

## A Novel Lithium Salt with a Chelate Compound of Phosphorus for Lithium Battery Electrolytes

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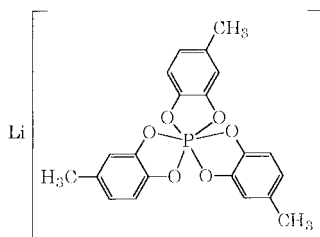
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We have synthesized a novel Li salt with a chelate compound of phosphorus, lithium tris[4-methyl-1,2-benzenediolato(2-)-*O,O'*]phosphate (4-MLTBP). The thermal stability and electrolytic properties of 4-MLTBP, and the charge-discharge characteristics of a lithium electrode are investigated. The thermal decomposition temperature of 4-MLTBP is higher than those of a common lithium salt with phosphorus,  $\text{LiPF}_6$ , and lithium tris[1,2-benzenediolato(2-)-*O,O'*]phosphate, which we previously synthesized. The specific conductivities and the cycling efficiencies become higher in an ethylene carbonate- and a propylene carbonate-dimethyl carbonate equimolar binary solutions containing a mixture of 4-MLTBP with  $\text{LiPF}_6$ .

Numerous investigators have attempted to develop inexpensive, nontoxic, and thermally, chemically, and electrochemically stable lithium salts with sufficiently high solubility. Barthel et al. reported several lithium salts with chelate compounds of boron such as lithium bis[1,2-benzenediolato(2-)-*O,O'*]borate (LBBB), lithium bis[2,3-naphthalenediolato(2-)-*O,O'*]borate (LBNB).<sup>1-6</sup> These chelate compounds are highly thermally stable. The electrolyte solutions tend to exhibit prominent charge-discharge characteristics of a lithium electrode, as compared to solutions of common lithium salts such as  $\text{LiBF}_4$ .<sup>7,8</sup> Recently, Xu and Angell synthesized a lithium organoborate of a weakly coordinating anion, lithium bis[1,2-tetra(trifluoromethyl)ethylenediolato(2-)-*O,O'*]borate.<sup>9</sup> This salt was found to be fused at 120 °C. We previously synthesized a chelate compound of phosphorus, lithium tris[1,2-benzenediolato(2-)-*O,O'*]phosphate (LTBP), and investigated the thermal stability, the electrolytic properties, and the discharge characteristic.<sup>10</sup> LTBP is thermally more stable than a common lithium salt of phosphorus,  $\text{LiPF}_6$ . The oxidative stability of LTBP is higher than that of LBBB, but lower than that of LBNB.

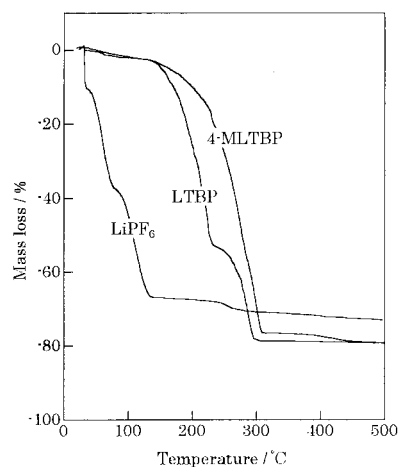
In this paper we report the thermal characteristic and electrolytic behavior of lithium tris[4-methyl-1,2-benzenediolato(2-)-*O,O'*]phosphate (4-MLTBP, see Figure 1), which we have newly synthesized. The charge-discharge characteristics of a lithium electrode are also described.



