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Electronic Supplementary Information

UV-cured Gel Polymer Electrolytes with Improved Stability for Advanced Aqueous Li-ion Batteries

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Experimental Section

Materials: Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium trifluoromethanesulfonate (LiOTf) were purchased from TCI America. 2-hydroxyethyl acrylate (HEA), poly(ethylene glycol) methyl ether acrylate (MPEGA, M_n = 480), poly(ethylene glycol) diacrylate (PEGDA, M_n = 700), 2,2-dimethoxy-2-phenylacetophenone (DMPA), N-methyl pyrolidone (NMP) and aluminum foil were purchased from Sigma Aldrich. $Li_4Ti_5O_{12}$ (LTO) and $LiMn_2O_4$ (LMO) powders were either provided by Saft America (MD, USA) or purchased from NEI Corporation (NJ, USA). $LiFePO_4$ (LFP) was purchased from MTI Corporation (CA, USA). Carbon black (C65) was purcased from MTI Corporation (CA, USA), and polyvinylidene fluoride (PVDF, HSV900) was obtained from Arkema.

Water-in-bisalt stock solution preparation: Water-in-bisalt (WiBS) liquid stock solution was prepared in ambient laboratory conditions by mixing 19.9 g of LiTFSI, 3.60 g of LiOTf, and 3.30 g of H_2O to a total molality of 21m LiTFSI + 7m LiOTf. The mixture was heated at 80° C for 1 hour and stirred until the salt was fully dissolved.

Gel polymer electrolyte pre-polymer preparation: Gel polymer electrolytes (GPEs) pre-polymer solutions were prepared in ambient laboratory conditions by mixing the WiBS stock solution with a monomer mixture in a 3:1 weight ratio. The monomer mixture consisted of a combination of HEA, MPEGA, and PEGDA. Specifically for the W-GPE formulation, a solution containing 89% MPEGA, 9 % HEA, and 2% PEGDA (by weight) was mixed directly from the stock solutions without further pre-processing. DMPA was added at 0.5% by weight of total polymer content. Then, one part of the mixture and three parts of WiBS were mixed to the final concentration. For the C-W-GPE formulation, the pre-polymer solution contained 58% WiBS, 17% LiTFSI, and 25% of the monomer mixture.

Gel Polymer Electrolyte cross-linking: The GPE pre-polymer mixture was cured either directly on an electrode (for cell testing), a stainless steel disk (for ionic conductivity measurement) or on a carrier substrate (for GPE characterization) followed by peeling off with a blade. The curing apparatus involved two glass slides coated with FEP (fluorinated ethylene propylene) tape to prevent electrolyte adhesion the glass. The bottom slide served as a substrate while the top slide served a two-fold purpose to a) control thickness and b) prevent oxygen inhibition from interfering with polymerization. Thickness was controlled either through two glass cover-slips (~0.125 mm, for cell testing) or stainless steel disks (for material characterization). The apparatus was placed in a Uvitron Intelliray 600 UV lamp with UVB bulbs (365 nm) and exposed for a total dose of 6 Joules.

Ionic conductuvity measurement: GPEs with different formulations were prepared with the aforementioned procedure. The GPEs were cured on stainless steel disks and then placed in 2032 coin cell. Top contact was made with two additional stainless steel disks and the coin cell was crimped. The actual thickness of the GPEs was measured by subtracting the total coin cell thickness from the thickness of the case and the spacer disks. The coin cells were placed in a temperature controlled chamber at 20, 0, 20, 40, and 60 degrees celsius, and allowed to rest for at least 1 hour at each temperature set point before measurement. Ionic conductivity was measured using a Gamry Reference 3000 potential using Electrochemical Impedance Spectroscopy with a 25 mV amplitude in the 0.1 Hz to 1 MHz range. The resistance of the electrolyte was extracted through the intercept of the Nyquist plot with the real axis.

Thermogravimetric Analysis (TGA) measurement: A TA Instruments (New Castle, DE, USA) Q5000 IR TGA was used to measure the mass loss of the samples in sealed aluminum pans (punctured before testing with an autosampler). The experiments were run in nitrogen with a 5 minute isothermal hold at the beginning followed by a 10 °C/min ramp from room temperature to 600°C.

Differential Scanning Calorimetry (DSC) measurement: A Mettler-Toledo (Columbus, Ohio, USA) Stare DSC was used to measure the heat flow of samples in aluminum pans. An autosampler and piercing device was used to pierce the pans before being loaded into the instrument. The experiments were run in nitrogen with a heating/cooling rate of 10°C/min over 3 steps: 1) cool from RT to -70°C 2) Heat from -70°C to 50°C, and 3) Cool from 50°C to -70°C.

Dynamic Mechanical Analysis (DMA) measurement: A TA Instruments (New Castle, DE, USA) RSA-G2 DMA was used to measure the mechanical responses versus frequency of the samples. A 20mm disk (approximately 2mm tall) was cut and placed on 25mm diameter platens and compressed with an initial force of 5 grams. Two main steps were used: 1) An oscillation amplitude test at 10 Hz sweeping strain from 0.01% to 2.0%; 2) An axial test to measure the adhesion (same sample) at a 0.05mm/s platen separation rate.

Fourier Transform Infrared Spectroscopy (FTIR) measurement: A Perkin Elmer (Waltham, MA, USA) Spectrum 100 FT-IR was used to characterize the infrared absorption for both liquid and solid/polymer samples. Approximately 20 mg of each sample was analyzed to see the effect of the polymer matrix on free water.

Electrochemical stability window measurement: GPEs were cured directly in three electrode cell glass vials. For the reduction stability, an Al wire with exposed area of 0.3 cm^2 was used as the working electrode, an LFP coated Al foil was used as the counter electrode, and Ag/AgCl (saturated KCl) was used as the reference electrode. The working electrode was scanned at 1mV/s from 0 to -3.0V vs. the reference for two cycles and the reduction data from the 2nd scan was used to compare the voltage stability of the electrolyte. For the oxidation stability, a Ti mesh with exposed area of 0.4 cm^2 was used as the working electrode, a $Li_4Ti_5O_{12}$ coated Al foil was used as the counter electrode, and Ag/AgCl (saturated KCl) was used as the reference electrode. The working electrode was scanned at 1mV/s from 0 to 3.0V vs. the reference

electrode for two cycles and the data from the oxidation data from the 2nd scan was used for the comparison.
Electrode fabrication (for coin cell testing): LTO and LMO electrodes with areal capacities of 0.4 mAh/cm^2 and 0.46 mAh/cm^2 were graciously provided by Saft America (MD, USA). All other LTO and LFP electrodes were fabricated in house. LTO slurries were prepared by mixing active material, carbon black, and PVDF dissolved in NMP in a weight ratio of 90:3:7. LFP slurries were prepared with a weight ratio of 88:4:8 among active material, carbon black, and PVDF. The slurries were homogenized using a Thinky planetary centrifugal mixer (AR-100) and blade coated on an aluminum foil using an automated blade coater (MTI Corporation). After coating, electrodes were dried in a vacuum oven at 120°C and calendered using an MTI Corporation calender press. The LTO and LFP active electrode loadings were 5.4 mg/cm^2 and 7.2 mg/cm^2, respectively.

