High Performance Asymmetric Supercapacitors Based on Dual Phosphorus (P) and Nitrogen (N) co-Doped Carbon and Graphene-Polyaniline Electrodes

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We report an asymmetric type hybrid supercapacitor device with ultrahigh-energy density by employing a dual phosphorus and nitrogen co-doped carbon (PNDC) and a graphene (G)–polyaniline (PANI) nanocomposite electroactive electrodes. Dual-doped carbon is synthesized by the microwave assisted technique and G-PANI was synthesized by the chemical oxidative polymerization technique. An asymmetric PNDC/G-PANI electrodes with ionic liquids (IL) as electrolytes in supercapacitor are found capable of increasing the operating voltage up to 4 V and electrodes with aqueous electrolytes in supercapacitor are capable of increasing the operating voltage up to 2 V. The size-uniform porous nanostructures of PNDC and G-PANI provide a continuous electron pathways and facilitate short ionic transportation process. Further, IL increases the wettability of the electrodes and exhibited ultra-high energy density of 114 Wh/kg and 13.7 kW/kg power density at a 2 A/g current density. Therefore, the asymmetric type hybrid supercapacitor based on G-PANI nanocomposite and microwave assisted PNDC electrodes is a cost effective ultra-high energy density supercapacitor with high rate capability.

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An energy storage device called “Supercapacitors” or electrochemical capacitors (ECs) attracted extensive attention because of their outstanding properties over other energy storage devices, such as, fuel cells, batteries, and dielectric capacitors. ECs can provide instantaneous higher power density than batteries and higher energy density than dielectric capacitors, and therefore under consideration for applications in transportation, hybrid vehicles, modern electronics, and grid-connected power plants.1–4 Even though, high power uptake can be achieved by ECs, the energy densities are significantly lower than rechargeable battery systems, which limit their applications as a main power source.5 Advanced supercapacitors must be developed with higher operating voltage and higher energy density (>100 Wh/kg) without sacrificing power delivery and cycle life for future practical applications.6 A method of improving energy density is to design asymmetric supercapacitors by combining electrodes of the double layer capacitance with redox capacitance, which can make use of the different voltage windows of two electrodes.6–9 For such type of supercapacitors, one electrode stores charge through a reversible nonfaradaic process of ion movement on the surface of an activated carbon, carbon nanotubes (CNTs) or graphene,10–12 and other electrode is to utilize a reversible faradaic reaction of electroactive material, such as metal oxides (MnO2 and RuO2) and conducting polymers (CPs); (a) polyaniline (PANI), (b) polypyrrole (PPy) and (b) poly(3-4-ethylenedioxythiophene) (PEDOT).13,14 Maximizing the specific capacitance(C) and cell voltage (V) are the key purposes of fabricating excellent supercapacitors to improve their energy densities by employing high-reactivity electrode materials and proper electrolytes. Several asymmetric type supercapacitors with increased energy density have been reported in literature, for example, RuO2-TiO2/activated carbon (12.07 kW/kg of power density and 5.7 Wh/kg energy density at current density of 120 mA/cm2 with operating voltage of 0–1.4 V in KOH electrolyte),41 MnO2/activated carbon (10.1 kW/kg power density and 18.2 Wh/kg energy density at discharge current of 10 mA with operating voltage of 2 V in Na2SO4,14 and MnO2/PEDOT (13.5 Wh/kg energy density at current density of 250 mA/g with operating voltage of 1.8 V in H2SO4 electrolytes).

Recently, graphene have attracted much attention for potential applications in energy storage devices due to its excellent properties, such as, large specific surface area, excellent electrical/thermal conductivities and good mechanical properties. Graphene has been studied for supercapacitor application and a capacitance in the rage of 70–180 F/g15–21 has been observed. Also, graphene (G)-based supercapacitor with high energy density of 85.6 Wh/kg at current density of 1 A/g comparable to that of the Ni metal hydride battery has been reported using ionic liquids (IL); 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4), with an increased voltage up to 4 V.18 Graphene and metal oxide based asymmetric type hybrid supercapacitors have been studied and the maximum energy density of 50.8 Wh kg−1 has been calculated in Na2SO4,48 Nitrogen doped activated carbon, CNTs and graphene have been used as electrodes for supercapacitors in enhancing the capacitance and surface wettability.22,23,24 However, to date, asymmetric supercapacitors have been designed mainly to increase the operating voltage and most of the reported material synthesis methods are extensive and limited to laboratory scale design and fabrication.

