Nanocomposites of Graphene Nanosheets/Multiwalled Carbon Nanotubes as Electrodes for In-plane Supercapacitors

João Paulo C. Trigueiro, Rodrigo L. Lavall, Glaura G. Silva*

Departamento de Química, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Pampulha, CEP 31270-901 Belo Horizonte, MG, Brazil

ARTICLE INFO

ABSTRACT

Flexible supercapacitors with large power and energy densities, long life cycles and good operational safety are necessary devices for various applications. In this work, we demonstrate the integration of a composite based on graphene nanosheets/multiwalled carbon nanotubes in an in-plane supercapacitor configuration by using a straightforward preparation involving the filtration of nanomaterials to produce an electrode film. Reduced graphene oxide (RGO) received 15 wt % carbon nanotubes to act as a conducting additive, which led to a flexible and transferable thin film (RGO/MW) with an average conductivity of $20.0 \, S \, cm^{-1}$. Three ionic liquids were tested as electrolytes for the supercapacitor, among which 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) was observed to exhibit the best performance. The specific capacitance of the supercapacitor based on RGO/MW-EMITFSI reached $153.7 \, F \, g^{-1}$ at a current density of $0.2 \, A \, g^{-1}$ and exhibited a capacitance retention of 88% after 2000 cycles. The maximum energy and power densities were calculated to be $41.3 \, Wh \, kg^{-1}$ and $3.5 \, kW \, kg^{-1}$, respectively, for the RGO/MW-EMITFSI supercapacitor.

1. Introduction

The growing demand for clean energy generation and storage is contributing to an increase in the research and development of advanced energy storage systems, such as batteries and super-capacitors (SCs) [1]. An electrochemical capacitor, also called supercapacitor, is a device able to provide higher capacitance values than conventional capacitors because of (1) the electrostatic attraction that occurs between the ions and the charged surface of the electrode (electrochemical double-layer capacitor, EDLC) or (2) fast surface Faradaic redox reactions (pseudocapacitor) [2–8]. These devices can be used in several applications, including portable electronics, digital communications, roll-up displays and hybrid electric vehicles [2,9–11]. Supercapacitors offer great advantages compared to other energy sources (batteries), such as a large number of charge-discharge cycles, a robust thermal operating range, low weight and an extraordinary power density [2,12]; however, their energy density is somewhat lower than that of batteries [13].

Great efforts have been made toward developing new materials for use in SCs and controlling their structures and geometries with the aim of achieving better electrochemical and mechanical properties [12,14–18]. In this context, flexible electrodes developed from carbon nanomaterials have been proposed as next-genera-tion materials for flexible supercapacitors with desirable proper-ties, such as large power and energy densities, long life cycles and good operational safety [19–23].

Graphene nanosheets (GNSs) have become one of the most promising materials for use in supercapacitor electrodes because of their unique physical and chemical properties (e.g., high electrical conductivity, large surface area, chemical inertness, high thermal conductivity and optical transmittance) [24–29]. Howev-er, the integration of their excellent properties into macroscopic structures for practical applications remains a challenge.

Recent research has demonstrated that the capacitive behavior of GNSs, as a result of their aggregation during the stages of preparation, is much lower than the predicted value estimated from their ultrahigh surface area [14,30]. Individual sheets tend to irreversibly agglomerate because of van der Waals interactions. Thus, the capacitive performance is significantly lower than expected because GNS stacks limit the access of the electrolyte ions into the inner layers to form an electric double layer, as shown schematically in Fig. 1a. In such a case, the ions mainly accumulate at the external surfaces of the GNS aggregates, significantly decreasing the supercapacitor performance [26,31].

To inhibit self-restacking of GNSs and to increase the conductivity of the electrodes, several authors have proposed