**Figure 1.** Structure of lithium tris[4-methyl-1,2-benzenediolato(2-)-*O,O'*]phosphate (4-MLTBP).

4-MLTBP has been synthesized according to the procedure for synthesizing LTBP,<sup>10</sup> except that a penta-coordinate compound, which is an intermediate in the reaction, was not isolated from the benzene solution. The calculated composition of 4-MLTBP was almost agreed with the results of elemental analyses<sup>11</sup> including inductively coupled plasma emission spectroscopy. 4-MLTBP was also identified by <sup>1</sup>H, <sup>13</sup>C, and <sup>1</sup>H-<sup>13</sup>C COSY NMR spectra recorded on a JEOL JNM-LA500 FT-NMR system in acetone-*d*<sub>6</sub> containing 1% tetramethylsilane.<sup>12</sup> Thermogravimetry was carried out on a Seiko Instruments, Inc., TG/DTA220 system with a sample mass of ca. 10 mg. The apparatus and techniques for measurements of the conductivity,<sup>8,10</sup> viscosity,<sup>13</sup> and voltammogram<sup>8,10</sup> were previously reported. Charge-discharge coulombic efficiency of a lithium electrode, lithium electrode cycling efficiency, was measured with a 6-channel charge-discharge unit (Hokuto Denko, Model HJ-101SM6) and estimated by a galvanostatic plating-stripping method reported by Koch and Brummer.<sup>14</sup> All solvents used were battery-grade and dehydrated by purified molecular sieves (4A) before preparation of solutions.

Figure 2 shows thermogravimetric (TG) curves of 4-MLTBP, LTBP, and  $\text{LiPF}_6$  in air. As the temperature increased, the mass of LTBP greatly decreased at ca. 150 °C, and the lithium salt started to decompose. Thermal decomposition temperature of  $\text{LiPF}_6$ , ca. 30 °C, was considerably lower. It is well-known that a related hexa-coordinate compound with phosphorus,  $\text{LiPF}_6$ , is extremely sensitive to both temperature and moisture and that  $\text{LiPF}_6$  is readily hydrolyzed in the presence of moisture at room temperature. A heating rate was also as slow as 1 K min<sup>-1</sup>, and  $\text{LiPF}_6$  can be partially decomposed due to moisture. The mass of 4-MLTBP gradually decreased with increasing temperature, and the thermal



**Figure 2.** Thermogravimetric curves of 4-MLTBP, LTBP, and  $\text{LiPF}_6$  at a heating rate of 1 K min<sup>-1</sup> in air.  $\alpha$ -Alumina was used as the reference.

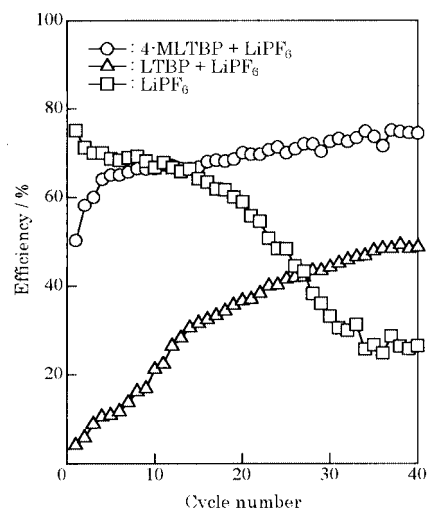
decomposition temperature of 4-MLTBB, ca. 160 °C, was higher than those of LTBP and LiPF<sub>6</sub>. LTBP and 4-MLTBP, which contain bidentate ligands, are highly thermally robust due to the chelate effect. Furthermore, the substituent effect was observed for 4-MLTBP. The hyperconjugation arising from the overlap of  $\sigma$ -orbitals in the methyl group with the  $\pi$ -system in the benzene ring can increase the thermal stability of the chelate anion. TG curves of mixtures of LTBP or 4-MLTBP with LiPF<sub>6</sub> were not obtained, because the sample mass is very small, and large molecular weights of LTBP and 4-MLTBP lead to difficulty in preparing mixtures with LiPF<sub>6</sub> exactly.

**Table 1.** Specific conductivities ( $\kappa$ ) in an EC–DMC and a PC–DMC equimolar binary solutions containing LiPF<sub>6</sub>, LTBP, 4-MLTBP, or equimolar binary electrolytes. The concentration of the single or the mixed lithium salt was adjusted to 0.5 mol dm<sup>-3</sup>

Electrolytes	$\kappa / \text{mS cm}^{-1}$	
	EC–DMC	PC–DMC
4-MLTBP	2.25	1.69
4-MLTBP + LiPF <sub>6</sub>	5.26	4.48
LTBP	2.62	2.24
LTBP + LiPF <sub>6</sub>	5.66	5.03
LiPF <sub>6</sub>	9.66	8.75

