Surface Modified Carbon Cloth via Nitrogen Plasma for Supercapacitor Applications

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The irregularity of renewable energy resources induced by environmental pollution and global warming has driven the development of efficient and pollution-free energy-generating and storage devices. Among the different available technologies, the production of hydrogen via the electrocatalysis of water and storing electricity in electrochemical energy storage devices are promising approaches. The critical factor for such devices is the design and development of advanced electrode materials and electrolytes using cost-effective techniques. In previous research, various electroactive materials and electrolytes have been utilized to enhance the electrochemical performance of energy-generating and -storing devices. Current collectors are also important in determining the overall electrochemical performance of such devices, but current collectors are rarely explored in existing literature toward enhancing the electrochemical performance of devices. Typically, metal-based current collectors like stainless steel (SS), nickel foam, and plates of copper and titanium are used for electrochemical devices because they offer high electrical conductivity and ductility. Despite this advantage, the bulky and heavy nature of metallic current collectors limit their large-scale application. Moreover, the corrosion of metal-based current collectors in liquid electrolytes constrained the working lifetimes of metal-based electrochemical devices. From a practical perspective, high areal and volumetric electrochemical performances (like the areal capacitance) are very important. For metal-based current collectors, achieving the desired area- or volume-normalized electrochemical performance requires larger current collectors, thereby lowering the weight-normalized electrochemical performance in the final product.

Carbon-based current collectors such as carbon cloth (CC) and graphite paper have numerous advantages over metal-based current collectors, including ultra-low weights, 3D structures, and high porosities, and are thus suitable for developing high-energy and lightweight energy-generating and energy-storage devices. However, less attention has been given to the direct use of CC as an electrode material for various electrochemical devices because of its lower energy storing capacity, lower surface area, hydrophobic nature, and poor compatibility with electrolyte ions. To overcome this issue, different strategies have been developed, including the introduction of numerous structural defects and oxygen-containing groups on CC microfibers via oxidative treatments, as well as the incorporation of different heteroatoms by functionalization. Wang et al. reported the chemical and electrochemical exfoliation approach by using acidic solutions to enhance the capacitance of the CC. In their approach, the surface area of the CC was increased but large number of oxygen containing functional groups are incorporated in the CC. In general, the oxygen-containing groups provide unsatisfactory electrochemical results because they decrease the electrical conductivity of the entire electrode. Therefore, it is necessary to determine a simple yet effective strategy to improve the coupling interaction between electrolyte ions and carbon-based current collectors to upgrade this technology for advanced electrochemical devices.

To overcome the abovementioned issues, in the present work we have proposed a very simple, convenient, one-step nitrogen plasma process for commercial CC to induce fine nanostructuring over the carbon thread as well as nitrogen doping on the surface of CC. In testing of the nanostructured and nitrogen-doped CC (NCC) for energy storage applications, it shows excellent electrochemical features compared to those of the commercial CC. Moreover, the proposed strategies for activating carbon materials is more simple, effective, time/energy-saving, environmentally friendly and low-cost than the previous reports.

Experimental

Preparation of the nitrogen plasma-treated CC.—The NCC was prepared by using an Advanced Energy RFX-600 radio-frequency (RF)-plasma system with nitrogen plasma. Before the plasma treatment, commercial CC (2 cm²) was cleaned with acetone, ethanol, and water and then dried in an oven for 10 h at 60 °C. The cleaned CC was placed within the chamber of the RF-plasma system and the chamber was evacuated using rotary pumps to a vacuum of ~0.014 Torr. The chamber was then filled with nitrogen at a flow rate of 50 standard cubic centimeters per minute (sccm) by adjusting the base pressure to ~0.114 Torr. Finally, nitrogen plasma was formed inside the chamber by applying 400 W RF power for 10 min to convert the CC to NCC.

Electrochemical measurements.—Supercapacitive measurements were performed in a standard three-electrode system with 2 M KOH as an electrolyte, platinum as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and the NCC as a working electrode. Cyclic voltammetry (CV), galvanostatic charge–discharge measurements, and stability measurements were performed with an automatic battery cyler (WBCS3000). The electrochemical impedance was measured using an electrochemical workstation over the frequency range 100 mHz–100 kHz at a constant bias potential of 10 mV.

