



Enhancing the capacitance and active surface utilization of supercapacitor electrode by graphene nanoplatelets



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ABSTRACT

The potential application of graphene nanoplatelets as electrode material in supercapacitors with high energy density was investigated. The electrode were prepared with commercially available graphene nanoplatelets before and after being functionalized with MnO₂ particles, and with those electrochemically exfoliated from graphite. The morphology, structure and the specific surface area properties of each material were analyzed prior to test the electrochemical performance of the corresponding electrodes under the design constraints of real devices by cyclic-voltammetry (CV) and charge/discharge (CD) measurements. The results indicated that graphene nanoplatelets show potential in replacing activated carbon for the fabrication of supercapacitors with high energy density, while the efficient usage of active surfaces available of the electrode material should be considered.

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1. Introduction

The advancements of complex electronics systems over the last years have led to the increasing demand of portable energy usage and storage [1,2]. In this instance, powerful and reliable energy storage systems are sought after as power supply units for emerging applications in the field of electro-mobility. In the automotive field, many applications, such as the device actuation, heating of seats and starting of the engine or energy recuperation during braking require not only a device with high energy density, but also one that is able to deliver/store the energy within a short period of time (i.e. high power and high charging rate). In spite of their low power densities [3], batteries are the most commonly applied solution to the aforementioned challenges thanks to the high energy density they offer [4].

In recent times, supercapacitors are thought to be among promising candidates to replace or to be coupled with batteries for these applications with the aim of enhancing the power densities of the devices [5]. In comparison to batteries, a supercapacitor modus operandi offers higher power densities, faster charging

rates and theoretically unlimited cyclability [6]. However, the main drawback of the commercially available supercapacitors is their limited energy densities. Therefore, one of the main focal point of today's research in this field is oriented at increasing the energy density of supercapacitors. In this aspect, advancements have been assisted by the discovery of novel advanced materials which are capable of bringing the energy density of supercapacitors to a level more comparable to batteries [7,8]. A common approach to enhance the capacitance of a supercapacitor cell, and its energy density lies in providing the electrodes with more active sites for the storage of charge compounds, such as the ions of the electrolyte. To achieve this goal, supercapacitors have been fabricated with materials that are able to provide high surface area. Till date, the commercially available supercapacitors constitute mainly of carbon-based electrodes and among them, activated carbon ones are the most commonly employed due to its high specific surface area, ranging from a few hundreds to 1500 m²g⁻¹, low cost and long cycling life [9,10]. However their complex pore structures of irregular pore sizes have been reported to impede the access of electrolyte ions resulting in an increased electrode's resistance and reduced capacitance [10].

Amid the search for systems with high efficiency, graphene has emerged as one of the most promising alternative for electrode developments in devices including batteries [11], fuel-cells [12]

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supercapacitors [13,14], in optoelectronics [15,16] and nanofillers [17]. This is accredited to the high intrinsic electrical conductivity and high specific surface area [18–20] obtainable from this material; from the point of view of a capacitive device, these properties translate to high power and high energy density [21,22]. On top of that, graphene can be structured on the current collectors to provide paths with higher accessibility for ions within the electrolytes as compared to activated carbon.

In the present work three different types of multi-stacked graphene, also known as graphene nanoplatelets are studied for supercapacitor electrode materials. The first type of graphene nanoplatelets was obtained commercially and will be referred to as “GNP”, while the second type – “MnO₂/GNP” – represents GNP which has been functionalised with MnO₂ particles in order to increase the material’s energy density through the pseudocapacitive effect it demonstrates in protic and certain aprotic electrolytes [23,24]. Finally, the last type was obtained through electrochemical exfoliation of graphite and will be referred to as “eGNP”.

A series of investigations have been carried out to characterize the properties of these three GNPs before and after being processed into electrodes. For the electrochemical characterisations of the electrodes, a 2-electrode electrochemical cell was specifically designed to mimic the setup of a supercapacitor in order to compare each electrode performance under the design constraints of a real device. Therein the most important parameters of a supercapacitor required in specific power electronics to serve end-user applications were evaluated.

2. Experimental

2.1. Material synthesis

All reagents were of analytical grade and used without further treatment. Distilled water was used in relevant situations. Commercial GNP (from XG Sciences, www.xgsciences.com, trade name *xGnP C-750*) was used as-obtained for electrode preparation and also as the scaffold for MnO₂ functionalization in case of MnO₂/GNP. The functionalization process was performed in accordance with the process described by Yu [25]. The commercial GNP was first dispersed in a 0.01 mol L⁻¹ KMnO₄ followed by the drop wise addition of 0.05 mol L⁻¹ citric acid until the solution turned brown-purple. The mixture was further heated up to 80 °C in a distillation column with full reflux for 7 h. The functionalised GNP was filtered out and dried at 80 °C for 12 h.

