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Full Length Article

Insight into capacitive performance of polyaniline/graphene oxide composites with ecofriendly binder

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ABSTRACT

The behaviour of gold electrode modified with polyaniline/graphene oxide composites (PGO) was studied for electrochemical and charge storage properties in aqueous acidic media. The surface of gold electrode was modified with aqueous slurry of PGO by using Carboxymethyl cellulose (CMC) as binder. The intercalation of polyaniline in the GO layers, synthesized by *in situ* polymerization was confirmed by scanning electron microscopy (SEM). The electrochemical behaviour and charge storing properties were investigated using cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS). A high specific capacitance of 1721 F g^{-1} was obtained for PGO with 69.8% retention of capacitance even after 1000 voltammetric cycles in the potential range of 0–0.9 V at 20 mV s^{-1}. EIS indicated low charge transfer resistance (*R*ct) and solution resistance (*R*s) values of 0.51 Ω and 0.07 Ω, respectively. This good performance of PGO coated electrode is attributed to the use of CMC binder which generate a high electrode/ electrolyte contact area and short path lengths for electronic transport and electrolyte ion.

1. Introduction

To meet energy demands of modern world researchers are trying to design and develop more efficient and portable energy devices. Supercapacitors with good energy storage capability, high power density, high charge/discharge rates and good cycling stability are considered as maintenance free energy storage devices [1–3]. Based on the charge storage mechanism supercapacitors are categorized as electric double layer (EDL) capacitors and pseudocapacitors [4]. Carbon nanotubes (CNT) [5], graphene [6], activated carbon [7] and metal organic framework (MOF) derived nanoporous carbon [8–11] based materials are usually used in fabrication of electrodes for EDL supercapacitors which accumulate charge at electrode/electrolyte interface under applied electric field. Such supercapacitors are very stable but associate with disadvantage of low specific capacitances. Conducting polymers and metal oxides are used in the fabrication of pseudocapacitors which store charge because of fast reversible redox or faradic processes across the electrode/solution interface occur. Though pseudocapacitors show high values of specific capacitances the materials used in their fabrication quickly suffer from degradation with continuous cycling [12]. A possible solution is provided by making composites of both the materials used in EDL and pseudocapacitors. Such materials are reported to show an enhancement in the specific capacitances, charging-discharging rate and cycling life [13,14].

Carbon based materials (diamond, fullerene, graphene) have been widely studied in supercapacitor fabrication. Graphene, initially reported by Novoselov et al. in 2004 [15], is reported to have high electrical and thermal conductivity, exceptional high surface area, chemical inertness, good cycling stability and large capacitance values [16–19]. These properties make graphene very attractive for application in the field of sensors [20], field effect transistors [21], fuel cells [22], batteries [23] and supercapacitors [24,25]. However, graphene is poorly soluble in water and is therefore commonly used in its oxide form. Graphene oxide (GO) which forms stable dispersion in water can easily be obtained by simple oxidation of graphite [26]. A large number of oxygen containing functional groups (epoxide, hydroxyl, carbonyl and carboxylic groups) in GO structure are responsible for its dispersiveness in water. The epoxide and alcohol functionalities decorate basel plane of GO sheet whereas carboxylic and carbonyl are present along the sheet edge [27] resulting in GO flakes with a negative surface charge [28–30].

Intrinsically conducting polymers (ICPs) have also received great research interest ever since their discovery in 1977. ICPs such as Polyaniline (PANI), Polypyrole (PPy), Poly (3,4-

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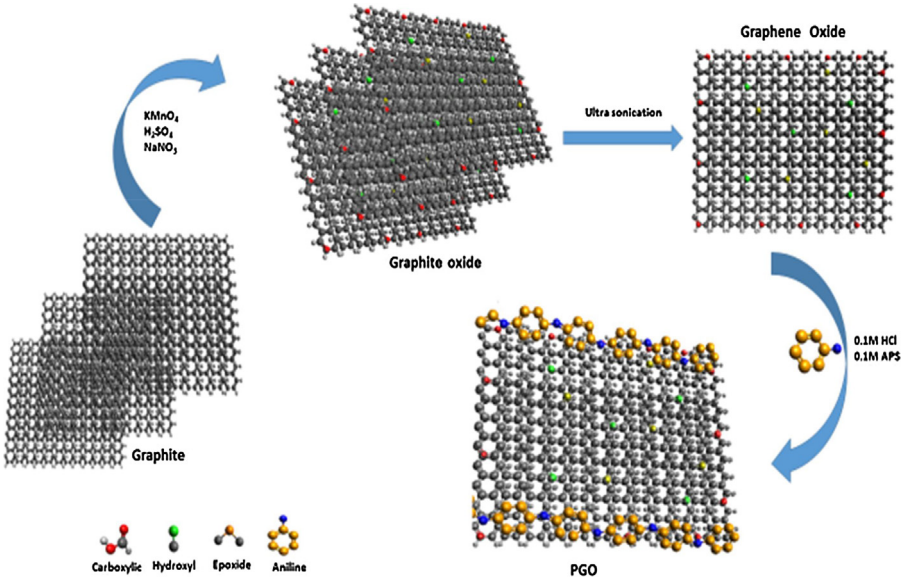
ethylenedioxythiophene) (PEDOT) and their derivatives have been tested as active electrode materials in supercapacitors. PANI has been emerged as a promising pseudocapacitive material because of its high conductivity in doped state, low cost, easy synthesis, good environmental stability and high storage capacity [31–34]. However, PANI also degrades during the charging and discharging process which limits its application in supercapacitors. A combination of GO and intrinsically conducting polymers into one material offers the advantages of both the components and is found to be eff ;ective for improving the electrochemical performances of supercapacitors.

