^{-1}, and a power density greater than 4 kW kg^{-1}[13]. However, it must be noted that the strong tendency of RGO sheets to stack-up, decreases the active area dramatically over time, which reduces the SC and energy density, thus restricting their scale-up for commercial supercapacitors.

In a similar vein, functionalized CNTs and templated porous carbon structures obtained by using sacrificial ordered zeolites have also delivered high SCs in the past. A supercapacitor based on a phosphate-functionalized CNT containing carbon composites with a hierarchical porous structure gave a SC of ~160 F g^{-1} at 0.1 A g^{-1} and it was able to retain ~78% of its SC at a very high current density of 10 A g^{-1}[14]. This was accomplished in a 6 M KOH electrolyte in a 3-electrode cell. In another report, for a symmetric supercapacitor based on functionalized CNT fiber assemblies using UV-generated ozone with a polymer membrane electrolyte and an exceptionally high cell voltage of 3.5 V, the SC increased from 27.5 to 43.9 F g^{-1}, and the energy density reached a maximum value of 15.4 Wh kg^{-1} at 1 mA cm^{-2} compared to 10.9 Wh kg^{-1} for the pristine fibers[15]. Hollow carbon nanorods with graphitic walls with a surface area of 771 m^2 g^{-1} were prepared from a La(OH)$_3$ nanorod template via

chemical vapor deposition. The coin cell type symmetric supercapacitor with the hollow carbon nanorods delivered a SC of 128 F g^{-1}, an energy density of 55 Wh kg^{-1}, and a power density of 1.7 kW kg^{-1} at 1 A g^{-1} in an ionic liquid electrolyte[16]. Again, scaling-up such processes, be it large scale functionalization of CNTs or the templating methods for the preparation of large quantities of porous carbons is challenging.

Despite these advancements, the low accessible energy density (typically ranging between 1 to 10 Wh kg^{-1}), a fast self-discharge rate (ranging from a few seconds to a few minutes), the inaccessibility of the electrolyte to the bulk of the carbon nanomaterial electrode notwithstanding a high effective surface area (typically ~500 m^2 g^{-1}) limits their performance. Furthermore, the high processing cost of carbon nano-materials is also an issue which restricts their more widespread use. As a consequence, there is ample scope for developing novel low cost nano-carbons with superior attributes. In view of the challenges particularly pertaining to (a) the ease of synthesis and (b) scale-up, here we present the synthesis of holey graphitic carbon nano-flakes (HGCNF) from an extremely low cost carbon source, puffed rice, which can be bought in large quantities at a price as low as ~35 cents/kg. Subsequent to carbonization and chemical activation by an alkali, the product obtained is HGCNF, which is applied over Ni foam current collectors, and symmetric supercapacitors are assembled using an aqueous alkaline electrolyte. Since no harmful or toxic chemicals were used for processing the HGCNF, the possibility of any trapped contaminants in the final product is also eliminated, rendering it to be non-toxic. The benefit of using HGCNF is the mesoporous and macroporous structure, which enables facile penetration of the electrolyte ions and provides a large interfacial contact area during charge-discharge. Although similar hierarchical carbon structures having a combination of micro-, meso- and macro- pores derived from bio-mass have been reported in the past[17–20], superior electrochemical energy storage performance for the HGCNF device was demonstrated in this work, by using ion-permeable carbon fabric

Such a cell configuration has not been reported before. The Ni/HGNCF//HGNCF/Ni supercapacitor cell performance was improved by including a self-supporting electrolyte wetted porous carbon fabric (CF) layer adjacent to each side of the separator. The layers serve as electrolyte reservoirs, increasing the amount of ions available for forming the EDL at the two half-cells. By increasing the volume of electrolyte available, ion depletion in the electrolyte is mitigated and the conductivity is maintained within an optimal range.

Besides studying the conventional electrochemical parameters and the impact of integrating the Carbon-fabric (C-fabric) into the supercapacitor, a comprehensive analysis on the effect of temperature (from 5 to 55 °C) and bending angle (from 15 to 60°) on the charge storage properties of the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni supercapacitor is presented. The HGCNF coatings are also scaled-up to yield heat sealed pouch cell supercapacitors, and their performance is also demonstrated highlighting the potential scalability of this approach.

2. Experimental

2.1. Chemicals

Puffed rice was purchased from a local vendor and used as acquired. Potassium hydroxide (KOH), sodium hydroxide (NaOH), acetone, concentrated nitric acid (HNO_3, 69%), concentrated sulfuric acid (H_2SO_4, 98%) were procured from Merck. C-fabric was procured from Alibaba Pvt Ltd and treated with a 1:1 volume ratio of concentrated HNO_3 and concentrated H_2SO_4 for 12 h. It was then washed sequentially in water and acetone and dried at 80 °C for 12 h in air. Poly(vinylidene fluoride) (PVdF, average Mw: 534000), carbon black (CB) and N-methyl pyrrolidone (NMP) were purchased from Sigma-Aldrich and used directly. Nickel foam current collectors were procured from Gelon and used directly after washing with acetone. Ni tabs and laminated Al were also procured from Gelon. Throughout

the experiments, ultrapure deionized water with a resistivity of ~18.2 MΩ cm was used, which was obtained from a Millipore Direct-Q3 UV system.

