Crystal-structure-matched FePO_4 Surface-coating on LiCoPO_4 /MWCNT Nanocomposites for Long Lifecycle 5 V Class Lithium Ion Batteries

Naohisa OKITA,^a Etsuro IWAMA,^{a,b,*} Yusuke TAKAMI,^a Shingo ABO,^a Wako NAOI,^c McMahon Thomas Homer REID,^{b,d,e} and Katsuhiko NAOI^{a,b,d,*}

^a Department of Applied Chemistry, Tokyo University of Agriculture & Technology,
2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

^b Global Innovation Research Organization, Tokyo University of Agriculture & Technology,
2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

^c Division of Art and Innovative Technologies, K & W Inc., 1-3-16-901 Higashi, Kunitachi, Tokyo 186-0002, Japan

^d Advanced Capacitor Research Center, Tokyo University of Agriculture & Technology,
2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

^e Simpetus LLC., 1 Fitchburg St, Somerville, MA 02143, USA

* Corresponding authors: iwama@cc.tuat.ac.jp, k-naoi@cc.tuat.ac.jp

ABSTRACT

Stable high-voltage operation of LiCoPO_4 (LCP) was successfully achieved via crystal-structure-matched surface coating using FePO_4 (FP) with an identical olivine structure to the LCP. The efficient formation of Fe^{3+} -rich surface together with the partial dissolution of Fe^{3+} into LCP matrix yielded the excellent cycle performance with 99% of capacity retention at 100th cycle, with a minimized Fe^{3+} dosage compared to the methods previously reported. This work confirms that the existence of the Fe^{3+} on the LCP surface is an important factor to bring about the stability of electrode/electrolyte interface.

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1. Introduction

In the ongoing quest to identify high-performance cathode materials for lithium-ion batteries, one particularly promising candidate is LiCoPO_4 (LCP), in which P-O covalent bonding gives rise to a high redox potential of 4.8 V—significantly exceeding that of conventional materials such as $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM: 4.5 V vs. Li/Li^+), LiCoO_2 (LCO: 4.2 V), and LiFePO_4 (LFP: 3.5 V)—without sacrificing thermal stability.^{1–3} To date, however, practical application of LCP has been hindered by poor cycle performance, with LCP cathodes exhibiting a drastic loss of capacity within just a few cycles. Mechanisms proposed to explain the dramatic reduction in capacity include instability of the ethylene carbonate (EC)-based electrolyte,⁴ cleavage of P-O bonds by nucleophilic attack of F^- in LiPF_6 -containing electrolytes,⁵ and instability of the delithiated phase (Li_xCoPO_4 , $x \ll 1$).^{6,7} Attempts to improve cycle performance to inhibit the undesirable decomposition of the electrolyte at delithiated Li_xCoPO_4 ($x \ll 1$) were conducted by adding protective coating layers of carbon, AlF_3 , or LiFePO_4 (LFP), but failed to prolong cycle life beyond 50 cycles. Others considered alternative electrolytes or additives such as fluorinated ethylene carbonate (FEC),^{4,8} but achieved only modest improvement in cycle life. More successful was the 2011 study of Allen et al.,⁹ which achieved cyclability as high as 500 cycles—albeit with only 80% retention of initial capacity—but only at the cost of adding tris (trimethylsilyl) phosphite to EC+EMC, reducing the potential for practical applications. These authors proposed that aliovalent Fe^{3+} substitutions at Li^+ (M1) and transition metal Co^{2+} (M2) sites stabilize the delithiated Li_xCoPO_4 phase. An alternative approach was pursued by Hanafusa et al.,¹⁰ who used a conventional EC+DMC electrolyte without additives and achieved improved cycle performance—up to 150 cycles with 95% capacity retention—by restricting the operating voltage range to the range [3.5–5.0] V

vs. Li . Although several studies have used additives or other means to yield improved cycle life in laboratory settings up, the possibility of using LCP as a cathode material for practical batteries has continued to seem remote.

