

## Electronic Structures and Electrochemical Properties of LiPF<sub>6-n</sub>(CF<sub>3</sub>)<sub>n</sub> (2)

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### 1. Introduction

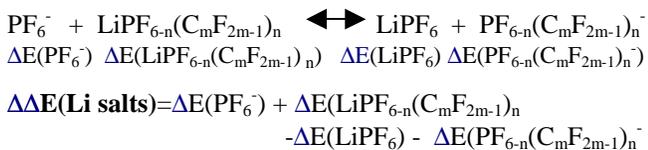
LiPF<sub>6</sub> salt is widely used as an effective electrolyte salt for lithium-ion battery due to its high conductivity. But it is thermally unstable and easily decomposed by hydrolysis. Our strategy to design new organic lithium salts LiPF<sub>6-n</sub>(CF<sub>3</sub>)<sub>n</sub> is to replace unstable P-F bonds of PF<sub>6</sub> anion by P-CF<sub>3</sub> bonds keeping their high conductivity and electrochemical stability<sup>1)</sup>. On the other hand, Merck group also reported on LiPF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub><sup>2)</sup>. We report here the structural effect of PF<sub>6-n</sub>(CF<sub>3</sub>)<sub>n</sub> and PF<sub>6-n</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>n</sub> anions on their properties such as HOMO energy level, thermal stability factor ( $\Delta\Delta E(\text{Anions})$ ), dissociation constant factor ( $\Delta\Delta E(\text{Li salts})$ ) by DFT (Density Functional Theory) calculation methods. We report also some performance of lithium battery with LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub> which showed better cycle characteristics than that with LiPF<sub>6</sub>, and electrode analysis results by XPS.

### 2. Results and Discussion

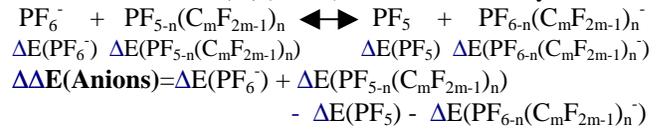
#### 2.1 DFT calculation of PF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub><sup>-</sup> (m=1,2, n=2,3)

The relative stabilizing energies of LiPF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> and PF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> anions ( $\Delta\Delta E$ ) are obtained by the following isodesmic reactions(I,II) with total energy ( $\Delta E$ ) of optimized structures of PF<sub>6</sub><sup>-</sup>, PF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub><sup>-</sup>, LiPF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub>, LiPF<sub>6</sub>, PF<sub>5</sub> and PF<sub>5-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> by B3LYP/6-31G\* or GGA(pw91)/DND calculation.

#### Isodesmic reaction (I) (n=2,3) : Ion Dissociation



#### Isodesmic reaction (II) (n=2,3) : Thermal Stability



where  $\Delta\Delta E(\text{Li salts})$  becomes positive when lithium salts LiPF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> are more dissociative than LiPF<sub>6</sub>, and  $\Delta\Delta E(\text{Anions})$  becomes positive when the PF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> anion is more thermally stable than PF<sub>6</sub> anion.

Table 1 shows that the conductivity ratio of LiPF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> does not decrease so much in spite of its large anion size, because of high dissociation of PF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub><sup>-</sup>. Thermal stability is calculated by  $\Delta\Delta E(\text{anion})$ . PF<sub>4</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>2</sub><sup>-</sup> with two perfluoroalkyl(Rf) substituents is more thermally stable than PF<sub>3</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>3</sub><sup>-</sup> with three substituents.

HOMO energy order was as follows: PF<sub>4</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub><sup>-</sup> < PF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub><sup>-</sup> < or = PF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> < PF<sub>6</sub><sup>-</sup> < PF<sub>3</sub>(CF<sub>3</sub>)<sub>3</sub><sup>-</sup>. Higher oxidation potential was also predicted for the salts with two Rf substituents compared with the salts with their Rf substituents.

#### 2.2 Battery Performances and XPS Analysis Result

We checked the battery performance of the cell with LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub> because of its high conductivity and good stability. LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub>-cell showed almost same capacity as LiPF<sub>6</sub>-cell but better cycle characteristics than LiPF<sub>6</sub>-cell. Moreover, the impedance increase of LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub>-cell for 60 °C- 20 days storage was smaller than that of LiPF<sub>6</sub>-cell.

We analyzed the surface characteristics of anode by XPS analysis to investigate the reason for the difference in cycle characteristics. The anode surface of the LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub>-cell is mainly covered by organic compounds with Li compounds such as LiF and LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub> salt component. The large F 1S peak was observed at 687-688 eV (organic F such as CF<sub>3</sub>-) for only LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub> surface. These results suggest that the LiPF<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub> salt might exist on anode surface or be involved as surface film with other organic compounds. This surface layer might assist Li ion transportation.

#### References

- (1) F. Kita, H. Sakata, S. Shinomoto, A. Kawakami, H. Kamizori, T. Sonoda, H. Nagashima, N. Pavlenko and Y. L. Yagupolskii, IMLB 10, May.28- June.2, Como/Italy, Abs.283 (2000)
- (2) M. Schmidt, U. Heider, A. Kuehner, R. Oesten, M. Jungnitz, N. Ignat'ev and P. Sartori, IMLB 10, May.28- June.2, Como/Italy, Abs.22 (2000).

Table 1.  $\Delta\Delta E$  and Electrochemical Properties of LiPF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> (m=1,2, n=2,3)

Anion	Conductivity Ratio <sup>*1</sup>	$\Delta\Delta E(\text{Li salt})$ <sup>*2</sup> /kcal/mol		$\Delta\Delta E(\text{anion})$ <sup>*3</sup> /kcal/mol		HOMO Energy <sup>*4</sup> /eV	LUMO Energy /eV
		B3LYP /6-31G*	GGA(pw91) /DND	B3LYP /6-31G*	GGA(pw91) /DND		
PF <sub>6</sub> <sup>-</sup>	1.00(0.1M)	0	0	0	0	-3.64	4.49
trans-PF <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	0.88(0.1M)	2.1	5.2	7.3	7.0	-3.92	4.46
mer-PF <sub>3</sub> (CF <sub>3</sub> ) <sub>3</sub> <sup>-</sup>	0.88(0.1M)	8.6	9.9	4.1	5.0	-3.60	3.90
trans-PF <sub>4</sub> (C <sub>2</sub> F <sub>5</sub> ) <sub>2</sub> <sup>-</sup>	-	-	8.4	-	13.4	-4.05	3.44
mer-PF <sub>3</sub> (C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> <sup>-</sup>	0.82(0.1M)	-	10.4	-	8.3	-3.91	2.75

\*1 Conductivity Ratio=(conductivity of electrolyte)/(conductivity of LiPF<sub>6</sub> electrolyte) in PC:DME(1/2 v/v) at 0.1 mol/l.

\*2  $\Delta\Delta E(\text{Li salts})$  becomes positive when lithium salts LiPF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> is more dissociative than LiPF<sub>6</sub>.

\*3  $\Delta\Delta E(\text{Anions})$  becomes positive when the PF<sub>6-n</sub>(C<sub>m</sub>F<sub>2m-1</sub>)<sub>n</sub> anion is more thermally stable than PF<sub>6</sub> anion.

\*4 HOMO Energy : For low value, high oxidation potential expected.