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Synthesis and characterization of a novel electrolyte based on bis[(perfluoroalkyl)sulfonyl]triimide trianion

Jin Nie*, Xiaoyong Li, Dafan Liu, Rong Luo, Liqiong Wang

Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074, Hubei, PR China

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Abstract

The facile preparation and characterization on a novel trisodium salt based on bis[(perfluoroalkyl)sulfonyl]triimide trianion were reported for the first time. High oxidation potential was observed for the new salt in organic solvent. Ionic conductivities of this new salt and other monomeric sodium salts were determined in different organic solvents over a temperature range between 10 and 100 °C.

Keywords: Bis[(perfluoroalkyl)sulfonyl]triimide; Imidobis(sulfuryl chloride); Polyfluorinated sulfonylimide; Electrolyte

1. Introduction

In recent years, extensive study has been carried out on the novel electrolytes and their applications for high energy density batteries. Alkaline metal electrolytes based on perfluorosulfonylimides and other weakly coordinating anions have been receiving increasing attention due to their high stability and high conductivity [1–4].

Most prior research has focused on monoanionic salts with large anions like $(CF_3SO_2)_2N^-$ (TFSI anion) [1–3], $((CF_3)_2CHOSO_2)_2N^-$ (HFPSI anion) [4] and $(C_4F_9SO_2)(CF_3SO_2)N^-$ [4]. Polyanionic salts are also of particular interest in battery technology. DesMarteau [5] synthesized a kind of dianionic sodium salt for preparation of a imide-type ionomer which demonstrated excellent electrochemical property as fuel cell. But many challenges have to be met in its synthetic work. Very recently, DesMarteau prepared a series of similar dilithium salts based on bis[(perfluoroalkyl)sulfonyl] diimides dianions [6]. PEO electrolyte containing these salts exhibited comparable ionic conductivity to PEO-LiTFSI. Besides these researches, no other synthetic study on monomeric polysulfonylimide and its derivatives was seen in a literature survey.

Previously, we reported one-step synthesis [7] of a series of bis(polyfluoroalkoxyl)sulfonyl imides through the reaction of polyfluoroalkyl alcohols with $HN(SO_2Cl)_2$ in benzene. These imides were fairly strong acids according to ^1H NMR determination, which means very weak coordination ability of the anions. But, these ester-type compounds were not very stable due to cleavage of ester bond. Similar synthetic method was also employed in our continuous study on sulfonylimide-type polymeric electrolytes [8,9]. The results showed that their lithium salts had very good electrochemical properties [4,9,10].

In this paper, we would like to report the facile synthesis of a new type of triimide salt based on large and weakly coordinating triimide trianion for the first time. This monomeric species (I) (as shown in Fig. 1) is expected to exhibit good electrochemical properties due to relatively higher concentration of cation in the molecule structure and low dissociation energy.

2. Results and discussions

2.1. Synthesis

As shown in Scheme 1, the trisodium salt (I) can be prepared by the reaction of $C_4F_9SO_2NHNa$ [11] with $HN(SO_2Cl)_2$ [12] in CH_3CN under an argon atmosphere. In this reaction, 5 equiv. of sodium perfluorinated sulfone amide were used because we assumed that the reaction proceeded as shown in Scheme 2. CH_3NO_2 was also found to be a suitable solvent for the reaction. This sodium salt product was soluble in water, alcohol and *N*,*N*-dimethylformamide (DMF).

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* Corresponding author. Tel.: +86-27-8754-3232; fax: +86-27-8754-3632.

E-mail address: niejin@mail.hust.edu.cn (J. Nie).

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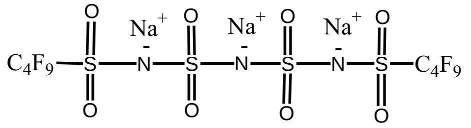


Fig. 1. Trisodium bis[(perfluoroalkyl)sulfonyl]triimide (I).

The sodium bis[(perfluoroalkyl)sulfonyl]triimide was characterized by FT-IR, NMR spectroscopy and elemental analysis. First, the FT-IR spectrum exhibited no strong N–H absorption beyond 3000 cm^{-1}, and the characteristic peaks at 990, 800, 698, 504 cm^{-1} in $C_4F_9SO_2NHNa$ disappeared in the product's spectrum. As to ^1H NMR spectrum, besides the signal of solvent, the single peak of $C_4F_9SO_2NHNa$ or $C_4F_9SO_2NH_2$ was not found in product's ^1H NMR spectrum indicating a high purity. The ^{19}F NMR spectrum showed four different resonance at δ −80.9 (triplet), −113.4 (multi peak), −121.5 (multi peak) and −125.3 (triplet) representing the fluorine atoms on C^A, C^B, C^C and C^D $[(C^AF_3C^BF_2C^CF_2C^DF_2\text{-}SO_2NNaSO_2)_2NNa]$, respectively. The relative area ratio was 3:2:2:2 as required for the structure I.

