Synthesis and Characterization of Alkylsilane Ethers with Oligoethylene Oxide Substituents for Safe Electrolytes in Lithium-Ion Batteries

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SUPPORTING INFORMATION

Experimental

1. Materials

Di(ethylene glycol) monomethylether (99.6+%), tri(ethylene glycol) monomethylether (95%), tri(ethylene glycol) (99%), and tetra(ethylene glycol) (99%) were purchased from Aldrich and distilled prior to use, except for tetra(ethylene glycol) which was dried over molecular sieves before use. Tosylates of (di-, tri-) ethylene glycol monomethyl ether and allyl methoxy triethylene glycol ether were synthesized as described previously.[1] Chloromethyltrimethylsilane and Chloropropyltrimethylsilane were purchased from Gelest; their iodination was carried out by reacting with NaI in dry acetone. Sodium hydride (NaH, 60% dispersion in mineral oil) was purchased from Acros. Lithium bis(trifluoro methanesulfonyl) imide (LiTFSI) was donated by 3M Co.. Lithium bis(oxalate)borate (LiBOB) was supplied by Chemetall and purified by recrystallization in dried, distilled acetonitrile (Aldrich). $LiNi_{0.8}Co_{0.05}Al_{0.05}O_2$ cathode materials and MCMB graphite were obtained from Sumitomo Co. and OSAKA Gas Co., respectively.

2. Measurements

^{1}H NMR was determined on a Bruker AC300 spectrophotometer; ^{13}C and ^{29}Si NMR were performed on a Varian Unity 500 spectrophotometer. All doping levels are reported as the number of lithium cations (Li^+) per EO unit. Elemental analyses were performed at Chemisar Laboratories Inc., Guelph, ON, Canada.

Viscosity (η) measurements were performed on a Brookfield LVDV-I+ viscometer. The dielectric constants (ε) were measured on an 870 Liquid Dielectric Constant Meter (Scientifica). Differential scanning calorimeter (DSC) data were obtained using a Perkin-Elmer Pyris Diamond instrument, calibrated with indium and polydimethylsiloxane. All samples were loaded under dry argon. Undoped samples were cooled with liquid nitrogen down to -160 °C, followed by heating from -160 °C to 20 °C at a rate of 10 °C/min. This cooling-heating cycle was repeated a second time. The glass transition temperature (T_g) value was determined from the onset of the glass transition of the second heat run. The conductivity was measured in cells using a Princeton Applied Research (PAR) potential galvanostat model 273A and a PAR frequency response detector model 1025, which applied an AC current and measured impedance (Z) and phase shift (θ) over a frequency from 100 to 100 000 Hz. The four lowest θ values were used to calculate an average conductivity (σ) for both conductivity experiments and cell calibrations. The cell assembly was carried out in an argon-filled dry box.[2] Variable temperature conductivity measurements were conducted in a copper Faraday cage for temperatures ranging between 0°C and 60°C. A condenser was wrapped in cotton and attached to a circulating ethylene glycol bath regulated cell temperature, which was monitored with a thermocouple taped directly to the cell. The flammability test of the electrolytes was based on UL Flame Rating-UL 94 which is the stardard test for plastic materials. Some test conditions of UL 94 were modified to make it suitable for testing the electrolyte by incorporating a fiberglass wick. The detailed test procedures and the calculation of propagation rate was described earlier.[3] The hydrolysis percentage of 1NM3 was calculated from the integration ratio of trimethylsilyl peak of the hydrolyzed product (hexamethyldisiloxane, δ=0.13 ppm) and 1NM3 (δ=0.10 ppm). The cycling performance tests were conducted on an electrochemical analyzer (Maccor Inc.) using 2032 coin cells containing $LiNi_{0.8}Co_{0.05}Al_{0.05}O_2$ as the cathode and MCMB graphite as the anode. The separator (Celgard 3501) was soaked with the electrolytes before being placed in the cell. After three formation cycles, typically between 3.0 and 4.0 V at C/20 (0.1 mA) and C/10 (0.2 mA), the coin cells were cycled continuously at room temperature at a C/5 (0.4 mA) rate.

3. Synthesis of alkylsilanes with one methylene spacer

3.1 Synthesis of acetatomethyltrimethylsilane[4]

To a suspension of NaOAc (18.5g, 0.22mol) and tetrabutylammoniumchloride (2.8g, 1.0 mmol) in 300 mL carbon tetrachloride was added chloromethylpentamethyldisiloxane (40.0g, 0.20mol). The mixture was heated to reflux for 3 days. The solid salt was removed by filtration. After removing the solvent, the pure product was obtained by distillation. Yield: 24g (80%); b.p. 123-125 ^{o}C.

