Electronic Supplementary Information

Hybrid Composite Polymer Electrolytes: Ionic Liquid as a Magic Bullet for the Poly(ethylene glycol)-Silica Network

Tyler Blensdorf[1], Anisha Joenathan[1], Marcus Hunt[2], Ulrike Werner-Zwanziger[3], Barry D. Stein[4], Waleed E. Mahmoud[5], Ahmed A. Al-Ghamdi[5], John Carini[6], Lyudmila M. Bronstein[1,5,7]

[1] Indiana University, Department of Chemistry, 800 E. Kirkwood Av., Bloomington, IN 47405,

[2]The Chemours Company, 22828 Hwy 87 W, Fayetteville, NC 28306

[3]Department of Chemistry, Dalhousie University, Halifax, NS, Canada

[4]Indiana University, Department of Biology, Bloomington, IN 47405, USA

[5]King Abdulaziz University, Faculty of Science, Department of Physics, Jeddah, Saudi Arabia

[6]Indiana University, Department of Physics, Bloomington, IN 47405, USA

[7]A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 119991 Russia

Table S1. HCPE composition and conductivities.

Sample notation	PEG molecular weight, Da	IL type	IL amount, wt. %	Conductivity, S/cm
200-IL1-10	200	1	10	7.58×10^{-5}
200-IL1-20	200	1	20	2.68×10^{-4}
200-IL1-30	200	1	30	3.55×10^{-4}
200- IL1-40	200	1	40	3.59×10^{-4}
200- IL1-50	200	1	50	3.77×10^{-4}
200- IL1-55	200	1	55	8.50×10^{-4}
300- IL1-10	300	1	10	9.21×10^{-5}
300- IL1-30	300	1	30	2.70×10^{-4}
300- IL1-40	300	1	40	2.87×10^{-4}
300- IL1-55	300	1	55	9.49×10^{-4}
400- IL1-10	400	1	10	4.45×10^{-5}
400- IL1-20	400	1	20	1.48×10^{-4}
400- IL1-30	400	1	30	1.95×10^{-4}
400- IL1-40	400	1	40	3.57×10^{-4}
400- IL1-50	400	1	50	6.82×10^{-4}
400- IL1-55	400	1	55	4.91×10^{-4}
600- IL1-10	600	1	10	4.06×10^{-5}
600- IL1-20	600	1	20	8.86×10^{-4}
600- IL1-30	600	1	30	1.55×10^{-4}
600- IL1-40	600	1	40	2.39×10^{-4}
600- IL1-50	600	1	50	4.13×10^{-4}
600- IL1-55	600	1	55	3.71×10^{-4}
1000 IL1-10	1000	1	10	4.36×10^{-5}

1000- IL1-20	1000	1	20	1.02×10^{-4}
1000- IL1-30	1000	1	30	1.50×10^{-4}
1000- IL1-40	1000	1	40	1.81×10^{-4}
1000- IL1-50	1000	1	50	2.91×10^{-4}
1000- IL1-55	1000	1	55	4.87×10^{-4}
2000- IL1-10	2000	1	10	5.49×10^{-6}
2000- IL1-20	2000	1	20	8.87×10^{-6}
2000- IL1-30	2000	1	30	1.89×10^{-5}
2000- IL1-40	2000	1	40	3.11×10^{-5}
2000- IL1-50	2000	1	50	9.70×10^{-5}
2000- IL1-55	2000	1	55	3.05×10^{-4}
300- IL2-10	300	2	10	3.51×10^{-5}
300- IL2-30	300	2	30	1.65×10^{-4}
300- IL2-40	300	2	40	1.97×10^{-4}

^{1}H and ^{29}Si Solid State NMR

Similar to the solution state NMR spectra (Figure S1, center), in the ^{1}H MAS NMR spectra (Figure 2 and example in top of Figure S1), the peaks around 9.1 ppm, and 7.8 ppm originate from the protons within the imidazolium rings. The resonances between 1.2 and 2.1 ppm stem from the methyl and methylene groups in the IL butyl-side chains. The peaks around 4.2, and 4.5 ppm derive from the N-bound methyl, (NCH_3), and the N-bound methylene group, (NCH_2), of the 1-butyl-3-methylimidazolium (IL1). While in solution, the NCH_3 group resonates at 3.82 ppm, the concentration dependent, the concerted signal increase of the peaks at 4.2 and 4.5 ppm supports their assignment to the IL. Such shift differences between solution state and solid state NMR are common. In addition, the PEG protons resonate in this area (between 3.9 ppm and 4.8 ppm). The strong intensity of the peak at 3.9 ppm in the solid state ^{1}H MAS NMR spectra at low IL concentrations supports the assignment of this peak to the polymer backbone. Related to their lower mobility, these resonances are not as sharp as those from the ionic liquid molecules and cause the spinning sidebands (marked by ss) seen above 10 ppm and below -2 ppm.

