Synthesis and Characterization of Organosilane Electrolyte Containing Silphenylene

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Abstract

Organosilicon compound containing silphenylene unit as an eletrolyte for the application of lithium-ion batteries was synthesized by hydrosilylation method between 1,4-bis(dimethylsilylhydro)benzene and 3-[2-(2-methoxyethoxy)ethoxy]-1-propene. As-prepared new organosilicon compounds containing spacer such as propyl group with ethylene glycol are synthesized to improve thermal stability and to promote conductivity. The products are characterized by spectroscopic analysis.

Keywords: Silane, Silphenylene Unit, Electrolyte, Lithium Ion Battery

1. Introduction

Lithium-ion batteries (LIB) as secondary rechargeable batteries are used in various consumer electronic devices, such as mobile phones, portable computers and others. LIB as a renewable energy in electric vehicles and energy storage system (ESS) exhibits a potential application. Typically in commercial batteries, solvents are blended to obtain an optimum set of properties that promote conductivity including low viscosity (h), a high dielectric constant (E), and solvation of the lithium salt. Commercial electrolyte in lithium ion batteries is a mixture of lithium hexafluorophosphate (LiPF$_6$) with ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC) and propylene carbonate (PC), which exhibit low flash point as well as highly flammable property. It is necessary for better battery performance, that the additives should be able to: (1) facilitate formation of solid electrolyte interface/interphase (SEI) on the surface of anode materials such as graphite, (2) reduce gas generation and irreversible capacity for the SEI formation and long-term cycling, (3) enhance thermal stability of lithium salt against the organic electrolyte solvents, (4) protect cathode material from dissolution and overcharge, and (5) improve physical properties of the electrolyte such as ionic conductivity, viscosity, wettability to the polyolefine separator, and so forth[1]. It is also required for better battery safety, that the additives of electrolyte should be able to: (1) lower flammability of organic electrolytes, (2) provide overcharge protection or increase overcharge tolerance, and (3) terminate battery operation in abuse conditions[1]. As mentioned above, to overcome the required performance for electric vehicles and ESS, the safety and energy density issues should be solved first[2]. More recently, there are increasing concerns about the safety of the conventional electrolytes due to the explosion involving lithium-ion batteries. Especially, safety concern, which is greatly related to the high flammability of the liquid electrolytes in the LIB application, has been a main obstacle in hybrid electric vehicles and electric vehicles. Therefore, many researches have been focused on the development of fire-retardant (FR) additive to lower the flammability of the liquid electrolytes. The concept of the FR additives has been long known and studied for the protection of the solid polymers and woods[3,4]. Up to now, most of FR additives used in the liquid electrolytes are based on organic phosphorus compounds[5-9] and their halogenated derivatives[10-12]. Since the siloxane compound is well known for FR additives, the research for the siloxane compounds in LIB is rare. Siloxane compounds in LIB have several advantages over current commercial electrolytes. The characteristics of siloxanes are nonvolatile, nontoxic, nonflammable, and biocompatible. In addition, their low glass transition temperatures and

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high free volumes promote conductivity[13] at low temperature. Since the lithium ion transport properties of an electrolyte depend on complexation of the Li cations by the electrolyte, the silicon oxide units of the siloxane structures provide coordination binding site to lithium ion. West et al reported the synthesis of organosilicons such as trimethylsilyl oligo(ethylene glycol) ethers, which showed high ionic conductivity, great electrochemical stability, and good cycling performance when used as electrolyte solvents in lithium-ion batteries[13-15].

In this study, we report new type of siloxane such as a silphenylene-containing organosilicon compound. Since the silphenylene unit is well known for the high thermal stability, they open used in the field of polymer application such as elastomer[16], film polymer[17], LED encapsulant[18].

2. Experimental Section

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. All reagents such as tetrahydrofuran, methylene chloride, Mg powder, KOH, diethylene glycol monomethyl ether, allyl bromide, platinum(0)-1,3-divnyl-1,1,3,3-tetramethyl-disiloxane complex solution, NaOH, $MgSO_4$, 1,4-dibromobenzene, and chlorodimethylsilane were purchased directly from Aldrich and used without any purification. NMR spectra were recorded by using Bruker AC-300 MHz spectrometer (^{1}H NMR, 300.1 MHz and ^{13}C NMR, 75 MHz). Chloroform-d was stirred over CaH_2 for 1 day, transferred by vacuum distillation onto P_2O_5, stirred for 2 h, and then vacuum-distilled for purification. Chemical shifts are reported in parts per million (δ ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) standard at 0.00 ppm.

