Supporting Information

Disiloxane-functionalized phosphonium-based ionic liquid as electrolyte for lithium-ion battery

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Experimental

All manipulations were carried out under argon atmosphere with standard Schlenk techniques using dried solvents. Chloromethylpentamethyldisiloxane was purchased from Gelest Inc. (the purity identified by ^{1}H NMR is less than 94%). All other reagents were purchased from Sigma Aldrich and used as received.

^{1}H and ^{13}C NMR experiments were performed on a Bruker model DMX 500 NMR spectrometer (11.7 T).

Ionic conductivity was determined by YSI 3200 Conductivity Instrument equipped with an YSI 3253 conductivity cell. The viscosity of ionic liquids was measured on a programmable viscometer (Brookfield, DV-II+). Cyclic voltammetry experiments using a Solartron Analytical 1470E system were performed in a custom-made three-electrode cell with a 1.6-mm-diameter Pt working electrode, a Li metal reference electrode, and a Li counter electrode.

The charge–discharge cycling performance was tested on a Maccor Electrochemical Analyzer using 2032 coin cells with NCM as the cathode, MCMB graphite as the anode, and a Celgard 3501 separator. The effective electrode area was $1.6 cm^2$. Performance data were acquired and analyzed by the software associated with the instrument.

XPS Experiment

All XPS measurements were made using a Kratos™ Axis Ultra DLD surface analysis instrument. The base pressure of the analysis chamber during these experiments was 3×10^{-10} Torr, with operating pressures around 1×10^{-9} Torr. Spectra were collected using a monochromatic Al Kα source (1486.7 eV) and a 300 x 700 micron spot size. The Al source was operated at 13 mA of emission current with the target anode set to 15 kV, for a resulting power of 195 W. For survey spectra the data were collected using a pass energy of 160 eV (fixed analyzer transmission mode), a step size of 1 eV and a dwell time of 200 ms. High resolution regional spectra were collected using a pass energy of 20 eV (fixed analyzer transmission mode), a step size of 0.1 eV and a dwell time of 300 ms. For low signal to noise regions, multiple passes were made and the results averaged together as noted.

Prior to introduction into the load lock vacuum chamber of the instrument, all air sensitive samples were loaded into an inert transfer module which interfaces with the instrument. Samples were prepared for analysis in an Ar-filled glove box, with no more than 1 ppm O_2 and 1 ppm H_2O. Non-conductive samples showed evidence of differential charging, resulting in peak shifts and broadening. Photoelectron peak positions were shifted back towards their true values and their peak widths were minimized by flooding the samples with low-energy electrons and ions from the charge neutralizer system on the instrument. Further peak position correction was made by referencing the C 1s peak position of adventitious carbon for a respective sample (284.8 eV, PHI Handbook), and shifting all other peaks in the spectrum accordingly.

Fitting was done using the program XPS Peak. Each relevant spectrum was fit to a Shirley type background to correct for the rising edge of backscattered electrons that shifts the baseline higher at high binding energies, or a Linear type background otherwise. The end points of the background region were averaged over the 7-9 nearest points to increase the accuracy. Peaks were fit as asymmetric Guassian/Lorentzians, with 0-30 % Lorentzian character. The FWHM of all sub-peaks were constrained to 0.7-2 eV, as dictated by instrumental parameters, lifetime broadening factors, and broadening due to sample charging. With this native resolution set, peaks were added and the best fit, using a least squares type fitting routine, was obtained while adhering to the constraints mentioned above.

Synthesis of Iodomethylpentamethyldisiloxane.
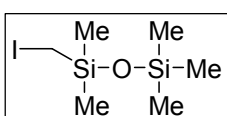
$(CH_3)_3SiOSi(CH_3)_2CH_2I$ was prepared according to a published procedure.[1,2] $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$ (81g, 0.41 mol), NaI (61g, 0.41 mol) and dry acetone (500 mL) are placed in a 2-liter round-bottom flask fitted with a reflux condenser. The mixture is refluxed for 24 h. A lot of white precipitation is formed. The solid is filtered through a pad of celite and the resulting filtrate was concentrated until the most of the acetone is removed. The residue was distilled under reduced pressure and the major fraction is collected to afford the title compound (60 $^\circ$C at 0.5 mmHg). Yield: 85.7 g (72%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.98 (s, 2H, IC*H$_2$*), 0.24 (s, 6H, -CH$_2$Si*Me$_2$*O-), 0.10 (s, 9H, -OSi*Me$_3$*). ^{13}C NMR (500 MHz, CDCl$_3$): δ 1.9 (s, IC*H$_2$*), -0.3 (s, -CH$_2$Si*Me$_2$*O-), -12.4 (s, -OSi*Me$_3$*).