In our previous work,¹¹ this paradigm have been shifted by demonstrating that a combination of novel fabrication techniques, and modified operating parameters was able to yield LCP-based materials, namely Fe-substituted LCP (LCFP), whose performance lied in an entirely different regime from that of previous studies and one much closer to what is required for practical applications: our LCFP cells exhibited cycle life in excess of 5,000 cycles with >85% capacity retention despite requiring no additives of any kind. This dramatic improvement was the product of multiple factors: the formation of Fe^{3+} -rich surface layer assisted by the novel fabrication step of ultracentrifugation (UC) that served to stabilize the crystal against lattice expansion during high-voltage operation, the creation of vacancies at M2 sites in the crystal structure that enhances the Li^+ diffusivity in LCFP crystals and decreases its charge transfer resistance, and the restriction of the operating voltage range to ensure that Fe remained oxidized at valence state 3+, preventing its reduction to Fe^{2+} . Although an excellent cyclability in Fe^{3+} -substituted LCP was achieved, an excess Fe dosage is required so that the Fe^{3+} can migrate towards the surface via oxidation and then form the Fe^{3+} -rich layer. Such excess of Fe leads to an inevitable sacrifice of the specific capacity, due to the restricted operating voltage range between 4.3 and 5.0 V vs. Li which is above the voltage range of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox below 3.5 V vs. Li .

In this work, the addition of Fe dopants to the original mixture was dispensed, instead applying a coating of FePO_4 (FP) to LCP nanoparticles after synthesis. This yielded the same protective Fe^{3+} -rich surface layer as previously reported¹¹ as confirmed by X-ray photoelectron spectroscopy (XPS) with a lower overall dose of Fe, reducing mass and thereby improving specific capacity. Our updated

techniques yielded improvement of the performance relative to that of LCFP (95 mAh g^{-1}),¹¹ increasing specific capacity to 106 mAh g^{-1} while retaining the outstanding cycle performance observed previously. Our findings may suggest new techniques for prolonging cycle-life performance without unnecessarily decreasing capacity. These strategies may pave the way toward practical use of LCP in 5 V-class Li-ion batteries.

2. Experimental

LCP/MWCNT and LCFP/MWCNT composites were synthesized via ultracentrifugation (UC) treatment as previously reported.¹¹ In case of FePO_4 (FP) coating, two kinds of solutions (solution A and B) were prepared. The solution A was composed of 0.2500 g of synthesized LCP/MWCNT composite and 0.0183 g of H_3PO_4 (1.0 eq.) mixed in 10 ml of ultrapure water. The solution B was composed of 0.0276 g of $\text{Fe}(\text{CH}_3\text{COO})_2$ (1.0 eq.), 0.0107 g of CH_3COOLi (1.0 eq.) and 0.0306 g of citric acid (1.0 eq.) dissolved in 10 ml of ultrapure water. Mixture of solution A and B were then subjected to UC treatment at 80°C for 5 min. The UC-treated sol was further dried at 130°C under vacuum for 12 h. The obtained powder made of FP-coated LCP/MWCNT precursor was pre-annealed at 350°C in air for 1 h to remove absorbed water and citric-acid-derived amorphous carbon, then left to cool to room temperature (RT). The pre-annealed powder was then fast annealed at 700°C under N_2 flow (RT to 700°C in 3 min, dwell for 5 min, 20 min to cooling to RT) to form the LFP-coated LCP/MWCNT composite. The pristine LFP-coated LCP/MWCNT composite was further annealed at 350°C for 3 h under air in order to form FP-coated samples.

Structure analysis on LCP/MWCNT, and FP-coated LCP/MWCNT composites were performed by X-ray diffraction [XRD, Smart-lab (Rigaku)] using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). XRD patterns were recorded in the 10° – 90° 2θ range at a scan speed of $0.0033^\circ \text{ s}^{-1}$. XRD patterns were recorded in the 10° – 60° 2θ range at a scan speed of $0.167^\circ \text{ s}^{-1}$. The carbon content of LCP/MWCNT, and FP-coated LCP/MWCNT composites were determined by thermogravimetric analysis under a synthetic air (O_2 : 20%, N_2 : 80%) using a thermogravimetric/differential thermal analyzer (TG/DTA, Seiko Instruments TG/DTA6300) (see Fig. S1). X-ray photoelectron spectroscopy [XPS, JPS-9200 (JEOL)] was carried out using Mg X-ray source. Prior to the XPS characterization, the sample electrodes were thoroughly washed by dimethyl carbonate (DMC) and dried overnight.