* Corresponding author. Tel.: +55 31 34095768; fax: +55 31 34095711.
E-mail addresses: joaopcampos@yahoo.com.br (J.P.C. Trigueiro),
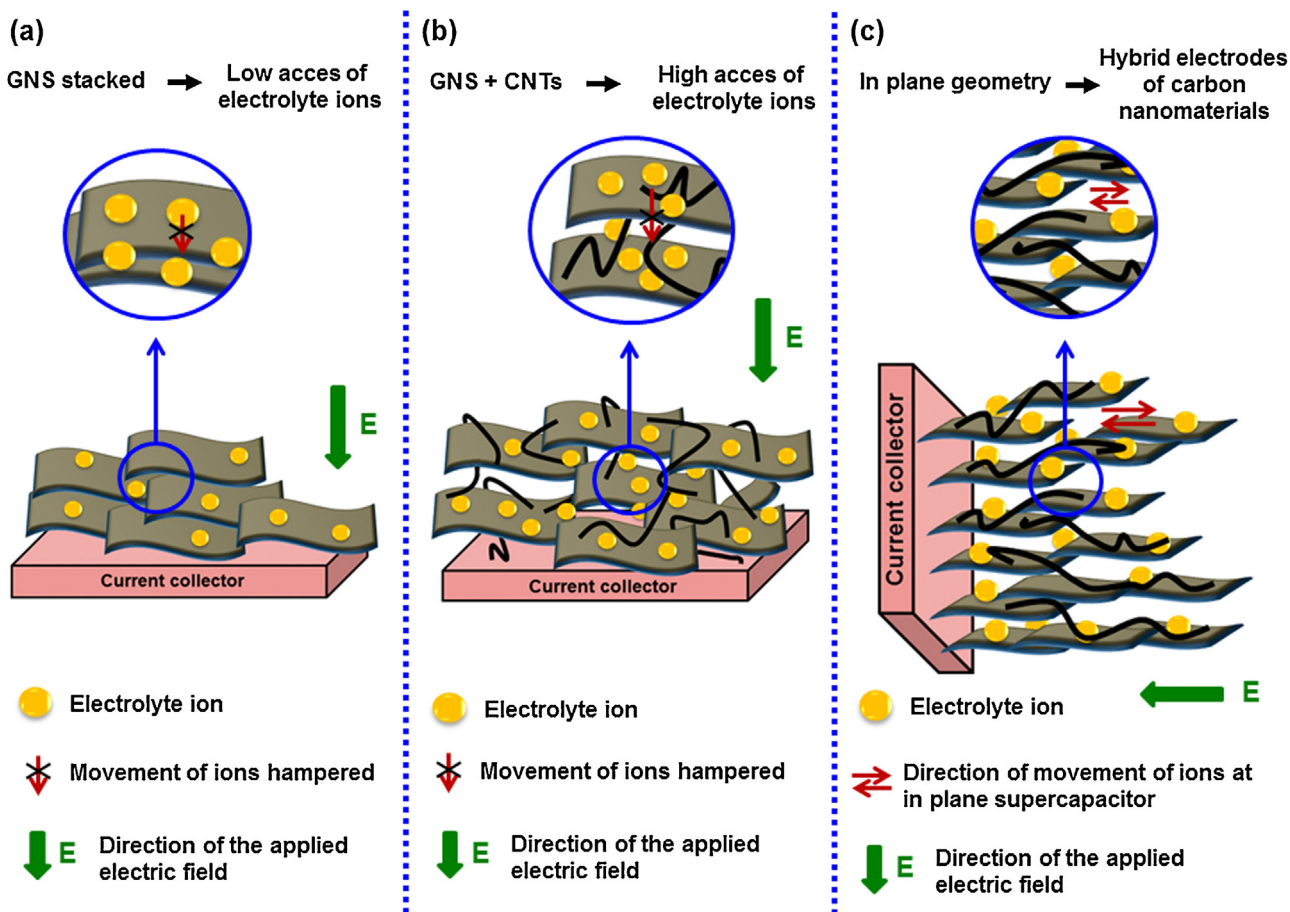rodrigo.lavall@qui.ufmg.br (R.L. Lavall), glaura.goulart@gmail.com (G.G. Silva).

Fig. 1. Schematic models of supercapacitors in the stacked and in-plane configurations. (a) GNS aggregated in the typical stacked configuration, inhibiting the access of electrolyte ions. (b) Graphene/CNT composite used in the preparation of a supercapacitor in the stacked configuration. The CNTs act as conducting additive between the GNS to give rise to a more rapid diffusion pathway for the electrolyte ions. CNTs can also increase the electrical conductivity of the electrode. (c) The in-plane configuration allows for better use of the surface area of the carbon nanomaterials, facilitating the transport of ions and electrons in the electrode.

combining GNSs and carbon nanotubes (CNTs) to design hierarchically structured carbon-carbon nanocomposites [32–37]. In this material, the CNTs are used to inhibit the aggregation of GNSs, thereby significantly improving the surface area that is accessible to electrolyte ions compared to that of pure GNSs. Furthermore, CNTs are also able to interconnect GNSs, which provides conductive pathways for electron transport and reduces the internal resistance in the electrode, as shown in Fig. 1b [14,31]. Efforts have also been made to insert other materials, such as mesoporous carbon [38], porous silica [39], cation surfactants [40] and other structures [41] into the interlayer spaces of GNSs to form sandwich structures with the aim of improving the ability of ions to access the electrode structures.

Typically, supercapacitors are assembled in a conventional stacked geometry [13,15,26]. This geometry can hinder penetration of electrolyte ions into the graphitic layers of the electrode, which are composed of stacked and well connected GNSs. This fact limits the extension of the electric double layer formed at the electrode/electrolyte interface since the electrolyte ions move towards the electrode surface with the electric field applied perpendicular to the electrode surface, as shown in Fig. 1a. To populate the entire electrode, the ions must overcome the barrier formed by the stacked GNSs to reach the carbonaceous surfaces.

Planar supercapacitors built with graphene electrodes have emerged as a promising candidate for the next-generation of energy-storage devices [30,42,43]. These devices are built with each one of the two electrodes onto the same plane (or surface). This is a new configuration for the assembly of supercapacitors, which more efficiently exploits the surface of the GNSs used in energy storage devices. This configuration, named "in-plane" by some authors, allows for ultrathin and planar devices to be obtained. The main advantage of this configuration is that it improves the interaction of the electrolyte ions with the carbon nanomaterials of the electrode, leading to full utilization of the high surface area provided by the carbon nanomaterials. Its design allows for the electrolyte ions to move more efficiently since the electric field is applied in the same direction of the preferential arrangement of the electrode materials as show in Fig. 1c (which illustrates hybrid carbon nanotubes/GNSs as electrode material). A significant increase in the surface area of the electrode accessible to the electrolyte to produced electrical double layer is thus possible [30,42,43].

Yoo et al. [30] describes the preparation of an in-plane ultrathin supercapacitor using electrodes based on pristine graphene and multilayer reduced graphene oxide. Effect of graphene edges and the open architecture of electrode allows the construction of an ultrathin device, produced from of a 1–2 graphene layers, which reached specific capacities up to $80\,\mu F\,cm^{-2}$, while exhibited a much higher ($394\,\mu F\,cm^{-2}$) specific capacitance values for device with multilayer reduced graphene oxide electrodes (with 10 nm thick). The multilayer graphene films were prepared by chemical reduction of the graphene oxide films obtained through layer-by-