On the characteristics of electrolytes with new lithium imide salts

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Abstract

In our continuous study on organic lithium salts, we found that the imide salt $(RfSO_2)(R'fSO_2)NLi$ shows high conductivity in organic solvents, and that the modification of the imide salts change the anodic oxidation potential and the dissolution potential of aluminum current collector. Lithium imide with long fluoroalkyl groups such as $(C_4F_9SO_2)(CF_3SO_2)NLi$ and the new ester-type imide salts, $((CF_3)_2CHOSO_2)_2NLi$ do not dissolve the aluminum collector up to 4.8 and 4.3 V, respectively. We also examined the polymer analogue of the ester-type imide salt such as $(-CH_2(CF_2)_4CH_2OSO_2N(Li)SO_2O-)_{9-10}$. © 1997 Elsevier Science S.A.

Keywords: Organic lithium salts; Imide; Conductivity; Oxidation potential; Orbital energy

1. Introduction

Lithium imide $(CF_3SO_2)_2NLi$ is noteworthy as a potential-supporting electrolyte for high energy density lithium batteries because of its high stability and high conductivity [1–3]. For 4 V rechargeable lithium batteries, however, the electrolyte with this lithium imide has a key problem to dissolve aluminum current collector at more than 4 V [4]. In the course of our continuous study to develop practical electrolytes for lithium batteries for the next generation, we designed the lithium salts of various polyfluorinated organic anions with high electrochemical stability and high conductivity, and found a new lithium imide salt $(C_4F_9SO_2)(CF_3SO_2)NLi$ which does not dissolve the aluminum collector up to 4.8 V. We also developed new polyfluorinated lithium salts $(RfOSO_2)_2NLi$ (ester-type imides), and show here their attractive characteristics for high voltage batteries.

Moreover, we studied the polymer analogue. One of the polymeric structure of anion sites is well known as a Nafion®-type membrane. The anion sites of this-type polymer with $-SO_3^-$ or $-CO_2^-$ groups do not show a high dissociation constant in organic electrolytes, while the imide anion sites are better because of their high dissociation constant. DesMarteau [5] already showed some examples of the imide-type polymer. Our polymer showed here is a new ester-type imide polymer such as $(CH_2(CF_2)_4CH_2OSO_2$
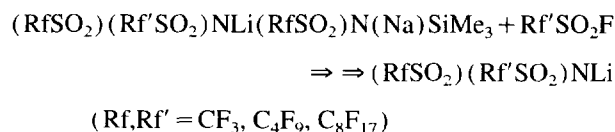
$N(Li)O_2SO)_{9-10}$ (mol. wt $= \sim 4300$), which showed extremely high molar conductivity in organic solvents.
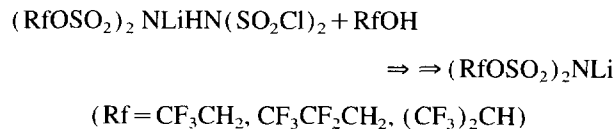
2. Experimental

2.1. Syntheses of lithium salts

We synthesized the following lithium imide salts [6]:

(a)

$(RfSO_2)(Rf'SO_2)NLi(RfSO_2)N(Na)SiMe_3 + Rf'SO_2F$

$$\Rightarrow \Rightarrow (RfSO_2)(Rf'SO_2)NLi$$

$$(Rf,Rf' = CF_3, C_4F_9, C_8F_{17})$$

(b)

$(RfOSO_2)_2 NLiHN(SO_2Cl)_2 + RfOH$

$$\Rightarrow \Rightarrow (RfOSO_2)_2NLi$$

$$(Rf = CF_3CH_2, CF_3CF_2CH_2, (CF_3)_2CH)$$

2.2. MNDO calculation

The energy levels for the highest occupied molecular orbitals (HOMO) were calculated by MNDO semi-empirical methods using MOPAC Ver.6 [7] on Cache system (Cache Scientific).

2.3. Conductivities and oxidation potentials

Conductivities were measured by a conductance meter (CM40S, Toa Electronics).

Anodic oxidation potentials were measured by potential sweep method. The 0.3 mm diameter platinum wire (Nilaco) was used for a working electrode, and 21 mm wide lithium foil (Kyokuto) was used for the counter electrode (substantial area = 0.2 cm²). A polyethylene separator was placed between the working electrode and the counter one. Cell potential was swept at the rate of 50 mV/s with a potentiostat (HA-501, Hokuto Denko) and a function generator (HA-501, Hokuto Denko). The potential at a current density (0.5 mA/cm²) was regarded as the oxidation potential.