2.2. Synthesis of HGCNF and fabrication of symmetric supercapacitors

Puffed rice was ground to a fine powder by using a motorized grinder. The resulting powder was carbonized at 750 °C in a muffle furnace for 4 h with a ramp rate of 3 °C.min^{-1} in air. The formed carbon was treated with NaOH in a 1:1 (w/w) ratio with water and stirred continuously for 12 h (generally, for 1 g of carbon, a maximum of 5 mL of water was used). Finally, it was washed with deionized water thoroughly to remove excess NaOH, treated with acetone, dried overnight at 80 °C and the resultant powder was labelled as HGCNF, which was stored in a desiccator. HGCNF, CB and PVdF were then combined in a weight ratio of 80:10:10 and dry-ground in a pestle and mortar for 2 h. NMP solvent was added dropwise and the mixture was ground for another 1 h till a homogeneous slurry was obtained. The slurry was diluted by adding extra drops of NMP and drop-cast on two different current collectors: C-fabric and Ni foam, each having an active geometrical area of 1 cm × 1 cm. The weight of HGCNF on each of the two electrodes was ~1.6 mg. Two different HGCNF electrodes were obtained; one over Ni foam and the other over the C-fabric, after drying at 70 °C in a hot air vacuum oven for 12 h. An aqueous 6 M KOH solution was used as the electrolyte. Prior to assembling the cells, the HGCNF/CF electrode was pre-wetted with the electrolyte on both sides and the HGCNF/Ni electrode was wetted only at the active material side. Symmetric cells were fabricated with the following architectures: Ni/HGCNF//HGCNF/Ni, CF/HGCNF//HGCNF/CF and Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni. Whatman filter paper soaked with the electrolyte acted as a separator and it was sandwiched between the electrodes. Scheme 1 provides a schematic for the fabrication of this symmetric supercapacitor, starting from puffed rice.

2.3. Measurement techniques

Cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) measurements for the individual electrodes of HGCNF/Ni and HGCNF/CF were conducted in a three electrode system with a reference electrode of Ag/AgCl/KCl (3 M) and a Pt rod counter electrode. For HGCNF/Ni and HGCNF/CF, the potential window was taken from 0 to -1 V. For all the symmetric cells, the potential window was also taken from 0 to 1 V. SCs were calculated using Equation 1, where the SC of a full cell in a two- electrode configuration is given by SC, and that of a single electrode is given by: 4 * SC.

$$SC = \frac{I * \Delta t}{m * V} \qquad (1)$$

In Equation (1), I is the applied discharge current (A), Δt is the discharge time (s), m is total active mass at both electrodes (g) and V is the voltage window. The energy density (E) and power density (P) were calculated using equations 2 and 3.

$$E = \frac{SC * V^2}{2 * 3.6} \qquad (2)$$

$$P = \frac{I * V}{2} \qquad (3)$$

In Equations (2) and (3), E is the specific energy density in Wh kg^{-1} and P is the specific power density in kW kg^{-1}. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer with Cu Kα radiation (1.5418 Å), as the X-ray source. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi machine, operating at a base pressure of ~5 × 10^{-11} Torr with a non-monochromatized Al Kα line at 1,486.7 eV. The acquired resolutions of survey and core levels were 1 and 0.1 eV and the spectra were acquired at 200 and 50 eV pass energies, respectively. The core level spectra were deconvoluted using a non-linear iterative least squares Gaussian fitting procedure. Corrections due to charging effects were accounted for by using C(1s) as an internal reference and the Fermi edge of a gold sample. A Jandel Peak FitTM (version 4.01) program

was used for the analysis. Surface morphology analysis was performed using a scanning electron microscope (SEM) (Carl Zeiss EV018). Transmission electron microscopy (TEM) images were obtained on a JEOL 2100 microscope operating at an acceleration voltage of 200 kV by using samples deposited over carbon coated copper grids by using a suspension and evaporation method. GCD, CV, linear sweep voltammetry, self-discharge and electrochemical impedance spectroscopic (EIS) studies were performed on an Autolab PGSTAT 302 frequency response analyzer. Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size and volume analysis were performed for HGCNF under a nitrogen atmosphere at 77.3 K, after degassing at 300 °C for 4 h. Pouch cells were fabricated using equipment from Gelon including: an automatic film coating machine with cover heater (GN-AFA-III-220) for coating the active material over the Ni foam or C-fabric current collectors, a semi-automatic die cutter for cutting the coated pouch cell electrode sheets to required dimensions (GN-QM180), a pouch cell case forming machine (GN-120) for fabricating cups from aluminum laminated films, an ultrasonic welding machine with digital control (GN-800W) for welding the Ni tabs to the electrodes and a compact heating sealer for sealing the laminated aluminum case or pouch cell (GN-140) for the final sealing of the pouch cell along the four edges.

