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Electronic structures and electrochemical properties of $\text{LiPF}_{6-n}(\text{CF}_3)_n$

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Abstract

We evaluated (1) thermal and electrochemical stability and (2) ion-dissociation ability of $\text{PF}_{6-n}(\text{CF}_3)_n^-$ anions by computational method. The thermal stability order by $\Delta\Delta E$ (anion) is $\text{PF}_4(\text{CF}_3)_2^- > \text{PF}_5(\text{CF}_3)^- > \text{PF}_3(\text{CF}_3)_3^- > \text{PF}_6^-$. The ion-dissociation ability order by $\Delta\Delta E$ (Li salts) is $\text{LiPF}_3(\text{CF}_3)_3 > \text{LiPF}_4(\text{CF}_3)_2 > \text{LiPF}_5(\text{CF}_3) > \text{LiPF}_6$. The conductivity of electrolyte solution with $\text{LiPF}_4(\text{CF}_3)_2$ (3.9 mS/cm) was a little lower than that of LiPF_6 (4.4 mS/cm) in 0.1 mol/l Li salt/PC:DME electrolyte, while the oxidation potential of $\text{LiPF}_4(\text{CF}_3)_2$ in PC was higher than that of LiPF_6 . The $\text{LiPF}_4(\text{CF}_3)_2$ -cell showed better cycle characteristics than LiPF_6 -cell. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiPF_6 ; $\text{LiPF}_4(\text{CF}_3)_2$; Thermal stability; HOMO; Oxidation potential; Cycle characteristics

1. Introduction

We have developed some new organic lithium salts for lithium battery electrolyte such as $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$ [1]. A most advantageous feature of designing organic lithium salts is in a wide range of structural modification for improving their electrolyte properties. Although, LiPF_6 salt is widely used as an effective electrolyte for lithium battery due to its high conductivity, it is thermally unstable and easily decomposed by hydrolysis. Our strategy to design new organic lithium salts $\text{LiPF}_{6-n}(\text{CF}_3)_n$ is to replace unstable P–F bond(s) of PF_6^- anion by P– CF_3 bond(s) keeping their high conductivity and electrochemical stability [2]. We report here the structural effect of $\text{PF}_{6-n}(\text{CF}_3)_n^-$ anions on their properties for electrolyte such as highest occupied molecular orbital (HOMO) energy level, dissociation constant, conductivity, and oxidation potential. We report also some performance of lithium battery with $\text{LiPF}_4(\text{CF}_3)_2$ which showed better cycle characteristics than that with LiPF_6 .

2. Experimental

2.1. HOMO calculation

The energy levels for the HOMO of geometry-optimized different kinds of electrolyte anions were calculated by B3LYP/6-31G* on SPARTAN V 5.0.

2.2. Conductivity and oxidation potential

Conductivities were measured by a conductance meter (CM40S, Toa Electronics Ltd.). Anodic oxidation potentials were measured by potential sweep method. The 0.3 mm \varnothing platinum wire (Nilaco) was used for working electrode, and 21 mm wide lithium foil (Kyokuto) was used for 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 (HB-104, ditto). The potential at a current density (0.5 mA/cm²) was regarded as the oxidation potential.

2.3. Battery performance test

LiCoO_2 was used as a cathode with PVdF binder and conductive carbon. Graphite was used as an anode with

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PVdF binder. A 14 500 cell (14 mm diameter and 50 mm height) was made using LiPF₆ or LiPF₄(CF₃)₂ electrolyte. After pre-charge and aging, we checked the capacity and cycle characteristics of the batteries.

3. Results and discussion

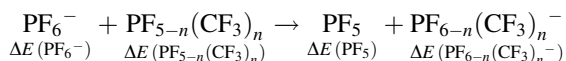
3.1. Syntheses of PF_{6-n}(CF₃)_n salts

LiPF_{6-n}(CF₃)_n salts are prepared [3]. Recently, Ignat'ev and his co-workers have reported the syntheses and conductivities of LiPF₄(i-C₃F₇)₂ and LiPF₃(C₂F₅)₃ [4,5].

