



## Short communication

## High-performance solid polymer electrolytes for lithium batteries operational at ambient temperature



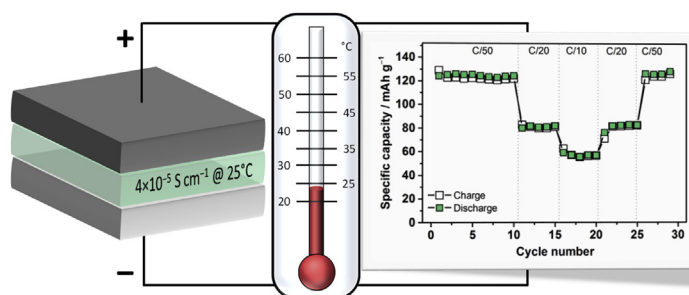
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## HIGHLIGHTS

- Polymer electrolytes were prepared based on poly( $\epsilon$ -caprolactone).
- Optimal performance was attained by addition of 20 mol% carbonate repeating units.
- High total ionic conductivity;  $4.1 \times 10^{-5} \text{ S cm}^{-1}$  at 25 °C,  $1.1 \times 10^{-4} \text{ S cm}^{-1}$  at 40 °C.
- High  $\text{Li}^+$  transference numbers; 0.62 at 40 °C, 0.66 at 60 °C.
- Li polymer half-cells were cycled with high stability at room temperature.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 9 June 2015

Received in revised form

19 July 2015

Accepted 10 August 2015

Available online 24 August 2015

## Keywords:

Polymer electrolytes

Polyester

Polycarbonate

Lithium batteries

Ionic conductivity

## ABSTRACT

Incorporation of carbonate repeating units in a poly( $\epsilon$ -caprolactone) (PCL) backbone used as a host material in solid polymer electrolytes is found to not only suppress crystallinity in the polyester material, but also give higher ionic conductivity in a wide temperature range exceeding the melting point of PCL crystallites. Combined with high cation transference numbers, this electrolyte material has sufficient lithium transport properties to be used in battery cells that are operational at temperatures down to below 23 °C, thus clearly demonstrating the potential of using non-polyether electrolytes in high-performance all-solid lithium polymer batteries.

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## 1. Introduction

One major challenge in the development of Li batteries is finding a suitable electrolyte [1]. The low-molecular-weight organics currently used as electrolyte solvents are inherently unstable at the electrode/electrolyte interfaces, leading to irreversible loss of capacity during the first cycle due to the formation of a solid

electrolyte interphase (SEI) layer as well as the risk of continuous further decomposition of solvent and salt during the operational lifetime of the battery [2,3]. The volatility and flammability of these solvents are also sources of great concern, as runaway reactions in such batteries may have devastating consequences [4]; notable examples being the recent Boeing 787 Dreamliner battery incidents [5]. One possible way to mitigate these problems is to replace the liquids with solid-phase electrolytes with concomitant improvements in stability and safety while also providing enhanced flexibility in cell design [6,7].

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Ever since first suggested by Armand et al. [8,9], solid (solvent-free) polymer electrolytes (SPEs) have been intensively researched for potential use in Li battery applications. Compared to other solid electrolytes, SPEs are potentially both low-cost and easily processable [1,3,6]. Furthermore, they offer all the versatility and flexibility of polymer chemistry, allowing for facile synthesis of tailored materials with specific functionalities for specific applications, ranging from self-assembling crosslinkable oligomers for 3D-microbatteries [10] to electrolytes with tailored mechanical properties for structural batteries [11].

The vast majority of Li<sup>+</sup>-conducting SPEs are based on polyethers, and in particular the oxyethylene motif; the most prominent example being poly(ethylene oxide) (PEO). Few alternatives exist that are not subpar to this standard material [6] and most electrolytes typically fall short of either the demand for high ionic conductivity or sufficient mechanical properties [1,3,11,12]. In the case of PEO, this is exacerbated by semicrystallinity at low to moderate temperatures, which severely restricts ion transport in the material [13]. Other issues that have been highlighted include compatibility with the highly porous electrodes and good wetting of the active materials [3]. These challenges have so far limited the practical use of SPEs and despite the wealth of literature on solid polymer electrolytes, there is a notable lack of cycling data.

