

Fluoride phosphate $\text{Li}_2\text{CoPO}_4\text{F}$ as a high-voltage cathode in Li-ion batteries

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Abstract

As a new high-voltage cathode candidate for post 4 V cathodes, ordered-olivine LiCoPO_4 and fluoride phosphate, $\text{Li}_2\text{CoPO}_4\text{F}$ were synthesized by solid-state reaction. Their structures were identified by neutron diffraction. The 5 V discharge profiles were demonstrated using coin-type cells. Two important issues for commercial use, metal dissolution and oxygen release at elevated temperatures, were also tested with an atomic absorption spectrophotometer and differential scanning calorimeter, respectively.

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1. Introduction

Recently, polyanionic cathodes such as olivine type LiCoPO_4 have attracted much attention as next-generation cathodes with high voltage. Fluorides, however, have been expected to be useful as high-voltage cathodes because the electronegativity of fluorine is greater than that of oxide [1]. We anticipate that not only ordered phospho-olivine LiCoPO_4 but also its relative, fluoride phosphate $\text{Li}_2\text{CoPO}_4\text{F}$, would be strong candidates for new high-voltage cathodes with large capacity, as the theoretical capacity of $\text{Li}_2\text{CoPO}_4\text{F}$ is twice as large as that of LiCoPO_4 . The two compounds were synthesized in the present study by means of the solid-state reaction method, and their structures were identified by neutron diffraction. The 5 V discharge profiles were demonstrated using coin-type cells. In addition, two significant issues regarding commercial use, metal dissolution of cathodes into electrolytes and oxygen release from cathodes in cells at elevated temperature, were investigated.

2. Experimental

Conventional solid-state reactions were employed to synthesize the phospho-olivines. LiCoPO_4 was prepared from stoichiometric amounts of reactants Li_2CO_3 , P_2O_5 and CoO . The mixtures were pre-sintered at 500 °C for several hours. After firing at 780–820 °C for 2 days with intermittent grinding, the mixtures were quenched using liquid nitrogen. Moreover, the obtained LiCoPO_4 was mixed with LiF and heated at 780 °C for 78 h in a vacuum quartz tube. Both of the obtained powders, LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$, were indexed as orthorhombic in the space group $Pnma$ by XRD (Rigaku RINT2100HLR/PC), using monochromatized $\text{Cu K}\alpha$ radiation. Neutron diffraction data were obtained using a powder diffractometer, HERMES [2], at the JRR-3M reactor of the Japan Atomic Energy Research Institute. The structural parameters were refined by Rietveld analysis using RIETAN 97 β [3].

Cathode pellets were fabricated by mixing the identified cathode powder with 25 (w/o) AB (acetyleneblack, Denki Kagaku Co. Ltd.) and 5 (w/o) PTFE Teflon binder (Polyflon TFE F-103, Daikin Industry Ltd.). We evaluated the electrochemical cathode performance in coin-type Li cells using a non-aqueous electrolyte (1 M $\text{LiPF}_6/\text{EC-DMC}$ (1:1 vol%), Mitsubishi Chemical Co., and 1 M LiPF_6/EMS , Tomiyama

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Table 1
Comparison of obtained and reported lattice parameters for LiCoPO₄

LiCoPO ₄	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	SG	Rwp
This work	10.200	5.919	4.697	<i>Pnma</i>	6.81
ICDD #32-0552	10.206	5.922	4.701	<i>Pnma</i>	–

Table 2
Comparison of lattice parameters for Li₂CoPO₄F and Li₂NiPO₄F [4]

Li ₂ MPO ₄ F	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	SG	Rwp
Li ₂ CoPO ₄ F	10.444	6.381	10.864	<i>Pnma</i>	7.26
Li ₂ NiPO ₄ F	10.473	6.289	10.846	<i>Pnma</i>	–

Pure Chemicals Co.) and a polypropylene separator (Celgard 3501) against a Li metal anode.

3. Result and discussion

3.1. Synthesis and characterization

Both synthesized powders, LiCoPO₄ and Li₂CoPO₄F, were indexed as orthorhombic space group *Pnma* by X-ray diffraction. The observed, calculated and difference plots for neutron diffraction patterns of LiCoPO₄ and Li₂CoPO₄F are shown in Fig. 1. The lattice parameters in Tables 1 and 2 were derived from least-squares refinement of the powder diffraction data in Fig. 1.