2.1. Synthesis of 1,4-Bis(dimethylsilylhydro)benzene
In a 500 mL round bottom flask, Mg powder (6.2 g, 0.255 mol) in tetrahydrofuran (80 mL) was stirred under argon at room temperature for 1 hour. Chlorodimethylsilane (24.1 g, 0.255 mol) was added dropwise and the mixture was stirred under argon for 10 min. 1,4-diboromobenzene (20 g, 0.085 mol) in tetrahydrofuran (100 mL) was added dropwise to reaction mixture at 0°C and the reaction mixture was stirred for 2 days. After reaction completed, a solvent was removed under

reduced pressure and the salt was precipitated in n-hexane or pentane and filtered off. The filtrate was evaporated with rotary evaporator and crude product was obtained as yellow liquid. The crude product was purified by vacuum distillation and was obtained as colorless liquid (isolated yield = 63%). B.p. 70°C at 10^{-2} torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, 4H, J = 1.2 Hz), 4.42 (dtd, 2H, J = 7.4, 3.7, 1.3 Hz), 0.34 (dd, 12H, J = 3.7, 1.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.60, 133.47, -4.00.

2.2. Synthesis of 3-[2-(2-Methoxyethoxy)ethoxy]-1-propene
The 3-[2-(2-methoxyethoxy)ethoxy]-1-propene was prepared with previous reported literature procedure[19]. In a 250 mL two-necked round bottom flask, equipped with a reflux condenser and a dropping funnel, diethylene glycol monomethyl ether (10 g, 0.083 mol) was dissolved in 30 mL THF. KOH(9.2 g, 0.166 mol) was added and then stirring at room temperature. After 30 min, allyl bromide(13 g, 0.107 mol) in tetrahydrofuran (10 mL) was added dropwise to reaction mixture. The reaction mixture was heated to reflux for 1 day. After reaction was finished, the reaction mixture was cooled to room temperature and filtered. The filtrate was washed three times with 1 M NaOH, dried over $MgSO_4$ filtered and concentrated with rotary evaporator. The crude product was The crude product was purified by vacuum distillation and was obtained as colorless liquid (isolated yield = 80%). B.p. 60°C at 10^{-2} torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93-5.69(m, 1H), 5.24-5.01(m, 2H), 3.93 (dt, 2H, J = 5.8, 1.3 Hz), 3.61-3.38(m, 8H), 3.28(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.57, 116.81, 71.91, 71.64, 70.34, 70.25, 69.12, 58.68.

2.3. Synthesis of 1,4-Bis{3-[2-(2-methoxyethoxy)ethoxy]-1-propyl}dimethylsilylbenzene
In a 250 mL round flask, as-prepared 1,4-bis(dimethylsilylhydro)benzene (5 g, 0.026 mol), 3-[2-(2-methoxyethoxy)ethoxy]-1-propene (9.85 g, 0.057 mol) and platinum(0)-1,3-divnyl-1,1,3,3-tetramethyl-disiloxane complex solution (15 mg, 0.1 wt % of all reactant weight) as catalyst was added under argon and heated at 70°C to reflux for 12 h. After reaction finished, solvent was removed with rotary evaporation and then the crud product was purified by vacuum distillation and was obtained as bright yellow color liquid (isolated yield = 68%). B.p. 240~250°C at

10^{-2} torr. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.48 (s, 4H), 3.68-3.60(m, 8H), 3.60-3.51(m, 8H), 3.46-3.35(m, 5H), 1.61(ddd, 2H, J = 14.5, 12.3, 7.2 Hz), 0.77-0.67 (m, 2H), 0.26 (s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.94, 131.0, 72.31, 70.0, 68.71, 68.59, 68.06, 57.09, 21.98, 9.53, -5.25.

3. Results and Discussion

Although the siloxane compounds as an electrolyte in LIB have nonvolatile and nonflammable properties, they have a weak point such as hydrolysis by moisture. Previously, we reported the synthesis of perfluorosilane[20] as shown in Fig. 1. The results of the charge/discharge cycling performance with perfluoresilane electrolyte exhibited good specific capacity in the beginning, but low specific capacity after 100 cycle numbers. This result might be come from low lithium ion transport properties of an electrolyte due to the low complexation of the Li cations by ethylene glycol moiety of the perfluoresilane.