^{1}H NMR ($CDCl_3$), δ (ppm) = 0.05 (s, 9H, Si-CH_3), 2.02 (s, 3H, CH_3 of Ac), 3.73 (s,2H, CH_2); ^{13}C NMR ($CDCl_3$), δ (ppm)=0.0; 23.80; 60.82; 174.73.

3.2 Synthesis of hydroxymethytrimethylisilane:

To a suspension of $LiAlH_4$ (7.0g, 0.184 mol) in 500mL dry ethyl ether was added acetatomethyltrimethylsilane (26.3g, 0.174mol) dropwise at 0 ^oC. After addition, the mixture was stirred at room temperature for 24 h. The reaction mixture was then poured cautiously onto ice. The organic phase was separated, and washed with 5% H_2SO_4 solution and then water until neutral. The ether solution was dried over magnesium sulfate, filtered, and distilled to give the product. Yield: 16g (88%); b.p. 118-120 ^oC.

^1H NMR ($CDCl_3$), δ (ppm) = 0.04 (s, 9H, Si-CH_3), 0.97 (s, 1H, OH), 3.36 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$), δ (ppm)=0.00; 59.20.

3.3 General procedures of Method A:

To a solution of hydroxymethyltrimethylsilane (0.1 mol) in 350 mL THF was added BuLi (0.11 mol) dropwise at 0 ^oC. After addition, the solution was warmed to room temperature and stirred for 1 h. The corresponding tosylate with differrent EO chain length was then added at room temperature. The mixture was heated to 80 ^oC and refluxed for 16 h. After removing the tosylate lithium salt via filtration, the product was obtained by vacuum distillation as a colorless liquid in a yield of 70-85%.

3.4 General procedures of Method B:

A mixture of excess (di-, tri-) ethylene glycol (0.2mol) monomethyl ether and Na metal in small pieces (1.2g, 0.05mol) was vigorously stirred at room temperature (heated at 60 ^oC when necessary) until Na was completely consumed. After adding iodomethyltrimethylsilane (10.7g, 0.05 mol), the reaction mixture was then heated to 100 ^oC. When the reaction was completed, the product was obtained by extracting with hexane, evaporating the volatiles, and distillation as colorless liquid in a yield of 60-70%.

Methoxyethoxymethyl-trimethylsilane (1S1M1):

b.p. 119-120 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ =0.00 (s, 9H, CH_3-Si), 3.12 (s 2H, Si-CH_2-), 3.28 (s, 3H, CH_3-O), 3.40-3.48 (m, 4H, OCH_2CH_2O); ^{13}C NMR (300 MHz, $CDCl_3$): 0.05, 62.09, 68.56, 74.92, 77.63; ^{29}Si NMR (500 MHz, $CDCl_3$): -2.68; Anal. Calcd. For $C_7H_{18}O_2Si$: C, 51.80; H, 11.18. Found: C, 51.64, H, 11.01.

[Methoxydi(oxyethylene)methpyl]-trimethylsilane (1S1M2):

b.p. 193-194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 9H, CH_3-Si), 3.12 (s, 2H, Si-CH_2-), 3.35 (s, 3H, CH_3-O), 3.50-3.65 (m, 4H, OCH_2CH_2O); ^{13}C NMR (300 MHz, $CDCl_3$): 0.0, 62.06, 68.49, 73.51, 75.09, 77.80; ^{29}Si NMR (500 MHz, $CDCl_3$): -2.83; Anal. Calcd. For $C_9H_{22}O_3Si$: C, 52.38; H, 10.75. Found: C, 51.99, H, 10.72.

[Methoxytrioxyethylene]methyl]-trimethylsilane (1S1M3,):

b.p. 53-54 °C/0.5 Torr; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.001 (s, 9H, CH_3-Si), 3.12 (s, 2H, Si-CH_2-), 3.36 (s, 3H, CH_3-O-), 3.53-3.65 (m, 12H, $O(CH_2CH_2)_3O$); ^{13}C NMR (300 MHz, $CDCl_3$): 0.003, 62.03, 68.38, 73.42, 73.55, 73.73, 74.99, 77.75; ^{29}Si NMR (300 MHz, $CDCl_3$): -2.99; Anal. Calcd. For $C11H_{26}O_4Si$: C, 52.76; H, 10.75. Found: C, 52.36, H, 11.27.

