



Fluorosilane compounds with oligo(ethylene oxide) substituent as safe electrolyte solvents for high-voltage lithium-ion batteries



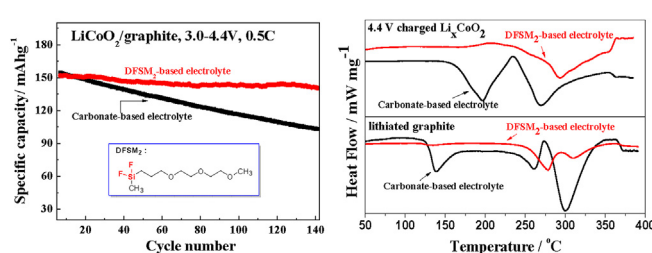
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HIGHLIGHTS

- Fluorosilanes synthesized as novel electrolytes for lithium-ion batteries.
- Fluorination resulting in lower viscosity and higher oxidative potential.
- Excellent cycling performance for 4.4 V LiCoO₂/graphite cell at 0.5 C rate.
- Better safety due to high thermal stability with charged graphite and Li_xCoO₂.

GRAPHICAL ABSTRACT



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ABSTRACT

Two fluorosilanes with oligo(ethylene oxide) unites were synthesized through hydrosilylation of chlorosilane with allyl substituted oligo(ethylene oxide) ether followed by fluorination with potassium fluoride. The synthesized fluorosilane compounds exhibited lower viscosity, higher dielectric constant and higher oxidation potential, compared with their non-fluorination counterparts. Difluoro(3-(2-(2-methoxyethoxy)ethoxy)propyl)methylsilane (DFSM₂), one of the two compounds, was evaluated as high-voltage and thermal stable electrolyte co-solvent with the conventional carbonate-based electrolytes. Using an optimized electrolyte of 1M LiPF₆ in EC/DFSM₂/EMC (2/3/5 in vol.) with addition of 5 wt% fluoroethylene carbonate (FEC), high-voltage LiCoO₂(LCO)/graphite full cell displayed outstanding cycling stability of 92.5% capacity retention after 135 cycles at 4.4 V upper cutoff voltage. Characterized by differential scanning calorimetry (DSC) analysis, the DFSM₂-based electrolyte demonstrated higher thermal stability with lithiated graphite anode and delithiated LCO cathode, thus better safety feature compared with the conventional electrolyte.

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1. Introduction

With the growing demands for lithium-ion batteries (LIBs) in such applications as advanced consumer electronics, energy storage system, plug-in hybrid electric vehicles and electric vehicles, there are increasing concerns about the safety of the conventional

carbonate-based electrolytes used widely in the commercial LIBs. Great attention has been paid to develop new electrolyte systems with improved safety features by using flame retardant additives [1,2] or less flammable (even non-flammable) solvents [3–8].

Among them, organosilicon compounds have received considerable attention as electrolyte solvents for energy storage devices due to their thermal and electrochemical stability, low flammability, and environmentally benign characters [9,10]. Specifically, {2-[2-(2-methoxyethoxy)ethoxy]ethoxy}trimethylsilane (1NM3) has been identified as a focus of interest mainly due to the

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combined merits of high safety and electrochemical stability of organosilicon group and good lithium salt-solvating capability of a oligo(ethylene oxide) moiety. Moreover, the electrolyte of 1NM3 with lithium bis(oxalato)borate (LiBOB) salt can well support some mainstream cell chemistries such as $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2/\text{graphite}$ [11], $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2/\text{graphite}$ [12], and $\text{LiMn}_2\text{O}_4/\text{graphite}$ [13]. However, an upper cutoff voltage of 4.2 V is critical for this 1NM3-LiBOB electrolyte [12], limiting its application to high potential cathode materials [14–17]. To remedy this drawback, we introduced oxidative resistant nitrile group for a series of organosilicon compounds for their high voltage application. Such organosilicon electrolytes with nitrile group demonstrated excellent cycling stability in $\text{LiCoO}_2(\text{LCO})/\text{graphite}$ full cell with an upper cutoff voltage of 4.4 V [18,19].

On the other hand, fluorination is reported to be a helpful strategy to improve the electrochemical anodic stability of electrolytes, expecting that they can be used in high-voltage LIBs [8,20]. For instance, commercially available FEC-based electrolytes of 1M LiPF_6 in FEC/DMC (1/4 by wt.) was proved to be practical and efficient for enhancing the electrochemical performance for 5.0 V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO)/silicon and 5.2 V $\text{LiCoPO}_4/\text{Li}$ cells [21,22]. Zhang et al. also found that fluorinated electrolytes, including fluorinated cyclic/linear carbonate and fluorinated ether, appeared to be a suitable electrolyte candidate for 5.0 V LNMO cell chemistries [7,23,24].

In this work, two novel fluorosilane compounds with oligo(ethylene oxide) moiety was synthesized for our continuous effort on developing high safety and high-voltage organosilicon electrolytes. Their basic physiochemical properties, such as viscosity, dielectric constant, ionic conductivity, and electrochemical stability were systematically characterized. One fluorosilane compound (DFSM₂) was evaluated as thermal stable and high-voltage electrolyte co-solvent by mixing with organic carbonate solvents. The compatibility of the fluorosilane based electrolytes with graphite anode, high-voltage LCO cathode, and LCO/graphite full cells at an upper cutoff voltage of 4.4 V were investigated, respectively. The safety property was characterized by the thermal stability of the electrolytes with lithiated graphite anode and delithiated LCO cathode using differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

Potassium hydroxide, 2-(2-methoxyethoxy)ethanol, allyl bromide, dimethylchlorosilane, dichloromethylsilane, potassium fluoride, acetonitrile, and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aladdin Reagent Co. (China) and used without further purification. Lithium oxalyldifluoroborate (LiODFB), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and lithium hexafluoro-phosphate (LiPF_6) were donated by Dongguan Shanshan Battery Material Co. (China) and used as received. LiBOB, ethylene carbonate (EC), methyl ethyl carbonate (EMC), FEC and vinylene carbonate (VC) were supplied by Guangzhou Tinci Materials Technology Co. (China). Graphite powder and high-voltage LCO powder were offered by Amperex Technology Limited (China). A Celgard 2400 microporous polypropylene membrane was used as the separator.