Herein we report an asymmetric supercapacitor device to increase both capacitance and operating voltage by using microwave-assisted phosphorous and nitrogen co-doped carbon (PNDC) and Graphene-Polyaniline (G-PANI) as negative and positive electrodes in BMIMPF6– ionic liquid (IL) based electrolytes. Recently, we have reported synthesis and characterization of microwave-assisted phosphorous and nitrogen co-doped carbon (PNDC) with a BET surface area of 1000 m2/g25 for potential application in energy storage devices, such as, fuel cells and supercapacitors. Furthermore, the synthesis and application of G-PANI nanocomposites for symmetric supercapacitors was investigated and a high specific capacitance of 500 F/g was reported. The physical and chemical analysis of PNDC and G-PANI have been carried out extensively by different material
characterization techniques, such as X-ray photoelectron spectrometer (XPS), Raman spectrometer, UV-Visible spectrometer, Furrier Transform Infra-Red spectrometer (FTIR), and Brunauer–Emmett–Teller (BET) surface area.

Asymmetrical supercapacitors were fabricated with PNDC and G-PANI and evaluated in different electrolytes, such as IL aqueous and organic electrolytes to study the electrochemical behavior of asymmetric supercapacitor.

Experimental

Material synthesis.—Synthesis of G-PANI nanocomposite.—

Graphene-polyaniline was synthesized by chemical oxidative polymerization method. Nanocomposite of graphene and polyaniline was prepared by in-situ polymerization of aniline in a suspension of graphene in acidic solution. The weight ratio of aniline to graphene was kept as 1:1 during the synthesis. The purified 0.8 M aniline was dissolved in 200 ml of 1 M HCl and stirred for 30 minutes. Graphene was dispersed in the resulting solution by sonication for 1 hour. A 0.2 M ammonium peroxydisulfate (APS) in 1 M HCl was rapidly poured into the mixture of aniline and graphene while maintaining vigorous stirring at room temperature. Polymerization of aniline was identified by the change of reaction mixture color into green. The mixture was allowed to stir at 4–5 °C temperature for 24 hours. The precipitate was washed repeatedly with deionized water and methanol. The composite was vacuum dried at 100 °C for several hours to remove the water.

Synthesis of P- and N- co-doped carbon.—In this study, nitrogen and phosphorous co-doped carbon was prepared by microwave-assisted method reported recently by the authors of this manuscript. The synthesis method was carried out in three steps; Step 1: 7.56 g of melamine was dissolved in 275 ml of hot distilled water followed by the addition of 17.28 g of unmodified tannin and stirred for several minutes. Step 2: 2.85 g of hexamine was dissolved in 10 ml of distilled water and added to the above solution mentioned in step 1 while stirring continuously. Then the resultant solution was heated to obtain a brown color polymer and the mixture was transferred to an evaporating dish and heated at 70 °C to 80 °C for 12 hours to remove the moisture. Step 3: The water removed brown color resultant polymer mixture was mixed with phosphoric acid and the mixture was microwaved at 1.25 kW and 2.4 GHz for 30 minutes to obtain the PNDC powder.

Preparation of electrode materials.—The anode electrode was made of PNDC, mixed with 15 wt% Nafion binder and the cathode electrode was made G-PANI mixed with 15% Nafion binder. The active electrode materials were spin coated on 9 mm diameter size copper foil. The mass of each electrode was 6.6 mg. Coin-size capacitor cells were assembled. A unit cell supercapacitor comprising of two electrodes, PNDC and G-PANI, were electrically isolated from each other by a porous filter paper membrane. The ionic liquid electrolyte was 1-ethyl-3-methylimidazolium hexafluoroborate (1 M BMIM-PF$_6$). Also, 2 M H$_2$SO$_4$ and 0.2 M LiClO$_4$ electrolytes were used to investigate the electrochemical properties of asymmetric supercapacitors.