Coin cell fabrication and testing: The electrochemical performance of the GPEs was characterized in 2032 coin cells. All cells were assembled in a N_2 filled dry box with relative humidity < 10%. Cells were made with and without separators. A disk of glassfiber paper (STERlITECH, GRADE C) was used as the separator, soaked in GPE solution, and UV cured as described above. LTO and LFP thickness for these cells was not controlled by a glass cover slip. For LTO/LMO cells without separator, the GPEs were cured directly on either electrode. The two coated cells were placed between stainless steel spacers after curing and crimped into a cell using a spring. Electrochemical characterization was performed using Landt Instruments (CT2001A, China) battery analyzers. LTO/LFP cells were cycled in the 1 to 2.4 V range, while LTO/LMO cells were cycled in the 1.5 to 2.8 V range.

Scanning Electron Microscopy (SEM): SEM images were obtained on samples after testing to evaluate GPE penetration and thickness. Coin cells were decrimped and the anode/GPE/cathode stacks were manually sectioned with scissors. Specimens were subsequently sputtered coated with iridium to make a conductive path from the top of the samples to the bottom of the SEM stubs. Images were taken using a Thermo Scientific Scios SEM at an accelerating voltage of 5 kV.

Flexible battery fabrication: Aluminum/Titanium current collectors were e-beam evaporated on Kapton films resulting in a stack of 1µm Ti/1µm Al/1mil Kapton for the LMO electrode and 0.5µm Ti/1µm Al/1mil Kapton for the LTO electrode. LTO and LMO electrode slurries were prepared using the process described for LTO above except active material, carbon black, and PVDF were mixed together in a ratio of 90:5:5 before being homogenized with NMP in a Thinky planetary centrifugal mixer. Electrode tabs were cut manually after electrode coating and the top and bottom edges of the electrodes were trimmed with Kapton tape prior to GPE application to prevent shorting near the edges. GPEs with a formulation of 25 wt% monomer mixture and 75wt% WiBS were coated and cured on either side of the Kapton substrates. The monomer mixture used in the GPE was a mixture of MPEGA, HEA, and PEGDA mixed by weight in a ratio of 90:9:1, respectively, with 0.5% DMPA added by weight of total polymer content. The two electrodes were aligned after curing the GPE and gently pressed together.

Supporting Figures and Tables

TABLE S1 - COMPOSITION FOR THE THREE PRIMARY ELECTROLYTES

Electrolyte	LiTFSI (%wt)	LiOTf (%wt)	H_2O (%wt)	Polymer (%wt)
28m WiBS	74.2	13.4	12.3	0.0
W-GPE	55.7	10.1	9.2	25
C-W-GPE	60	7.8	7.2	25

