Ultrafast and High-Voltage Lithium Ion Batteries using Polyanionic Positive Electrode Material/Carbon Nanocomposites

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Chapter 1

Introduction
1.1. Lithium ion batteries

Electrical energy storage devices (EESDs) have attracted much attention as key enabling technologies for sustainable societies. The combination of EESDs with technologies such as electric vehicles, zero-emission buildings, and renewable energy sources enable efficient use of electric power.\(^1\) Perhaps the most famous EESD is the lithium ion battery (LIB). Compared to other EESDs—such as lead-acid batteries or nickel-metal-hydride batteries—LIBs offer both higher cell voltages and larger capacities, and have consequently found widespread application to portable devices, electric vehicles, and other technologies requiring batteries confined to restricted spaces. The central challenge in the material design of LIBs is to achieve high energy density and rapid charge/discharge capability (power density) while ensuring long lifetimes and safe operation.\(^2\)-\(^4\)

LIBs consist of multiple components, each presenting its own unique material-design challenges, as we now briefly review.

- **Positive-electrode materials**

  The energy density of a LIB is determined by the product of capacity and cell voltage (the difference between the redox potentials of the positive and negative electrodes). Positive-electrode materials for LIBs must thus be engineered to exhibit high redox potential and large capacity without sacrificing cycle performance or thermal stability. In particular, higher cell voltages reduce the number of cells that must be series-connected to achieve a given battery voltage; however, excessive cell voltages (> 4.5 V vs. Li/Li\(^+\)) degrade cycle performance by inducing electrolyte decomposition.

  At present, rock-salt lithium cobalt oxide (LiCoO\(_2\))\(^5\)-\(^6\) is the most common positive-electrode material for commercial LIBs. Ni- and Al- substituted rock-salt lithium cobalt oxide (LiCo\(_0.8\)Ni\(_{0.15}\)Al\(_{0.05}\)O\(_2\))\(^7\)-\(^8\) spinel lithium manganese oxide (LiMn\(_2\)O\(_4\))\(^9\) and polyanion-based lithium iron phosphate (LiFePO\(_4\))\(^10\) are also in practical use. Properties of these materials are described in Section 1.2 below.
**Negative-electrode materials**

Mirroring the requirements for positive-electrode materials, negative-electrode materials for LIBs must have low redox potential and high capacity without sacrificing cycle performance or thermal stability. At present, negative electrodes in commercial LIBs are typically made from carbon materials such as graphite, which boasts high theoretical capacity (372 mAh g\(^{-1}\)) and low redox potential (0.1 V vs. Li/Li\(^+\)). The basic reaction at the negative electrode is then

\[ 6C + xLi^+ + xe^- \rightleftharpoons Li_xC_6 \quad (1-1) \]

However, graphite suffers from a number of intrinsic disadvantages, including low volumetric and gravimetric capacities, low power density, and risk of deposition of Li metal. Therefore, other carbon materials—such as hard carbon, alloying-type materials (such as Si and Sn), conversion-type materials (such as Mn\(_3\)O\(_4\) and SnO\(_2\)), and intercalation-type metal oxides (such as Li\(_4\)Ti\(_5\)O\(_12\) and Li\(_3\)V\(_2\)O\(_8\)) have attracted attention as candidate negative-electrode materials.

One particularly promising negative-electrode material is lithium titanate oxide (Li\(_4\)Ti\(_5\)O\(_12\), LTO), which boasts long lifetime, high power, and good safety properties. For LTO negative electrodes, the redox potential is 1.55 V vs. Li/Li\(^+\), the theoretical capacity is 175 mAh g\(^{-1}\), and the basic reaction is

\[ Li_4Ti_5O_{12} + 3Li^+ + 3e^- \rightleftharpoons Li_7Ti_5O_{12} \quad (1-2) \]

Pristine LTO is a spinel structure with low electronic conductivity, which upon charging becomes a rock-salt structure with high electronic conductivity; in the event of a short circuit the LTO immediately forms a spinel structure with low electronic conductivity, preventing thermal runaway. LTO also exhibits good cycle performance due to (a) the vanishingly small change in lattice volume (0.2 %) it experiences during charge and discharge, and (b) the fact that its redox potential is higher than the potential at which the electrolyte suffers reduction. In our laboratory, we have used innovative techniques for synthesizing nanometer-scale particles of LTO and its composites to achieve huge improvements in the power (C-rate) capability of LTO, which now rivals that of activated
carbon: our LTO electrodes achieve C-rates of 300 or greater, corresponding to charge/discharge times of just 12s, without sacrificing the outstanding safety and cycle performance (>10,000 cycles).21

● Electrolyte

The electrolytic solution is composed of an organic solvent and a lithium salt. General requirements for solvents include high dielectric constant, low viscosity, high electrochemical stability, high boiling point, low freezing point, high ignition point, and low toxicity; at present, alkyl organic carbonates (EC, DEC, DMC, PC, and so on)22 are widely used as solvents. Requirements for lithium salts include high solubility, small ion size, high electrochemical stability, high thermal stability, low cost, and low toxicity; commonly used lithium salts in commercial LIBs include LiPF6, LiBF4, and LiTFSI.22-24

● Separator

The separator prevents electrical contact between positive and negative electrodes without inhibiting lithium-ion diffusion through the electrolyte during the charge and discharge processes. Polypropylene/polyethylene membranes25 are commonly used for commercial LIBs.

1.2. Positive-electrode materials for lithium-ion batteries

The reversible capacities of positive-electrode materials—such as rock-salt LiCoO2 (148 mAh g⁻¹, theoretical: 274 mAh g⁻¹)26 and olivine LiFePO4 (165 mAh g⁻¹, theoretical: 170 mAh g⁻¹)27—are lower than the capacity of typical negative-electrode materials such as graphite (372 mAh g⁻¹, theoretical: 372 mAh g⁻¹).28 Therefore, increasing the energy density of LIBs requires the development of novel positive-electrode materials. As shown in Figure 1-1, the positive-electrode materials in use today may be classified into three families: rock-salt, spinel, and polyanion.
As shown in Figure 1-2, rock-salt materials can be described by a hexagonal structure (space group $R\bar{3}m$) consisting of layered (111) planes of oxide ions interspersed with aggregations of lithium and cobalt ions.

The most common rock-salt material for LIB positive electrodes is LiCoO$_2$, for which the average redox potential is 3.8 V vs. Li/Li$^+$, the theoretical capacity is 274 mAh g$^{-1}$, and the basic reaction is
\[
\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- (0 \leq x \leq 1) \quad (1-3)
\]

Due to the two-dimensional character of Li\(^+\) diffusion in LiCoO\(_2\), the Li\(^+\) diffusion coefficient is higher in this material than in LiMn\(_2\)O\(_4\) or polyanion-based LiFePO\(_4\). However, the capacity of LiCoO\(_2\) is limited by the fact that the crystal structure of the de-intercalated material Li\(_{1-x}\)CoO\(_2\) transforms from hexagonal to monoclinic for values of \(x\) greater than 0.5, effectively restricting operation to the range \(x < 0.5\).\(^6\) To overcome this issue, Ni-, Mn-, and Al-substituted lithium cobalt oxides (LiCo\(_{0.8}\)Ni\(_{0.15}\)Al\(_{0.05}\)O\(_2\) and LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\))\(^7, 29\) have been developed to achieve stabilization of lithium-removed CoO\(_2\). LiCo\(_{0.8}\)Ni\(_{0.15}\)Al\(_{0.05}\)O\(_2\) shows high reversible capacity of 200 mAh g\(^{-1}\) at 3.7 V vs. Li/Li\(^+\). These rock-salt materials are promising as high-capacity positive electrodes. However, cells using these oxide-based materials pose risks of ignition due to release of oxygen from the crystal structure during charge and discharge.

- **Spinel**

  The well-known spinel LiMn\(_2\)O\(_4\) may be described by a cubic structure (space group \(Fd\) \(3m\)), as illustrated in Figure 1-3.

![Figure 1-3 Structure of spinel LiMn\(_2\)O\(_4\).](image)

For LiMn\(_2\)O\(_4\) electrodes, the basic reaction is

\[
\text{LiMn}_2\text{O}_4 \rightleftharpoons \text{Mn}_2\text{O}_4 + \text{Li}^+ + e^- \quad (1-4)
\]
The redox potential of spinel LiMn$_2$O$_4$ is 4.0 V vs. Li/Li$^+$—higher than that of rock-salt materials—although the theoretical capacity (148 mAh g$^{-1}$) is only around one-half that of rock-salt materials. An even higher redox potential—4.7 V vs. Li/Li$^+$—is observed for Ni-substituted lithium manganese oxide [Li(Ni$_{1/2}$Mn$_{3/2}$)O$_4$]$^{30}$. These spinel materials are promising as high-redox-potential positive electrodes. However, these lithium manganese oxides suffer capacity loss caused by manganese dissolution into electrolyte at high temperature (60 °C) or high state of charge (60 - 70 %).$^{31-32}$ Furthermore, these materials also pose risks of ignition due to release of oxygen.

- **Polyanion materials**

  Polyanion-based materials are characterized by strong covalent AO$_x$ bonds (A=B, P, S, Si, and so on). The olivine-structured polyanion compound LiFePO$_4$ (LFP) is shown in Figure 1-4.

![Figure 1-4 Structure of polyanion-based LiFePO$_4$.](image)

Olivine LFP can be described by an orthorhombic structure (space group Pnma), with Li insertion/deinsertion occurring along the $b$ axis. Electrochemical reactions at LFP electrodes proceed via a two-phase reaction scheme

\[
\text{LiFePO}_4 \rightleftharpoons \text{FePO}_4 + \text{Li}^+ + e^- \quad (1-5)
\]

The redox potential of LiFePO$_4$ is 3.4 V vs. Li/Li$^+$ (theoretical capacity: 170 mAh g$^{-1}$), higher than that of iron oxides (redox potential of Fe$_2$O$_3$ : 1.5-1.6 V vs. Li/Li$^+$). This high
redox potential for $M^{2+/3+}$ (where $M=$Fe, V, Mn, Co, Ni, etc.) is generated by the presence of phosphates with strong $P\text{--}O$ covalent bonding, which serves to stabilize the antibonding $M\text{--}O$ energy level through an $M\text{--}O\text{--}P$ inductive effect.\textsuperscript{27} Unfortunately, this effect leads to low electronic conductivity ($10^{-9}\text{ to }10^{-10} \text{ S cm}^{-1}$) because the transition metal ions are separated by the phosphate groups. However, the strong $P\text{--}O$ covalent bonding also ensures that there is no release of oxygen from the crystal structure during charge and discharge, and thus minimal risk of ignition.\textsuperscript{33} Consequently, polyanion-based materials offer excellent thermal stability compared to other common positive-electrode materials such as rock-salt LiCoO$_2$ or spinel LiMn$_2$O$_4$. In this thesis, we focus on polyanion-based positive-electrode materials to design next-generation LIBs without sacrificing safety.

### 1.3. Polyanionic positive-electrode materials

As discussed above, research to date has focused on three primary families of candidate materials for positive electrodes in high-energy-density, high-power-density LIBs; however, two of the three families—rock-salt compounds and spinel compounds—are plagued by intrinsic safety problems. This leaves the remaining family—polyanion-based compounds—as the strongest candidate materials for positive electrodes in next-generation LIBs with high energy density and high power density while preserving long lifetimes and safe operation. Figure 1-5 shows crystal structures and electrochemical properties for some common polyanionic materials.
Among the polyanion compounds, lithium nickel phosphate (LiNiPO₄) has the highest redox potential of 5.1 V vs. Li/Li⁺. However, the structure of LiNiPO₄—and of conventional electrolytes—is unstable at potentials above 5 V, and there have been no reports of reversible charging/discharging of this material. Instead, research on high-energy-density LIBs has focused on the lithium cobalt phosphate (LiCoPO₄) which has the second highest redox potential of 4.8 V vs. Li/Li⁺. There have also been reports of attempts to construct ultrafast LIBs using lithium vanadium phosphate [Li₃V₂(PO₄)₃] which has the highest Li⁺ diffusivity and electronic conductivity among polyanion compounds.

1.3.1. Lithium cobalt phosphate (LiCoPO₄: LCP)

Lithium cobalt phosphate (LiCoPO₄: LCP) is a promising positive-electrode candidate material for high-voltage, high-energy-density LIBs because of its high reaction potential of 4.8 V vs. Li/Li⁺, with theoretical capacity of 167 mAh g⁻¹. The basic scheme of electrochemical reactions at LCP electrodes is

\[
\text{LiCoPO}_4 \rightleftharpoons \text{Li}_{0.7}\text{CoPO}_4 + 0.3 \text{ Li}^+ + 0.3 \text{ e}^- \quad (1-6)
\]

\[
\text{Li}_{0.7}\text{CoPO}_4 \rightleftharpoons \text{CoPO}_4 + 0.7 \text{ Li}^+ + 0.7 \text{ e}^- \quad (1-7)
\]
The crystal structure of lithium cobalt phosphate (LiCoPO$_4$ : LCP) is orthorhombic (space group $Pnma$) with good thermal properties (remaining structurally stable up to high temperatures above 400 °C) due to P-O covalent bonding. Co and Li are located at octahedral sites, while P occupies tetrahedral sites, and LiO$_6$ octahedra define a 1-dimensional Li$^+$ diffusion path along the $b$-axis.

Practical use of LCP is hampered by the poor rate-cycling capability of the material, which derives both from its inherently low electron conductivity ($< 10^{-9}$ S cm$^{-1}$) and the poor Li$^+$ diffusivity ($<10^{-13}$ cm$^2$ s$^{-1}$) associated with the one-dimensional character of Li$^+$ diffusion along $b$-axis-oriented diffusion paths. A further impediment to practical use of LCP is the dramatic capacity degradation the material exhibits upon charge/discharge cycling, caused by electrolyte decomposition and structure deterioration. Consequently, many studies have proposed methods for enhancing the practical utility of the material, including improving its electrical conductivity, doping with metal ions, coating with electrically conductive materials, and shortening Li$^+$ diffusion paths. However, despite significant research efforts spanning many years, the cycle performance of LCP remains inadequate for practical applications, and the detailed mechanism responsible for improved cycle performance remains unclear.

Motivated by this background, the objective of this thesis is to elucidate the influence of aliovalent substitutions on the cycle performance of LCP electrodes, taking into account both crystal structure and the nature of the electrode/electrolyte interface.