Electrochemical experiments.—Electrochemical properties were investigated on PNDC/G-PANI asymmetric capacitor cells by employing the electrochemical measurement techniques, such as cyclic voltammetry (CV), galvanostatic charging-discharging and electrochemical impedance spectroscopy (EIS). The CV was recorded at different scan rates, such as, 100, 50, 25, 10 and 5 mV/s. EIS measurements were employed for frequencies between 100 kHz to 100 mHz frequencies. Supercapacitor cells were evaluated in both symmetric (PNDC/PNDC and G-PANI/G-PANI) and asymmetric (PNDC/G-PANI) arrangements in electrolytes of IL, 2 M H$_2$SO$_4$ or 0.2 M LiClO$_4$. Specific capacitances were calculated from both CV and charging-discharging curves according to the equation, $C = \frac{I}{V} \times \Delta t$, where I is the current, V is the voltage scan rate, $\Delta t$ is the discharging time.

Results and Discussion

The scanning electron microscope (SEM), Transmission electron microscope and X-ray photoelectron spectrometer (XPS) techniques were used to study the surface morphology and structure of nanocomposite G-PANI and PNDC materials. Figure 1 shows the SEM (a-d) and TEM (e and f) images of PNDC electrode and G-PANI nanocomposites electrode. Spherical structures of PNDC with diameter of spheres between 600 nm to 1 µm are clearly seen in SEM images of the Figures 1a and 1b. Graphene agglomeration into the fibrous structure of conducting PANI with fiber diameters between 20 nm to 100 nm diameters are also shown in Figures 1c and 1d. TEM study revealed that PANI has nanowire-like structure and the agglomeration of graphene to form a conductive network in the nanocomposite G-PANI. XPS study on PNDC was carried out and the detailed research on the synthesis and characterization was reported elsewhere.

Figure 2 illustrate the nitrogen adsorption-desorption isotherms and pore size distribution of PNDC. The nitrogen adsorption isotherms were found to be Type II according to IUPAC classification, and PNDC has a primarily mesoporous structure. The average pore size and total pore volume of the PNDC were found to be 2 nm and 0.5 cm$^3$/g, respectively. The BET surface area of the material was estimated to be 974 m$^2$/g. Further, the BET surface area of G-PANI was found to be about 35 m$^2$/g. Electrochemical behavior of both PNDC and G-PANI was measured in electrochemical cell of three-electrode configuration G-PANI or PNDC coated glassy carbon electrode as working electrode, Pt as counter electrode and Ag/AgCl as reference electrode in
aqueous electrolyte 2 M H₂SO₄. Figure 3 shows the recorded CVs for two electrochemical systems and observed a working potentials range of −200 mV to 1750 mV for G-PANI and −2000 mV to 200 mV for PNDC electrodes. The oxidation and reduction peaks due to faradaic reaction of PANI is clearly observed from Figure 3b. Specific capacitances have been reported as 425 F/g and 275 F/g for G-PANI and PNDC symmetric supercapacitor cells, at 5 mV/s scan rate.

In order to make progress toward the application of G-CPs in supercapacitor technologies, an attempt was made to improve the materials quality and their electrochemical properties by employing co-doped carbon structures. Figure 4 shows the CV curves of G-PANI/PNDC supercapacitor cell in ionic liquid electrolyte with the potential window of −2 V to ~2 V. In particular, when PNDC are used, the supercapacitors demonstrated resilience high-voltage of ~4 V unlike G-PANI symmetric supercapacitors in IL reported in our previous studies. This approach can also be considered as an approach for overcoming the stability issues of G-PANI symmetric type supercapacitors. Further, relatively rectangular shapes of the curves at low scan rates, 10 and 5 mV/s, indicate prominent ideal capacitive behavior of asymmetric supercapacitor cells.

Figure 5a shows typical discharge characteristic of the PNDC/G-PANI supercapacitor at different discharge current with an operating voltage of about 4 V. The discharge curves are somewhat deviated from linearity due to pseudocapacitive effect. The calculated energy density for the corresponding discharge experiments are shown in Figure 5b. The energy density calculated for PNDC/G-PANI supercapacitors is 114 Wh/kg at the current density of 2 A/g with energy density of 13.7 kW/h/kg in IL electrolyte, which are much higher values than those reported for asymmetric type supercapacitors. However, the calculated high energy density is due to the excellent electroactivity of PNDC, the high capacitance G-PANI electrode as well as wide operating potential ability of IL. PNDC electrode and graphene filler in G-PANI nanocomposite contribute to the performance of the capacitor by increasing the conductivity, rate capability and stability in IL electrolyte. In comparison with literature, an increased voltage of 4 V symmetric supercapacitors using curved graphene-based supercapacitor has been reported in with energy density of 85.6 Wh/kg at 1 A/g in IL electrolyte; 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄).  

