Fabrication of an LiMn$_2$O$_4$@LiMnPO$_4$ composite cathode for improved cycling performance at high temperatures

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ABSTRACT
The cyclability of LiMn$_2$O$_4$ (LMO), a spinel cathode used in Li-ion batteries (LIBs), at high temperatures (>50°C) should be improved. In this study, we use an olivine-type LiMnPO$_4$ (LMP) cathode with a composite structure as the surface material to improve the cyclability of LMO. The fabrication strategy includes mechanical coating of the LMO core with shell precursor particles and their subsequent transformation into LMP rod particles via hydrothermal vapor conversion. The core-shell precursor particles (composing NH$_4$MnP$_4$O$_{12}$H$_2$O (AmMP) plates) are successfully converted into LMO@LMP composite particles with a rod-like surface layer. The composite cathode fabricated with 7 mass% AmMP exhibits improved capacity retention of 72% after 30 cycles at 60°C, while that of the uncoated LMO cathode decreases to 63%. Further structural arrangement of the surface particles can lead to the development of a suitable cathode material for large-scale applications of LIBs.

1. Introduction
Li-ion batteries (LIBs) are indispensable energy storage systems that can be used in both portable electric devices (e.g. mobile phones, cameras, and laptops) and much larger systems such as vehicles, aircraft, and renewable-energy power plants. The high energy density of LIBs compared with that of other secondary batteries can satisfy the increasing emerging demand for new energy storage applications [1]. Large-scale applications require low-cost, stable electrode active materials. Lithium manganese oxide, LiMn$_2$O$_4$ (LMO), is a suitable cathode material for large-scale LIB applications because Mn is found abundantly in nature in the form of minerals as well as in spent alkaline–manganese batteries [2,3] and has a stable spinel-type crystal structure. However, the LMO cathode suffers from cycling performance degradation at high temperatures (>50°C) [4–6]. The Mn$^{3+}$ ions in LMO dissolve as a result of chemical reactions with decomposed species from the LiPF$_6$ organic electrolyte. This triggers a disproportionation reaction (2Mn$^{3+}$ → Mn$^{4+}$ + Mn$^{2+}$) during charge–discharge cycles, leading to the formation of resistive layers on both electrodes [6].

Surface coating of LMO particles is a direct method of suppressing Mn$^{3+}$ dissolution. Coating materials are divided into the following three categories: (1) transition metal oxides, (2) conductive materials, and (3) other active materials. Transition metal oxides, including Al$_2$O$_3$ [7–9], ZnO [10,11], SiO$_2$ [12,13], and TiO$_2$ [14], act as a physical protection layer on the particle surface of LMOs to prevent or suppress chemical reactions with electrolytes. The cyclability of LMOs at high temperatures is improved by deposition of chemically stable materials, while electrochemically inactive features of oxides exhibiting low ion and electron conductivities lead to a loss of rate or power capabilities [15]. As opposed to oxides, surface coating with conductive materials including carbon, silver, or gold satisfies the role of a protective layer and provides the LMO cathode with electrochemical activities [16–18]. A common disadvantage of both approaches is that an excessive content of coating materials causes the coating layer to turn into an inhibitor of the cathode performance of LMO.

In the third approach, the fabrication of particles designed with electrode active materials in the core and shell can elicit synergy effects from the components. Generally, core-shell cathodes are fabricated using active materials with a similar crystal structure to reduce the interfacial resistance, i.e. core-shell cathode particles constructed using two types of layered materials [19–21] or materials with a spinel structure. Spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) is used as the shell material for the LMO core because of its high stability [22–25]. However, different redox voltages are obtained when a core-shell LMO@LNMO cathode is used: ~4.1 V (vs. Li$^+$/Li) for LMO, which is due to the redox reaction of Mn$^{3+}$, and ~4.7 V for LNMO, which is due to the redox reaction of Ni$^{2+}$. The overall capacity in a voltage range based on the LMO core decreases compared with that of the LMO single-phase cathode. Thus, the core-shell LMO@LNMO cathode attains high cycling stability at high temperatures, albeit at the
expensive of the high working voltage of LNMO [22,23]. In this study, we used the olivine-type LiMnPO$_4$ (LMP) cathode as the protective material on LMO particles. LMP exhibits excellent thermal and chemical stability, which is attributed to its phosphate framework, and possesses the same working voltage as that of LMO (~4.1 V) [26]. Recently, core-shell LMO@LMP cathodes were fabricated [27,28] and exhibited good cyclability at room temperature, which is attributed to the coating [28]. However, the cycling performance of the core-shell LMO@LMP cathode and that of the non-coated LMO cathode decreased at 55°C. This unexpected result was due to the coating of LMP with lower ionic and electric conductivities than LMO. The core-shell structure of LMO@LMP may actually degrade the cycling performance of LMO. In order to improve the cyclability of LMO cathodes at high temperatures, designing a more suitable particle structure, including the morphology and contents of the protective layer, is necessary.