3. Results and discussion

3.1. Structural and compositional features of HGCNF

SEM images of the HGCNF (Figure 1a and b), reveal corrugated and rough textures, typical of graphene[21,22] except for one distinguishing feature, which are the hierarchical macroscopic holes that prevail across multiple length scales. These holes are uniformly distributed, and are approximately 50 to 100 nm. During the charge-discharge process, they allow easy diffusion of the charge carriers, thus enabling more electrochemically active reaction sites, across the depth of HGCNF to participate in the charge storage process and

maximize the SC. The TEM image (Figure 1c) highlights the crumpled sheet like nature of the material, suggestive of a high effective surface area and the flaky texture is also visible. The high magnification images (Figure 1d and e), showcase the mesoporous and macroporous microstructure of the HGCNF very clearly. The macropores and mesopore are clearly visible in the carbon nano-flakes. The mesopore diameters vary from 5 to 20 nm, and their dimensions are conducive for ingress and egress of K^+ and OH^- ions during electrochemical cycling. The graphitic structure of the carbon nano-flakes or the walls of the pores, is evidenced from the lattice scale images displayed in Figure 1f and g. The walls are composed of consecutive parallel fringes; the inter-fringe distance is 0.34 nm, which matches with the (002) plane of hexagonal graphite (PDF: 75-1621). Figure 1g shows two conjoined mesopores where, each mesopore is enclosed by tens of graphitic planes oriented parallel relative to each other. The corresponding selected area electron diffraction (SAED) pattern comprises of concentric rings with bright spots, with the successive rings originating from the (002), (100) and (004) planes of the graphite, concurring with the inter-planar spacings of 0.34, 0.21 and 0.17 nm respectively. Previously, holey graphene was prepared by a catalyst free, thermal oxidation method, but the hole density appeared to be low from the micrograph[23]. In another report, nitrogen doped holey graphene was synthesized and while it was composed of a plethora of macropores[24], the mesopores were not distinctively observable. Here, the macropores permit the electrolyte solution to seep through the thickness of the HGCNF, and the mesopores, concurrently to allow facile ion propagation, by the virtue of their size. This perforated 3D graphitic flake-like structure achieved for the activated carbon is favorable for electrolyte permeability and ion accessibility.

The XRD pattern of the HGCNF (Figure 2a) shows three distinct but broad peaks at 2θ = 24.07°, 43.4° and 79.5° corresponding to d = 3.40, 2.14 and 1.23 Å, and these are assigned to the (002), (101) and (110) planes of graphite, thus re-affirming that the HGCNF have a

hexagonal lattice of carbon atoms. The formation of the graphitic structure is explained as follows. Puffed rice is primarily made up of starch, which is a polymeric carbohydrate comprising of glucose units linked via covalent glycosidic bonds. During the annealing process, when the puffed rice powder is heated slowly to 750 °C, chemical transformations such as depolymerization, fragmentation, ring opening and ring contraction occur because of the heat. It further degrades via parallel pathways either to volatile organic compounds or to char and gases such as CO, CO_2, H_2O, which are expelled on further heating. Similar chemical changes are reported for cellulose, which is also composed of similar repeating glucose based monomer units[25]. When the temperature is increased to 400 °C or more, a major product formed is anhydrous sugar levoglucosan along with hydroxy-methylfurfural and formic acid[25]. Condensation of these intermediate products leads to the formation of soluble polymers by intermolecular dehydration or aldol condensation eventually resulting in the aromatization of polymers[26]. Graphitization takes place through the following steps: (a) removal of defects within each graphite layer plane as well as between the planes, (b) gradual shifting and growth of the crystallites, (c) removal of cross-linking bonds, (d) evolution of the ABAB stacking sequence, and (e) shifting of carbon rings or single atoms to fill vacancies and eliminate dislocations[27] .

Compositional features of HGCNF were analyzed by XPS; the survey spectrum of the HGCNF (Figure 2b) shows multiple peaks due to C, N and O. The corresponding deconvoluted core level spectra of C1s, N1s and O1s signals are shown in Figure 2(c,d) and inset of Figure 2b. The C1s spectrum shows three components at 284.6, 285.1 and 286.3 eV with integrated areas of 45.3, 41.5 and 13.2%, which are attributed to C-C, C-O and C-N groups, respectively. The O1s and N1s spectra show almost symmetric peaks at 532.2 and 399.8 eV respectively. The strong alkali treatment results in the formation of C-OH groups along the edges of the graphitic carbon and these groups produce the strong O1s signal in the

spectrum. <mark>The N1s signal arises from the nitrogen that fail to escape from the puffed rice, during the starch heat treatment.</mark> This nitrogen possibly originates from the impurities in puffed rice and is most likely present as a pyrrolic nitrogen (-NH-) species, as the peak position matches with a reported value of 399.8 eV for porous carbon fabricated from cross-linked monomers[28]. The presence of the hetero-atoms: O and N, along the carbon backbone is advantageous in enhancing the electrical conductivity of HGCNF[28]. BET data for the HGCNF is presented in Figure 2e,f. The BET surface area is calculated to be 600 m^2 g^{-1}. Since the technique is sensitive to mesoporous materials, the porosity analysis shows that ~5 nm pores are predominant in the material. Figure 2e represents a reversible type II isotherm, which is an isotherm typical of a macroporous absorbent having unrestricted monolayer and multilayer adsorption[29]. The total volume of pores is about to 0.2 cc g^{-1}.