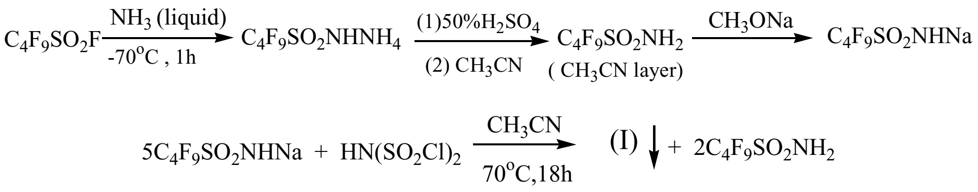
An attempt to obtain the bis[(perfluoroalkyl)sulfonyl]triimide (a potential strong triacid) directly by the reaction of $C_4F_9SO_2NH_2$ with $HN(SO_2Cl)_2$ (Scheme 3) was not satisfactory. The reaction occurred very slowly and we got a highly hygroscopic and strongly acidic compound containing byproducts that were hard to remove. This might be attributed to the reduced nucleophilicity of $C_4F_9SO_2NH_2$ on $HN(SO_2Cl)_2$, compared with $C_4F_9SO_2NHNa$. We also tried to extend the reaction to $C_4F_9SO_2NHLi$, but it was unsuccessful because of the fairly low solubility of $C_4F_9SO_2NHLi$ in acetonitrile and other organic solvents. Further synthetic effort to obtain the trilithium salt is in progress.

2.2. Oxidation potential

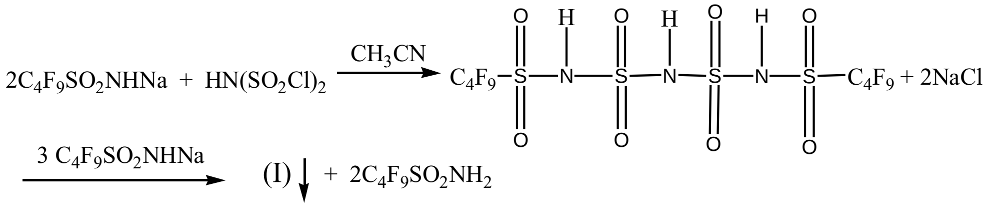
In the preliminary electrochemical measurements, potential sweep was conducted to evaluate the anodic stability of the new electrolyte. As exhibited in Fig. 2, $((CF_3)_2CHO\text{-}SO_2)_2NNa$ (NaHFPSI) gave higher oxidation potential (5.8 V) than NaTFSI. This agrees well Kita et al.'s previous report [4] about LiTFSI and LiHFPSI. Compared with those two salts, our new salt demonstrates good electrochemical stability (6.0 V). This may reveal a promising prospect for the application of the new salt in high voltage battery technology. A detailed electrochemical investigation on this new salt will be discussed elsewhere.

2.3. Conductivity

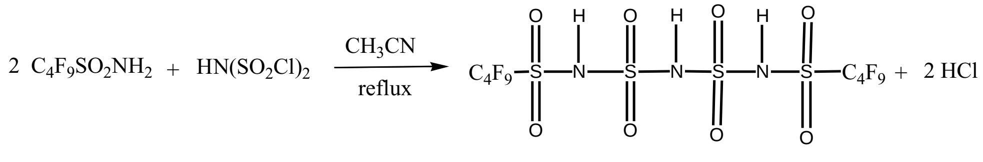
Fig. 3 shows the ionic conductivities of three kinds of electrolyte solutions in PC–EC (1:2, v/v). According to this figure, our new salt shows higher conductivity than NaTFSI and NaHFPSI. But due to high viscosity of the mixed solvent, the difference between conductivities of NaTFSI and NaHFPSI is not very clear. So DMF, another solvent



Scheme 1. Reaction scheme for preparation of trisodium salt (I).



Scheme 2.



Scheme 3.