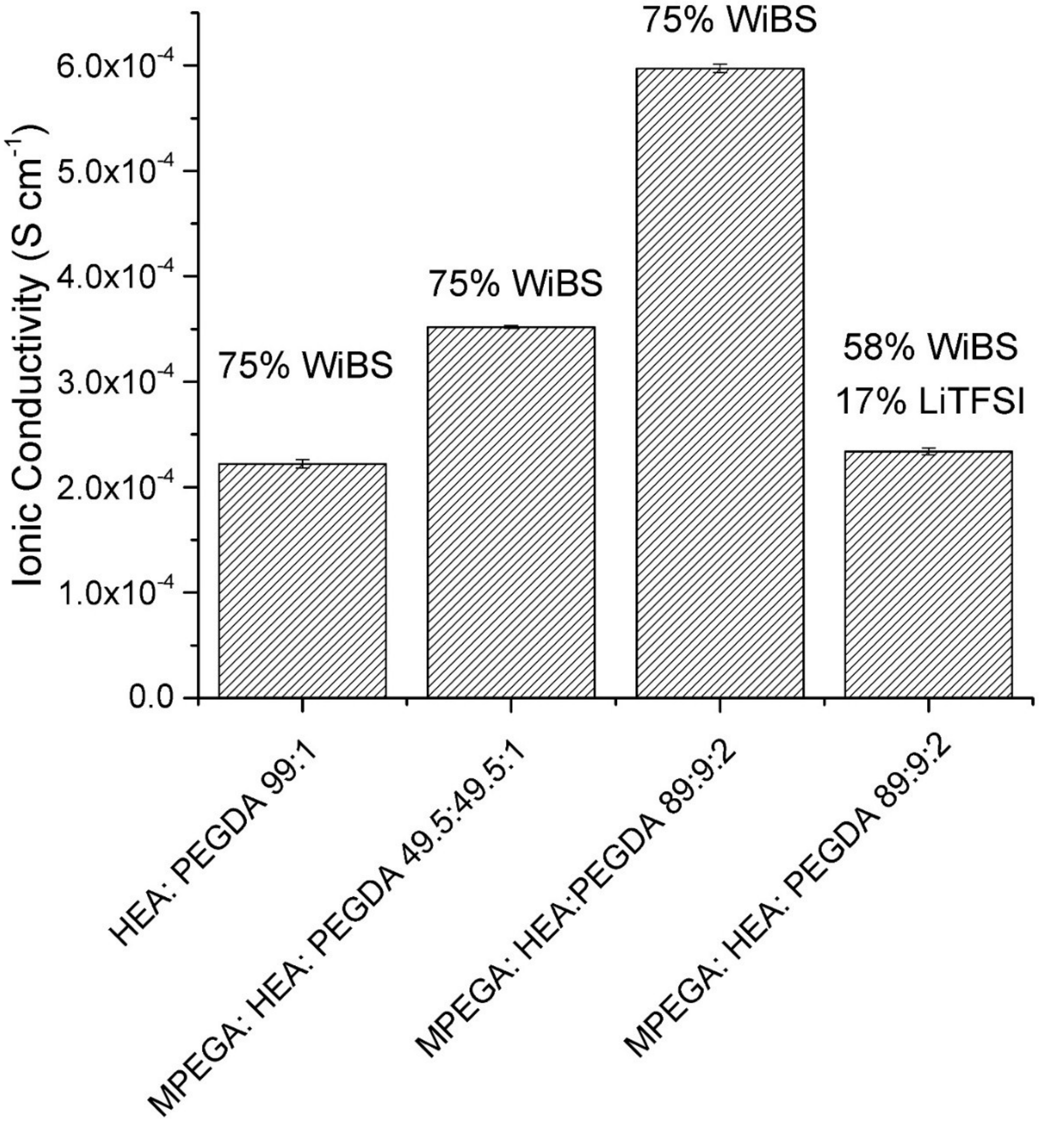

Figure S1: *Room temperature ionic conductivity for different GPE formulations*

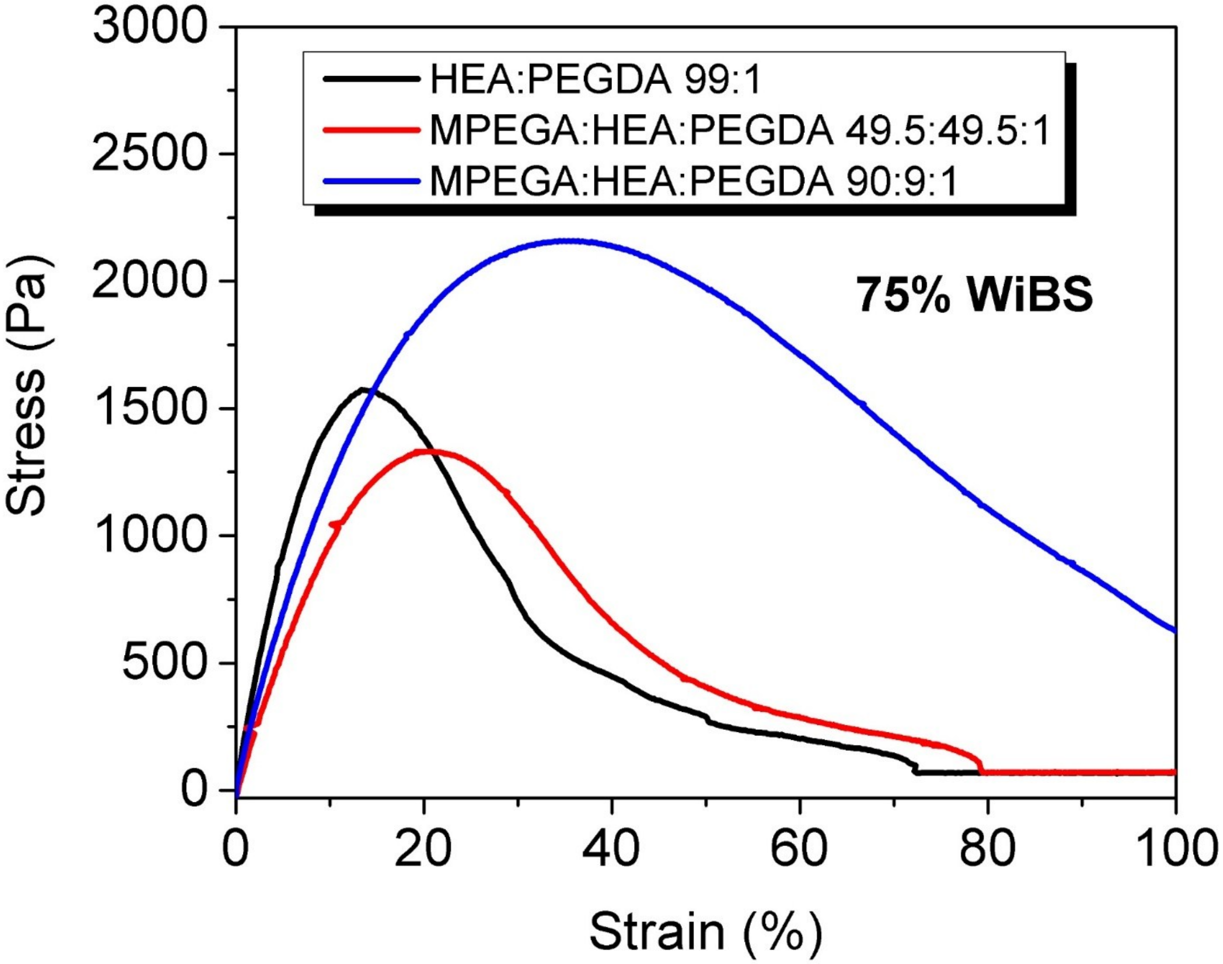

Figure S2: *DMA analysis of GPEs with different MPEGA, HEA, PEGDA ratios showing the axial adhesion stress vs strain.*

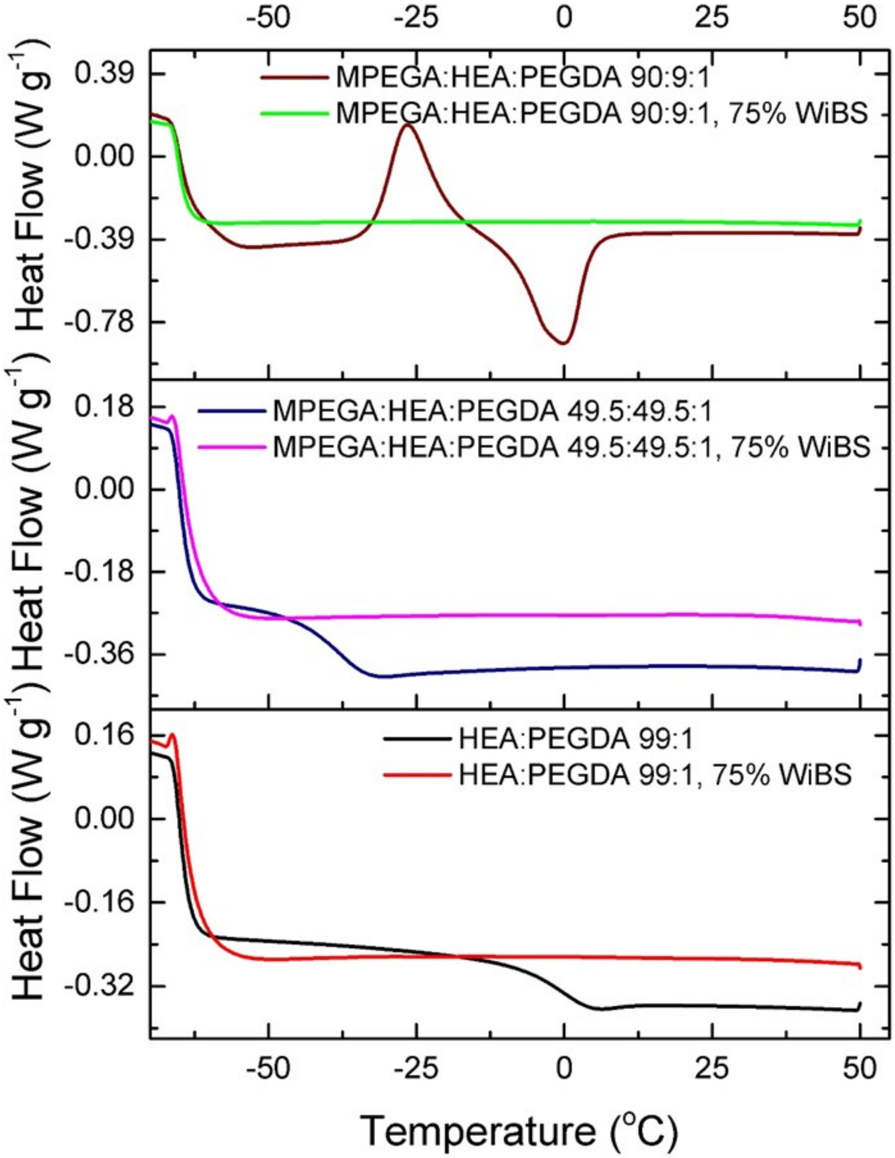

Figure S3: *Differential scanning calorimetry scans for different polymer formulations with and without WiBS. Glass transition peaks disappear with WiBS addition. The first formulation on top shows a behavior of poly(ethylene glycol) side chain crystallization followed by melting.*