Beside electrode composition and electrolyte systems, choice of binder is crucial factor for electrochemical performance. Binder helps in adhesion of active material and conductive additive simultaneously with current collector. Consequently, electron can flow through current collector-active material-conductive additive chain to/from the outside circuit. The type of binder in the electrode architecture is very important to optimize specific capacitance, electrode cost, energy density, stability, and fabrication procedure. A binder retains the structural integrity, capacity and cyclability of electrode. Most commonly used binders are fluoropolymer or functional fluoropolymer binders such as, Polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVDF) and Nafion *etc*. along with conductive additive for active material deposition. Xu et al. prepared hierarchical nanocomposite of PANI on GO by dilute polymerization technique [35]. Gold grid electrode was used as a current collector and active material was pressed on the electrode by using PTFE as a binder. The specific capacitance was reported to be as high as 555 F g^{-1} at a current density of 0.2 A g^{-1}. Zhe-Fei et al. have reported covalently grafted PANI on GO sheet by simple route [36]. The supercapacitor electrode was prepared by making a slurry of the active material in NMP and casting on a glassy carbon electrode. PVDF was employed as a binder and a capacitance of 442 F g^{-1} was recorded. Guiheng et al. synthesized PGO nanocomposite by *in situ* polymerization with the assistance of super critical CO_2. The test electrode (steel) was prepared by pressing the active material using PTFE as a binder. The specific capacitance of this material was recorded to be 425 F g^{-1} at the current density of 0.2 A g^{-1} [37]. However, PTFE or PVDF binders require expensive and highly toxic organic solvent such as *N*-methyl-pyrrolidone (NMP) in the processing. Moreover, according to migration controlled kinetics of drying, binder migrated towards the top surface of electrode sheet because of the solvent flow during drying. As the evaporation rate of NMP is very low and take longer time to dry, resulting in the non-homogeneity in the dried electrode sheet comparing to the identical electrode fabricated with water soluble binder (*e.g.* naturally abundant cellulose) [38]. Hence the performance of water soluble binder coated electrode in term of resistance, charge–discharge efficiency and adhesion is much better than fluoropolymer based coated electrode.

In the last decade, Cellulose based materials especially Sodium salt of Carboxymethyl cellulose (CMC) have gained considerable attention as binding material. It has several benefits over conventional binder such as: a) the overall electrode fabrication processes is low cost and water based, b) there is no usage of toxic and expensive organic solvent, c) self-standing electrode films with high mechanical properties, d) the end products of cellulose based materials are renewable and eco-friendly, e) cellulose binder material are suitable for flexible electrodes fabrication [39–41]. Since 2005, after the first report by Lee et al. CMC has been widely tested as binder for carbon based material in anode fabrication of Li-ion batteries [42]. Wang et al. suggested that, the capillary effect of the binder solution (CMC + acetylene black) may become concentrated near the contact points between graphite spheres which effectively improve the electrical contact during cycling performance [43]. Buqa et al. reported for the first time that Si electrode fabricated from 1% CMC binder compared to identical electrode fabricated from 10% PTFE binder showed same cycling stability [44]. Due to these enrich property of CMC as binding agent in field of batteries, a wide space of research is available for electrode fabrication in supercapacitor, solar cell and sensor.

We report a greener approach for the fabrication of PGO composite on gold substrate using economical, fluorinated free CMC as a binder for supercapacitor application. The intercalation of PANI in GO layers was confirmed from spectral and morphological investigation of PGO with UV–vis, FTIR and SEM techniques. The electrochemical and charge storing properties were investigated using CV, GCD and EIS. The specific capacitance obtained was as high as 1721 F g^{-1} and show 69.8% retention even after 1000 voltammetric cycles at a scan rate of 20 mV s^{-1}. Moreover, the electrode shows very low *R*s and *R*ct values of 0.07 Ω and 0.51 Ω, respectively. This good performance of PGO material is attributed to the use of CMC binder which generates a high electrode/ elec-



Scheme 1. Synthetic route of Graphene oxide and its composite with PANI.