The obtained lattice parameters for LiCoPO₄ agreed well with literature values (ICDD #32-0552). In addition, it was confirmed that Li₂CoPO₄F is isostructural with Li₂NiPO₄F [4]. Interatomic distances for LiMPO₄ and Li₂MPO₄F

Table 3
Interatomic distances for LiMPO₄

M–O bond length [Å]	Co	Mn [5]	Fe [5]	Ni [5]
M–O(1)	2.150	2.23	2.25	2.150
M–O(2)	2.084	2.14	2.00	2.070
M–O(3) × 2	2.187	2.13	2.03	2.072
M–O(3) × 2	2.060	2.30	2.30	2.150
Average	2.151	2.205	2.151	2.110

Table 4
Interatomic distances for Li₂MPO₄F

M–O bond length [Å]	Li ₂ CoPO ₄ F	Li ₂ NiPO ₄ F [11]
M(1)–O(2) × 2	1.9960	2.011
M(1)–O(5) × 2	2.0872	2.070
M(1)–F(2) × 2	2.1637	2.081
M(2)–O(6) × 2	2.0092	2.013
M(2)–O(4) × 2	2.0606	2.036
M(2)–F(1) × 2	2.1552	2.082
Average	2.0382	2.032

Table 5
M–O interatomic distances in MO₆ octahedra calculated by Shannon's ion radii [6]

M–O interatomic distance [Å]	Co ²⁺	Mn ²⁺	Fe ²⁺	Ni ²⁺
M (high spin)–O	2.145	2.23	2.18	2.09
M (low spin)–O	2.05	2.07	1.98	–

obtained from Rietveld refinements of neutron diffraction by OLFEE are shown in Tables 3 and 4, respectively. According to Shannon's ion radius [5] in MO₆, the M–O interatomic distances in Table 5 suggest that both Co and Fe have a 2+ high spin state in the initial LiMPO₄ olivine matrix. Actually,

