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# Cathode properties of phospho-olivine $\text{LiMPO}_4$ for lithium secondary batteries

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## Abstract

Four types of orthorhombic olivine  $\text{LiMPO}_4$  (M:Co, Fe, Ni and 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 versus  $\text{Li/Li}^+$  after initial charging to 5.1 V and its energy density was comparable to that of layered rocksalt  $\text{LiCoO}_2$  ( $120 \text{ mAh/g} \times 4 \text{ V} = 480 \text{ mWh/g}$ ). In contrast, the open circuit voltage profile of  $\text{LiFePO}_4$  was 160 mAh/g on the 3 V plateau. The  $\text{Co}^{2+}$  state in  $\text{LiCoPO}_4$  was confirmed using HRXRF. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Olivine  $\text{LiMPO}_4$ ; High-voltage cathode; HRXRF

## 1. Introduction

Fey's paper on  $\text{LiNiVO}_4$  [1] 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 [2], Cr [3]) and inverse spinel  $\text{LiNiVO}_4$  and their reported capacities over 4.5 V versus  $\text{Li/Li}^+$  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. Then, the olivine and inverse spinel structures both 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 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 also 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.

## 2. Experimental

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  $\text{Li}_2\text{CO}_3$ ,  $\text{P}_2\text{O}_5$  ( $\text{NH}_4$ ) $_2\text{HPO}_4$  and CoO (NiO,  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ). The mixtures were pre-sintered at 500°C for several hours. After firing at 780–850°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°C for 2 days in a nitrogen atmosphere to avoid oxidation of  $\text{Fe}^{2+}$

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Table 1  
Typical high-voltage cathodes over 4.5 V

Structure	Spinel	Inverse spinel	Olivine
Symmetry	Cubic	Cubic	Orthorhombic
Space group	Fd3m	Fd3m	Pmnb
Li site	Tetrahedral	Octahedral	Octahedral
Framework	ccp	ccp	hcp
Example	LiCoMnO <sub>4</sub>	LiNiVO <sub>4</sub>	LiCoPO <sub>4</sub>
References	[2]	[1]	[4,5]

and cooled slowly to room temperature. They were all indexed as orthorhombic in the space group Pmnb. We fabricated the cathodes for electrochemical characterization by blending powders of the active material LiMPO<sub>4</sub> with acetylene black (Denki Kagaku Co. Ltd.) and 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) with a non-aqueous electrolyte (1 M LiPF<sub>6</sub>/EC: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 Cu K $\alpha$  radiation. After it had reached potential equilibrium, each cathode pellet was adequately rinsed with dimethyl carbonate and dried in a vacuum.

The differential scanning calorimetry (DSC) of the initial and electrochemically-charged cathode pellets of LiCoPO<sub>4</sub> were also measured using Rigaku 8230L at heating rate of 5°C/min in air.

In addition, we analyzed the oxidation states of Co in LiCoPO<sub>4</sub> cathode pellets using a high resolution X-ray fluorescence spectrometer (HRXRF) with an XFRA 190 double-crystal spectrometer (Technos).

### 3. Results and discussion

Of these investigated olivine cathodes, LiCoPO<sub>4</sub> exhibited the highest 4.8 V (versus Li/Li<sup>+</sup>) discharge plateau after initial charging. The rechargeable capacity of LiCoPO<sub>4</sub> depended on the charge-cut-off voltage caused by the electrolyte decomposition. The maximum capacity, 100 mAh/g

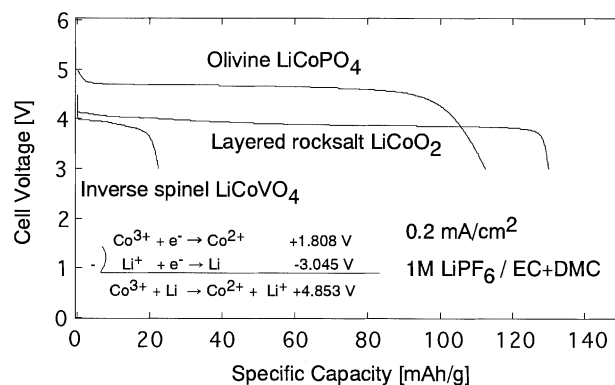


Fig. 1. First discharge profiles of Co-based high-voltage cathodes.

was obtained after charging to 5.1 V in a rate of 0.2 mA/cm<sup>2</sup> and its energy density was comparable to that of LiCoO<sub>2</sub> (120 mAh/g  $\times$  4 V = 480 mWh/g) as shown in Fig. 1.

During charging to 5.1 V, there were no other phases except Pmnb and the lattice constants *a* and *b* decreased, while *c* increased. This behavior is in good agreement with that of Li<sub>1-x</sub>FePO<sub>4</sub> during chemical delithiation using NO<sub>2</sub>PF<sub>6</sub> [6]. As shown in Table 2, the cell volume change ratio ( $\Delta V/V$ ) of Li<sub>1-x</sub>CoPO<sub>4</sub> during the charging process was -4.6%, while  $\Delta V/V$  is reported to be -6.5% for Li<sub>1-x</sub>FePO<sub>4</sub> [6].

In contrast, LiNiPO<sub>4</sub> and LiMnPO<sub>4</sub> 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 LiNiPO<sub>4</sub> between 3 and 5.5 V with a scan rate of 0.2 mV/s as shown in Fig. 2.

