Graphene/Polyaniline flexible supercapacitors using non-metallic electrodes

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Abstract. Flexible supercapacitors are attractive devices for portable applications including those integrated in clothes. Highly conducting flexible electrodes can easily be fabricated by graphene powder and PE polymer foil but reliable fabrication of supercapacitor structure is still a challenge. A promising solution could be the incorporation of conducting polymer as polyaniline (PANI) intended to stabilize the mesoporous carbon and graphene plates, to form a conductive porous composite and to increase the capacitance. Low-cost aqueous electrolyte (1V) supercapacitor devices based on graphene/PANI composite were developed, tested in series configurations and compared in electrical performance. Preliminary applications in portable solar chargers are discussed.

1. Introduction
In Standalone-powering systems with small renewable energy generator (series of solar cells, small wind-generators or Peltier elements) are popular in smart energy microsystems as a reliable, low-cost and environmentally independent source of energy. Nowadays, the bottleneck in energy production pipeline has been transferred from energy generation to short-time energy storage devices capable of withstanding the increasing need for electricity. By this reason storage unit (for example, series of supercapacitor devices) have recently attracted more and more attention for use in novel applications especially for flexible electronics [1-3].

The principle of energy storage in a supercapacitor can be either electrostatic surface charge accumulation in double layers capacitors (EDLC) or charge transfer, via reversible (Faradaic) redox reactions known as pseudo capacitance. The high surface area and high cycle life, makes these novel devices preferred energy storage banks for many applications based on non-constant renewable energy sources and also regenerative braking in vehicles.

Carbon nanomaterials, especially graphene and carbon nanotubes (CNTs), are very promising candidates to replace activated carbons due to their large surface area, high mesoporosity and electrolyte accessibility, and excellent electrical conductivity. The mesoporous structure of nanocarbon materials have been introduced by many authors [4, 5] due to its low cost and easy fabrication. In various papers [6], research efforts have been focused on design of 3-D structures based on graphene oxide (GO), reduced graphene oxide (rGO), CNTs materials as well as novel hybrid composites based on graphene and conducting polymer or metal oxides.
Graphene sheet is a two-dimensional (2-D) honeycomb lattice of one-atom-thick layer of sp²-hybridized carbon with good mechanical properties and additional flexibility. Of particular interest, graphene sheets with tunable through-thickness p–p stacking interactions and/or edge functionalities have been shown [7]. Within a reasonable range of oxygen functional groups content in graphene sheets, a large specific area and high conductivity could be obtained.

In this paper recent results are reported on low-cost technologies for fabrication of flexible flat all-carbon supercapacitors using graphite conducting electrodes prepared on PE polymer substrate.

2. Experimental

2.1. Graphene exfoliation

Nano graphene plates has been produced by many authors [6] using oxidation of graphite. The carbon sheets can be easily “unfolded” by applying liquid-assisted exfoliation procedures [8]. In our study, electrochemical procedure of graphite electrodes exfoliation in (NH₃)₄SO₄ is applied. Electrochemical potential of 10 V DC between graphite cathode and anode electrodes for 2 hours and electrolyte solution of 0.1M (NH₃)₄SO₄ are effective low-cost method for graphene plate extraction. Next step is cleaning of SO₄ radicals by rinsing 3 times in DI water at 80°C for 30 min followed by carbon microcrystal separation by filter paper. Graphene-based powder has been dried and prepared for electrodes fabrication. Microscopic photos of dispersed graphene plates on glass surface are presented in figure 1.

Homogeneous conducting graphene layers has been further obtained by rubbing the powder carefully in between two 125 µm Polyethylene sheets (PE) and by hot laminating the sandwich structure at 70°C together. After lamination the PE sheets was exfoliated mechanically. Double-exfoliated graphene layers have been obtained on the internal surfaces of laminated PE foils. Graphene oxide platelets form highly developed surface as can be seen at figure 2.

2.2. Supercapacitor based on Graphene/PANI composite

The problem with aggregation and re-stacking of graphene sheets caused by Van der Waals force tends to result in a loss of surface area and reduced capacitance. Therefore, intermediate external particles or structures between graphene sheets could improve mesoporosity. Conducting polymers are being explored as supplementary materials for supercapacitors owing to their flexibility, low cost and
high conductivity in doped states with little environmental hazards. Graphene layer can serve as a underlying conductive network, while polyaniline (PANI) can serve as a spacer to separate neighboring graphene sheets. Capacitance values higher than EDLC capacitors are possible to achieve due to fast pseudo-faradaic charge-transfer in the polymer. The GO/PANI composite material is expected to improve the overall capacitance values and cycling stability, as conducting polymers enhance the capacitance of carbon nano-materials by introducing voltage-dependent pseudo capacitance.

Moreover, the GO/PANI composite displays an excellent electrochemical performance due to an extra synergistic effect between PANI and GO. 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 and doping of conducting polymers. GO with oxygen-contenting groups can provide a large number of active sites for the nucleation of PANI and for reversible modulation of conductivity.

It seems that smart engineering of advanced 3-D structures is a promising option for next generation of energy storage devices. The performance can be further enhanced by coating of graphene underlayered matrix with PANI polymer caps or preparation of multi-layered GO/PANI construction.

2.3. Electropolymerization of PANI
It is well known that PANI exists in three states: leucoemeraldine, emeraldine, and pernigraniline. In general, conducting polymer is a semicrystalline material and the crystallinity can be attributed to the systematic alignment of the polymer chains by chain folding or the formation of single or multiple helices. In this study, emeraldine salt of PANI has been prepared by electrochemical deposition of aniline monomer in HClO₄ solution on Palladium working electrode and on PE polymer/graphene electrode. The electrochemical potential of 0.75 V is sufficient to extract electron and to start polymerization of green conducting state of PANI.

