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Synthesis of Sodium Poly[4-styrenesulfonyl(trifluoromethylsulfonyl) imide]-*co*-ethylacrylate] Solid Polymer Electrolytes

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ABSTRACT

Sodium-based batteries are being considered to replace Li-based batteries for the fabrication of large-scale energy storage devices. One of the main obstacles is the lack of safe and conductive solid Na-ion electrolytes. A Na-ion polymer based on the (4-styrenesulfonyl(trifluromethylsulfonyl) imide anion, Na [STFSI], has been prepared by a radical polymerization process and its conductive properties determined. In addition, a number of multi-component polymers were synthetized by co-reaction of two monomers: Na[STFSI] and ethyl acrylate (EA) at different ratios. The structural and phase characterizations of the polymers were probed by various techniques (DSC, TGA, NMR, GPC, Raman, FTIR and Impedance spectroscopy). Comparative studies with blends of the homopolymers Na[PSTFSI] and poly(ethyl-acrylate) (PEA) have also been performed. The polymers are all thermally stable up to 300 °C and the ionic conductivity of EA copolymers and EA blends are about 1-3 orders of magnitude higher than that of Na [PSTFSI]. The highest conductivity measured at 100 °C was found for Na[PSTFSI-*blend*-5EA] at $7.9 \times 10^{-9}\,\mathrm{S\,cm^{-1}}$, despite being well below its T_g. Vibrational spectroscopy indicates interaction between Na^+ and the EA carbonyl groups, with a concomitant decrease in the sulfonyl interaction, facilitating Na^+ motion, as well as lowering T_g.

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1. Introduction

There is an increasing need for cost-effective, sustainable and environmentally friendly energy-storage systems [1,2]. Large-scale stationary electric storage devices and electric vehicles are among the key applications for such energy storage systems. Due to the low-cost and abundant availability of sodium (Na), Na-ion batteries (NIB) are an emerging and competitive candidate to replace current Li-ion batteries (LIB) [3]. One of the key developments needed for the success of NIBs is the development of safe and conductive Na-ion electrolytes, capable of supporting efficient cycling of the Na anode. The recent research focus has largely been centered on the design and preparation of high energy density Na cathode materials, such as $Na_{1.5}VPO_{4.8}F_{0.7}$ [4], $Na_x[Fe_{1/2}Mn_{1/2}]O_2$ [5], $Na_4Fe(CN)_6$ [6], bipolar porous organic electrode/$NaClO_4$ (BPOE/$NaClO_4$) [7]. Electrolyte materials are not as heavily researched, with most investigations using organic solvent based systems [8,9], however, as for Li based devices, a safe high performance electrolyte is just as important for Na devices.

Traditional liquid based electrolytes containing organic solvents, such as propylene carbonate, with dissolved $NaPF_6$ or $NaClO_4$ as the solute, are problematic due to unfavorable reactions at the anode which cause low capacity and Columbic inefficiency [3] as well as safety concerns. Solid polymer electrolytes (SPEs), which are safer and more shape-conformable than other solid-state electrolytes such as ceramic electrolytes, have shown great potential to serve as an alternative to the traditional liquid based electrolytes [10–12]. Some SPE designs contain a polymeric anionic framework, in which only the cations are capable of diffusion; the transference number of such electrolytes can approach unity [13,14]. This can effectively prevent the accumulation of anions on the anode and curb the occurrence of salt concentration gradients during the cell charge/discharge process [15]. A number of SPEs have been prepared and studied during the last two decades, including composite polymers [16,17], comb-shape polymers [18,19], cross-linked polymers [20] and linear polymers [18]. The ionic conductivity of those polymer electrolytes is mainly

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dependent on polymer crystallinity and/or segmental motion of the polymer backbones, which is associated with the glass transition temperature (T_g). However, the room temperature conductivity of those single-ion polymer electrolytes is normally quite low ($<10^{-7}$ S cm^{-1}), which is inadequate for practical applications [21,22].

Recently, Meziane et al. synthesized a single Li-ion polymer (lithium poly[(4-styrene sulfonyl) (trifluoromethanesulfonyl) imide], denoted as Li[PSTFSI]), which was blended with poly(ethylene oxide) (PEO) to form Li-ion electrolytes with conductivity as high as 10^{-6} S cm^{-1} at 70 °C [23]. The conductivity of the Li[PSTFSI]/PEO blend was compared and found to be better than the blend of lithium poly(styrene sulfonate) and PEO. It was explained that the higher conductivity of the Li[PSTFSI]/PEO blend is related to the charge delocalization on the perfluorinated sulfonimide group ($CF_3SO_2NSO_2$–, denoted as STFSI) in the polymer structure. This idea was initially addressed by the DesMarteau [24,25] and Watanabe [26] groups. Similar ideas have been applied to the fields of NIB, including SiO_2-PEG-STFSI (PEG = poly-ethylene glycol) [27], Na[PSTFI] [28], polyphosphazenes [29], and PFSI zwitterions (PFSI = diazonium (perfluoroalkyl) benzenesulfonylimide) [30]. More recently, Feng et al. synthesized a series of Li[PSTFSI]/MPEGA copolymers (MPEGA = methoxy-polyethylene glycol acrylate), which show ionic conductivity as high as 7.6×10^{-6} S cm^{-1} at 25 °C and 10^{-4} S cm^{-1} at 60 °C [31]. The higher conductivities of the Li[PSTFSI]/MPEGA copolymers compared with Li[PSTFSI]/PEO blends can be attributed to their segmental mobility. At about the same time, Bouchet et al. prepared several tri-block polymers (LiPSTFSI-*b*-PEO-*b*-PS, PS = polystyrene) with a maximum conductivity of 1.3×10^{-5} S cm^{-1} at 60 °C, which is strongly related to the amorphous character and segmental mobility of the polymer backbone [32]. Taking advantage of the charge delocalization character of STFSI and the low T_g nature of the well known acrylate backbones, we were encouraged to investigate the conductivities of Na-ion polymer electrolytes which contain both STFSI and acrylate segments. We also studied the homogeneous blends of Na [PSTFSI] and PEA at different ratios. To provide insight into the conduction mechanism, we want to understand two factors in these materials; what is the role of PEA and how strong is the interaction of Na^+ and STFSI anion?

