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Chemically Reduced Graphene Oxide as Electrodes for

Energy Storage Applications

By

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Abstract:

Supercapacitors have attracted increasing attention due to their widespread applications, such as hybrid electric vehicles, power tools, portable electronic equipment and other devices. Using larger surface area of graphene electrodes and thinner dielectrics to achieve larger capacitances is a new trend for increasing capacitance of supercapacitors. This allows for energy densities greater than those of conventional capacitors and power densities greater than those of batteries.. In this paper, graphene oxide was synthesized by improved Hummers method. polyaniline PANI/grapheneoxide (GO) nanocomposite electrode materials were prepared from aniline (ANI), GO and ammoniumpersulfate (APS) by insitu chemical polymerization in ice bath. GO in composite was reduced for 5h and 20h. The crystal structure and the surface topography of all materials were characterized by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The electrochemical properties were evaluated by cyclic voltammetry (CV), charge-discharge measurements, electrical impedance spectroscopy (EIS) and a four-point probe, respectively. The results show that with increasing reduction time, the oxygen content on the surface of GO was decreased, leading to increased ID/IG ratio in the Raman spectra of GO and increased conductivity of composite. Consequently, the capacitance properties of RGO/PANI composites could be significantly improved by the reduction of GO for 20h. The GO /PANI composite reduced for 20h had a specific capacitance as high as 1405.68 F/g at scan rate of 1 mV/s compared with 291.73 F/g for pristine graphene film.

<u>Keywords:</u>

Graphene oxide, Graphene; Polyaniline, Hybrid supercapacitor and Composite.

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1.Introduction:

Supercapacitors represent an attractive alternative for portable electronics and automotive applications due to their high specific power and extended life. In fact, the growing demand of portable systems and hybrid electric vehicles, memory protection in CMOS, logic circuit, VCRs, CD players, PCs, UPS in security alarm systems, remote sensing, smoke detectors, etc. require high power in short-term pulses[1, 2]. So, in the last 20 years, electrochemical capacitors have been required for the development of large and small devices driven by electrical power [3].

Hybrid capacitors attempt to exploit the relative advantages and mitigate the relative disadvantages of EDLCs and pseudocapacitors to realize better performance characteristics. Utilizing both Faradaic and non-Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without the sacrifices in cycling stability and affordability that have limited the success of pseudocapacitors. Such limitations may be overcome by combining PANI with carbon materials [4-6], because the combination improves the electrochemical performances of PANI, such as conductivity, specific capacitance, and cyclic stability.

In this work, GO/aniline composite was synthesized by an in situ polymerization. Sodium hydroxide is used for reduction of graphene oxide for different time. Supercapacitor electrochemical performance was assessed using cyclic voltammetry (CV), electrical impedance spectroscopy (EIS), and galvanostatic charge/discharge measurements.

2.EXPERIMENTAL WORK

2.1.Materials

Graphite powder was purchased from Fischer Scientific. Sulphuric acid (98 wt.%), nitric acid (70 wt.%), potassium permanganate and sodium nitrite were purchased from Sigma-Aldrich Ltd. Barium chloride (99%) was purchased from ALEC. Potassium hydroxide, silver chloride, sodium hydroxide and hydrogen peroxide (30 wt.%) were obtained from local chemical companies. Aniline (99%) was purchased from CDH. Ammonium persulphate (98.5%) was purchased from WINLAB. Hydrochloric acid (37%) and camphor sulfonic acid were obtained from Mereck.

2.2.Reduced GO/PANI Composite Preparation

Graphene oxide was prepared by modified Hummers method [7-10]. Graphene/polyaniline composite was prepared. Weight of 0.4 mg mL^{-1} GO (20% weight) in 180 mL distilled water was ultrasonicated for 1 h to obtain a yellow brown

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suspension. Aniline of 1.6 mg (0.1171 M) was slowly added into the suspension and a stable GO/aniline suspension was obtained after stirring violently. A mixture of concentrated hydrochloric acid, ammonium persulphate (APS) in 20 mL distilled water was then slowly added to the suspension with stirring. The molar ratio of aniline, hydrochloric acid and APS was 1:1:1. The reaction was conducted by the insitu polymerization method in ice bath for 1 h and the yellow-brown suspension gradually changed to deep green color. The prepared composite was filtered, rinsed with distilled water. Then, the GO was reduced and the PANI was dedoped by 14.4 mL 8 M sodium hydroxide at 95 °C for 5 h and 20h. In the basic medium, the color was changed from deep green to dark purple. The composite was filtered and rinsed with distilled water until the filtrate became neutral. Thirdly, the product was mixed with campher sulfonic acid (ratio 1:3) and stirred for 24 h for PANI redoping. The graphene/PANI composite of different reduction time of GO are shown in Table 1 with their abbreviated name.

