



Correlation between Properties and Conductivity Mechanism in Poly(vinyl alcohol)-based Lithium Solid Electrolytes

Gioele Pagot^{a,b}, Federico Bertasi^{a,c}, Keti Vezzù^a, Graeme Nawn^a, Giuseppe Pace^d, Angeloclaudio Nale^a, Vito Di Noto^{a,b,c,e,*}

^a Section of “Chemistry for the Technology” ChemTech, Department of Industrial Engineering, University of Padova, Via Marzolo 1, I-35131 Padova (PD), Italy

^b Centro Studi di Economia e Tecnica dell’Energia Giorgio Levi Cases, Via Marzolo 9, I-35131 Padova (PD), Italy

^c INSTM, Via Marzolo 1, I-35131 Padova (PD), Italy

^d CNR-IENI, Via Marzolo 1, I-35131 Padova (PD), Italy

^e Material Science and Engineering Department, Universidad Carlos III de Madrid, Escuela Politécnica Superior, Av.de la Universidad, 30, 28911 Leganes, Spain



ARTICLE INFO

Keywords:

Polyelectrolyte
Lithium
Conductivity mechanism
Poly(vinyl alcohol)

ABSTRACT

In this study, a new family of poly(vinyl alcohol)-based solid membrane electrolytes is proposed. The single ion conducting polyelectrolytes are obtained by direct lithiation of partially hydrolyzed poly(vinyl alcohol), forming a lithium-poly(vinyl alkoxide) macromolecular salt. Furthermore, in order to improve the ionic conductivity, the obtained polymer is plasticized with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) ionic liquid. Thermogravimetric analysis demonstrates a thermal stability higher than 215 °C. Differential Scanning Calorimetry studies show a polymer associated glass transition event and a melting transition related to the ionic liquid domains at ca. +80 and –40 °C respectively. Fourier-transform infrared spectroscopy proves that: a) lithiation of the membrane results in an increase to the amorphous character of the polymer backbone; and b) after ionic liquid addition to the lithiated membrane, the effective coordination of lithium cations by the TFSI anions of the ionic liquid augments the ionic conductivity of the proposed materials. Broadband electrical spectroscopy (BES) investigations reveal that this system is characterized by several polarization phenomena and dielectric relaxation events. Analysis of the BES results, using suitable models, allows for the conductivity mechanism in the proposed polymer electrolytes to be hypothesized. Finally, the ionic conductivity values of $1.29 \cdot 10^{-5} \text{ S cm}^{-1}$ and $1.92 \cdot 10^{-3} \text{ S cm}^{-1}$ at 30 and 80 °C render these materials very promising for application in electrochemical devices.

1. Introduction

Polymer electrolytes (PEs) were first proposed in the early 1970s [1]. Since then, this class of materials has attracted the attention of many scientists, becoming one of the most prolific research fields in solid-state electrochemistry [2–4]. PEs are able to overcome many of the disadvantages of classic liquid organic electrolytes, which typically exhibit: a) high flammability and high vapor pressure; b) low thermal, chemical, and electrochemical stability; and c) dendrites formation when combined with lithium metal electrodes. Classical solid PEs typically show lower values of ionic conductivity ($\sigma < 10^{-6} \text{ S cm}^{-1}$) with respect to those necessary for practical electrochemical applications [2]. One play adopted to increase the conductivity of solid polymer electrolytes is the addition of plasticizers that permeate into the polymer matrix, thus increasing the mobility of polymer chains

[5,6]. In classic lithium PEs, as well as in plasticized PEs, the total ionic conductivity is mainly modulated by the migration of the anionic species [7]. Indeed, in these materials, the Li^+ transference number (t_{Li^+}) is usually lower than 0.3 [8–10]. It is well known that the overall conduction selectivity toward lithium ion mobility can be achieved by doping the polymer with salts endowed with enlarged anion size [10–12]. Taken all together, two different strategies are used to improve t_{Li^+} in PEs: 1) the addition of a lithium salt consisting of large anions, or 2) the direct bonding of anions to the polymer backbone. In the latter case the polymer chain behaves as a huge poly-anionic species [10]. In order to obtain a PE with high conductivity for practical applications, there is generally a compromise between the overall ionic conductivity and Li^+ transference number of the material.

