

New Synthetic Method of Perfluoro-Silanes for the Stable Electrolyte of Lithium Ion Battery Application

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Abstract

Non-hydrolyzable fluorinated organosilicon compounds as an electrolyte for the application of lithium-ion batteries (LIB) are synthesized. New synthetic method for the perfluorinated organosilicon compound containing spacer such as ethyl and propyl group with cyano moiety instead of ethylene glycol to prevent hydrolysis and to promote conductivity are developed in one pot reaction with moderately high yield. Air-sensitive boron trifluoride etherate is no longer required in this reaction. The products are characterized by spectroscopic analysis.

Keywords: Silane, Perfluoro Compound, Synthesis, 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. However, to overcome the required performance for electric vehicles and ESS, the safety and energy density issues should be solved first^[1]. More recently, there are increasing concerns about the safety of the conventional electrolytes due to the explosion involving lithium-ion batteries. Typically in commercial batteries, solvents are blended to obtain an optimum set of properties that promote conductivity including low viscosity (η), a high dielectric constant (ϵ), and solvation of the lithium salt^[2]. 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. Siloxane compounds might be an excellent candidate as an electrolyte in LIB. Electrolytes contain-

ing siloxane compounds have several advantages over current commercial electrolytes. They are nonvolatile, nontoxic, nonflammable, and biocompatible with low glass transition temperatures and high free volumes, which promote conductivity^[3]. Since the lithium ion transport properties of an electrolyte depend on complexation of the Li cations by the electrolyte, the introduction of silicon oxide units into the siloxane structures provide lithium ion binding sites. West et al reported the synthesis of trimethylsilyl oligo(ethylene glycol) ethers though a trimethylsilylation reaction by directly refluxing oligo(ethylene glycols) or oligo(ethylene glycol) monomethyl ethers with trimethylchlorosilane or hexamethyldisilazane, which showed high ionic conductivity, great electrochemical stability, and good cycling performance when used as electrolyte solvents in lithium-ion batteries^[3-5]. However, these trimethylsilyl ethers may be hydrolyzed by moisture. More recently, they published that fluorinated organosilicon compounds are non-hydrolyzable at room temperature which expected a much higher tolerance for moisture. They also reported that the voltage stability of the organosilicon compounds is greatly improved due to the effect of halogen substitutions. In this study, we have developed new synthetic method for the perfluorinated organosilicon compound which containing spacer such as ethyl and propyl group with cyano moiety instead of ethylene glycol to prevent hydrolysis and to promote conductivity.

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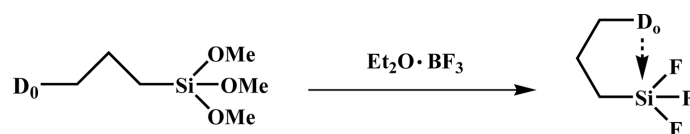


Fig. 1. Synthetic scheme for the synthesis of pentacoordinate silicon compounds.

2. Experimental Section

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. All reagents such as HF (48%), isopropyl alcohol, diethyl ether, MgSO_4 , 3-cyanopropyltriethoxysilane, and 2-cyanoethyltriethoxysilane were purchased directly from Aldrich and used without any purification. NMR spectra were recorded by using Bruker AC-300 MHz spectrometer (^1H 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 4-(Trifluorosilyl)butanenitrile

In a 250 mL round bottom flask, 3-cyanopropyltriethoxysilane (20 g, 0.086 mol) in isopropyl alcohol (150 mL) was stirred under argon at 0°C for 30 min. Hydrogen fluoride (11.83 g, 0.284 mol) was added dropwise and the mixture was stirred under argon at 0°C for 24 h. After removal of volatiles, diethyl ether (50 mL) was added. After dried over anhydrous MgSO_4 , the solvent was removed with a rotary evaporator. The product was purified by vacuum distillation and was obtained as colorless liquid (isolated yield = 67%). B.p. $63 - 68^\circ\text{C}$ at 10^{-2} torr. ^1H NMR (300 MHz, CDCl_3): $\delta = 2.44$ (t, 2H, $J = 5$ Hz), 1.90 (m, 2H), 1.17 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 118.57$, 19.46, 17.54, 6.18 (q, $J = 19.50$ Hz).