Herein, we report a new fabrication strategy for LMO@LMP composite cathode particles to improve their cycling behavior at high temperatures. First, LMO core particles are coated with LMP precursor particles. Then, the coated precursor particles are converted into LMP. The converted LMO particles exhibit a rod-like shape and play a role in contacting electrolytes instead of LMO, resulting in lowering of the interfacial resistance. This fabrication strategy can control the morphology of the protective layer of core-shell/composite cathodes.

2. Experimental

2.1. Preparation of starting materials

All reagents were of analytical grade, purchased from Wako Pure Chemical Industries and Kanto Chemical, Japan, and used in as-received condition without further purification. Deionized water was used in all the experiments.

Spherical LMO particles (core particles) were synthesized using composite precursor particles of Mn$_2$O$_3$ spheres and a Li source. This synthetic process was slightly modified from our previous method [29]. First, spherical MnCO$_3$ particles were prepared by the scalable precipitation method using MnSO$_4$ and (NH$_4$)$_2$CO$_3$ [30]. Subsequently, the MnCO$_3$ powder was decomposed into Mn$_2$O$_3$ at 800°C for 2 h in air. The obtained Mn$_2$O$_3$ particles acquired the morphology of porous spheres. Next, LiOH·H$_2$O was suspended in ethanol. The prepared Mn$_2$O$_3$ powder was added to this solution in a stoichiometric amount to form LMO. The resulting solution was stirred for 1 h and then gradually dried at 40°C in a vacuum using a rotary evaporator. Finally, the LiOH-impregnated Mn$_2$O$_3$ powder was calcined at 800°C for 6 h in air to form spherical LMO particles.

Plate-like NH$_4$MnPO$_4$·H$_2$O (AmMP) particles were prepared as the precursor of LMP via the wet mechanical method using a planetary ball mill (High-G BX254E; Kurimoto, Ltd., Japan) [31]. The raw powders (NH$_4$H$_2$PO$_4$ and MnCO$_3$, total 3 g) and water (20 mL) were entered into a stainless-steel vessel (170 cm$^3$) along with 2-mm diameter Y$_2$O$_3$-stabilized ZrO$_2$ balls (100 g). The vessel was sealed and subsequently rotated for 1 h under centrifugal acceleration of 50 G. Following the wet-milling, the product was collected via centrifugation, washed several times with water, and dried at 100°C.

2.2. Preparation of core-shell precursor particles

The preparation of core-shell LMO@AmMP precursor particles was performed via a dry mechanical process. The mechanical treatment of LMO and AmMP powders was conducted using an attrition-type mill that consisted of a circular chamber (inner diameter 80 mm and height 50 mm) and an internal elliptical rotor. The gap between the chamber and rotor was fixed at 0.6 mm. The starting powders of LMO (20 g) and AmMP (3, 5, 7, and 10 mass%) were entered into the chamber, and the inside rotor was then rotated at a speed of 2500 rpm. Each mechanical treatment was performed for 25 min while gradually adding AmMP powder. The obtained core-shell precursor particles are denoted as LMO@AmMP3, LMO@AmMP5, LMO@AmMP7, and LMO@AmMP10 based on the mass ratio of AmMP.

2.3. Conversion to LMO@LMP composite particles

In order to convert the AmMP shell layer into LMP particles, core-shell LMO@AmMP precursor powders were treated using hydrothermal vapor treatment. The LMO@AmMP powder (0.5 g) contained in a Teflon cylinder was entered into a Teflon-lined autoclave (inner volume 50 cm$^3$) with 1 M LiNO$_3$ (7.5 mL). Direct contact between the powder and solvent was avoided. Hydrothermal vapor treatment of the LMO@AmMP powders was performed at 120°C for 12 h, with the exception of the LMO@AmMP10 sample, which was treated at 160°C. After treatment, the products were washed with water and subsequently dried. The products converted from each LMO@AmMP sample are conveniently denoted as LMO@LMP3, 5, 7, and 10, respectively.