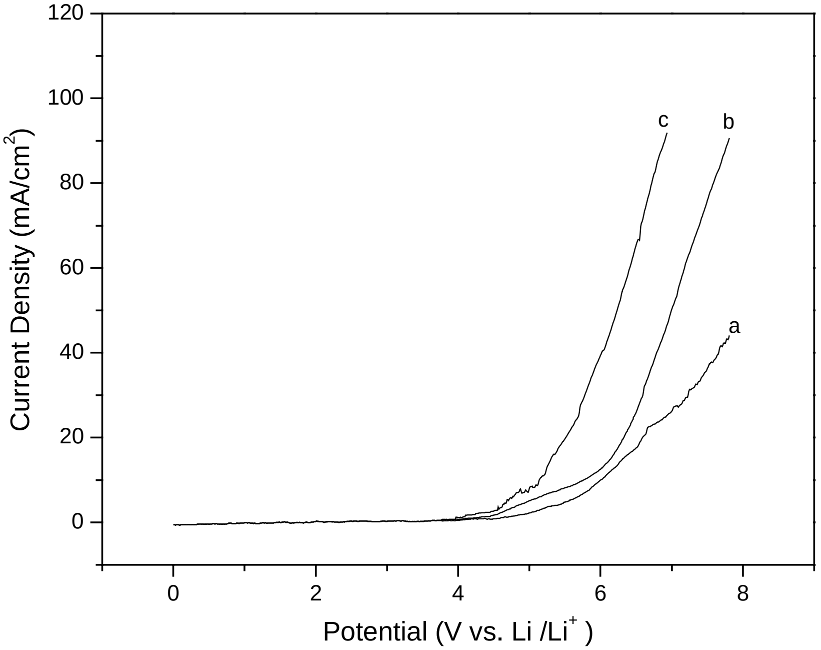


Fig. 2. Comparison between potential sweep curves of 0.01 M sodium salt in PC–EC (1:2) at 25 °C; electrode: Pt (9.08×10^{-4} cm^2); sweep rate: 10 mV/s; oxidation limit current: 10 mA/cm^2. (a) Trisodium salt (I)—6.0 V; (b) NaHFPSI—5.8 V; (c) NaTFSI—5.2 V.

with lower viscosity, was used in conductivity measurement. As shown in Fig. 4, the differences of ionic conductivities among three electrolyte solutions are apparent and reproduce the trend in Fig. 3. As expected, due to low viscosity of DMF, all the salts demonstrate higher conductivity in DMF than in PC–EC mixed solvent. Good linear relationships of the plots were obtained in all cases.

Generally, the high ionic conductivity of electrolyte reflects its low dissociation energy in the solvent. To confirm this notion, a theoretical approach on the dissociation energy $(E_{\text{dis}} = (E_{\text{free anion}} + E_{\text{Na cation}}) - E_{\text{sodium salt}})$ was employed in our study.

Geometry optimizations on electronic structures of three sodium salts and their anions were performed using PM5

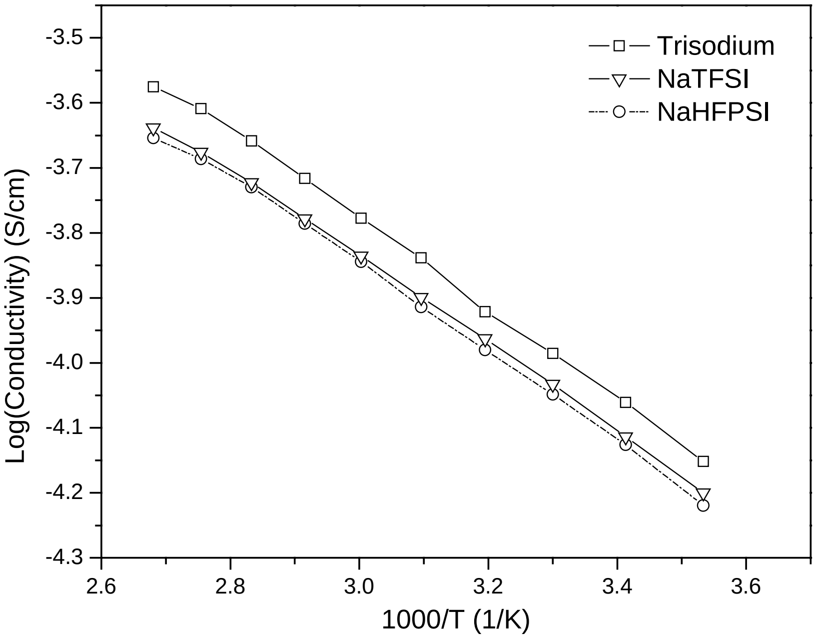


Fig. 3. Comparison between Arrhenius plots for liquid electrolytes of 0.01 M sodium salt in PC–EC (1:2). Trisodium salt (I)—□; NaTFSI—▽; NaHFPSI—○.