**Synthesis of Iodomethylpentamethyldisiloxane-Triethyl phosphonium Iodide (P222Si-I).**
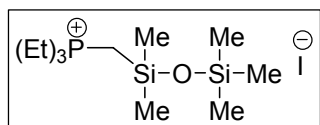
P222Si-I: A mixture of PEt$_3$ (20g, 0.17 mol) and the prepared (CH$_3$)$_3$SiOSi(CH$_3$)$_2$CH$_2$I (48g, 0.17) was stirred at ambient temperature for 24 h. The resulting white solid was washed with diethyl ether and then dried under vacuum. Yield: 54 g (81%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.37 (dq, 6H, $^3J_{H-H}$= 7Hz, $^2J_{H-P}$= 16 Hz, PCH_2Me), 1.83 (d, 2H, P-CH_2Si-, $^2J_{P-H}$ = 18 Hz), 1.26 (dt, 9H, $^3J_{H-H}$= 7Hz, $^3J_{H-P}$= 18 Hz, PCH$_2$$Me$), 0.33 (s, 6H, -CH$_2SiMe_2$O-), 0.08 (s, 9H, -OSi$Me_3$). ^{13}C NMR (500 MHz, CD$_3$CN): δ 14.9 (d, $^1J_{C-P}$ = 51 Hz, PCH$_2$Me), 6.3 (d, $^1J_{C-P}$ = 40 Hz, PCH$_2$Si), 6.0 (d, $^2J_{C-P}$ = 5 Hz, PCH$_2$$Me$), 2.8 (s, -CH$_2SiMe_2$O-), 1.7 (s, -OSi$Me_3$).

**Synthesis of Disiloxane-Functionalized Triethylphosphonium**

Bis(trifluoromethanesulfonyl) Imide (P222Si-TFSI).
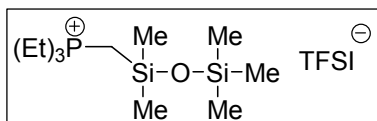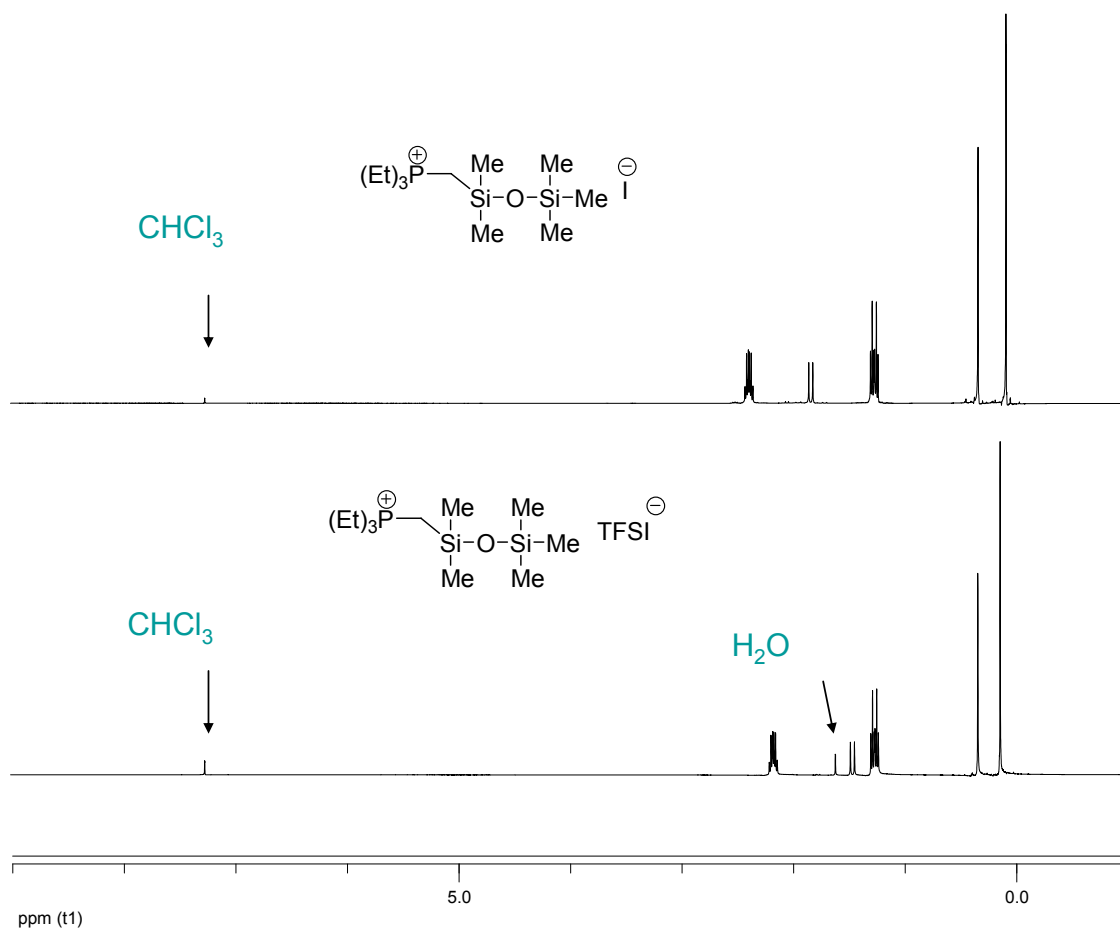
The metathesis of I$^-$ in P222Si-I by TFSI$^-$ was performed in water. The desired product P222Si-TFSI is not soluble in water and forms hydrophobic globules at the bottom of the flask. A solution of 44.6 g (0.155 mol) of LiTFSI in 40 ml of water was added into a solution of 48.8 g (0.155 mol) P222Si-I in 30 ml of distilled water and stirred overnight at ambient temperature. CH$_2$Cl$_2$ (200 mL) was added to extract the ionic liquid. The organic layer was washed with deionized water several times to remove LiI. The absence of iodide anions was confirmed by performing the test with AgNO$_3$. The organic layer was stirred with activated carbon and then filtered to afford a colorless solution. The solution was passed through a pad of alumina. The final filtrate was concentrated in a rotary evaporator to remove CH$_2$Cl$_2$ and followed by drying in a vacuum oven at 100 ^{o}C for 24. The final product was stored in He-filled glove box. Yield: 65 g (90%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.17 (dq, 6H, $^3J_{H-}$