1.3.2. Lithium vanadium phosphate [Li$_3$V$_2$(PO$_4$)$_3$: LVP]

Lithium vanadium phosphate [Li$_3$V$_2$(PO$_4$)$_3$, LVP] is a promising positive-electrode candidate material with applications to high-safety LIBs due to its high thermal stability, good cyclability, and outstanding safety performance provided by stable P-O covalent bonding. LVP exists in a monoclinic structure (space group $P2_1/n$) with a 3-dimensional network built from distorted VO$_6$ octahedra and PO$_4$ tetrahedra sharing oxygen vertices. LVP has also attracted much attention as a candidate material for high-energy, high-power LIBs due to its high theoretical capacity of 197 mAh g$^{-1}$ at high potential up to 4.8 V vs. Li/Li$^+$ and its relatively high Li$^+$ diffusivity (10$^{-7}$-10$^{-9}$ cm$^2$ s$^{-1}$), attributable to the 3-dimensional character of Li$^+$ diffusion through the material. The basic electrochemical
reactions at LVP electrodes proceed according to the schema\textsuperscript{36}

\begin{align*}
\text{Li}_3\text{V}_2(\text{PO}_4)_3 & \rightleftharpoons \text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 + 0.5 \text{ Li}^+ + 0.5 \text{ e}^- & (1-8) \\
\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 & \rightleftharpoons \text{Li}_2\text{V}_2(\text{PO}_4)_3 + 0.5 \text{ Li}^+ + 0.5 \text{ e}^- & (1-9) \\
\text{Li}_2\text{V}_2(\text{PO}_4)_3 & \rightleftharpoons \text{LiV}_2(\text{PO}_4)_3 + \text{ Li}^+ + \text{ e}^- & (1-10) \\
\text{LiV}_2(\text{PO}_4)_3 & \rightleftharpoons \text{V}_2(\text{PO}_4)_3 + \text{ Li}^+ + \text{ e}^- & (1-11)
\end{align*}

When operated at voltages sufficient to induce 3-electron (Li\textsuperscript{+}) extraction, LVP experiences a degradation in capacity due to strong repulsion among $[\text{V}_2(\text{PO}_4)_3]^{3-}$ units and the destabilization of its crystal structure. Thus, a more practical choice for applications to cathode materials for ultrafast LIBs is to use LVP over a restricted voltage range that ensures at most 2-electron reactions (specific capacity of 131 mAh g\textsuperscript{-1} at a potential up to 4.3 V vs. Li/Li\textsuperscript{+}). One of the challenges associated with the use of the LVP is to circumvent the limitations posed by its intrinsically low electronic conductivity ($10^{-8}$-$10^{-9}$ S cm\textsuperscript{-1}).\textsuperscript{49} Strategies that have been investigated for addressing this issue include reduced particle sizes,\textsuperscript{49-52} synthesis of carbon-composite materials,\textsuperscript{50-51, 53} and doping with other metals,\textsuperscript{52} but to date all efforts have failed to increase charge/discharge speeds above 100C. Achieving ultrafast LVP charge/discharge at rates beyond 100C will require considerably faster paths for electron transport between LVP and carbon. In our laboratory, we have used ultracentrifugation (UC) to synthesize LVP nanocrystals, of sizes in the range 10-100 nm, highly dispersed throughout a matrix of multiwalled carbon nanotubes (MWCNTs).\textsuperscript{54} Synthesized uc-LVP/MWCNT composites exhibit ultrafast charge/discharge capability of 96 mAh g\textsuperscript{-1} at 300C, more than twice the capacity of the activated carbon electrodes used in supercapacitors (SCs). The SCs available today are safe, long-lived devices with high power density; nonetheless, in the near future, uc-LVP/MWCNT composites may replace activated-carbon electrodes to form the basis of a new generation of energy-storage devices—called SuperRedox Capacitors (SRCs) in this thesis—that combine the energy densities of LIBs with the high-speed charge/discharge capability of supercapacitors. In addition to the task of improving high power density, the assembly and operation of full cells using LVP positive electrodes is a challenge addressed by few previous studies.\textsuperscript{55-57}

In this thesis, we design full cells of LVP-based SRCs that simultaneously achieve high
energy density, high power density, and long cycle lifetime.

1.4. Objectives

In this thesis, we investigate three novel polyanion-based composite nano-materials: (a) Fe$^{3+}$-substituted lithium cobalt phosphate (LiCo$_{0.8}$Fe$_{0.2}$PO$_4$), (b) iron-phosphate-(FePO$_4$)-coated Ti$^{4+}$-substituted lithium cobalt phosphate (LiCo$_{0.90}$Ti$_{0.05}$PO$_4$), and (c) lithium vanadium phosphate [Li$_3$V$_2$(PO$_4$)$_3$]. Materials (a) and (b) are designed for applications to high-voltage LIBs, while material (c) is intended for applications to ultra-fast LIBs, also known as SuperRedox Capacitors.

In Chapter 2, we use a novel ultracentrifugation (UC) process to synthesize Fe$^{3+}$-substituted LiCoPO$_4$ nanoparticles (average diameter 100 nm) highly dispersed within a multi-walled carbon nanotube (MWCNT) matrix. The goal of this effort is to achieve stable cycle performance, and we investigate the influence of Fe$^{3+}$-substitutions on the cyclability of LiCoPO$_4$, taking into account both crystal structure and the electrode/electrolyte interface.

In Chapter 3, we again use UC techniques to synthesize nanocrystals of FePO$_4$-coated LiCoPO$_4$, and of the aliovalent substitution LiCo$_{0.90}$Ti$_{0.05}$PO$_4$, highly-dispersed within a MWCNT matrix; the goal of this effort is to clarify the mechanisms responsible for the improved performance of LiCoPO$_4$-based positive electrodes. Additionally, we synthesize FePO$_4$-coated LiCo$_{0.90}$Ti$_{0.05}$PO$_4$ to achieve increased capacity (relative to that of uc-LiCo$_{0.8}$Fe$_{0.2}$PO$_4$) without sacrificing cycle performance.

In Chapter 4, we design full cells of Li$_3$V$_2$(PO$_4$)$_3$-based SuperRedox Capacitors that simultaneously achieve high energy density, high power density, and long cycle lifetime. As part of this effort, we elucidate the mechanism of capacity degradation during full-cell cycling and take steps to mitigate its effect on cycle performance.

1.5. References


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Chapter 2

Stabilizing the structure of LiCoPO$_4$ nanocrystals via addition of Fe$^{3+}$: Formation of Fe$^{3+}$ surface layer, creation of diffusion-enhancing vacancies, and enabling high-voltage battery operation
2.1. Introduction

Growing global demands for electric and hybrid electric vehicles necessitate the development of 5V-class lithium ion batteries (LIBs) in view of their potential for higher specific energy and voltage compared to the 4V-class LIBs. From this perspective, LiCoPO$_4$ (LCP) is an interesting material that offers advantages complementary to those of conventional cathode materials such as LiCoO$_2$ and LiFePO$_4$ (LFP): high reaction potential of 4.8 V vs. Li/Li$^+$, theoretical capacity of 167 mAh g$^{-1}$, and thermal stability thanks to the P-O covalent bonding.\(^1\)\(^-\)\(^3\) Although the low electron conductivity ($<10^{-9}$ S cm$^{-1}$)\(^4\) and Li$^+$ diffusivity ($<10^{-13}$ cm$^2$ s$^{-1}$)\(^5\) of LCP were initially thought to be problematic, it has since become clear that these difficulties can be remedied by controlling particle size/morphology,\(^6\) doping metal ions,\(^7\),\(^8\) carbon coating,\(^9\) and/or synthesizing composites with conductive nanocarbons.\(^4\),\(^10\) A more serious obstruction to practical utilization of LCP—and the primary focus of this study—is its poor cyclability: LIBs with LCP cathodes exhibit a dramatic decrease in capacity within just a few 10s of cycles. Mechanisms proposed to explain the plummeting capacity include instability of the ethylene carbonate (EC)-based electrolyte,\(^11\) cleavage of P-O bonds by nucleophilic attack of F$^-$ in LiPF$_6$-containing electrolytes,\(^12\) and instability of the delithiated phase (Li$_x$CoPO$_4$, $x << 1$).\(^13\),\(^14\) Formation of a protective surface film on LCP using alternatives to EC-based solvents, such as fluorinated ethylene carbonates\(^11\) and other electrolyte additives,\(^15\) has succeeded in prolonging useful life to 100 cycles. Allen et al. recently showed that Fe substitution into LCP in combination with a phosphite electrolyte additive enhances electrochemical performance, extending cyclability to 500 cycles with 80% retention of initial capacity.\(^16\) Fe substitution—specifically, aliovalent Fe$^{3+}$ substitution in Li$^+$ (M1) and transition metal M$^{2+}$ (M2) sites obtained by such a simple air-annealing process—has been well known for other phosphates such as LFP and LiMn$_{1-x}$Fe$_x$PO$_4$ (LMFP) to cause changes in the structural characteristics (defective) and in the electrochemical signature (slope).\(^17\)-\(^19\) In case of LCP, the Fe$^{3+}$ substitution yields structural stabilization at high potential such 4.5 V vs. Li/Li$^+$ and the creation of vacancies in the Li$^+$ (M1) sites.\(^16\),\(^20\) It is reported that these vacancies contribute to increased Li mobility, thus enhancing rate capability.\(^16\),\(^21\) Hanafusa et al. demonstrated that Fe$^{3+}$-substituted LCP can charge and discharge with negligible capacity loss ($< 5\%$) over 150
cycles even in conventional EC-based electrolyte. However, achieving such an excellent cyclability in Fe$^{3+}$-substituted LCP requires restricting the operating voltage range between 3.5-5.0 V vs. Li, thus sacrificing capacity contributed by the Fe$^{3+}$/Fe$^{2+}$ redox below 3.5 V vs. Li. Moreover, the detailed mechanism responsible for improved cyclability, and the role played by the presence of Fe$^{3+}$ within the LCP crystal structure, remains unclear.

This study aims at elucidating the influence of Fe$^{3+}$ substitution on LCP cyclability by focusing on electrode/electrolyte interface. Using LCP nanoparticles (100 nm diameter in average) highly dispersed within multi-walled carbon nanotube (MWCNT) matrix prepared via ultracentrifugation (UC), we have synthesized different LCP-based materials with different Fe$^{3+}$ amounts. Electrochemical characterizations of the synthesized materials gave clear evidence of improved electrochemical stability of LCP as well as enhanced rate capability, with Fe$^{3+}$ substitution. Surface analysis using X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) suggested that Fe enrichment of the surface of LCP nanoparticles occurred through the oxidation of Fe$^{2+}$ into Fe$^{3+}$ along with the creation of vacancies at Co$^{2+}$ (M2) sites during the synthesis process. The Fe$^{3+}$-rich phase on the LCP surface enhanced the stability of the delithiated phase, preventing oxidative reactions with electrolytes during high-voltage operation. This surface protection persisted over 1,000 cycles at 0.2C and 5,000 cycles at 1.0C as long as the electrochemical reduction of Fe$^{3+}$ was avoided by ensuring that the full range of operating voltages lied above the Fe$^{3+}$/Fe$^{2+}$ redox potential. Additionally, we first demonstrated for LCP or LCFP materials that the vacancies in Co/Fe M2 sites were responsible for the Li$^+$ diffusivity enhancement within LCFP crystals and thus for the improvements of C-rate capability. Our findings may offer new approaches for stabilizing the structure of LCP and other high-voltage positive electrodes for use in 5V-class Li-ion batteries.

2.2. Experimental

2.2.1. Materials

Co(CH$_3$COO)$_2$ • 4H$_2$O (>99%, Wako Pure Chemicals), Fe(CH$_3$COO)$_2$ (>99%, Sigma-Aldrich Corp.), CH$_3$COOLi (>98.0%, Wako Pure Chemicals), and H$_3$PO$_4$ (>85.0%, Wako
Pure Chemicals) were used to prepare LCFP. Citric acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}) (>99.5%, Sigma-Aldrich Corp.) was used as a chelating agent. MWCNTs\textsuperscript{23} with a specific surface area of 240 m\textsuperscript{2} g\textsuperscript{-1} were used for the preparation of carbon composite. Distilled water (17 MΩ cm) was used as a medium for the entire preparation scheme.

2.2.2. Preparation of LCFP/MWCNT composite under UC treatment

First, two kinds of solutions (solution A and B) were prepared. The solution A was composed of 0.4000 g of MWCNT and 0.6714 g of H\textsubscript{3}PO\textsubscript{4} (1.0 eq. for LCFP) mixed in 50 ml of ultrapure water. The solution B was composed of 1.1725 g of Co(CH\textsubscript{3}COO)\textsubscript{2} \cdot 4H\textsubscript{2}O (0.8 eq.), 0.2027 g of Fe(CH\textsubscript{3}COO)\textsubscript{2} (0.2 eq.), 0.3922 g of CH\textsubscript{3}COOLi (1.0 eq.) and 1.1247 g of citric acid (1.0 eq.) dissolved in 20 ml of ultrapure water. The solution A was subjected to the \textit{ultracentrifugation} (UC) treatment\textsuperscript{22} at 80 °C for 5 min before and after the addition of the solution B. The uc-treated sol was further dried at 130 °C under vacuum for 12 h. The obtained powder made of LCFP precursor and MWCNT 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 650 °C under N\textsubscript{2} flow (RT to 650 °C in 3 min, dwell for 5 min, 20 min to cooling to RT) to form the LCFP/MWCNT composite (pristine LCFP/MWCNT). The pristine LCFP/MWCNT composite was further annealed at 350 °C for 3 h under air in order to oxidize Fe\textsuperscript{2+} into Fe\textsuperscript{3+} without incinerating MWCNTs (air-annealed LCFP/MWCNT).

2.2.3. Physicochemical characterizations of LCFP/MWCNT composite

Structure analysis on pristine and air-annealed LCFP samples was performed by X-ray diffraction [XRD, Smart-lab (Rigaku), Cu K\textalpha{} radiation (\(\lambda\)=1.54 Å), operating at 45 kV, 200 mA]. XRD patterns were recorded in the 10° - 90° 2\theta range at a scan speed of 0.0033° s\textsuperscript{-1}. Time-of-flight neutron powder diffraction (NPD) measurements were performed at the iMATERIA (BL20) facility of the Japan Photon Accelerator Research Complex (J-PARC, Ibaraki, Japan) to obtain NPD patterns corresponding to 0.5-4.8 Å in d-spacing. \textsuperscript{57}Fe Mössbauer spectra were collected at room temperature in transmission geometry on a constant acceleration spectrometer using a \textsuperscript{57}Co source in a Rh matrix. Isomer shift (IS)
calibrations were performed using $\alpha$-Fe as a standard at room temperature. The obtained spectrum was fitted by two Lorentzian doublets ($\text{Fe}^{2+}$ and $\text{Fe}^{3+}$). The LCFP/MWCNT nanostructure and the particle size were characterized by high-resolution transmission electron microscopy (HRTEM, Hitachi model H9500). Thermogravimetric analysis was performed under a synthetic air ($\text{O}_2$: 20%, $\text{N}_2$: 80%) using a thermogravimetric/differential thermal analyzer (TG/DTA, Seiko Instruments TG/DTA6300). X-ray photoelectron spectroscopy (XPS JEOL Ltd. JPS-9200) 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. X-ray adsorption fine structure (XAFS) measurements at the Co and Fe K-edges for the composite 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 LCFP/MWCNT composite 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 using references selected to exhibit different oxidation states, such as $\text{Co}^{2+}$ ($\text{LiCoPO}_4$ bulk sample), $\text{Co}^{3+}$ (Cobalt acetylacetonate), $\text{Fe}^{2+}$ ($\text{LiFePO}_4$ bulk sample) and $\text{Fe}^{3+}$ ($\text{FePO}_4$ bulk sample oxidized by the chemical method using $\text{NO}_2\text{BF}_4$).

### 2.2.4. Electrochemical characterization of LCFP/MWCNT composite

Half-cells were assembled using a negative Li metal electrode and a positive LCFP/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 ($\text{LiPF}_6$). LCFP/MWCNT electrode was prepared by mixing 90 wt.% of the composite and 10 wt.% 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 loading mass of the composite was 1.4 mg cm$^{-2}$ on etched Al current collector (1.54 cm$^2$). Charge–discharge tests were performed in constant-current constant-voltage mode between 2.5 and 5.0 V or 4.3 and 5.0 V vs. Li/Li$^+$ at current density of 0.2C-rate, assuming that 1C-rate equals 167 mA g$^{-1}$. The cut-off current density at the constant-voltage mode was 8.35 mA g$^{-1}$ (0.05C).
Before charge–discharge tests, a pre-cycling was conducted at 0.1C in the same potential range as charge–discharge tests.

2.3. Results and discussion

2.3.1. Crystal structure of the air-annealed LCFP/MWCNT composite

Figure 2-1 shows XRD patterns of the air-annealed LCFP, pristine LCFP, and air-annealed LCP/MWCNT composites. Lattice parameters for the air-annealed LCFP, pristine LCFP, and air-annealed LCP were determined through Rietveld refinements on the XRD data, as shown in Table 2-1. Main peaks of the air-annealed LCFP composite were indexed with an olivine structure (Space group. Pnma LiCoPO$_4$; JCPDS card no. 85-0002). As same as for the air-annealing LCFP, all peaks of the pristine LCFP composite corresponded to a single phase of an olivine structure with the Pnma space group. Apart peaks attributed to MWCNT and Co$_3$O$_4$ with very small intensity, no other peaks due to possible impurities such as Fe$_2$O$_3$, LiFePO$_4$ and FePO$_4$ were detected, indicating successful substitution of Fe into the LCP crystalline structure.