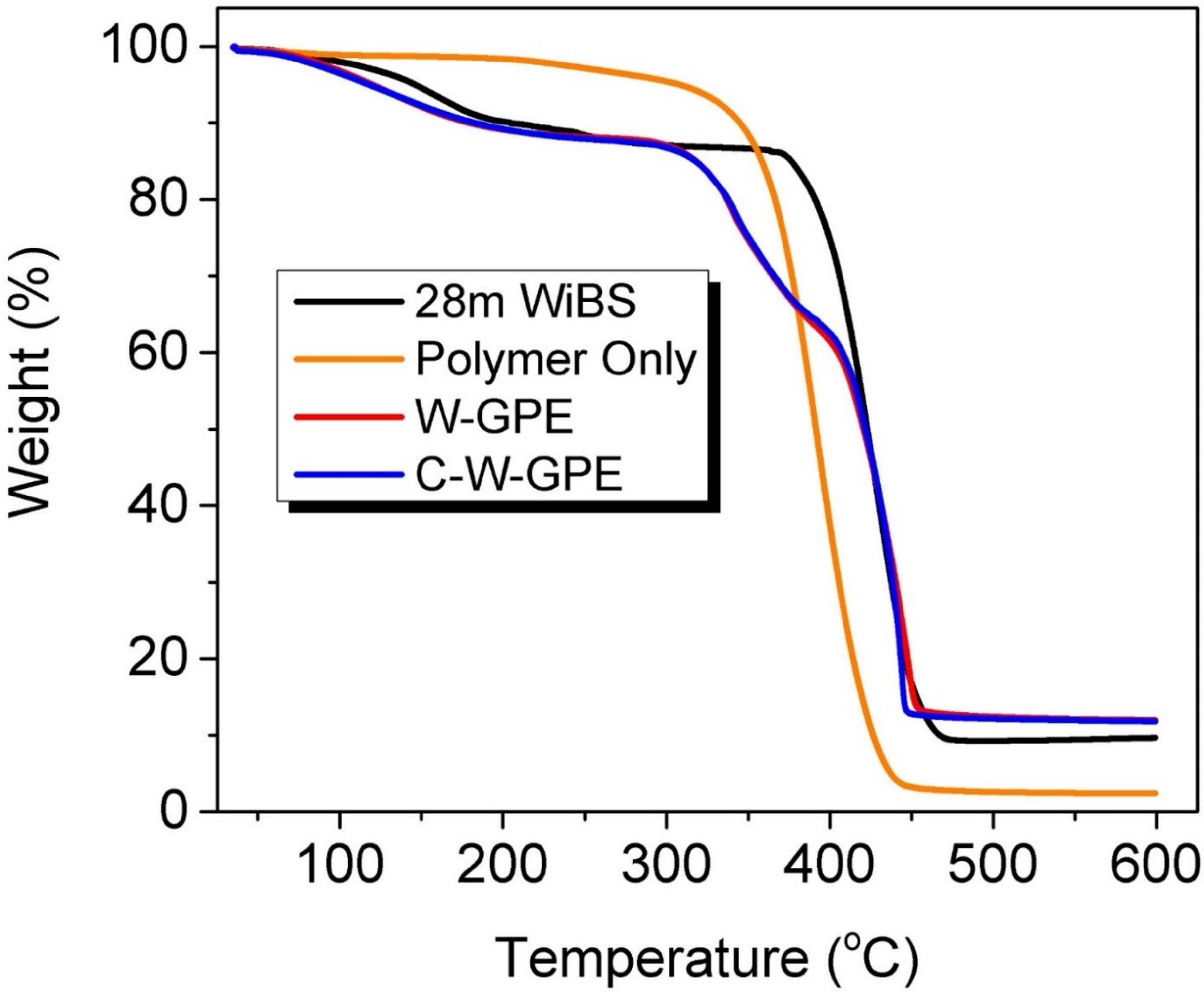

Figure S4: *TGA data from the three different electrolytes studied in this work. The lower mass observed in the W-GPE and C-W-GPE cases around 130-150°C is attributed to some partial polymer decomposition (due to HEA)*

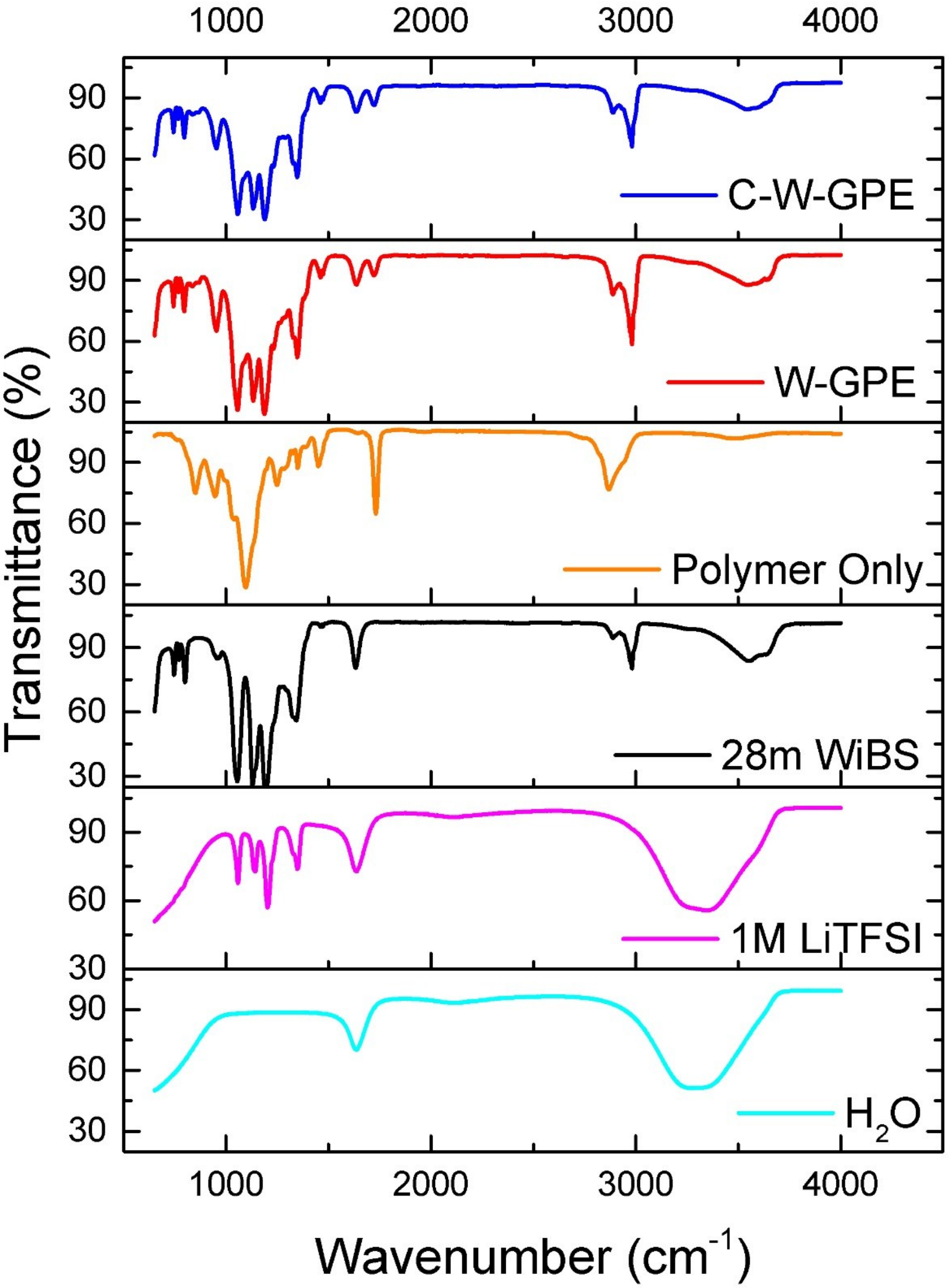

Figure S5*: FTIR data for different samples, including water only, 1M LiTFSI, polymer only, and the two GPE concentrations. GPEs exhibit the same shift for water peaks as the WiBS, validating that the mechanism is similar as the liquid*