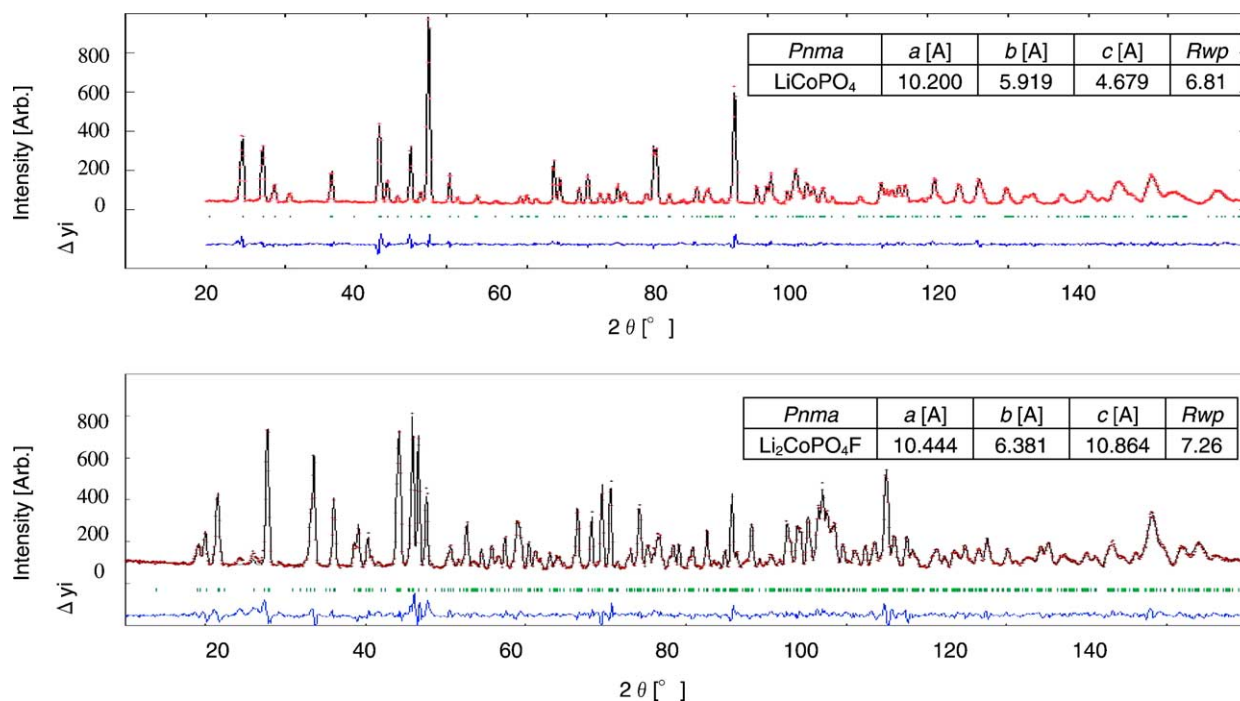


Fig. 1. Rietveld profiles of neutron diffraction for LiCoPO₄ and Li₂CoPO₄F.

Table 6
Atomic distribution in LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ *Pnma* matrixes

<i>Pnma</i>	4a	4b	4c	8d
LiCoPO_4	Li	–	P, Co, O(1), O(2)	O(3)
$\text{Li}_2\text{CoPO}_4\text{F}$	Co(1)	Co(2)	F(1), F(2), P(1), P(2), Li(2), Li(3), O(2), O(3), O(4), O(5)	Li(1), O(1), O(6)

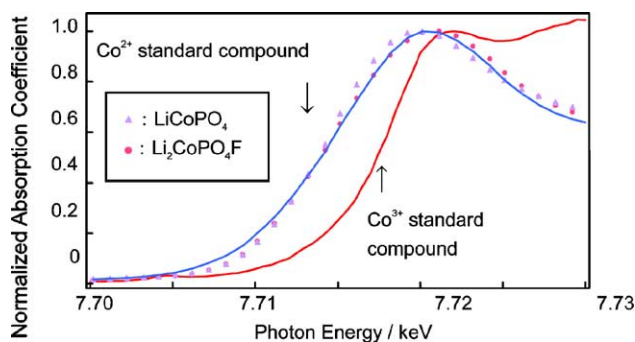


Fig. 2. Co K-edge XANES spectra of LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$.

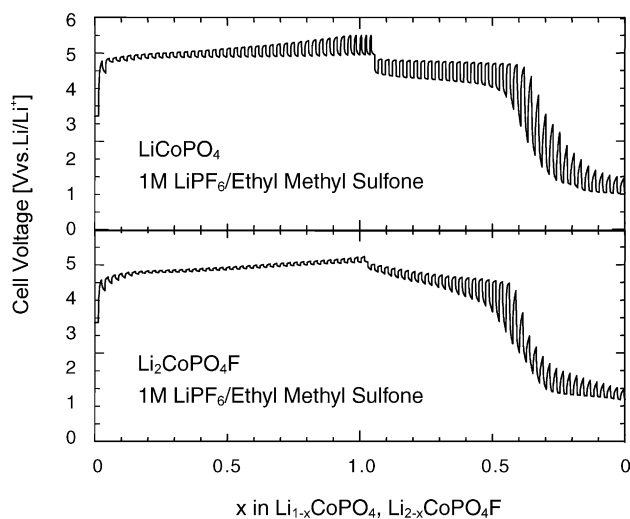


Fig. 3. Quasi-open circuit voltage profiles of LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$.

