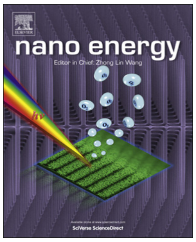
Nano Energy (2013) 2, 403–411

Available online at www.sciencedirect.com
SciVerse ScienceDirect
journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

Outstanding performance of activated graphene based supercapacitors in ionic liquid electrolyte from −50 to 80 °C

Wan-Yu Tsai[a], **Rongying Lin**[a], **Shanthi Murali**[c], **Li Li Zhang**[c], **John K. McDonough**[d], **Rodney S. Ruoff**[c], **Pierre-Louis Taberna**[a], **Yury Gogotsi**[d],*, **Patrice Simon**[a,b],**

[a]*Université Paul Sabatier, CIRIMAT UMR CNRS 5085, 118 route de Narbonne, 31062 Toulouse, France*
[b]*Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*
[c]*Department of Mechanical Engineering and the Materials Science and Engineering Program, The University of Texas at Austin, One University Station C2200, Austin, TX 78712, United States*
[d]*Department of Materials Science and Engineering & A.J. Drexel Nanotechnology Institute, Drexel University, 3141 Chestnut St., Philadelphia, PA 19104, United States*

Received 8 October 2012; received in revised form 7 November 2012; accepted 12 November 2012
Available online 22 November 2012

KEYWORDS
Electrochemical capacitors;
Activated graphene;
Ionic liquid mixture;
Wide temperature range

Abstract

High specific surface area (SSA ~2000 m^2/g) porous KOH-activated microwave exfoliated graphite oxide ('a-MEGO') electrodes have been tested in a eutectic mixture of ionic liquids (1:1 by weight or molar ratio N-methyl-N-propylpiperidinium bis(fluorosulfonyl)imide (PIP_{13}-FSI) and N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR_{14}-FSI)) as electrolyte for supercapacitor applications. By optimizing the carbon/electrolyte system, outstanding capacitive performance has been achieved with high capacitance (up to 180 F/g) and wide electrochemical window (up to 3.5 V) over a wide temperature range from −50 °C to 80 °C. This is the first demonstration of a carbon-ionic liquid system capable of delivering capacitance in excess of 100 F/g below room temperature. The excellent electrochemical response of the proposed couple shows that optimization of the carbon/electrolyte interface is of great importance for improving capacitive energy storage.

Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, store electrical charges between electrode materials and electrolyte ions by electrostatic

---

*Corresponding author. Tel.: +1 215 895 6446.
**Corresponding author. Tel: +33 5 615 568 02
E-mail addresses: simon@chimie.ups-tlse.fr (P. Simon), Gogotsi@drexel.edu (Y. Gogotsi).

2211-2855/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.nanoen.2012.11.006

attractions. Supercapacitors had their debut mainly in CMOS memory back-up and are now widely used in power electronics for peak power shaving and back-up supplies (as support for power disruption). Today, one of the most promising applications is their use in transportation (in hybrid-electric vehicles (HEVs) in particular) for harvesting braking energy and for faster start-up of the engine [1-3]. Their increasing use for energy storage is due to a number of factors including (i) their high power densities ($>$10 kW/kg), (ii) moderate energy density ($\sim$5-6 Wh/kg), (iii) that they can be fully charged/discharged in a matter of seconds [4,5], (iv) the cost competitiveness of the materials that they are comprised of, (v) high charge/discharge efficiency, and (vi) their high cycle life, which is generally longer than the life of the device being powered.

Generally, EDLCs are made up of two symmetrical activated carbon electrodes that display symmetric charge/discharge power capability over the complete range of potential operation (i.e., from the maximum rated voltage to near zero). Carbon/carbon supercapacitors can be used over the complete voltage range without damage for at least 1 million cycles [6]. Carbon-based electrodes are of great interest because they are light, of moderate cost, abundant, easy to process, and possess high electronic conductivity and high specific surface area (yielding high charge storage). A variety of different carbon nanostructures can be produced that have very high surface areas and a wide variety of physical properties, which allows targeting of different types of applications. Templated carbons [7], carbide-derived carbons (CDCs) [8-10], 'onion-like' carbons (OLCs) [11], carbon fabrics (cloth, fibers) [12], nanotubes [13], activated graphene [14] and nanohorns [15] have been used as electrodes for EDLC applications [16].

