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# Cathodes Properties of Phospho-olivine for Lithium Secondary Batteries

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Four types of orthorhombic olivine  $\text{LiMPO}_4$  (M:Co, Fe, Ni, Mn) were investigated as high voltage cathode active materials for lithium secondary batteries.  $\text{LiCoPO}_4$  exhibited the highest 4.8 V discharge plateau of 100 mAh/g vs.  $\text{Li/Li}^+$  after initial charging to 5.1 V and its energy density was comparable to that of layered rocksalt  $\text{LiCoO}_2$  (120 mAh/g  $\times$  4 V = 480 mWh/g). In contrast, the open circuit voltage profile of  $\text{LiFePO}_4$  was 160 mAh/g on the 3 V plateau. TG-DSC measurements showed that the thermal stability of charged  $\text{Li}_{1-x}\text{CoPO}_4$  is better than that of fully-charged  $\text{Li}_{1-x}\text{CoO}_2$ . The chemical state of Co in  $\text{LiCoPO}_4$  was also analyzed using HRXRF.

## Introduction

Fey's paper<sup>1)</sup> on  $\text{LiNiVO}_4$  prompted the discovery of several high-voltage cathodes as post 4 V cathodes. However, they consist solely of normal spinel  $\text{LiMnMO}_4$  (M:Co<sup>2+</sup>, Cr<sup>3+</sup>) and inverse spinel  $\text{LiNiVO}_4$  and their reported capacities over 4.5 V vs.  $\text{Li/Li}^+$  are less than 100 mAh/g. We anticipated that ordered olivine  $\text{LiMPO}_4$  would be a candidate for a new high-voltage cathode with superior capacity.

The similarities and differences between their structures are summarized in Table 1. They can all be represented by a similar general formula  $\text{LiMnMO}_4$  in which half the octahedral sites and one-eighth of the tetrahedral sites are occupied by cations. Unlike the normal spinel and inverse spinel structures with a cubic-closed packed (ccp) oxygen framework, ordered olivine has a hexagonal closed-packed (hcp) oxygen array and these tetrahedral sites occupied  $\text{P}^{5+}$  form  $\text{PO}_4$  tetrahedral oxo-

anions as shown in Fig.1. Then, both olivine and inverse spinel structures have octahedral Li sites in their matrix. In inverse spinel  $\text{LiMVO}_4$ , Li and M are randomly situated on the 16d octahedral sites. M ions at the 16d site disturb Li conduction through the 16d – 8b – 16d path in an inverse spinel, while there is no obstacle cation except Li itself on the 16c – 8a – 16c diffusion path in a normal spinel. However, in the ideal olivine, two types of octahedral site are crystallographically distinct and differ in size. The ordered olivine has orthorhombic symmetry with alternate *a-c* planes of Li and M occupying the octahedral sites, which makes it possible for there to be the two dimensional Li diffusion paths between the hcp oxygen layers.

This paper describes the electrochemical, structural and spectroscopic characteristics of  $\text{LiMPO}_4$  and introduces  $\text{LiCoPO}_4$  as the first 4.5 V cathode material with a rechargeable capacity of 100 mAh/g.

Table 1. Typical high-voltage cathodes over 4.5 V.

Structure	Spinel	Inverse spinel	Olivine
Symmetry	Cubic	Cubic	Orthorhombic
Space Group	Fd3m	Fd3m	Pnma
Li site	Tetrahedral (8a)	Octahedral (16d)	Octahedral (4a)
Oxygen Framework	Cubic closed pack	Cubic closed pack	Hexagonal closed pack
Example	$\text{LiCoMnO}_4$	$\text{LiNiVO}_4$	$\text{LiCoPO}_4$
Reference	(2)	(1)	(4, 5)