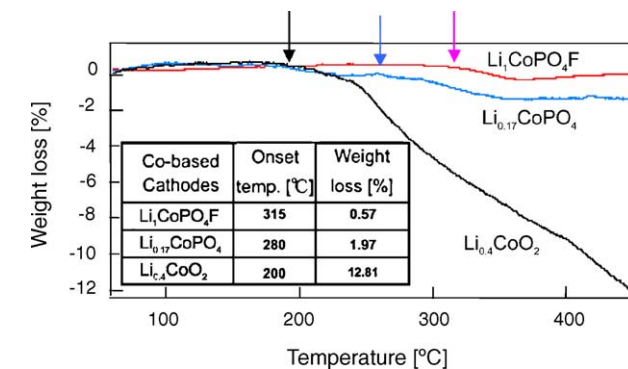
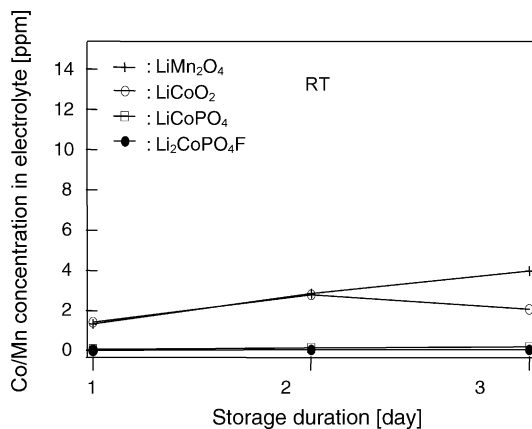


Fig. 5. TG profiles of charged LiCoO_2 , LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ cathode pellets.

the Thomas group proved that Fe in LiFePO_4 has a 2+ high spin state by ^{57}Fe Mössbauer spectroscopy [7]. On the other hand, Co seems to have a 2+ low spin state in $\text{Li}_2\text{CoPO}_4\text{F}$.

Although the space groups are the same, there are remarkable differences between the structures from a crystallographic point of view. LiCoPO_4 has CoO_6 octahedra, LiO_6 octahedra and PO_4 tetrahedra. In contrast, $\text{Li}_2\text{CoPO}_4\text{F}$ has CoO_4F_2 octahedra instead of CoO_6 octahedra. In addition, $\text{Li}_2\text{CoPO}_4\text{F}$ has two kinds of Li sites, 4c and 8d. The atom distributions in the matrixes are shown in Table 6.

3.2. XANES spectra

The XANES spectra for LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ are shown in Fig. 2. We used CoO and $\text{Co}(\text{CH}_3\text{COCHCOCH}_3)_3$ as Co^{2+} and Co^{3+} standard compounds, respectively. The Co K-edge photon energy of initial LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ agreed well with that of the Co^{2+} standard compound. These results of the Rietveld analysis and XANES spectra suggest that the $\text{Li}_2\text{CoPO}_4\text{F}$ sample must be stoichiometric.

3.3. Cathode properties

The quasi-open circuit voltage charge–discharge profiles of LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ are shown in Fig. 3.

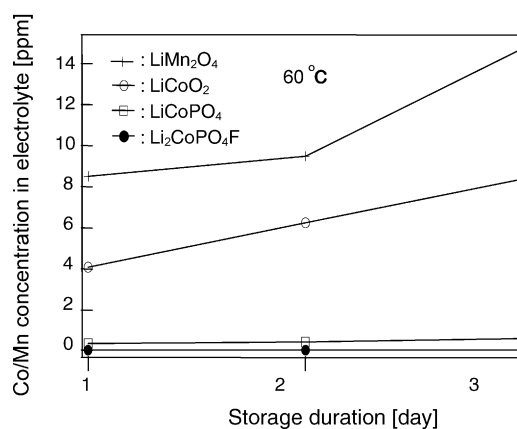


Fig. 4. Co and Mn concentrations in electrolyte solution at room temperature and 60°C .

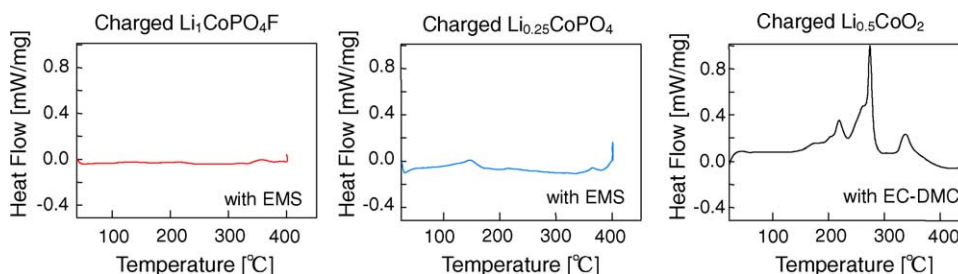


Fig. 6. DSC profiles of charged LiCoO_2 , LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ cathode pellets without electrolytes.