Batteries have much higher energy densities (up to 250 Wh/kg for Li-ion) than current commercial supercapacitors (5 Wh/kg) [17]. One approach to increase energy density of supercapacitors is with ionic liquid electrolytes that offer better electrochemical stability than that of the aqueous (1.23 V) and organic (2.7 V) electrolytes currently used. Ionic liquids (IL) - salts (mainly, organic) that are liquid at room temperature - are being explored as electrolytes for Electrical Energy Storage (EES) systems owing to their high thermal (up to 350 °C) and electrochemical (up to 6 V) stability [18]. Their high heat capacity, a large cohesive energy, and negligible vapor pressure at elevated temperatures make them safe and non-flammable electrolytes. This is especially important in energy storage applications when devices need to perform under extreme temperature conditions that can raise/cause safety issues. The *raison d'être* for exploring eutectic mixtures of ionic liquids is their large stable liquidus temperature range (the span of temperatures between the freezing point and boiling point of a liquid, such as from $-80\,^{\circ}$C to $\geq 250\,^{\circ}$C). The size and symmetry of cations strongly influence the melting points of ionic liquids. Usually, one of the two pairing ions (usually the cation) is particularly large and possesses a low degree of symmetry, leading to inefficient packing of the large irregular cations with small charge-delocalized anions, which is why organic salts have a reduced crystal lattice energy and hence a lower melting point compared to inorganic salts [19]. Binary and ternary eutectic mixtures have been studied for EES systems. Binary eutectic systems first appeared with the discovery by Wilkes et al. in 1982 of a MeEtImCl/$AlCl_3$ molten salt mixture that was liquid over a wide range of compositions and to temperatures as low as $-98\,^{\circ}$C for a composition of 67% $AlCl_3$ [20]. Other binary systems have been investigated by Hou et al. [21] using imidazolium-based ILs with organic salts. Every et al. [22] reported a eutectic mixture of pure ILs (mixing ethyl-methyl-immidazolium tri-fluorosulfonyl-imide (EMI-TFSI) and EMI-$CF_3SO_3^-$ (triflate)) with no evidence of a melting point, indeed only a glass transition was observed. Pyrrolidinium-based mixtures with TFSI-FSI-based ILs were also found by differential scanning calorimetry to form eutectic mixtures [23]. Deeper eutectics ($-95\,^{\circ}$C) were however observed to be mainly in mixtures of a common cation with two different anions compared to eutectics ($-25\,^{\circ}$C) in mixtures of a common anion with two different cations. Other binary systems include IL-LiX mixtures as electrolytes for battery applications [24-26]. Henderson et al. [24] reported decreasing the eutectic temperatures of pyrrolidinium-based ILs by using different alkyl chain lengths and Li salt concentrations.

As reported before, we have designed IL mixtures with exactly the same anion (FSI) but two different cations: piperidinium (PIP) and pyrrolidinium (PYR) [27]. These cations have the same molecular weight and the same number of atoms of the same nature, with the only difference being their cation molecular structure, namely a five-member (piperidinium) or six-member (pyrrolidinium) heterocycle. Methyl+propyl substituent groups (total of 4 carbons on side chains) are used for synthesizing the PIP-based cation and methyl+butyl substituent groups (total of 5 carbons on side chains) for synthesizing the PYR-based cation. The concept is to maintain similar intermolecular interactions due to the similar constituent atoms of the two cations, while also increasing disorder and asymmetry among the cations to hinder lattice formation to lower the melting point, but still maintaining good miscibility. Amongst common anions such as hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), bis(trifluorosulfonyl)imide ($TFSI^-$) and bis(fluorosulfonyl)imide (FSI^-) anions, the imides ($TFSI^-$ and FSI^-) have emerged as popular alternatives to the PF_6^- and BF_4^- anions due to the susceptibility of the PF_6^- and BF_4^- anions to hydrolysis, leading to the production of hazardous hydrogen fluoride [28-32]. This is why hydrophobic $TFSI^-$ and FSI^- anions are increasingly being studied as electrolytes for energy storage [33-35]. The FSI^- ion has been selected to be the anion for the electrolyte used in this study due to its generally higher conductivity and lower viscosity as compared to the $TFSI^-$ ion when paired with the same cation [36], because of the smaller size and hence higher mobility of the FSI^- ion. Cations were chosen by comparing their stability. The electrochemical stability of commonly used cations of ILs decreases in the order of Ammonium $\approx$ Piperidinium $\geq$ Pyrrolidinium $>$ Imidazolium [37]. Hence, cations with functional groups of pyrrolidinium (PYR) and piperidinium (PIP) with relatively higher electrochemical stability were explored.

A eutectic mixture composed of (1:1 by weight or molar ratio) N-methyl-N-propylpiperidinium bis(fluorosulfonyl)imide (PIP_{13}-FSI) and N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR_{14}-FSI) was prepared and used as electrolyte. The measured melting points of constituents of this IL mixture were $6\,^{\circ}$C (PIP_{13}-FSI) and $-18\,^{\circ}$C (PYR_{14}-FSI), in good agreement with