Materials Chemistry and Physics 148 (2014) 48–56

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Stretchable supercapacitors based on highly stretchable ionic liquid incorporated polymer electrolyte

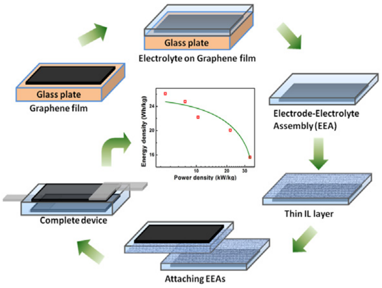
P. Tamilarasan, S. Ramaprabhu*

Alternative Energy and Nanotechnology Laboratory (AENL), Nano Functional Materials Technology Centre (NFMTC), Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

HIGHLIGHTS

- A stretchable supercapacitor has been fabricated using stretchable electrolyte.
- Here ionic liquid incorporated polymer plays dual role as electrolyte and stretchable support.
- The developed device shows low equivalent series resistance.
- The device has specific capacitance of 83 F g^{-1}, at the specific current of 2.67 A g^{-1}.
- The energy density and power density of 25.7 Wh kg^{-1} and 35.2 kW kg^{-1}, respectively.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 September 2013
Received in revised form
26 June 2014
Accepted 9 July 2014
Available online 1 August 2014

Keywords:
Polymers
Nanostructures
Chemical synthesis
Evaporation
Mechanical properties
Electrochemical techniques

ABSTRACT

Mechanical stability of electrolyte in all-solid-state supercapacitor attains immense attention as it addresses safety aspects. In this study, we have demonstrated, the fabrication of stretchable supercapacitor based on stretchable electrolyte and hydrogen exfoliated graphene electrode. We synthesized ionic liquid incorporated stretchable Poly(methyl methacrylate) electrolyte which plays dual role as electrolyte and stretchable support for electrode material. The molecular vibration studies show composite nature of the electrolyte. At least four-fold stretchability has been observed along with good ionic conductivity (0.78 mS cm^{-1} at 28 °C) for this polymer electrolyte. This stretchable supercapacitor shows a low equivalent series resistance (16 Ω) due to the compatibility at electrode–electrolyte interface. The performance of the device has been determined under strain as well.

1. Introduction

All-solid-state supercapacitors have great advantage as it offers mechanical robustness. Several attempts are experimented towards a high performance, mechanically robust, electrochemically stable supercapacitors [1–3]. In this regards, solid state electrolytes, especially gel polymer electrolytes, attain more interest as they offer excellent mechanical stability and ionic conductivity [4–10]. Here, mobile phase is imbibed in host polymer, where polymer matrix gives mechanical stability and the mobile phase gives ionic conductivity to the electrolyte. In general, gel polymer electrolytes contain aqueous or organic solutions of suitable salts. Here, aqueous solutions limit the potential window of the electrolyte to the maximum of 1.23 V, whereas the flammability of organic solvents make the device non-robust and results in safety issues. Ionic liquids (ILs) attain more importance as electrolytes for energy

---

* Corresponding author.
E-mail address: ramp@iitm.ac.in (S. Ramaprabhu).

http://dx.doi.org/10.1016/j.matchemphys.2014.07.010
0254-0584/© 2014 Elsevier B.V. All rights reserved.

storage applications due to their wide operating potential, high ionic conductivity, wide liquid range along with high thermal and electrochemical stability [11–13]. In addition, ILs are generally known as a unique mixture of 100% salt and 100% solvent, which accounts electrolyte depletion problem. Hence, conventional salt based electrolytes have been replaced by ionic liquids for superior performance. The scientific community have employed ionic liquid as mobile phase in gel polymer electrolyte. Recently, Ye et al., have reviewed the progress and development in various aspects of ionic liquid based polymer electrolytes [14]. Since, ionic liquid ions are made up of bulk organic moieties, the interaction with other organic molecules, like solvents, polymers, gases etc., is unique. In ionic liquid based gel polymer electrolyte, the ionic conductivity, electrochemical stability and mechanical properties, depend on the interaction between the host polymer and the mobile phase [15,16]. Several host polymers have been studies including, polyvinylidene fluoride (PVDF), polyvinylidene fluoride–hexafluoropropylene (PVDF–HFP), polyacrylonitrile (PAN), polyethylene oxide (PEO) and poly (methyl methacrylate) (PMMA) [17]. Among them, PMMA and its co-polymers are well known for their mechanical strength with good electrochemical properties [5–8,18]. Duluard et al., made a detail investigation on PMMA based gel polymer electrolytes with ionic liquid as mobile phase [19].

In the recent past, graphene grabbed the interest of material science community, due to its unique physical, electrical and electrochemical properties, which promote graphene as a better choice for energy storage applications, especially in supercapacitors [20–22]. The electrode–electrolyte interface plays a major role in all-solid-state supercapacitors as it is one of the factor decides the equivalent series resistance (R_{ESR}) of the device. Hence, graphene based supercapacitors with mechanically robust, highly conductive electrolytes, which can make unique interface with electrode, are anticipated to have potential advantages. Graphene based all-solid-state supercapacitors with ionic liquid incorporated PVDF–HFP [23,24], PEO [24], PAN [25,26] electrolyte have been reported. But, much studies have not been done on ionic liquid incorporated PMMA as electrolyte for graphene based supercapacitor though it has good mechanical, thermal and electrochemical properties [19].

