



# Electrochemical performance of polymer electrolytes based on Poly (vinyl alcohol)/Poly(acrylic acid) blend and Pyrrolidinium ionic liquid for lithium rechargeable batteries



Savitha Thayumanasundaram<sup>a,\*</sup>, Vijay Shankar Rangasamy<sup>a</sup>, Jin Won Seo<sup>b</sup>, Jean-Pierre Locquet<sup>a</sup>

<sup>a</sup> Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D, B-3001, Belgium

<sup>b</sup> Department of Materials Engineering, Kasteelpark Arenberg 44, KU Leuven, B-3001, Belgium

## ARTICLE INFO

### Article history:

Received 31 January 2017

Received in revised form 19 April 2017

Accepted 20 April 2017

Available online 21 April 2017

### Keywords:

Pyrrolidinium ionic liquid  
lithium transference number  
polymer electrolyte  
LiFePO<sub>4</sub>  
PVA

## ABSTRACT

Polymer electrolytes offer the most promising solution to address the all-solid-state battery requirements such as flexibility, leak-proof packing and easy processing. In this study, a polymer blend of 25 mol% poly(acrylic acid) (PAA) and 75 mol% poly(vinyl alcohol) (PVA) was optimized based on its thermal, mechanical and structural properties. The ionic liquid (IL) electrolyte, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYRTFSI) with 0.2 m lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), was added to the polymer blend in different molar ratios. A maximum ionic conductivity of 1 mS cm<sup>-1</sup> is observed at 90 °C in the membrane with 70 mol% IL. Cyclic voltammetry of the polymer electrolytes shows peaks corresponding to lithium stripping (+0.25 V vs. Li<sup>+</sup>/Li) and deposition (−0.3 V vs. Li<sup>+</sup>/Li) processes indicating the occurrence of a highly reversible redox process. The electrochemical stability window of these polymer electrolytes, as determined by linear sweep voltammetry, extends up to 5 V, suggesting that these electrolytes could be suitable for batteries that use high voltage cathode materials. A lithium transference number ( $t_{Li^+}$ ) of 0.4 was determined for the polymer electrolytes by using chronoamperometry and impedance measurements. Galvanostatic charge-discharge studies of the polymer electrolytes in a lithium half-cell with LiCoO<sub>2</sub> (LCO) as cathode delivers a capacity of about 100 mAh g<sup>-1</sup> at 60 °C. Coin-type half-cell with LiFePO<sub>4</sub> (LFP) cathode and the polymer electrolyte containing 70 mol% IL delivered a capacity of 172 mAh g<sup>-1</sup>. Interestingly, the LFP/polymer composite cathode (LFP-C) delivers a higher capacity (215 mAh g<sup>-1</sup> at 60 °C) than the pristine LiFePO<sub>4</sub> cathode.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

To realize a polymer-based solid-state battery, it is necessary to design a solid polymer electrolyte (SPE) film with favorable properties, which include a high ionic conductivity and a good mechanical stability [1]. Certain side reactions that normally take place between lithium metal and organic liquid electrolytes are avoided by using a solid electrolyte. The plastic nature of SPEs facilitates flexibility, thin cell configurations, and leak proof cell assembly which are highly desirable in the context of advanced battery applications [2]. Polyethylene oxide (PEO)-based SPE films have been regarded as the ideal electrolytes for lithium batteries, as they eliminate the need for a separator [3,4]. Although these

electrolytes possess good mechanical strength and dimensional stability, their conductivity is rather low (10<sup>-6</sup>–10<sup>-4</sup> S cm<sup>-1</sup>) at ambient temperature [5]. Other problems in PEO-based electrolytes include their low Li<sup>+</sup> transference number (0.3 to 0.5) which leads to high polarization and interfacial resistance, and the incompatibility of their anions (BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> etc.) with the anode. These anions react with the anode to form a passivation layer, which eventually results in the formation of lithium ‘dendrites’ [6]. To overcome these problems, gel polymer electrolytes (GPE), which contain a liquid electrolyte retained in a polymer gel, were proposed [7]. The ionic conductivity of GPEs at ambient temperature is in the range of 1 × 10<sup>-4</sup> S cm<sup>-1</sup> to 1 × 10<sup>-3</sup> S cm<sup>-1</sup> [8]. However, the mechanical stability of GPEs is significantly lower than that of SPEs. Moreover, the thermal stability of GPEs is affected by the high vapor pressure of the organic solvents. Safety issues such as cell leakage and the presence of volatile, highly flammable solvents are not fully addressed by GPEs. Cell processing

\* Corresponding author.

