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Electronic Supplementary Information

for

Inhibiting Li-ion battery operation at high temperature with thermally responsive polymers

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Experimental Section

Preparation of LiTFSI, PBMA, [EMIM][TFSI] Electrolytes. Ionic liquid electrolytes were prepared by the co-solvent evaporation method in which select amounts of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIM][TFSI], IoLiTec, 99%), poly(benzyl methacrylate) (PBMA, Sigma, M_W 100,000) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Acros, 99%) were mixed. Specifically, PBMA (1.21 g) and LiTFSI (0.215 g) were dried under vacuum for 12 hours (at 60 ^{0}C and 150 ^{0}C, respectively), dissolved in anhydrous THF (3 mL) and sealed under nitrogen. Separately, [EMIM][TFSI] (2 mL) was dried under vacuum at 80 ^{0}C for 6 hours and sealed under nitrogen. PBMA and LiTFSI solutions were mixed with [EMIM][TFSI], heated to 80 ^{0}C under nitrogen and dried under vacuum (50 mTorr) at 80 ^{0}C for a minimum of 12 hours to remove the THF. The remaining electrolyte consisted of a 5 wt % PBMA in a 0.5 M LiTFSI/[EMIM][TFSI] solution. Solutions were transferred to a glove-box vacuum antechamber for 1 hour and sealed under argon prior to electrochemical testing.

Electrolyte Solution Characterization. Cloud points (CP) of responsive electrolytes were determined using optical transmittance. Solutions were mixed and dried in test cells according to the previous section and purged with nitrogen prior to transmission measurements. Temperature-controlled cells with sapphire windows were placed in a UV-Vis spectrophotometer (Varian Cary 50 Bio) and heated at 2 ^{0}C/min while recording UV-Vis scans. An average transmittance was calculated over a range of wavelengths (600-800 nm). The CP was defined as the temperature at which the transmittance dropped below 80% of its initial value. Bulk conductivity measurements were conducted on electrolytes over a temperature range of 60 to 180 ^{0}C between stainless steel electrodes separated by poly(ether ether ketone) (PEEK) spacer (2mm thick, 2.5 diameter ID) (Figure S1). Electrolyte solutions were mixed and dried according to the previous section and assembled in the argon glove-box. Electrochemical impedance spectroscopy was performed over a frequency range of 1 Hz to 1 MHz at a potential of 0.0V (amplitude of 20 mV). Ionic conductivity was determined from the high frequency resistive component of the impedance spectrum and calculated using a cell constant calibrated from a standardized 1M NaCl solution at 25 ^{0}C (85 mS/cm).

Electrode Preparation. Lithium titanate (LTO, Sigma, 99%) electrodes were prepared by dispersing LTO, conductive graphite (CG, MTI Corp), and carboxymethylcellulose (CMC, MTI Corp) in an 80/10/10 weight percent ratio in DI water (18 MΩ). Specifically, CMC (1.0 g) was dissolved in water (12-15 mL) at 80 ^{0}C and ultrasonicated for 30 minutes to fully dissolve. LTO (8.0 g) and CG (1.0 g) were ground and mixed in a mortar and pestle and slowly added to the CMC solution. The resulting viscous LTO solution was ultrasonicated for 30 minutes and coated on 9 µm copper substrates using the doctor blade method. Resulting electrodes were heated slowly from room temperature to 90 ^{0}C over 6 hours and then dried under vacuum at 90 ^{0}C for 12 hours. The resulting electrodes were approximately 40 µm thick. Lithium iron phosphate electrodes (LFP, MTI Corp, 93% active material, 15 mm diameter) were 100 µm thick on 15 µm aluminum foil. Electrodes were dried for at least 12 hours at 80 ^{0}C under vacuum. LTO and LFP electrodes (15 mm diameter) were soaked in their respective electrolyte for at least 6 hours under vacuum (~30 in Hg vacuum) prior to electrochemical testing.

Electrochemical Measurements. Electrochemical measurements were performed with a Gamry REF600 galvanostat/potentiostat in a 2-electrode setup using a split test coin cell (MTI, EQ-STC) mounted in a modified convection oven. Solutions were heated at approximately 2 ^{0}C/min and allowed to equilibrate at set temperatures for 30 minutes prior to electrochemical measurements. Measurements were conducted on PBMA/[EMIM][TFSI]/LiTFSI electrolytes with an LTO anode and LFP cathode separated by a 40 µm nonwoven fiber separator (Dreamweaver Intl.) over a temperature range of 60 to 150 ^{0}C. Electrodes, electrolyte, and separator were assembled in standard 2025 button cells (MTI Corp) under argon, crimped at pressures >2,000 psi, and placed in the split test coin cell. Electrolytes and Li-ion cells were characterized using charge-discharge, electrochemical impedance spectroscopy (EIS), and open circuit voltage (OCV) measurements. Charge-discharge was performed at currents that resulted in discharge times of approximately 1000 seconds (C-rate of 3.6) over a potential range of 1.0 to 2.5V. EIS analysis was performed over a frequency range of 10 mHz to 1 MHz (0V vs. OCV, 20 mV RMS).