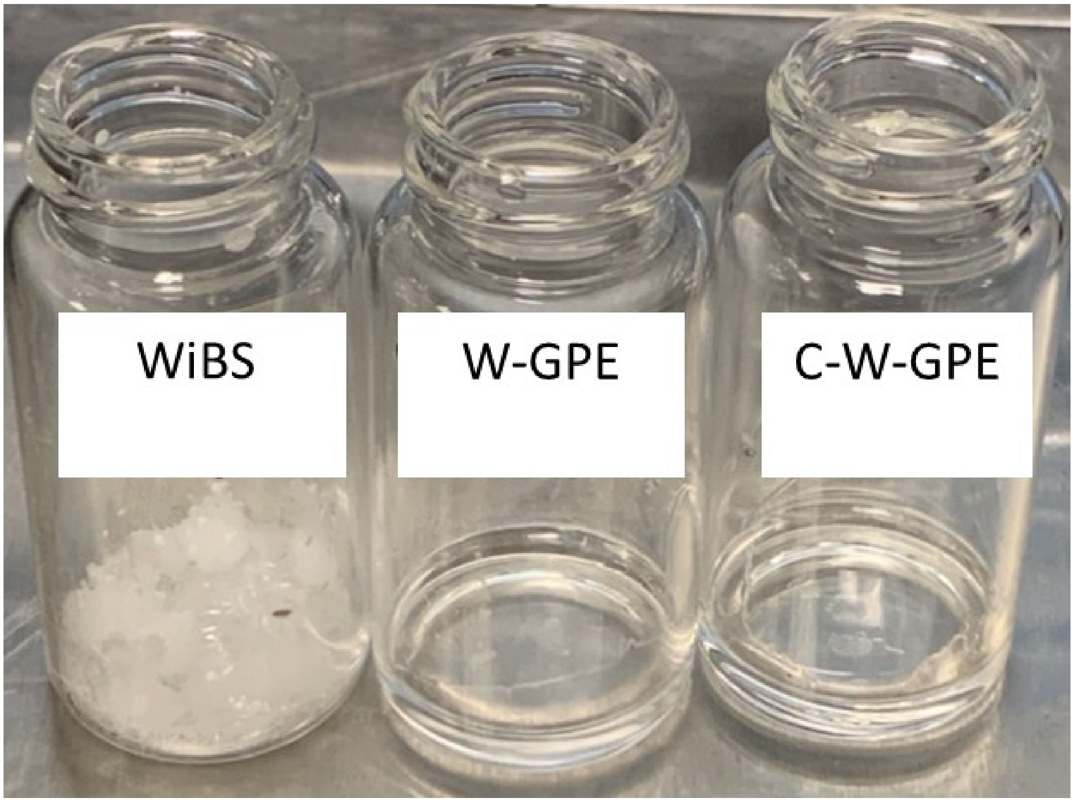

Figure S6: *Optical images of WiBS, W-GPE, and C-W-GPE electroltyes after 167 hours in the glove box*

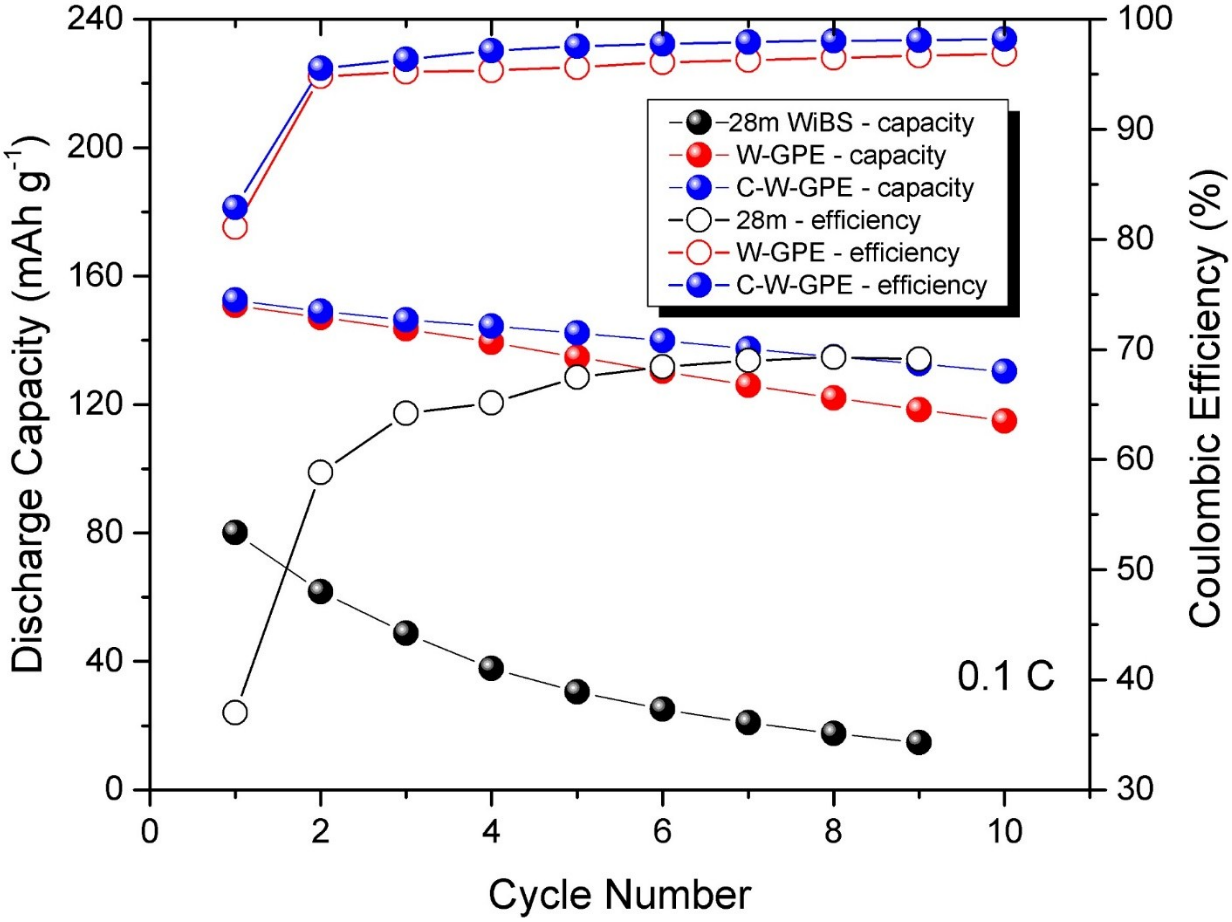

Figure S7: *LTO/LFP cell discharge capacity and coulombic efficiency for the first 9 and 10 cycles of oepration for WiBS and W-GPE/C-W-GPE electrolytes, respectively, showing the significantly improved stability with the polymer*