Half-cells were assembled using a negative Li metal electrode and a positive LCP/MWCNT, and FP-coated LCP/MWCNT electrode in 2032 coin-type cells. The electrolyte was a mixture of ethylene carbonate, propyl carbonate and dimethyl carbonate (EC:PC:DMC = 1:1:3) containing 1.0 M of lithium hexafluorophosphate (LiPF_6). LCP/MWCNT and FP-coated LCP/MWCNT electrodes were prepared by mixing 90 wt.% of composites and 10 wt.% of weight of polyvinylidene difluoride (PVdF) in N-methyl pyrrolidone (NMP). The mixture was coated on an etched-Al foil (current collector) and dried at 80°C in vacuum for 12 h. The electrode density, calculated from the loading mass of the composite, was 1.4 mg cm^{-2} on 1.54 cm^2 of etched Al current collector. Charge/discharge tests were performed at constant-current constant-voltage (CC-CV) mode between 4.3 and 5.0 V vs. Li/Li^+ at current density of 0.2 C-rate, assuming that 1 C-rate equals 167 mA g^{-1} . The cut-off current density at the constant-voltage mode was 8.35 mA g^{-1} (0.05 C).

X-ray adsorption fine structure (XAFS) measurements at the Co and Fe K-edges for composites were performed in transmission mode at the beam line BL01 of the synchrotron radiation facility SPring-8 (Hyogo, Japan). Laminate-type two-electrode cells (pouch cells) were assembled using lithium metal foil as a negative

electrode and composites as a positive electrode. The obtained XAFS spectra were analyzed using the spectral fitting software REX2000 (Rigaku Corp.) to evaluate the ratio of Co and Fe species with references at different oxidation states, such as Co^{2+} (LiCoPO_4 bulk sample), Co^{3+} (Cobalt acetylacetonate), Fe^{2+} (LiFePO_4 bulk sample) and Fe^{3+} (FePO_4 bulk sample oxidized by the chemical method using NO_2BF_4).

3. Results and Discussion

In the previous work,¹¹ the formation of Fe^{3+} -rich layer on Fe-doped LiCoPO_4 ($\text{LiCo}_{0.8}\text{Fe}_{0.2}\text{PO}_4$, LCFP) particles was achieved via the air annealing process of LCFP/MWCNT composites. In this study, we applied the same annealing process on the LiFePO_4 (LFP, Fe^{2+})-coated LCP/MWCNT in order to yield FePO_4 (FP, Fe^{3+})-coated LCP/MWCNT as a final product. To minimize the dosage of Fe^{3+} which may lead to the sacrifice of the capacity, we prepared the LCP/MWCNT with 10 wt.% of FP-coating, whose stoichiometry equals to that of $\text{LiCo}_{0.87}\text{Fe}_{0.13}\text{PO}_4$ /MWCNT.

X-ray diffraction patterns (XRD) were recorded for uncoated LCP/MWCNT and FP-coated LCP/MWCNT compounds, as shown in Fig. 1a. First, all primary peaks in the XRD patterns of the LCP/MWCNT composite were reproduced by an olivine structure (S.G. *Pnma* LiCoPO_4 ; JCPDS card no. 85-0002). Except low-intensity peaks attributable to MWCNT and Co_3O_4 , no other peaks were detected, indicating successful synthesis of crystalline LCP. All XRD peaks of the FP-coated LCP agrees well with the peaks of LCP structure, while the positions of some Bragg peaks were shifted by FP-coating. To interpret the observed peak shifts, lattice parameters for two compounds were determined from the observed XRD patterns (Table 1). Compared to the uncoated LCP, lattice parameters for FP-coated LCP changed in all directions: the *a* and *b* parameters decrease, while *c* increases. Such lattice parameter changes well agree with the previous reports on Fe^{3+} -substituted LCP,^{10,12} suggesting the oxidation of Fe^{2+} (LFP) into Fe^{3+} (FP) by the annealing process. This also indicates that FP not only coated the surface of the LCP crystal but also partially dissolved into the bulk LCP crystal structure, which may enhance the compatibility between the FP coating (surface) and the LCP matrix (bulk).