NPD analysis of the air-annealed LCFP confirmed the existence of vacancies in the synthesized crystal structure [Figure 2-2(a) and (b)]. Lattice parameters, atomic positions and occupancies, including Li and expected vacancy sites, for the air-annealed LCFP were determined through Rietveld refinements on the NPD data. Observed NPD peaks were indexed by an olivine structure with lattice constants of $a = 10.1592(7)$ Å, $b = 5.9114(4)$ Å, and $c = 4.7091(3)$ Å and a unit-cell volume of $V = 282.80(3)$ Å$^3$, as shown in Table 2-2. These values of the $a$ and $b$ lattice parameters and the cell volume were smaller than those of the air-annealed LCP, in good agreement with the previous report. The obtained stoichiometry of the air-annealed LCFP crystal structure was $(\text{Li}_{0.98}\text{Fe}_{0.02})_{\text{M1}}(\text{Co}_{0.785}\text{Fe}_{0.13}\square_{0.085})_{\text{M2}}\text{PO}_4$, where M1, M2, and $\square$ respectively represent Li, Co, and vacancy sites. Fe$^{3+}$ was present primarily at transition metal sites (M2), whereupon vacancies were present at the same M2 site to compensate the valence, unlike previous reports which suggested the creation of vacancies in Li (M1) sites. One has to note that vacancies appeared overestimated as the composition $(\text{Li}_{0.98}\text{Fe}_{0.02})_{\text{M1}}(\text{Co}_{0.78}\text{Fe}_{0.13}\square_{0.085})_{\text{M2}}\text{PO}_4$, was expected to insure charge compensation. However, this result was related to the evidence of the inhomogeneous composition of
the particles as described latter.

![XRD patterns of the air-annealed LCFP, pristine LCFP, and air-annealed LCP/MWCNT composites.](image)

**Figure 2-1** XRD patterns of the air-annealed LCFP, pristine LCFP, and air-annealed LCP/MWCNT composites.

**Table 2-1** Rietveld refinement results of XRD patterns from Figure 2-1 for the air-annealed LCFP pristine LCFP, and air-annealed LCP/MWCNT composites.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Space Group</th>
<th>a / Å</th>
<th>b / Å</th>
<th>c / Å</th>
<th>V / Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air annealed LCFP / MWCNT</td>
<td><em>Pnma</em></td>
<td>10.1589</td>
<td>5.9105</td>
<td>4.7090</td>
<td>282.75</td>
</tr>
<tr>
<td>Pristine LCFP / MWCNT</td>
<td><em>Pnma</em></td>
<td>10.2237</td>
<td>5.9376</td>
<td>4.6985</td>
<td>285.22</td>
</tr>
<tr>
<td>Air annealed LCP / MWCNT</td>
<td><em>Pnma</em></td>
<td>10.2018</td>
<td>5.9217</td>
<td>4.7003</td>
<td>283.95</td>
</tr>
</tbody>
</table>
Figure 2-2  NPD patterns for (a) the air-annealed LCFP / MWCNT and (b) LCP / MWCNT composites.
Mössbauer spectroscopy was conducted on the air-annealed and pristine LCFP/MWCNT, in order to verify the idea that the air-annealing of pristine LCFP/MWCNT was the responsible process to create Fe$^{3+}$ in the structure [Figure 2-3(a) and (b)]. The obtained spectrum for the air-annealed LCFP was best fitted by two doublets: one with an isomer shift (IS) = 0.43 mm s$^{-1}$ and a quadrupole splitting (QS) = 0.83 mm s$^{-1}$, and the other with IS = 1.2 mm s$^{-1}$ and QS = 2.9 mm s$^{-1}$. The former, accounting for 94% of the absorption area, corresponded to the Fe$^{3+}$ present on M1 and disordered M2 sites, and the latter, accounting for 6% of the spectra, corresponded to Fe$^{2+}$ on M2 sites. The drastic increase in the Fe$^{3+}$ ratio from 12% to 88% was due primarily to the oxidation of Fe$^{2+}$ in pristine LCFP through the air-annealing process, as pristine LCFP contained only 12% Fe$^{3+}$ (88% Fe$^{2+}$). Most of the Fe$^{3+}$ oxidized from Fe$^{2+}$ was found to remain on the M2 site including also all created vacancies thus leading to highly distorted octahedral surrounding.
HRTEM observations of the air-annealed LCFP indicated the presence of nanocrystals of ca. 100 nm highly dispersed within the MWCNT matrix [Figure 2-4(a)]. The high magnification HRTEM image [Figure 2-4(b)] showed the highly crystalline bulk part of LCFP nanocrystal surrounded by an amorphous phase. The crystalline bulk part showed clear lattice fringes with interplanar lattice distances of 3.86, 5.10 and 5.92 Å, corresponding respectively to the (210), (200), and (010) planes of the olivine structure.

TG/DTA curves for the air-annealed LCFP, pristine LCFP, air-annealed LCP/MWCNT composites, and MWCNTs are shown in Figure 2-5. The calculated weight ratios of MWCNT in the air-annealed LCFP, pristine LCFP, air-annealed LCP/MWCNT composites were 26, 27, and 27 wt.%, respectively.

**Figure 2-3** Mössbauer spectra of (a) the air-annealed and (b) pristine LCFP/MWCNT composites fitted with two Fe environments (Fe$^{2+}$ and Fe$^{3+}$).
Figure 2-4  (a) Lower-magnification (20,000×) higher-resolution TEM image for highly dispersed LCFP nanocrystalline within the MWCNT matrix. (b) Magnified (400,000×) HRTEM image of the air-annealed LCFP nanocrystalline. Clear lattice fringes of $d = 3.86$, $5.10$ and $5.92$ Å appear, corresponding to the (210), (200) and (010) planes of LCFP, respectively.

Figure 2-5  TG/DTA curves for the air-annealed LCFP, pristine LCFP, air-annealed LCP/MWCNT composites, and MWCNTs.

2.3.2. Surface structure of the air-annealed LCFP nano-crystals

XPS analysis of Co 2p$_{3/2}$ and Fe 2p$_{3/2}$ energy levels was performed on the air-annealed and pristine LCFP [Figure 2-6(a)-(f)] subjected to different Ar ion etching duration. The
Co/Fe ratio was determined quantitatively by computing the areas under the Co 2p$_{3/2}$ and Fe 2p$_{3/2}$ peaks [Figure 2-6(c) and (f)]. The examination of the results showed that the distribution of Fe and Co varied from the surface to the bulk of the particles. While an average Co/Fe ratio of 83/17 was calculated from NDP refinement, the XPS experiments showed that at the surface (no Ar ion etching) this ratio was equal to 57.4/42.6 and progressively increased when moving toward the center of the particle (increasing Ar ion etching duration). In contrast, the Co/Fe ratio of pristine LCFP/MWCNT composite remained fixed at approximately 80/20 independent of location between surface and center of the particle (independent of Ar ion etching duration), which well agreed with the dosage of the synthesis process (Co = 0.8 eq. and Fe = 0.2 eq.). This suggested that the air-annealing process induced, beside the oxidation of the Fe and creation of Co vacancies to balance the charge, the migration of Fe$^{3+}$ ions toward the surface of the particles in the amorphous domain.

To support the hypothesis of Fe-rich phase on the surface of air-annealed LCFP crystals based on the analysis of XPS spectra, we conducted the EELS analysis on the sample. Here, to compensate for the low ratio of Fe/Co in the composite and the corresponding low intensity of Fe in synthesized LCFP/MWCNT structures, we prepared the pristine and air-annealed samples of a composite with higher Fe concentration, namely LiCo$_{0.5}$Fe$_{0.5}$PO$_4$/MWCNT. As shown in Figure 2-7(a), elemental mapping of the air-annealed LiCo$_{0.5}$Fe$_{0.5}$PO$_4$/MWCNT composite showed an Fe-rich surface layer on the nanoparticle surface which was supported by its line analysis [Figure 2-7(c)], where as that of the pristine in Figure 2-7(b) showed uniform distribution of Fe, Co, O, and P within the particle. This inhomogeneous distribution of Fe allowed, in addition, interpreting the apparently overestimated vacancy amount as deduced from the NDP analysis. The migration of Fe$^{3+}$ was associated with equivalent migration of vacancies in the opposite ways leading to an excess of vacancies in the bulk part of the particle and an excess of Fe at the surface. As this surface was amorphous, as revealed by HRTEM, the refinement of NDP took to account only the vacancy rich part of the particle thus explaining the apparent overestimation.
Figure 2-6  Consecutive XPS measurements with data acquisition at 5 s intervals during 0–30 s Ar ion etching (2 keV), yielding a depth profile of (a), (b), (c) the air-annealed and (d), (e), (f) pristine LCFP/MWCNT composites: (a), (d) Co 2p$_{3/2}$ peak and Co satellite peak, (b), (e) Fe 2p$_{3/2}$ peak and Co LMM Auger electron peak. (c), (f) Atomic ratio of Co and Fe calculated from Co 2p$_{3/2}$ and Fe 2p$_{3/2}$ peaks.
(a) Air annealed LiCo$_{0.5}$Fe$_{0.5}$PO$_4$ / MWCNT

(b) Pristine LiCo$_{0.5}$Fe$_{0.5}$PO$_4$ / MWCNT
Figure 2-7  Elemental mapping line analysis of (a) the air annealed LiCo_{0.5}Fe_{0.5}PO_4/MWCNT and (b) pristine LiCo_{0.5}Fe_{0.5}PO_4/MWCNT composites, (c) line analysis of the air annealed LiCo_{0.5}Fe_{0.5}PO_4/MWCNT composite [shown in white frame in Figure 2-7(a)] obtained from electron energy loss spectroscopy.
2.3.3. Electrochemical performance of the air-annealed LCFP/MWCNT composite

The electrochemical behavior of LCFP/MWCNT composites were investigated in half-cells versus Li anode at a rate of 0.2C (1C = 167 mA g⁻¹) (Figure 2-8). During the charge/discharge processes, a voltage shoulder around 3.5 V and two plateaus were observed at 4.76 V and 4.83 V [Figure 2-8(a)]. The shoulder corresponded to the redox reaction of Fe²⁺/Fe³⁺ in LiCo₀.₈Fe₀.₂PO₄. The two plateaus at high potentials corresponded to a two-step redox reaction of Co²⁺/Co³⁺ in Li₀.₈Co₀.₈Fe₀.₂PO₄, which well agreed with previous reports.²⁰, ²⁴, ²⁵ The air-annealed LCFP/MWCNT composites showed a high initial discharge capacity of 130 mAh g⁻¹ [Figure 2-8(a)], and increased stability of the cycle performance with 86% capacity retention after 50 cycles compared to LCP/MWCNT and pristine LCFP/MWCNT composites [Figure 2-8(d)]. During cycling between 2.5 and 5.0 V, dQ/dV plots showed an increase near the Fe²⁺/Fe³⁺ redox peak at 3.5 V and a decrease near the broad redox peak at 3.4 V [Figure 2-8(c)]. Such change in redox peaks suggested that Fe³⁺ in the air-annealed LCFP was gradually reduced into Fe²⁺ at low potentials, and that the energy level of the resultant Fe³⁺ produced by re-oxidation of Fe²⁺ was different from that for Fe³⁺ originally existed in the air-annealed LCFP. To avoid this phenomenon, we performed charge and discharge tests of the composites with operating voltages confined to the range of 4.3-5.0 V. This resulted in excellent cycle performance, with 96% capacity retention at 0.2C after 1,000 cycles, and 85% at 1C after 5,000 cycles [Figure 2-8(e)] largely exceeded the best reported one by Hanafusa et al.²⁰ Additionally, the air-annealed LCFP/MWCNT composite enabled discharge at a 100C rate with capacity of 45 mAh g⁻¹, larger than observed for LCP/MWCNT and pristine LCFP/MWCNT composites [Figure 2-8(f)].

In order to elucidate the factor for the C-rate capability enhancement as shown in Figure 2-8(f), galvanostatic intermittent titration technique (GITT) measurements were conducted and calculated $D_{Li^+}$ was compared between the air-annealed LCFP (Fe³⁺ and resulted vacancies in Co/Fe M₂ sites) and pristine (Fe²⁺) LCFP. As shown in Figure 2-9(a)-(c), $D_{Li^+}$ for the air-annealed LCFP (Fe³⁺ giving vacancy in Co site) was higher in both charge and discharge compared to the pristine (Fe²⁺) especially in the high potential region [high state of charge (SOC) and low depth of discharge (DOD)], which was
consistent with the results of C-rate capability tests. Such results indicated that the creation of vacancies in M2 sites resulting from the oxidation/migration of Fe ions enhanced the Li\(^+\) diffusivity within LCFP crystal, unlike previous reports which suggested the enhancement of Li\(^+\) mobility due to the vacancies in Li (M1) sites\(^{16,21}\).

As shown from GITT measurement, the apparent \(D_{Li^+}\) was enhanced for the air-annealed LCFP (with a Fe\(^{3+}\) rich surface) compared with pristine LCFP. However, GITT analysis generally represents overall diffusion kinetics of active materials, thus, it is hard to distinguish between effects of charge transfer and diffusional properties. We made additional electrochemical impedance spectroscopy (EIS) experiments using symmetric cells\(^{26}\) on (a) the air-annealed LCFP (with a Fe\(^{3+}\) rich surface) and (b) pristine LCFP at two different SOCs, namely 0 and 70\% (middle range of second plateau as shown in Figure 2-8(b). Both the charge transfer and mass transport processes were improved for Fe\(^{3+}\)-rich LCFP: the relevant absolute impedance became roughly 1/10 for the charge transfer process and 1/5 for the diffusion process when moving from pristine LCFP to the air-annealed LCFP [Figure 2-10(a) and (b)].
Figure 2-8 (a) Constant-current charge/discharge curves of a half-cell consisting of Li/1M LiPF₆ EC:PC:DMC(vol. 1:1:3)/(air-annealed LCFP/MWCNT composite) at a 0.2C rate between 2.5 and 5.0 V. (b) Constant-current charge/discharge curves of a half-cell consisting of Li/1M LiPF₆ EC:PC:DMC(vol. 1:1:3)/(air-annealed LCFP/MWCNT composite) at a 0.2C rate between 4.3 and 5.0 V. (c) dQ/dV plots for the air-annealed LCFP/MWCNT composite from Figure 2-8(a). (d) Cycle performance for the composites at a 0.2C rate. (e) Cycle performances for the air-annealed LCFP/MWCNT composites of Figure 2-8(b). (f) Rate performance for the composites over the range 2.5-5.0 V.
Figure 2-9  Plots of Li diffusion coefficients vs. state of charge/discharge calculated from GITT curves during (a) charge and (b) discharge for the pristine and air-annealed LCFP. GITT was conducted with 0.1C (1C = 167 mAh g\(^{-1}\) per active material) for 20 min. and rest time for 1h in the potential range of between 4.3-5.0 V vs. Li/Li\(^+\). Before GITT measurements, a pre-cycling was conducted at 0.1C in the same potential range as GITT.

Figure 2-10  Impedance spectroscopy on (a) the air-annealed LCFP with Fe\(^{3+}\)-rich-surface and (b) pristine LCFP at two different SOCs, namely, 0 and 70% (middle range of second plateau). The measurement was made on symmetric cells comprising of both LCFP or LCFP (Fe\(^{3+}\)-rich) electrodes. Perturbation amplitude was ±10 mV (peak to peak). Frequency ranges was 10 mHz to 65 kHz.
2.3.4. Stability of LCP and LCFP crystal structure at different voltage range operation; 2.5 - 5.0 V and 4.3 - 5.0 V

HRTEM observation and XPS analysis of the C 1s energy level were performed on air-annealed LCP/MWCNT and LCFP/MWCNT composites during cycling to confirm the electrochemical behavior (Figure 2-11). HRTEM images of air-annealed iron-free LCP/MWCNT composites after 30 cycles between 2.5 and 5.0 V showed amorphization of LCP nanocrystals and solid-electrolyte-interface (SEI) production on the surface of LCP nanocrystals and MWCNTs [Figure 2-11(a)]. XPS measurements showed an increase of the peak intensity for carboxyl, carbonyl and alkoxy groups [Figure 2-11(e)] which evidenced the decomposition of the electrolyte. This suggested that these degradations were caused by unstable CoPO4, which reacted readily with an electrolyte. Normally, a stable SEI produced during charge (oxidation) should protect such CoPO4 from reacting with an electrolyte. However, SEI decomposition might occur during discharge from 5.0 to 2.5 V. Then, exposed CoPO4 may degrade by reaction with electrolyte, yielding new SEI upon subsequent charging back to 5.0 V. This new SEI obstructs the Li insertion/deinsertion and increases the resistivity. To prevent this, we restricted the voltage range to 4.3-5.0 V to ensure protection of the SEI. The clear difference was able to be seen both in TEM images and XPS spectra, as neither SEI production nor LCP amorphization were observed after several cycles in the “4.3 - 5.0 V” voltage range [Figure 2-11(b) and (f)]. In contrast, the air-annealed LCFP/MWCNT composite, exhibited no electrolyte decomposition even upon cycling between 2.5 and 5.0 V [Figure 2-11(c), (d), (g) and (h)] which confirmed that the Fe-rich surface layer contributed to stabilize the delithiated (Co0.8Fe0.2PO4) structure and prevent for electrolyte decomposition. Despite that, cycling the air-annealed LCFP/MWCNT composite between 2.5 and 5.0 V still resulted in decreasing capacity indicating the existence of another process. This phenomenon was similar to the reported one by Paolella et al. who reported a progressive capacity decay for LiFePO4 due to the mixing of Fe and Li cations as deduced from cell parameters evolution.27 Also, the cell volume deduced from lattice parameter refinement (Figure 2-12) increased with increasing number of cycles in agreement with a progressive Li-Co mixing in LCFP crystals. Differently, the refinement of the lattice parameters showed that the cell volume remained...
constant for the air-annealed LCFP operated within the high voltage range (4.3-5.0 V) to avoid the Fe$^{3+}$/Fe$^{2+}$ redox couple. Such results strongly supported the hypothesis that Fe$^{3+}$ and vacancies at M2 sites served to stabilize the LCFP crystal structure.
Figure 2-11  Higher-resolution TEM images of the air annealed (a), (b) LCP/MWCNT and (c), (d) LCFP/MWCNT composites after 30 cycles. XPS measurements of the air annealed (e), (f) LCP/MWCNT and (g), (h) LCFP/MWCNT composites after 1, 10 and 30 cycles. (a), (c), (e) and (g) are conducted in potential range between 2.5 and 5.0 V. (b), (d), (f) and (h) are conducted in potential range between 4.3 and 5.0 V.
Figure 2-12  Unit cell volumes of four different samples after charge and discharge up to 30 cycles; the air-annealed LCP/MWCNT and air-annealed LCFP/MWCNT composites at 2 different operation voltage ranges (2.5 - 5.0 V and 4.3 - 5.0 V). Each unit cell volume was calculated from the cell parameters obtained from corresponding XRD-pattern analysis.