West et al reported the synthesis of organosilicons such as trimethylsilyl oligo(ethylene glycol) ethers[15]. Although, conductivities close to 10^{-4} S/cm have been reported for siloxane-PEO electrolyte as shown in Fig. 2, the charge/discharge cycling performance was not reliable. The decomposition of electrolytes based on siloxane-PEO electrolyte with the industry-standard LiPF$_6$ salt caused by PF$_5$ which is formed by decomposition of the PF$_6$ anion. Decomposition of LiPF$_6$ produces PF$_5$, which fluorinates siloxane-PEO molecules and catalyzes decomposition of siloxane-PEO electrolyte hydrolysis reaction.

Easy hydrolysis reaction of siloxane-PEO molecules by decomposition of LiPF$_6$ might due to the strong π-
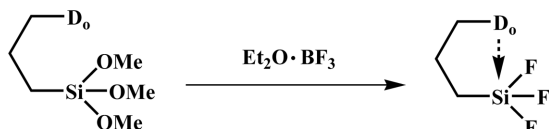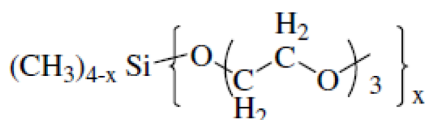
back bonding between silicon and oxygen which leads weaker s bond between oxygen and carbon. Illustration of this concept is shown in Fig. 3.

Fig. 4 showed the orbital diagram of HOMO and LUMO energy level for methylsilyl ether molecule which was calculated based on hf/6-31G(d). Less electron density between oxygen and carbon in the LUMO energy level of methylsilyl ether causes weaker bond and easy hydrolysis.

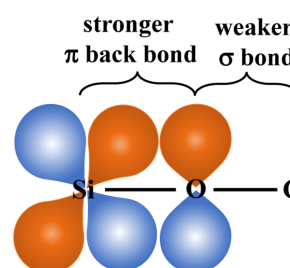Therefore, we introduced spacer between silicon and oxygen to prevent hydrolysis of organosilicon electro-

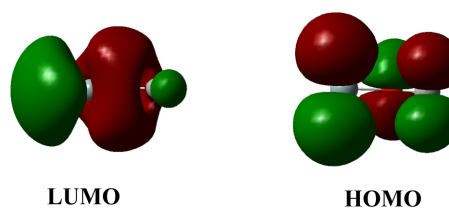**Fig. 3.** Diagram for p-back bond between silicon and oxygen in siloxane-PEO.

Fig. 4. HOMO and LUMO molecular orbital diagrams of methylsilyl ether.

Fig. 1. Synthesis of perfluorosilane.

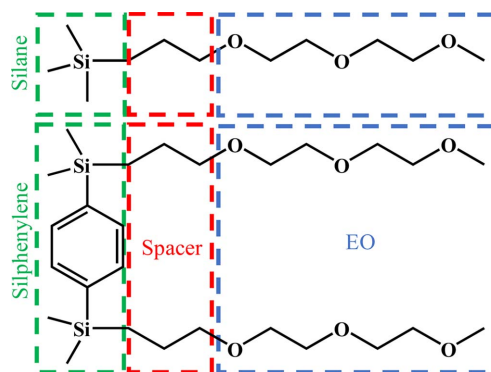**Fig. 2.** Chemical structure of siloxane-PEO.

Fig. 5. Chemical structures of oganosilicon compounds having one ethylene glycol moiety and two ethylene glycol moieties.
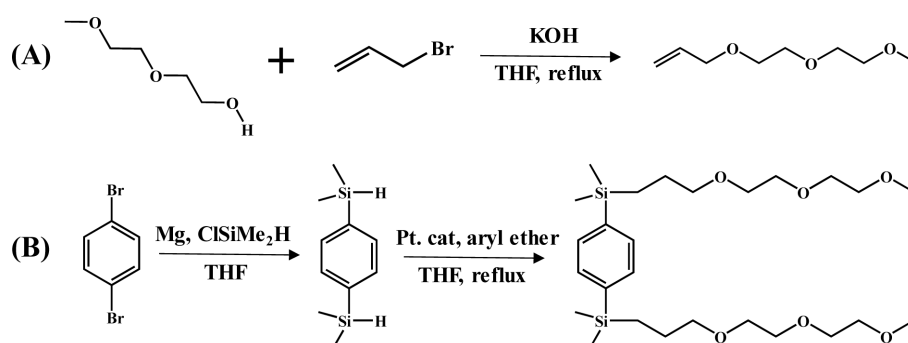
Fig. 6. Synthetic scheme for the silaphenylene-containing organosilane compound.

