Electrochimica Acta 230 (2017) 189–195

Contents lists available at ScienceDirect

Electrochimica Acta

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

Mechanical Stabilization of Solid Polymer Electrolytes through Gamma Irradiation

Jonas Mindemark*, Adam Sobkowiak, Gabriel Oltean, Daniel Brandell, Torbjörn Gustafsson

Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form 30 January 2017
Accepted 2 February 2017
Available online 3 February 2017

Keywords:
polymer electrolytes
crosslinking
lithium batteries
mechanical properties
gamma irradiation

ABSTRACT

Attaining sufficient mechanical stability is a challenge for high-performance solid polymer electrolytes, particularly at elevated temperatures. We have here characterized the viscoelastic properties of the non-polyether host material poly(ε-caprolactone-*co*-trimethylene carbonate) with and without incorporated LiTFSI salt. While this electrolyte material performs well at room temperature, at 80 °C the material is prone to viscous flow. Through γ-irradiation at a dose of 25 kGy, the material stabilizes such that it behaves as a rubbery solid even at low rates of deformation while retaining a high ionic conductivity necessary for use in solid-state Li batteries. The performance of the irradiated electrolyte was investigated in Li polymer half-cells (Li vs. $LiFePO_4$) at both 80 °C and room temperature. In contrast with the notably stable battery performance at low temperatures using the non-irradiated material, during cycling of the irradiated electrolytes detrimental instabilities were noted at both 80 °C and room temperature. The possible effects of both radiation damage to the electrolyte and impaired interfacial contacts due to the crosslinking indicate that a different procedure may be necessary in order to stabilize these electrolytes for use in battery cells capable of stable long-term operation.

1. Introduction

While large-scale energy storage in general and Li battery technology in particular is a key component of the sustainable energy system of the future, regular catastrophic high-profile battery failures involving the Boeing Dreamliner, the Tesla Model S and, more recently, the Samsung Galaxy Note 7, serve as reminders of the inherent dangers of high-density energy storage in combination with volatile and flammable organic electrolyte solvents [1,2]. A possible way to mitigate these hazards is through the use of solid polymer electrolytes, which precludes the use of liquid electrolytes to allow for a more stable battery without the need for containment of toxic and flammable liquids and gaseous discharge products [3]. Of course, this places demands on the polymer electrolyte material, not only in terms of ion transport properties and electrochemical stability, but also the mechanical properties of the material. This is not least related to the formation of dendrites during the deposition of metallic Li, which has been suggested to be suppressed if the shear modulus of the electrolyte is sufficiently large [4]. The modulus is largely dependent on the electrolyte host material; here, modifications to the polymer architecture may be used to tune the modulus, *e.g.*, through the use of block copolymers [5] or other architectural variations – including crosslinking [6,7]. Alternatively, this end can also be accomplished by incorporating stiff fillers into a composite electrolyte matrix [8]. However, measures such as these that are intended to increase the modulus also tend to simultaneously limit the ionic conductivity [5–7].

Recent research on new types of host materials has pushed the limits of solid polymer electrolyte performance and we have recently seen several examples of materials that can be used in cells that are operational down to room temperature, whereas traditional solid polymer electrolytes have required elevated temperatures for sufficiently fast Li-ion conduction [9,10]. In this context, we recently presented an amorphous polyester–polycarbonate (PCL–PTMC) copolymer that shows a combination of high ionic conductivity and high Li transference number, allowing for stable battery cycling at temperatures down to 22 °C [11]. The dilemma here, however, is that the ionic conductivity and the mechanical properties of polymer electrolytes generally both

---

* Corresponding author.
E-mail address: jonas.mindemark@kemi.uu.se (J. Mindemark).

http://dx.doi.org/10.1016/j.electacta.2017.02.008
0013-4686/

depend on the molecular flexibility of the host polymer backbone, such that an increase in conductivity – induced by faster segmental motions of the polymer [12] – will have a negative impact on the mechanical properties [5,6]. Thus, it is commonly seen that high-performance polymer electrolytes, although solvent-free, display notably liquid-like characteristics to the point where mechanical reinforcement is needed for the material to be able to function reliably in battery cells [9,13,14]. This is unfortunate, since it adds complexity to cell construction and undermines one of the basic premises of SPEs, *i.e.,* that the electrolyte membrane itself can act as an electrode separator [15,16].

In this context, the PCL–PTMC copolymer is no exception. The fact that it is an amorphous material with sub-ambient T_g means that, while solid and rubber-like on a macroscopic level, on a molecular level it is best described as essentially a (very viscous) liquid. Although this is hardly noticeable at room temperature – battery cells using this material have been shown to function reliably at up to 40 °C without any form of mechanical reinforcement or additional separators [11] – at higher temperatures these properties will eventually manifest themselves as liquid flow. To put things into perspective, even electrolytes based on the much more stable trimethylene carbonate (TMC) homopolymer ($T_g = -16$ °C vs. -57 °C for the PCL–PTMC copolymer [11]) show sufficient mobility at 60 °C to eventually move into and infiltrate a porous electrode when applied as a self-supporting membrane in a battery assembly [17,18].