The evolution of Co and Fe valence state along cycling has been determined by XAFS measurements. The X-ray absorption near edge structure (XANES) spectra of Co and Fe K-edge for the air-annealed LCFP/MWCNT composite before cycling and at cut off voltages of the two investigated voltage ranges of “2.5 - 5.0 V” and “4.3 - 5.0 V” are shown in Figure 2-13 while calculated average oxidation states for Co and Fe are reported in Table 2-3. In the air-annealed LCFP/MWCNT composite material before cycling, valence states of Co and Fe were +2.1 and +2.9, respectively, in good agreement with previous Mössbauer spectroscopy results [Figure 2-3(a)]. During cycling in the “2.5 - 5.0 V” voltage range, the Fe valence state changed between +2.3 and +3.0 at lower and upper cut-off voltages respectively and these values remained stable along cycles. The Co valence state at low cut off voltage was equal to +2.1 and remained stable along cycles while at 5.0 V at the end of the first charge it was equal to +2.8 and progressively decreased along cycles to reach +2.55 at the 30th charged state. During cycling in the “4.3 – 5.0 V” voltage range, Fe valence state, as expected, increased during the first charge from +2.9 in the sample before cycling up to +3. The valence state of +3 was maintained then whatever the voltage along cycles. For the Co atom, valence states were +2.1 and
+2.8 at 4.3 V and 5.0 V, respectively. These values were stable along cycles. This stable cycle performance confirmed the specific role of Fe$^{3+}$ which together with vacancies at M2 sites of LCFP effectively prevented irreversible changes in the crystal structure. This stabilizing effect added to the prevention of decomposition of the electrolyte during charge and discharge processes, resulted in stable cycle performance with improved rate performance for Fe substituted samples.

Based on the results of XRD, NPD analysis, Mössbauer, XANES and XPS studies, we proposed the schematic picture illustrated by Figure 2-14 for the structural changes occurring during cycling. Upon cycling, LCP as a reference material suffered from both structural degradation (Li-Co cation mixing) and SEI accumulation on the particle surface, while only the latter can be restrained by a high cut-off voltage operation within the range of 4.3 and 5.0 V [Figure 2-14(a)]. Fe$^{3+}$ was introduced as a partial substitute for Co in our material. It was observed that, upon air annealing, some of the introduced Fe$^{3+}$ cations migrated to the nanoparticle surface, producing vacancies at M2 sites. However, the vacancies disappeared during cycling between 2.5 and 5.0 V, due to the reduction of Fe$^{3+}$ into Fe$^{2+}$ at 3.5 V, resulting in a destabilization of the charged Co$_{0.8}$Fe$_{0.2}$PO$_4$ structure. In contrast, the Fe$^{3+}$ surface-rich structure with vacancies at M2 sites and intact SEI remained stable as long as the charge/discharge potential was confined between 4.3 and 5.0 V to avoid redox reactions of Fe$^{2+}$/Fe$^{3+}$[Figure 2-14(b)]. This structure resulted in stable cycle performance.
Figure 2-13  XAFS measurements on a pellet of (a)-(b) air-annealed LCFP/MWCNT composite and (c)-(f) half-cell consisting of Li/1M LiPF$_6$ EC:PC:DMC(vol. 1:1:3)/(air annealed LCFP/MWCNT composite). The XANES spectra at the Co K-edge of the composite are shown in (a), (c) and (e). The XANES spectra at the Fe K-edge of the composite are shown in (b), (d) and (f). (c) and (d) are conducted in potential range between 2.5 and 5.0 V. (e) and (f) are conducted in potential range between 4.3 and 5.0 V.

Table 2-3  Valence states of Co and Fe of air annealed LCFP/MWCNT composite obtained from XANES spectra shown in Figure 2-13

<table>
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<tr>
<th>Cycle No.</th>
<th>Co valence state</th>
<th>Fe valence state</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Before charge/dischARGE</td>
<td>Discharge</td>
</tr>
<tr>
<td>2.5-5.0 V</td>
<td>+2.10 +2.11 +2.78</td>
<td>+2.82 +2.33 +3.01</td>
</tr>
<tr>
<td>10$^{th}$</td>
<td>+2.11 +2.11 +2.78</td>
<td>+2.33 +2.00 +3.01</td>
</tr>
<tr>
<td>30$^{th}$</td>
<td>+2.08 +2.09 +2.80</td>
<td>+2.55 +2.36 +3.02</td>
</tr>
<tr>
<td>4.3-5.0 V</td>
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<td>+3.02 +3.02 +3.02</td>
</tr>
<tr>
<td>10$^{th}$</td>
<td>+2.11 +2.11 +2.78</td>
<td>+3.02 +3.02 +3.02</td>
</tr>
<tr>
<td>30$^{th}$</td>
<td>+2.09 +2.09 +2.80</td>
<td>+3.01 +3.01 +3.01</td>
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</table>
Figure 2-14  Structural changes of synthesized (a) LCP and (b) LCFP during charge and discharge.
2.4. Conclusions

In conclusion, a detailed understanding of the mechanism of LCP structure stabilization by Fe$^{3+}$ substitution suggested that the Fe$^{3+}$-rich phase formed on the LCP surface played a significant role in yielding stable charge-discharge performance. The oxidation of Fe$^{2+}$ into Fe$^{3+}$ during air annealing of the pristine LCFP resulted in diffusion of Fe ions to the surface due to the increased repulsion between Fe$^{3+}$ and Co$^{2+}$. The Fe$^{3+}$-rich phase on the surface stabilized the unstable delithiated phase of $(\text{Li}_{x}\text{Fe}_{0.02}\text{M}_{1}\text{Fe}_{0.76}\text{Co}_{0.13}\text{Fe}_{0.11})\text{PO}_{4}$ ($x << 1$), preventing both the crystal structure degradation and continuous SEI formation on the LCFP nanoparticle surface. The phase stabilization yielded excellent cyclability, with 85% capacity retention over 5,000 cycles at 1C and 96% capacity retention over 1,000 cycles even at a slow C-rate of 0.2C. The importance of Fe$^{3+}$ retention in the crystal structure, which required to prevent Fe$^{3+}$ reduction to Fe$^{2+}$ around 3.5 V vs. Li/Li$^+$, was demonstrated by a combination of XRD and XAFS analysis on samples with and without operation-voltage extending below 3.5 V vs. Li. Meanwhile, different from previous reports, it was found that the vacancies on Co/Fe M2 sites improved the overall electrochemical performances such as the capacity and C-rate capability, thanks to the enhancement of Li$^+$ diffusivity within LCFP crystals. By demonstrating the existence of the Fe-rich phase on LCFP nanoparticles and its critical impact on electrochemical performance, this study may open the way to the design of stable 5V cathode materials via fine-tuning of surface phenomena.

2.5. References


Chapter 3

The origin of stability and high $\text{Co}^{2+/3+}$ redox utilization for FePO$_4$-coated LiCo$_{0.90}$Ti$_{0.05}$PO$_4$ / MWCNT nanocomposites for 5V class lithium ion batteries
3.1. **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 LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (4.5 V vs. Li/Li$^+$), LiCoO$_2$ (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$_x$CoPO$_4$, x << 1).$^6$ Attempts to improve cycle performance to inhibit the undesirable decomposition of the electrolyte at delithiated Li$_x$CoPO$_4$ (x << 1) were conducted by adding protective coating layers of carbon, AlF$_3$, or 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$_x$CoPO$_4$ 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 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 (LiCo$_{0.8}$Fe$_{0.2}$PO$_4$, 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 enhanced the Li$^+$ diffusivity in LCFP crystals and decreased 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 each of these factors was clearly identified in our previous work, the interrelations among them were left unexplored, as were optimal recipes for material fabrication and device configuration.

In this work, we extended our work in several ways, clarifying the mechanisms responsible for the improved performance of our LCFP and exploiting this understanding to optimize material design and fabrication, ultimately yielding cells with improved performances. A key breakthrough enabling this progress was an improved understanding of the distinct mechanisms governing the relevant surface and bulk phenomena and of their mutual interactions. In particular, having established in our previous work that a primary role of Fe dopants in UC-processed LCP nanoparticles was to diffuse outward to form Fe-rich protective layer at the nanoparticle surface, 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 reported$^{11}$ as confirmed by X-ray photoelectron spectroscopy (XPS) with a lower overall dose of Fe, reducing mass and thereby improving specific capacity. In addition, we showed that the UC step was crucial for maximizing effective surface area, improving several aspects of electrochemical performance. Having clarified this surface-related behavior, we turned next to a consideration of bulk phenomena. As replacements for the Fe dopants, we considered doping with different elements and used X-ray and neutron-diffraction analysis to study the effect of dopant concentration on the formation of vacancies in the crystal structure. We found that among various tested elements Ti$^{4+}$ was the most effective dopant, and we suggested possible explanations for this finding. Finally, Our updated techniques yielded improvement of the performance relative to that of LCFP (95 mAh g$^{-1}$),$^{11}$ increasing specific capacity to 116 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—namely, retaining M2-site vacancies and stabilizing the LCP surface layer. These strategies may pave the way toward practical use of LCP in 5V-class Li-ion batteries.

3.2. Experimental

3.2.1. Materials

Co(CH₃COO)₂ • 4H₂O (>99%, Wako Pure Chemicals), Fe(CH₃COO)₂ (>99%, Sigma-Aldrich Corp.), CH₃COOLi (>98.0%, Wako Pure Chemicals), Ti₂(SO₄)₃ aq. (45% in H₂SO₄, Sigma-Aldrich), and H₃PO₄ (>85.0%, Wako Pure Chemicals) were used to prepare LCP, LCFP, LiCo₀.₉Ti₀.₀₅PO₄ (LCTP), and FP-coated compounds. Citric acid (>99.5%, Sigma-Aldrich Corp.) was used as a chelating agent. Multiwalled carbon nanotubes (MWCNTs) with a specific surface area of 240 m² g⁻¹ were used for the preparation of carbon composite. Distilled water (17 MΩ cm) was used a medium for the entire preparation scheme.

3.2.2. Preparation of LCP/MWCNT and LCTP/MWCNT composites under UC treatment

LCP/MWCNT and LCFP/MWCNT composites were synthesized via UC treatment as previously reported. Similar scheme of LCP was applied to synthesize LCTP/MWCNT composite; First, two kinds of solutions (solution A and B) were prepared. The solution A was composed of 0.4000 g of MWCNT and 0.6714 g of H₃PO₄ (1.0 eq. for LCTP) mixed in 50 ml of ultrapure water. The solution B was composed of 1.3432 g of Co(CH₃COO)₂ • 4H₂O (0.9 eq.), 0.1265 g of Ti₂(SO₄)₃ (0.05 eq.), 0.3994 g of CH₃COOLi (1.0 eq.) and 1.1454 g of citric acid (1.0 eq.) dissolved in 20 ml of ultrapure water. The solution A was subjected to the UC treatment at 80˚C for 5 min before and after the addition of the solution B. The UC-treated sol was further dried at 130 ˚C under vacuum for 12 h. The obtained powder made of LCTP precursor and MWCNT 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 650 °C under N\textsubscript{2} flow (RT to 650 °C in 3 min, dwell for 30 min, 20 min to cooling to RT) to form the LCTP/MWCNT composite. The pristine LCTP/MWCNT composite was further annealed at 350 °C for 3 h under air in order to oxidize Ti\textsuperscript{3+} into Ti\textsuperscript{4+} and to obtain vacancy in LCTP crystals without incinerating MWCNTs.

### 3.2.3. Preparation of FP-coated LCP/MWCNT and LCTP/MWCNT composites

In case of FP coating, another two kinds of solutions (solution C and D) were prepared. The solution C was composed of 0.2500 g of synthesized LCP/MWCNT or LCTP/MWCNT and 0.0183 g of H\textsubscript{3}PO\textsubscript{4} (1.0 eq. for FP) mixed in 10 ml of ultrapure water. The solution D was composed of 0.0276 g of Fe(CH\textsubscript{3}COO)\textsubscript{2} (0.05 eq.), 0.0107 g of CH\textsubscript{3}COOLi (1.0 eq.) and 0.0306 g of citric acid (1.0 eq.) dissolved in 10 ml of ultrapure water. Mixture of solution C and D 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. Then, same annealing process was applied to dried powder to obtain FP-coated samples. The obtained powder was pre-annealed at 350 °C in air for 1 h, then left to cool to RT. The pre-annealed powder was then fast annealed at 700 °C under N\textsubscript{2} flow (RT to 700°C in 3 min, dwell for 5 min, 20 min to cooling to RT). The pristine LFP-coated composite was further annealed at 350 °C for 3 h under air in order to form FP-coated samples.

### 3.2.4. Physicochemical characterizations of LCP/MWCNT, LCTP/MWCNT, FP-coated LCP/MWCNT, and FP-coated LCTP/MWCNT composites

Structure analysis on LCP/MWCNT, LCTP/MWCNT, FP-coated LCP/MWCNT, and FP-coated LCTP/MWCNT composites were performed by X-ray diffraction [XRD, Smart-lab (Rigaku)] using Cu K\textsubscript{\alpha} radiation (\lambda=1.54 Å). XRD patterns were recorded in the 10°- 90° 2θ range at a scan speed of 0.0033° s\textsuperscript{-1}. XRD patterns were recorded in the 10°- 60° 2θ range at a scan speed of 0.167° s\textsuperscript{-1}. Time-of-flight neutron powder diffraction (NPD) measurements were performed at the iMATERIA (BL20) facility of the Japan Photon Accelerator Research Complex (J-PARC, Ibaraki, Japan) to obtain NPD patterns.
corresponding to 0.5-4.8 Å in d-spacing. The carbon contents of composites were determined by thermogravimetric analysis under a synthetic air (O₂: 20%, N₂: 80%) using a thermogravimetric/differential thermal analyzer (TG/DTA, Seiko Instruments TG/DTA6300). X-ray photoelectron spectroscopy [XPS, JPS-9200 (JEOL)] was carried out using Mg X-ray source. X-ray adsorption fine structure (XAFS) measurements at the Co, Fe, and Ti 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 Co²⁺ (LiCoPO₄ bulk sample), Co³⁺ (Cobalt acetylacetonate), Fe²⁺ (LiFePO₄ bulk sample) and Fe³⁺ (FePO₄ bulk sample oxidized by the chemical method using NO₂BF₄).