Characterizations.—The surface morphology of the prepared samples was characterized using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) and atomic force microscopy (AFM, Park system). X-ray diffraction analysis (XRD, X’Pert Pro...
using Cu Ka radiation), X-ray photoelectron spectroscopy (XPS, ESCALAB-MKII), and Raman spectroscopy (NRS-5100) were performed to confirm the structure and composition of the prepared material.

Results and Discussion

Structural and morphological study of the nitrogen plasma-treated CC.—The process to prepare the nitrogen plasma-treated CC is shown in Scheme 1. The commercial CC is composed of interlinked carbon microfibers having excellent electrical conductivity and the mechanical flexibility, which are very useful for electrochemical applications. Consequently, the poor compatibility of commercial CC with electroactive materials and electrolyte ions, constraining its use at the grid level. In our approach, we treated the commercial CC with high-power nitrogen plasma to simultaneously induce nanostructuring and nitrogen-doping of the CC microfibers to improve its compatibility with electroactive materials and electrolyte ions. Plasma is the fourth state of matter and contains negatively charged electrons, positively charged ions, neutral atoms, neutral molecules, or mixtures of these. The main purpose of the plasma process is to modify the chemical and physical properties of the CC. The high-power plasma process can enhance the surface energy of the carbon fibers to promote the wetting properties of the CC. Moreover, it can induce fine nanostructuring and nitrogen doping over the carbon fiber to improve the porosity and specific surface area (Scheme 1). The high-power nitrogen plasma may expand the graphite layers of the carbon microfibers, thus allowing the insertion of nitrogen into the graphite structure. In addition, some of the carbon atoms are replaced by nitrogen to form $\text{CN}_x$ bonds.

The morphological study of the untreated CC and NCC was performed by SEM and AFM observation. Figs. 1a, 1b shows the morphology and the microstructure of the untreated CC. As seen in the SEM image, the untreated CC is composed of numerous interlaced carbon fibers with very smooth surfaces. The AFM results confirm that the surface of the untreated CC microfiber is uniform and smooth (Fig. 1c). The high-power nitrogen plasma treatment induces nanostructuring by forming a very fine and uniform nanoparticle-like structure over the carbon microfiber, thus improving the electroactive surface area for electrochemical reactions, as seen in Figs. 1d, 1e. Further, AFM analysis was performed to confirm the effectiveness of the nitrogen plasma treatment on the CC. As seen in Fig. 1f, NCC shows a highly porous surface compared to that of the untreated CC. Energy-dispersive X-ray (EDX) spectroscopy mapping was performed for the NCC sample to confirm the uniform distribution of nitrogen on the surface. As seen in the EDX results (Figs. 1g–1i), nitrogen is observed throughout the NCC surface.

The efficiency of the nitrogen plasma process for electrochemical applications was further studied by measuring the wettability features of the untreated and plasma-treated CC. In general, high wettability of the current collector is necessary for electrochemical applications, as it enhances the coupling interaction of the current collector with the electrolyte ions and electroactive material. As seen in Figs. 1b, 1e, the water contact angle for the CC is drastically decreased from 130.07° to 0° after the nitrogen plasma process. The superhydrophilic nature of the NCC demonstrates the effectiveness of the nitrogen plasma process in improving the compatibility of CC with electrolyte ions.

Raman spectroscopy, XPS, and XRD were performed to study the functionalization and surface modification of the CC after nitrogen plasma processing. The Raman spectra for the untreated CC and plasma-treated CC are shown in Fig. 2a, showing the two major contributions of the D (~1350 cm$^{-1}$) and G (~1580 cm$^{-1}$) bands. Typically, the D-to-G peak intensity ratio corresponds to the disorder or defects present in carbon-based materials. In the present case, the D-to-G peak intensity ratio for the NCC is about 1.48, which is much higher than that of the untreated CC (0.91). The higher ratio and slight upward shifts in the frequencies of the D and G band for the NCC signify higher disorder are present over the carbon microfibers after nitrogen plasma process. From the perspective of electrochemical applications, higher disorder levels or defects in the material are favorable, as they enhance the number of electrochemically active sites for electrochemical reactions. The chemical composition and surface electronic state of the untreated CC and plasma-treated CC were further investigated by XPS measurements. Fig. 2b shows the broad-scan XPS spectra for NCC and untreated CC. As seen in the broad-scan spectrum, no nitrogen species are detected in the untreated CC. However, 5.52% nitrogen species appear in the NCC broad-scan spectrum after plasma treatment, confirming their presence on the NCC surface. Moreover, the narrow-scan XPS spectrum of the N 1s orbital

Scheme 1. Schematic of showing the preparation of NCC by the nitrogen plasma process.
Figure 1. The SEM images for the (a, b) commercial CC and (d, e) NCC. Inset of the SEM images showing the water contact for the commercial CC and NCC. The AFM images for the (c) commercial CC and (f) NCC. (g-i) EDX elemental mapping for the NCC electrode.