X-ray photoelectron spectroscopy (XPS) analyses of Co $2p_{3/2}$ and Fe $2p_{3/2}$ energy level was performed on the synthesized FP-coated LCP with different Ar ion etching duration. The XPS spectrum of the surface of the sample (pristine) shows a peak with a maximum at 712 eV which well corresponds to the signal of Fe^{3+} (FP),¹³ confirming successful FP-coating on LCP surface. The change in peak intensity with etching times differed depending on Co and Fe atoms (Fig. 1b and 1c), indicating the difference of a composition ratio between surface (pristine) and the inner bulk (after etching up to 30 sec). The Co/Fe ratio was calculated by computing the areas under the Co $2p_{3/2}$ and Fe $2p_{3/2}$ peaks. As shown in Fig. 1d, the surface composition of FP-coated LCP particles is Fe^{3+} -rich (Co/Fe = 61/39) compared to that for the inner bulk (Co/Fe = 77/23), suggesting the partial substitution of Co for Fe into LCP nanocrystals which agrees well with the results of XRD analysis. High-resolution TEM images observed on two composites indicate that both composites contain nanocrystals of ca. 100 nm highly dispersed within the MWCNT matrix (Fig. 2a and 2c). Magnified images for the LCP/MWCNT show a highly crystalline bulk part of LCP surrounded by amorphous phase (Fig. 2b). The crystalline bulk part shows clear lattice fringes with interplanar lattice distances of $4.3 \text{ \AA}$ corresponding to the (101) plane of the olivine structure. Contrary to the LCP, the most of HRTEM images for FP-coated LCP shows clear lattice fringes even close to the edge parts of the nanocrystalline. The interplanar lattice distance observed in Fig. 2d is $2.5 \text{ \AA}$, which well agrees with the (311) plane of the olivine structure, indicating the successful FP-coating and partial

Figure 1. (a) X-ray diffraction patterns for the LCP and FP-coated LCP/MWCNT composites. Consecutive XPS measurements with data acquisition at 5 s intervals during 0–30 s Ar ion etching (2 keV). Depth profiles of (b) Co and (c) Fe, and (d) atomic ratio of Co and Fe calculated from depth profiles for FP-coated LCP/MWCNT composites.

Table 1. Lattice parameters calculated by X-ray diffraction patterns for the LCP and FP-coated LCP/MWCNT composites.

Sample	Space group	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	<i>V</i> /Å ³
LiCoPO ₄ /MWCNT	<i>Pnma</i>	10.2018(6)	5.9217(3)	4.7003(3)	283.95(3)
10 wt.% FePO ₄ coated LiCoPO ₄ /MWCNT	<i>Pnma</i>	10.1875(4)	5.9179(2)	4.7037(2)	283.58(2)

dissolution of Fe³⁺ into the LCP crystalline as discussed in the previous paragraphs.

Charge discharge curves for LCP, LCFP,¹¹ and FP-coated LCP within the restricted voltage range of 4.3–5.0 V vs. Li during 100 cycles are shown in Fig. 3. All three compounds showed the large irreversible capacity (40–50 mAh g⁻¹ per composite) only at the initial cycle, most of which attributed to the irreversible capacity of MWCNT (*ca.* 100 mAh g⁻¹ per MWCNT during 1st charge). Figure 3a showed LCP curves with two plateau regions, corresponding to two redox reactions: i) LiCoPO₄ ↔ Li_{0.7}CoPO₄ + 0.3Li⁺ + 0.3e⁻, and ii) Li_{0.7}CoPO₄ ↔ CoPO₄ + 0.7Li⁺ + 0.7e⁻; this agrees with reports of previous studies.¹⁴ The exhibited discharge capacity at the 1st cycle is 76 mAh g⁻¹, which corresponds 46% of the efficiency against the theoretical capacity (167 mAh g⁻¹). During cycling, the discharge capacity contentiously decreased and then fell to 47% of the initial capacity at 100th cycle. Contrary to LCP, both LCFP and FP-coated LCP showed excellent stable cycling performances as seen in Fig. 3b and 3c. Here, the amount

