



Liquid type of fluorosulfonyl lithium salts containing siloxane for Li-ion electrolyte



Jaeseong Ha, Seungbin Im, Soonho Lee, Hohyoun Jang, Taewook Ryu, Chaekyun Lee, Youngjin Jeon, Whangi Kim*

Department of Applied Chemistry, Konkuk University, Chungju 380-701, Republic of Korea

ARTICLE INFO

Article history:

Received 27 January 2016
Received in revised form 9 March 2016
Accepted 27 March 2016
Available online 4 April 2016

Keywords:

RTILs
Lithium ion battery
Electrolyte
Ionic liquid
Additive

ABSTRACT

Our goal in the present work is to synthesize liquid type of electrolyte that can be used in lithium-ion battery, based on fluorosulfonyl group. We synthesized a precursor of fluorosulfonyl isocyanate, and followed to prepare fluorosulfonyl carbamic acid ester lithium salt (SiFSC 1)s and fluorosulfonyl urea lithium salt (SiFSC 2)s containing siloxane electrolytes. Four electrolytes with carbamic or urea structures were prepared by changing the siloxane moieties with different chain length. The synthesized electrolytes are viscous liquid with different color. The resulting electrolytes were characterized by ^1H NMR spectroscopy and thermogravimetric analysis (TGA). The ionic conductivity of SiFSCs was compared by LiPF_6 and LiFSI .

© 2016 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

Introduction

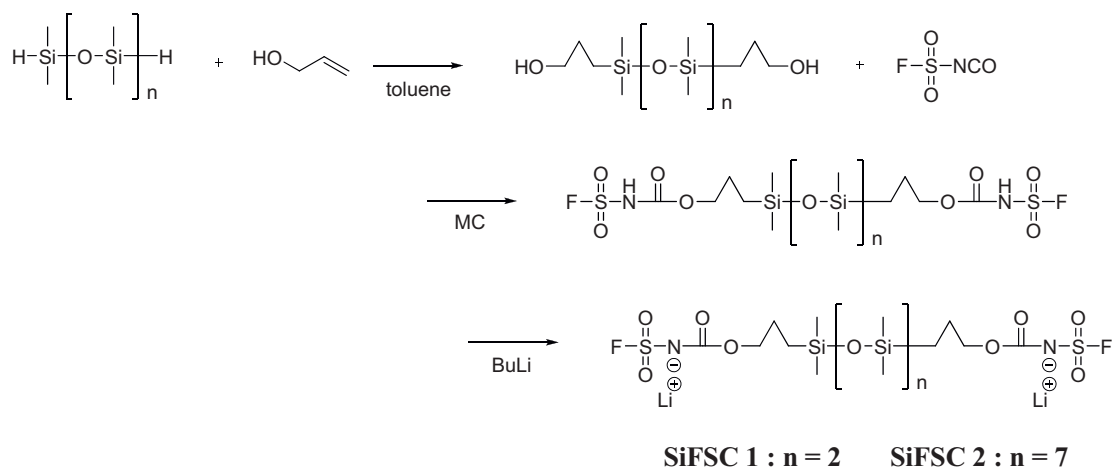
These numerous features provide using in high energy lithium batteries: negligible volatility, relatively high decomposition temperatures when compared to traditional lithium battery electrolytes [1–6]. Liquid type of room temperature ionic liquids (RTILs) is showing low vapour pressure, high ionic conductivity, and chemical and electrochemical stability [1,2]. RTILs as a potential electrolyte have been extensively studied chemical modification of imidazolium, tetraalkylammonium, pyrrolidinium, and piperidinium cations. To improve the ion conductivity of the RTILs, the introduction of ether functional group plays key role to low the melting point, and also prevents the crystallization, which is depending on the counter anion [7–10]. However they have drawback of low concentration ($>0.6 \text{ mol kg}^{-1}$) because of solubility. In most commercial lithium-ion batteries, a concentration of $0.8\text{--}1.2 \text{ mol kg}^{-1}$ Li salt in organic liquid electrolyte is used to maximize cell performance by achieving a balance between conductivity and viscosity [11]. The effects of Li concentration were studied, and resulted that the important factor for charging and discharging of Li batteries is Li salt concentration in RTIL,

because increasing the Li salt concentration increases the viscosity and decreases the conductivity [12].

Seki et al. [12] reported the concentration effect of LiTFSI salt ($0\text{--}0.8 \text{ mol kg}^{-1}$) on the performance of 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (DMPImTFSI). Zhou et al.'s [13] electrochemical and physicochemical studies on N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)-imide (C3mpyr FSI) and N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)-imide (C4mpyr FSI). Paillard et al. [14] added different amounts of LiFSI salts (mole ratios from 0 to 0.6, where a mole ratio of 0.6 LiFSI : 0.4 C4mpyr is equivalent to an LiFSI concentration of 4.9 mol kg^{-1}) to C4mpyr FSI and performed physical and electrochemical studies.

Recently, lithium bis(fluorosulfonyl)imide $\text{Li}[\text{N}(\text{SO}_2\text{F})_2]$ (LiFSI) was extensively studied as a electrolyte salt because imido-bis(sulfuric acid) difluoride ($\text{HN}(\text{SO}_2\text{F})_2$) contains a strong nitrogen acid that forms with metals, such as, K, Na, Li, Mg, Zn etc. [15–17]. LiFSI is more likely to dissociate into ions to produce lithium ions than LiPF_6 or the like because sulfonyl groups shield lithium ions. Nevertheless new LiFSI derivatives have been not studied because of difficulty of the synthetic scheme and harmful chemicals handling in laboratory. The purpose of this study is to synthesize liquid type of LiFSI containing with siloxane in which siloxane group provides low melting point. The flexibility characteristic of siloxane is caused by the large angle and the low bending force constant of Si–O–Si bonds [18–20].