Table 1 shows specific conductivities in an ethylene carbonate (EC)–dimethyl carbonate (DMC) and a propylene carbonate (PC)–DMC equimolar binary solutions containing LiPF<sub>6</sub>, LTBP, 4-MLTBP, or equimolar binary electrolytes. The solubilities of LTBP and 4-MLTBP in an EC– and a PC–DMC binary solvent were ca. 0.5 mol dm<sup>-3</sup>. Accordingly, the concentration of the single or the mixed lithium salt was adjusted to 0.5 mol dm<sup>-3</sup>. The conductivities of LTBP and 4-MLTBP in the solutions were much lower than those of LiPF<sub>6</sub>. However, such lower conductivities were improved by mixing with LiPF<sub>6</sub>. The conductivity of 4-MLTBP was lower than that of LTBP, because the molecular weight of 4-MLTBP is larger, and the viscosity in the solution containing 4-MLTBP was higher. In addition, the electron-donating effect of the methyl group can bring about the localization of electrons around the phosphorus, precluding the electrolytic dissociation. The localization of electrons in 4-MLTBP also resulted in the oxidative decomposition voltage (ca. 3.6 V vs Li/Li<sup>+</sup>) slightly lower than that of LTBP (ca. 3.7 V vs Li/Li<sup>+</sup>). A voltage reached at 0.5 mA cm<sup>-2</sup> in a PC solution was regarded as the oxidative decomposition voltage of a lithium salt.

Figure 3 shows the variation in lithium electrode cycling efficiency in an EC–DMC equimolar binary solution containing LiPF<sub>6</sub> or equimolar binary electrolytes. It was difficult to measure the cycling efficiency in a solution containing 4-MLTBP or LTBP singly, because the conductivity was considerably lower. Thus, mixtures of 4-MLTBP or LTBP with LiPF<sub>6</sub> were used as the electrolytes. The electrolyte solution of LiPF<sub>6</sub> exhibited lower cycling efficiency in a high cycle number. Although the cycling efficiency in the electrolyte solution containing the mixture of LTBP with LiPF<sub>6</sub> increased with an increase in a cycle number, the highest value was ca. 50% at the most. On the other hand, the cycling efficiency in the solution containing the mixture of 4-MLTBP with LiPF<sub>6</sub> was stable and as high as ca. 75% in a high cycle number. Such tendencies were also observed for



**Figure 3.** Variation in lithium cycling efficiency in an EC–DMC equimolar binary solution containing LiPF<sub>6</sub> or equimolar binary electrolytes at 25 °C. The concentration of the single or the mixed lithium salt was adjusted to 0.5 mol dm<sup>-3</sup>. The plating and the stripping current densities were 1 mA cm<sup>-2</sup>, and the plated charge density was 300 mC cm<sup>-2</sup>.

a PC–DMC equimolar binary solution. The morphology and chemical composition of the surface film on a substrate may be suitable for the deposition and dissolution of a lithium metal in the presence of both 4-MLTBP and LiPF<sub>6</sub>.

In conclusion, we have newly synthesized 4-MLTBP, which is a derivative of LTBP. The substituent effect on the electrolytic properties was observed. The cycling efficiencies in the electrolyte solutions containing a mixture of 4-MLTBP with LiPF<sub>6</sub> were more excellent than those in the solutions of LiPF<sub>6</sub>, which is commonly used as a battery electrolyte. Surface analyses can clarify the relationship between the cycling efficiency and the morphology and chemical composition of the surface film.

#### References and Notes

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- Results of elemental analyses. Found: C, 61.77; H, 4.73; Li, 1.43; P, 7.49%. Calcd for 4-MLTBP: C, 62.39; H, 4.49; Li, 1.72; P, 7.66%.
- <sup>1</sup>H NMR: 2.15 (s, 3H), 6.3–6.4 (m, 3H); <sup>13</sup>C NMR: 29.80, 109.30, 110.87, 119.09. These peaks were crossed on a <sup>1</sup>H–<sup>13</sup>C COSY NMR spectrum.
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