A solid polymer electrolyte for aluminum ion conduction

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ABSTRACT

We report on the synthesis and characterization of a solid polymer electrolyte for aluminum ion conduction. The solid polymer electrolyte is produced via the copolymerization of a low molecular weight polytetrahydrofuran and a cycloaliphatic epoxy. The crosslinked copolymer is swollen in THF solutions of different concentrations of aluminum nitrate as the aluminum ion source. The conductivity as a function of concentration is measured via AC impedance spectroscopy over a temperature range of 20–110 °C. We attain conductivities that increase with salt loading, reaching a value of 2.86×10^{-5} S·cm^{-1}. Thermogravimetric analysis shows the electrolytes are stable up to 150 °C. Raman spectroscopy reveals complete dissociation of the aluminum nitrate salt in the electrolyte over the concentration range explored. This study establishes a polymer system and synthetic route towards solid polymer electrolytes for aluminum ion conduction, for the development of all solid-state aluminum ion batteries.

Introduction

Solid polymer electrolytes (SPEs) are a safe, promising alternative to meet the challenges of battery applications. SPEs address concerns about overheating, electrolyte leakage, fire safety, as well as effective separator operation to avoid short circuits between anode and cathode. In addition, they provide additional advantages of flexible, compliant shapes and processability during manufacturing. SPEs also provide the opportunity to obtain a true all solid-state battery, with the inherent benefits of better thermal and mechanical stability. SPEs have been developed for lithium, sodium and magnesium ion batteries [1]; however, there have been no reports of an SPE for aluminum ion conduction.

Aluminum ion batteries show some of the highest potentials, greatest charge densities, and greatest capacities, in addition to being an abundant, low-cost alternative, multi-valent ion species [1]. After oxygen and silicon, aluminum is the third most abundant element in the earth's crust. An aluminum metal anode is a superior multivalent system in terms of volumetric capacity (8040 mAh/cm^3), four times greater than lithium and twice that of magnesium. Aluminum also has a rich history due to the well-established aluminum electroplating industry, and an aluminum ion battery offers Coulombic efficiencies close to 100%.

In this report, we examine an SPE for aluminum ion conduction. The SPE is synthesized via photo-crosslinking using visible light to form a copolymer consisting of polytetrahydrofuran and a cycloaliphatic epoxy. The SPEs are loaded with aluminum nitrate salt, and the conductivity, thermal stability, and composition are interrogated. This SPE shows good conductivity and thermal stability, which provides opportunities towards further SPE development and expansion of the system for improved aluminum ion conduction and future battery prototyping.

Experiment

Materials

Polytetrahydrofuran (PTHF) of M$_n$ = 250, 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (Epoxy), and visible-light photosensitizer camphorquinone (CQ) were purchased from Sigma Aldrich. The cationic initiator (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate (OPPI) was purchased from Hampford Research Inc.

SPE preparation

Photocurable mixtures were prepared by mixing equal weights of PTHF and Epoxy with CQ (2.5 wt% of total mixture) and OPPI (1.5 wt% of total mixture). CQ sensitizes the photoreactive blend to blue light (λ_{max} = ~470 nm), and initiates the polymerization of the PTHF and Epoxy via the active monomer mechanism [2]. The mixtures were loaded into wells constructed from a Teflon ring over a transparent plastic substrate. The mixture height was ~100 μm. The mixture was

irradiated from below with collimated blue light from a light-emitting diode (LED) (λ_{max} = 470 nm, Thorlabs Inc.) at an exposure intensity of 15 mW/cm^2. The resulting solids were washed in THF for a day, then dried under vacuum at 55 °C for one day. The PTHF-Epoxy copolymers samples were swollen in various concentrations (0.05–0.6 M) of aluminum nitrate in THF for 3 days, then dried under vacuum for a day.

Impedance spectroscopy

The ion conductivity of each sample was determined from AC impedance spectroscopy using a Solartron EnergyLab XM instrument, over a frequency range 0.1 Hz to 1 MHz at an amplitude of 30 mV. The temperature range was from 20 (approx. room temperature) to 110 °C at 10 °C intervals. Two stainless steel block electrodes were employed, and the bulk resistance determined from the Nyquist plot of the impedance. The conductivity (σ) of each sample was calculated from:

$$\sigma = \frac{d}{R_b A}$$

where A is the area of contact of the electrolyte with the block electrodes, d the electrolyte thickness, and R_b the bulk resistance. The measurements were carried out inside an Argon-filled glovebox, and the results fitted with the instruments' software using an equivalent circuit.