3.2. Thermal stability of PF_{6-n}(CF₃)_n⁻ anions

As PF₆⁻ anion decomposes to give PF₅ and fluoride ion in pyrolysis, we evaluated the thermal stability of PF_{6-n}(CF₃)_n⁻ anions by computational method considering a similar decomposition of PF_{6-n}(CF₃)_n⁻ anions to give PF_{5-n}(CF₃)_n and fluoride ion. The relative stabilizing energy of PF_{6-n}(CF₃)_n⁻ anions ($\Delta\Delta E$ (anions)) is obtained by the following isodesmic reaction (I) with total energy (ΔE) of optimized structures of PF₆⁻ and PF_{6-n}(CF₃)_n⁻ anions and PF₅ and PF_{5-n}(CF₃)_n by B3LYP/6-31G* calculation.

Isodesmic reaction (I): ($n = 1-3$)



Relative stabilizing energies: $\Delta\Delta E$ (anions)

$$\begin{aligned} \Delta\Delta E(\text{anions}) &= \Delta E(\text{PF}_6^-) + \Delta E(\text{PF}_{5-n}(\text{CF}_3)_n) \\ &\quad - \Delta E(\text{PF}_5) - \Delta E(\text{PF}_{6-n}(\text{CF}_3)_n^-) \end{aligned}$$

where $\Delta\Delta E$ (anions) becomes positive when the PF_{6-n}(CF₃)_n⁻ anion is more stable than PF₆⁻ anion.

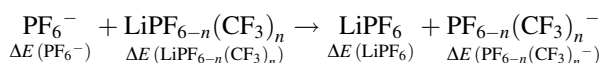
Table 1 shows that PF₄(CF₃)₂⁻ anion is most stable among PF₆⁻ and PF_{6-n}(CF₃)_n⁻ ($n = 1-3$) anions:

$$\begin{aligned} \Delta\Delta E(7.3, \text{PF}_4(\text{CF}_3)_2^-) &> \Delta\Delta E(4.4, \text{PF}_5(\text{CF}_3)^-) \\ &> \Delta\Delta E(4.1, \text{PF}_3(\text{CF}_3)_3^-) > \Delta\Delta E(0, \text{PF}_6^-) \end{aligned}$$

3.3. Conductivities of LiPF_{6-n}(CF₃)_n electrolytes

The conductivity of electrolyte solution is closely related with the dissociation level of lithium salt. The intrinsic and relative dissociation level of LiPF_{6-n}(CF₃)_n salts is evaluated by the following isodesmic reaction (II).

Isodesmic reaction (II): ($n = 1-3$)



Relative stabilizing energies: $\Delta\Delta E$ (Li salts)

$$\begin{aligned} \Delta\Delta E(\text{Li salts}) &= \Delta E(\text{PF}_6^-) + \Delta E(\text{LiPF}_{6-n}(\text{CF}_3)_n) \\ &\quad - \Delta E(\text{LiPF}_6) - \Delta E(\text{PF}_{6-n}(\text{CF}_3)_n^-) \end{aligned}$$

Table 1

$\Delta\Delta E$ and HOMO energies of PF_{6-n}(CF₃)_n anion^a

| Li salt | $\Delta\Delta E$ (kcal/mol) | | HOMO energy of anion (eV) |
|---|-----------------------------|---------|---------------------------|
| | Anion | Li salt | |
| LiPF ₆ | 0 | 0 | -4.26 |
| LiPF ₅ (CF ₃) | 4.4 | 0.5 | -3.99 |
| LiPF ₄ (CF ₃) ₂ | 7.3 (<i>trans</i>) | 2.1 | -4.30 |
| LiPF ₃ (CF ₃) ₃ | 4.1 (<i>mer</i>) | 8.6 | -3.72 |

^a B3LYP/6-31G*.

The relative stabilizing energies of Li salts compared with LiPF₆ are shown in Table 1. As all $\Delta\Delta E$ (Li salts) values of LiPF_{6-n}(CF₃)_n salts are positive, these lithium salts are considered to be more dissociative than LiPF₆.

Table 2 shows the conductivities of electrolyte solution with LiPF_{6-n}(CF₃)_n (0.1 mol/l) in PC/DME(1/2, v/v). Although, decreasing mobility of PF_{6-n}(CF₃)_n⁻ anions with increasing number of CF₃ groups is predicted to reduce the conductivity of the electrolyte solution with LiPF_{6-n}(CF₃)_n due to increased molecular weights of the anions, the conductivity of LiPF_{6-n}(CF₃)_n electrolyte does not decrease so much because of their increased dissociation level.