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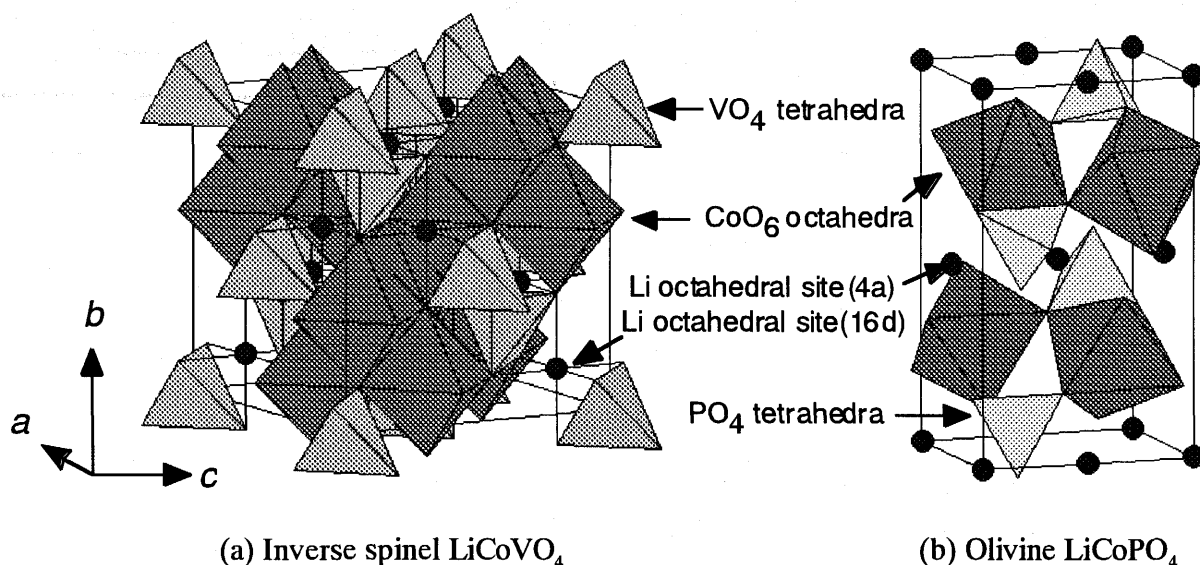


Fig.1 CCP and HCP oxygen framework in inverse spinel and olivine  $\text{LiCoXO}_4$ .

### Experiment

Conventional solid-state reactions were employed to synthesize four types of phospho-olivine.  $\text{LiMPO}_4$  (M: Co, Ni and Mn) were prepared from stoichiometric amounts of reactants  $\text{Li}_2\text{CO}_3$ ,  $\text{P}_2\text{O}_5$  ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and  $\text{CoO}$  ( $\text{NiO}$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ). The mixtures were presintered at  $500^\circ\text{C}$  for several hours. After firing at  $780 - 820^\circ\text{C}$  for 2 days with an intermittent grinding, the mixtures were quenched using liquid nitrogen.  $\text{LiFePO}_4$  was prepared similarly with  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  as the source of iron. It was fired at  $800^\circ\text{C}$  for 2 days in a nitrogen atmosphere to avoid oxidation of  $\text{Fe}^{2+}$  and cooled slowly to room temperature. They were all indexed as orthorhombic in the space group Pnma. We fabricated the cathodes for electrochemical characterization by blending powders of the active material  $\text{LiMPO}_4$  with acetylene

black (Denki Kagaku Co., Ltd.) and F-210L PTFE Teflon binder (Daikin Industry Ltd.) in a weight ratio of 70 : 25 : 5. We measured the cathode properties in a coin-type cell (type 2032 made from SUS316) with a nonaqueous electrolyte (1M  $\text{LiPF}_6/\text{EC}:\text{DMC} = 1 : 1$  vol%, Tomiyama Pure Chemical Industries, Ltd.) and polypropylene separator (Celgard 3501) against a Li metal anode.

We measured the structural changes that occurred in the cathode during the charge/discharge cycle by XRD using  $\text{Cu-K}\alpha$  radiation. After it had reached potential equilibrium, each cathode pellet was rinsed with dimethyl carbonate and dried in a vacuum. The differential scanning calorimetry of electrochemically-charged pellets of  $\text{Li}_{0.4}\text{CoPO}_4$  and  $\text{Li}_{0.45}\text{CoO}_2$  were also measured using Rigaku 8230L at heating rate of  $5^\circ\text{C}/\text{min}$  in air.

In addition, we analyzed the oxidation states of Co in  $\text{LiCoPO}_4$  cathode pellets using a high resolution X-ray

Table 2. Lattice change of  $\text{Li}_{1-x}\text{CoPO}_4$  and  $\text{Li}_{1-x}\text{FePO}_4$  with charging.

