Molecular Design and Electrochemical Characteristics of Fluorine Containing Electrolytes for Lithium Battery

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In our course of designing new types of lithium battery electrolyte we have developed some new organic salts such as $LiB(C_6H_3R_{f2})_4$, $RfSO_3Li$, $(R_fSO_2)_2NLi$, $(R_fOSO_2)_2NLi$, and $(R_fOSO_2)_3CLi$, where R_f is a fluoroalkyl group[1-2]. Although $LiPF_6$ is widely used as an electrolyte for lithium battery due to its high conductivity, this salt decomposes easily by hydrolysis[3].

To improve the thermal stability, we replaced unstable P-F bonds by P-CF_3 bonds[4] as Merck group has reported about $LiPF_3(C_2F_5)_3$ with a similar idea[5].

We report here some new organic lithium salts designed as electrolytes for lithium battery from the points of their anodic oxidation stability and ion conductivity by MO calculations.

Anodic oxidation stability is estimated by HOMO energy of anion. The oxidation potential of anion correlates well with its HOMO energy[4]. The stabilization of HOMO level is expected by modification of anion with electron-withdrawing group. Table 1 shows the HOMO energies and oxidation potentials of $(R_fSO_2)_nY^-$ type anion, where Y represents O, N, or C. The anion with more electron-withdrawing group such as CF_3SO_2 shows low HOMO energy level and high oxidation potential.

Ion conductivity of electrolyte depends on ion-mobility and ion-concentration, which relates to the degree of dissociation. Electron-withdrawing group delocalizes the charge on anion and reduces the anion-cation interaction, while the ion-mobility decreases with the increase of the size of the ion. Relative degree of dissociation can be estimated by calculating the total energy change ΔΔE(LiX) for the following isodesmic reaction[4]. Positive ΔΔE(LiX) represents that LiX is more dissociative than reference salt, LiX_o. ΔΔE calculated by DFT method and conductivities salts are listed in Table 2. $((CF_3)_2CHOSO_2)_2NLi$ shows quite a high conductivity as expected from ΔΔE in spite of its large anion size.

Table 3 shows ΔΔE and HOMO of $LiPF_{6-n}(Rf)_n$ calculated by DFT. ΔΔE increases with the molecular weight and bulky structure such as $LiPF_3(Rf)_3$ or $LiPF_4(CF(CF_3)_2)_2F_4$ is particularly effective. However the HOMO level of $PF_3(Rf)_3^-$ is higher than that of $PF_4(Rf)_2^-$.

Table 1

Anion	HOMO/MNDO eV	HOMO/DFT eV	Oxidation potential V
$CH_3SO_2O^-$	-5.72	-0.53	(insoluble)
$CF_3SO_2O^-$	-6.94	-1.55	4.8
n-$C_4F_9SO_2O^-$	-7.17	-1.86	6.0
n-$C_8F_{17}SO_2O^-$	-7.25		6.5
$(CF_3SO_2)_2N^-$	-8.20	-3.22	5.2
$(CF_3SO_2)_3C^-$	-8.72	-3.49	5.3

$$LiX_o + X^- \rightarrow X_o^- + LiX$$

$$\Delta\Delta E(LiX) \equiv E(LiX) + E(X_o^-) - E(LiX_o) - E(X^-)$$
$$= \{E(LiX) - E(X^-)\} - \{E(LiX_o) - E(X_o^-)\}$$

Table 2

Li salt	ΔΔE (LiX) (X_o= $CF_3SO_2O^-$) (kcal/mol)	MW	Conductivity (mS/cm)
CH_3SO_2OLi	-5.4	102	(insoluble)
CF_3SO_2Oli	(0.0)	145	2.3
n-$C_4F_9SO_2OLi$	3.3	306	2.3
$(CF_3SO_2)_2NLi$	6.2	287	4.0
$((CF_3)_2CHOSO_2)_2NLi$	12.2	483	3.1

Table 3

Li salt	ΔΔE (LiX) (X_o= PF_6^-) / kcal/mol	MW	HOMO of anion eV
$LiPF_6$	(0.0)	145	-3.6
$LiPF_5(CF_3)$	1.8	195	-3.7
trans-$LiPF_4(CF_3)_2$	5.1	245	-3.9
mer-$LiPF_3(CF_3)_3$	9.9	295	-3.6
$LiPF_5(C_2F_5)$	4.1	245	-3.7
trans-$LiPF_4(C_2F_5)_2$	8.4	345	-4.1
mer-$LiPF_3(C_2F_5)_3$	10.4	445	-3.9
trans-$LiPF_4(C_3F_7)_2$	8.4	445	-4.1
trans-$LiPF_4(CF(CF_3)_2)_2$	10.2	445	-4.4

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