For the synthesis of eGNP, graphite (from Mueller & Roessner, tradename *MREG-E*) was subjected to anodic electrochemical exfoliation [26] at a potential of 7 V. The exfoliation took place in a setup consisting of five graphite electrodes (two of which served as anode, while the other three were placed on each side of the anode acting as the cathode) partially submerged in a 0.1 mol L⁻¹ NaOH and placed 15 mm apart. The exfoliated materials were filtered through polycarbonate membranes (Millipore, 0.4 μm) with a pressure aided filtration setup (Sartorius 16249). Successive washings were performed with de-ionized water until filtrate of neutral pH was obtained.

2.2. Material characterization

The morphology and structure of the employed materials were analyzed by means of scanning electron microscopy (SEM, QUANTA FEG 650, FEI microscope), Raman spectroscopy (HR UV 800 (JYV-Jobin Yvon), laser wavelength 532 nm) and X-ray diffraction (XRD) (diffractometer D5000 Siemens using Cu K α radiation). Nitrogen adsorption/desorption isotherms were analyzed to

determine the specific surface areas (ASAP 2010 Micromeritics nitrogen adsorption apparatus).

2.3. Electrode fabrication

The three types of stacked multi-layer graphene, (1) GNP, (2) MnO₂/GNP and (3) eGNP, were employed for the fabrication of electrodes with accordance to common industrial practices as follows. The graphene materials (10 wt%) were dispersed in 1:1 (w/w) H₂O/2-propanol mix with the help of a rotor/stator homogeniser (Silent Crusher M, Heidolph Instruments) for 20 min at 20,000 rpm. Thereafter, pre-prepared poly(vinylidene fluoride-hexafluoropropene) (PVDF-HFP 1% in 2-propanol) was added drop-wise as a binder (10% w/w ratio with respect to the amount of graphene materials) at a homogeniser rotation speed of 26,000 rpm. The resulting ink was allowed to homogenize for a further 20 min at 26,000 rpm. Once prepared, the inks were coated onto collectors, made of aluminum foil, with the bar-coating method to a wet coating thickness of 300 μm. The coatings were left to dry in air for 60 min at 70 °C before the dried mass loadings of the active electrode material were measured and reported as 1.93, 2.05, 2.03 and 7.26 mg cm⁻², respectively for GNP, eGNP, MnO₂/GNP and activated carbon. The active material loading should not be confused with the amount of carbonaceous materials. In the case of electrodes prepared with MnO₂/GNP, the mass of the electrode coating is shared between graphene nano-platelets and MnO₂. For benchmarking purposes, the results were compared to performance of commercial supercapacitor electrodes consisting in activated carbon coated on aluminum foil current collectors.

2.4. Electrochemical testing

The performance of the prepared electrodes was evaluated within the potential window of 0–2.5 V using an aprotic electrolyte consisting of 1 M TEABF₄/acetonitrile solution. The tests were conducted in a 2-electrode cell configuration [27]. The electrode cell was designed specifically to mimic the build-up and the working principle of an actual supercapacitor. Two graphite current collectors were used to sandwich the two electrode samples in order to avoid chemical interactions between the copper collectors and the electrolyte in case of possible leakage. A glass microfiber filter (Whatman, 934-AH™) pre-soaked in the electrolyte was used as the separator and two sheets of rubber insulators, each with a 2 × 2 cm² window, were aligned between the electrode samples to prevent short circuit between the two pieces of graphite and also to limit the amount of surface exposed to the electrolyte.

The electrochemical performance of the fabricated electrodes was evaluated by means of cyclic voltammetry (CV) and constant-current charge/discharge measurements (CD) with an AMEL 500 potentiostat. The specific capacitance values were obtained from the CV and CD curves [18], by integrating the area under the charging cycle and from the discharge slopes of the response curves using the equation $C = I/(dV/dt)$. The absolute capacitance measured from the exposed surface was thereafter converted into the specific capacitance of the electrode with the following equation $C_{sp} = 4 \times C/m$, where C is the capacitance measured from the exposed surface and m the total mass of the cell. The factor of 4 was included to adjust the cell’s absolute capacitance to the electrodes specific one (C_{sp}) in case of symmetrical capacitors. The equivalent series resistance (R) was also measured from the discharge CD curves, usually associated to ohmic effects. R represents the sum of all resistances present in the setup (i.e. arising from electrodes, electrolyte, interfacing contacts, leads, etc.). The R value was calculated from the voltage and current values with the formula $R = \Delta V/\Delta I$ [18].

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