Figure 2. The (a) Raman and (b) broad scan XPS spectra for the commercial CC and NCC. The narrow scan XPS spectra for the (c) N1s, (d) C1s for the NCC sample, (e) the XRD patterns for the commercial CC and NCC sample.
Supercapacitive study for the nitrogen plasma-treated CC.—The electrochemical performance of a supercapacitor depends upon the different components, such as the current collector, active electrode material, and electrolyte. In existing research, most work has investigated on the active electrode material and electrolyte to enhance supercapacitive performance, and very few attempts have been investigated to functionalize of the current collector to improve the energy storage capacity of the supercapacitor. Commercial CC holds great promise as a current collector in supercapacitor devices because it offers high conductivity and excellent mechanical flexibility, but it has received little attention in direct utilization as an active electrode material only when carbon atoms are substituted by nitrogen. Moreover, the similar atomic size of carbon and nitrogen permits strong covalent bonding, which is useful for enhancing the electrochemical performance and charge-carrier density of the electrode. Ultimately, the XPS analysis confirms that nitrogen doping on the surface of CC after nitrogen plasma processing. Furthermore, nitrogen doping of carbon-based materials creates positive charge centers to accept electrons, thereby enhancing the resultant electrical conductivity of the CC. Following nitrogen plasma treatment, the C 1s spectrum can be deconvoluted into three contributions, which are due to the C–C sp² graphite-like carbon, carbon bound to nitrogen (C–N sp²), and carbon bound to oxygen (C–O). The XRD results for the untreated CC and NCC are presented in Fig. 2d, which shows a broad single peak at ∼26° specifying that both the samples are composed of amorphous carbon.

Figure 3. (a) the comparative CV curves for the commercial CC and NCC electrode in 2 M KOH electrolyte, (b) CV curves for the NCC electrode at different scan rates, (c) the charge-discharge curves for the NCC electrode at different current densities, (d) the plot of specific areal capacitance to the current density for NCC electrode, (e) the capacitance retention for the NCC electrode for 5000 cycles. Inset shows the initial and final charge-discharge cycles and (f) the Nyquist plot for commercial CC and NCC electrode.

contains the two major contributions from pyridinic N and graphitic N, as shown in Fig. 2c. Typically, graphitic nitrogen is observed in a material only when carbon atoms are substituted by nitrogen. Moreover, the similar atomic size of carbon and nitrogen permits strong covalent bonding, which is useful for enhancing the electrochemical performance and charge-carrier density of the electrode. Ultimately, the XPS analysis confirms that nitrogen doping on the surface of CC after nitrogen plasma processing. Furthermore, nitrogen doping of carbon-based materials creates positive charge centers to accept electrons, thereby enhancing the resultant electrical conductivity of the CC. Following nitrogen plasma treatment, the C 1s spectrum can be deconvoluted into three contributions, which are due to the C–C sp² graphite-like carbon, carbon bound to nitrogen (C–N sp²), and carbon bound to oxygen (C–O). The XRD results for the untreated CC and NCC are presented in Fig. 2d, which shows a broad single peak at ∼26° specifying that both the samples are composed of amorphous carbon.