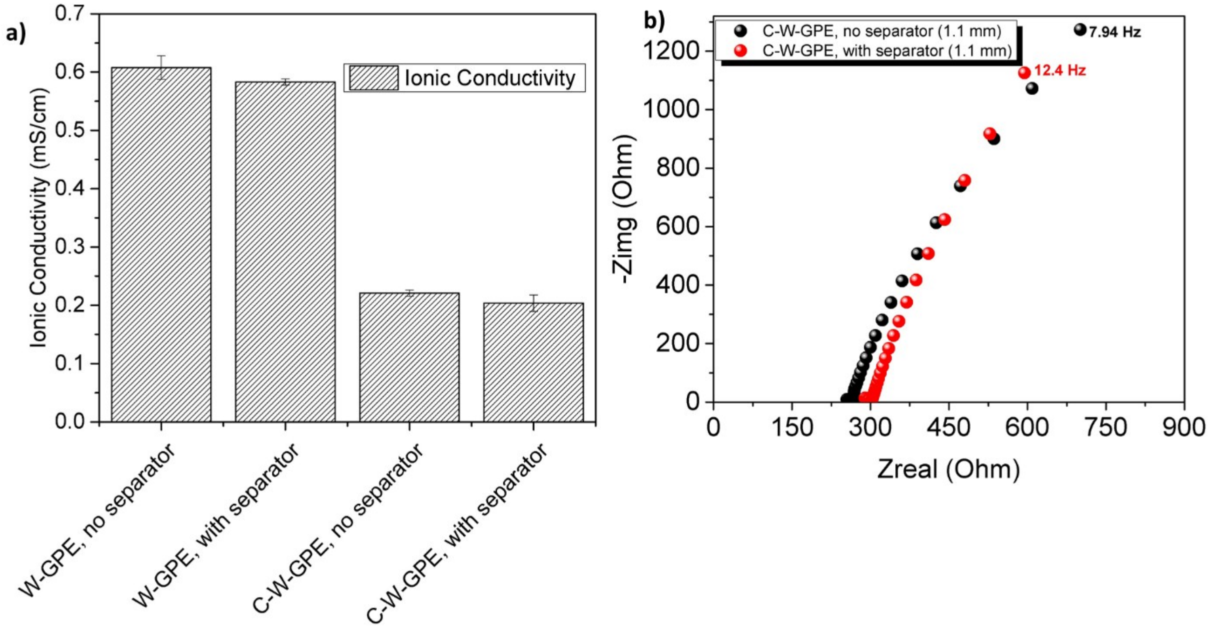

Figure S8*: a) ionic conductivity of W-GPE and C-W-GPE with and without separator and b) a representative set of electrochemical impedance spectra (portion of plot shown from the marked frequencies to the 1 MHz range) for the C-W-GPE with and without separator. Both figures show that when GPEs are cured inside a separator, their ionic conductivity decreases slightly*

