A 1 V supercapacitor device with nanostructured graphene oxide/polyaniline composite materials

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Abstract. Polyaniline and graphene oxide composite on activated carbon cum reduced graphene oxide-supported supercapacitor electrodes are fabricated and electrochemically characterized in a three-electrode cell assembly. Attractive supercapacitor performance, namely high-power capability and cycling stability for graphene oxide/polyaniline composite, is observed owing to the layered and porous-polymeric-structured electrodes. Based on the materials characterization data in a three-electrode cell assembly, 1 V supercapacitor devices are developed and performance tested. A comparative study has also been conducted for polyaniline and graphene oxide/polyaniline composite-based 1 V supercapacitors for comprehending the synergic effect of graphene oxide and polyaniline. Graphene oxide/polyaniline composite-based capacitor that exhibits about 100 F g^{-1} specific capacitance with faradaic efficiency in excess of 90% has its energy and power density values of 14 Wh kg^{-1} and 72 kW kg^{-1} , respectively. Cycle-life data for over 1000 cycles reflect 10% capacitance degradation for graphene oxide/polyaniline composite supercapacitor.

Keywords. Supercapacitor; pseudocapacitance; polyaniline; graphene oxide; cycling stability.

1. Introduction

Carbon-based supercapacitors,^{1–3} both with aqueous and non-aqueous electrolytes, have dominated the R&D activity on electrochemical capacitors during the last few decades. Ironically, however, low energy density of such supercapacitors has been the limiting factor for wider exploitation. To overcome the aforesaid limitation, researchers are introducing fast surface faradaic charging with the electrical-double-layer capacitors. In the arena of pseudocapacitors,^{3,4} transition metal oxides and ceratin nitrides have looked attractive due to their long cycling stability. On the other hand, in recent years, conducting polymers are being explored as possible materials for supercapacitors owing to their flexibility,⁵ low cost⁶ and high conductivity in doped states^{7,8} with little environmental hazards.⁹ Besides, capacitance values higher than with electrical-double-layer capacitors are possible to achieve due to fast pseudo-faradaic charge-transfer. However, a drawback of conducting polymer-based supercapacitors is their poor cycling capability due to structural instability during charge/discharge processes. The large volumetric swelling and shrinking during doping and dedoping lead to poor lifetime.¹⁰ Due to the low internal resistance in doped state of conducting polymers, such as polyaniline and polypyrrole, the power capabilities for the supercapacitors are high but their poor cycling stability continues to be a limiting factor.

In the literature, efforts are being expended to mitigate the aforesaid problems by forming composites between the carbon nanomaterials and conducting polymers.¹¹ The composite materials have improved capacitance values and good cycling stability, as conducting polymers enhance the capacitance of carbon nanomaterials by introducing voltage-dependent pseudocapacitance, while carbon nanomaterials, such as multiwalled carbon nanotubes, graphene, graphene oxide (GO) and reduced graphene oxide (rGO), help to increase their mechanical stability and cycle-life. In this context, GO and conducting polymer composites have been extensively investigated due to their exceptional mechanical and electrical properties.¹² The availability of functional groups on GO, such as hydroxyl, epoxide, carbonyl and carboxyl groups on its basal planes and edges, can be utilized for chemical functionalization of conducting polymers.¹³ Typically, its good dispersion stability in aqueous and other common organic solvents provides a facile route to prepare GO/polymer composites, which are considered to be attractive attributes for these materials in improving the performance of supercapacitors.

Various methods are reported to improve the cycle-life of conducting polymer-based supercapacitors. For example, Zhu *et al*¹⁴ showed that polyaniline/sulphonated multi-walled carbon nanotubes composite loses ~10% of its initial capacitance after 1000 cycles. Zhang and Zhao¹⁵ reported that polyaniline and polypyrrole deposited on rGO substrate can reach capacitance degradation of ~18 and ~19%, respectively, after 1000 cycles. Fu *et al* reported that carbon nanotube embedded in polypyrrole nanowire electrode loses