Delithiation	Electrochemical (This work)		Chemical (Ref.6)	
	$\text{LiCoPO}_4$	$\text{Li}_{0.25}\text{CoPO}_4$	$\text{LiFePO}_4$	$\text{FePO}_4$
Space Group	Pnma	Pnma	Pnma	Pnma
$a[\text{\AA}]$	5.97	5.62 (-5.9%)	6.008	5.792 (-3.6%)
$b[\text{\AA}]$	10.24	10.05 (-1.9%)	10.334	9.821 (-4.9%)
$c[\text{\AA}]$	4.72	4.87 (3.2%)	4.693	4.788 (2.0%)
V	288.5	275.1 (-4.6%)	291.39	272.36 (-6.5%)

fluorescence spectrometer (HRXRF) with an XFRA 190 double-crystal spectrometer (Technos).

## Results and Discussion

Of these investigated olivine cathodes,  $\text{LiCoPO}_4$  exhibited the highest 4.8 V discharge plateau of 100 mAh/g vs.  $\text{Li/Li}^+$  after initial charging to 5.1 V and its energy density was comparable to that of  $\text{LiCoO}_2$  ( $120 \text{ mAh/g} \times 4 \text{ V} = 480 \text{ mWh/g}$ ) as shown in Fig.2.

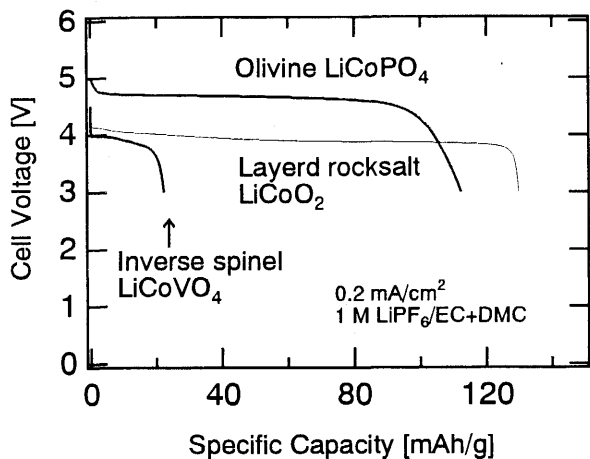


Fig.2 First discharge curves of Co-based high-voltage cathodes.

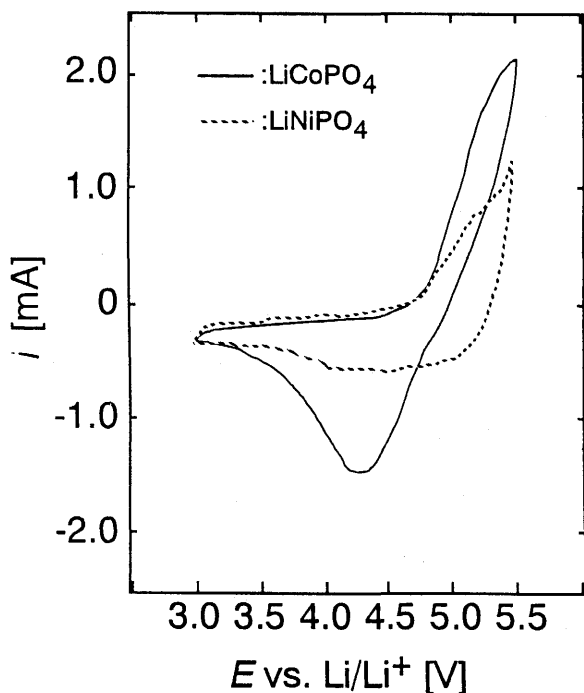


Fig.3 Cyclic voltammograms for  $\text{LiCoPO}_4$  and  $\text{LiNiPO}_4$  (diameter: 10 mm) obtained at 0.2 mV/s between 3.0 and 5.5 V vs.  $\text{Li/Li}^+$  in 1 M  $\text{LiPF}_6/\text{EC} + \text{DMC}$ .