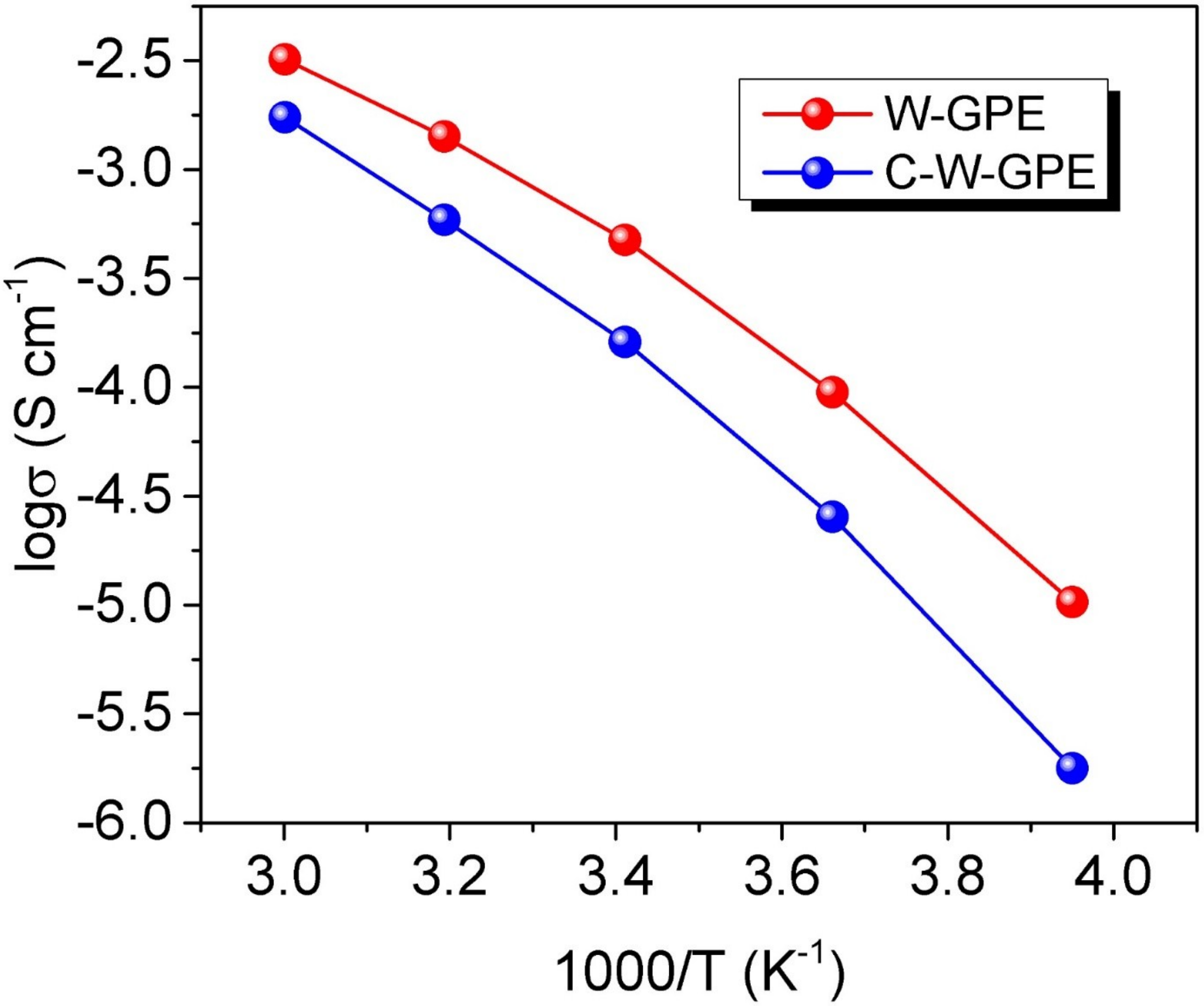

Figure S9: *Ionic conductivity vs temperature for the two GPEs*

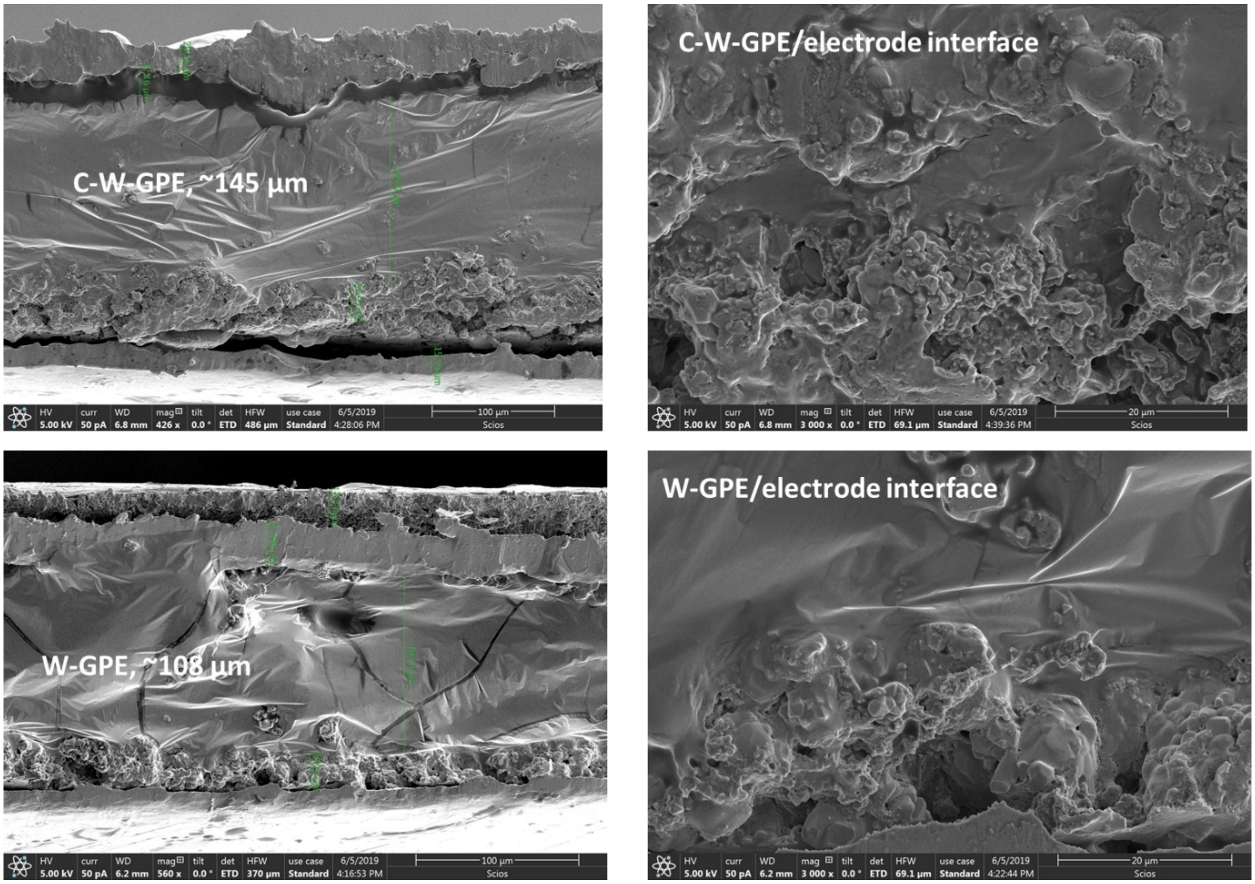

Figure S10: *SEM images of C-W-GPE and W-GPE cells after testing. Even though as cured thicknesses are on the order of 100 microns on either side, cell crimping changes the final thickness. The variation is attributed to differences in pressure as well as curing morphology. Higher magnification SEM images show excellent electrolyte penetration inside the porous electrodes for both formulations.*

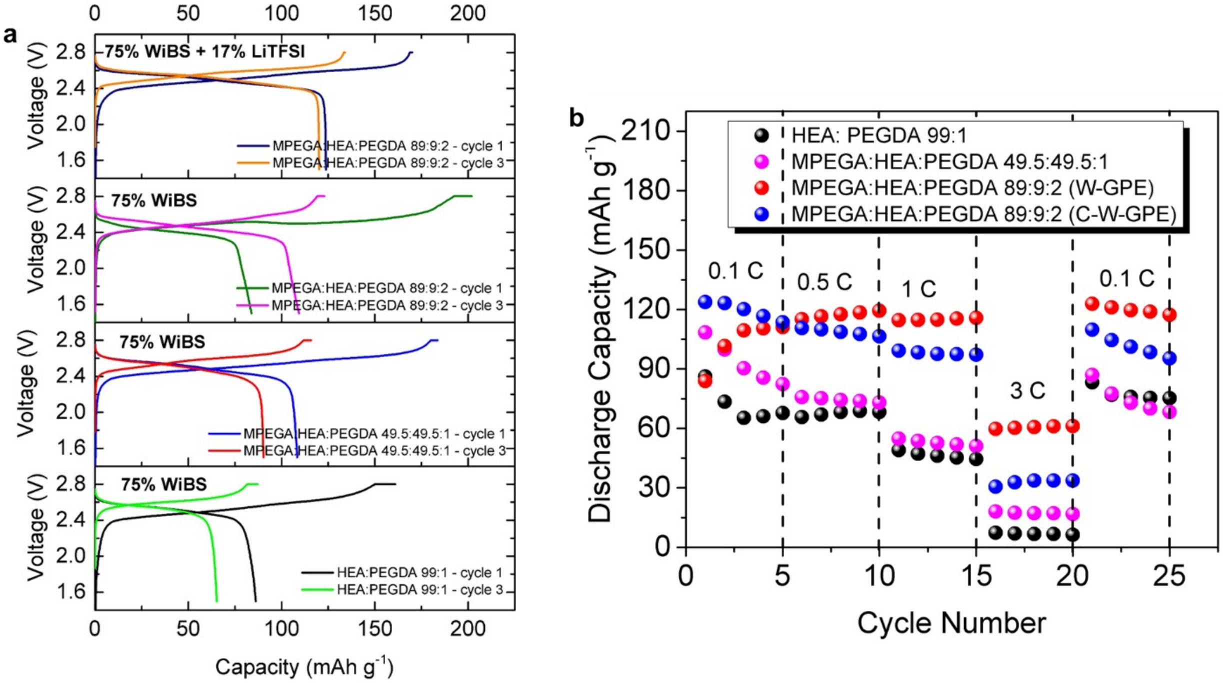

Figure S11: *Electrochemical cell performance of GPEs at 25% polymer: a) 1st and 2nd cycle profile for different formulations. Results are in agreement with ionic conductivity and DMA data in Figures S1 and S2, further validating polymer selection. b) rate capability for different recipes*