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about 15% of capacitance after testing for 1000 cycles at 1 A g⁻¹ current density.¹⁶ Wang *et al*¹⁷ demonstrated that supercapacitor electrode with polyaniline deposited on coral-like monolithic carbon achieves capacitance degradation of about 22% after 1000 cycles at a scan rate of 100 mV s⁻¹. Cycling stability of polymer electrodes is also studied beyond 1000 cycles, for example, Liu *et al*¹⁸ demonstrated that the capacitance degradations for carbonaceous shell-coated polyaniline and polypyrrole electrodes are ~5 and ~15%, respectively, after 10000 cycles at a scan rate of 100 mV s⁻¹. Kim *et al*,¹⁹ in one of his studies, synthesized polyaniline/reduced graphene nanosheet composites by polymerization through chemical oxidation while changing the weight ratio of aniline monomers and characterized the capacitance behavior of the materials using a three-electrode system. It is noteworthy that most of the reports in the literature on the conducting polymer-based supercapacitors are single-electrode characterization studies and their performance as a device is lacking.

To exploit the aforesaid attributes of nanomaterial/polymer composites, in this study, we have attempted to improve the cycling stability of polyaniline by *in situ* electropolymerization of aniline in the presence of GO templates. The effect of GO on the electrochemical performance of supercapacitors was studied in a three-electrode as well as in a two-electrode electrochemical cell assembly. The rated specific-capacitance values for polyaniline-based 1 V supercapacitor devices are 100 and 80 F g⁻¹ with the capacitance degradation of about 10 and 30% after 1000 cycles with and without GO, respectively. The power density is also higher for GO/polyaniline composite-based supercapacitor due to its shorter response time.

2. Experimental

2.1 Synthesis and characterization of GO and rGO

GO and rGO were synthesized from graphite flakes by modified Hummer's method and hydrazine hydrate, respectively,

Table 1. Active material compositions for three-electrode cell assembly.

Working electrode designation	Active material composition
WE A	85% Activated carbon + 10% rGO + 5% PVDF binder
WE B	PANI coating on top of WE A
WE C	GO/PANI coating on top of WE A

Table 2. Electrode combinations for 1 V supercapacitor devices in two-electrode cell assembly.

	Positive electrode	Negative electrode
Supercapacitor A	(85% Activated carbon + 10% rGO + 5% PVDF binder) + PANI coating (WE B)	85% Activated carbon + 10% rGO + 5% PVDF binder (WE A)
Supercapacitor B	(85% Activated carbon + 10% rGO + 5% PVDF binder) + GO/PANI coating (WE C)	85% Activated carbon + 10% rGO + 5% PVDF binder (WE A)

as reported elsewhere.^{20,21} The detailed synthesis is described in the supplementary information. Synthesized GO and rGO were characterized by Fourier transform infrared (FT-IR) spectroscopy (supplementary figure S1) and Raman spectroscopy (supplementary figure S2). Characteristic peaks in FT-IR spectra and bands in Raman spectra support the formation of GO from graphite flakes and further modification to rGO was analysed by chemical method.

2.2 Fabrication of working electrodes

Activated carbon-coated graphite working electrodes were fabricated using dimethyl formamide as a solvent and 5 wt.% poly(vinylidene fluoride) (PVDF) as a binder. Subsequently, the mixture was blended with 85 wt.% activated carbon and 10 wt.% rGO to form an ink. Resulting carbon ink was applied onto the graphite substrate followed by drying in an air-oven at 80°C for 6 h.

2.3 Electropolymerization of polyaniline and GO/polyaniline composite

rGO-embedded activated carbon working electrodes were amperometrically coated with a thin layer of polyaniline (PANI) in a three-electrode cell assembly using 0.5 M sulphuric acid and 0.2 M aniline solution under nitrogen purging at 0.75 V vs. Ag/AgCl reference electrode.²² The optimized duration for PANI electrodeposition was 5 min. Electrodeposition of GO and PANI composite was carried out at the same potential as mentioned above. The water suspension of GO was prepared by 1 h ultrasonic agitation, while the optimized concentration of GO was 60 mg l⁻¹. Subsequently, aniline and sulphuric acid were added to GO suspension. Resulting solution was used for electrodeposition of GO/PANI composite under nitrogen purging; optimized period for electrodeposition was 3 min. Amperometric profiles for electrodeposition of PANI and GO/PANI composite are presented in supplementary figure S3. Resulting PANI and GO/PANI composite were characterized by FT-IR spectroscopy, and corresponding data are shown in supplementary figure S4.

