



# Highly efficient gel polymer electrolytes for all solid-state electrochemical charge storage devices

P. Pal, A. Ghosh\*

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India



## ARTICLE INFO

### Article history:

Received 24 February 2018

Received in revised form

12 April 2018

Accepted 2 May 2018

Available online 4 May 2018

### Keywords:

Gel polymer electrolytes

Ionic conductivity

Supercapacitor

Lithium ion battery

## ABSTRACT

Gel polymer electrolytes are prepared using poly(vinylidene fluoride-co-hexafluoropropylene) polymer matrix and 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ionic liquid and also by adding lithium bis(trifluoromethanesulfonyl)imide salt and plasticizer mixture (ethylene carbonate: propylene carbonate in the ratio 1:1). Thermal and electrical properties of these electrolytes are first investigated. The electrical conductivity of these electrolytes is analyzed over a wide frequency range using a universal power law coupled with modified Poisson-Nernst-Planck model for electrode polarization. All electrolytes show excellent thermal stability up to 340 °C, high ionic conductivity ( $\sim 1 \times 10^{-3} \text{ S cm}^{-1}$ ) and wide potential window ( $\sim 4.0 \text{ V}$ ). Supercapacitors are fabricated with these electrolytes using activated carbon as electrodes and their electrochemical properties are studied. The cyclic voltammetry curves show almost box-like shape corresponding to an ideal and reversible capacitive characteristic. The specific capacitance of supercapacitors increases with the addition of lithium salt and plasticizer mixture. The cycle stability of these supercapacitors up to 4000 cycles confirms their electrochemical stability. A lithium ion coin cell is also fabricated using electrolytes containing plasticizer mixture. At ambient temperature, the fabricated cell delivers high specific discharge capacity ( $\sim 165.8 \text{ mAh g}^{-1}$ ) for the first discharge cycle at a constant current rate  $C/12$ .

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Nowadays, a rapid growing demand has been received from our modern society to develop high performing solid-state electrochemical charge storage devices operating at ambient condition due to the limited source of fossil fuels and global warming, etc. Over last few years, researchers have delivered their efforts in developing alternative green energy storage devices, such as polymer based supercapacitors, lithium ion batteries, etc. [1–4]. There are some basic differences in their charge storage mechanisms of polymer supercapacitors and lithium ion batteries. Supercapacitors store charge through electrostatic interaction between electrode surfaces and charge carriers of polymer electrolytes, whereas lithium ion batteries store energy via electrochemical reactions [5]. The cycle life of supercapacitors is higher than that of batteries [6], while batteries can store more energy than supercapacitors. Currently, gel polymer electrolytes (GPEs) have received extensive attention for their applications in

energy storage devices as an electrolyte/separator due to their higher ionic conductivity ( $> 1 \times 10^{-3} \text{ S cm}^{-1}$ ) at ambient temperature, wider electrochemical voltage window and better stability of electrode-polymer interface than that of liquid electrolytes [7,8]. Besides device applications, the studies of  $\text{Li}^+$  ion conduction mechanism in GPEs are an important aspect for investigation [9–11].

In general, among various polymer matrices [12–17], poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-HFP)] copolymer is the most widely studied host polymer matrix used for the preparation of high performance GPEs, because the crystalline part P(VdF) of this polymer supports the mechanical property and amorphous part P(HFP) helps to trap the liquid electrolytes [16,18]. Furthermore, to improve the ionic conductivity, interfacial stability, thermal/mechanical stability, flexibility and electrochemical voltage stability different approaches, such as addition of ceramic fillers ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , graphene oxide) [16,17,19], blending with other polymers [20], aqueous and organic liquid electrolyte consisting of different salts and polar solvents [21–24], etc. have been adopted. However, development of high performance gel polymer electrolytes has been an active research area. Recently, ionic liquids

\* Corresponding author.

E-mail address: [sspag@iacs.res.in](mailto:sspag@iacs.res.in) (A. Ghosh).