3.2.5. Electrochemical characterization of LCP/MWCNT, LCTP/MWCNT, FP-coated LCP/MWCNT, and FP-coated LCTP/MWCNT composites

Half-cells were assembled using a negative Li metal electrode, a positive LCP/MWCNT, LCTP/MWCNT, FP-coated LCP/MWCNT, and FP-coated LCTP/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 (LiPF₆). Positive electrode was prepared by mixing 90 wt.% of the composite and 10 wt.% 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 loading mass of the composite was 1.4 mg cm⁻² on etched Al current collector (1.54 cm²). 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 0.2C-rate, assuming that 1C-rate equals 167 mA g⁻¹. The cut-off current density at the constant-voltage mode was 8.35 mA g⁻¹ (0.05C). Before charge–discharge tests, a pre-cycling was conducted at 0.1C in the same potential range as charge–discharge tests.
3.3. Results and discussion

3.3.1. Structural determination and surface composition

In the previous work,\textsuperscript{11} we considered Fe-doped LCP (LCFP), which brought about two key features to LCP: (i) a formation of protecting Fe\textsuperscript{3+}-rich surface layer to improve cyclability of LCP, and (ii) a creation of vacancies in M2 (Co\textsuperscript{2+}) sites to improve the Li diffusivity in LCP crystals. In this study, we attempted to attain same effect of Fe\textsuperscript{3+}-rich surface layer but by coating LCP with FP instead of Fe-doping in order to minimize Fe\textsuperscript{3+} amount and thus sacrifice of the capacity.

To determine the crystal structures of for all four samples—uncoated LCP, uncoated LCTP, FP-coated LCP, and FP-coated LCTP—, XRD were recorded for various samples as shown in Figure 3-1. First, all main diffraction peaks can be indexed using an olivine-type structure (S.G. Pnma LiCoPO\textsubscript{4}: JCPDS card no. 85-0002). Apart low-intensity peaks attributable to MWCNT and Co\textsubscript{3}O\textsubscript{4}, no other peaks were detected, indicating successful synthesis of crystalline LCP and of all other LCP derivatives synthesized in this study including LCTP, FP-coated LCP, and FP-coated LCTP. The evaluated ratios of Co\textsubscript{3}O\textsubscript{4} in the different samples [Table 3-1(a)] showed that the Ti doping was effective to suppress the formation of Co\textsubscript{3}O\textsubscript{4} phase (almost 0%), while the FP-coating on LCP also contributed to decrease such impurity phase (6%) possibly due to the air annealing process. For LCTP with or without FP-coating, no traces of other possible impurities such as TiO\textsubscript{2}, LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} and Ti\textsubscript{2}O\textsubscript{3} were detected. Meanwhile, the positions of some Bragg peaks being shifted by Ti-substitution or FP-coating, lattice parameters were refined from both XRD [Table 3-1(a)] and NPD [Table 3-1(b)] patterns. The refined lattice parameters were consistent and showed that the 0.05 Ti substitution in LCP induced little changes in the lattice parameters. In contrast to uncoated LCP and LCTP, lattice parameters for FP-coated samples changed in all directions: the $a$ and $b$ parameters decreased, while $c$ increased. This indicated that FP not only coated the surface of crystals but also partially dissolved into the bulk crystal structure, which may enhance the compatibility between the FP coating (surface) and the LCP or LCTP matrix (bulk). Such speculation was further supported by the NPD analysis which confirmed, in FP coated samples, the presence of Fe ions in the M2 sites [Table 3-1(c)]. Refinement of site occupancies led also to suggest
presence of vacancies for all samples apart uncoated LCP once matching perfectly the calculated values considering Ti\(^{4+}\) and/or Fe\(^{3+}\) substitution. It was consistent with our previous report\(^{11}\) that the vacancies lied in M2 (Co\(^{2+}\)) sites, unlike other reports which suggest the creation of vacancies in M1 (Li\(^{+}\)) sites. The highest amount of vacancies was obtained for the FP-coated LCTP which combined both effect of Ti\(^{4+}\) and Fe\(^{3+}\) substitution for Co\(^{2+}\).

Figure 3-1 (a) XRD patterns for the four composites: LCP, FP-coated LCP, LCTP, and FP-coated LCTP/MWCNT composites. (b) NPD patterns for LCP, FP-coated LCP, LCTP, and FP-coated LCTP/MWCNT composites. Grey area corresponds to the noise related to synchrotron measurements, which was not taken account for any fitting.
Table 3-1  Lattice parameters calculated by (a) XRD patterns and (b) NPD patterns for the four composites: LCP, FP-coated LCP, LCTP, and FP-coated LCTP/MWCNT composites. (c) The results of Rietveld refinement of NPD patterns for the four composites.

(a) Lattice parameters calculated by XRD patterns

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<tr>
<th>Sample</th>
<th>Space group</th>
<th>a / Å</th>
<th>b / Å</th>
<th>c / Å</th>
<th>V / Å³</th>
<th>CoOx ratio calculated by XRD / %</th>
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<tbody>
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(b) Lattice parameters calculated by NPD patterns

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(c) Rietveld refinement results of NPD patterns

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<td>1.0016(7)</td>
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</tr>
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<th>z/c</th>
<th>B_m</th>
<th>Occupancy</th>
</tr>
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<td>0.250.9922(3)</td>
<td>1.90(4)</td>
</tr>
<tr>
<td></td>
<td>Ti⁴⁺</td>
<td>4c</td>
<td>0.2761(1)</td>
<td>0.250.9922(3)</td>
<td>1.90(4)</td>
</tr>
<tr>
<td></td>
<td>Fe²⁺</td>
<td>4c</td>
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<td>0.250.9922(3)</td>
<td>1.90(4)</td>
</tr>
<tr>
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<td>4c</td>
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<td>0.250.4182(1)</td>
<td>0.86(1)</td>
</tr>
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<td></td>
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<td>4c</td>
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<td>0.250.7469(1)</td>
<td>0.79(1)</td>
</tr>
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<td></td>
<td>O</td>
<td>4c</td>
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<td>0.250.2022(1)</td>
<td>0.86(1)</td>
</tr>
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<td>8d</td>
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<td>0.0468(6)</td>
<td>0.2813(8)</td>
</tr>
<tr>
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<td></td>
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XPS analyses of Co 2p\textsubscript{3/2}, Ti 2p\textsubscript{3/2}, and Fe 2p\textsubscript{3/2} were performed on the LCP or LCTP particles with or without FP coating, subjected to different Ar ion etching duration to screen the evolution of the composition from the surface toward the bulk of the corresponding particles. The evolutions of the XPS spectra collected for the different samples and at different etching time (Figure 3-2) confirmed the evolution of the composition between the surface and the bulk of the particles. The Co/Ti, Co/Fe, and Co/Ti/Fe ratios were calculated by computing the areas under the Co 2p\textsubscript{3/2}, Ti 2p\textsubscript{3/2}, and Fe 2p\textsubscript{3/2} peaks and reported in the Figure 3-3. Examination of the results for LCTP particles showed that the distribution of Co and Ti at the surface (Co/Ti = 88/12) slightly differed from that in the bulk (Co/Ti = 93/7), suggesting the existence of a Ti-rich phase on the surface of LCP. The FP coating drastically changed the surface composition (Co/Fe = 61/39, Co/Ti/Fe = 50/15/35) from the bulk composition (Co/Fe = 77/23, Co/Ti/Fe = 62/10/28), indicating the successful formation of an Fe\textsuperscript{3+}-rich phase on the LCP or LCTP surface, as we previously reported for Fe\textsuperscript{3+}-substituted LCP (LCFP).\textsuperscript{11}
Figure 3-2  Consecutive XPS measurements with data acquisition at 5 s intervals during 0–30 s Ar ion etching (2 keV). Depth profiles of Co, Fe, and Ti for (a) FP-coated LCP, (b) LCTP, and (c) FP-coated LCTP/MWCNT composites.
Figure 3-3  Consecutive XPS measurements with data acquisition at 5 s intervals during 0–30 s Ar ion etching (2 keV). Atomic ratio of Co, Fe, and Ti calculated from depth profiles (see Figure 3-2) for (a) FP-coated LCP, (b) LCTP, and (c) FP-coated LCTP / MWCNT composites.

High-resolution TEM images observed on four composites indicated that all composites contain nanocrystals of \( ca. \) 100 nm highly dispersed within the MWCNT matrix [Figure 3-4(a), (c), (e), and (g)]. Magnified images for the LCP/MWCNT and LCTP/MWCNT composites showed a highly crystalline bulk part of LCP or LCTP surrounded by amorphous phase [Figure 3-4(b) and (f)]. The crystalline bulk part showed clear lattice fringes with interplanar lattice distances of 4.3 and 3.5 Å corresponding to the (101) and (111) planes of the olivine structure, respectively. Contrary to the uncoated LCP and LCTP, the most of HRTEM images for FP-coated LCP or LCTP showed clear lattice fringes even close to the edge parts of the nanocrystalline. The interplanar lattice distance observed in Figure 3-4(d) and (h) are 2.5 and 5.1 Å, which well agreed with the (311) and (200) planes of the olivine structure, respectively, indicating the successful FP-coating and partial dissolution of Fe\(^{3+}\) into the LCP or LCTP crystalline as discussed in the previous paragraphs. The TG/DTA curves of the LCP/MWCNT or LCTP/MWCNT with or without FP-coating are shown in Figure 3-5. The calculated weight ratios of MWCNT in composites—LCP/MWCNT, LCTP/MWCNT, FP-coated LCP/MWCNT, and FP-coated LCTP/MWCNT—were 27, 30, 23, 25 wt.%, respectively.
Figure 3-4  HRTEM images for (a), (b) LCP, (c), (d) FP-coated LCP, (e), (f) LCTP, and (g), (h) FP-coated LCTP/MWCNT composites.
3.3.2. Surface phenomena: Formation of Fe$^{3+}$-rich layer

Charge discharge curves for LCP, LCFP, and FP-coated LCP within the restricted voltage range of 4.3-5.0 V vs. Li during 100 cycles are shown in Figure 3-6. 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, see Figure 3-7). Figure 3-6(a) showed LCP curves with two plateau regions, corresponding to two redox reactions: i) LiCoPO$_4$ $\leftrightarrow$ Li$_{0.7}$CoPO$_4$ + 0.3Li$^+$ + 0.3e$^-$, and ii) Li$_{0.7}$CoPO$_4$ $\leftrightarrow$ CoPO$_4$ + 0.7Li$^+$ + 0.7e$^-$; this agreed with reports of previous studies$^{12}$. The exhibited discharge capacity at the 1$^{st}$ cycle was 76 mAh g$^{-1}$, which corresponded 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 100$^{th}$ cycle. Contrary to LCP, both LCFP and FP-coated LCP showed excellent stable cycling performances as seen in Figure 3-6(b) and (c). Here, the amount of FP-coating on LCP/MWCNT was optimized to be 10 wt.% [Figure 3-6(d)]: 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/MWNCT equaled to be that of LiCo$_{0.87}$Fe$_{0.13}$PO$_4$/MWCNT, meaning ca. 10% increase of active Co compared to the LCFP (LiCo$_{0.8}$Fe$_{0.2}$PO$_4$), which well corresponded to an increase in exhibited capacity [10 wt.% FP coated LCP/MWNCT: 106 mAh g$^{-1}$, LCFP/MWNCT: 95 mAh g$^{-1}$, 73% and
71% of the efficiency against the theoretical capacity of 10 wt.% FP coated LCP/MWNCT (145 mAh g\(^{-1}\)) and LCFP/MWNCT (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 AlPO\(_4\) coating was ineffective on cyclability only with 52% of capacity retention and even exhibited smaller capacity compared to the FP-coating. Meanwhile, the LFP-coating on LCP in previous report\(^{13}\) was even detrimental to its cycle performance. These facts highlighted 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 Figure 3-8. 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 was 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 was probably due to the large submicron size of LCP particles, where the ratio of its surface to the bulk part of particles was much smaller compared to the LCP nanoparticles within the composite. These results showed that the synthesis of LCP using MWCNT brought 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.
Figure 3-6 Charge discharge curves of (a) LCP, (b) LCFP, (c) FP coated LCP/MWCNT cathodes in 1 M LiPF$_6$ in EC+PC+DMC (1:1:3 in vol.) operated at CC-CV charge (0.2C-rate) and CC discharge (0.2C-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, AlPO$_4$ coated LCP, uncoated LCP, and LCFP/MWCNT cathodes at a 0.2C-rate.
Figure 3-7 Charge discharge curves of MWCNTs.

Figure 3-8 Charge discharge curves of (a) LCP bulk (supplied from Toshima Manufacturing), (b) 10 wt.% FP coated LCP bulk cathodes in 1 M LiPF$_6$ in EC+PC+DMC (1:1:3 in vol.) operated at CC-CV charge (0.2C-rate) and CC discharge (0.2C-rate). Confined operation voltage: 4.3-5.0 V vs. Li was applied, the protocol of which has been discovered in our previous paper. (c) Capacity plots against cycle number for a Li metal half-cell using 10 wt.% FP-coated LCP/MWCNT composite, 10 wt.% FP-coated LCP bulk, uncoated LCP/MWCNT composite, and uncoated LCP bulk cathodes at a 0.2C-rate.

3.3.3. Bulk phenomena: Effect of M2 site vacancies

As evidenced in the discussion of section 3.3.2, it was demonstrated that the 10 wt.% of FP-coating can stabilize the redox reaction of LCP similar to the Fe-substituted LCP reported in our previous work. We then considered another substitution species such as Ti, Sn, and V to yield alicovalent-substituted LCP [LiCo$_{1-x}$(Ti, Sn, V)$_x$PO$_4$] to further
enhance the electrochemical properties of bulk LCP. These three atoms were chosen as a multivalent element, which can exist at valence states equal to or higher than that of Fe (namely, 3+), allowing creation of vacancies in the bulk LCP crystal. Among tested samples with different dopant concentrations, the highest discharge capacity of 102 mAh g⁻¹ at the initial cycle was obtained for Ti with \( x = 5 \) at.\% (see Figure 3-9). This composition was then selected for further investigation. As shown in Figure 3-10, the capacity retention for such LiCo₀.₉₀Ti₀.₀₅PO₄ (LCTP) fell to be 72% of the initial capacity after 100 cycles, which was better than uncoated LCP but failed to be as stable as Fe-substituted or FP-coated samples. Having identified LCTP as a material offering high capacity but limited cycle performance, we attempted to improve its cyclability by FP-coating. As shown in Figure 3-10, FP coating also led in that case to a drastic improvement of the capacity retention which reached 100% over 100 cycles with the highest capacity of 116 mAh g⁻¹ among tested samples. Comparison of charge/discharge curves for LCP and LCTP with and without FP coating indicated that the surface protection of LCP/LCTP particles was the dominant mechanism responsible for stable cycle performance, and the creation of vacancies with an aliovalent substitution, especially for Ti, was effective to enhance the capacity related to Co²⁺/Co³⁺, which will be discussed in the following sections.

![Figure 3-9](image)

**Figure 3-9**  (a) Discharge curves of Ti⁴⁺, V⁵⁺, and Sn⁴⁺ substituted LCP/MWCNT composites. Confined operation voltage: 4.3-5.0 V vs. Li was applied. (b) Discharge curves of x wt.% (x = 0.03, 0.05, 0.07, and 0.10) Ti⁴⁺ substituted LCP/MWCNT composites. Confined operation voltage: 2.5-5.0 V vs. Li was applied.
Figure 3-10  Charge discharge curves of (a) LCTP and (b) FP coated LCTP/MWCNT cathodes in 1 M LiPF₆ in EC+PC+DMC (1:1:3 in vol.) operated at CC-CV charge (0.2C-rate) and CC discharge (0.2C-rate). Confined operation voltage: 4.3-5.0 V vs. Li was applied, the protocol of which has been discovered in our previous work. (c) Capacity plots against cycle number for a Li metal half-cell using composites at a 0.2C-rate.