We and other authors have recently started investigating polycarbonates as alternative host materials for SPEs [14,15]. Although polycarbonate electrolytes have shown good stability and cycling efficiency in Li half-cells at elevated temperature, the low ionic conductivity currently limits the use of these materials to low-power and/or high-temperature applications [14,16]. We were recently able to demonstrate increased ionic conductivity and better cycling performance for electrolytes based on poly(trimethylene carbonate) (PTMC) on incorporation of  $\epsilon$ -caprolactone repeating units in the polymer chains (from 10 to 40 mol%), attributed to increased chain flexibility [17]. Based on these results, it could be anticipated that optimal performance would be obtained in electrolytes based on the poly( $\epsilon$ -caprolactone) (PCL) homopolymer [18–20]. However, while showing decent ionic conductivity at elevated temperatures, much like PEO, polymer electrolytes based on PCL are semicrystalline at room temperature, thereby severely limiting their ionic conductivity. In this short communication, we demonstrate how crystallinity can be suppressed in PCL-based polymer electrolytes by copolymerization with trimethylene carbonate (TMC), thereby improving the ionic conductivity in a broad temperature range to the point where use in batteries functional at room temperature becomes feasible.

## 2. Experimental

### 2.1. Materials

$\epsilon$ -Caprolactone (CL; Aldrich) was distilled under reduced pressure over CaH<sub>2</sub> and stored in a glovebox under argon. Trimethylene carbonate (TMC; Boehringer Ingelheim) was handled and stored in a glove box under argon and used as received. Copolymers of CL and TMC were synthesized through bulk ring-opening polymerization according to the same procedure as previously published for the homopolymerization of TMC [14]. Lithium bis(trifluoromethanesulfonimide) (LiTFSI; Purolyte, Ferro Corporation) was dried in vacuum at 120 °C for 24 h before use. All other chemicals were obtained from commercial sources and used as received.

### 2.2. Polymer electrolyte preparation

Electrolyte films were prepared by casting from solutions in anhydrous acetonitrile (0.5 g polymer in 0.75–1 ml solvent). The

solvent was removed using a vacuum oven setup inside the glovebox where the samples were initially kept at ambient temperature while the pressure was gradually decreased from an initial 200 mbar to <1 mbar during 20 h, followed by heating at 60 °C and <1 mbar for 40 h. After cooling to room temperature, circular samples with a diameter of 14 mm were punched from the resulting films. Great care was taken to avoid moisture contamination, including conducting all monomer, polymer and electrolyte handling in a glovebox under argon. The polymer is obtained anhydrous from synthesis, as any trace amounts of water in the reaction mixture will be consumed during polymerization.

### 2.3. Thermal properties

The thermal properties of copolymers and electrolytes were determined through differential scanning calorimetry on a TA Instruments DSC Q2000. Samples were hermetically sealed in aluminum pans under argon. The pans were rapidly cooled to –80 °C and subsequently heated at a rate of 10 °C/min to 130 °C for measurement. This cycle was repeated to assess the tendency for recrystallization of the polymers.

### 2.4. Ionic conductivity

The ionic conductivity of the electrolyte films was measured using electrochemical impedance spectroscopy. Samples were sandwiched between stainless steel blocking electrodes and sealed in Swagelok-type cells. The thickness of the electrolyte films was measured prior to cell assembly using a Mitutoyo digital indicator. The measurement cells were designed to exert a minimum amount of pressure on the electrolyte film to ensure proper electrical contact while avoiding deformation of the sample. The cells were heated to 100 °C in an oven while monitoring the cell temperature using a thermocouple inserted a few mm from one of the electrodes. The cells were kept at 100 °C for 30 min to ensure good interfacial contacts and were then allowed to cool and left at room temperature for 20 h to allow for recrystallization. The ionic conductivity was measured during heating using an SI 1260 Impedance/Gain-Phase Analyzer (Schlumberger) at a frequency range of 1 Hz–10 MHz and an amplitude of 10 mV. The ionic conductivity was obtained from the Nyquist plots as the (low-frequency) intercept with the real axis.

### 2.5. Transference number

Lithium transference numbers were measured using potentiostatic polarization [21]. Symmetric Li/SPE/Li cells were assembled and thermally equilibrated for 20 h (60 °C measurement) or 48 h (40 °C measurements) and the impedance in the cell was monitored until a stable SEI was observed (no obvious change in resistance). Impedance and polarization measurements were carried out using a VMP2 (Biologic). The cells were polarized at 10 mV and the impedance spectra were obtained from 1 Hz to 200 kHz (40 °C measurements) or 1 Hz to 1.5 MHz (60 °C measurement) at an amplitude of 10 mV. Temperature fluctuations were maintained within 0.1 °C.

### 2.6. Battery cycling

The preparation of LiFePO<sub>4</sub> cathodes and Li half-cell assembly has already been described elsewhere [14]. The full capacity of the active material, as reported by the manufacturer, is approximately 150 mAh/g. The active mass loadings of the electrodes was in the range of 1.8–2.5 mg/cm<sup>2</sup> and the thickness around 13–16  $\mu$ m. Electrolytes for Li half-cell assembly were solution-cast directly

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