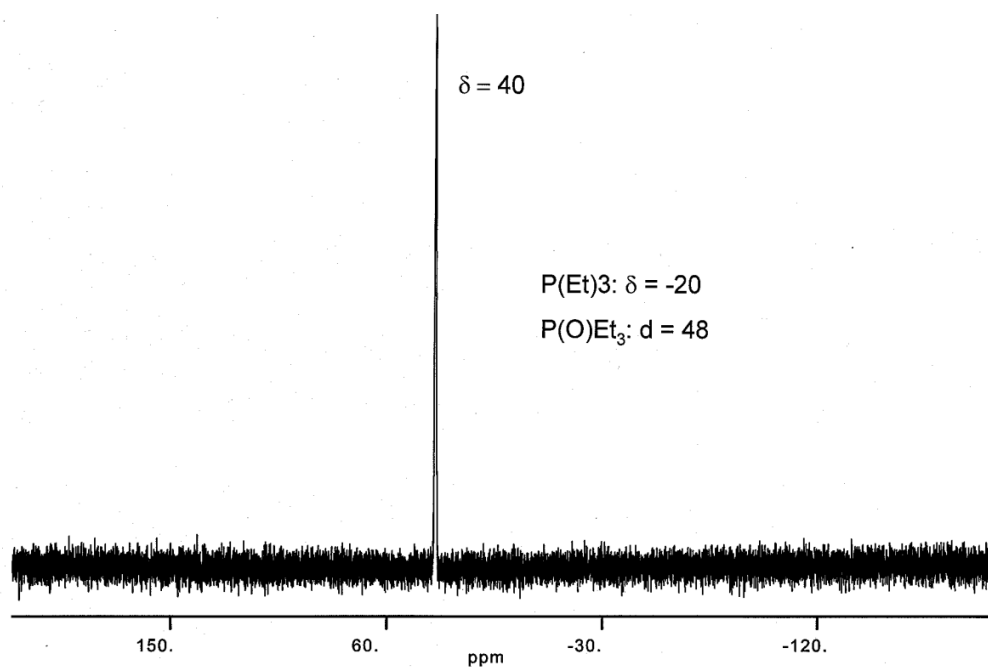$_H$= 8 Hz, $^2J_{H-P}$= 13 Hz, PCH_2Me), 1.45 (d, 2H, P-CH_2Si-, $^2J_{P-H}$ = 18 Hz), 1.26 (dt, 9H, $^3J_{H-H}$= 8 Hz, $^3J_{H-P}$= 18 Hz, PCH$_2$$Me$), 0.33 (s, 6H, -CH$_2SiMe_2$O-), 0.13 (s, 9H, -OSi$Me_3$). ^{13}C NMR (500 MHz, CDCl$_3$): δ 119.7 (q, $^1J_{C-F}$ = 321 Hz, CF$_3$), 13.9 (d, $^1J_{C-P}$ = 51 Hz, PCH_2Me), 5.3 (br, PCH_2Si), 5.0 (br, PCH$_2$$Me$), 2.4 (s, -CH$_2SiMe_2$O-), 1.4 (s, -OSi$Me_3$). ^{31}P NMR (202.4 MHz, CDCl3):δ 40 (s).
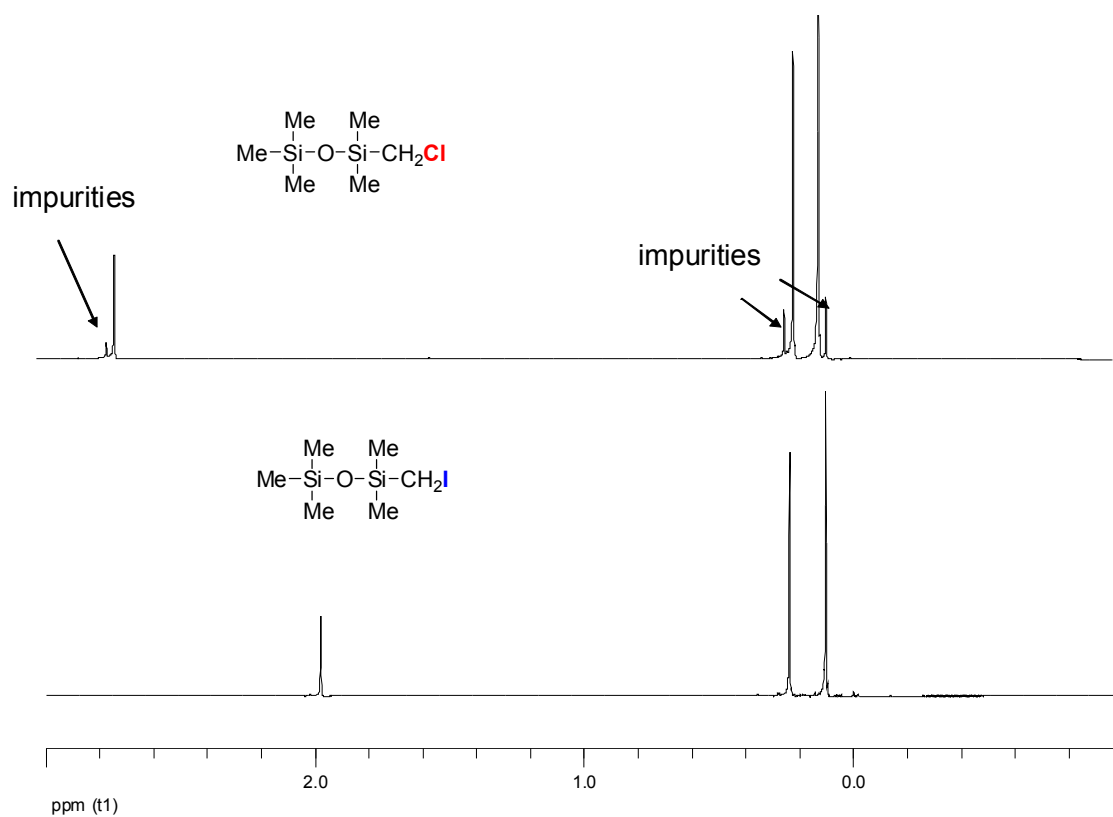
Figure S1: ^{1}H NMR spectra of $ClCH_2SiMe_2OSiMe_3$ (commercial) and synthesized $ICH_2SiMe_2OSiMe_3$ in $CDCl_3$.

CHCl₃

(Et)₃P⁺—Si(Me)(Me)—O—Si(Me)(Me)—Me I⁻

CHCl₃

(Et)₃P⁺—Si(Me)(Me)—O—Si(Me)(Me)—Me TFSI⁻

H₂O

5.0   0.0

ppm (t1)

Figure S2: ^{1}H NMR spectra of P222Si-I and P222Si-TFSI in CDCl$_3$.

$\delta = 40$

P(Et)3: δ = -20

P(O)Et$_3$: d = 48

150.   60.   -30.   -120.

ppm

Figure S3. ^{31}P NMR of P222Si-TFSI in CDCl$_3$

Reference

1. Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.*, **1946**, *68*, 481.
2. Roedel, G. F. *J. Am. Chem. Soc.*, **1949**, *71*, 269.