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High performance electrode material prepared through *in-situ* polymerization of aniline in the presence of zinc acetate and graphene nanoplatelets for supercapacitor application

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ABSTRACT

This study discusses a simple and feasible method that involves *in-situ* polymerization of aniline in the presence of zinc acetate dihydrate $[Zn(CH_3COO)_2.2H_2O]$ and graphene nanoplatelets (GNP) for the preparation of high performance electrode material (PZG composite) for supercapacitor application. In the presence of metal salt $[Zn(CH_3COO)_2.2H_2O]$, the capacitance value is changed and increased enormously compared to the capacitance value of PANI/GNP (PG) composite. Thus, the proposed method gives specific capacitance value for the PZG composite is ~688 F/g at a 10 mV/s scan rate which is very high compared to the specific capacitance value (~340 F/g) of PG composite at the same scan rate. In the PZG composite, zinc acetate and GNP are successfully coated by PANI, which provides more active sites for nucleation and electron transfer path. In addition, the inter- and intra-molecular interactions among them facilitate the electron transfer path which plays an important role to enhance the capacitance value of the composite. Moreover, the prepared composite is electrically conducting in nature and shows electrical conductivity in the order of $\approx 4.67 \times 10^{-2}\ \mathrm{S\,cm^{-1}}$. In addition, PZG composite shows semi-conducting behavior. Field Emission Scanning Electron Microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM) have been studied for the morphological analysis of the PZG composite.

1. Introduction

Supercapacitor has become a new generation energy storage device in the current science and technologies. It has been used as a bridge between low power devices (low temperature fuel cells and batteries) and low specific energy devices (conventional capacitors). In addition, it has been considered most promising material for various energy storage devices due to its long cycle life (>100,000 cycles), high rate capability, low maintenance cost, rapid charging–discharging rates, environmental friendliness and light weight [1–4]. Two types of capacitors are generally classified depending on their charge storage mechanism, such as, (a) electrical double-layer capacitors (EDLCs) composed of porous carbonaceous materials of high surface area as electrodes, where achievement of electrostatic charge storage of the electrical energy occurs due to the separation of charge at the interface between the surface of a conductor electrode and an electrolytic solution and this whole process is non-Faradaic in nature and (b) pseudocapacitors, often called redox electrochemical capacitors, where storage of the electrical energy occurs due to some fast, reversible redox reactions of the electrode materials generally composed of conducting polymers and transition metal oxides, with the electrolyte and this process is Faradaic in nature [5].

Since pseudocapacitors deal with fast and reversible redox reactions, comparatively higher capacitance value will be obtained for pseudocapacitors than EDLCs. To improve the capacitance value, different electro-active transition metal oxides such as RuO_2, MnO_2, TiO_2, Fe_3O_4, MoO_x, CoO_x, NiO_x [6–13] have been used for the preparation of supercapacitor materials. Besides these, various conducting polymers like polypyrrole (PPY), polyaniline (PANI), and polythiophene (PTH) have been extensively used along with metal oxides or metal salts to enhance the ability of the energy storage of the materials. Among all of them PANI has been much more attractive and promising basic material due to its low cost, high electrical conductivity [14], high capacitive characteristic, environmental stability, ease of synthesis, simple acid doping-base dedoping chemistry [15–17]. However, electrodes comprised of conducting polymers, such as PANI suffer from some serious

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problems such as low electronic conductivity, degradation through mechanical shrinkage and swelling during charging–discharging and hence, high resistance during cycling [18–21]. So for improving electrochemical energy storage property of PANI, concept of using composite electrode had evolved, where PANI is combined with a particular amount of porous, highly conducting carbonaceous materials of high surface area [19,22]. Capacitance can further be improved by doping conducting polymers with transition metal ions like Zn^{2+}, Cu^{2+} and Fe^{3+}, as these serve as catalysts in the redox process increasing the energy density.

Many research groups have prepared electrode materials for supercapacitors based on different transition metal ions, PANI along with highly surface reactive conducting nanofillers. For instance, Maiti and Khatua [23] have prepared $CoCl_2$ doped PANI/GNP composite (PGC) as a supercapacitor electrode material through *in-situ* polymerization and the reported specific capacitance value was ≈634 F/g at a 10 mV/s scan rate. Li et al. [24] have synthesized Zn^{2+} and H^+ co-doped PANI by simple chemical polymerization method and the obtained capacitance value of the composites was ≈369 F/g. Wang et al. [25] have synthesized a flexible graphene/PANI hybrid material as an electrode material by *in-situ* polymerization–reduction/dedoping–redoping process. They have achieved high specific capacitance value (≈1126 F/g) with 84% retention of life after 1000 cycles. Baek et al. [18] have studied the specific capacitance value of PANI/reduced graphene oxide (rGO) composite. The obtained capacitance value was ≈250 F/g with high electrical conductivity of ≈8.66 S cm^{-1}. The composite has been synthesized through *in-situ* polymerization. Cong et al. [26] have achieved high specific capacitance value of ≈763 F/g for PANI/graphene composites. They have prepared flexible composite paper using *in-situ* electro-polymerization technique. Xia et al. [27] have prepared PANI/rGO/molybdenum oxide (MoO) ternary composites as electrode material and reported specific capacitance value was ≈553 F/g in 1 M H_2SO_4 at a scan rate of 1 mV/s. Sahoo et al. [28] have prepared PANI/surface modified graphene composites as supercapacitor materials. They have observed that specific capacitance value of the composite decreased from ≈242 F/g to ≈193 F/g for modification of graphene. Giri et al. [29] have developed an electrically conducting (70.8 S cm^{-1}) PANI/graphene/zirconium oxide (ZrO) nanocomposite with high specific capacitance value of ≈1360 F/g at 1 mV/s.