2.4 Configuration of electrochemical cells

Electrochemical characterization of electrode-active materials was carried out by assembling a three-electrode cell in a Plexiglass container, in which active materials were applied on the working electrode (1.5 × 1.5 cm² geometric area). A graphite sheet with a similar geometric area and an Ag/AgCl

electrode were used as the counter and the reference electrodes, respectively. Three different kind of working electrodes were made, namely 85% activated carbon + 10% rGO + 5% PVDF (WE A), 85% activated carbon + 10% rGO + 5% PVDF + PANI (WE B) and 85% activated carbon + 10% rGO + 5% PVDF + GO/PANI (WE C), which are summarized in table 1. Optimum concentration of sulphuric acid electrolyte was chosen as 2 M. Detailed optimization data are presented in supplementary figure S5.

2.5 Evaluating the supercapacitor performance

Two-electrode cell assemblies were designed for 1 V supercapacitor devices. The electrode combinations of supercapacitor devices are presented in table 2. Geometric areas of electrodes were $3 \times 3.5 \text{ cm}^2$, and the two electrodes were separated by 0.5 mm polyethylene mesh. Sulphuric acid (2 M) was used as electrolyte. 1 V supercapacitor devices thus assembled were performance tested by various dc and ac electrochemical methods using Autolab Potentiostat/Galvanostat-Model 30 at room temperature ($\sim 25^\circ\text{C}$).

3. Results and discussion

3.1 Electrode materials characterization

Figure 1a–c shows surface morphologies for various working electrodes, namely WE A, WE B and WE C, respectively. However, figure 1a shows the activated carbon and rGO composite-based active material structure, wherein the respective particle size values for activated carbon and rGO range between 5–10 and 2–5 μm . A scanning electron micrograph of rGO is also shown in the inset to figure 1a. Smaller-sized and highly conducting rGO improves the inter-particle contacts among comparatively larger-sized and less conducting activated carbon particles and helps reducing the internal resistance. Besides rGO contributes to the voltage-dependent pseudocapacitive component along with electrical-double-layer capacitance, and, consequently, resulting capacitance value is increased substantially. A quantitative data on the effect of rGO in reducing internal resistance that concomitantly improves capacitance is presented in supplementary figures S6 and S7. Figure 1b shows PANI nano-fibres with about 100 nm diameter. Porous, fibrous and random polymer matrix covers the basement of activated carbon and rGO composite layer, and enhances the effective surface area of the electrode. Effective capacitance increases due to the increase in electrical-double-layer capacitance owing to higher surface area and pseudocapacitance for fast electron transfer among the different redox states of PANI. Figure 1c shows porous, fibrous and layered polymer matrix with about 100 nm fibre thickness, which also covers the carbon layer. The layered structure of the polymer matrix is clearly seen in high magnification image in the inset to figure 1c. Layered structure of GO particles acts as template for layered polymeric matrix in electropolymerization. Non-covalent H-bonding interactions between oxygen containing functionalities of

Figure 1. Scanning electron surface micrograph for (a) WE A (inset: structural morphology of rGO), (b) WE B and (c) WE C (inset: layered polymeric matrix at higher magnification).

GO, such as hydroxyl, epoxide, carbonyl and carboxyl groups on its basal planes and edges, and amine functionalities of aniline monomer and polymer direct the nucleation/growth of polymeric matrix.¹¹ Consequently, GO particles are

covered with polymer layers bringing about improved mechanical stability of polymer matrix. To further investigate the structure of GO/PANI composite, transmission electron microscopic (TEM) studies were carried out. Figure 2a shows TEM image of GO/PANI, while the dark/bright contrast on the polymer rod indicates the core-shell structure. Inset to figure 2a shows selected area electron diffraction (SAED) pattern, which reflects that the composite material is not highly crystalline. In the high-resolution transmission electron microscopy (HR-TEM) image, shown as figure 2b, good lattice fringes are visible in darker region compared to the lighter region, which justifies the coating of only a meagre amount of crystalline PANI on top of more

crystalline GO supports. Furthermore, HR-TEM image shows inter-planer spacing of GO, namely 0.21 and 0.34 nm for (100) and (311) lattice planes at $2\theta = 42.7^\circ$ and 25.7° , respectively, which synchronize well with the PXRD pattern of GO.^{23,24} This study strongly validates the composite core-shell structure for GO and PANI.