3.2. Electrochemical energy storage properties of HGCNF

The charge storage behavior of HGCNF was determined in a three electrode assembly, using a 6 M KOH aqueous electrolyte, with HGCNF/CF or HGCNF/Ni layers as the working electrode, Ag/AgCl/KCl as the reference electrode, operated over a negative potential range of -1 to 0 V. On comparing the CV plots with Ni and CF current collectors, quasi-rectangular ideal curves are achieved (Figure 3a,b). While the area enclosed in the voltammogram, and the corresponding SC is larger with CF, the HGCNF/Ni electrode showed higher limiting current densities. Variation of SC with scan rate (Table S1) illustrates that CF is superior, due to the mesh like framework of C-fabric, which allows a better distribution of the active material, HGCNF, and as a consequence, enhances the capacitance compared to what is achieved with Ni foam. Although both Ni foam and CF are porous, CF is denser than Ni foam, and therefore ion-adsorption is better with CF. For instance, at 1 mV s^{-1}, the areal capacitances are 0.38 and 5.4 F cm^{-2}, for HGCNF/Ni and HGCNF/CF. At a low scan rate, there are multiple peaks in the CV observed for HGCNF/Ni, which are attributed to the Ni

foam, as Ni reacts in KOH to form $Ni(OH)_2$. What distinguishes Ni foam from CF is perceptible from the differences in the GCD plots (Figure 3c,d). The plots are quasi-triangular with the CF, but the Ohmic drop is larger, compared to the Ni foam. The non-linear charge discharge profile for HGCNF/Ni at low current density (0.5 A g^{-1}) is as a result of its pseudocapacitive nature which further confirms the reaction of the Ni foam with the electrolyte. There is no distinguishable iR drop observed for the HGCNF/Ni electrode whilst HGCNF/CF shows an iR drop of 0.12 V at a current density of 1 A g^{-1} with it increasing to 0.24 and 0.33 V at 2 and 3 A g^{-1}. SC values of 195 and 1,142 F g^{-1} are obtained at the same current density of 1 A g^{-1} for HGCNF/Ni and HGCNF/CF respectively. This difference in performance highlights the importance of the two current collectors. While the CF, undoubtedly, assists in utilizing the full potential of the HGCNF, the Ni foam electrode is endowed with both mechanical integrity, flexibility and high electronic conductivity, therefore enabling the fabrication of structurally stable devices. Furthermore, almost 71% of the maximum SC is retained even at a high current density of 3 A g^{-1} for the HGCNF/CF, implying fast and efficient utilization of the active sites. The SCs obtained for the single HGCNF/CF electrode over a current density range of 1-3 A g^{-1}, are extraordinarily higher than those reported for other carbon nanomaterials. Generally, for all practical supercapacitor devices, it is the two-electrode capacitance or the net cell capacitance (if the device contains multiple cells connected in a combination of series or parallel) which is relevant, but the magnitude of single electrode capacitance, demonstrates the potential that any electroactive material has for energy storage, which is the reason for reporting single electrode capacitances here.

The values obtained in this study are higher than the single electrode capacitances reported for carbons derived from waste bio-mass, at the same current density of 1 A g^{-1}, in the same KOH electrolyte, and in three electrode configurations. The values are summarized here. In

an earlier report on porous carbon with a specific surface area of 3404 m^2 g^{-1} produced from waste celtuce leaves, a SC of 361 F g^{-1} was achieved at a current density of 1 A g^{-1} in 6 M aqueous KOH electrolyte[30]. In another work, twisted, tubular and porous carbon fibers obtained after the carbonization of low-cost natural cotton with surface area of 2436 m^2 g^{-1} and high electrical conductivity (~860 S m^{-1}), delivered a SC of 283 F g^{-1} (1 A g^{-1})[31]. In yet another study, microporous and microporous structured carbon derived from lotus leaf as the bio-mass source offered a SC of 379 F g^{-1} at 1 A g^{-1}[32]. Nitrogen doped porous carbon with an effective surface area of 1212 m^2 g^{-1} derived directly by a pyrolysis method from a bio-mass source of stem bark of broussonetia papyrifera delivered a SC of 310 F g^{-1} at 1 A g^{-1}[33].

Table 1: Fitted EIS parameters for the electrodes in a three electrode system.

Electrode	R_s Ω cm^2	R_{ct} Ω cm^2	C_{dl} F cm^2	Y_o S $s^{1/2}$ cm^2
HGCNF/Ni	0.5	31	6.8×10^{-3}	4.8×10^{-2}
HGCNF/CF	2.1	3.5	3.4×10^{-5}	1.6×10^{-2}

A comparison of impedance spectra recorded under a potentiostatic AC bias of 20 mV, over a frequency range of 1 MHz to 0.01 Hz is shown in Figure 3e and f. From the fitted data (Table 1) it is shown that the resistance to charge transfer (R_{ct}), which is equal to the diameter of the semi-circle, is lower for the CF (4.2 Ω cm^2) based cell compared to the Ni foam (31 Ω cm^2) one. Cation and anion accumulation from the KOH electrolyte at the electroactive sites on HGCNF deposited over carbon fibers is more facile compared to Ni. But ionic conductivity and double layer capacitance are higher for the Ni foam based cell. This could

be due to the lower sheet resistance of Ni foam compared to CF and a more open pore structure for the former.