2.2. Synthesis

Scheme 1 presents synthetic route of the fluorosilane compounds. The detail synthetic processes are described as follow:

2.2.1. Synthesis of 3-(2-(2-methoxyethoxy)ethoxy)prop-1-ene (AOEM₂)

AOEM₂ was synthesized by a etherification reaction starting from allyl bromide and 2-(2-methoxyethoxy)ethanol. The synthetic procedures were detailed as follow: allyl bromide (121.0 g, 1.0 mol) was added slowly to a mixture of potassium hydroxide (40.4 g, 1.1 mol) and 2-(2-methoxyethoxy)ethanol (240.0 g, 2.0 mol). The mixture was stirred at 50 °C for 10 h, then quenched with water (100 mL), and followed by extracting with hexane (4 × 50 mL). The combined organic layer was dried over anhydrous magnesium sulfate; the solvent was removed by rotary evaporation after filtration. AOEM₂ was obtained as a colorless liquid (144.0 g, with the yield of 89%) by distillation under reduced pressure (b.p.: 46 °C/3 mmHg).

2.2.2. Synthesis of fluoro(3-(2-(2-methoxyethoxy)ethoxy)propyl)dimethylsilane (MFSM₂)

MFSM₂ was synthesized by a two-step reaction of hydrosilylation AOEM₂ with chlorohydrosilane compound followed by fluorination with KF. The detail synthetic procedures were as follow: dimethylchlorosilane (15.4 g, 0.16 mol) was added slowly to a mixture of chloroplatinic acid (0.1 g, 0.19 mmol) and AOEM₂ (25.1 g, 0.15 mol) with argon atmosphere in ice-salt bath. After 24 h reaction at 70 °C, chloro(3-(2-(2-methoxyethoxy)ethoxy)propyl)dimethylsilane was obtained by distillation under reduced pressure (b.p.: 122 °C/3 mmHg) as a colorless liquid (28.7 g, with the yield of 75%). Then, the obtained product (28.7 g, 0.11 mol) was added slowly to a mixture of potassium fluoride (7.0 g, 0.12 mol) and anhydrous acetonitrile (80 mL). After 10 h reaction at 70 °C, MFSM₂ was obtained as colorless liquid (21.3 g, with the yield of 81%) by distillation under reduced pressure (b.p.: 105 °C/3 mmHg). The chemical structure of MFSM₂ was characterized by NMR as follow:

¹H NMR (600 MHz, CDCl_3): 3.62 (m, 4H, $\text{CH}_2\text{-O-CH}_2$), 3.55 (m, 4H, $\text{CH}_2\text{-O-CH}_2$), 3.42 (t, 2H, $\text{Si-CH}_2\text{CH}_2\text{CH}_2$), 3.35 (s, 3H, $-\text{OCH}_3$), 1.65 (m, 2H, SiCH_2CH_2), 0.66 (m, 2H, Si-CH_2), 0.16 (d, 6H, $-\text{Si}(\text{CH}_3)_2$). ¹³C NMR (150.4 MHz, CDCl_3): 73.5, 71.9, 70.6, 70.5, 70.4, 70.0, 59.0, 22.8 (d), 12.66 (d), -1.5 (d).

2.2.3. Synthesis of difluoro(3-(2-(2-methoxyethoxy)ethoxy)propyl)methylsilane (DFSM₂)

The detail synthetic procedures of DFSM₂ were similar to those for MFSM₂ except for using dichloromethylsilane as a starting material for hydrosilylation reaction of AOEM₂. DFSM₂ was obtained as colorless liquid (with the yield of 79%) by distillation under reduced pressure (b.p.: 98 °C/3 mmHg). The chemical structure of DFSM₂ was characterized by NMR as follow:

¹H NMR (600 MHz, CDCl_3): 3.63 (m, 4H, $-\text{CH}_2\text{-O-CH}_2$), 3.59 (m, 2H, $\text{O-CH}_2\text{CH}_2$), 3.54 (m, 2H, OCH_2), 3.44 (t, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 3.36 (s, 3H, OCH_3), 1.72 (m, 2H, SiCH_2CH_2), 0.82 (m, 2H, SiCH_2), 0.33 (t, 3H, SiCH_3). ¹³C NMR (150.4 MHz, CDCl_3): 72.5, 71.9, 70.5, 70.5, 70.1, 59.0, 21.9, 10.1 (t), -4.21 (t).

2.3. Apparatus and measurements

¹H NMR and ¹³C NMR spectra were recorded on a Bruker avance600 spectrophotometer using CDCl_3 as solvent. All the synthesized fluorosilane compounds were dried over 4 Å molecular sieves before using, and their water contents were less than 20 ppm, determined by Karl-Fisher coulometric moisture titrator (831 KF, Metrohm Co., Sweden). Viscosity (η) and dielectric constant (ϵ) measurements were performed on Viscometer (SPb-2, Nirun Intelligent Technology Co., China) and Liquid Dielectric Constant Meter (870, Scientifica), respectively. Variable temperature ionic conductivity measurements of 1M LiTFSI in the fluorosilane solutions were conducted using a conductivity meter

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