3.2 Cyclic voltammetric study

Figure 3a–c depicts cyclic voltammograms for various working electrodes, namely WE A, WE B and WE C, respectively, in a three-electrode cell assembly between -0.2 and 0.8 V working voltage windows with respect to the reference

Figure 2. (a) TEM and (b) HR-TEM images for GO/PANI composite material. Inset of a shows the SAED pattern of composite.

Figure 3. Cyclic voltammograms at different scan rates for (a) WE A, (b) WE B and (c) WE C. (d) Scan rate vs. specific capacitance profiles for WE A, WE B and WE C.

electrode at varying scan rates. The specific-capacitance values are calculated from the cyclic voltammograms using equation (1), and respective data are presented in figure 3d.

$$\text{Specific capacitance} = \frac{\text{Area under the cyclic voltammogram}}{\nu \times \Delta V \times m} \quad (1)$$

In equation (1), ν , ΔV and m are the scan rate, working voltage window and mass of active materials, respectively. High specific capacitance values are achieved for WE C, owing to the synergistic effect of GO/PANI composite. WE B shows higher capacitance than WE A for the larger pseudocapacitance component of PANI. Due to the presence of rGO in WE A, certain amount of facilitated pseudocapacitance is observed in addition to electrical-double-layer capacitance, as shown in figure 3a, which improves the resulting capacitance of carbon-based layers in the working electrodes. It is seen from figure 3b and c that the pseudocapacitance overpotential is reduced and the shifts in overpotentials at fast scan rates are lowered in the presence of GO. The diffusion path-length for ions through the layered porous matrix in WE C is shorter compared with random porous matrix in WE B, and therefore the resistive component arising from mass-transport limitation is lesser for WE C than WE B.

3.3 Impedance analysis

Frequency-response analysis through electrochemical impedance spectroscopy is performed for WE A, WE B and WE C. Figure 4a shows Nyquist plots for aforementioned working electrodes. X-intercept in Nyquist plots at higher frequency is considered as internal resistance,²⁵ and the estimated internal-resistance values are: 0.533, 0.478 and 0.389 Ω for WE A, WE B and WE C, respectively. Conducting polymer structures improve the internal resistance for WE B and WE C in relation to WE A. The layered-polymer matrix in WE C further reduces its internal-resistance value in relation to WE B. Also, the π - π stacking interaction between GO sheet and PANI enhances the electron-transfer efficiency for the composite material, which reduces the internal resistance.²⁶ The response-time data are calculated from Bode plots (frequency vs. phase);²⁵ these data follow the same trend as internal-resistance values. The shorter ionic-diffusion pathway through the layered porous matrix is responsible for a shorter response-time for WE C in relation to WE B. The higher response-time for WE A is due to higher internal-resistance value. Figure 4b shows the Bode plots for different working electrodes. Response-time values are: 1.7, 1.2 and 0.6 s for WE A, WE B and WE C,

Figure 4. Frequency-response analysis by electrochemical impedance spectroscopy for different working electrodes: (a) Nyquist plots, (b) Bode plots, (c) real capacitance vs. frequency plots and (d) imaginary capacitance vs. frequency plots.

respectively, as derived from the frequency values (f) at phase angle -45° using equation (2).²⁷

$$\text{Response time} = \frac{1}{2 \times \pi \times f} \quad (2)$$

The frequency dependent capacitance (C) is a combination of real (C') and imaginary (C'') parts according to equation (3). The imaginary part of capacitance signifies the irreversible energy dissipation and corresponds to the relaxation process during ion transport.²⁸ A measure has been taken to separate out these two parts from impedance spectroscopy using equations (4) and (5),²⁸

$$C(f) = C'(f) + iC''(f), \text{ where } i = \sqrt{-1} \quad (3)$$

$$C'(f) = \frac{-Z''(f)}{2 \times \pi \times f \times |Z(f)|^2} \quad (4)$$

$$C''(f) = \frac{Z'(f)}{2 \times \pi \times f \times |Z(f)|^2} \quad (5)$$

where Z' , Z'' and $|Z|$ represent the real part (resistance), imaginary part (reactance) and modulus of total impedance, respectively, and $Z = Z' + iZ''$. Figure 4c shows the frequency response for real part of capacitance, and it is