Thermal analysis

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA Q500 with a heating rate of 10 °C/min, up to 600 °C, under nitrogen. The remaining percent mass after heating was used to calculate the O:Al^{3+} ratio for the SPEs, and all samples are referred to hereon by their respective ratio.

Raman spectroscopy

Raman spectra were collected using a confocal Raman spectrometer (Renishaw, InVia), using a 785 nm continuous wave (CW) diode laser, connected to a Leica DM2700P microscope.

Results and discussion

We were motivated to explore PTHF as the polymer chain to facilitate Al^{3+} conduction for three reasons: (1) Polyethyelene oxide (PEO) used for monovalent ion conduction (i.e., Li$^+$ and Na$^+$) [3–7] shows strong electrostatic interactions with multivalent cations and the counterion, which can render dissociation difficult; (2) the strong electrostatic interaction between Al^{3+} and the ether oxygen units of the PEO chains in the matrix polymer might lead to low cation mobility, yet sufficient electrostatic interactions are still required to promote salt dissociation, hence the greater spacing of the oxygens (tetramethylene ether units) found in PTHF might balance these two factors, alleviating tight binding of ion pairs while still inducing salt dissociation to provide free ions for conduction; (3) PTHF is a liquid at room temperature, and its greater chain flexibility affords greater segmental motion, whereby Al^{3+} ions can be driven to percolate along the polymer network. Polytetrahydrofuran has shown reasonable conductivity in its liquid form [8], and we infer that its conductive properties can be captured in solid form via crosslinking with an epoxy [9]. While other low molecular weight polymers such as PEO are also liquid, it is common that moderate to high molecular weights (that are solid at room temperature) are employed in SPE synthesis. Cycloaliphatic epoxies are known to confer thermal stability and mechanical rigidity to their networks [10–12]. We selected aluminum nitrate as a simple, cost-effective salt species to initiate the investigation of Al^{3+} conduction in our work.

Fig. 1 shows plots of the conductivity over a range of temperatures and salt loadings employed. The conductivity increases with increased aluminum salt loading as well as with increased temperature. With the
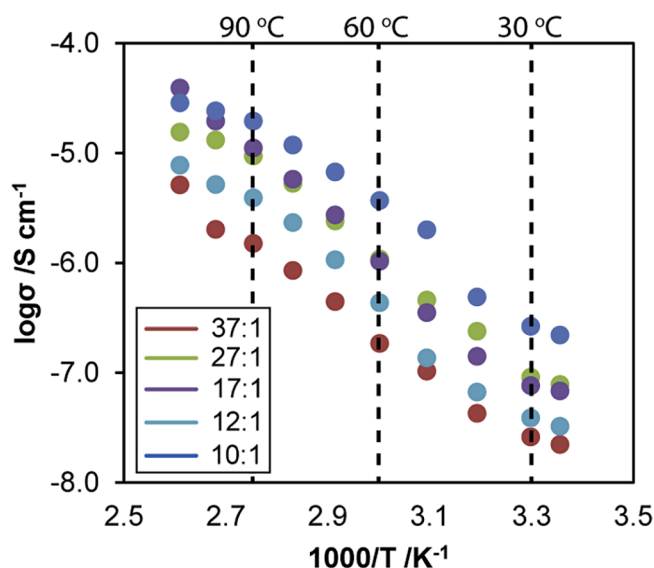

Fig. 1. Ion conductivity of PTHF-Epoxy crosslinked networks over a range of aluminum salt loadings (O:Al^{3+} ratio). Approximate temperatures in °C are provided as a reference.

highest salt loading explored, we attained a conductivity as high as 2.86×10^{-5} S·cm^{-1}. All plots show the well-known Vogel–Tammann–Fulcher (VTF) nonlinear temperature response [13]. Specifically, there is a clear inflection point near 60 °C, indicating different temperature dependencies: when T > 60 °C the data follows more closely a VTF dependence; when T < 60 °C the data is more Arrhenius-like yet it flattens at lower temperature possibly because the liquid nature of the PTHF allows for sufficient segmental motion to facilitate greater conductivity than predicted by the Arrhenius model.

Fig. 2 shows TGA curves for the SPE samples. All samples are thermally stable up to approximately 150 °C, well above the common operating temperatures of batteries. Above this range, the SPE begins to lose mass owing to thermal degradation. This onset of thermal degradation occurs at lower temperatures with increase in salt loading, most likely due to the aluminum ions catalyzing breakdown of the polymer network. Nevertheless, the thermal stability of the SPEs within the required operating temperature range is notable.