During charging to 5.1 V, there were no other phases except  $\text{Pnma}$  and the lattice constants  $a$  and  $b$  decreased, while  $c$  increased. This behavior is in good agreement with that of  $\text{Li}_{1-x}\text{FePO}_4$  during chemical delithiation using  $\text{NO}_2\text{PF}_6$ <sup>6)</sup>. Table 2 shows that the cell volume change ratio ( $\Delta V/V$ ) of  $\text{Li}_{1-x}\text{CoPO}_4$  during the charging process was -4.6 %, while  $\Delta V/V$  is reported to be -6.5 % for  $\text{Li}_{1-x}\text{FePO}_4$ <sup>6)</sup>. In contrast,  $\text{LiNiPO}_4$  and  $\text{LiMnPO}_4$  had no voltage plateaus in their discharge profiles even after initial charging to 5.2 V. In addition, we did not detect any reduction peaks in the cathodic wave in the cyclic voltammogram of  $\text{LiNiPO}_4$  between 3 and 5.5 V with a scan rate of 0.2 mV/s as shown in Fig.3.

As shown in Fig.4, the rate capability of  $\text{LiCoPO}_4$  seems to be better than that of  $\text{LiFePO}_4$ . However, the capacity of  $\text{LiFePO}_4$  in the QOCV (quasi open circuit voltage) profile almost reached the theoretical value for 1 Li intercalation per mole of 170 mAh/g. It is worthy to note that the Hydro-Québec group was successful in obtaining the theoretical capacity of  $\text{LiFePO}_4$  at 80 °C by using an advanced processing technique<sup>7, 8)</sup>. NTT has also reported a good cyclability of  $\text{LiFePO}_4$  of 100 mAh/g at room temperature<sup>9)</sup>. We expect that there is considerable room for improvement up to the theoretical upper limit of about 167 mAh/g for  $\text{LiCoPO}_4$ , too.

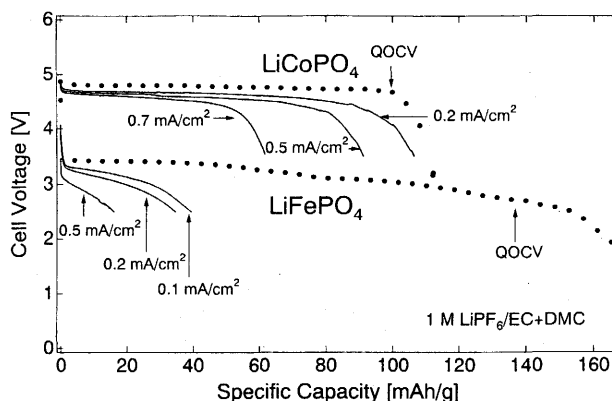


Fig.4 Rate capability of  $\text{LiCoPO}_4$  and  $\text{LiFePO}_4$ .

Figure 5 and 6 shows the DSC and TG profiles of charged  $\text{LiCoPO}_4$  and  $\text{LiCoO}_2$  cathode pellets without an electrolyte, respectively. The cathode pellet of  $\text{Li}_{0.45}\text{CoO}_2$  exhibited a broad exothermic peak around 210 °C corresponding to oxygen release<sup>10)</sup>. The weight loss of  $\text{Li}_{0.45}\text{CoO}_2$  is started from 200°C, while any gas generation was observed in  $\text{Li}_{0.17}\text{CoPO}_4$  under 280°C as shown in Fig.5. The thermal instability must be due to the existence of chemically unstable  $\text{Co}^{4+}$  in charged  $\text{Li}_{1-x}\text{CoO}_2$ . In contrast, the cathode pellet of  $\text{Li}_{0.4}\text{CoPO}_4$  has no strong exothermic peak up to 550 °C, because there is

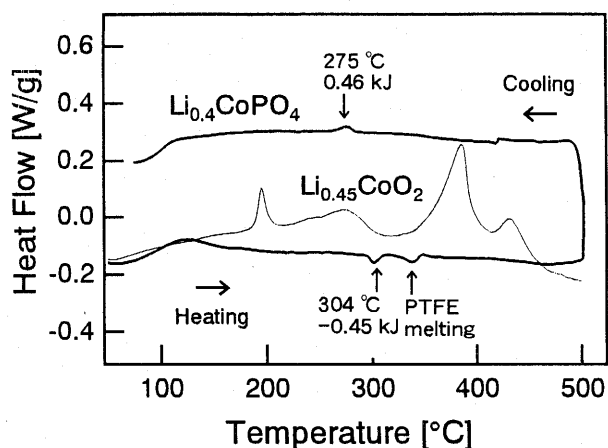


Fig.5 DSC curves of charged  $\text{Li}_{0.4}\text{CoPO}_4$  and  $\text{Li}_{0.45}\text{CoO}_2$ .