of FP-coating on LCP/MWCNT was optimized to be 10 wt.% (Fig. 3d): as 5 wt.% coating improved its capacity retention to a certain degree (87% over 100 cycles), but not as stable as 10 wt.% coating with an 100% capacity retention, while the sample with a 12 wt.% coating showed the same level of capacity retention to that of 10 wt.% coating. The stoichiometry of 10 wt.% coating of FP on LCP/MWCNT equaled to be that of LiCo_{0.87}Fe_{0.13}PO₄/MWCNT, meaning *ca.* 10% increase of active Co compared to the LCFP (LiCo_{0.8}Fe_{0.2}PO₄), which well corresponds to an increase in exhibited capacity [10 wt.% FP coated LCP/MWCNT: 106 mAh g⁻¹, LCFP/MWCNT: 95 mAh g⁻¹, 73% and 71% of the efficiency against the theoretical capacity of 10 wt.% FP coated LCP/MWCNT (145 mAh g⁻¹) and LCFP/MWCNT (134 mAh g⁻¹) in confined operation voltage 4.3–5.0 V vs. Li, respectively]. Interestingly, when it is compared on the condition of the same amount of coating as 10 wt.%, it was found that the AlPO₄ coating was ineffective on cyclability only with 52% of capacity retention and even exhibited smaller capacity compared to the FP-coating.

Figure 2. High-resolution TEM images for (a), (b) LCP and (c), (d) FP-coated LCP/MWCNT composites.

Meanwhile, the LFP-coating on LCP in previous report¹⁵ was even detrimental to its cycle performance. These facts highlight the importance of i) crystal-structure-matching between coating material and LCP matrix, and ii) the existence of Fe^{3+} -rich phase on its surface, in order to attain the excellent cyclability as demonstrated in this study. To further demonstrate the importance of surface stabilization by FP coating, we compared two FP-coated LCP samples with different particle sizes; LCP/MWCNT composites containing LCP nanoparticles with a diameter of *ca.* 100 nm, and the submicron-sized LCP which we termed *LCP bulk*. Results of electrochemical characterizations are shown in Fig. S2. The FP-coated LCP bulk showed higher discharge capacity, 101 mAh g^{-1} , compared to that for uncoated LCP bulk (61 mAh g^{-1}). This tendency is consistent with the obtained results for the LCP/MWCNT with FP coating. After 100 cycles, however, the capacity for the FP-coated LCP bulk fell to 39 mAh g^{-1} , corresponding to the 39% of the initial capacity. Such poor capacity retention for the FP-coated LCP bulk is probably due to the large submicron size of LCP particles, where the ratio of its surface to the bulk part of particles is much smaller compared to the LCP nanoparticles within the composite. These results show that the synthesis of LCP using MWCNT brings about not only the enhancement of exhibited capacity thanks to the downsizing of LCP and high electrical conductivity of MWCNT, but also the effective stabilization of the electrode/electrolyte interface for FP-coated LCP particles.

To see the effect of FP-coating on the redox state of Co and Fe, *in situ* X-ray absorption measurements were conducted for the four different samples at 1st and 50th cycles. The X-ray absorption near edge structure (XANES) spectra of Co and Fe K-edge for the LCP/MWCNT and FP-coated LCP/MWCNT composites are shown in Fig. 4a–4c. Note that, for the FP-coated LCP, the XANES spectra at