2.2. Synthesis of 3-(Trifluorosilyl)propanenitrile

In a 250 mL round bottom flask, 2-cyanoethyltriethoxysilane (20 g, 0.092 mol) in isopropyl alcohol (150 mL) was stirred under argon at 0°C for 30 min. Hydrogen fluoride (12.66 g, 0.304 mol) was added dropwise and the mixture was stirred under argon at 0°C for 24 h. After removal of volatiles, diethyl ether (50 mL)

was added. After dried over anhydrous MgSO_4 , the solvent was removed with a rotary evaporator. The product was purified by vacuum distillation and was obtained as colorless liquid (isolated yield = 60%). B.p. $50 - 55^\circ\text{C}$ at 10^{-2} torr. ^1H NMR (300 MHz, CDCl_3): $\delta = 2.56$ (t, 2H, $J = 6$ Hz), 1.42 (t, 2H, $J = 5$ Hz); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 118.78$, 9.69, 3.95 (q, $J = 20.75$ Hz).

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. Since the Si-F bond is stable at water, perfluorosilane might be one of excellent candidate as an electrolyte additive in LIB. We have developed easy synthetic method for 4-(trifluorosilyl)butanenitrile and 3-(trifluorosilyl)propanenitrile by using HF. The synthesis of perfluorosilanes has been reported and isolated as a pentacoordinate silicon species. In this case, they required an electron donor moiety at the end of alkyl chain such as $\text{C}=\text{O}$ ^[6], P ^[7], $\text{N}=\text{N}$ ^[8,9], N ^[10], and $\text{P}=\text{O}$ ^[11] to form stable hypervalent silicon compounds through five membered ring formation due to the electron withdrawing property of three fluorine atoms as shown in Fig. 1.

In this reaction method, boron trifluoride etherate, which is air-sensitive compound, is used as a fluorination source. Recently, the synthesis of perfluorosilanes without electron donor moiety has been reported as shown in Fig. 2. However, it requires two step reactions

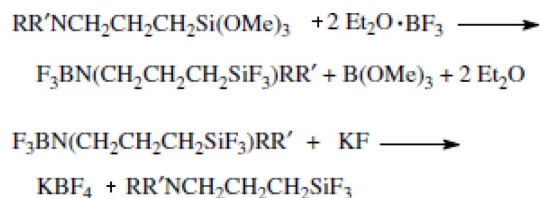


Fig. 2. Synthetic scheme for the synthesis of perfluorosilanes.

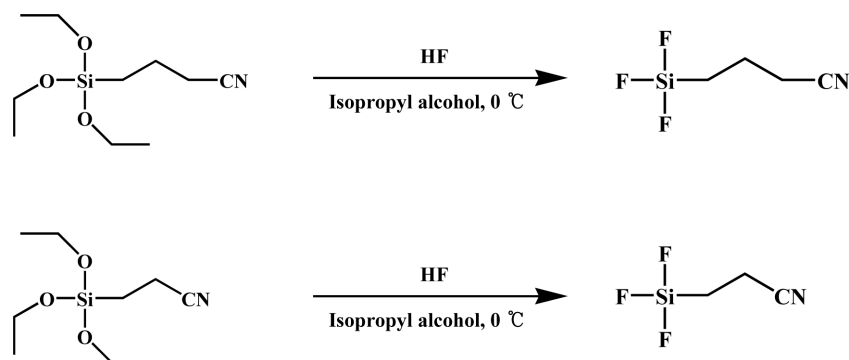


Fig. 3. New synthetic method for the synthesis of perfluorosilanes.