As shown in Fig. 3, the rate capability of LiCoPO<sub>4</sub> seems to be better than that of LiFePO<sub>4</sub>. However, the capacity of LiFePO<sub>4</sub> in the QOCV profile almost reached the theoretical value for one 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 LiFePO<sub>4</sub> at 80°C by an advanced processing technique using few weight percent polypropylene [7–10]. NTT has also reported a good cyclability of LiFePO<sub>4</sub> of 115 mAh/g at room temperature [11]. We expect that there is considerable room for improvement up to the theoretical upper limit of about 167 mAh/g for LiCoPO<sub>4</sub>, too.

Table 2  
Lattice change of Li<sub>1-x</sub>CoPO<sub>4</sub> and Li<sub>1-x</sub>FePO<sub>4</sub> with charging

Delithiation Olivine	Electrochemical (this work)		Chemical [6]	
	LiCoPO <sub>4</sub>	Li <sub>0.25</sub> CoPO <sub>4</sub>	LiFePO <sub>4</sub>	FePO <sub>4</sub>
Space group	Pmnb	Pmnb	Pmnb	Pmnb
<i>a</i> [Å]	5.97	5.62 (-5.9%)	6.008	5.792 (-3.6%)
<i>b</i> [Å]	10.24	10.05 (-1.9%)	10.334	9.821 (-4.9%)
<i>c</i> [Å]	4.72	4.87 (3.2%)	4.693	4.788 (2.0%)
<i>V</i>	288.5	275.1 (-4.6%)	291.39	272.36 (-6.5%)

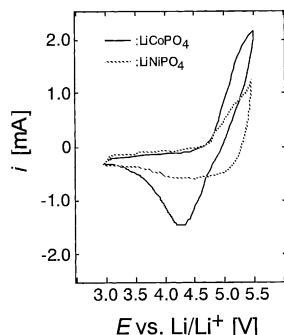


Fig. 2. Cyclic voltammograms for LiCoPO<sub>4</sub> and LiNiPO<sub>4</sub> (diameter: 10 mm  $\varnothing$ ) obtained at 0.2 mV/s between 3.0 and 5.5 V vs. Li/Li<sup>+</sup> in 1 M LiPF<sub>6</sub>/EC + DMC.

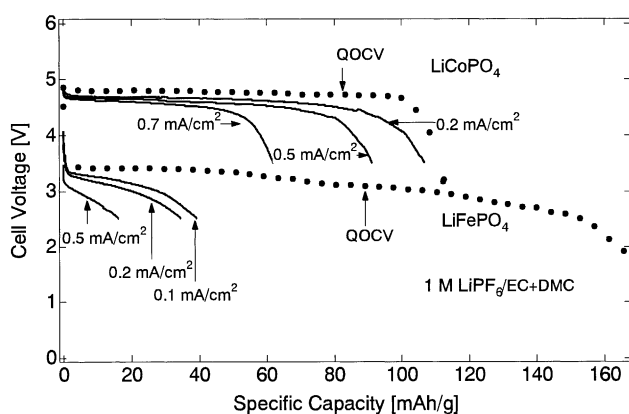


Fig. 3. Rate capability of LiCoPO<sub>4</sub> and LiFePO<sub>4</sub>.

The DSC profiles of fully-charged Li<sub>0.4</sub>CoPO<sub>4</sub> showed that the reversible endothermic peak at 304°C on heating and the exothermic peak at 275°C on cooling which suggests the existence of the first order phase transition of Li<sub>1-x</sub>CoPO<sub>4</sub> around 290°C. However, we have not confirmed the structure of the high temperature region, 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 FePO<sub>4</sub> [6]. The couple of peaks disappeared in discharged LiCoPO<sub>4</sub> cathode pellet.

Table 3  
The chemical shift and FWHM values of Co in LiCoPO<sub>4</sub>

Valence state of Co	Compound	$\Delta E$ (ev)	FWHM (ev)
Initial	LiCoPO <sub>4</sub>	0.313	4.572
Co <sup>2+</sup> compounds	CoSO <sub>4</sub> ·7H <sub>2</sub> O	0.316	4.578
	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.292	4.542
	CoO	0.264	4.434
Co <sup>2.7+</sup> compounds	Co <sub>3</sub> O <sub>4</sub>	0.078	3.841
Co <sup>3+</sup> compounds	CoOOH	0.023	3.585
	LiCoO <sub>2</sub>	0.013	3.520

We use HRXRF to analyze the oxidation states of Co in initial LiCoPO<sub>4</sub> 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 chemical shift and the full width at half-maximum (FWHM) values suggest that initial LiCoPO<sub>4</sub> have Co<sup>2+</sup> state as shown in Table 3.

#### 4. Conclusion

Of the four olivine cathodes, LiCoPO<sub>4</sub> exhibited the highest 4.8 V discharge plateau without a Co<sup>4+</sup> anomalous valence state. The energy density was comparable to that of layered rocksalt LiCoO<sub>2</sub> (120 mAh/g  $\times$  4 V = 480 mWh/g). The volume change after a charge-discharge cycle was less than -5%. Moreover, the thermal trace of the reversible phase transition of the fully-charged Li<sub>0.4</sub>CoPO<sub>4</sub> was detected around 290°C. We could confirm Co<sup>2+</sup> state in LiCoPO<sub>4</sub> by HRXRF. The further HRXRF measurements during cycling will reveal the high-voltage discharge mechanism of Li<sub>1-x</sub>CoPO<sub>4</sub>.

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