* Corresponding author. Tel.: +82 43 840 3579.
E-mail address: wgkim@kku.ac.kr (W. Kim).



Scheme 1. Preparation of SiFSCs.

A new route for the synthesis of LiFSI (Si-LiFSI) derivatives containing siloxane was presented. Si-LiFSI derivatives were shown viscous liquid and solid depending on the different chemical structures. The structures of Si-LiFSI derivatives were analyzed and interpreted by NMR and. Some of the properties of Si-LiFSI, such as thermal stability, conductivity, were comparatively performed with those of the two common salts, LiPF₆ and LiFSI. The prepared liquid type of Si-LiFSI was shown the possibility to use as an ionic liquid.

Experimental

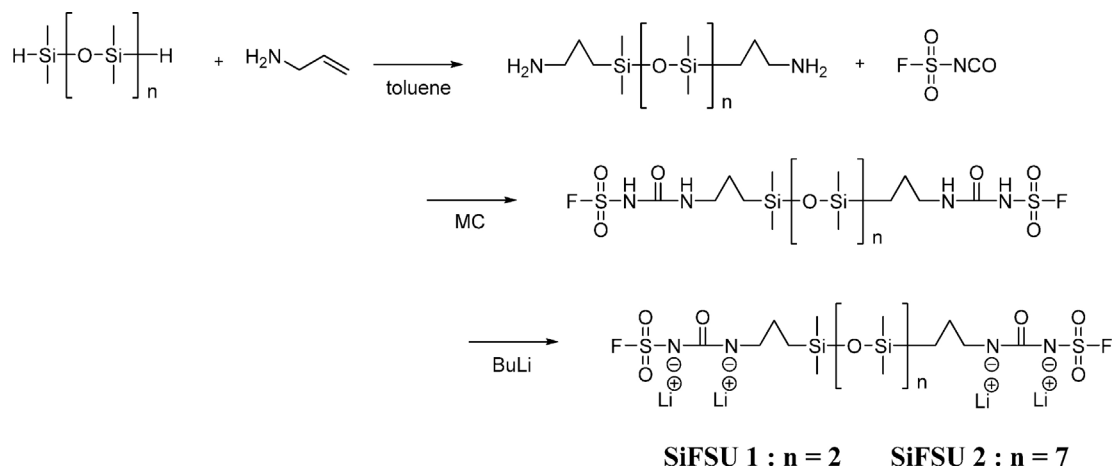
Materials

Allyl alcohol, allyl amine, 1,1,3,3,5,5-hexamethyltrisiloxane (HMTS, 97%), poly(dimethylsiloxane) hydride terminated (number average molecular weight, Mn ~ 580), lithium hexafluorophosphate (LiPF₆) platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (karstedt's catalyst), N-butyllithium (solution 2.5 mol in hexane) were purchased from Sigma-Aldrich. Bis(fluorosulfonyl) imide lithium salt (LiFSI) was purchased from Chunbo Co. (>99%, Korea). The other reagents were used as received without purifications unless otherwise specified.

Synthesis of 1,5-bis(1-propyl fluorosulfonyl carbamic acid)-1,1,3,3,5,5-hexamethyltrisiloxane, lithium salt (SiFSC 1)

A mixture of 1,1,3,3,5,5-hexamethyltrisiloxane (3.0 g, 14.39 mmol) and allyl alcohol (2.01 g, 34.54 mmol) was dissolved in toluene (30 mL), and follows added an 1 drop catalytic amount of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (0.145 g, 0.4 mmol). The reaction mixture was gradually increased and refluxed for 24 h. After the reaction, the reaction mixture was cooled down and evaporated. The liquid product was dissolved in methyl alcohol and passed through a plug of celite to remove the catalyst. The final product of 1,5-bis-(3-hydroxypropyl)-(1,1,3,3,5,5-hexamethyltrisiloxane) was yielded (4.44 g, 95% yield). Into a two-necked round-bottom flask (100 mL) equipped with a dropping funnel were charged with fluorosulfonyl isocyanate (1.77 g, 14 mmol) and dichloromethane (20 mL). The mixture was cooled to 0 °C under nitrogen atmosphere and with magnetic stirring in an ice bath. 1,5-bis-(3-hydroxypropyl)-(1,1,3,3,5,5-hexamethyltrisiloxane) (2 g, 6 mmol) was added in drops to the mixture. The mixture was stirred for about 30 min with temperature under 5 °C. The product of 1,5-bis(1-propyl fluorosulfonyl carbamic acid)-1,1,3,3,5,5-hexamethyltrisiloxane (3.1 g, 87.5% yield) was obtained after vacuum evaporation.

1,5-Bis(1-propyl fluorosulfonyl carbamic acid)-1,1,3,3,5,5-hexamethyltrisiloxane (1.5 g, 3 mmol) was dissolved in dichloromethane



Scheme 2. Preparation of SiFSUs.

Download English Version:

<https://daneshyari.com/en/article/227299>

Download Persian Version:

<https://daneshyari.com/article/227299>

[Daneshyari.com](https://daneshyari.com)