(ILs) have received considerable attention as an electrolyte component or single liquid electrolyte due to their high ionic conductivity, good electrochemical stability, wide electrochemical voltage range, non-flammability, non-volatility, negligible vapor pressure and environmental compatibility [24,25]. It is important to note that ILs plays dual roles in polymer electrolytes such as supplier of additional charge carriers as well as critical role of plasticizers [26,27].

In this paper, we have prepared GPEs using copolymer P(VdF-HFP) and 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (PMIMTFSI) ionic liquid. We have investigated the effect of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt and a mixture of plasticizers ethylene carbonate (EC): propylene carbonate (PC) on physicochemical properties and electrochemical performance of the GPEs. We have fabricated three supercapacitor cells using gel polymer electrolytes and activated carbon (AC) as an electrode material and studied electrochemical performance of these supercapacitors. Finally, we have also fabricated a lithium ion battery using best performing gel electrolyte in the configuration: graphite//gel electrolyte//LiFePO<sub>4</sub> and studied its electrochemical performance.

## 2. Experimental

### 2.1. Materials

Poly(vinylidene fluoride-hexafluoropropylene) (P(VdF-HFP), having average molecular weight ~455,000 g/mol) was used as a host polymer. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, ≥ 99.0%) was used as salt. The used ionic liquid was 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (PMIMTFSI, ≥ 98.0%) which offers low viscosity (40 cP at 30 °C) [28]. Plasticizers were ethylene carbonate (EC, anhydrous 99.0%) and propylene carbonate (PC, anhydrous 99.7%). All chemicals were procured from Sigma Aldrich and stored inside the argon gas filled glove box (mBRAUN LAB star ECO) with <0.5 ppm H<sub>2</sub>O and <0.5 ppm O<sub>2</sub>. These chemicals were used without further purification. Acetone (Merck purity ≥ 99.5%) was used for the preparation of the polymer electrolyte. N-methyl-2-pyrrolidone (NMP, analytical grade, Sigma Aldrich), polyvinylidene fluoride as a binder (PVdF, powder, MTI Corp.), acetylene carbon black (CB, MTI Corp.), active cathode material LiFePO<sub>4</sub> powder (<5 μm particle size, Sigma Aldrich), anode material graphite powder (MTI Corp.), activated carbon (AC, TCI Chemicals, Japan), flexible graphite sheets with 0.5 mm thickness (NICKUNJ Eximp Entp P LTD) aluminum (Al) and copper (Cu) foil (MTI Corp.) were used to prepare the supercapacitor and lithium ion battery electrodes.

### 2.2. Preparation of gel polymer electrolytes (GPEs)

The ionic liquid based P(VdF-HFP) gel polymer electrolyte films of following compositions were prepared using 'standard solution cast' technique:

- (i) PMIMTFSI/P(VdF-HFP) with ratio 80:20 (w/w) (**GPE-1**),
- (ii) 0.4 M LiTFSI in PMIMTFSI/P(VdF-HFP) with ratio 80:20 (w/w) (**GPE-2**) and
- (iii) 0.4 M LiTFSI in PMIMTFSI/P(VdF-HFP)/(EC:PC) with ratio 60:20:20 (w/w) (**GPE-3**).

First, the host polymer P(VdF-HFP) was dissolved in acetone. The liquid electrolyte solutions were prepared by dissolving 0.4 M LiTFSI in PMIMTFSI and 0.4 M LiTFSI in PMIMTFSI/(EC:PC) (60:20). 20 wt% ionic liquid of the total amount of PMIMTFSI was partially substituted by a mixture of plasticizers EC and PC in the ratio 1:1 v/

v. The ionic liquid PMIMTFSI or LiTFSI/PMIMTFSI or LiTFSI/PMIMTFSI/EC:PC solution was mixed with the P(VdF-HFP)/acetone solution under stirring condition. The weight ratio of liquid electrolyte to host polymer P(VdF-HFP) was fixed at 80:20 (w/w). The solutions became viscous and homogeneous after stirring for 5–6 h due to evaporation of the solvent in ambient condition. Finally, the solutions were cast onto polytetrafluoroethylene containers to get homogeneous and free standing films by slow evaporation of the solvent at ambient condition. The thickness of the prepared free-standing polymer films was in the range from 0.35 mm to 0.5 mm.