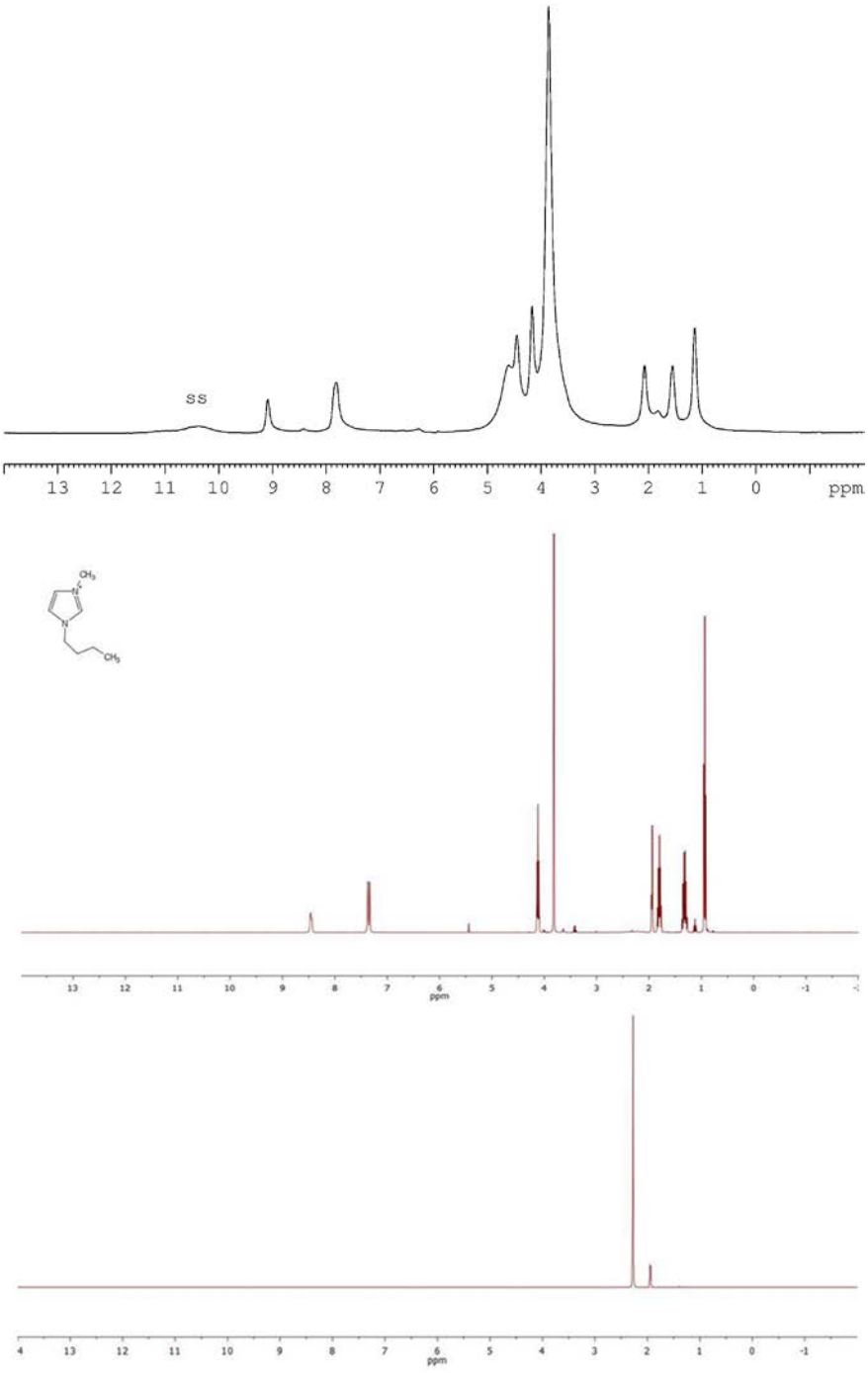

Figure S1. ^{1}H MAS NMR spectra of 300-IL1-50 (top), ^{1}H solution NMR spectra of IL1 (center) and the fifth THF extract after extraction of IL1 from 300-IL1-50 (bottom). (top) In addition to the lines observed in the solution spectrum (compare to center), PEG signals resonate between 3.9 - 4.8 ppm and cause spinning sidebands, marked by ss. (center) ^{1}H NMR(400 MHz, CD_3CN δ/ppm): 0.94(3H, t, but-CH_3), 1.31(2H, m, CH_2), 1.80(2H, m, CH_2), 1.94(3D, s, solvent), 3.82(3H, s, NCH_3), 4.12(2H, t, NCH_2), 7.34(1H, d, NCH), 8.34(1H, s, NCHN). (bottom) ^{1}H NMR(400 MHz, CD_3CN δ/ppm): 1.94(3D, s, solvent), 2.27(2H, s, H_2O impurity)

