



RAPID COMMUNICATION

Conjugated polyfluorene imidazolium ionic liquids intercalated reduced graphene oxide for high performance supercapacitor electrodes



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Abstract

We report a new concept of using conjugated polyfluorene imidazolium ionic liquids (PILs) intercalated reduced graphene oxide for high performance supercapacitor electrode materials. Two polyfluorene homo-polymer (hoPIL) and co-polymer (co-PIL) carrying hexyl imidazolium bromide side chains were designed and synthesized. Their corresponding intercalated reduced graphene oxide materials hoPIL-RGO and coPIL-RGO exhibited good electrochemical performance in aqueous electrolytes as well as in ionic liquid electrolyte 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄). High specific capacitances of 222 F g⁻¹ at a current density of 0.2 A g⁻¹ and 132 F g⁻¹ at 0.5 A g⁻¹ were obtained for coPIL-RGO in 6 M KOH and BMIMBF₄ accordingly. When assembled into a symmetric two-electrode cell with graphene materials as electrodes and BMIMBF₄/acetonitrile (1:1) as electrolyte, an energy density of 14.7 Wh kg⁻¹ was obtained for coPIL-RGO at a current density of 0.5 A g⁻¹, and a maximum power density of 347 kW kg⁻¹ was achieved for hoPIL-RGO at a current density of 5 A g⁻¹ with good cycling stability.

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Introduction

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted much attention because they can provide much higher power density than lithium ion batteries, and much larger energy density than conventional capacitors. Bridging the gap between capacitors and rechargeable batteries makes supercapacitors promising energy storage devices in a wide range of applications, such as consumer electronics, memory back-up systems, industrial power and energy management, where high power density and long cycle-life are highly desirable [1-3]. While the energy density of supercapacitors is very high compared to conventional dielectric capacitors, it is still significantly lower than batteries or fuel cells. Thus, research has been focused on developing advanced supercapacitors with higher energy without sacrificing power delivery and cycle life [1,4]. A large capacitance value and high operating cell voltage are required for a supercapacitor to have good performance [5,6]. Hence, the development of both novel electrode materials with increased capacitance, such as graphene based materials [7-11,51-52], and electrolytes with wider potential windows, such as ionic liquid electrolytes or organic electrolytes is required to optimize the overall performance of the supercapacitor [12].

Graphene, a lightweight two-dimensional all-sp²-hybridized carbon, is a promising material for supercapacitor electrodes owing to its low mass density, excellent electronic conductivity, and high surface area (~2630 m²/g, theoretically). Chemical reduction of exfoliated graphene oxide (GO) is commonly regarded to be an efficient technique for the low-cost and bulk production of graphene sheets [13-19,53-54]. However, irreversible agglomeration of graphene sheets resulted from van der Waals interaction during reduction process is inevitable, and will cause the possibly decrease of the effective surface area, resulting in a lower specific capacitance [4]. Previously, our group prepared surfactant-stabilized graphene materials as electrodes for supercapacitors through the reduction of organic ionic surfactant-intercalated GO, and much higher specific capacitances compared with chemically reduced graphene (GR) were obtained [20]. Currently, both covalent [21-27] and non-covalent functionalizations [28-39] of graphene are widely used to improve its dispersibility [28,37]. Among these methods, non-covalent functionalization of graphene with π - π interactions as the binding force between graphene and stabilizers is regarded to be a more effective and non-destructive method, which enables the modification of material properties without altering the chemical structure of graphene [39,40]. Recently, Ghosh et al. reported 1-pyrenecarboxylic acid (PCA) functionalized graphene and discussed the effect of PCA functionalization of graphene on its electrochemical properties [41].

Ionic liquids (ILs), known as room temperature molten salts, are attractive candidates for electrolytes used in energy storage because of their unique properties, such as negligible vapor pressure, low toxicity, high thermal stability, high electrochemical stability over a wide potential window, acceptable conductivity at elevated temperature, etc. However, they are typically high viscosity liquids and have low ionic conductivity at room temperature, which make their performance inevitably

affected [12]. Thus, how to take the advantages of ionic liquid electrolytes at room temperature is a practical issue to be addressed. Kim et al. reported that the performance of a polyethylene based ionic liquid-modified reduced graphene oxide electrode in ionic liquid electrolyte could be greatly enhanced due to the improved wettability resulting from the structural similarity of the chosen polymer and IL [42]. Hence, it demonstrates that a combination of good dispersible graphene sheets, enhanced operating voltage, and improved accessibility of ions from electrolyte to the active regions of electrode materials should afford supercapacitors with good electrochemical performance.

In this context, herein, we present the design and synthesis of novel conjugated polyfluorene imidazolium ionic liquids (PILs) modified graphene composites as supercapacitor electrodes with good electrochemical performance. Conjugated PILs are rigid-rod polymers, composed of one electron-delocalized planar backbone and two hexyl flexible side chains ending with or partially with 1-methylimidazolium bromide moieties. With such unique molecular architecture, it is anticipated that they should have much stronger interaction with GO and RGO sheets than other molecules due to their unique electronic backbones, and the strong π - π interaction between planar conjugated PILs backbone and GO/RGO sheets can have conjugated PILs easily adsorb on the surface of GO/RGO sheets and effectively stabilize graphene sheets. Meanwhile, RGO materials modified by conjugated PILs are expected to exhibit improved surface wettability due to the presence of imidazolium bromide tails. Two imidazolium bromide ionic liquids derived from polyfluorene were designed and synthesized, as shown in Figure 1. hoPIL has two charged ionic-liquid end groups on each fluorene unit, while coPIL has two charged ionic-liquid end groups for every two fluorene units. To the best of our knowledge, it is the first time that conjugated polymer imidazolium ionic liquids were introduced to graphene materials and their composites were tested as supercapacitor electrode materials. These conjugated PILs intercalated reduced graphene oxide were named as hoPIL-RGO and coPIL-RGO, respectively, and can be obtained in gram quantities. Conjugated PILs intercalated between graphene sheets can effectively prevent the agglomeration of graphene sheets during reduction through π - π interactions due to their unique electronic backbones. Meanwhile, imidazolium bromide moieties contained in conjugated PILs may also improve the surface wettability of electrode materials and result in better electrochemical performance. The applications of these conjugated PILs stabilized graphenes as supercapacitor electrodes were systematically studied in aqueous electrolytes, 1 M H₂SO₄ and 6 M KOH, as well as in ionic liquid electrolyte 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄).

Experimental section

Sample preparation

Graphite oxide was synthesized from natural flake graphite (crystalline, 300 mesh, Alfa Aesar) using a modified Hummers method [43]. Neutral conjugated polymers hoP and coP (Figure 1) were synthesized according to a previously

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