3.3.4. Valence states changes of Co and Fe before and after cycling

To see the effect of FP-coating and Ti substitution on the redox state of Co and Fe, in situ XAFS measurements were conducted for the four different samples at 1st and 50th cycle. The X-ray absorption near edge structure (XANES) spectra of Co, Fe and Ti K-edge for the LCP/MWCNT or LCTP/MWCNT composites with or without FP-coating are shown in Figure 3-11. 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 remained identical over 2nd cycle with 99% capacity retention. The valence states of Co and Fe in the composite were determined by deconvolving the spectra using the contributions of Co²⁺, Co³⁺, Fe²⁺ and Fe³⁺. As shown in Table 3-2, different Co valence states were determined for the four as-prepared electrodes, where those in LCTP samples correspond to Co = +2 regardless of FP-coating, while LCP samples with and without FP-coating showed Co = +2.06 and +2.13, respectively. Interestingly, the difference of Co valence states between uncoated LCP and LCTP, which equaled to 0.13, cannot be simply explained by the different amounts of Co₃O₄ (average valence state Co = +2.66) impurity phase evaluated
from the XRD patterns fitting (10%, see Table 3-1). Although the explanation of such difference was still unspecified, a role of Ti and generated vacancies can be suggested to favor the stabilization of Co in electrochemically active +2 valence state leading to increased capacity compared to samples with already some Co in inactive +3 valence state. Along the 1st cycle, at the charged state, the Co valence states increased, and reached much higher values for FP-coated samples (+2.82 - +2.85) compared to uncoated ones (+2.66 - +2.67). This indicated an enhancement of kinetics in Co redox (Li$_4$CoPO$_4$ or Li$_x$Co$_{0.9}$Ti$_{0.05}$PO$_4$, 0<x<1) thanks to the FP-coating, which was well consistent with the obtained galvanostatic intermittent titration technique (GITT) measurements plots (Figure 3-12). The comparison of the Co valence state at charged state along cycles showed that after 50 cycles FP coated samples were stable while uncoated ones showed a clear decrease in agreement with already discussed capacity retention capabilities. Ex-situ XRD analysis (Figure 3-13) supported such stability of FP-coated samples indicating that the unit cell volume for coated samples remained constant after 50 cycles, while the one for uncoated samples increased. This increase suggested the existence of a progressive cation mixing in uncoated LCP or LCTP crystals, accompanied by the decay of crystal structure as observed in TEM images after cycling (Figure 3-14). Combining the XAFS analysis with XPS and results obtained in our previous report, the surface Fe$^{3+}$ enrichment brought about the stability and kinetic enhancement of the delithiated phase, leading to excellent long term cyclability, while Ti$^{4+}$-substitution created the vacancies which contributed to the higher utilization of Co in LCTP crystals.
Figure 3-11  Co-K XANES spectra for (a) LCP, (b) FP-coated LCP, (c) LCTP, and (d) FP-coated LCTP/MWCNT composites. Fe-K XANES spectra for (e) FP-coated LCP and (f) FP-coated LCTP/MWCNT composites. Ti-K XANES spectra for (g) LCTP and (h) FP-coated LCTP/MWCNT composites.

Table 3-2 Formal valence number of Co and Fe evaluated from XANES spectra for the half-cells consisting of Li/1M LiPF$_6$ EC:PC:DMC(vol. 1:1:3)/composite at 1$^{st}$ and 50$^{th}$ cycles.

<table>
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<th>Cycle No.</th>
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<th>Co valence state</th>
<th>Fe valence state</th>
<th>Co$_{3+x}$ ratio calculated by XAFS / %</th>
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<td>LCP/MWCNT</td>
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<td>+2.13</td>
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<td>+2.47</td>
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<td>10 wt.% FP coated LCP/MWCNT</td>
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<td>+2.85</td>
<td>0.79</td>
<td>+2.76</td>
</tr>
<tr>
<td></td>
<td>50$^{th}$</td>
<td>+2.06</td>
<td>+2.85*</td>
<td>0.79</td>
<td>+3.02</td>
</tr>
<tr>
<td>LCTP/MWCNT</td>
<td>1$^{st}$</td>
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<td></td>
</tr>
<tr>
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<td>+2.57</td>
<td>0.54</td>
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</tr>
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<td>+2.82</td>
<td>0.82</td>
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<tr>
<td></td>
<td>50$^{th}$</td>
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<td>+2.81</td>
<td>0.81</td>
<td>+2.93</td>
</tr>
</tbody>
</table>

*Value corresponds to 10$^{th}$ cycle
Figure 3-12  GITT polarization curves for (a) LCP, (b) FP-coated LCP, (c) LCTP, and (d) FP-coated LCTP. GITT was conducted with 0.1 C (1C = 167 mAh g\(^{-1}\) per active material) for 20 min. and rest time for 1 h in the potential range of between 4.3-5.0 V vs. Li/Li\(^{+}\). Before GITT measurements, a pre-cycling was conducted at 0.1C in the same potential range as GITT.

Figure 3-13  Calculated unit cell volumes from XRD patterns of pristine and 50\(^{th}\) cycled samples for LCP, FP-coated LCP, LCTP, and FP-coated LCTP/MWCNT composites.
Summarizing and combining results of the different sections, we may reach to the following conclusions illustrated in the Figure 3-15. The FP-coating on LCP samples brought about the formation of Fe$^{3+}$-rich surface, which prevented an irreversible crystal structure change and SEI production during cycling, resulting in the stable cycle performance. At the same time, partially-dissolved Fe into LCP structure created vacancies in M2(Co$^{2+}$) sites, which contributed to the enhancement of electrochemical characteristics such as Li$^+$ mobility. Doping with Ti$^{4+}$ allowed, by charge compensation mechanism, mastering the creation of vacancies in M2(Co$^{2+}$) sites together with an unexpected phenomenon which consisted in the stabilization of Co in 2+ valence state in the pristine material and resulted in the enhancement of exhibited capacity. Like for Fe
doped LCFP sample, a partial migration of Ti toward the surface of the particle was also evidenced yet, unlike "Fe$^{3+}$-enrichment", the effect of such "Ti$^{4+}$-enrichment" was not enough to stabilize the delithiated phase of LCTP. Nevertheless, the combination of those two, FP-coating and Ti$^{4+}$-substitution, brought about the stable cycling with the high Co utilization.

![Diagram](https://via.placeholder.com/150)

**Figure 3-15  Role of FP-coating and Ti$^{4+}$-substitution.**

### 3.4. Conclusions

In conclusion, highly-dispersed 10 wt.% FP-coated LCP and its aliovalent-substitution, LCTP nanocrystals were successfully synthesized within the MWCNT via our original UC process. The 10 wt.% FP-coated LCP and LCTP materials showed a higher discharge capacity than the previously-reported uc-LCP and the uc-LCFP without sacrificing its cycle performance (99% of capacity retention at 100$^{th}$ cycle). Combination of XRD, NPD, XPS, and XAFS analyses suggested that (i) Ti$^{4+}$-substitution increased the utilization of Co redox (capacity increase) in LCP crystals by suppressing the Co$_3$O$_4$ formation and creating the vacancies in M2(Co$^{2+}$) sites, and (ii) the FP-coating prevented an irreversible crystal structure change and SEI production during cycling, resulting in the stable cycle performance. Our finding may offer new idea of retaining M2-site vacancies and crystal-structure-matched surface coating—where the crystal structure between the coating
material and the matrix is identical—to stabilize the cycling performance without unnecessarily decreasing capacity of not only LCP but also other high-voltage cathode materials.

3.5. References


Chapter 4

Prolonged Cycle Life for
Li$_4$Ti$_5$O$_{12}$/[Li$_3$V$_2$(PO$_4$)$_3$/Multiwalled Carbon
Nanotubes] Full Cell Configuration “SuperRedox
Capacitor” via Electrochemical Preconditioning
4.1. Introduction

Electrical energy storage devices (EESDs), in conjunction with technologies such as electric vehicles and renewable power sources, are crucial tools for efficient utilization of electric power in sustainable societies. The central challenge in the design of EESDs is to maximize energy density and power density while ensuring long lifetimes and safe operation. Perhaps the most famous EESD is the lithium-ion battery (LIB); although the current research and development for LIBs are mainly focused on targeting high energy and power densities, their disturbing propensity to ignite or explode poses serious challenges of safety and reliability. In contrast, electrochemical capacitors, and specifically supercapacitors (SCs), are safe and long-lived devices with high power densities but low energy densities due to limitations on capacity and operating voltage imposed by their charge-storage mechanism, which involves ionic adsorption/desorption on the surface of activated carbon (AC) electrodes. Thus, the challenge of increasing the energy density of SCs is an active topic of current research. One promising strategy is the design of hybrid supercapacitors, which combine an AC electrode with an electrode made from a high-capacity faradic (pseudocapacitive or battery-like) material such as lithium titanate (Li$_4$Ti$_5$O$_{12}$, LTO). Efforts to synthesize nanoscale particles of LTO and its composites have dramatically increased the power (C-rate) capability of LTO electrodes, enabling operating speeds comparable to those of AC electrodes (> 300 C-rate). In particular, in previous work we fabricated nano-LTO//AC hybrid capacitors—which we term Nanohybrid Capacitors (NHCs)—which offer the outstanding safety, cycle performance (>10,000 cycles), and power density (6 kW L$^{-1}$ at charge/discharge rates of 300 C or above) of SCs, but with high energy densities on the order of 30 Wh L$^{-1}$, an 3-fold improvement over SCs. Still, the low volumetric energy density of AC positive electrodes (< 40 mAh cm$^{-3}$) continues to limit the volumetric energy density of such hybrid capacitors. This suggests the possibility of dramatically increasing volumetric energy density by replacing the AC positive electrode with an electrode made from battery materials and treated to facilitate ultra-high-speed operation. Such cell configuration offers tantalizing possibilities for realizing a new generation of energy-storage devices, called SuperRedox Capacitors (SRCs) in this thesis that combine the energy densities of LIBs with the high-speed charge/discharge capability of
supercapacitors.

Lithium vanadium phosphate \([\text{Li}_3\text{V}_2(\text{PO}_4)_3, \text{LVP}]\) is a positive-electrode material of polyanion type characterized by strong \(\text{AO}_x\) bonds \((\text{A}=\text{B, P, Si})\); this ensures that there is no release of oxygen from the crystal structure during charge and discharge, and thus minimal risk of ignition. Consequenty, LVP offers excellent thermal stability compared to other common positive-electrode materials such as rock-salt \(\text{LiCoO}_2\) or spinel-form \(\text{LiMn}_2\text{O}_4\). LVP also exhibits high reaction potentials due to inductive effects of phosphoric acid and is thus a promising candidate for positive electrodes. Moreover, lithium ions diffuse in all three dimensions within the solid of LVP, yielding a large value of the \(\text{Li}^+\) diffusion coefficient \((10^{-9} - 10^{-11} \text{ cm}^2 \text{ s}^{-1})\). This property distinguishes LVP from other phosphate-based polyanionic materials—such as lithium iron phosphate \((\text{LiFePO}_4)\), in which the diffusion of lithium ions is constrained to be one-dimensional—and enables device operation at capacitor-grade speeds. One of the challenges associated with the use of LVP cathodes is to circumvent the limitations imposed by the intrinsically low electronic conductivity of LVP \((10^{-8} - 10^{-9} \text{ S cm}^{-1})\). Strategies such as reducing particle sizes, creating carbon-composite materials, and doping with other metals have been pursued, but have failed to increase charge/discharge speeds above 100C.

Beyond the challenge of improving power performance, an important issue which has been addressed by only a small number of studies thus far is the performance of full cells using LVP positive electrodes. To date, the reported values of volumetric energy density \((30-40 \text{ Wh L}^{-1})\) and maximum power density \((2-12 \text{ kW L}^{-1})\) for such LVP-based cells have remained limited by the low volumetric density of the negative electrodes, which have involved materials such as AC, hard carbon, and LTO nanowires. A more serious drawback is that the cycle performance of previous devices has been limited to 500 - 4,000 cycles. The possibility that this capacity degradation might be caused by the elution of vanadium from LVP was suggested in the patent, but the relationship was left unspecified.

In this study, we designed LVP-based SRC full cells that simultaneously achieved high energy, high power density, and long cycle life. First, to realize the full high-power potential of LVP electrodes, we used LVP materials synthesized via our unique technique of ultracentrifugation (UC) treatment. UC-treated LVP contained highly crystalline
LVP particles, sized 10-100 nm, highly dispersed throughout a matrix of multiwalled carbon nanotubes (MWCNTs). The uc-LVP/MWCNT composites enabled high C-rate operation of 96 mAh g\(^{-1}\) at 300C—more than twice the rate possible with AC electrodes—and excellent cycle performance over 10,000 cycles. We assembled full cells consisting of positive electrodes made from the uc-LVP/MWCNT paired with negative electrodes made from standard commercially-available LTO. Then, we successfully identified the mechanism of capacity degradation during full cell cycling and devised a strategy for minimizing its effect on the cycling performance. As we showed, capacity degradation was caused by gradual shifts of the state of charge (SOC) between two electrodes—namely, an upward SOC shift for uc-LVP/MWCNT and a downward SOC shift for LTO. The SOC shifts were due to a decrease in the coulombic efficiency of the reaction on the LTO side. This, in turn, was due to the deposition of vanadium species on the LTO surface, after elution from LVP particles and diffusion to the negative electrode. Having diagnosed this mechanism for capacity degradation, we proposed a cure: electrochemical preconditioning of the LTO electrode with Li to minimize SOC shifts. The strategy of electrochemical preconditioning not only allowed adjustment of SOC, but also gave rise to the formation of a protective covering layer on the LTO surface consisting of electrolyte-decomposition products such as LiF and Li\(_2\)CO\(_3\). As we showed, this covering layer prevented deposits of vanadium species on the LTO surface and mitigated capacity degradation, resulting in outstanding cycle performance (>10,000 cycles) for the LTO//uc-LVP/MWCNT full-cell configuration.

4.2. Experimental

4.2.1. Materials

NH\(_4\)VO\(_3\) (>99%, Kanto Chemicals), CH\(_3\)COOLi (>98.0%, Wako Pure Chemicals), and H\(_3\)PO\(_4\) (>85.0%, Wako Pure Chemicals) were used to prepare LVP. Citric acid (>99.5%, Sigma-Aldrich Corp.) and ethylene glycol (>99.5%, Wako Pure Chemicals) were used as a chelating agent. MWCNTs\(^{26}\) with a specific surface area of 240 m\(^2\) g\(^{-1}\) were used for the preparation of carbon composite. Ultrapure water (17 M\(\Omega\) cm) was used as a medium for the entire preparation scheme. LTO (Toho Titanium) was used as a negative electrode in the full cell assembling.
4.2.2. Preparation of uc-LVP/MWCNT composite under UC treatment

Firstly, three kinds of solution (solution A, B and C) were prepared. Solution A was composed of 0.8000 g of MWCNT and 1.5840 g of H$_3$PO$_4$ mixed in 50 ml of ultrapure water. Solution B was composed of 1.0823 g of NH$_4$VO$_3$, 0.9251 g of CH$_3$COOLi and 1.7685 g of citric acid (1.0 eq.) dissolved in 20 ml of ultrapure water. Solution C was composed of 2.2854 g of ethylene glycol dissolved in 10 ml of ultrapure water. Solution A was subjected to the UC treatment at 80 °C for 5 min before and after the addition of solution B and C. The uc-treated sol was further dried at 130 °C under vacuum for 12 h. The obtained precursor was pre-annealed at 300 °C for 3 h in air to remove citric acid and ethylene-glycol-derived amorphous carbon and absorbed water, then left to cool to room temperature (RT). The pre-annealed powder was further annealed at 800 °C for 30 min under N$_2$ flow (RT to 800 °C in 3 min, dwell for 30 min, 30 min to cooling to RT) to form the uc-LVP/MWCNT (70/30) composites.

4.2.3. Physicochemical characterizations of uc-LVP/MWCNT composite

Structure analysis on LVP/MWCNT composite was performed by X-ray diffraction [XRD, MiniFlex (Rigaku), Cu Kα radiation (λ=1.54 Å), operating at 40 kV, 15 mA]. XRD patterns were recorded in the 10°- 60° 2θ range at a scan speed of 0.167° s$^{-1}$. The carbon content of uc-LVP/MWCNT composite was 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). Surface morphologies on uc-LVP/MWCNT and LTO electrodes before and after charge/discharge were observed by scanning electron microscopy (SEM, Hitachi model S5500) and high-resolution transmission electron microscope (HRTEM, Hitachi model H9500). X-ray photoelectron spectroscopy (XPS JEOL Ltd. JPS-9200) was carried out using Al X-ray source without Ar etching. Prior to the SEM observation and XPS characterization, the sample electrodes were thoroughly washed by diethyl carbonate (DEC) in the glove box under Ar atmosphere with a dew point < -80°C and then dried for 12 h under vacuum. The quantitative analysis of vanadium in electrolytes and the surface of LTO electrodes was
conducted by inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Fisher Scientific, ELEMENT XR) in Toray Research Center. H$_2$O contents in the electrolytes were measured based on the Karl Fisher method (Mitsubishi Chemical Analytic, CA-6).

