



Supercapacitors based on modified graphene electrodes with poly(ionic liquid)



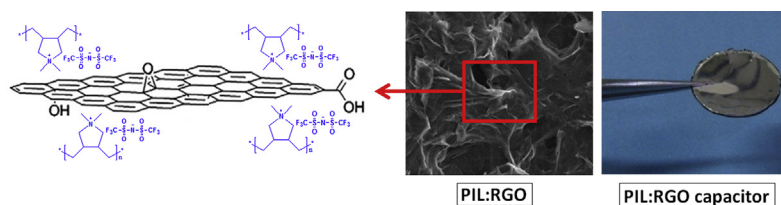
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HIGHLIGHTS

- The PIL:RGO electrode increases the compatibility with the ionic liquid electrolyte.
- The use of polymeric PILTFSI showed to be a promising strategy for capacitive devices.
- The PIL:RGO supercapacitor exhibits high capacitance and indication of good cycle stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The improved accessibility of the electrolyte to the surface of carbon nanomaterials is a challenge to be overcome in supercapacitors based on ionic liquid electrolytes. In this study, we report the preparation of supercapacitors based on reduced graphene oxide (RGO) electrodes and ionic liquid as the electrolyte (specifically, 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide or [MPPy][TFSI]). Two types of electrodes were compared: the RGO-based electrode and a poly(ionic liquid)-modified RGO electrode (PIL:RGO). The supercapacitor produced with the PIL:RGO electrode and [MPPy][TFSI] showed an electrochemical stability of 3 V and provided a capacitance of 71.5 F g^{-1} at room temperature; this capacitance is 130% higher with respect to the RGO-based supercapacitor. The decrease of the specific capacitance after 2000 cycles is only 10% for the PIL:RGO-based device. The results revealed the potential of the PIL:RGO material as an electrode for supercapacitors. This composite electrode increases the compatibility with the ionic liquid electrolyte compared to an RGO electrode, promoting an increase in the effective surface area of the electrode accessible to the electrolyte ions.

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1. Introduction

In supercapacitors (also known as electrochemical double layer capacitors), the electric charge is accumulated in a double layer, mainly by electrostatic forces, without any chemical change in the electrode materials [1,2]. Energy storage is based on the separation of charged species in the double layer formed on the electrode/electrolyte interface [3,4]. Supercapacitors have attracted much attention in recent years due to their important characteristics,

such as high capacitance, high power density ($\sim 10 \text{ kW kg}^{-1}$), medium energy density ($\sim 5 \text{ Wh kg}^{-1}$) and a large number of life cycles ($> 100,000$). One further advantage is that they can be fully charged or discharged in a few seconds [5]. These devices have a high power density and a relatively large energy density compared to conventional capacitors, which enables their application to energy storage systems [6]. Supercapacitors may complement or replace batteries where high power densities are required for short time intervals [7].

To generate high capacitance, the specific surface area of the electrode material must be as high as possible to accommodate a large number of ions at the electrode/electrolyte interface, promoting the capacitance of the electrical double layer [8,9]. Among the different materials studied for application as the electrodes of

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supercapacitors, carbon materials in a variety of forms (for example, carbon nanotubes, carbon felts and activated carbon) have been widely investigated. However, there are many possibilities for great advances in the characteristics of supercapacitors and the discovery of graphene has become an important event in this context.

Graphene is a single atomic layer of sp^2 carbon atoms and is a promising material for supercapacitors electrodes due to its fascinating physical and chemical properties [10,11]. Supercapacitors based on graphene materials and aqueous electrolytes have been produced, and the results show great potential for this new class of carbon material for high-performance devices [12,13]. Du et al. developed electrodes with free standing graphene nanosheets that were prepared using a coating method that exhibited a stable specific capacitance of 150 F g^{-1} in KOH aqueous solution (30 wt.%) as the electrolyte [14]. Recently, Sun et al. fabricated a supercapacitor using reduced graphene oxide paper synthesized using a flame-induced reduction; this supercapacitor had a specific capacitance of 212 F g^{-1} in 2 mol L^{-1} of KOH electrolyte [15].

A critical factor influencing the properties of a supercapacitor is the characteristics of the electrolyte. Organic electrolytes provide a greater potential window when compared to aqueous electrolytes. However, organic electrolytes have the drawback of low thermal stability and toxicity, which limits their use in supercapacitors [16].

Ionic liquids (IL), i.e., molten salts with melting points below 100°C , have been intensively used as the electrolyte in various electrochemical systems, including supercapacitors because IL have unique physicochemical properties such as high thermal and chemical stability, low vapor pressure and a wider electrochemical stability window [17,18].