3. Results and discussion

3.1. Conductivity

The conductivities of several kinds of electrolyte solution (0.1 M lithium salts in 1:2 v/v PC:DME) with polyfluorinated organic lithium salts are shown in Table 1 [8].

The conductivities of the ester-type lithium salts such as $(CF_3CH_2OSO_2)_2NLi$, $(CF_3CF_2CH_2OSO_2)_2NLi$, $(HCF_2-CF_2CH_2OSO_2)_2NLi$, and $((CF_3)_2CHOSO_2)_2NLi$ (3.0, 3.0, 2.9, and 3.1 mS/cm, respectively) were higher than that of CF_3SO_2OLi (2.3 mS/cm) in 0.1 M PC:DME(1:2 v/v) solution of lithium salts at 25 °C.

3.2. Oxidation stability

The effects of the structure and polyfluoro-substituents on the oxidation stability of the organic anions were investigated theoretically and experimentally in terms of the oxidation potentials. Theoretical MNDO calculations on the HOMO

Table 1
Conductivities of electrolytes with fluorinated lithium imide salts at 25 °C, 0.1 M salts in PC:DME(1:2 v/v)

Lithium salt	Conductivity (mS/cm)	Mol. wt
CF₃CO₂Li	0.4	120
(CF₃CO)₂NLi	0.8	215
CF₃SO₃Li	2.3	156
(CF₃SO₂)₂NLi	4 0	287
(C₄F₉SO₂)(CF₃SO₄)NLi	3.5	437
(FSO₂C₆F₄)(CF₃SO₂)NLi	3.0	347
(FSO₂C₆F₄)(CF₃SO₂)NLi ᵃ	3 1	347
(C₈F₁₇SO₂)(CF₃SO₃)NLi	3.2	637
(CF₃CH₂OSO₂)₂NLi	3 0	347
(CF₃CF₂CH₂OSO₂)₂NLi	3.0	447
(HCF₂CF₂CH₂OSO₂)₂NLi	2.9	411
((CF₃)₂CHOSO₂)₂NLi	3.1	483
(CF₃SO₂)₃CLi	3 6	418
LiPF₆	4.4	152

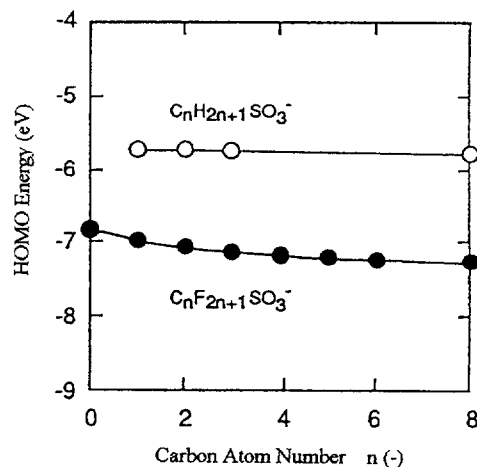ᵃ Mixture with (C₆F₅SO₂)(CF₃SO₂)NLi

Fig. 1. Effects of alkyl-length on HOMO energy; anion, $C_nF_{2n+1}SO_3^-$, $C_nH_{2n+1}SO_3^-$ (MOPAC Ver. 6 MNDO method)
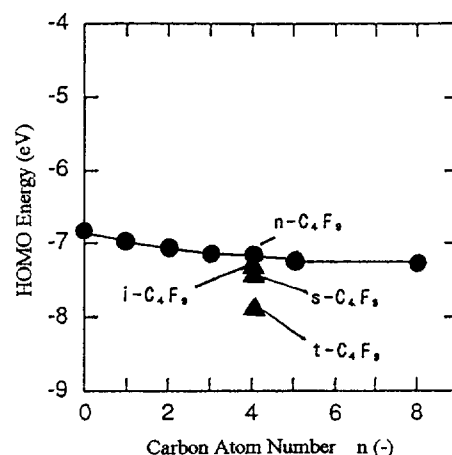

Fig. 2. HOMO energies of linear and branched $C_4F_9SO_3^-$ anions
$n-C_4F_9SO_3^- = CF_3CF_2CF_2CF_2SO_3^-$;
$i-C_4F_9SO_3^- = (CF_3)_2CFCF_2SO_3^-$;
$s-C_4F_9SO_3^- = CF_3CF_2CF(CF_3)SO_3^-$, and
$t-C_4F_9SO_3^- = (CF_3)_3CSO_3^-$.
(MOPAC Ver. 6 MNDO method).

energy levels of organic anions indicated that the anions with fluoro- or polyfluoroalkyl groups have lower HOMO energy levels (i.e. more stable to oxidation) compared with the anions without these groups as shown in Figs. 1 and 2.