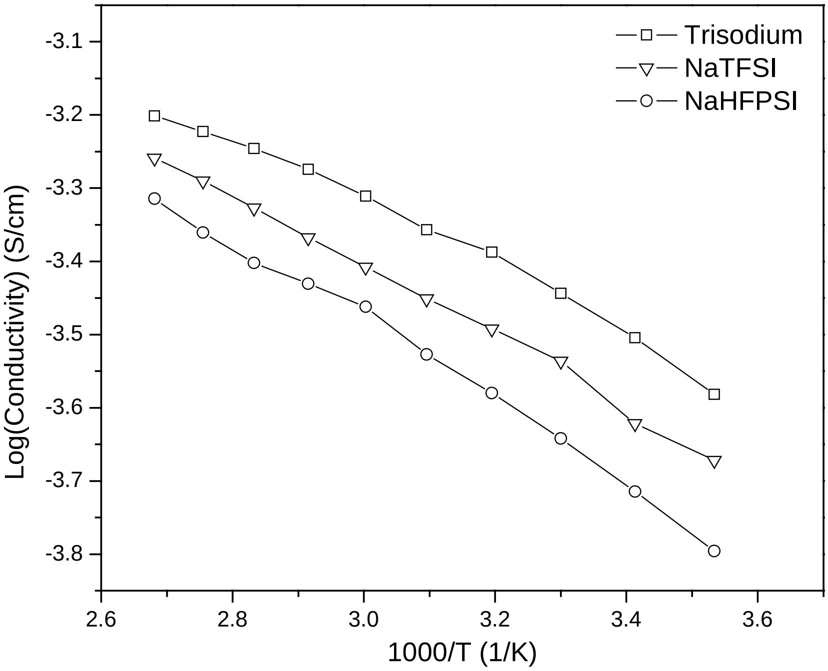


Fig. 4. Comparison between Arrhenius plots for liquid electrolytes of 0.01 M sodium salt in DMF. Trisodium salt (I)—□; NaTFSI—▽; NaHFPSI—○.

Table 1
Dissociation energy for different salts[a]

Anion	Dissociation energy (kcal/mol)	
	PM5	3-21G*//PM5
$C_4F_9SO_2N^-$–SO_2–N(Na)–SO_2–N(Na)–SO_2–C_4F_9(II)	$E_{dis1} = 100.1$	122.8
$C_4F_9SO_2N^-$–SO_2–N^-–SO_2–N(Na)–SO_2–C_4F_9	$E_{dis2} = 193.2$	264.8
$C_4F_9SO_2N^-$–SO_2–N^-–SO_2–N^-–SO_2–C_4F_9	$E_{dis3} = 246.2$	324.3
$(CF_3SO_2)_2N^-$	116.4	152.1
$(CH(CF_3)_2OSO_2)_2N^-$	125.3	187.8

[a] Optimize using PM5 method in MOPAC 2002.

semi-empirical method. Single point energies were also calculated at B3LYP/3-21G* level to obtain the dissociation energies of three salts. The E_{dis} (PM5 and B3LYP/3-21G*//PM5 levels) listed in Table 1 testified that the species with higher conductivity has lower dissociation energy. Optimization result also reveals that in the new salt, three cations prefer to coordinate with oxygen atoms in –SO_2-group and fluorine atoms in C_4F_9-group. This is in very good accordance with Arnaud et al.'s ab initio study on LiTFSI [13]. According to energetic comparison, the single anion with a structure depicted in Fig. 5 is preferred. This is reasonable because in such a structure, the negative charge center is close to the strong electron-withdrawing perfluoroalkyl group ($C_4F_9SO_2$–) facilitating the delocalization of negative charge. Further energy calculation indicates that the dissociation energy for anion II to render the second sodium cation is relatively high, needless to say the dissociation of the third cation. So the remaining sodium cations in anion II are not able to disassociate completely (see Table 1).