3.3. Comparative analysis of symmetric supercapacitors

A series of electrochemical studies were performed on symmetric supercapacitors: having the configurations: Ni/HGCNF//HGCNF/Ni, CF/HGCNF//HGCNF/CF and Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni which are described through cartoons in Figure 4(a-c). Figure 4(d-f) shows the CV profiles for the three cells at scan rates of 5, 20 and 100 mV s^{-1} respectively. The enclosed areas in the CV curves maintain the following sequence: Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni > CF/HGCNF//HGCNF/CF > Ni/HGCNF//HGCNF/Ni. The differences in the curves suggests that the redox behavior is a strong function of both scan rate and cell configuration. While the cell without CF, shows a pseudocapacitive response at all scan rates, the two cells based on the CF-electrodes, show a leaf like response at 5 mV s^{-1}, that transforms to quasi-rectangular and almost-ideal capacitive plots at 20 and 100 mV s^{-1}. Figure 4(g-i) compares the GCD profiles for the cells recorded at current densities of 0.5, 2 and 5 A g^{-1}. The pattern of charging and discharging plots are arc-type but having an overall triangular appearance implying that charge storage takes place mainly by the electrical double layer mechanism. The calculated SCs or C$_{cell}$ for Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni, CF/HGCNF//HGCNF/CF and Ni/HGCNF//HGCNF/Ni cells are: 8.3, 0.6, 0.1 F g^{-1}, 457, 111, 11 F g^{-1} and 488, 134, 54 F g^{-1} respectively at the current densities of 0.5, 2 and 5 A g^{-1}. The SC trends are also compared in Figure 4j. Unlike Ni foam which makes a negligible contribution to the SC, the C-fabric contributes to the SC. Therefore, the SCs for the CF based cells were calculated by deducting the contribution towards ion-storage from the CF current collector. This was accomplished by fabricating a blank symmetric cell with C-fabric without any HGCNF but having an architecture of CF/6 M KOH-separator/CF, where the C-fabric was pre-wetted with a 6 M

KOH electrolyte for 12 h. For this cell, CV and GCD plots were measured at the same scan rate and current densities as done for the above three cells (plots are provided in supporting information). SC (C_{cell}) calculations for Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni and CF/HGCNF//HGCNF/CF cells were performed by using the equation: $C_{cell} = C_{total} - C_{blank}$, where C_{total} is the SC obtained from the respective GCD plots for the aforesaid two cells, C_{blank} is the SC obtained from blank CF//CF cell. C_{cell} gives the actual SC of the two aforementioned cells as C-fabric is in parallel connection with the electrode coated with the active material or HGCNF or HGCNF itself, thus justifying the direct subtraction. The calculated SCs at different current densities with and without the CF's contributions are tabulated in supporting information (Table S2).

The SC magnitudes unambiguously confirm that among the three cells, the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell has the best performance due to the following reasons. (1) The CF/HGCNF interlayer electrodes are the primary contributors to charge storage and they are well supplemented by the additional ions stored by HGCNF tethered to the Ni foam based outer layers. (2) At each half-cell, the electrolyte availability is abundant (owing to pre-wetted electrodes) and its' infiltration is deep due to the open hierarchical porosity of the HFCNF and the mesh like framework of carbon fibers. This implies that the maximum possible number of electrochemically active sites on the HGCNF are accessed by the electrolyte, thus maximizing the observed SC. (3) Apart from the ease of ion-movement across the multiple layers at the cathode or the anode, the high electrical conductivities of the three main components: Ni foam, CF and HGCNF, also permit the unrestricted transfer and propagation of electrons, during cycling. In comparison with literature studies on activated carbon, our cell exhibits favorable properties, particularly at a current density of 0.5 A g^{-1}. For instance, a symmetrical coin cell of nanoporous carbon synthesized from jute sticks, as a waste bio-mass source, exhibited a maximum cell

capacitance of 80 F g^{-1} at 0.5 A g^{-1} in an aqueous 6 M KOH electrolyte[34]. Hierarchically-porous carbon obtained from organic waste having very high surface area of 3000 m^2 g^{-1} delivered a cell capacitance of 200 F g^{-1} at a current density of 0.5 A g^{-1}[35]. A symmetric cell consisting of nitrogen doped porous carbon obtained from the pyrolysis of the bark of a plant delivered a SC of 130 F g^{-1} at a current density of 0.5 A g^{-1}[33]. All of the above described cells employed the same aqueous KOH electrolyte, which is used in this work. In comparison with other reported carbon based supercapacitors, the storage performance for this cell is substantially improved.