The ^{29}Si NMR spectra show two signal groups reflecting the T-species between -50 and -70 ppm, and the Q-groups, between -85 and -110 ppm. The assignments are in particular T^2 [C-$SiO_2(O^-)$] around -58 ppm, T^3 [C-SiO_3] around -66 ppm, Q^2 [$SiO_2(O^-)_2$] around -91 ppm, Q^3 [$SiO_3(O^-)$] around -102 ppm, and Q^4 [SiO_4)] groups around -109 ppm.

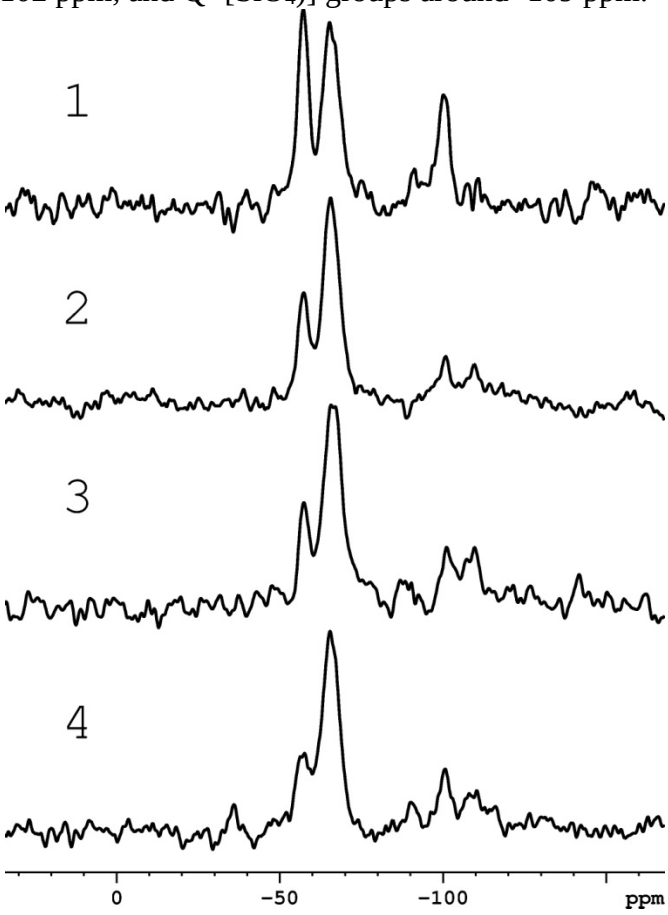

Figure S2. ^{29}Si CP/MAS (1) and directly excited ^{29}Si MAS NMR spectra of 300-IL1-10 (2), 300-IL1-30 (3), and 1000-IL1-30 (4)

TEM

Table S2. The HCPE OIN sizes from TEM.