Methoxyethoxypropyl-trimethylsilane (1S3M1):

b.p. 192 -193 °C; H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 9H, CH_3-Si), 0.43-0.47 (m, 2H, Si-CH_2-), 1.53-1.63 (m, 2H, $SiCH_2$-CH_2), 3.38-3.42 (m, 5H, CH_3-O and CH_2-$OCH_2CH_2OCH_3$), 3.50-3.58 (m, 4H, OCH_2CH_2O); ^{13}C NMR (300 MHz, $CDCl_3$): 0.01, 14.25, 25.81, 60.76, 71.71, 73.78, 76.22; ^{29}Si NMR (500 MHz, $CDCl_3$): 0.487; Anal. Calcd. For $C_9H_{22}O_2Si$: C, 56.79; H, 11.65. Found: C, 56.41, H, 11.21.

[Methoxydi(oxyethylene)propyl]-trimethylsilane ($1S_3M_2$):

b.p. 50 – 51 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 9H, CH_3-Si), 0.41-0.46 (m, 2H, Si-CH_2-), 1.53-1.61 (m, 2H, $SiCH_2$-CH_2), 3.36-3.42 (m, 5H, CH_3-O and CH_2-$O(CH_2CH_2O)_2CH_3$), 3.52-3.65 (m, 8H, $O(CH_2CH_2)_2O$); ^{13}C NMR (300 MHz, $CDCl_3$): 0.001, 14.26, 25.82, 60.72, 71.78, 72.29, 72.43, 73.73, 76.10. ^{29}Si NMR (300 MHz, $CDCl_3$): 0.500; Anal. Calcd. For $C_9H_{22}O_2Si$: C, 56.36; H, 11.18. Found: C, 55.93, H, 11.40.

[Methoxytrioxyethylene]propyl]-trimethylsilane ($1S_3M_3$):

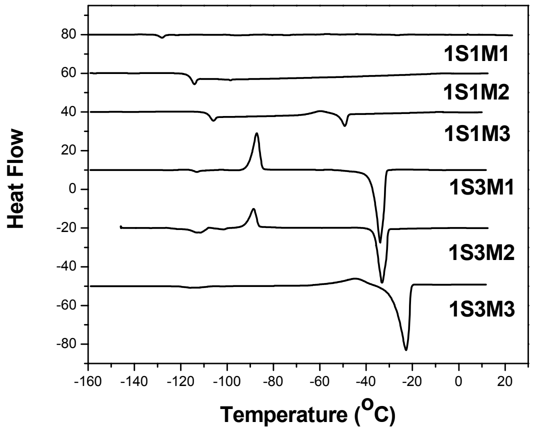
b.p. 72 - 74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 9H, CH_3-Si), 0.41-0.46 (m, 2H, Si-CH_2-), 1.53-1.58 (m, 2H, $SiCH_2$-CH_2), 3.36-3.41 (m, 5H, CH_3-O and CH_2-$O(CH_2CH_2O)_3CH_3$), 3.51-3.65 (m, 8H, $O(CH_2CH_2)_3O$); ^{13}C NMR (300 MHz, $CDCl_3$): 0.001, 14.25, 25.81, 60.70, 71.77, 72.26, 72.38, 73.70, 76.07; ^{29}Si NMR (300 MHz, $CDCl_3$): 0.439; Anal. Calcd. For $C_9H_{22}O_2Si$: C, 56.07; H, 10.86. Found: C, 56.40, H, 10.63.

1-(3-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-propyl)-1,1,3,3,3-pentamethyl-disiloxane (2SM3):

To a three-neck flame dried flask was charged 1,1,3,3-pentamethyldisiloxane (20g, 0.135mol) and allyl methoxy triethylene glycol ether (34.1g, 0.167mol). While stirring, 200μL Karlstedt's catalyst was added to the mixture, and then the reaction was heated to 75 °C and stirred for 24 h. After the completion of the reaction, the pure product was obtained by fractional distillation (yield: 95%).

b.p. 105 °C/0.5 Tor; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.022 (s, 9H, $(CH_3)_3SiO$), 0.033 (s, 6H, $(CH_3)_2SiOSi(CH_3)_3$), 0.45(m, 2H, CH_2SiOSi), 1.58(m, 2H, 3.12 (s, 2H, CH_2CH_2SiOSi), Si-CH_2-), 3.36 (s, 3H, CH_3-O-), 3.39 (t, *J*=7.2 Hz, $CH_2(CH_2)_2SiOSi$), 3.51-3.65 (m, 12H, $O(CH_2CH_2)_3O$); ^{13}C NMR (300 MHz, $CDCl_3$): -0.001, 0.043, 62.107, 68.465, 73.459, 73.595, 73.743, 75.02, 77.748,; ^{29}Si NMR (300 MHz, $CDCl_3$): 6.1, 6.5; Anal. Calcd. For $C_{16}H_{38}O_4Si_2$: C, 54.81; H, 10.92. Found: C, 54.77, H, 11.07.

Fig. S1 DSC curves of alkylsilane ethers.



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