The HOMO levels of the anions with longer and branched polyfluoroalkyl groups are much lower than those with shorter and linear groups.

We also calculated the HOMO energies for the imide anions $(RfSO_2)(Rf'SO_2)N^-$ and the new ester-type imide anions $(RfOSO_2)_2NLi$ in Table 2. The HOMO levels of the new ester-type imide anions were lower compared with the imide anion $(CF_3SO_2)_2N^-$.

The experimental oxidation potentials of the new ester-type imide salts were also higher than the value of $(CF_3SO_2)_2NLi$ (5.2 V) in PC solvent as shown in Figs. 3–5 [7]. Especially, branched ester-type imide, $((CF_3)_2CH-OSO_2)_2NLi$ showed the highest oxidation potential (5.8 V vs. Li/Li⁺).

Table 2
Effect of a new imide structure on HOMO energy [a]

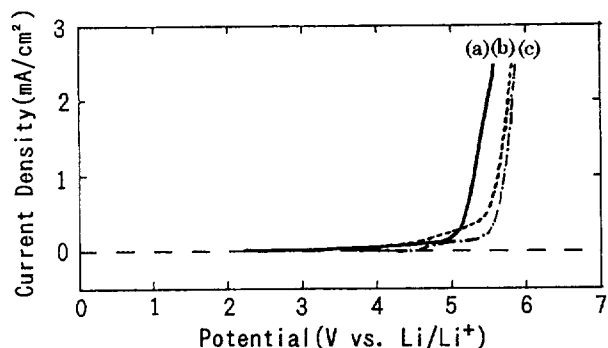| Anion	HOMO energy (eV)
(CF₃OSO₂)₂N⁻	−8 6
(CF₃CH₂OSO₂)₂N⁻	−8.3
(CF₃CF₂CH₂OSO₂)₂N⁻	−8 4
((CF₃)₂CHOSO₂)₂N⁻	−8.9
(CF₃SO₂)₂N⁻	−8 2

[a] MOPAC Ver 6 MNDO method.

Fig 3 Potential sweep curves of imide ((CF₃SO₂)₂NLi) and new imide salts (0 1 M) in PC at 25 °C. Electrode: Pt (0 2 cm²), sweep rate: 50 mV/s, and oxidation limit current: 0.5 mA/cm²
(a) (CF₃SO₂)₂NLi (5.2 V);
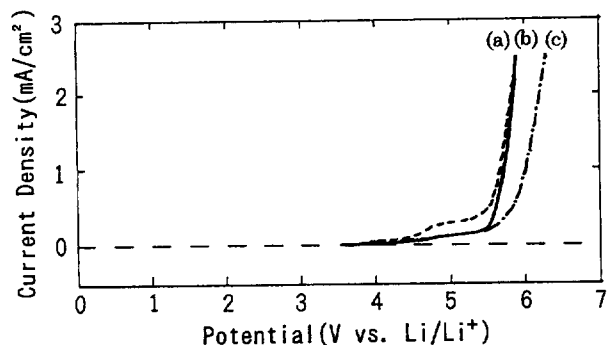(b) (CF₃CH₂OSO₂)₂NLi (5.4 V), and
(c) (CF₃CF₂CH₂OSO₂)₂NLi (5.6 V).

Fig. 4. Potential sweep curves of different types of new imide salts (0 1 M) in PC at 25 °C. Electrode: Pt (0.2 cm², sweep rate· 50 mV/s, and oxidation limit current· 0 5 mA/cm²
(a) HCF₂CF₂CH₂OSO₂)₂NLi (5.5 V),
(b) (CF₃CF₂CH₂OSO₂)₂NLi (5.6 V), and
(c) ((CF₃)₂CHOSO₂)₂NLi (5.8 V).