2. Experimental

2.1. Materials

Sodium 4-vinylbenzenesulfonate was purchased from Sigma-Aldrich Pty. Ltd. Triethylamine and thionyl chloride were received from Merck Pty. Ltd. 4-tert-butylpycocatechol and trifluoromethanesulfonamide were purchased from Tokyo Chemical Industry Co., Ltd. All the above commercial chemicals were used as received. Ethyl acrylate was purchased from Tokyo Chemical Industry Co., Ltd. The stabilizer (mono methyl ether hydroquinone, MEHQ) in ethyl acrylate was quenched with 5 *wt.%* NaOH aqueous solution and the neat ethyl acrylate was dried over Na_2SO_4. The organic solvents used in this study are anhydrous and received without further purification. All synthesized materials/compounds were dried in high vacuum for 48 hours at high temperatures before instrumental measurements.

2.2. Instrumentation

All the manipulations related to synthesis, handling and storage of air/moisture sensitive materials/chemicals were carried out using standard Schlenk and glove box techniques under a high purity N_2 atmosphere.

2.2.1. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA)

DSC measurements (DSC Q100 series instrument (TA Instruments)) were carried out on the as prepared polymer electrolytes. The data was evaluated with Universal Analysis 2000 software. Approximately 5 to 10 mg of the polymer electrolyte samples were hermetically sealed in aluminium pans under N_2 in a glove box and measured over a temperature range of -60 °C to 250 °C/350 °C at a scanning rate of 10 °C min^{-1}. The glass transition temperature (T_g), measured at the onset of the heat-capacity change, was determined during the heating ramp. TGA samples were hermetically sealed under N_2 in a glove box and the measurements were performed on a Pyris 1 TGA (PerkinElmer) in a nitrogen atmosphere between 25 and 400 °C with a heating rate of 10 °C min^{-1}

2.2.2. Ionic Conductivity

The ionic conductivity measurement of the as prepared polymer electrolytes was carried out by ac impedance spectroscopy using a high frequency response analyser (HFRA; Solartron 1296). The cell used for the measurement was fabricated locally and is composed of two round flat stainless electrodes contained within a heated cell. The electrolyte samples were pressed into pellets under a hydraulic pressure of 10 ton for 0.5 hr. The pressed pellets were then aged in the oven at 150 °C over 2 hrs. The measurement cell was assembled under N_2 in a glove box and the data was collected over a frequency range of 0.1 Hz to 10 MHz (ten points per decade) with a 30 mV amplitude over a temperature range of 40 to 130 °C in 10 °C intervals. The raw data was measured and processed using the series circuit in Z-view (Version 2.3).

2.2.3. Nuclear magnetic resonance (NMR)

For solution NMR measurements, ^1H and ^{19}F NMR spectra were recorded with a Bruker AvanceIII 400 spectrometer and were referenced to the resonances of the solvent used.

2.2.4. Gel Permeation Chromatography (GPC)

The molecular weights of the synthesized polymer electrolytes were determined by GPC performed with a Gel Permeation Chromatography apparatus (Tosoh EcosHLC- 8320), which has been equipped with both refractive index (IR) and ultraviolet (UV) detectors (UV detection, $\lambda = 280$ nm). In this study, the UV detector was used as the detector. Tosoh alpha 4000 and 2000 columns were used for the measurement. DMF, containing LiBr, 0.01 M, was used as the solvent. Calibration curves were obtained by using polystyrene standards ranging between M_n 500–2.89×10^6 g mol^{-1}.

2.2.5. Raman Spectroscopy

For Raman mapping measurements, a confocal Raman system, Witec 300 R, based on an integral Olympus BX40 microscope with a 50x objective (8 mm) was used. The spatial resolution was about 2 μm. The calibration was undertaken referring to the 520.5 cm^{-1} line of silicon. A 785 nm laser source was used for excitation with the power of 15 mW. The collection time for each spectrum was 50 s with one accumulation. The spectrometer grating had 80 points/line. An automatic motorized translator X–Y stage was used to perform Raman mapping.

2.2.6. Attenuated total reflectance (ATR)-Fourier transform infrared spectroscopy (FTIR)

ATR-FTIR measurements were carried out on solid samples using an Agilent Cary 630 attenuated total reflectance spectrometer equipped with KBr optics in the 600–4000 cm^{-1} frequency range. The data was determined based on 32 scans with a resolution of 2 cm^{-1}.

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