Previous studies demonstrated that PEs based on poly(vinyl alcohol) (PVA) are able to dissolve large amounts of lithium salts, giving rise to

* Corresponding author at: Section of “Chemistry for the Technology” ChemTech, Department of Industrial Engineering, University of Padova, Via Marzolo 1, I-35131 Padova (PD), Italy.

E-mail address: vito.dinoto@unipd.it (V. Di Noto).

<https://doi.org/10.1016/j.ssi.2018.03.001>

Received 28 September 2017; Received in revised form 11 January 2018; Accepted 1 March 2018

0167-2738/ © 2018 Elsevier B.V. All rights reserved.

materials that present conductivity values higher than those of any other solid and solvent-free polymer electrolyte [13]. Here, a new family of ion conducting solid polymer electrolytes based on a partially lithiated PVA macromolecular salt is proposed. In these materials, Li^+ ions are provided by alkoxide side groups ($-\text{RO}^-\text{Li}^+$) grafted on to the backbone polymer chains. In this study, lithium alkoxide groups are formed by direct reaction of lithium methoxide with the acetate groups of a poly(vinyl alcohol-co-vinyl lithium alkoxide) co-polymer. The conductivity of the obtained macromolecular salt is then improved by plasticizing the material with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) ionic liquid (IL). The structure and interactions in both pristine and doped PEs are investigated in order to understand the role of the dopant IL on the overall conductivity. Furthermore, insights into the phenomena responsible for the long range charge migration events in these materials are elucidated and the conductivity mechanism is proposed.

2. Experimental

2.1. Reagents

Poly(vinyl alcohol-co-vinyl acetate), obtained by a partial hydrolysis process of a poly(vinyl acetate) is provided by INEOS Technologies Italia Srl. The degree of polymerization (sum of vinyl acetate ($m=60$) and vinyl alcohol repeat units ($n=440$), see Scheme 1) is equal to 500, the hydrolysis degree ($n/(n+m)$) is 0.88, and the polymer average molecular weight is 25 kDa. Methanol, ethanol, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), and lithium metal are purchased from Sigma-Aldrich.

2.2. PVA lithiation

Poly(vinyl alcohol-co-vinyl lithium alkoxide), namely lithiated poly(vinyl alcohol) (Li_PVA), is prepared by mixing 5.003 g of ball-milled PVA and 8.611 g of lithium methoxide (MeOLi) in 75 mL of methanol (see Scheme 1a). This reaction is carried out in a Teflon autoclave which is heated up to 85 °C for 20 h. The MeOLi precursor is obtained by reacting lithium metal directly with dry methanol. Li_PVA is recovered by centrifuge precipitation, and washed 5 times with 30 mL of ethanol. The powder of the co-polymer is then dried in vacuum at 80 °C for 48 h and finally stored into an argon filled glove-box. The complete removal of MeOLi is confirmed by FT-IR analyses (see Fig. S1 of Supporting Information).

2.3. PVA and Li_PVA membrane preparation

PVA and Li_PVA powders are dissolved in bidistilled water (ca. 5% by weight). Membranes with a thickness on the order of 60 μm are obtained by casting ca. 5 mL of a prepared polymer water solution on a Teflon Petri dish at 80 °C.

2.4. Li_PVA plasticization

IL doped lithiated poly(vinyl alcohol) (Li_PVA + IL) is prepared by mixing 0.070 g of EMImTFSI ionic liquid into 0.288 g of Li_PVA powder. The obtained mixture is dissolved into 4 mL of bidistilled water before heating to 85 °C for 10 min. 7 mL of methanol is then added to the solution which is then cast onto a Teflon Petri dish at 80 °C. The Li_PVA + IL_{soak} membrane with a high degree of IL doping is prepared by soaking the pristine Li_PVA + IL membrane directly into EMImTFSI at 70 °C for 18 days. The above described protocols allow for the preparation of four different membranes which consist of: 1) a pristine partially hydrolyzed poly(vinyl alcohol) (PVA); 2) a lithiated PVA (Li_PVA); 3) a moderately plasticized Li_PVA (Li_PVA + IL); and 4) a strongly IL doped Li_PVA + IL membrane (Li_PVA + IL_{soak}).