3.3. Aluminum dissolution

As shown in Fig. 6, (CF₃SO₂)₂NLi electrolyte dissolved aluminum current collector at more than 4 V. On the other hand, lithium imides with a long fluoroalkyl groups such as (C₄F₉SO₂)(CF₃SO₂)NLi and the new ester-type imide salt, ((CF₃)₂CHOSO₂)₂NLi did not dissolve the aluminum up to 4.8 and 4.3 V, respectively, the aluminum dissolution potential of the lithium imide electrolyte can be changed by modifying the structure of the imide anions.
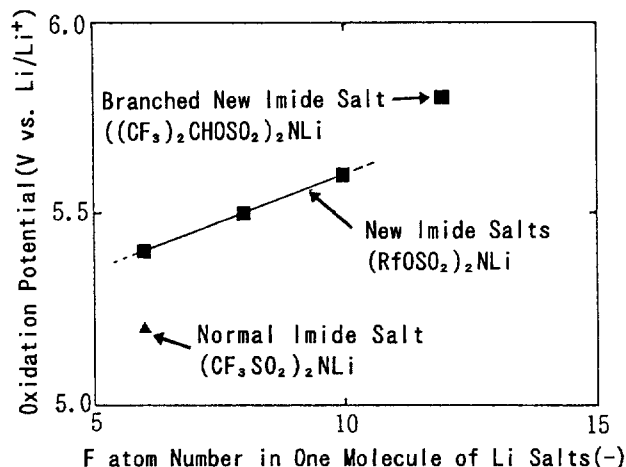

Fig. 5. Oxidation potentials of new imide salts (0.1 M) in PC at 25 °C. Electrode: Pt (0.2 cm²), sweep rate: 50 mV/s, and oxidation limit current: 0.5 mA/cm².
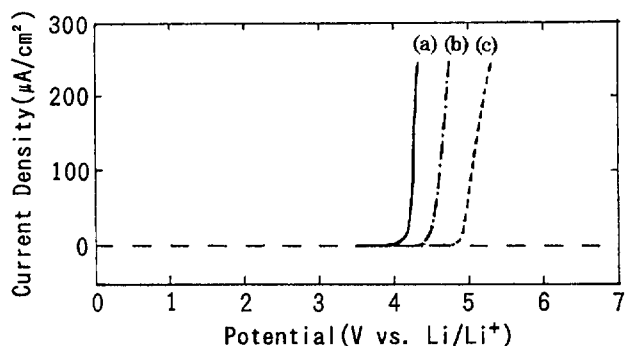

Fig. 6. Aluminum dissolution potentials for normal and new imide electrolytes (0.1 M) in PC at 25 °C Electrode: Pt (0.2 cm²), sweep rate: 5 mV/s.
(a) (CF₃SO₂)₂NLi (4 0 V);
(b) ((CF₃)₂CHOSO₂)₂NLi (4.3 V), and
(c) (C₄F₉SO₂)(CF₃SO₂)NLi (4.8 V)

3.4. Application of lithium salt of the polymer analogue

When we used a diol such as HOCH₂(CF₂)₄CH₂OH instead of RfOH for the new ester-type imide salts, we can obtain an ester-type polymer salt, (−CH₂(CF₂)₄CH₂O-SO₂N(Li)SO₂O−)₉₋₁₀ (mol. wt. = ~4300). This polymer salt electrolyte showed 8.9 mS/cm in polymer salt:AN = 1.1:4.7 w/w, 25 °C). In PC:DME (1:2 v/v) solvent, this polymer salt electrolyte showed extremely high conductivity of 1.7 mS/cm even at 0.01 M (molar conductivity was ~170 S cm²/mol).

4. Conclusions

In our continuous study on organic lithium salts, we focused on the imide-type lithium salts because of their high conductivity and found that the modification of imide salts changes the anodic oxidation potential and the dissolution potential of aluminum current collector.

Lithium imide with a long fluoroalkyl groups such as (C₄F₉SO₂)(CF₃SO₂)NLi and the new ester-type imide salt,

$((CF_3)_2CHOSO_2)_2NLi$ do not dissolve aluminum up to 4.8 and 4.3 V, respectively.

We examined a polymer analogue of ester-type imide salt, $(-CH_2(CF_2)_4CH_2OSO_2N(Li)SO_2O-)_{9-10}$ (mol. wt. = ~4300). In PC:DME (1:2 v/v) solvent, the conductivity of this polymer salt electrolyte was as high as 1.7 mS/cm even at ~0.01 M (molar conductivity was ~170 S cm^2/mol).

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