3.4. Oxidation potentials of LiPF_{6-n}(CF₃)_n salts

We investigated the oxidation stability of the PF_{6-n}(CF₃)_n⁻ anions by calculating the HOMO energy levels of the anions as shown in Table 1. The HOMO level of PF₄(CF₃)₂⁻ anion is lower than that of PF₆⁻ anion and the electrolyte of LiPF₄(CF₃)₂ (0.1 mol/l) in PC solution showed higher oxidation potential (6.2 V) than that of LiPF₆ (6.0 V) as shown in Table 2.

3.5. Battery performance

We checked the battery performance of the cell with LiPF₄(CF₃)₂. Since the conductivity of electrolyte solution with LiPF₄(CF₃)₂ (3.9 mS/cm) is lower than that of LiPF₆ (4.4 mS/cm) as shown in Table 2, the impedance increase of LiPF₄(CF₃)₂-cell for 60°C — 20 days storage was smaller than that of LiPF₆-cell (LiPF₄(CF₃)₂ and LiPF₆: 30 and 41% increased for initial impedance, respectively).

Table 2

Conductivities and oxidation potentials of LiPF_{6-n}(CF₃)_n electrolytes at 25°C

| Salt | Conductivity (mS/cm) ^a | Oxidation potential (V versus Li/Li ⁺) ^b |
|--|-----------------------------------|---|
| LiPF ₆ | 4.4 | 6.0 |
| Li PF ₆ + 3DME | — | 5.3 |
| LiPF ₅ (CF ₃) | 4.2 | 6.2 |
| LiPF ₄ (CF ₃) ₂ | 3.9 | 6.2 |
| LiPF ₃ (CF ₃) ₃ + 3DME | 3.9 | 5.1 |

^a An amount of 0.1 mol/l salts in PC/DME (1/2, v/v).

^b An amount of 0.1 mol/l salts in PC.

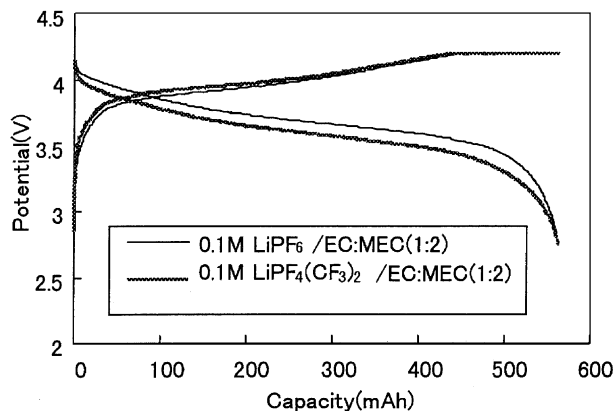


Fig. 1. The charge and discharge curves of $\text{LiPF}_4(\text{CF}_3)_2$ - and LiPF_6 -cell at 0.1 C rate.

Fig. 1 shows the battery discharge curves of $\text{LiPF}_4(\text{CF}_3)_2$ - and LiPF_6 -cell at 0.1 C rate. The discharge potentials of the $\text{LiPF}_4(\text{CF}_3)_2$ -cell are lower than that of LiPF_6 -cell, because of the difference of their conductivities. But discharge capacities of both cells are almost same.

As shown in Fig. 2, the cycle characteristics of the $\text{LiPF}_4(\text{CF}_3)_2$ -cell with 0.1 mol/l lithium salt is better than that of LiPF_6 -cell. We analyzed the surface characteristics of anode by XPS analysis to investigate the reason for the difference in cycle characteristics. Tables 3 and 4 show the