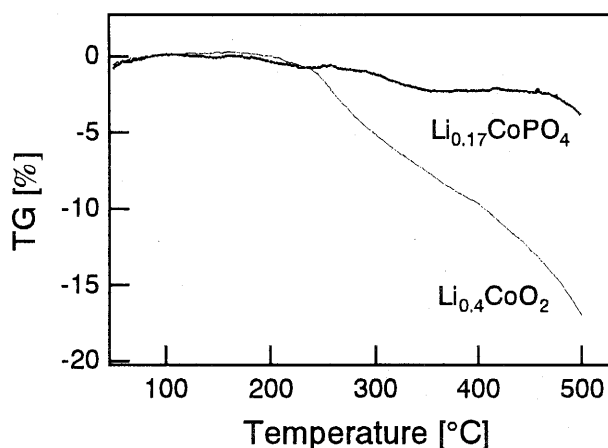


Fig.6 TG curves of charged  $\text{Li}_{0.17}\text{CoPO}_4$  and  $\text{Li}_{0.4}\text{CoO}_2$ .

no  $\text{Co}^{4+}$  in charged  $\text{Li}_{1-x}\text{CoPO}_4$ .

The reversible endothermic peak at 304 °C on heating and the exothermic peak at 275 °C on cooling suggests the existence of the first order phase transition of  $\text{Li}_{1-x}\text{CoPO}_4$  around 290 °C. The transition enthalpies are - 0.45 and 0.46 kJ/mol, respectively. Similar reversible endothermic and exothermic peaks are also reported around 315 °C for  $\text{FePO}_4$ <sup>6)</sup>. The couple of peaks disappeared in discharged  $\text{LiCoPO}_4$  cathode pellet. The additional endothermic peak around 330 °C is attributed to the melting of PTFE binder (m.p.: 327 °C), because it was observed in discharged  $\text{LiCoPO}_4$  cathode pellet with PTFE binder and it was not observed in discharged  $\text{LiCoPO}_4$  powder without PTFE binder.

We use HRXRF to analyze the oxidation states of Co in initial  $\text{LiCoPO}_4$  cathode pellet, because X-ray photoelectron spectroscopy (XPS) is not suitable for the chemical state analysis of Co. In comparison with typical Co-based compounds with various valence state, the

Table 3. Chemical shift ( $\Delta E$ ) and FWHM values of  $\text{LiCoPO}_4$  and Co-based compounds.

Valence state of Co	Compound	$\Delta E$ [ev]	FWHM [ev]
Initial	$\text{LiCoPO}_4$	0.313	4.572
$\text{Co}^{2+}$ compounds	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	0.316	4.578
	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.292	4.542
	$\text{CoO}$	0.264	4.434
$\text{Co}^{2.7+}$ compounds	$\text{Co}_3\text{O}_4$	0.078	3.841
$\text{Co}^{3+}$ compounds	$\text{CoOOH}$	0.023	3.585
	$\text{LiCoO}_2$	0.013	3.520

chemical shift and the full width at half-maximum (FWHM) values suggest that initial  $\text{LiCoPO}_4$  have  $\text{Co}^{2+}$  state as shown in Table 3. Further HRXRF measurements during cycling will reveal the high-voltage discharge mechanism of  $\text{Li}_{1-x}\text{CoPO}_4$ .

## Conclusion

Of the four olivine cathodes,  $\text{LiCoPO}_4$  exhibited the highest 4.8 V discharge plateau without a  $\text{Co}^{4+}$  anomalous valence state. The energy density was comparable to that of layered rocksalt  $\text{LiCoO}_2$  (120 mAh/g X 4 V = 480 mWh/g). The volume change after a charge-discharge cycle was less than - 5 %. Moreover, the thermal stability of fully-charged  $\text{Li}_{0.4}\text{CoPO}_4$  cathode pellet without electrolyte was better than that of  $\text{Li}_{0.45}\text{CoO}_2$ . We could confirm  $\text{Co}^{2+}$  state in  $\text{LiCoPO}_4$  by HRXRF.

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