The chemical reactions when charging the asymmetric G-PANI/PNDC supercapacitor cell at anode and cathode are represented in a schematic shown in Figure 6. The schematic figure clearly shows the double layer formation and electrochemical reactions. The changes in chemical structures are based on hypothetical structures derived from the previous studied on G-PANI and PNDC.

The capacitive properties of PNDC/G-PANI supercapacitors in different electrolytes, such as 2 M H₂SO₄ and 0.2 M LiClO₄ were studied. Figure 7 indicates the CV measured at different scan rate and the specific capacitance was calculated. As shown in Figure 7, the highest capacitance (340 F/g) value was calculated for PNDC/G-PANI supercapacitor in 2 M H₂SO₄ electrolytes. The oxidation and reduction peaks are not prominent for two electrodes asymmetric cells due to higher film thickness unlike the CV recorded for G-PANI three electrode cells. The operating voltage was increased up to 2 V with the novel asymmetric electrode design, compared with the 1.2 V G-PANI symmetric type supercapacitors in aqueous electrolyte. The stable increased voltage can be attributed to the PNDC cathode electrode. The G-PANI and pyridinic-Ni in PNDC play main roles for improving pseudo-capacitance by the redox reaction. Therefore, the energy density was increased by PNDC/G-PANI supercapacitors by increasing the operating voltage as well as by increasing the capacitance.

The magnitude of equivalent series resistances (ESR) which can be derived from equivalent distribution resistance (EDR) due to porous nature of the electrodes surfaces, are obtained from the x-intercept of the Nyquist plot in Figure 8. The ESRs values are 3.4, 6.3 and 21.5 ohms for aqueous H₂SO₄, IL and LiClO₄ electrolytes based PNDC/G-PANI supercapacitors. A high rate capability is observed for aqueous based PNDC/G-PANI supercapacitor due to the low ESR values (3.4 ohm). The impedance curve for organic electrolyte (0.2 M LiClO₄) exhibits a semicircle over the high frequency range, due to high charge transfer resistance.

Figure 2. (a) Nitrogen sorption linear isotherm and (b) pore size distribution of PNDC compound.

Figure 3. CV curves of (a) PNDC and (b) G-PANI electrodes in three-electrode system.

Figure 4. (a) CV curves of PNDC/G-PANI asymmetric supercapacitor in IL electrolyte at different scan rate, (b) charging and discharging curve of PNDC/G-PANI asymmetric supercapacitor in IL at current density of 2 A/g.

Figure 5. (a) Galvanostatic discharge curve of a PNDC/G-PANI asymmetric type supercapacitor at a constant current density of 2, 10 and 20 A/g, using IL electrolyte, and (b) relationship between the energy density and current density of PNDC/G-PANI supercapacitor in IL electrolyte.

Figure 6. The schematic figure clearly shows the double layer formation and electrochemical reactions. The changes in chemical structures are based on hypothetical structures derived from the previous studied on G-PANI and PNDC.
Conclusions

PNDC synthesized by a microwave assisted technique and the G-PANI synthesized by oxidative polymerization technique were used in the construction of asymmetric supercapacitors. PNDC/G-PANI asymmetric type hybrid supercapacitors were studied in different electrolytes and found improved operating voltage in IL (4 V) and aqueous electrolytes (2 V). The highest capacitance of 340 F/g was calculated in aqueous based 2 M H₂SO₄ electrolytes, whereas 194 F/g specific capacitance was calculated in IL electrolytes. High conductivity as well as high surface area with mesoporous structure of PNDC make asymmetric supercapacitor high rate capable in delivering power with high power density of 13.7 kW/kg at 2 A/g. Further, an ultra-high energy density of 114 Wh/kg was observed due to the N-doped nature of PNDC and the electro-activity of G-PANI electrodes in increasing...
capacitance and operating voltage of PNDG/G-PANI supercapacitor. Therefore, PNDG/G-PANI asymmetric supercapacitors reveal a new research direction to high performance cost effective next generation energy storage devices. We are conducting experiment to find the cycle stability of the asymmetric configuration and also fabricating the solid supercapacitor based on the flexible electrodes practical applications.

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