INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

Available online at www.sciencedirect.com

ScienceDirect

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

Synthesis and optimization of new polymeric ionic liquid poly(diallydimethylammonium) bis(trifluoromethane sulfonyl)imde based gel electrolyte films

Xingcheng Hu [a,1], *Ravi Muchakayala* [a,1], *Shenhua Song* [a,*], *Jingwei Wang* [a], *Jianjun Chen* [b], *Manlin Tan* [b,**]

[a] *Shenzhen Key Laboratory of Advanced Materials, Department of Materials Science and Engineering, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen, 518055, China*

[b] *Research Institute of Tsinghua University in Shenzhen, Shenzhen, 518057, China*

ARTICLE INFO

Article history:
Received 22 November 2017
Received in revised form
28 December 2017
Accepted 3 January 2018
Available online xxx

Keywords:
Polymeric electrolyte
Polymeric ionic liquid
Ionic conductivity
Electrochemical stability window

ABSTRACT

Polymeric ionic liquid-based gel electrolyte films are a new generation of electrolyte materials for flexible energy storage device applications. In this work, Li-ion conducting gel electrolyte films are prepared with the polymeric ionic liquid poly(diallydimethylammonium) bis(trifluoromethane sulfonyl)imide (poly(DADMATFSI)) as the host polymer and the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt as the dopant. The crystalline nature, thermal stability, ionic conductivity and electrochemical stability window of the polymeric electrolyte films are analyzed by various characterization techniques. It is found that the polymeric electrolyte films exhibit high flexibility and excellent thermal stability. Their room-temperature electrical conductivity increases with increasing LiTFSI concentration and reaches a high value of 1.00×10^{-3} S cm^{-1} at 20 wt% LiTFSI. The ionic transference numbers of the polymeric electrolyte films are in the range of 0.98–0.99, indicating that they are perfect ion conductors. Finally, the electrochemical stability window of the 20 wt% LiTFSI-doped polymeric electrolyte film is determined as approximately 6 V, which is a promising value for flexible energy storage device applications.

Introduction

Currently, the flexible energy storage device is attracting much attention due to its widespread small scale electronic device applications in the modern society. All flexible energy storage devices, such as lithium batteries, supercapacitors and fuel cells, are composed of two electrodes along with electrolyte. The performance of the devices completely depends on these components [1–3]. Most of researchers have been focusing their attention on the development of new flexible electrode materials and optimizing their properties for device applications [4–7].

* *Corresponding author.*
** *Corresponding author.*
E-mail addresses: shsong@hit.edu.cn, shsonguk@aliyun.com (S. Song), tanml@tsinghua-sz.org (M. Tan).
[1] Co-first author.