The obtained NCC using a three-electrode system in a 2 M KOH electrolyte. Fig. 3a shows the comparative CV curves for the untreated CC and NCC within the potential window of 0 to 0.5 V vs. SCE at identical scan rates of 60 mV/s. The CV curve for NCC shows box-like characteristics and high current capability compared to the untreated CC. Moreover, we observed the well-defined redox peak in anodic and cathodic site which is due to interaction between the electrolyte ions and the N species of the CC. The pseudo-capacitance can be generated from the nitrogen rich species which is beneficial for the enhancing the energy storing capacity of the electrode. Further, the NCC electrode maintains this CV profile at both lower and higher scanning rates (Fig. 3b), indicating better rate capability. The CV curve for NCC shows higher areal capacitance of 741 mF/cm² at the lower current density of 0.5 mA/cm², which is much higher than that of the untreated CC. Moreover, NCC shows better rate capability, maintaining 322 mF/cm² of the initial capacitance at the higher current density of 2 mA/cm². From a practical viewpoint, long-term electrochemical stability is necessary for active electrode materials. Here, to measure the cycling stability for the NCC electrode by using the charge–discharge curves, as plotted in Fig. 3d. Significantly, the NCC electrode shows very high areal capacitance of 741 mF/cm² at the lower current density of 0.5 mA/cm², which is much higher than that of the untreated CC. Moreover, NCC shows better rate capability, maintaining 322 mF/cm² of the initial capacitance at the higher current density of 2 mA/cm². From a practical viewpoint, long-term electrochemical stability is necessary for active electrode materials. Here, to measure the cycling stability for the NCC electrode, charge–discharge measurements are performed for 5000 cycles. The NCC electrode shows excellent cycling stability over 5000 charge–discharge cycles without losing its initial capacitance, indicating the capability of the plasma process to functionalize commercial CC (Fig. 3e). The observed cycling stability and the capacitance are much larger than those of previously reported metal oxide-based electrodes. For instance, Wang et al. reported the areal capacitance of 88 mF/cm².
for oxidized CC. Xiong et al. achieved the areal capacitance of 71 mF/cm² with cycling stability over 5000 cycles for a porous reduced graphene oxide electrode.

EIS measurements were performed to gain insight regarding the charge transfer kinetics; the obtained results are plotted in Fig. 3f. As seen in the Nyquist plot, the NCC electrode shows much smaller charge transfer and equivalent series resistances than the CC electrode, representing the improved capabilities of the NCC for supercapacitor applications. Moreover, in the lower-frequency region, the Nyquist plot of the NCC is more tilted toward the Y-axis than that of the CC electrode, indicating a faster charge-transfer process in the NCC electrode. The magnified view of the Nyquist plot is shown in the inset of Fig. 3f. Further, the charge transfer resistance ($R_{ct}$) is calculated by considering the diameter of semicircle. The obtained $R_{ct}$ for the CC and NCC are 17.57 and 10.65 $\Omega$cm², respectively. On the same time, the equivalent series resistance ($R_s$) is estimated by considering the first intercept of the Nyquist plot to the X-axis. The lower value of $R_s$ is observed for the NCC (9.98 $\Omega$cm²) than the CC (14 $\Omega$cm²). The lower values of $R_s$ and $R_{ct}$ for the NCC electrode representing the improved electrochemical interaction in between the electrolyte ions and NCC electrode. The improved electrochemical features of the NCC electrode are attributed to the following reasons: 1) the superhydrophilic nature of the NCC electrode drastically enhances the coupling interaction between the active electrode and electrolyte to facilitate faster and easier electrochemical reactions, 2) the high-power plasma treatment forms fine nanostructuring over the CC, thus providing more active sites for electrochemical reactions, 3) nanopores formed by nanostructuring act as diffusion pathways for electrolyte ions to perform facile electrochemical reactions, 4) additional pseudocapacitance arises from the reversible redox reactions of the nitrogen-containing functional groups on the carbon microfibers, and 5) the nitrogen doping on the surface of the carbon microfibers can improve charge mobility of the electrode.

Conclusions

In summary, a simple strategy was developed for enhancing the electrochemical features of commercial CC for energy storage applications. We have established a simple yet effective nitrogen plasma process for commercial CC that improves its compatibility with electrolyte ions and drastically amplifies its electrochemical features. The NCC generated by the nitrogen plasma process exhibits superhydrophilicity and hierarchical nanostructuring, providing more abundant electroactive sites for electrochemical reactions. Moreover, the nitrogen doping of the backbones in the CC allows more electroactive species for facile electrochemical reactions. With these integrated merits, the NCC shows excellent supercapacitive features with a capacitance of 741 mF/cm² and excellent cycling stability over 5000 charge-discharge cycles without losing its initial capacitance. We believe that this plasma processing method provides a new route by which to develop efficient carbon-based electrodes for energy storage applications.

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