Extending the temperature range of the operation of supercapacitors is of great importance because supercapacitors can address the problems associated with operating in severe conditions, which is required for automotive, aerospace and power electronic applications. In this scenario, ionic liquids have an advantage because they are able to operate in high temperature extremes, which is not possible with conventional electrolytes.

Recent research has shown that the performance of supercapacitors using graphene with ionic liquids as the electrolyte may be improved [19,20]. In order to do this improvement is crucial enhance the accessibility of electrolyte ions at the electrode. A major challenge to overcome is the production of electrode materials based on graphene that can sustain high wettability with ionic liquid electrolytes. This may be accomplished by modifying the surface of the graphene.

Tamailarasan et al. developed a high-performance supercapacitor based on a multi-walled carbon nanotube, exfoliated graphene and a 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid ternary nanocomposite electrode; the same ionic liquid was used as the electrolyte [21]. Their study showed extremely high specific capacitance (201 F g^{-1}) for an ionic liquid-based device at a large specific current density of 2 A g^{-1} . The authors attributed the high performance of the device mainly to the presence of a layering of ionic liquid in the electrode material, forming a solid-like ionic liquid modifier to the carbonaceous surface. This layer of ionic liquid was supposed to enhance the electrolyte accessibility and facilitate ionic transport because it increases the number of ion diffusion paths inside electrode. In another study conducted by Kim et al., an interesting approach applying poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethylsulfonyl)imide to modify the reduced graphene oxide electrodes was developed; these authors used the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide to prepare the supercapacitors [22]. This work also reported outstanding values for an ionic liquid-based supercapacitor. Capacitance values between 127 and 187 F g^{-1} were obtained depending on the applied current

density. The authors believe that the wettability of the electrodes with an ionic liquid electrolyte was facilitated by the poly(ionic liquid) molecules electrostatically linked on the reduced graphene oxide surface, producing the high specific capacitance values.

In the present study, we employed a simple synthetic procedure for preparation of a polymeric ionic liquid and incorporation into a dispersion of reduced graphene oxide in dimethylformamide. From this dispersion, composite electrodes were prepared by the dripping technique, allowing control over the amount of deposited material to obtain self-supported films, which were used in the construction of a supercapacitor with ionic liquid as an electrolyte.

2. Experimental section

2.1. Materials

The ionic liquid 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide [MPPy][TFSI] with 99% purity and water content of less than 100 ppm (according to the supplier) was purchased from Iolitec (Germany) and was used as it was received. Other physicochemical properties for this ionic liquid are summarized in Table 1 (Supporting information), according to the literature data [23]. Handling of the ionic liquid was performed in a glove bag under a nitrogen atmosphere. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99.9%) and poly(diallyldimethylammonium) chloride solution (average Mw 400,000–500,000, 20 wt.% in H_2O) (PILCl) were obtained from Aldrich, Brazil. Natural graphite was purchased from Bay Carbon Co, USA.

2.2. Preparation of graphene oxide

Graphene oxide (GO) powder was prepared from natural graphite by an improved method (based on Hummers' method) according to the methodology previously reported in the literature. This method for producing GO has significant advantages over Hummers' method [24].

2.3. Preparation of chemically reduced graphene oxide

Hydrazine monohydrate was used as the reducing agent for production of RGO in a stoichiometric ratio of $1 \mu\text{L}$ of hydrazine to 3 mg of GO [25]. In a typical procedure, 150 mg of GO was dispersed in 50 mL of water with the aid of an ultrasound bath for 3 h, yielding a homogeneous yellow-brown dispersion (3 mg mL^{-1} of GO). Hydrazine monohydrate was subsequently added to the suspension, and the mixture was stirred at 80°C for 12 h resulting in a black precipitate of RGO powder. The synthesized RGO was washed with water to remove excess hydrazine and dried in a vacuum oven at 60°C for 12 h.

2.4. Synthesis of polymeric ionic liquid

The polymeric ionic liquid or poly(ionic liquid) (PIL) containing pyrrolidinium cation and bis(trifluoromethylsulfonyl)imide anion was synthesized by anion exchange reactions using a commercially available polymer poly(diallyldimethylammonium) chloride according to a procedure described in the literature [26]. Briefly, a solution of 8.52 g of LiTFSI salt in 10 mL of distilled water and a solution of 4 g of PILCl in 100 mL of distilled water were mixed for 5 min at room temperature to facilitate the exchange reaction of Cl^- ions by TFSI^- . After stirring, the resulting white solid (named PILTFSI) was separated by filtration and dried in a vacuum oven at 60°C for 12 h until it reached constant weight.

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