4.2.4. Electrochemical characterization of uc-LVP/MWCNT composite

2032 coin-type Li-metal half-cells were assembled using a negative Li metal electrode and a positive uc-LVP/MWCNT electrode. LTO/LVP Full-cells were assembled using negative LTO and positive uc-LVP/MWCNT electrodes in laminate-type cells. The electrolyte was a mixture of ethylene carbonate and diethyl carbonate (EC : DEC = 1 : 1) containing 1.0 M of lithium hexafluorophosphate (LiPF$_6$). The separator was a 25 µm-thick monolayer polypropylene separator (Celgard®2400, Celgard). The uc-LVP/MWCNT positive electrodes were prepared by mixing 90 wt.% of the composite and 10 wt.% of polyvinylidene difluoride (PVdF) in N-methyl pyrrolidone (NMP). LTO negative electrodes were prepared by mixing 70 wt.% of the sample, 20 wt.% of acetylene black and 10 wt.% of PVdF in NMP. The mixture was coated on an etched-Al foil (current collector) and dried at 80 °C under vacuum for 12 h. Before cell assembling, electrodes were further dried at 120 °C for 2 h under vacuum. Using prepared electrodes, cells were assembled in dry room (dew-point temperature < -40 °C). Loading masses of LTO and uc-LVP/MWCNT were 1.4 and 1.1 mg cm$^{-2}$ (18 and 20 µm of thickness) on etched Al current collector, respectively, corresponding to the N/P capacity ratio of 1.9. Electrode areas of half-cells and full-cells were 1.54 and 5.0 cm$^2$, respectively. Charge-discharge tests for the uc-LVP/MWCNT half-cells, LTO half-cells and LTO//(uc-LVP/MWCNT) full-cells were performed in constant-current (CC) charge and discharge modes between 2.5 - 4.3 V vs. Li/Li$^+$, 1.0 - 3.0 V vs. Li/Li$^+$ and 1.5 - 2.8 V, respectively. Current densities for half-cells and full-cells were 10C-rate for cycling tests and ranged from 1 to 480C-rate in rate tests, assuming that 1C-rate equals 131.5 mA g$^{-1}$[Li//(uc-LVP/MWCNT) and LTO//(uc-LVP/MWCNT)] and 175 mA g$^{-1}$[Li/LTO]. Electrochemical preconditining of LTO was conducted through charge discharge cycling with an additional Li metal electrode in the full cell laminated cells. The details of process are as following: LTO was (i) charged at constant-current constant-voltage (CC-CV) mode with cut-off potential of 1.0 V vs. Li/Li$^+$ and holding time of 1 h, (ii) rested for 24 h, (iii) discharged to 3.0 V at
CC mode, (iv) charged and discharged at CC mode between 1.0 - 3.0 V vs. Li/Li\(^+\) for 9 cycles, and then (v) charged at CC mode to the SOC 25 or 40%. At the same time, LVP underwent similar precycling using another additional Li metal in the cell as following: LVP was (i) charged at CC-CV mode with cut-off potential of 4.3 V vs. Li/Li\(^+\) and holding time of 1 h, (ii) rested for 24 h, (iii) discharged to 2.5 V at CC mode, and then (iv) charged and discharged at CC mode between 2.5 - 4.3 V vs. Li/Li\(^+\) for 9 cycles. After electrochemical preconditioning process, full cell packages were opened to remove Li metal electrodes, and the re-sealed full cells were cycled thereafter.

4.3. Results and discussion

4.3.1. Power capability and cyclability of SuperRedox Capacitors [LTO // uc-LVP/MWCNT]

Prior to any cell assembling, we have conducted the XRD and TG/DTA analysis on LVP/MWCNT composites synthesized via UC treatment.\(^{25}\) The XRD patterns of monoclinic LVP\(^{15}\) were found on the broad peak of the MWCNT (2\(\theta\) = 20 - 30°) as shown in Figure 4-1(a). Based on the TG/DTA curve under synthetic air atmosphere shown in Figure 4-1(b), the calculated weight ratio of LVP and MWCNT was 70/30.

![Figure 4-1](image)

Figure 4-1 (a) XRD pattern for uc-LVP/WMCNT composite and (b) TG/DTA curves for uc-LVP/WMCNT composite and MWCNTs.
As mentioned in the introduction, we have previously reported the LTO//AC hybrid capacitor system—called *Nanohybrid Capacitor* (NHC)*9*—where an AC negative electrode of supercapacitor (SC) was replaced by a nanocrystalline-LTO/MWCNT composite electrode.*7* The NHC showed the 3-fold energy density of SC, while attaining the high power comparative to SC.*9* To achieve further increase of energy density from NHC, replacement of the AC positive electrode was required by alternatives with higher capacity as well as ultrafast electrochemical characteristics and excellent cycle capability. Here, we assembled the *SuperRedox Capacitor* (SRC) full cells consisting of the uc-LVP/MWCNT positive and commercially-available LTO negative electrodes. The tested LTO//uc-LVP/MWCNT system exhibited excellent discharge C-rate capability [Figure 4-2(a)]; 92 mAh g⁻¹ at 100C, and then 55 mAh g⁻¹ at 300C, corresponding to the 76 and 46% of the capacity obtained at 1C. Ragone plots of SRC calculated based on the total volume of two electrodes are shown in Figure 4-2(b). SRC full cells exhibited high volumetric energy density of 60-63.5 Wh L⁻¹ within the region of low power requirement (100 – 1,000 W L⁻¹) which corresponded to the 2-folds volumetric energy density of NHC and 5-folds of SC. Even at a higher power (2,000 – 10,000 W L⁻¹), 63% of the energy density (40-56 Wh L⁻¹) can be maintained. Accordingly, the obtained Ragone characteristics for our SRC full cells demonstrated that this system can be operated at high power comparative to the SC, while showing the merit of this system in terms of volumetric capacity compared to SC and even NHC.
Figure 4-2  (a) Charge discharge curves of the assembled SRC full cells: [LTO//(uc-LVP/MWCNT)] using 1 M LiPF₆ in EC+DEC (1:1 in vol.) at different discharge C-rates from 1 to 300C. Charge C-rate was fixed at 1C. The gravimetric capacity was calculated per LVP. (b) Ragone plots of our full cells [LTO//(uc-LVP/MWCNT)], Nanohybrid Capacitor: NHC [uc-LTO/MWCNT (70:30)//AC],⁹ and supercapacitor: SC [AC/1 M TEMABF₆/PC/AC].⁹ All the volumetric capacity was calculated based on total volume of two electrodes.

Besides the Ragone characteristics, another important property for the capacitor application is the long term cyclability. In case of Li metal half cells, LTO and uc-LVP/MWCNT showed excellent cyclability [Figure 4-3(a) and (b)]: the capacity retentions of the initial capacity after 1,000 cycles were 86 and 98% for LTO and uc-LVP/MWCNT, respectively. Both materials showed high coulombic efficiency > 99.7%, where that for LTO showed slightly higher and stable plots (99.9%). We then simply assembled the LTO//uc-LVP/MWCNT full cells without any pretreatment. In full cell configurations, however, the capacity retention after 1,000 cycles was no more than 68% and continuously decreased to 63% until 2,000 cycles, and then gradually degraded down to 54% after 10,000 cycles as shown in Figure 4-3(c). At the 1ˢᵗ cycle, charge discharge curves of the full cell in Figure 4-3(d)—tagged as “no preconditioning”— showed clear three plateaus at 2.02, 2.10, and 2.51 V in average, corresponding to the typical LVP characteristic of 0.5, 0.5, and 1.0 of Li⁺ intercalation/deintercalation per LVP, respectively. With cycling up to 1,000 cycles, one can see the continuous decrease of the first plateau (0.5 Li⁺), and this plateau ended up to be almost disappeared. To identify the mechanism
responsible for capacity degradation and the disappearance of the first plateau in their charge discharge curves, we disassembled the full cells after 10,000 cycles, and used the cycled negative and positive electrodes to assemble two Li-metal half cells (see Figure 4-4). The OCV of the Li//uc-LVP/MWCNT just after reassembling was around 3.65 V vs. Li—slightly higher than the 1st plateau of LVP (3.60 V vs. Li)\textsuperscript{15}, which was consistent with the disappearance upon cycling of the 1st plateau [Figure 4-4(a)]. In the direction of discharge, however, the 1st plateau was recovered, and then at 10\textsuperscript{th} cycle, all three plateaus can be observed reversibly as the pristine one. Differently from the uc-LVP/MWCNT, the reassembled Li//LTO half cells exhibited \textit{ca.} 92% in capacity retention of the pristine LTO at the 1\textsuperscript{st} cycle and then 88% at the 10\textsuperscript{th} cycle, only with a small distortion in curve shapes [Figure 4-4(b)]. All experimental results, both for full cells and reassembled half cells, suggested that there was no significant degradation of electrode materials themselves, and thus that the capacity decrease during the initial 1,000 cycles was due to the appearance of shifts in the state of charge (SOC)\textsuperscript{27} between LTO negative and uc-LVP/MWCNT positive electrodes. The high OCV values of the Li//uc-LVP/MWCNT half cells were explained convincingly by the hypothesis that uc-LVP/MWCNT shifted to a higher SOC, and that the irreversibility of LTO reaction were responsible for such SOC shift of the positive electrode.\textsuperscript{27, 28} However, it was contradicted to the coulombic efficiencies obtained for the Li-metal half cells, whereas the LTO cells showed higher value (99.9%) than the uc-LVP/MWCNT (99.7%). This contradiction led to one conclusion that the coulombic efficiency of LTO became lower on the condition of the full cell cycling where the uc-LVP/MWCNT was used as a counter electrode of LTO instead of Li metal. Thus, to minimize the effects of such SOC shifts, electrochemical preconditioning process—electrochemical Li predoping on LTO—was conducted using Li//LTO cells, prior to the full cell assembling. The electrochemical preconditioning of LTO negative electrode provided a capacity margin to buffer the effects of SOC shifts regardless of the difference in coulombic efficiency of the reaction.\textsuperscript{21} We prepared two types of Li preconditioned LTO with different starting SOC conditions: 25 and 40%. As shown in Figure 4-3(c), the full cells using Li preconditioned LTO of 25 and 40% exhibited the high capacity retention even after 10,000 cycles: 66 and 77% of the initial capacity, respectively. Contrary to the no preconditioning sample, the clear 1\textsuperscript{st} plateau can be still observed in their charge discharge curves after 10,000 cycles [see Figure 4-3(e)
and (f)], showing the successful minimization of the SOC shifts of the uc-LVP/MWCNT. The corresponding uc-LVP/MWCNT electrodes (preconditioned LTO : SOC = 25 and 40%) in the Li metal half-cell exhibited the 105-118 mAh g\(^{-1}\) of charge capacity at the 1\(^{st}\) cycle with clear plateau at 3.60 V vs. Li [Figure 4-4(c) and (e)], while LTO exhibited the same capacity as the pristine and less distorted curve shape [Figure 4-4(d) and (f)] compared to the no preconditioning sample.

Figure 4-3  Plots of capacity and coulombic efficiency against cycle of (a) Li // (uc-LVP/MWCNT) and (b) Li // LTO, and (c) LTO // (uc-LVP/MWCNT) full cells with different ratio of Li preconditioning on LTO: SOC 0, 25, and 40%. Charge discharge curves of LTO // (uc-LVP/MWCNT) full cells (d) No preconditioning = SOC 0%, (e) Li preconditioning: SOC 25%, and (f) Li preconditioning: SOC 40%. Note that the capacity in (a) and (b) is per active material and (c) is per LVP, and also the different scales of x-axis in (a), (b), and (c).
Figure 4-4  Charge discharge curves for initial and 10th cycles of Li metal half cells reassembled by using electrodes removed from the full cells after 10,000 cycles with and without electrochemical preconditioning compared with pristine electrodes: (a) uc-LVP/MWCNT and (b) LTO after 10,000 cycling of full cell without any pretreatment (no preconditioning), (c) uc-LVP/MWCNT and (d) LTO after 10,000 cycling of full cell using preconditioned LTO (SOC = 25%), and (e) uc-LVP/MWCNT and (f) LTO after 10,000 cycling of full cell using Li preconditioned LTO (SOC = 40%). All the values of gravimetric capacity shown in the figures are normalized in the mass of LVP or LTO.

4.3.2. Elucidation of mechanism of SOC shifts in full cells and the effect of electrochemical preconditioning

As clarified in the section 4.3.1, the full cell degradation of LTO//uc-LVP/MWCNT was due to the shift to a high SOC of uc-LVP/MWCNT. However, the question still remains: why the reaction on the LTO negative electrode in full cells became less reversible than that on the uc-LVP/MWCNT positive—which was suggested to be the main reason of the SOC shifts on the positive side—, even though the results on Li-metal half cells suggested
that the LTO has slightly, but certainly higher coulombic efficiency compared to the uc-LVP/MWCNT. To elucidate such remaining question, we checked the overall surface composition of LTO with and without electrochemical preconditioning (Li preconditioning) by XPS, before and after 10,000 cycles in full cell configurations (Figure 4-5). Note that the XPS spectra intensity for the four atoms (C1s, O1s, Li1s, and F1s) shown in top of Figure 4-5 were normalized for the better comparison between three samples, while the peak intensity for other three atoms (P2p, Ti2p, and V2p) was kept as measured. For the no preconditioning sample after 10,000 cycles, the intensity of Ti2p peaks corresponding to Ti$^{4+}$ 2p$_{1/2}$ and 2p$_{3/2}$ decreased, compared to the sharp peak for the pristine one. This tendency was in good agreement with obtained results of O1s spectra for the no preconditioning sample, where the P-O/C-O peak intensity became comparative to the Ti-O, indicating that the LTO surface was covered by compounds containing those peaks. The peak corresponding to LiF appeared in Li1s and F1s spectra, while POF$_3$ (or Li$_x$PO$_y$F$_z$) can be also found in P2p spectra. These results suggested that the electrolyte-decomposed products such as LiPF$_6$, EC, and DEC were accumulated on the surface of LTO without Li preconditioning.\textsuperscript{29} Another large difference between the pristine and no preconditioning samples was the peaks of V$^{5+}$ 2p$_{1/2}$ and 2p$_{3/2}$ in the V2p spectra. The detection of such V$^{5+}$ peaks on the LTO surface after 10,000 cycling indicated the elution and subsequent diffusion of vanadium species (V$^{n+}$) from the uc-LVP/MWCNT positive electrode. Here, to determine the valence state of vanadium species (V$^{n+}$), whether V$^{5+}$ or its reduced states, is difficult, because of its minute amount (few $\mu$g as later shown in Table 4-1), and the possible redox of V$^{4+}$/V$^{5+}$ occurs in the potential region close to the LTO reaction (1.55 V vs. Li/Li$^+$) such as Li$_3$VO$_4$.\textsuperscript{30} Deposition/accumulation of transition metals such as Mn on the negative electrode in LIBs have been already studied,\textsuperscript{31-33} and it is well known that the existence of such transition metal/metal ions on the surface of negative electrodes induces the irreversible decomposition of electrolytes. Thus, it can be expected that the accumulated V$^{5+}$ on the LTO surface catalytically reduced the electrolyte components, leading to the lower coulombic efficiency of LTO side and the subsequent SOC shifts of the uc-LVP/MWCNT. On the Li preconditioned LTO (SOC = 25%), such V$^{5+}$ peaks can be detected but their intensity was much lower compared to the no preconditioning sample. The result well agreed with the quantitative analysis on the amount of vanadium detected from the LTO.
before and after full cell cycling by ICP-MS. As shown in Table 4-1, the vanadium amounts detected from the no preconditioning sample after 1,000 cycles was (8.0 µg) the highest compared to other two samples, Li preconditioned LTO after 1,000 cycles (2.4 µg) and the soaked LTO (1.3 µg) which was removed from the full cell after preserved for a week without any cycling. These results indicated that the Li preconditioning of LTO brought about the protective effect from the vanadium accumulation on its surface.

Figure 4-5  XPS spectra of LTO for the pristine (as prepared), no preconditioning (=SOC 0%) and Li preconditioning (=SOC 25%) after 10,000 cycles in LTO//(LVP/MWCNT) full cell configurations;(a)C1s, (b)O1s, (c)Li1s, (d)F1s, (e)P2p, (f)Ti2p, (g)V2p. Note that the peak intensity of (a)-(d) are normalized at the highest intensity for the better comparison between three samples.