PEG molecular weight, Da	IL2 amount, wt. %	NP size, nm
200	20	4.8±0.3
200	50	5.0±0.2
300	20	4.9±0.3
300	50	5.1±0.7
600	20	5.1±0.6
600	50	5.8±1.2

Conductivities and crosslinking densities

Table S3. Crosslinking densities

IL %	PEG300-IL1	PEG300-IL2	PEG400-IL1	PEG600-IL1	PEG1000-IL1
10	2.8×10^{-4}	1.5×10^{-4}	1.54×10^{-4}	1.73×10^{-4}	1.59×10^{-4}
30	4.6×10^{-4}	3.8×10^{-4}	1.49×10^{-4}	1.63×10^{-4}	1.46×10^{-4}
50	2.1×10^{-4}	1.1×10^{-4}	7.73×10^{-5}	1.21×10^{-4}	9.23×10^{-5}
None	8.1×10^{-2}	-	-	-	8.21×10^{-2}

Mechanical properties

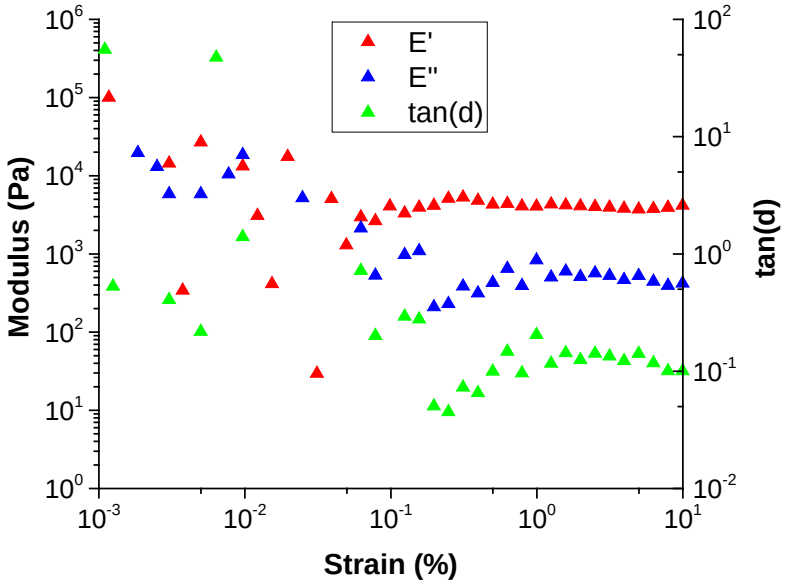

Figure S3. Strain sweep for 600-IL1-10 at 25 °C and 1 Hz.

HCPE cycling

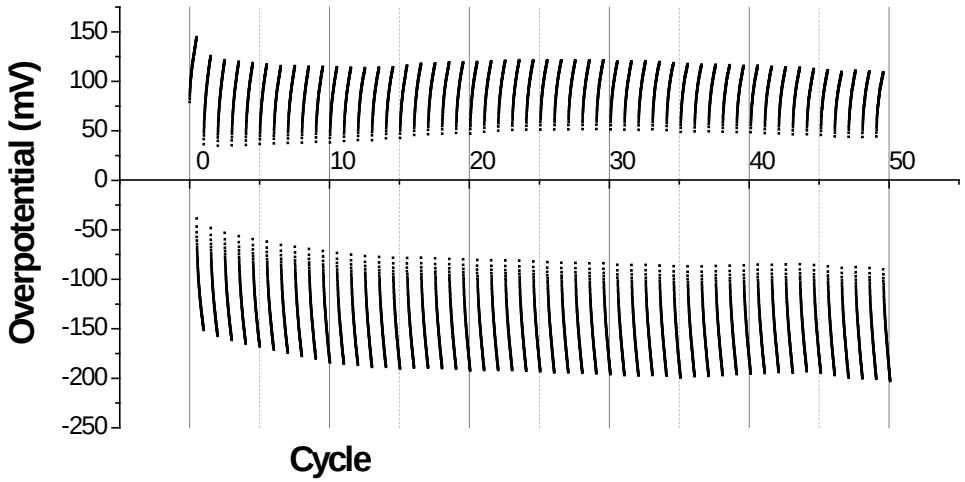

Figure S4. Overpotential versus cycle number for the 300-IL2-55 sample.

The cycling of 300-IL2-55 shows the final overpotential value plotted against the cycle number. There is an initial increase, but the final values stay fairly consistent after 10 cycles.

The high current density and voltage compared to those for the polymer electrolytes described elsewhere[1] demonstrate higher resistance than that implied by the bulk conductivity. This means the resistance is dominated by the contacts due to oxygen impurities in a glove box.

References

1. A. S. Fisher, M. B. Khalid and P. Kofinas, *J. Electrochem. Soc.*, 2012, 159, A2124-A2129.