Figure 3 presents optical reflection spectra of suitable emeraldine PANI film. The appearance of absorption bands at 330, 430 and 750nm for PANI is an indication of the emeraldine salt form. The characteristic bands were assigned as follows: 1) The lowest wavelength band around 330 nm was often related to the presence of cation radicals and corresponded to a $\pi-\pi^*$ transition in the benzenoid structure; 2) The mediate band was related to the $n-\pi^*$ transition and on behalf of the doping degree on polymer chains; 3) The band around 750nm was attributed to $\pi-n$ transition and it is also ascribed to exciton formation in the quinonoid rings.
3. Fabrication of flexible supercapacitors

3.1. Electrode preparation
Fine powder of graphene sheets (particles size < 50 um) were diluted in DMF binder to form graphene ink. The electrode is fabricated by sequential deposition of dry graphene powder on PE substrate to form current collecting electrode, electrodeposition of PANI film and screen-printing of graphene ink. The resultant multilayer composite has conducting graphene/PANI structure. Top surface and 3-D pictures of as prepared double layered structure are shown at Figure 4.

3.2. Gel electrolyte separator:
The electrolyte used is gel polymer electrolyte. The host polymer is PVA, the solution is water and the electrolytic salt is KCl. Filter paper (2-3 µm pore size) was dipped in the KCl/PVA electrolyte solution and dried in air at 90°C for 15 min.

3.3. Device assembling
Symmetric rectangular capacitor with 25 x 70 mm area is prepared in sandwich structure by pressing together two electrodes and separator film in between. As prepared EDLC-pseudo Cap is encapsulated in PE plastics foil pack using hot lamination, as can be seen at Figure 5.
4. Electrical testing

The electrochemical properties of the supercapacitors are investigated by means of galvanostatic charge-discharge techniques. Pseudocapacitive and hybrid systems can exhibit large deviations in linearity based upon varying capacitance with voltage compared to pure EDLC. After preparation of graphene/PANI composite the charge-discharge curves show that the discharge time has increased. The initial full charge to 1V and bending of the discharge curve only shows extended charge trapping. Redox reaction in polyaniline has appeared during charge-discharge process together with the electrostatic charging in graphene micropores which indicates the synergistic effect of the two phenomena and improved device performance.

5. Discussions

Figure 6 shows the galvanostatic initial charging curves at charge-discharge currents of 20mA/2mA in 20s for two individual supercapacitors with the same area and gel-electrolyte but prepared on different plates -metallic and non-metallic. The non-metallic graphene/PANI supercapacitor during initial charging period has a different electrical behavior compared to Cu/activated carbon capacitor produced by the same technology. It is assumed that activated carbon needs longer time to charge pores of the electrodes while graphene/PANI structure has bigger pores or even cavities able to capture ions. The second reason is the additional source of charge - not only electrolyte ions but also the extracted electrons from polymer chains of PANI. Obviously, graphene/PANI structure is more attractive for fast charging devices, for example in portable applications.
A key challenge is to design and assemble flexible electrode materials which can harvest/store human body energy through actions such as breathing, arm pressing, jogging, etc. The new flexible energy storage devices need to maintain high-quality performance under continuous mechanical deformation, such as bending, folding, twisting and stretching, for long cycles. For this reason, the importance of non-metallic supercapacitor has been increased due to the extended flexibility of the incorporated materials. Flexible electrodes can be assembled in thin, light and smart designs of any shape and size. Portable electronics needs operating voltages in the range of (1.5V -3V) which determines the voltage window of flexible energy storage devices. One reasonable approach is a single element to be used based on new organic electrolytes or ionic liquids operating at higher voltages (2.5V - 4V) instead of aqueous solutions. However, recent publications reveal effects of aging and fast degradation in organic electrolyte as for example acetonitrile [9, 10], which slows down the interest. On the other hand, ionic liquids are complex toxic metal-organic compositions at an early stage of development with high prices for mass applications. Obviously, a useful low-cost “battery” approach can be formed from connected in series identical supercapacitors each of them operating at (1.0-1.1 V) and based on human-friendly stable inorganic electrolyte. Our experiments reveal no degradation in performance of up to 4 identical supercapacitors in a 2D single plane configuration.

Possible light-weight application as a portable solar charger/powerbank could be graphene/PANI supercaps connected in series and suitable energy management circuitry assembled together on the back surface a small PV module. Such solar energy configuration could be feasible for daily in-house lighting applications.

Conclusions
All-carbon based thin film supercapacitors were successfully manufactured. These structures consist of conductive carbon/plastic films as current collectors and high surface area graphene-polyaniline (PANI) mixture films as electrodes. We developed a technique to increase the surface area as well as the capacitance of the electrode layer by electrochemical exfoliation of graphene and preparation of graphene/PANI multi-layered structure. The flexible rectangular shaped graphene/PANI supercapacitor (25 x 70 mm) were encapsulated by hot lamination. The manufacturing process has a good reproducibility. The rectangular supercapacitors can be used in various combinations of series to obtain desired energy or power. The in-plane assembly of supercapacitors in series will lead to space-saving integration of supercapacitors pack. The main advantages of the developed supercapacitors are the scalable low cost production, the inexpensive materials and the large variety of possible practical applications.

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