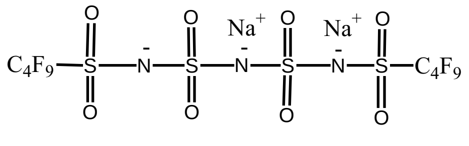

$$C_4F_9{-}\overset{O}{\underset{O}{S}}{-}\overset{-}{N}{-}\overset{O}{\underset{O}{S}}{-}\overset{Na^+}{\overset{-}{N}}{-}\overset{O}{\underset{O}{S}}{-}\overset{Na^+}{\overset{-}{N}}{-}\overset{O}{\underset{O}{S}}{-}C_4F_9$$

Fig. 5. Optimized structure for single anion of trisodium bis[(trifluoroalkyl)-sulfonyl]triimide (II).

3. Experimental

Infrared spectra were obtained with a Bruker EQUNIOX55 FT-IR spectrometer. Nuclear magnetic resonance was recorded on JEOL FX90Q spectrometer. The observation frequency was 90 MHz for ^1H and 84 MHz for ^{19}F. Elemental analysis was conducted by Vario EL-2 elemental analysis instrument. Unless otherwise mentioned, all other reagents were purchased from commercial sources.

3.1. Sodium bis[(perfluoroalkyl)sulfonyl]triimide

$C_4F_9SO_2NHNa$ (4.5 g, 14.0 mmol) and 50 ml dry CH_3CN were added to a 100 ml three-necked round bottom flask equipped with a bubbler and a calcium chloride drying tube. Imidobis(sulfuryl chloride) ($HN(SO_2Cl)_2$) (0.60 g, 2.80 mmol) was dissolved in 10 ml dry CH_3CN and added drop-wise into this solution under stirring. The reaction mixture was vigorously stirred for 18 h at 70 °C under dry argon atmosphere. When the reaction was over, a large amount of white precipitate was produced. After filtration, the crude product was further extracted by dry CH_3CN in Soxhlet extractor. Evaporation of the solvent and the remaining residue was dried under high vacuum for 12 h to afford 1.79 g white powder solid in 79% yield (m.p. >300 °C). IR (KBr): ν 1354 (w), 1304 (s), 1206 (vs) and 1173 (vs), 1140 (vs), 1073 (s), 826 (w), 657 (m), 612 (m), 543 (w); ^1H NMR (Me_2SO-d_6, TMS) no signals were observed; ^{19}F NMR (Me_2SO-d_6, $CFCl_3$) of $[(C^AF_3C^BF_2C^CF_2C^DF_2SO_2NNaSO_2)_2NNa]$ δ −80.9 (t, 3F, $J_{AB} = 11.8$ Hz, F–A), −113.4 (m, 2F, F–B), −121.5 (m, 2F, F–C), −125.3 (t, 2F, $J_{CD} = 13.5$ Hz, F–D); analytically calculated for $C_8O_8N_3S_4F_{18}Na_3$: C, 11.93; N, 5.22; H, 0.00. Found: C, 11.65; N, 5.06; H, 0.15.

3.2. Oxidation potential and conductivity measurements

Propylene carbonate (PC from Fluka) was dried over 4 Å molecular sieves. Ethylene carbonate (EC from Fluka) was used as received. NaTFSI and NaHFPSI were obtained by reacting HTFSI and HHFPSI, respectively, with $NaHCO_3$ in acetonitrile. The excess $NaHCO_3$ (not soluble in acetonitrile) was removed by filtration. After solvent evaporation, the sodium salts were dried under high vacuum for 12 h to afford white solid with >90% yield. No N–H absorption was observed in FT-IR spectra of both salts.

Preparation of electrolyte solutions and cell assembly were conducted in an argon-filled glove box. Conductivities of electrolytes were measured by a digital conductance meter (DDS-12A, Kinglong Ltd.) over a temperature range between 10 and 100 °C. The test cell used in potential sweep had a three-electrode configuration consisting of lithium foils as counter and reference electrodes, respectively. The working electrode was a 0.34 mm diameter platinum wire that was coated by epoxy with a small surface area (9.07×10^{-4} cm^2) exposed to electrolyte. Exposed section of this platinum wire was cleaned before each experiment by polishing with abrasive paper. The cell potential was swept at the rate of 10 mV/s with a HA-501 potentiostat (Hokuto Denko Ltd.). The potential at a current density (10 mA/cm^2) was regarded as the oxidation potential.

3.3. Calculations

All the molecular structures were constructed and optimized by PM5 semi-empirical method using MOPAC2002 on Cache 5.0 system [14]. We selected PM5 method instead of MNDO/d or PM3 method because it could give better description of molecules containing sodium atom. Single point energy calculation was also performed at B3LYP/3-21G* level.

Acknowledgements

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