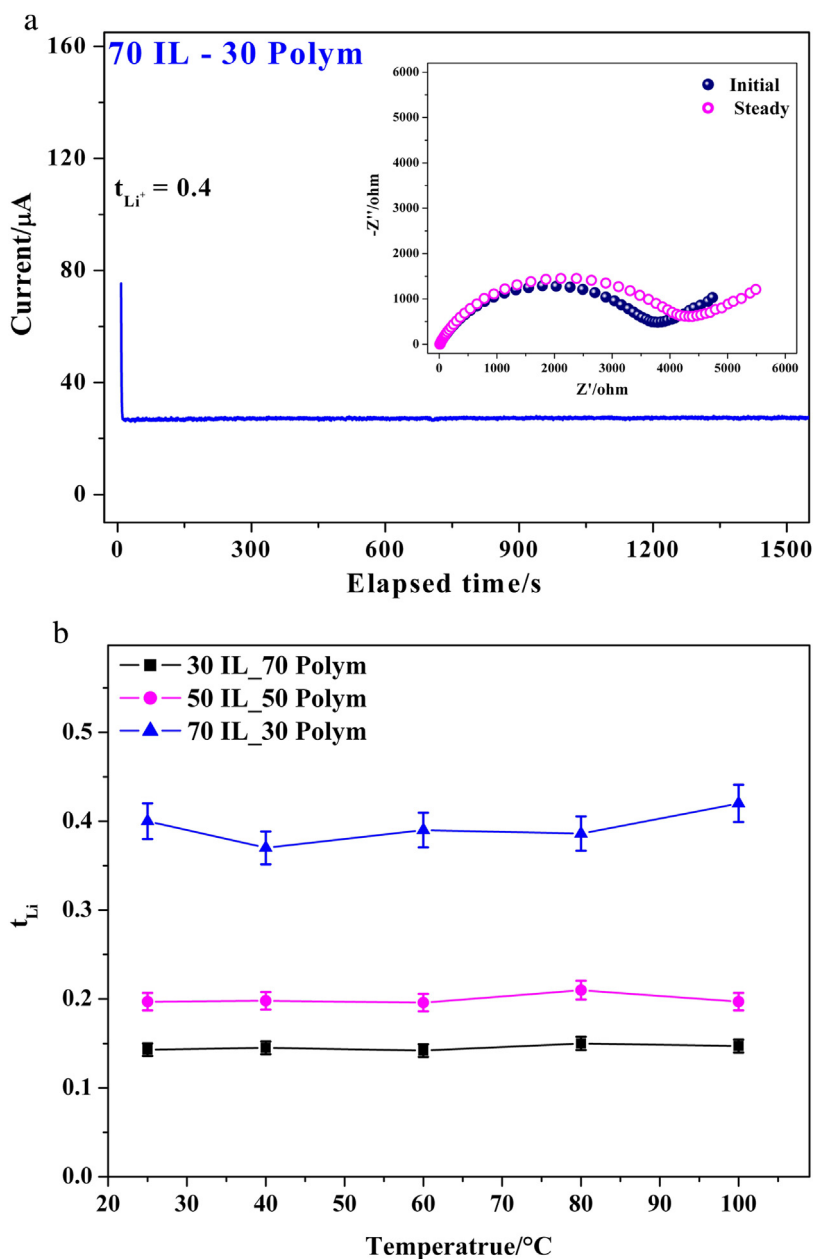
E-mail address: [Savitha.Sundaram@kuleuven.be](mailto:Savitha.Sundaram@kuleuven.be) (S. Thayumanasundaram).

becomes difficult due to their poor mechanical properties. In addition, the electrochemical stability window (ESW) of GPEs is limited by the narrow ESW of the incorporated organic solvents.

Another approach is to replace the classical electrolyte by molten salts, commonly known as ionic liquids (ILs). Room temperature ionic liquids (RTILs) containing lithium salts are extensively studied for application in batteries [9]. However, the conductivity and lithium ion transport strongly depend on the temperature in this case. The other drawback of using IL-based electrolytes is the poor cathodic electrochemical stability [10]. A recent strategy has been to replace the organic solvents by highly conductive, plasticizing liquids that enhance the electrochemical stability. Incorporation of ILs in solid polymer electrolytes has been proved as an effective approach to synthesize electrochemically stable electrolytes with enhanced ionic conductivity [11]. The incorporated ILs serve as non-flammable and nonvolatile plasticizers, as well as ionic carriers [12,13]. The  $\text{Li}^+$  transport in such polymer composite electrolytes is significantly

improved due to the plasticizing effect of the IL which enhances the polymer chain relaxation and reduces the glass transition temperature [14,15]. A ternary system consisting of PEO/PYR<sub>13</sub>TFSI/LiTFSI, was reported to show a remarkable ionic conductivity of  $10^{-4} \text{ Scm}^{-1}$  at 20 °C [16]. Recently, concentrated mixtures of oligo(ethylene glycol) dimethyl ethers (commonly known as glymes) and Li salts have been shown to form low-melting complexes and behave like ILs in the molten state [17].

Thus, lithium polymer batteries (LPBs) with lithium metal anode and solvent-free electrolyte are considered the next generation power sources that might overtake common lithium-ion batteries in terms of energy density, safety, reliability and electrochemical performance. In this study, we report the synthesis and characterization of an electrolyte system consisting of PVA-PAA polymer blend and an ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYRTFSI) with 0.2 m lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the anion. From various molar



**Fig. 1.** a Lithium ion transference number for the polymer membrane 70IL-30Polym. b Lithium ion transference number for all the polymer membranes at different temperatures.

Download English Version:

<https://daneshyari.com/en/article/6471313>

Download Persian Version:

<https://daneshyari.com/article/6471313>

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