lyte and two ethylene glycol moieties in the silphenyl-ene unit to improve the lithium ion transport properties as well as the complexation of the Li cations. Fig. 5 displays chemical structures of the organosilicon compounds having one ethylene glycol moiety[13-15] two ethylene glycol moieties (present work).

Fig. 6 shows overall synthesis procedure of 1,4-bis{3-[2-(2-methoxyethoxy)ethoxy]-1-propyl}dimethylsilylbenzene. In this reaction, 3-[2-(2-methoxyethoxy)ethoxy]-1-propene shown in Fig. 6(A) was synthesized by etherification reaction between diethylene glycol monomethyl ether and allyl bromide in the presence of KOH according to a method reported in detail elsewhere[19]. As shown in Fig. 6(B), silphenylene-containing silane was synthesized by Grignard reaction with 1,4-dibromobenzene and chlorodimethylsilane. Then 1,4-bis{3-[2-(2-methoxyethoxy) ethoxy]-1-propyl}dimethylsilylbenzene was synthesized by hydrosilation reaction with as-prepared products, 3-[2-(2-methoxyethoxy)ethoxy]-1-propene and 1,4-bis (dimethylsilylhydro)benzene, in the presence of Pt Karstedt's catalyst. Silphenylene-containing organosilicon compound were isolated as colorless liquids after distillation at reduced pressure. All chemical products were characterized by spectroscopic analysis (^{1}H and ^{13}C NMR, see supporting information).

Fig. 7. shows 3D structure of structure of trimethyl-silyl oligo(ethylene glycol) ethers and 1,4-bis{3-[2-(2-methoxyethoxy)ethoxy]-1-propyl}dimethylsilylbenzene, respectively. Since the lithium ion transport properties of an electrolyte depend on complexation of the Li cations by the electrolyte, the ethylene oxide units of the silaphenylene-containing organosilane compound the siloxane structures provide coordination binding site to lithium ion with reasonable cavity size.
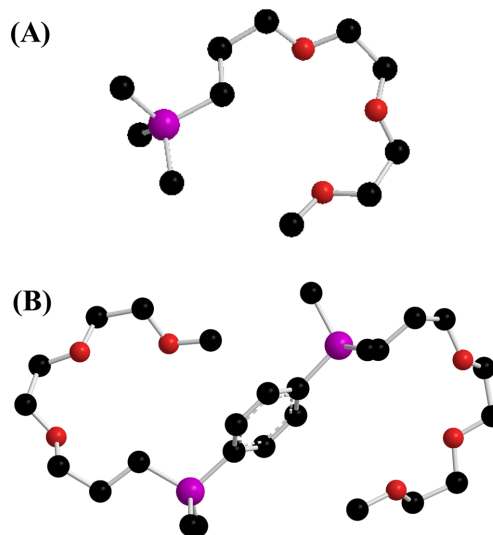

Fig. 7. 3D stereographic structure of (a) trimethylsilyl oligo(ethylene glycol) ethers and (b) 1,4-bis{3-[2-(2-methoxyethoxy)ethoxy]-1-propyl}dimethylsilylbenzene.

4. Conclusions

New synthetic method for 1,4-bis{3-[2-(2-methoxyethoxy)ethoxy]-1-propyl}dimethylsilylbenzene with silphenylene unit has been developed. Silphenylene-containing organosilicon compound have been successfully synthesized in 60-70% yield from the hydrosilation between 1,4-bis(dimethylsilylhydro)benzene and 3-[2-(2-methoxyethoxy)ethoxy]-1-propene. Silphenylene-containing organosilicon compounds were characterized by ^{1}H, and ^{13}C NMR spectroscopy. It is believed that the good conductivity and thermal stability can be improved by introducing silphenylene unit and ethylene glycol with

spacer such as propyl group for electrolyte in lithium-ion batteries.

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