No	Reduction time (hours)	Graphene/PANI composite undoped (After GO reduction)	Graphene/PAN I composite (doped with CSA)
1	5	GP5	GPD5
2	20	GP20	GPD20

Table (1): Graphene/PANI composites

2.3. Fabrication of the Introduced Supercapacitor

Graphene/PANI composites were deposited on the Stainless steel 304 current collector The separator was a filter paper soaked in aqueous potassium hydroxide (6 M). Supercapacitor was assembled by stacking two fabricated electrodes with a separator. The fabricated supercapacitor was sealed by laminating it with plastic foil and fixing the layers together by two clamps. Figure (1) shows the structure of supercapacitor.



Figure (1): Fabricated supercapacitor structure

2.4. Electrochemical Measurements

The electrochemical performance was analyzed for supercapacitor electrodes in a two-electrode system by CV and EIS using Potentiostat Gamry G750 instrument and the galvanostatic charge-discharge characteristic performance was carried out with a Gamry 3000. The CV response of the electrodes was measured at different scan rates varying from 1 mV/s to 100 mV/s. EIS measurements were carried out without dc bias with sinusoidal signal of 5 mA over the frequency range from 0.05 Hz to 1MHz. A four-point probe was used for measuring the sheet resistance by passing a current through the two outer probes and measuring the voltage through the inner probes.

3.RESULTS AND DISCUSSION

The FTIR spectra of GO, PANI and the chemically synthesized GP1 and GP2 are shown in Figure (2). PANI shows vibration bands at 3417, 2372, 1588, 1495, 1322, 1164 and 848 cm⁻¹. The peaks at 3418 and 2372 cm⁻¹ are attributed to NH_2^+ and N-Hstretching modes, The peaks at 1588 and 1495 cm $^{-1}$ are attributed to C=N and C=C stretching modes for the quinoid and benzenoid rings. The peak at about 1322 cm⁻¹ is attributed to C-N stretching mode for benzenoid ring. The vibration band at 1164 cm⁻¹ is due to presence of C-N double bond. The vibration band at 848 cm⁻¹ is attributed to C-H vibration [11, 12]. For the spectrum of GO, vibration bands at 3418, 1722, 1625, 1444, 1385 and 1120 cm⁻¹. The 3417 cm⁻¹ vibration band has been attributed to the vibrations of the O-H from the -COOH groups and/or the residual water. The band at 1722 cm⁻¹ was assigned to C=O vibration, and the vibration bands at 1625 was assigned to the vibration C=C. The vibration bands at 1444, 1385 and 1120 cm^{-1} were assigned to C-O in carboxyl (C-OH), epoxy and alkoxy groups respectively [19]. For graphene vibration bands at 3432, 1570, 1455 and 1120 cm⁻¹ [12]. A strong band located at 3432 cm⁻¹ to the stretching O-H vibration. The disappearance of C=O vibration (1722) shows the removal of -COOH groups by reduction. The band located at 1570 cm⁻¹ can be attributed to C=C vibration of graphene, confirming the recovery of the sp² hybrid carbon skeleton. For graphene, the vibrations of epoxy (C-O) and alkoxy (C-O) are disappeared. The residual C-OH (vibrational band at 1455 and 1120 cm⁻¹) groups may serve as a passage for the ions to the internal surface in the charge/discharge process and contributed to the wettability of the electrode [12,13]. With the increase of reduction time, the vibration at 1722 of C=O was weakened, tending to be finally disappeared. The FTIR spectra of GP5 and GP20 showed all characterization peaks as pure PANI, however the bands are shifted to 3417, 2371, 1620, 1503, 1382, 1160 and 834 cm⁻¹, respectively for GP5. In addition, the bands are shifted to 3470, 2373, 1638, 1460,1386, 1273, 1081 and 876 cm⁻¹, respectively for GP20. This shift arises from $\pi - \pi$ interaction between graphene and PANI chains. We can expect that this $\pi - \pi$ conjugated interaction allows faradic

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charges to be effectively transported from the PANI to and through the graphene [12,13].