The sheet resistances of Ni foam, CF and HGCNF were measured to be 0.1, 50 and 16 Ω cm^{-2}, suggesting that all the three principal components of the multilayered Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell are excellent electron conductors. This is further ratified from the I-V characteristics of Ni foam, CF and HGCNF, recorded by sandwiching them between two SS plates. Ohmic dependence was observed (Figure 5a) over short potential ranges for Ni foam as well as HGCNF. The current saturates over the high negative and positive voltage domains as the rate of diffusion of charge carries is equal to the rate of formation of EDL. From the slopes (Slope = $\Delta I/\Delta V$ = 1/R) of the linear fits over the Ohmic regions, the electrical conductivities (σ) are deduced to be 11.2, 8.8 and 10 mS cm^{-1} for Ni foam, C-fabric and HGCNF respectively, by applying the equation: $\sigma = (1/R \times (l/a))$, where 'l' is the thickness and 'a' is the active electrode area. The overall charge transport profile across the heterojunctions is shown through a cartoon in Figure 5b. The schematic evidences the ability of this dual electrode assembly to transfer, and transport charges (electrons and K$^+$ ions or positive charges and OH$^-$ ions) unobstructed, which is responsible for the good storage attributes at high rates shown by the full device. While C-fabric and Ni-foam are pure electronic conductors, their porosity allows charge storage via EDL formation, and this can be easily gauged from the micrographs/photographs of the CF and Ni foam

displayed in Figure 5c,d. The intertwined rope like structures in the CF and hierarchical highly porous framework offered by the Ni strands in Ni foam can be seen. The electrical conduction behavior and the morphologies of these two current collectors render them to be most suitable scaffolds for loading of HGCNF and assisting the latter in realizing its full potential for electrochemical energy storage.

The durability of the cells was studied by cycling them at a constant current density of 5 A g^{-1} (Figure 4k). Here, the SC drops from 54 to 52 F g^{-1} after 10,000 GCD cycles for the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell, implying a 96% SC retention. The remaining two cells of Ni/HGCNF//HGCNF/Ni and CF/HGCNF//HGCNF/CF exhibit 95 and 96% SC retention after 10,000 cycles. Since the initial SC of the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell is significantly higher compared to the other two cells, its' ability to endure 10,000 cycles without experiencing any major deterioration indicates its potential for commercial applications. Similarly, the same cell also shows slower self-discharge rate. All cells were charged to 1 V by applying a fixed current of 4 mA and the self-discharge time was monitored under no load (Figure 4l). After 3 min., the potential of the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell drops to 0.7 V whereas for CF/HGCNF//HGCNF/CF and Ni/HGCNF//HGCNF/Ni, it drops to 0.6 and 0.36 V. Thereafter, the potential decline is slow for both the CF based cells. The CF/HGCNF//CF/HGCNF cell reaches half of its' initial potential in 13 min. However, the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell takes 100 min. to reach the same potential of 0.5 V. Among the 3 cells, the Ni/HGCNF//HGCNF/Ni cell shows rapid decline, as it reaches zero volt within 21 min. This disparity in self-discharge response highlights the ability of the multi-layered half cells in Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni for storing charge effectively.

Ragone plots for the three cells with different configurations are presented in Figure 5e. A maximum energy density (E) of ~68 Wh kg^{-1} is measured at a power density (P) of 0.25 kW kg^{-1} for the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell. The CF/HGCNF//CF/HGCNF cell shows a E$_{max}$ of ~63 Wh kg^{-1} at the same P. In stark contrast, is the Ni/HGCNF//HGCNF/Ni cell shows a significantly lower E$_{max}$ of 1.2 Wh kg^{-1}. Energy densities of Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni and CF/HGCNF//CF/HGCNF cells drop to 7.5 and 1.5 Wh kg^{-1} respectively, when the P is raised to 2.5 kW kg^{-1}.

EIS spectra of the three cells are compared before and after 10,000 cycles (Figure 5f,g). An equivalent circuit comprising of equivalent series resistance (ESR) due to contacts and the electrolyte, charge transfer resistance (R$_{ct}$) and an infinite Warburg (Y$_o$) were used for fitting the data (Table 2).

Table 2: Fitted EIS parameters for symmetric cells before and after 10000 charge-discharge cycles.

Before Cycling						
Cell configuration	ESR Ω cm^2	R$_{ct1}$ Ω cm^2	C$_{dl1}$ F cm^2	R$_{ct2}$ Ω cm^2	C$_{dl2}$ F cm^2	Y$_o$ S s$^{1/2}$ cm^2
Ni/HGCNF//HGCNF/Ni	0.3	16.8	4.3×10^{-3}	-	-	2.2×10^{-3}
CF/HGCNF//HGCNF/CF	9.7	26.6	5.6×10^{-7}	-	-	8.5×10^{-4}
Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni	0.3	2.0	1.7×10^{-3}	5.0	3.0	3.4×10^{-3}
After Cycling						
Ni/HGCNF//HGCNF/Ni	0.3	8.0	2.1×10^{-3}	-	-	2.7×10^{-4}
CF/HGCNF//HGCNF/CF	8.8	47	1.6×10^{-6}	-	-	7.8×10^{-6}
Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni	0.4	1.8	1.1×10^{-4}	2.5	2.6	0.11