observed that from higher to lower frequency region the capacitance values increase from about zero to near saturation. The capacitance values at any particular frequencies decrease from WE C to WE B to WE A, and, as a result, the power capability is highest for WE C and lowest for WE A. The higher power capability is achieved for WE C due to the lower internal resistance and shorter response-time values. Figure 4d shows the imaginary part of capacitance vs. frequency profiles for WE A, WE B and WE C with maximum at relaxation or breaking frequencies,^{25,28} the maximum value indicates the maximum energy dissipation from the system.²⁸ The relaxation or breaking frequencies are the transition points from resistive (high frequency) to capacitive (low frequency) characteristics in systems, and the reciprocals of these frequencies (angular-frequency forms) match with response-time values. Response-time data from figure 4b and d match each other.

3.4 Galvanostatic charge/discharge data

Figure 5a–c exhibits galvanostatic charge/discharge profiles at varying current densities within working voltage window for WE A, WE B and WE C. Figure 5d shows the calculated specific-capacitance values from the galvanostatic discharge plots at varying current densities according to the

Figure 5. Galvanostatic charge/discharge profiles at different current densities for (a) WE A, (b) WE B and (c) WE C. (d) Current density vs. specific capacitance profiles for WE A, WE B and WE C.

Figure 6. Cycle-life data for working electrodes WE A, WE B and WE C at 10 A g^{-1} current density.

equation (6), where I and t represent the discharge current and time, respectively.

$$\text{Specific capacitance} = \frac{I \times t}{\Delta V \times m} \quad (6)$$

Faradaic efficiency values are calculated from galvanostatic charge/discharge profiles by using the ratio of charge (in coulomb) output and input, and it is observed that the faradaic efficiency values are $>95\%$ at all current densities as shown in figure 4. It is noteworthy that due to the non-uniform current distribution in the porous matrix, the specific-capacitance values decrease at higher current densities,²⁹ which is in accordance with the data obtained from cyclic voltammetry at different scan rates.

3.5 Cycle-life data

Cycle-life data for different working electrodes are obtained through galvanostatic charge/discharge at 10 A g^{-1} current density, and the data are shown in figure 6. The capacitance values decrease by 3, 17 and 8.5% after 3000 cycles for WE A, WE B and WE C, respectively. Scanning electron micrographs on the surfaces of WE A, WE B and WE C are recorded after 3000 cycling, and are presented in figure 7a–c. Figure 7a shows unaffected electrode surface morphology after 3000 cycles, which is responsible for better cycle-life of WE A. From figure 7b, it is clearly evident that the polymeric structures are disrupted, and the basement carbon layer is visible. By contrast, the polymeric structures are quite stable in figure 7c due to the increased mechanical stability of polymeric matrix in the presence of GO templates. The trend for capacitance degradation in WE B and WE C is reflected by the structural stability of polymer matrixes.

3.6 Electrochemical performance data for 1 V supercapacitors

In the light of the foregoing, 1 V supercapacitor devices, namely supercapacitor A and supercapacitor B (table 2) are

Figure 7. Scanning electron surface micrograph after 3000 cycling for (a) WE A, (b) WE B and (c) WE C.

Figure 8. Cyclic voltammograms at different scan rates for (a) supercapacitor A and (b) supercapacitor B. (c) Scan rate vs. specific capacitance profiles for supercapacitors A and B.

Figure 9. Frequency-response analysis by electrochemical impedance spectroscopy for supercapacitors A and B: (a) Nyquist plots, (b) Bode plots, (c) real capacitance vs. frequency plots and (d) imaginary capacitance vs. frequency plots.

developed. The electrochemical performance tests, using cyclic voltammetry, ac impedance analysis, galvanostatic charge/discharge and cycle-life data, are carried out for 1 V supercapacitors as discussed below.

3.6a Cyclic voltammetry: Cyclic voltammograms for 1 V supercapacitors are shown in figure 8a and b at varying scan rates between 0 and 1 V. Specific-capacitance values are calculated from cyclic voltammograms as reported in figure 8c. Little deterioration in specific-capacitance values are observed at high scan rates.