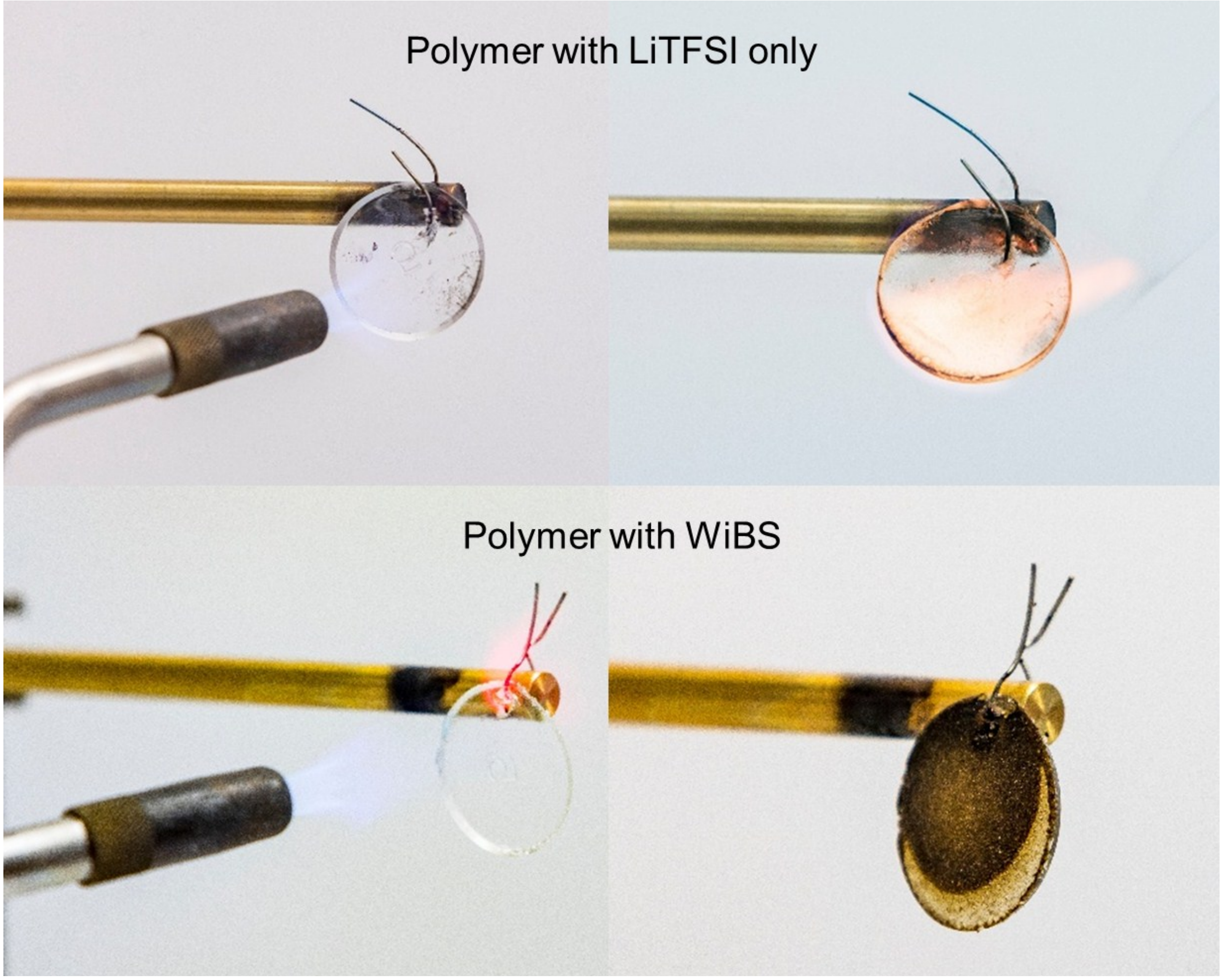

Figure S12: *Flammability test for UV cured GPEs with and without water; upon expoure to flame with a torch, a GPE with LiTFSI only (30% by weight, which is the maximum solubility in our polymer without co-solvent) the flame propagates within a few seconds; convversely, a GPE even with higher polymer content (30-32% roughly in this test) exhibits self-extinguishing properties upon repeated exposure to flame (video SV1 for real-time capture of a similar test)*

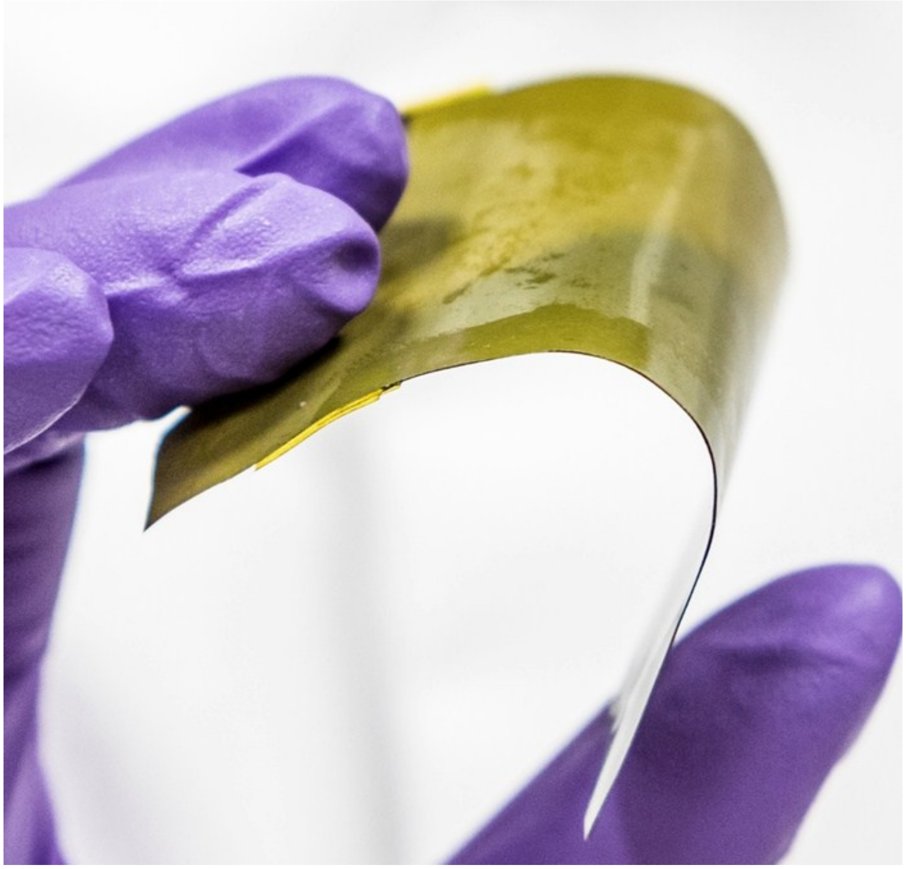

Figure S13: *Image of a flexible battery fabricated using a UV cross-linked WiBS GPE; the cell is completely exposed to air and contains tape only to prevent shorting at the electrode tabs*