For the Ni/HGCNF//HGCNF/Ni cell, the ESR is 0.3 Ω cm^2, which is 32 times smaller than that of the CF/HGCNF//HGCNF/CF cell (9.7 Ω cm^2). This may be because of the higher sheet resistance of CF (50 Ω cm^2) compared to that of Ni foam (0.1 Ω cm^2). The multi-layered Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell also has a low ESR of 0.3 Ω cm^2 which is equal to that observed for the Ni/HGCNF//HGCNF/Ni cell. The charge transfer resistances for Ni/HGCNF//HGCNF/Ni and CF/HGCNF//HGCNF/CF cells are 16.8 and 26.6 Ω cm^2, which are 8 and 13 times higher than that obtained for the multi-layered cell (2 Ω cm^2). The infinite Warburg element is represented by $Z = (1-j) \times \omega^{-1/2} / Y_o \times 2^{1/2}$, where ω is the angular frequency and Y_o is a measure of the diffusional conductance. The Y_o values are 2.2, 0.85 and 3.4 mS s$^{1/2}$ cm^2 for the Ni/HGCNF//HGCNF/Ni, CF/HGCNF//HGCNF/CF and Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cells respectively. The CF based cell shows the lowest diffusional conductance, due to the more constricting pore structure of the CF fibers compared to the Ni foam. The penetration of ions across the Ni foam is kinetically faster compared to CF. In the multilayered cell as well, the presence of the Ni foam layers facilitates ion transport. Additional RC parameters are obtained for the latter cell, possibly due to multiple interfaces. Post-cycling, the overall impedance is larger for the Ni/HGCNF//HGCNF/Ni cell, and the remaining two cells do not exhibit much change.

3.4. Effect of temperature and bending angle on cell performance

Since in real applications, the temperature of supercapacitor operation is not necessarily 25 °C, the dependence of the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell performance with temperature was investigated, by recording CV and GCD curves at 20 mV s^{-1} (Figure 6a) and 2 A g^{-1} (Figure 6b) respectively over a temperature range of 5 to 55 °C with a 10 °C interval. With increasing temperature, the area under the CV curve increases linearly at the beginning, up to 35°C, and after that it increases slowly. Over the low

temperature range of 5 to 25 °C, the increase in charge storage is facilitated by the improved ion-mobility afforded by the higher temperature operation. The SC changes from 42 to 627 F g^{-1} over the temperature range of 5 to 55 °C (Figure 6c). The cell exhibits an acceptable storage response even when the temperature is as low as 5 °C, implying that the supercapacitor can work in a cold climate, and no external heating is required.

The variation in the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell performance with bending was also examined; two bending angles are exhibited through as shown in Figure 6d. GCD plots were recorded at a current density of 2 A g^{-1} at different bending angles ranging from 15 to 60° (Figure 6e). The used carbon fabric is flexible and it can be bent any degree without any structural change of the fabric. The coated compound on carbon cloth is absorbed completely on tiny carbon fibers. The unbent cell delivers a SC of 200 F g^{-1} and higher SCs of 260 and 232 F g^{-1} were obtained when the cell was bent at angles of 15 and 30° respectively (Figure 6f). The reason for this could be that electrolyte is able to seep through the cross-section of the electrodes more effectively when it is bent or better electrical contact is made.

3.5. Scaling up to a pouch cell supercapacitor

Pouch cells were fabricated with 3 symmetric Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cells connected in series. The HGCNF/Ni electrodes were cut into square shapes using a die-cutter machine (Figure 7a), with a short extension on the side for taking contact. Once the individual cell was assembled with the KOH coated separator in between, the whole cell was encapsulated with Teflon tape to hold the assembly together. Three such cells were fabricated, and then stacked, and Ni tabs were ultrasonically welded onto the extensions prevalent on the Ni foam electrodes. The stacked cells with the welded contacts are shown in Figure 7b. Laminated aluminum foil was used for making a pouch, each side having a depth of 10 mm, using a cup forming machine (Figure

7c,d). The stacked cells were carefully placed in the cavity side of the pouch and the pouch was heat-sealed along all the four edges, with the Ni tabs protruding outwards as shown in Figure 7e. A pouch cell was also fabricated with 2 stacked cells. CV, GCD and EIS plots for 1, 2 and 3 cells are shown in Figure 7f-h. The CV and GCD plots show that 1, 2 and 3 cells could be charged to 1, 2 and 3 V, respectively. The cathodic and anodic current density maxima decrease with increasing number of cells in the CV plots, as anticipated. While the voltage window of operation is enhanced, but the discharge time remains almost constant ongoing from a single to a three cell or the pouch cell. The SC values for 1, 2 and 3 cells are 200, 110 and 80 F g^{-1} respectively. EIS spectra comparison, shows that that the ESR is slightly increased, from 0.3 to 0.8 and 1.3 Ω cm^2, ongoing from 1 to 2 and 3 cells respectively. This increase possibly originates from the resistance offered at the contacts, when the 3 cells are joined together. The resistive nature of the pouch cell is also visible from the intermediate to low frequency response, which shows a lowered contribution from the imaginary component compared to the single cell response. Table 3 summarizes the EIS parameters.

Table 3: Fitted EIS parameters for symmetric Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cells.