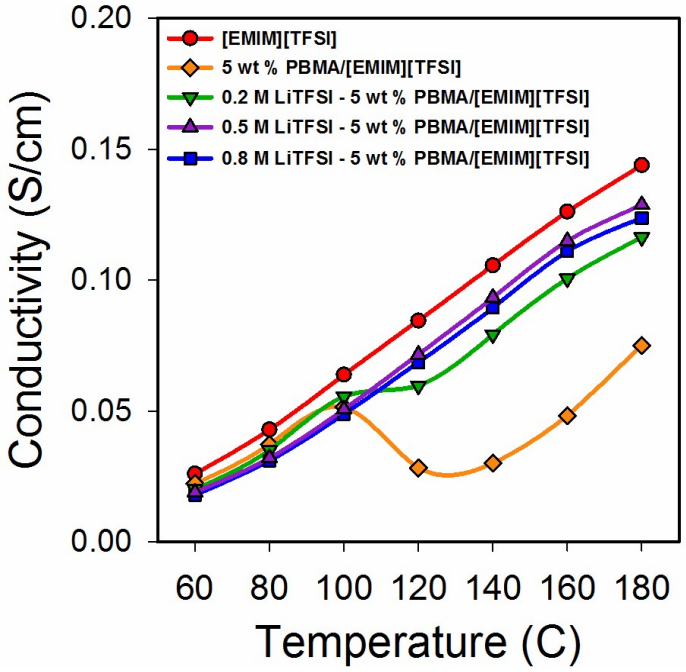

Figure S1. Conductivity vs. temperature of the pure IL, [EMIM][TFSI], and solutions of 5 wt % PBMA in [EMIM][TFSI] with varying concentrations of the lithium salt, LiTFSI.

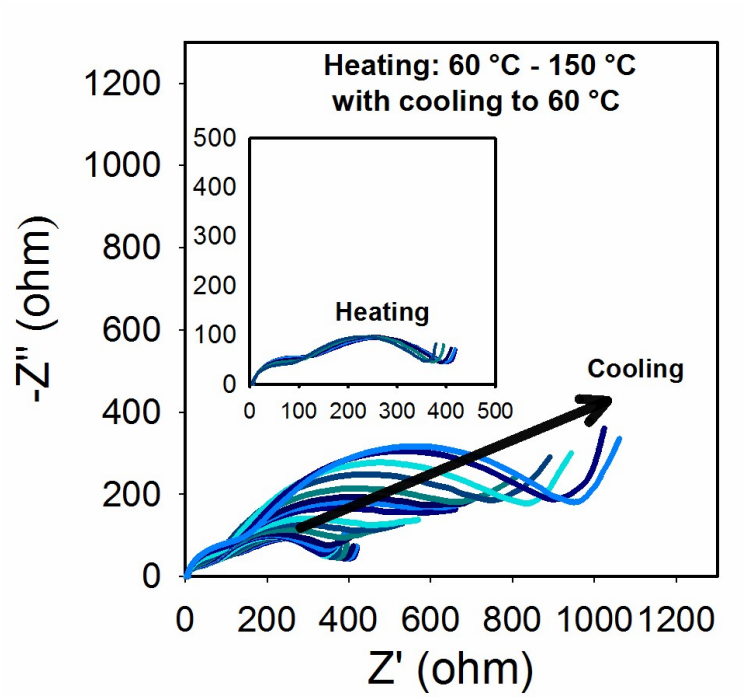

Figure S2. Continuous EIS measurements while heating from 60 ^{0}C – 150 ^{0}C at 1 ^{0}C/min, sitting at 150 ^{0}C for 10 minutes, and then cooling to 60 ^{0}C at 1 ^{0}C/min. Inset shows select EIS measurements between 60 ^{0}C – 150 ^{0}C with little or no change while the overall figure shows a combination of the heating and cooling runs. Upon cooling, reversibility in the system is not observed as the charge transfer resistance increases drastically even after cooling below the LCST. Measurements were performed at 0.0 V vs OCV at an amplitude of 20 mV over the frequency range of 1 MHz to 10 mHz.