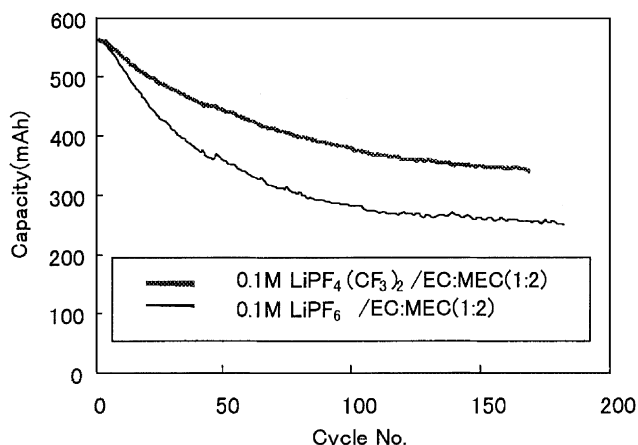


Fig. 2. The cycle characteristics of $\text{LiPF}_4(\text{CF}_3)_2$ - and LiPF_6 -cell at 0.1 C. $\text{LiCoO}_2/\text{graphite}$ type cell of 14 mm \varnothing , 50 mm height, charge current = 60 mA for 12 h (4.1 V CCCV), discharge current = 60 mA (2.75 V cut-off).

Table 3
The atomic ratio of anode surface by XPS analysis^a

| Salt used in the cell | C | F | Li | P | O |
|--|------|------|------|-----|------|
| 1.0 mol/l LiPF_6 | 33.0 | 19.6 | 10.7 | 3.8 | 32.6 |
| 0.1 mol/l LiPF_6 | 45.7 | 4.6 | 14.0 | 0.6 | 33.5 |
| 0.1 mol/l $\text{LiPF}_4(\text{CF}_3)_2$ | 43.2 | 6.0 | 15.2 | 0.5 | 33.4 |

^a ESCA LAB Mark 2 (VG), Mg K α 12 kV, 10 mA.

Table 4

The expected atomic ratio based on observed P atomic ratio

| Salt used in the cell | C | F | Li | P | O |
|--|-----|-----------|-----|-----|---|
| 1.0 mol/l LiPF_6 | 0.0 | 22.8 | 3.8 | 3.8 | – |
| 0.1 mol/l LiPF_6 | 0.0 | 3.6 | 0.6 | 0.6 | – |
| 0.1 mol/l $\text{LiPF}_4(\text{CF}_3)_2$ | 1.0 | 2.0 + 3.0 | 0.5 | 0.5 | – |

atomic ratio of anode surface by XPS and the calculated atomic ratio from P atom ratio for $\text{LiPF}_4(\text{CF}_3)_2$ and LiPF_6 salts. At low salt concentration (0.1 mol/l), $\text{LiPF}_{6-n}(\text{CF}_3)_n$ salt component ratio is small, while organic C, O atom ratio is large. This result means that the conductivity of surface layer might become lower and cell performance dropped. The anode surfaces of the $\text{LiPF}_4(\text{CF}_3)_2$ -cell is mainly covered by the organic compound with lithium atom and $\text{LiPF}_4(\text{CF}_3)_2$ salt component. These results suggest that the $\text{LiPF}_4(\text{CF}_3)_2$ salt related compound would exist on anode surface or be involved as a surface film with other organic compounds. The large F 1s peak was observed at 687–688 eV (organic F such as CF_3^-) only for $\text{LiPF}_4(\text{CF}_3)_2$ surface.

4. Conclusion

1. The thermal stability order by $\Delta\Delta E$ (anion) is $\text{PF}_4(\text{CF}_3)_2^- > \text{PF}_5(\text{CF}_3)^- > \text{PF}_3(\text{CF}_3)_3^- > \text{PF}_6^-$.
2. The ion-dissociation ability order by $\Delta\Delta E$ (Li salts) is $\text{LiPF}_3(\text{CF}_3)_3 > \text{LiPF}_4(\text{CF}_3)_2 > \text{LiPF}_5(\text{CF}_3) > \text{LiPF}_6$.
3. The high conductivities of $\text{LiPF}_{6-n}(\text{CF}_3)_n$ electrolytes (3.9–4.2 mS/cm) are a little lower than the conductivity of LiPF_6 .
4. The electrochemical stability against oxidation was estimated by HOMO energy level. $\text{PF}_4(\text{CF}_3)_2^-$ anion is most stable against oxidation by B3LYP/6-31G* calculation.
5. The oxidation potentials of $\text{PF}_5(\text{CF}_3)^-$ and $\text{PF}_4(\text{CF}_3)_2^-$ (6.2 V versus Li/Li^+) are higher than that of PF_6^- (6.0 V versus Li/Li^+).
6. The cycle characteristics of the $\text{LiPF}_4(\text{CF}_3)_2$ -cell with 0.1 mol/l lithium salt is better than that of LiPF_6 -cell.

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