Cell configuration	ESR Ω cm^2	R_{ct1} Ω cm^2	C_{dl1} F cm^2	R_{ct2} Ω cm^2	C_{dl2} F cm^2	Y_o S s$^{1/2}$ cm^2
One cell	0.3	2.0	1.7×10^{-3}	5.0	3.0	3.4×10^{-3}
Pouch Cell: 2 cells in series	0.8	10.0	3.1×10^{-3}	19.0	0.2	3.7×10^{-3}
Pouch Cell: 3 cells in series	1.3	8.0	7.6×10^{-3}	13.0	0.7	1.6×10^{-2}

Both C_{dl1} and C_{dl2}, as well as diffusional conductance increase with increasing number of cells. The increase in these parameters is due to an enhanced proportion of electroactive species available in the net circuit.

4. Conclusions

An innovative strategy, where dual electrodes of HGCNF tethered to Ni foam and CF were employed in a symmetric supercapacitor, yielded significantly enhanced energy storage characteristics compared to most of the nanostructured carbons reported in the literature. HGCNF comprises of layers of carbon arranged in a graphitic hexagonal lattice, interspersed with macro- and meso-pores, that permit easy flow of the electrolyte solution across deep recesses of the coated material, and widespread access of electrolyte ions to the electrochemically active sites. Propagation of electrons from the external circuit occurs easily across this multi-junction assembly of Ni/HGCNF/CF/HGCNF, primarily due to the high electrical conductivity of HGCNF, the Ohmic contact at the HGCNF/Ni and HGCNF/CF interfaces, and the direct contact between these two electrodes, established by the electrolyte (pre-)wetted surfaces. This flow of electrons and ions, imparts a SC of 487 F g^{-1}, energy and power densities of 68 Wh kg^{-1} and 0.25 kW kg^{-1}, negligible degradation over 10,000 cycles, slow self-discharge to the multilayered Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell relative to the individual supercapacitors based on sole Ni or sole CF. On scaling up the cell to a pouch cell comprising of 3 cells connected in series, it was charged to 3 V, corresponding to a SC of 80 F g^{-1}, thus illustrating the promise it holds for translating this cell architecture to a commercial level.

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Scheme 1. Photographs illustrating the step-wise fabrication of the symmetric Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell starting from the bio-resource, puffed rice.

Figure captions:

Figure 1. (a,b) SEM and (c) TEM images of HGCNF. (d,e) High magnification TEM images, (f,g) lattice scale images and (h) SAED pattern of HGCNF.

Figure 2. (a) XRD pattern of HGCNF. (b) XPS survey spectrum, (c) deconvoluted C1s- and (d) N1s- core level spectra of HGCNF; inset of (b) is the O1s core level spectrum of HGCNF. (d,e) BET- nitrogen adsorption-desorption isotherms and porosity distribution of HGCNF.

Figure 3. (a,b) CV plots, (c,d) GCD profiles, and (e,f) Nyquist plots of HGCNF/Ni and HGCNF/CF as working electrodes in 3-electrode set-ups with Ag/AgCl/KCl as the reference electrode, 6 M KOH as the electrolyte and a Pt rod as the counter electrode. Insets of: (a) is an enlarged view of the CV plot of HGCNF/Ni at 1 mV s^{-1}, (e,f) schematics of the 3-electrode cells, (f) equivalent circuit used for fitting the data.

Figure 4. Cartoons of symmetric cells of (a) Ni/HGCNF//HGCNF/Ni, (b) CF/HGCNF//HGCNF/CF   and   (c)   Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni. Comparison of the 3 cells: CV plots at scan rates of (d) 5, (e) 20 and (f) 100 mV s^{-1} and GCD plots at current densities of (g) 0.5, (h) 2 and (i) 5 A g^{-1}. (j) Variation of SC with current density, (k) cycling stability comparison, and (f) self-discharge plots for the 3-symmetric cells.

Figure 5. (a) I-V characteristics of Ni foam, C-fabric and HGCNF sandwiched between 2 SS plates. (b) Cartoon illustrating the charge transport mechanism in the Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni cell during charge or discharge. Photographs and SEM images of (c) C-fabric and (d) Ni foam current collectors. (e) Ragone plots and (f,g) Nyquist plots of the 3 symmetric cells of Ni/HGCNF//HGCNF/Ni, CF/HGCNF//HGCNF/CF and Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni, recorded under an ac amplitude of 20 mV, at open circuit voltage, over a frequency range of 1 MHz to

0.01 Hz: (f) before and (g) after 10000 GCD cycles (insets are enlarged views of the high frequency domains and the equivalent circuits used for fitting the data).

Figure 6. Variation in (a) CV curves, (b) GCD plots and (c) SC and % of change in SC with operational cell temperature for the symmetric cell of: Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni. (d) Photographs of the cell: Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni, bent at two different angles. Variation in (e) GCD plots and (f) SC and % of change in SC with bending angle.

Figure 7. Photographs of: (a) HGCNF/Ni, HGCNF/CF and related components for cell assembly, (b) 3-stacked symmetric cells of Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni with welded Ni tabs for contacts, laminated Al pouch: cavity side up (c) and down (d), (e) final heat sealed pouch cell. Comparison of (f) CV curves, (g) GCD profiles and (h) Nyquist plots of 1, 2 and 3 symmetric cells of Ni/HGCNF/CF/HGCNF//HGCNF/CF/HGCNF/Ni. Inset of (h) shows the equivalent circuit used for fitting the data.