### 2.3. Fabrication of supercapacitors

The activated carbon (AC) and acetylene carbon black (CB) powders were kept in vacuum overnight at ~90 °C before use. The electrodes for supercapacitor were prepared by coating a N-methyl-2-pyrrolidone (NMP) based homogeneous slurry containing AC powder, acetylene carbon black and PVdF in the ratio of 70:10:20 (w/w) on a flexible graphite sheet in a desktop coating machine (Ranga Techno Impex, India). After coating on the graphite sheet, the electrodes were dried at 90 °C under vacuum for 1 day. After drying at 90 °C, the electrodes were cut into 1 cm × 1 cm square shape (average area ~1 cm<sup>2</sup>). The average thickness of electrodes was about 150–160 μm for activated carbon mass loading of about 1.5 mg/cm<sup>2</sup>. The supercapacitors were fabricated by sandwiching gel polymer electrolytes between two symmetrical carbon electrodes and are denoted as **Cell-1**: AC||GPE-1||AC, **Cell-2**: AC||GPE-2||AC and **Cell-3**: AC||GPE-3||AC.

### 2.4. Fabrication of lithium ion battery (coin cell)

For lithium ion cell fabrication, LiFePO<sub>4</sub> powder was used as an active material for cathode due to its better cycle ability, low toxicity, low cost, and high thermal stability. LiFePO<sub>4</sub> cathode was prepared by coating on aluminum (Al) foil with a N-methyl-2-pyrrolidone (NMP) based homogeneous slurry containing LiFePO<sub>4</sub> powder, acetylene carbon black and PVdF in the ratio of 80:10:10 (w/w). After coating, the electrodes were dried at 100 °C under vacuum for 1 day. Similarly, negative electrode was prepared by coating on copper (Cu) foil with a NMP based homogeneous slurry of graphite powder, acetylene carbon black and PVdF in the ratio of 75:15:10 (w/w). After coating, the graphite electrodes were dried at 100 °C under vacuum for 1 day. The cathode and anode were cut into circular disc area of ~1.13 cm<sup>2</sup>. A graphite/GPE-3/LiFePO<sub>4</sub> CR2032 coin cell (MTI Corp.) was assembled in argon-filled glove box with H<sub>2</sub>O < 0.5 ppm O<sub>2</sub> < 0.5 ppm. Due to maximum ionic conductivity, GPE-3 was chosen to fabricate the coin cell of configuration graphite//GPE-3//LiFePO<sub>4</sub>.

### 2.5. Physicochemical characterization of gel polymer electrolytes

X-ray diffraction (XRD) patterns of the polymer electrolytes were recorded at room temperature in an X-ray diffractometer (Bruker AXS, model D8 advance) using Cu-K<sub>α</sub> radiation (λ = 0.154 nm) with a scan rate of 0.3° s<sup>-1</sup> and a step-size of 0.02° over the 2θ range of 10°–80°.

The differential scanning calorimetry (DSC) experiments of the polymer electrolytes were performed in a DSC instrument (TA, model Q2000) in N<sub>2</sub> atmosphere using a heating rate of 10 °C min<sup>-1</sup> from -60° to 200 °C in the heating cycle. The weights of the sample were maintained in the range of 7–10 mg and empty aluminum pan was used as a reference. The thermo-gravimetric (TGA) experiments of the polymer electrolytes were done in a TGA instrument (TA, model Q600) in N<sub>2</sub> atmosphere using a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> flowing at 50 cm<sup>3</sup>/min from 30° to 500 °C.

Download English Version:

<https://daneshyari.com/en/article/6602666>

Download Persian Version:

<https://daneshyari.com/article/6602666>

[Daneshyari.com](https://daneshyari.com)