https://doi.org/10.1016/j.ijhydene.2018.01.015
0360-3199/

However, flexible and good electrolyte materials are also required for the fabrication of highly flexible devices. Therefore, many research efforts have been focused on the development of polymer-based solid electrolytes for energy storage applications. Generally, solid polymer electrolytes (SPEs) are prepared in chemical methods by using host polymer and metal salt. The SPEs possess several advantages, such as good thermal stability, high mechanical strength, leakage proof, less reactivity and better manufacturing integrity [8,9]. However, the SPEs offer a low ionic conductivity ranging from 10^{-7} to 10^{-5} S cm^{-1} at room temperature, which is not high enough for practical device applications. To solve this problem and improve the room-temperature ionic conductivity of SPEs, various approaches have been adopted, such as blending, co-polymerization, incorporation of inorganic fillers and plasticizing. Based on the prepared materials and their approach, these polymer electrolytes have different names, such as complex, blend, nanocomposite and gel polymer electrolytes [10–12]. Some researchers prepared various flexible polymer electrolytes and clearly analyzed their properties [13–18]. Each type of polymer electrolyte has its own advantages and disadvantages. Among them, the gel polymer electrolyte systems receive much attention since they exhibit promising characteristics and behave like both liquid and solid. The gel polymer electrolytes have good physical, chemical, thermal, electrical and electrochemical properties. They are generally in the form of films or membranes and their transport properties are similar to those of liquid electrolytes along with intrinsic mechanical characteristics and safety features. Therefore, they are also called the hybrid electrolyte systems [19–22]. The gel polymer electrolytes have a flexible nature and smooth surface so that they can contact well with the electrodes, thereby increasing the device performance. Furthermore, the gel polymer electrolytes can reduce the size and weight of devices significantly by avoiding the strict shielding. Some researchers have prepared gel polymer electrolytes based on host polymer, lithium salt and organic plasticizer (EC, PC, DEC, etc.) and their properties were deeply analyzed [23–27]. It is seen that lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) doped polymer electrolyte exhibits better properties than others because of its bigger TFSI anion size [28–30]. In the present study, the LiTFSI was therefore selected as the dopant salt for the development of gel polymer electrolytes. However, the organic plasticizer-incorporated gel polymer electrolytes are highly volatile, corrosive and flammable, thereby limiting their applications in environment-friendly flexible energy storage devices [23,25,31,32]. To overcome these difficulties, there are two approaches: (1) ionic liquids (e.g., 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf), 1-butyl-3-methylimidazolium nonafluorobutanesulfonate (BMImNfO), 1-methyl-3-methylimidazolium-bis(trifluoromethyl-sulfonyl)imide (EMI-TFSI), 1-methyl-1-propylepyrrolidinium bis(trifluoromethylsulfonyl)azanide (MPPyrr-TFSA), and 1,2-dimethyl-3-propylimida zolium bis(trifluoromethylsulfonyl)imide (DMPImTFSI), etc.) are used as the plasticizer to develop safe and environment-friendly gel polymer electrolytes for flexible energy storage device applications [33–37]; (2) polymeric materials synthesized by using different chemical methods are used as the host polymer for the development of gel polymer electrolytes. These synthesized polymeric materials are a new class of polymer because their chemical structure contains both polymer and ionic liquid, and hence they are also termed the polymeric ionic liquids (PILs). Due to the special chemical nature of the polymeric ionic liquid, it exhibits some interesting properties, such as high solubility, high ionic conductivity and chemical compatibility towards other materials. Consequently, the development of polymeric ionic liquids is a growing research topic in polymer science for industrial applications [38,39]. For instance, some researchers have successfully synthesized polymeric ionic liquids with different anions, which were used as the host materials in the development of electrolyte films for different applications [40,41]. However, to the best of our knowledge, only a few research reports are available in the poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide [poly(DADMATFSI)] based gel polymer electrolytes [42–44]. The poly(DADMTFSI) works as the host polymer, i.e., it provides the mechanical integrity due to its polymer chain entanglements, and also provides $TFSI^-$ ions for conduction. Hence, the aim of the present study is to prepare and optimize the novel polymeric ionic liquid poly(DADMATFSI) based gel electrolyte films for flexible energy storage device applications. For achieving it, firstly we synthesized the polymeric ionic liquid poly(DADMATFSI) by using an anion exchange method and evaluated its purity by using different characterization techniques. Secondly, we developed gel electrolyte films by using the poly(DADMATFSI) as the host polymer and the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt as the dopant. Finally, all the prepared gel electrolyte films were analyzed by various techniques to identify the optimum composition for flexible energy storage device applications.

Experimental details

Synthesis of polymeric ionic liquid

Polymeric ionic liquids can be synthesized by two methods: polymerization and anion exchange reaction [45–47]. Each method has its own merits and drawbacks. Compared with the polymerization, the anion exchange reaction is fast, less expensive and simple. Hence, in the present study, the poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl) imide polymeric ionic liquid was synthesized by anion exchange reactions as shown in Fig. 1a. The predetermined quantities of commercially available lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI, Mw 287.09, Aldrich, 99%, China) and poly(diallyldimethylammonium) chloride (poly(DADMACl), Aldrich, average Mw 400,000–500,000, 20 wt % in H_2O, China) were separately dissolved in double distilled water. The poly(DADMACl) solution was taken in 250 ml round bottom conical flask and the LiTFSI solution was added dropwisely to mix with the poly(DADMACl) solution. Then the mixed solution was homogenized with magnetic stirring at a temperature of 25 °C. After stirring for 10 min, the anion exchange reaction occurred, producing white precipitates on the bottom of the conical flask. The precipitates were separated by vacuum filtration and washed several times with distilled water to remove the residual LiCl units, and then dried for 24 h at 120 °C in a vacuum oven to obtain the white poly(-DADMATFSI) polymeric ionic liquid powder. The $AgNO_3$

Please cite this article in press as: Hu X, et al., Synthesis and optimization of new polymeric ionic liquid poly(diallydimethylammonium) bis(trifluoromethane sulfonyl)imde based gel electrolyte films, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.01.015