In this study, we have prepared [BMIM][TFSI] incorporated PMMA electrolyte (PMMA/[BMIM][TFSI]) and studied its properties. PMMA/[BMIM][TFSI] (1:2) electrolyte exhibits high ionic conductivity (0.78 mS cm^{-1} at 28 °C) and has good transparency in visible range (>98%). The electrolyte is a highly stretchable film with at least four-fold stretchability. From the inspiration drawn from the recent report on buckled single walled carbon nanotube based stretchable supercapacitors, [27–29] we fabricated stretchable supercapacitor device with highly stretchable polymer electrolyte (PMMA/[BMIM][TFSI]) and hydrogen exfoliated graphene (HEG) electrode and demonstrated. To the best of our knowledge, this is the first study on supercapacitor based on PMMA/[BMIM][TFSI] electrolyte and graphene electrode.

2. Experimental section

2.1. Material synthesis

PMMA/[BMIM][TFSI] was synthesized as follows: 300 mg of PMMA (M.W = 550,000 g mol^{-1}) was dissolved in 10 ml of acetone by stirring at 1000 rpm for 30 min, which resulted in a transparent gel. Acetone has been chosen as solvent medium, since PMMA has good solubility and the solution has better miscibility with [BMIM][TFSI] ionic liquid. Appropriate amount of [BMIM][TFSI] was added in to the gel under stirring. Further the solution was stirred for 2 h at 1000 rpm. A transparent gel was obtained which was casted on a bare or graphene coated glass surface at ambient conditions for 24 h. Then the film was removed from the surface and dried under vacuum (400 mbar) and room temperature before use for further analysis. A solid state blending route is also employed to obtain PMMA/[BMIM][TFSI] blend, where PMMA powder was mechanically mixed with [BMIM][TFSI] using mortar and pestle. But the obtained blend was inhomogeneous at low IL to polymer ratios as IL interacts with polymer rapidly.

Graphene was prepared from graphite by a two step top–down approach, reported elsewhere [30]. Briefly, graphite was oxidized using water-free mixture of conc. H_2SO_4, $NaNO_3$ and $KMnO_4$ (Hummers' method [31]) to result graphite oxide (GO). Graphene was obtained by thermal exfoliation of GO at 200 °C under hydrogen atmosphere in a tubular furnace and labelled as HEG. The as-exfoliated HEG has the surface area as high as 443 $m^2\ g^{-1}$, with 1.64×10^3 S m^{-1} of electrical conductivity with 14.6 C/O ratio [32].

2.2. Fabrication of supercapacitor

The stretchable supercapacitor has been fabricated as follows: HEG was dispersed in the solution of 5 wt % PMMA/[BMIM][TFSI] blend as a binder in acetone medium under ultrasonic irradiation. We chose acetone medium because PMMA/[BMIM][TFSI] blend is either insoluble or phase separated in most of the solvents, other than acetone. But, graphene with large amount of residual functional groups cannot be dispersed in acetone. Hence, PMMA/[BMIM][TFSI] was first dissolved in acetone followed by the addition of required amount of graphene. We found a good dispersibility of graphene in this solution, which may be attributed to the deposition of PMMA/[BMIM][TFSI] blend on graphene surface. The dispersion was coated (~1 mg cm^{-2}) on a smooth glass surface. The PMMA/[BMIM][TFSI] electrolyte gel was poured on graphene film (50 mg cm^{-2}) and allowed to evaporate acetone for 24 h at ambient conditions. Then the electrode–electrolyte assembly (EEA) was removed from the surface. A thin layer of [BMIM][TFSI] was coated on electrolyte sides of two EEAs and the assemblies were joined as shown in Scheme 1. The device was dried for 1 h under vacuum (400 mbar) at room temperature in order to remove residual solvent molecules. Here, graphene film itself plays a role as current collector. In addition, electrolyte acts as support for electrode material, unlike the previous reports [27–29]. Stainless steel foils were used as electrical connections. This device was denoted as HEG – PMMA/[BMIM][TFSI] supercapacitor.

2.3. Characterization techniques

The structural analysis of synthesized materials was done by X'Pert Pro PANalytical powder X-ray diffractometer. The morphological analysis was carried out by electron microscopy (FEI Quanta and Technai G-20). WITec alpha 300 Confocal Raman spectrometer, equipped with a Nd:YAG laser as the excitation source, has been employed to acquire Raman spectra while Fourier transform infrared spectra were acquired by Perkin–Elmer FT-IR spectrometer. The transmittance studies were carried our using JASCO corp., V-570 spectrophotometer. Electrochemical behaviour was studied using CH instrument (CHI608C).

3. Results and discussions

3.1. Morphological analysis

The cross-sectional view of FESEM image of HEG – PMMA/[BMIM][TFSI] supercapacitor (Fig. 1) reveals the graphene electrode thickness of ~150–200 μm. The cross-sectional view of roughly tore PMMA/[BMIM][TFSI] shows a smooth morphology. It is a consequence of microscopic elastic deformation of the film which gives