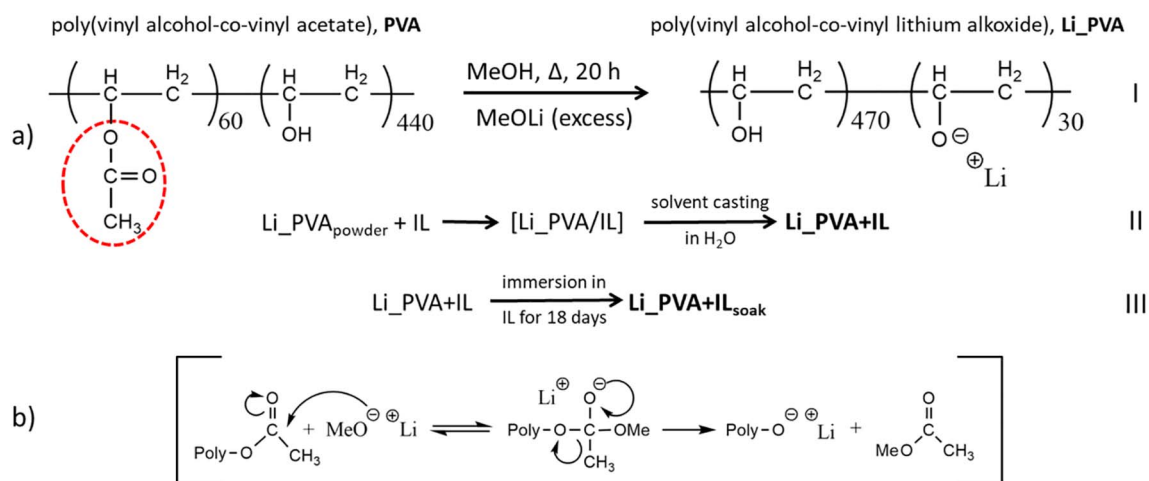
2.5. Membrane characterization

2.5.1. Elemental analysis

The content of Li in the polymer electrolytes is determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements. The analyses are carried out by digesting the samples in water solutions with a concentrated 3:1 mixture of HCl and HNO₃. The emission line of Li is 670.70 nm. The sulfur (S) weight percentage in the membranes is determined by using a FLASH 2000 CHNS-O Organic Elemental Analysis analyzer.

2.5.2. Thermal analysis

High resolution - thermo gravimetric analysis (HR-TGA) is carried out with a high resolution thermobalance (2950 model of TA Instruments). HR-TGA measurements are conducted in a temperature range from 30 to 950 °C under N₂. The heating ramp varies automatically following the first derivative of the weight loss, from 50 to 0.001 °C·min⁻¹. The instrument sensitivity ranges from 0.1 to 2% min⁻¹ and the weight resolution is 1 μg . Modulated differential scanning calorimetry (MDSC) measurements are performed from +160 to -150 °C with a scanning rate of 3 °C·min⁻¹, using a Q20 DSC by TA instruments. Measurements are carried out on samples of approximately 10 mg which are loaded and sealed in a hermetically-sealed aluminum pan under an Argon atmosphere within a glove-box.



Scheme 1. Preparation of Li_PVA, Li_PVA+IL, and Li_PVA+IL_{soak} samples (a). Steps I, II, and III are reported. Mechanism of reaction between MeOLi and carbonyl side groups (b).

Download English Version:

<https://daneshyari.com/en/article/7744302>

Download Persian Version:

<https://daneshyari.com/article/7744302>

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