The present study discusses about the capacitance performance of the PANI/$Zn(CH_3COO)_2$/GNP (PZG) composite. The PZG composite has been synthesized through *in-situ* polymerization of aniline in the presence of zinc acetate and GNP at low temperature. This is the one of the simplest and commercially successful methods. In addition, the composite has delivered high specific capacitance value which is ~688 F/g at 10 mV/s scan rate which is higher than the specific capacitance value (~340 F/g) of the PANI/GNP (PG) composite at the same scan rate. Thus, the presence of zinc acetate plays a crucial role to enhance the specific capacitance value of the PZG composite. In the PZG composite, a well ordered nanostructure is developed, which reduces the ionic diffusion path and facilitates ionic motion to the inner part. So, it can be considered as one of the most promising electrode materials for supercapacitor application. Moreover, the PZG composite shows high cycle stability and 83% of specific capacitance has retained after 500 cycles. In presence of conducting PANI and nanofiller like GNP, the PZG composite becomes highly electrically conducting and observed conductivity value is $\sim 4.67 \times 10^{-2}$ S cm^{-1}, indicating that it can also be used in various fields of application. We also studied the semi-conducting property of the composite. Thus, proposed simple cost effective method, high capacitance value, better cycle stability and high conductivity value of the PZG composite will play a key role for developing next generation high performance supercapacitor.

2. Experimental

2.1. Materials details

Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$], ammonium persulfate (APS) [$(NH_4)_2S_2O_8$] and cetyl trimethylammonium bromide (CTAB) were purchased from Loba Chemie Pvt. Ltd. India. Aniline and potassium chloride were purchased from Merck, Germany. Multi-layered graphene nanoplatelets (GNPs, carbon purity:>99.5%) having thickness and diameter of 8–10 nm and 5–25 μm respectively, were purchased from J.K. Impex, Mumbai, India. These GNPs have appreciable electrical conductivity of 10^7 S m^{-1}. All the chemicals were of analytical grade and used as received without any further chemical modification.

2.2. Preparation of the PZG composite

The PANI/$Zn(CH_3COO)_2$/GNP composite (PZG) was synthesized through simple *in-situ* polymerization of aniline in the presence of $Zn(CH_3COO)_2.2H_2O$ and GNP. At the beginning, the calculated amount of surfactant (CTAB) was dissolved in 150 ml of 1.5 (M) HCl solution and then required amount of GNP was added to this acidic solution followed by strong ultra-sonication for 30 min. The presence of CTAB plays a crucial role for homogeneous dispersion of multi-layered GNPs in the acidic solution. The acidic suspension of GNP was stirred vigorously in an ice-bath using magnetic stirrer for another 40 min. Then, aqueous solution of $Zn(CH_3COO)_2.2H_2O$ was prepared using de-ionized (DI) water and drop-wise added to the acidic solution at the same ice-cool condition under constant stirring for another 35 min. Finally, 1 ml of aniline was poured into the acidic reaction mixture followed by the controlled addition of acidic APS solution (prepared by dissolving of 2 gm APS in 150 ml 1.5 (M) HCl solution). The observation showed that the solution immediately changed to bluish color first and then deep green after sometime. The reaction mixture was stirred vigorously and kept for 6 h at this ice-cool condition. After 6 h of reaction, a deep greenish color solution was observed and filtered the reaction mixture. The residue was collected and washed with DI water followed by ethanol for several times. Finally, washed residue was air dried and then, kept in an air-oven at 60 °C for 24 h. The PANI/GNP (PG) composite was prepared following the same steps written above except the addition of zinc acetate salt during the polymerization of aniline. A schematic representation for the preparation of the PZG composite is shown in Fig. 1.

3. Characterizations

3.1. Fourier Transform Infrared (FTIR) Spectroscopic Analysis

FTIR studies of pure PANI, pristine GNP and PZG composite were done using a NEXUS 870 FTIR (Thermo Nicolet) to evaluate the bonding and structure of the PZG composite. The samples under investigation were prepared by mixing those with potassium bromide (KBr) in the ratio of 1:10 (w/w) and then were pelletized.

3.2. Wide Angle X-ray Diffraction (WAXD) Analysis

To investigate the crystal structures of pristine GNP, pure PANI and PZG composite, X-ray diffraction analysis was performed using a wide angle X-ray diffractometer (WAXD, X'pertPRO, PANalytical, Netherlands) with nickel-filtered Cu Kα line (λ = 0.15404 nm) at an accelerating voltage of 40 kV and 30 mA current density and a scanning rate of 0.5°/min. The sample-to-detector distance was 400 mm. All the materials were scanned in the range of 2θ = 10–70°.