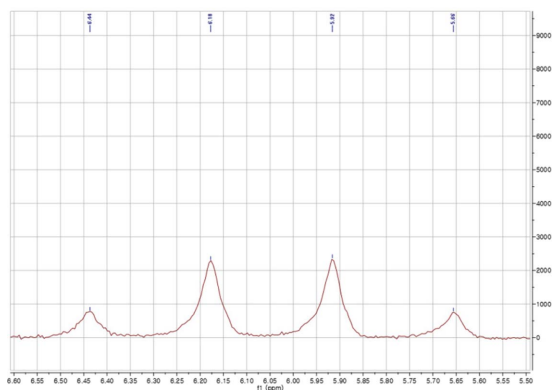


Fig. 4. Splitting pattern of CH₂SiF₃ moiety in ¹³C NMR spectra of 4-(trifluorosilyl)butanenitrile.

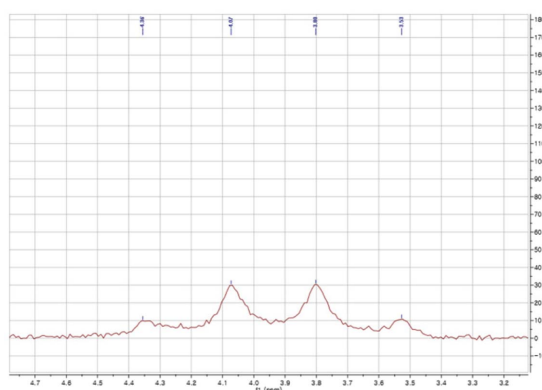


Fig. 5. Splitting pattern of CH₂SiF₃ moiety in ¹³C NMR spectra of 3-(trifluorosilyl)propanenitrile.

with a complicated method.

Here, we report new easy synthetic method for the synthesis of perfluorosilanes without donor moiety, which is one pot reaction with moderately high yield. Air-sensitive boron trifluoride etherate is no longer required in this reaction. 4-(Trifluorosilyl)butanenitrile and 3-(trifluorosilyl)propanenitrile in 60-70% yield shown in Fig. 3 have been successfully synthesized from the direct reaction of 3-cyanopropyltriethoxysilane and 2-cyanoethyltriethoxysilane with 48% HF, respectively. Especially, the synthesis of 3-(trifluorosilyl)propanenitrile was not reported yet.

Perfluorosilane compounds were isolated as colorless liquids after distillation at reduced pressure. They were characterized by spectroscopic analysis (FT-IR, ¹H, and ¹³C NMR, see supporting information). The intense Si-F stretching vibrations are observed at the wavenumbers ($\nu_{as} \sim 940 \text{ cm}^{-1}$ and $\nu_s \sim 880 \text{ cm}^{-1}$) and are typical of

tetravalent silanes. ¹H and ¹³C NMR spectra of 4-(trifluorosilyl)butanenitrile and 3-(trifluorosilyl)propanenitrile showed spin-spin coupling constants ¹⁹F-¹H and ¹⁹F-¹³C of the CH₂SiF₃ moiety. In ¹H NMR spectra, the coupling between H and F gives multiplet and the coupling between C and F gives quartet. The J_{C-F} coupling constants for 4-(trifluorosilyl)butanenitrile and 3-(trifluorosilyl)propanenitrile were 19.50 and 20.75 Hz, respectively. Fig. 4 and 5 show the splitting pattern of CH₂SiF₃ moiety in ¹³C NMR spectra of 4-(trifluorosilyl)butanenitrile and 3-(trifluorosilyl)propanenitrile, respectively.

3. Conclusions

New easy synthetic method for 4-(trifluorosilyl)butanenitrile and 3-(trifluorosilyl)propanenitrile by using HF has been developed. Perfluorosilanes without donor moiety with moderately high yield without using an air-

sensitive boron trifluoride etherate have been successfully synthesized in 60 -70% yield from the direct reaction of 3-cyanopropyltriethoxysilane and 2-cyanoethyltriethoxysilane with 48% HF, respectively. Perfluorosilane compounds were characterized by FT-IR, ^1H , and ^{13}C NMR spectroscopy. Spin-spin coupling ^{19}F - ^1H and ^{19}F - ^{13}C of the CH_2SiF_3 moiety for the perfluorosilanes were observed and measured.

Acknowledgments

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