In practical applications, this tendency for viscous flow translates into poor mechanical stability during long-term exposure also to low mechanical stresses. Thus, it remains a challenge to mechanically stabilize the material such that it may act as a physical separator also under more demanding operating conditions. To this end, crosslinking of the material is a potentially viable solution. In this paper, we have further investigated and characterized the mechanical properties of the polyester–polycarbonate copolymer electrolyte and the effects of γ-ray-induced crosslinking on both the mechanical and ion transport properties of the material as well as the cycling performance of γ-treated cathode–electrolyte assemblies in Li polymer solid-state battery cells.

2. Experimental

2.1. Materials

The PCL–PTMC copolymer was synthesized through tin(II)-catalyzed bulk ring-opening polymerization of ε-caprolactone and trimethylene carbonate as described elsewhere [11,19]. Lithium bis(trifluoromethanesulfonate) (LiTFSI; Purolyte, Ferro Corporation) was dried under vacuum at 120 °C for 24 h. Anhydrous acetonitrile was obtained from Acros Organics and used as received.

2.2. Polymer electrolyte preparation and γ-irradiation

All polymer electrolyte preparation and handling was performed in a glovebox under argon to prevent moisture contamination. Solutions of copolymer and LiTFSI were prepared in anhydrous acetonitrile and cast in PTFE molds. The solvent was evaporated in a vacuum oven setup where the pressure was gradually reduced from an initial 200 mbar to ≤ 1 mbar during 20 h followed by heating at 60 °C at this pressure for an additional 40 h, resulting in thin and transparent polymer electrolyte films. For γ-irradiation, polymer electrolyte samples were carefully packaged in airtight, laminated aluminum/plastic bags that were vacuum-sealed under argon. The packaged samples were subjected to 25 or 50 kGy γ-irradiation from a ^{60}Co source (Scandinavian Clinics Estonia).

2.3. Mechanical properties

The viscoelastic properties of the electrolytes were investigated using oscillatory rheology on a TA Instruments AR 2000 using an 8 mm aluminum parallel plate geometry. These measurements were done under a flow of nitrogen and the samples were loaded into the measurement setup under a blanket of flowing nitrogen as quickly as possible to minimize moisture contamination. The measurements were done at a strain of 0.5% while the oscillating frequency was ramped between 0.01–10 Hz at a controlled normal force of 0.5 ± 0.1 N.

2.4. Ionic conductivity

The total ionic conductivity of the electrolytes was determined from electrochemical impedance spectroscopy using a Schlumberger Impedance/Gain-phase Analyzer SI 1260. Circular samples (diameter 12 mm) were sandwiched between gold-plated stainless steel electrodes and sealed in Swagelok-type cells. The cells were heated to 100 °C in an oven, measuring the temperature using a thermocouple inserted into the cell assembly a few mm from one of the electrodes, and left at 100 °C for 30 min to improve the interfacial contacts. The impedance was measured from 1 Hz–1 MHz at an amplitude of 10 mV at regular intervals during cooling from 100 °C down to 25 °C. The bulk ionic resistance was obtained as the low-frequency *x*-axis intercept of the semicircle in the Nyquist plot.

2.5. Battery assembly and cycling

The cathodes consisted of a mixture of 75 wt% $LiFePO_4$ (Phostech, P2), 15 wt% PVdF (Solvay, Solef 5130) and 10 wt% conductive carbon (Timcal, Super C 65) which was ball-milled in *N*-methyl-2-pyrrolidone (NMP) for at least 2 h. The obtained slurry was cast onto aluminum foil with controlled and uniform coating thickness. After drying in a furnace at 80 °C, 13 mm diameter electrodes were cut and transferred to an argon-atmosphere glove box where they were further dried in a vacuum oven located inside the glovebox at 120 °C for 12 h prior to electrolyte casting. The copolymer electrolyte was cast directly onto the porous electrodes using the same procedure as described in section 2.2 for the electrolyte films. For the γ-irradiated samples, the entire electrode–electrolyte assembly was γ-treated, again using the same procedure as for the stand-alone electrolyte films.

The polymer electrolyte-coated $LiFePO_4$ electrodes were assembled against 13 mm diameter metallic Li disks as counter electrodes (the anode). The Li disk was stacked directly on top of the electrolyte film, without using any additional separator. The electrode/electrolyte stack was then sealed into a laminated aluminum/plastic pouch cell under vacuum, using nickel and aluminum as current collector tabs on the anode and cathode side, respectively.

All cells were cycled in galvanostatic mode between 2.7 and 4.2 V using a BTS600 battery testing system (Digatron) at either r.t. or 80 °C. Before starting the cycling at elevated temperature, the cells were held at open circuit voltage (OCV) at the intended cycling temperature for 20 h while recording the cell potential. This precycling step was employed to allow for an improved interfacial contact between the electrolyte and the electrodes, and to confirm that the cells could withstand short-circuiting solely due to their stack pressure. C-rates were calculated based on the theoretical capacity of the $LiFePO_4$ active material (170 mAh g^{-1})