It was found that the fluoride phosphate $\text{Li}_2\text{CoPO}_4\text{F}$ is a new 5 V class cathode like LiCoPO_4 with a slightly higher open circuit voltage than that of LiCoPO_4 . In contrast to LiCoPO_4 , the monotonical decrease profile of LiCoPO_4F suggests that it does not undergo a two-phase reaction in the 5 V region.

The large irreversible capacity of the first cycle is caused by electrolyte decomposition in the charging process over 5 V. Our other attempts to charge LiNiPO_4 and $\text{Li}_2\text{NiPO}_4\text{F}$ proved unsuccessful with the high anodic stable ethyl methyl sulfone (EMS) electrolyte [8]. According to the recent GGA + U calculation by Ceder et al. [9], the OCV of LiNiPO_4 is 5.1 V versus Li/Li^+ , likely due to its higher cell voltage than that of LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$. We expect that there is considerable room for improvement up to the theoretical upper limit of approximately 310 mAh g^{-1} for $\text{Li}_2\text{CoPO}_4\text{F}$ and $\text{Li}_2\text{NiPO}_4\text{F}$ by using a new, as yet unknown, oxidation-resistant electrolyte.

3.4. Chemical stability

Mn and Co concentrations in 1 M LiPF_6 EC:DMC (1:1) electrolyte for 3 days RT and 60°C storage of LiMn_2O_4 , LiCoO_2 , LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ are presented in Fig. 4. Mn concentrations in the electrolyte are close to the data reported in the literature by Okada et al. [10]. The polyanionic LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ samples showed lower solubility than the LiMn_2O_4 and LiCoO_2 oxide cathodes in all storage experiments at different temperatures and durations.

3.5. Thermal stability

Fig. 5 shows the TG profiles of charged LiCoO_2 , LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$ cathode pellets. The cathode pellet of $\text{Li}_{0.4}\text{CoO}_2$ exhibited a broad exothermic peak around 210°C corresponding to oxygen release [11]. The weight loss of $\text{Li}_{0.4}\text{CoO}_2$ began at 200°C , while no gas generation was observed in $\text{Li}_{0.17}\text{CoPO}_4$ and LiCoPO_4F under 280°C . The thermal instability of the oxide cathode must be due to the existence of chemically unstable Co^{4+} in charged $\text{Li}_{0.45}\text{CoO}_2$. In contrast, the cathode pellet of $\text{Li}_{0.4}\text{CoPO}_4$ and LiCoPO_4F had no strong exothermic peak

in DSC profiles of Fig. 6 up to 400°C , because there is no Co^{4+} in charged $\text{Li}_{1-x}\text{CoPO}_4$ and $\text{Li}_{2-x}\text{CoPO}_4\text{F}$.

4. Conclusion

Of the four olivine cathodes, LiCoPO_4 exhibited the highest 4.8 V discharge plateau without a Co^{4+} anomalous valence state. The energy density was comparable to that of layered rocksalt LiCoO_2 ($120 \text{ mAh g}^{-1} \times 4 \text{ V} = 480 \text{ mWh g}^{-1}$). Moreover, we discovered that the fluoride phosphate $\text{Li}_2\text{CoPO}_4\text{F}$ is a 5 V class cathode like LiCoPO_4 with a slightly higher open circuit voltage than that of LiCoPO_4 . Unfortunately, the true capacity and cyclability of $\text{Li}_2\text{CoPO}_4\text{F}$ are still unknown, because there is no good liquid electrolyte with oxidation resistance up to 5 V level. However, it is noteworthy that the theoretical capacity of $\text{Li}_2\text{CoPO}_4\text{F}$ is almost twice as large as that of LiCoPO_4 . Both polyanionic high-voltage cathodes, LiCoPO_4 and $\text{Li}_2\text{CoPO}_4\text{F}$, showed better stability than the traditional oxide cathodes, LiCoO_2 and LiMn_2O_4 , in metal dissolution and oxygen release tests at elevated temperatures.

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