Figure (2): FTIR spectra of PANI, GO, graphene, GP5 and GP20

Figure (3) shows the XRD patterns of undoped PANI, GO, graphene, GP1 and GP2 composite. For the PANI pattern, three characteristic peaks appear at 10.4°, 22.2° and 32.28° corresponding to (0 11), (0 20) and (200) amine salt crystals, respectively [14-16]. The amorphous nature of the sample is confirmed by the XRD spectrum, which shows a broad band at 22° and low intense peaks related to a poorly crystallized PANI. A sharp peak in GO pattern appears at 10.5° , which corresponds to a (0.01) plane of GO, with an interlayer spacing of 0.84 nm. The presence of oxygen containing groups (such as hydroxyl, epoxy and carboxyl) results in GO sheets more loosely stacked, and is attributed to the increase of the interlayer spacing. The graphene pattern shows peaks at 32.46°, 33.66° and 38.03°, respectively. The peak at 32.46° corresponds to single or a few layers of graphene sheet with the formation of a new lattice structure. Peaks at 33.66° and 38.03° indicate that the van der Waals force causes aggregate or stacking of the graphene due to oxygen removal with lower hydrophilicity. XRD pattern of GP5 composite show peaks at 22.4°, 23.84°, 24.7°, 30.88° and 39.84°. The XRD pattern of GP20 composite show peaks at 21.52°, 23.36°, 32.62°, 34.08° and 37.12°. The existing peaks around 32°, 34° and 37° are due to the presence of graphene in the composite,

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which indicate that the graphene has a strong interaction with the benzene ring of PANI and peak at 29° is due to PANI [11, 17]. GP20 composite shows high intensity graphene peaks while GP5 composite shows low intensity graphene peaks due to low reduction time.



Figure (3): XRD spectra of undoped PANI, GO, graphene, GP5 and GP20

Figure (4) shows the sheet resistance curves of GPD5 and GPD20 composites which deposited on a glass substrate. A four-point probe was used by passing a current through the two outer probes and measuring the voltage through the inner probes. From this figure, it is seen that For GPD5 composite when current increased the sheet resistance rapidly decreased from 511.89 at 1mA to 161.27 at 5mA. For GPD20 composite when current increased the sheet resistance slowly decreased from 36.24 at 1mA to 20.11 at 5mA. It can be clearly observed that GPD5 composite has higher values of sheet resistances compared to GPD20 composite. So with increasing reduction time of GO in the composite the sheet resistance decreased and conductivity increased.



Figure (4): Sheet resistance curves of GPD5 and GPD20 composites

Figure (5) shows the CV of graphene/PANI supercapacitor of GPD20 composite using two probes connection at differe scan rates with scanning potential window is from - 0.8 to 0.8V. The CV curve area is gradually enlarged with the increase of the scan rate. At low scan rate, there is sufficient time for electrolyte ions migration to the inner part of the electrode [12]. Oxidation and reduction peaks are appeared due to pseudocapacitance of PANI. The calculated specific capacitance was 1405.68 F/g at scan rate of 1 mV/s and weight of active material was 4.9 mg.



Figure (5): The CV curves of supercapacitor of GPD20 composite at different scan rates

Figure (6) shows Nyquist plot of GPD20. It shows a semicircle in the high frequency region. The semicircle corresponds to charge transfer resistance (Rct). The intersection of the curve at the x-axis represents the internal or equivalent series resistance (ESR). ESR is the sum of the electrolyte resistance, the intrinsic resistance of the active electrode material and the contact resistance at the interface of the active material and the current collector. The value of charge transfer resistance. From this Figure it is seen that the charge transfer resistance

(R_{ct}) was 39 Ω and the equivalent series resistance (ESR) was 2.9 Ω . Also, the maximum of $Z_{imag}(max)$ was 21.3 Ω .



Figure (6): The Nyquist plot of GP20 supercapacitor

Figure (7) shows the galvanostatic of GP20 supercapacitor at constant specific current of 1 A/g and 7 A/g. It exhibits semi triangular shape charge-discharge curves due to synergetic effect between graphene and PANI in the composite. The deviation from linearity is typically due to of pseudocapacitive contribution, which demonstrated that the capacitances of PANI mainly originate from pseudocapacitance plus electric double layer capacitance of graphene. The total charge-discharge time for GP20 supercapacitor is about 400s at 7 A/g and 2732s at 1 A/g.



Figure (7): Charge-discharge curves of GP20 supercapacitor at constant current of 1 A/g and 7A/g

4.CONCLUSIONS

Supercapacitors with graphene/PANI composite electrodes and filter paper separator were fabricated. GPD20 composite produced a specific capacitance of 1405.68 F/g at scan rate of 1 mV/s. The results show that with increasing reduction time, the oxygen content on the surface of GO was decreased, leading to increased ID/IG ratio in the Raman spectra of GO and increased conductivity of composite. With increasing reduction time of GO in the composite the sheet resistance decreased and conductivity increased. Consequently, the capacitance properties of GO/PANI composites were significantly improved by increasing reduction time from 5 h to 20 h.

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