10th was considered as the representative of longer cycle (50th cycle), regarding the fact that the curve shapes in electrochemical signal for the FP-coated sample remain identical over 2nd cycle with 99% capacity retention. The valence states of Co and Fe in the composite are determined by deconvolving the spectra using the contributions of Co^{2+} , Co^{3+} , Fe^{2+} and Fe^{3+} . As shown in Table 2, different Co valence states are determined for the as-prepared electrodes, where the samples with and without FP-coating show $\text{Co} = +2.06$ and $+2.13$, respectively. Such higher valence states of Co than 2.00 may be due to the presence of Co_3O_4 impurity within composites found in the XRD analysis. For the LCP/MWCNT, the K-edge jump in XANES spectra at 5.0 V shifts toward lower energy along cycling (Fig. 4a), suggesting that a decrease in the amount of active $\text{Co}^{2+}/\text{Co}^{3+}$ redox. Meanwhile, the XANES spectra for the FP-coated sample at 5.0 V remained identical as shown in Fig. 4b, where the valence state of Fe was kept to be *ca.* 3.00 thanks to the limited operation voltage¹¹ between 4.3 and 5.0 V. These results show that the FP-coating with the presence of Fe^{3+} -rich layer is effective on preventing the degradation of LCP, which are in good agreement with obtained capacity retention capabilities shown in Fig. 3.

Based on the results of XRD, XPS, XANES and electrochemical studies, it can be summarized that the Fe^{3+} -rich protective layer can be formed via simple FP-coating on LCP and prolong the cycle life of LCP. Such a protective layer is analogue to the one obtained by air-annealing of LCP,¹⁴ but more effective in terms of minimization of Fe dosage used to cover the LCP surface, leading to a higher capacity per composite. Further enhancement of LCP performance can be expected by combining such coating technique (surface) and other dopant into LCP bulk crystal (bulk), which will be the next topic of our research.

Figure 3. Charge discharge curves of (a) LCP, (b) LCFP, (c) FP coated LCP/MWCNT cathodes in 1 M LiPF₆ in EC+PC+DMC (1:1:3 in vol.) operated at CC-CV charge (0.2 C-rate) and CC discharge (0.2 C-rate). Confined operation voltage: 4.3–5.0 V vs. Li was applied, the protocol of which has been discovered in our previous paper. The x-axis shown in bottom corresponds to the capacity per active material without MWCNT; per LCP, LCFP, and FP-coated LCP. Then, the x-axis shown in top corresponds to the capacity per whole composites; per LCP/MWCNT, LCFP/MWCNT, and FP-coated LCP/MWCNT. (d) Capacity plots against cycle number for a Li metal half-cell using 12, 10, and 5 wt.% FP coated LCP, AlPO₄ coated LCP, uncoated LCP, and LCFP/MWCNT cathodes at a 0.2 C-rate.

Figure 4. Co-K XANES spectra for (a) LCP and (b) FP-coated LCP/MWCNT composites, and (c) Fe-K XANES spectra for the FP-coated LCP/MWCNT composite.

4. Conclusions

In conclusion, the stable cycle performance of LCP (*ca.* 100% over 100 cycles) was achieved by FP-coating on its surface via air-annealing process of the LFP layer. Combination of XRD and XPS analysis confirmed that such FP-coating brought about both the

formation of Fe³⁺-rich surface on LCP particles and the partial dissolution of Fe³⁺ into LCP crystals. This structure is analogue to the previously-reported Fe-substituted LCP (LiCo_{0.8}Fe_{0.2}PO₄: LCFP), yielding the same excellent cycle performance with 99% of capacity retention at 100th cycle, but with a minimum capacity sacrifice thanks to the minimized dosage of Fe³⁺ to cover the LCP

Table 2. Formal valence number of Co and Fe evaluated from XAFS spectra for the half-cells consisting of Li/1M LiPF₆ EC:PC:DMC(vol. 1:1:3)/(LCP/MWCNT composite with and without FP-coating) at 1st and 50th cycles.

Sample	Cycle No.	Co valence state			Fe valence state	
		OCV/Discharge state	Charge state	Charge in Co valence state	OCV/Discharge state	Charge state
LiCoPO ₄ /MWCNT	1 st	+2.13	+2.66	0.53	—	—
	50 th	+2.13	+2.47	0.34	—	—
10 wt.% FePO ₄ coated	1 st	+2.06	+2.85	0.79	+2.76	+3.05
LiCoPO ₄ /MWCNT	50 th	+2.06	+2.85*	0.79	+3.02	+3.04

*Value corresponds to 10th cycle.

surface. Our finding may offer new idea of crystal-structure-matched surface coating—where the crystal structure between the coating material and the matrix is identical—to stabilize the cycling performance of not only LCP but also other high-voltage cathode materials.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.18-00096>.

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