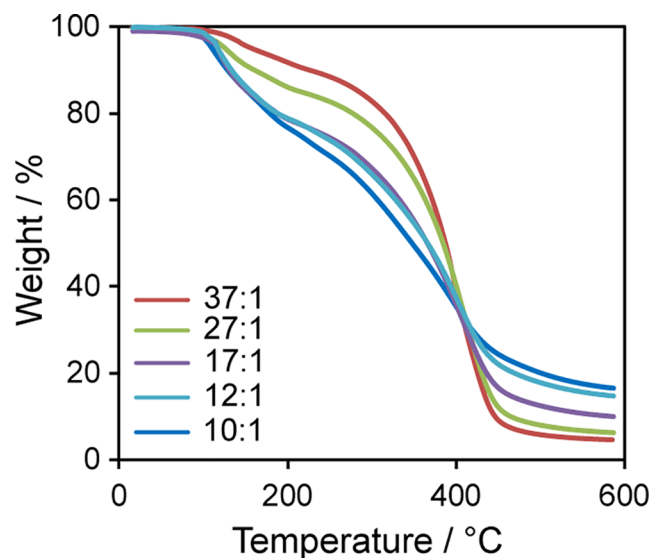Fig. 3 shows Raman spectra of the SPE samples. The spectra are

Fig. 2. TGA curves of PTHF-Epoxy copolymer networks over a range of aluminum salt loadings (O:Al^{3+} ratio).
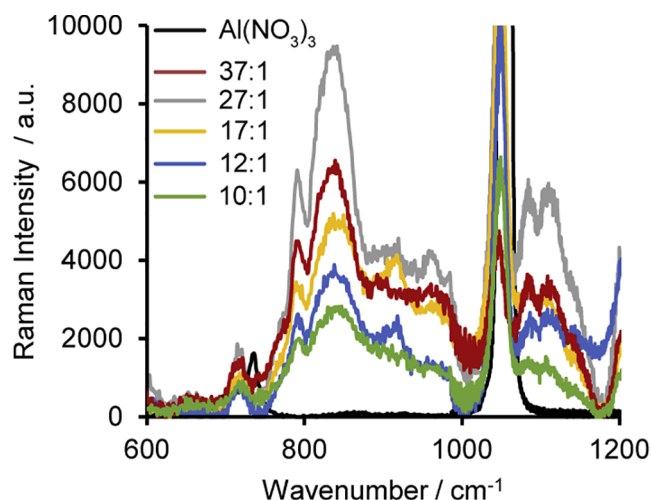
Fig. 3. Raman spectra PTHF-Epoxy copolymer networks over a range of aluminum salt loadings (O:Al^{3+} ratio).

generally dominated by the peaks of the PTHF and Epoxy. The Raman peaks between 900 and 1000 cm^{-1} are associated to the vibration modes of the C−O−C bond [14] of the PTHF and the ethylene oxide groups formed from the ring opening of the epoxide function. The strong and sharp band around 1050 cm^{-1} is associated to the ν_1 symmetric stretching of the nitrate group [15], and 724 cm^{-1} is associated to its ν_4 band. A critical observation is the absence of the band associated to the N−O−Al nitrato bond ($\nu_{\text{nitro-Al}}$ at ~1027 cm^{-1}) [15], which indicates thorough dissociation of aluminum nitrate in the SPE within the range of salt loadings explored. Hence, we infer that the increase in salt loading leads to more available aluminum ions, thereby contributing to the increase in conductivity.

Conclusion

We have demonstrated the synthesis and characterization of a copolymer network from PTHF and a cycloaliphatic epoxy as a solid polymer electrolyte for aluminum ion conduction. The SPE shows promising ion conductivities, and is thermally stable up to temperatures of 150 °C. This work shows the first demonstrable SPE system for aluminum ion conduction and opens opportunities for future work focused on exploring different aluminum salts and new SPE compositions (e.g., molecular weight, other polyether systems, different weight fractions, etc.), towards enhancing conductivity and improving thermal stability. As both the cation and anion can percolate across the polymer network, in-depth studies of the aluminum ion contribution to conductivity also need to be performed. Prototyping of all solid-state aluminum ion batteries is currently under study and will be reported in the future.

Acknowledgements

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