Table 4-1  Results of ICP-MS on vanadium detection among three LTO samples and corresponding electrolytes: as assembled (soaked in the electrolyte), no preconditioned after 1,000 cycles, and Li preconditioned after 1,000 cycles.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Vanadium on 5.7 mg of LiTiO2</th>
<th>Vanadium in 2,000 µL (1.3 g cm⁻²) of electrolyte</th>
<th>Total amount of vanadium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soaked LTO[(µ-LVP/MWCNT) fullcell]</td>
<td>230 ppm</td>
<td>1.3 µg</td>
<td>3.1 µg</td>
</tr>
<tr>
<td>No preconditioning LTO[(µ-LVP/MWCNT) fullcell, after 1,000 cycles]</td>
<td>1400 ppm</td>
<td>8.0 µg</td>
<td>8.8 µg</td>
</tr>
<tr>
<td>Li preconditioning LTO[(µ-LVP/MWCNT) fullcell, SOC 25%, after 1,000 cycles]</td>
<td>420 ppm</td>
<td>2.4 µg</td>
<td>4.6 µg</td>
</tr>
</tbody>
</table>
To see the effect of such minute vanadium dissolution on the morphology of uc-LVP/MWCNT composites, the SEM observation was conducted on different uc-LVP samples before and after cycling. As shown in Figure 4-6, the composite morphology such as dispersibility of LVP within MWNCT matrix did not change before [Figure 4-6(a) and (b)] and after [Figure 4-6(c) and (d)] 10,000 cycles of full cells. No clear SEI accumulation on the surface of LVP particles was observed, showing that the morphology of the composite and LVP particle’s surface were maintained regardless of the minute vanadium loss from the LVP crystalline. The SEM observation was conducted on another uc-LVP/MWCNT which was charged and discharged for 10,000 cycles within the full cell using Li preconditioned LTO. The observation results shown in Figure 4-6(e) and (f) just support what we observed in Figure 4-6(c) and (d), as no change in its morphology was observed. In contrast, SEM observation on the LTO samples provided us a clear view of such LTO protection from the vanadium accumulation (Figure 4-7). Compared to the smooth surface of the pristine LTO [Figure 4-7(a)], small dots (ϕ = ca. 10-50 nm)—which may be attributed to mixture of carbonated compounds or LiF—can be clearly seen on the surface of LTO without Li preconditioning after 10,000 cycles [Figure 4-7(b)], whose existences were also confirmed in the TEM image [Figure 4-8(a)]. Furthermore, besides the small dots, very thin film (2-3 nm) can be also observed in the TEM image of the LTO [Figure 4-8(b)]. Such thin film formed on the LTO surface may be originated from the decomposed organic compounds of electrolytes induced by the deposited vanadium species. Meanwhile, the surface of the Li preconditioned LTO was already covered by the flake-like compounds even before the full cell cycling [Figure 4-7(c)], and then the thickness of the surface accumulation was increased with similar morphology after 10,000 cycles [Figure 4-7(d)]. This coverture on the surface of Li preconditioned LTO well supported the disappearance of Ti 2p peaks and significant increase of the peaks attributed to the LiF, carbonates (C-O and C=O), and POF₃. Such coverture on the LTO surface—produced during the Li preconditioning—may play an important role in the protection from the vanadium species deposition during the full cell cycling. Interestingly, these flake-shape compounds on the LTO can be easily removed by ultrasonication of the samples—as observed in Figure 4-8(c) and (d)—, indicating their weak adhesion on the LTO surface due to the flake morphology (minimum contacts on the surface). Therefore, this minimum-contact coverture was considered to provide the protection of LTO surface
without hampering the Li intercalation/deintercalation into LTO.

Figure 4-6 SEM images of uc-LVP/MWCNT electrodes: (a), (b) pristine, (c),(d) after 10,000 cycles in full cells using no preconditioning LTO, (e),(f) after 10,000 cycles in full cells using preconditioned LTO (SOC =25%) before cycling.
Figure 4-7  SEM images of LTO electrodes: (a) pristine, (b) No preconditioning after 10,000 cycles, (c) Li preconditioning (SOC =25%) before cycling, and (d) Li preconditioning (SOC =25%) after 10,000 cycles.
Figure 4-8  TEM images of LTO samples after the LTO//uc-LVP/MWCNT full cell cycling: (a) and (b) no preconditioning LTO after 10,000 cycles. (c) and (d) preconditioned LTO (SOC = 25%) after 10,000 cycles. All the LTO samples were ultrasonicated for 30 min. in diethyl carbonate to prepare LTO dispersion and then to drop it on TEM grids.
Combining results of XPS, ICP-MS, and SEM observation, the mechanism of vanadium elution/deposition and the resultant SOC shift of the uc-LVP/MWCNT, as well as its prevention by Li preconditioning of LTO can be drawn as shown in the schematic images of Figure 4-9. Even on the condition of soaking of the LTO and uc-LVP/MWCNT in the electrolyte for a week, minute amounts of vanadium were dissolved from the uc-LVP/MWCNT into the electrolyte as detected 3.1 µg (see Table 4-1) and also 1.3 µg deposited on the LTO surface. The elution of the vanadium may occur due to the produced HF via hydrolysis of LiPF$_6$\textsuperscript{29} in the electrolyte [Figure 4-9(a)], where the adsorbed H$_2$O may be released from the surface of MWCNT and/or LTO. Here, the differences of the measured H$_2$O contents among the different conditions were within 1-2 ppm or even 0.5 ppm, which were far below the detection limit as 10 ppm (10 µg of H$_2$O: as the limitation of general Karl Fisher titration apparatus) considering the amount of electrolyte (1 g) used in our laminate-type cells. In the case of the full cell using LTO without Li preconditioning (without any preconditioning of LTO), the vanadium species deposition occurred on the pristine/bare LTO surface, and the deposited vanadium species—which were detected as V$^{5+}$ in XPS spectra—catalytically reacted with the electrolyte, resulted in the formation of thin layer (2-3 nm) and dotted compounds (10-50 nm) on the LTO surface [Figure 4-9(b)]. Such electrolyte decomposition and further release of H$_2$O from the LTO surface may induce the production of HF in the electrolyte, which further attacked the LVP particles on the other side and thus provoked further elution of vanadium species.\textsuperscript{29} The results of ICP-MS confirmed the increase of vanadium after cycling, as the total amount of dissolved/deposited vanadium (= LTO + electrolyte) doubled from the just soaked sample (4.4 µg) to the no preconditioning sample after 1,000 cycles (8.8 µg). It was considered that, for the no-preconditioning cells, most of vanadium eluted from the LVP was deposited on the LTO surface (8.0 µg). This may be the reason why the amount of vanadium in the electrolyte for the no-preconditioning cells was lower or similar to that for Li preconditioning cells. Such minute amount of vanadium eluted from the uc-LVP does not change its composite morphology [see Figure 4-6] nor degrade any electrochemical properties of LVP itself. However, the accumulation of continuous irreversible decomposition on the LTO surface—induced by the deposited vanadium species—gave rise to the difference in the coulombic efficiencies between the LTO and uc-LVP/MWCNT electrodes, and then led to the gradual SOC shifts as schematically
explained in Figure 4-9(c) and (d). At the initial cycling of the full cell operation, the polarization curves of two electrodes were as originally designed (cell voltage: 1.5-2.8 V) as shown in Figure 4-9(c) highlighted in orange. Due to the continuous SOC shifts up to 10,000 cycles, the operation potential range of the uc-LVP/MWCNT shifted towards the higher SOC region and thus the LTO went to the other direction (lower SOC), leading to the capacity degradation with a disappearance of the 1st plateau of LVP [Figure 4-9(d)]. Furthermore, deposited film and dots on the LTO may inhibit the Li\(^+\) diffusion access from the electrolyte and thus increase overpotential of LTO intercalation, resulted in the slight distortion of LTO polarization and degrades of its exhibited capacity as observed in the reassembled Li//LTO cells [Figure 4-4(b)]. Applying the preconditioning, LTO was offered to be at higher SOC than no preconditioning sample, which acted as a capacity margin against the SOC shifts regardless of the difference in coulombic efficiency between positive and negative electrodes. Moreover, the surface of the Li preconditioned LTO was covered by flake-shape compounds containing LiF, and Li\(_2\)CO\(_3\), which minimize the deposition of vanadium species on the LTO surface (2.4 µg) as shown in Figure 4-9(e) and (f). Such LTO surface protection may prevent the subsequent events leading to the vanadium elution from the positive electrode [Figure 4-9(f)], as confirmed by ICP-MS where the total vanadium amount (4.6 µg) remained almost the same as the soaked sample (4.4 µg). Combination of these two factors—capacity margin against SOC shifts and surface protection of LTO—assured stable charge discharge behavior in the full cell cycling [Figure 4-9(g) and (h)], and brought about the excellent cycle performance: 77% of the initial capacity retention over 10,000 cycles.
Figure 4-9  Schematic images of events on the LTO surface during the full cell cycling: (a) just soaked cell (no preconditioning before cycling), (b) no preconditioning during cycling, (c) Li preconditioning before cycling, and (d) Li preconditioning after cycling. Model polarization curves corresponding to LTO negative and uc-LVP/MWCNT positive electrodes in full cell cycling: (e) at initial cycling and (f) after 1,000 cycles for the no preconditioning sample, and (g) at initial cycling and (h) after 1,000 cycles for the Li preconditioning sample.
4.4. Conclusions

In conclusion, we successfully assembled SRC full cell system based on the uc-LVP/MWCNT positive paired with a commercially-available LTO negative electrode. The SRC full cell showed excellent Ragone characteristics—60 Wh L\(^{-1}\) at 100 W L\(^{-1}\) and 40 Wh L\(^{-1}\) at 10,000 W L\(^{-1}\) (per volume of two electrodes), corresponding to a 2-folds and 5-folds increase in the energy density from the LTO//AC configuration (= NHC) and SC, respectively—, and the outstanding long cycle life configuration—over 10,000 with 77% capacity retention of its initial capacity—for the full cell cycling. Such stable cycle performance was achieved thanks to the electrochemical preconditioning (=Li preconditioning of LTO, SOC = 25 and 40%) conducted prior to the full cell assembling, while the capacity retention without preconditioning fell to 54%. In the process of elucidation of the Li-preconditioning effect on cycle performances, it was found that minimization of the vanadium elution from the LVP and the subsequent deposition on the LTO surface played an important role for the stable cycling. Combined results of XPS, ICP-MS and SEM observation suggested that the deposited vanadium species on the LTO surface induced the decomposition of electrolytes and production of HF. The irreversible electrolyte decomposition led to a decrease in the coulombic efficiency of Li\(^+\) intercalation/deintercalation into LTO crystals, resulted in the gradual shift between two electrodes: higher SOC for uc-LVP/MWCNT positive and lower SOC for LTO negative electrodes. Additionally, the produced HF was considered to induce further elution of vanadium from the uc-LVP/MWCNT, accelerating the SOC shifts and degradation in the full cell capacity. Li preconditioning of LTO was found to be effective as a countermeasure, because of the given capacity margin to minimize the effect of SOC shifts, and the formation of the protective coverture on the LTO surface—composed of such as LiF and Li\(_2\)CO\(_3\)—from the undesirable vanadium deposition.

4.5. References


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Chapter 5

General conclusion
In this thesis, we investigated three novel polyanion-based composite nano-materials: (a) Fe$^{3+}$-substituted lithium cobalt phosphate (LiCo$_{0.8}$Fe$_{0.2}$PO$_4$, LCFP), (b) iron-phosphate-(FePO$_4$, FP)-coated Ti$^{4+}$-substituted lithium cobalt phosphate (LiCo$_{0.90}$Ti$_{0.05}$PO$_4$, LCTP), and (c) lithium vanadium phosphate [Li$_3$V$_2$(PO$_4$)$_3$, LVP]. Materials (a) and (b) are designed for applications to high-voltage lithium ion batteries (LIBs), while material (c) is intended for applications to ultra-fast LIBs, also known as SuperRedox Capacitors (SRCs).

In chapter 1, backgrounds and previous studies of positive electrode materials including high safety polyanion based materials for lithium ion batteries were introduced. The significance and objectives of this thesis were also described.

In chapter 2, factors affecting the cyclability of the LCFP material were elucidated, including both the structural and electrode/electrolyte stability. Electrochemical characterization of the synthesized LCFP nanoparticles lent clear evidence for improved electrochemical stability of LCP, as well as enhanced rate capability, with Fe$^{3+}$ substitution. Surface analysis using X-ray photoelectron spectroscopy and electron energy loss spectroscopy suggested that Fe enrichment on the surface of LCFP occurred through the oxidation of Fe$^{2+}$ into Fe$^{3+}$ in the synthesis process. The Fe$^{3+}$-rich phase on the LCP surface enhanced the stability of the delithiated phase, preventing oxidative reactions with electrolytes during high-voltage operation. This surface protection persisted as long as the electrochemical reduction of Fe$^{3+}$ was avoided by ensuring that the full range of operating voltages lied above the Fe$^{3+}$/Fe$^{2+}$ redox potential. The phase stabilization yielded excellent cyclability, with 85% capacity retention over 5,000 cycles at 1C and 96% capacity retention over 1,000 cycles even at a slow C-rate of 0.2C.

In chapter 3, highly-dispersed 10 wt.% FP-coated LCP and its aliovalent-substitution, LCTP nanocrystals were successfully synthesized within the multiwalled carbon nanotube via our original ultracentrifugation process. The 10 wt.% FP-coated LCP and LCTP showed a higher discharge capacity than the previously-reported uc-LCP and the uc-LCFP without sacrificing its cycle performance, 99% of capacity retention at 100$^{th}$ cycle. Combination of X-ray diffraction, neutron powder diffraction, X-ray photoelectron spectroscopy, and X-ray adsorption fine structure analyses suggested that (i) Ti$^{4+}$-substitution increased the utilization of Co redox (capacity increase) in LCP crystals by suppressing the Co$_3$O$_4$ formation and creating the vacancies in M2(Co$^{2+}$) sites, and (ii)
the FP-coating brought about the Fe enrichment of the surface of LCP and LCTP which prevented an irreversible crystal structure change and SEI production during cycling, resulting in the stable cycle performance. Our finding may offer new idea of retaining M2-site vacancies and crystal-structure-matched surface coating—where the crystal structure between the coating material and the matrix is identical—to stabilize the cycling performance without unnecessarily decreasing capacity of not only LCP but also other high-voltage cathode materials.

In chapter 4, novel full cells called SRCs consisting of nanocrystalline LVP positive and standard commercial \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) (LTO) negative electrodes have been demonstrated outstanding cyclability: capacity retention of 77% over 10,000 cycles. We achieved this stable cycle performance by electrochemical preconditioning of LTO with Li prior to full-cell cycling. The strategy of Li preconditioning not only allowed adjustment of the state of charge between negative and positive electrodes, but also gave rise to the formation of a protective covering layer on the LTO surface. As we showed, this covering layer played an important role in preventing a key performance-limiting phenomenon—namely, the deposition of vanadium eluted from LVP onto LTO, which degraded the coulombic efficiency of \( \text{Li}^+ \) intercalation/deintercalation into LTO crystals—yielding minimal state of charge shifts and stable full-cell cycling.

Our findings in stabilizing the LCP nanocrystal surface layer by \( \text{Fe}^{3+} \)-rich phase and retaining vacancies offered new approaches to stabilize the structure of LCP and other high-voltage positive electrodes for use in 5-V class lithium ion batteries. New design of ultrafast LIBs, namely SRCs also demonstrated outstanding energy density, power density, and cyclability. By strategically controlling such as fine-tuning of nano-structures and surface phenomena, open the way to the design of high energy density, high power, long lifetime, and safety energy storage devices.
Reference materials
List of publications


List of international conferences

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List of awards

1. Student Poster Award, 5th International Symposium on Enhanced Electrochemical Capacitors (Jul 2017).
2. 2nd Poster Prize, 2016 International Conference on Advanced Capacitors (May 2016).
List of Japanese conferences

1. 沖田 尚久, 木須 一彰, 酒井 祐輝, 林 怡瑤, 高見 祐介, Brousse Thierry, Rozier Patrick, Simon Patrice, 直井 和子, 直井 勝彦
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