Figure 10. Galvanostatic charge/discharge profiles at different current densities for (a) supercapacitor A and (b) supercapacitor B. (c) Current density vs. specific capacitance profiles for supercapacitors A and B.

3.6b Impedance analysis: Internal resistance and response-time values are estimated from Nyquist plots (figure 9a) and Bode plots (figure 9b), respectively. For supercapacitor A, the internal resistance and response-time values are 0.33 Ω and 1.3 s, respectively, whereas for supercapacitor B, these respective values are 0.25 Ω and 0.7 s. The frequency response data for real and imaginary parts of capacitance are analysed, and respective profiles are shown in figure 9c and d. These profiles correspond to single-electrode study and the response-time values from figure 9d match with abovementioned data.

3.6c Galvanostatic charge/discharge data: Galvanostatic charge/discharge experiments are carried out between 10 mA (120 mA g⁻¹) and 50 mA (600 mA g⁻¹) load currents within 0 to 1 V for supercapacitor A and supercapacitor B, and respective profiles are shown in figure 10a and b. Specific-capacitance values are calculated at each load current, and presented in figure 10c, where small degradation is observed at higher current loads. From figure 10c, the rated specific-capacitance values for supercapacitor A and supercapacitor B are estimated as 80 and 100 F g⁻¹, respectively, with more than 90% faradaic efficiencies.

3.6d Energy and power densities: Energy and power densities are calculated from rated specific-capacitance values (C) using equations (7) and (8), respectively,²⁸ where $V_{\max}$ and $V_{\min}$ are 1 and 0 V, respectively.

$$\text{Energy density} = \frac{C(V_{\max}^2 - V_{\min}^2)}{2 \times m} \quad (7)$$

$$\text{Power density} = \frac{\text{Energy density}}{\text{Response time}} \quad (8)$$

Energy and power density values for supercapacitor A were estimated to be 11 Wh kg⁻¹ and 30 kW kg⁻¹, respectively, while the respective values for supercapacitor B were 14 Wh kg⁻¹ and 72 kW kg⁻¹. Higher power density value for supercapacitor B is attributed to the presence of GO template.

Figure 11. Cycle-life data for supercapacitors A and B at 50 mA current load.

Figure 12. Nyquist plots with internal-resistance data after 1000 cycling for supercapacitors A and B.

Figure 13. Photographic image of 2 V supercapacitor device pack under 1.5 V LED operation.

3.6e Cycle-life data: Cycle-life test was also performed at 50 mA (600 mA g^{-1}) load current for supercapacitor devices, and 1000 cycle data are presented in figure 11. It is seen that only 30 and 10% capacitance loss are observed after 1000 cycles for supercapacitors A and B, respectively.

Internal-resistance values are measured after 1000 cycles for supercapacitors A and B, with respective values being 0.48 and 0.30Ω (figure 12). The increase in internal resistance is much higher for supercapacitor A in relation to supercapacitor B due to the breakdown of polymeric structure in supercapacitor A. It is noteworthy that the high cycling stability for supercapacitor B is owing to the retention of polymeric structures in GO/PANI.

3.6f Demonstration of 2 V supercapacitor pack with LED lamp: Figure 13 shows the design of 2 V supercapacitor pack with two 1 V cells in series under 1.5 V light emitting diode (LED) lamp operation. The real-life performance testing under 1.5 V LED load demonstrates the fabrication of functioning supercapacitor devices with nanostructured GO/polyaniline composite materials.

4. Conclusions

A GO/PANI composite-based supercapacitor device is reported, and a comparative study with PANI-based device is performed. *In situ* potentiostatic electropolymerization processes are followed for synthesizing PANI and GO/PANI composites, which are devoid of impurities, and contribute lesser internal resistance to the electrodes. Various electrochemical methods, namely cyclic voltammetry, impedance spectroscopy, galvanostatic charge/discharge and cycling stability, are used for characterization of polymer-based active materials in a three-electrode cell assembly and performance tests for 1 V supercapacitor devices. It is surmised that high-power capability and cycling stability make the GO/PANI composite-based supercapacitor a potential system for practical applications.

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Electronic Supplementary Material

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