2.4. Characterization

The crystalline phases of the products were characterized using powder XRD (D2 PHASER, Bruker AXS, Japan) with Cu Ka radiation generated at 30 kV and 10 mA. The diffraction patterns were acquired at steps of 0.02° (2θ) and a counting time of 1 s/step. The particle morphologies of the products were observed using scanning
electron microscopy (SEM; JSM-6010LA, JEOL, Japan) and transmission electron microscopy equipped with energy dispersive X-ray spectrometry (TEM-EDS; JEM-2100F, JEOL, Japan). The specific surface area ($S_w$) of the products was calculated by the Brunauer-Emmett-Teller method used in $N_2$ adsorption measurements (3Flex, Micromeritics, Japan). Prior to each measurement, the powder was outgassed under vacuum at 120°C for 3 h. The particle size distribution was determined using the laser diffraction/scattering method (Microtrac MT3300EXII, NIKKISO, Japan). Small amounts of the samples were dispersed in 0.05 mass% sodium hexametaphosphate solution using an ultrasonic homogenizer.

**2.5. Electrochemical measurements**

The cathode performances of LMO@LMP composite products were evaluated via CR2032 coin-type cells with Li metal as the anode. The LMO@LMP composite powder was mixed with acetylene black carbon (DENKA, Japan) and polyvinylidene difluoride (Kishida Chemical, Japan) in a weight ratio of 80:15:5 in N-methyl-2-pyrrolidone (Kishida Chemical). The obtained homogeneous cathode slurry was coated onto Al foil using a doctor blade, and subsequently dried at 100°C for 12 h in a vacuum. The dried cathode was uniaxially pressed and punched out of the foil. A polypropylene membrane (#2400, Celgard, USA) and 1 M LiPF$_6$ (Kishida Chemical) solution in a mixed electrolyte, respectively. The coin-type cells were assembled (50:50 vol%) were used as the separator and electrolyte, respectively. The charge and discharge tests were performed using an electrochemical workstation (VMP3, Bio-Logic, France) with a voltage range of 3.0–4.4 V at 25°C and 60°C.

**3. Results and discussion**

Figure 1 illustrates the scheme for the fabrication of the LMO@LMP composite particles. The LMO sphere used as the core was synthesized using spherical Mn$_2$O$_3$ particles as the starting material. AmMP plates (synthesized via wet planetary ball milling) were deposited on the LMO sphere via a mechanical method. The prepared core-shell LMO@AmMP particles were treated hydrothermally with LiNO$_3$ vapor to convert AmMP into LMP rods. The resulting product was composed of the LMO core sphere and LMP rod particles.

The powder properties of LMO and AmMP prepared by each synthesis method are shown in Figure 2. The LMO spheres were synthesized via a solid-state reaction of LiOH-impregnated Mn$_2$O$_3$ precursor particles. The product corresponded to a spherical secondary particle with a diameter of several micrometers that consisted of sub-micrometer primary particles (Figure 2(a)). The median size ($D_{50}$) of the LMO powder corresponded to 3.9 µm. Each primary particle exhibited a well-developed crystallographic facet. The synthesis of LMO spheres from LiOH-impregnated Mn$_2$O$_3$ precursor particles formed a hollow structure, as shown in Figure 3. This followed a formation mechanism analogous to the Kirkendall effect [32]. Given the exposed primary particles and the hollow structure, the powder exhibited a specific surface area ($S_w$) of 23 m$^2$/g. Meanwhile, the AmMP plate particles were obtained via wet planetary ball milling, and their lateral size and thickness were below 1 µm and 50 nm, respectively (Figure 2(b)). The XRD patterns of the two materials exhibited a highly crystalline phase (Figure 2(c)).

Mechanical treatment of LMO spheres and AmMP plates using an attrition-type mill was conducted with different additive amounts of AmMP. Figure 4 shows the XRD patterns of the treated products. The diffraction peak intensity of AmMP increased with increases in the additive amount. No reaction between LMO and AmMP occurred under any treatment conditions. Figure 5 shows SEM and TEM-EDS images of LMO@AmMP. The spherical shape of LMO was maintained after the mechanical treatment (Figure 5(a)). The rugged particle surface of the original LMO spheres (Figure 2(a)) was changed into a relatively smooth surface. The TEM observation of LMO@AmMP revealed the surface coating of AmMP plates (Figure 5(b)). According to the surface contrast (arrow area), the thickness of the AmMP coating layer was estimated to be just under 200 nm. Given that the thickness of the AmMP plates was <50 nm, approximately four layers were deposited on the LMO spheres for the LMO@AmMP sample. The EDS elemental maps of Mn and P indicated homogenous coating with AmMP plates (Figure 5(c,d)). The overlay image of these elemental maps strongly supported a core-shell structure as the LMO core and AmMP shell, moreover, as shown in Figure 6. The AmMP plates were homogeneously deposited on the LMO spheres due to the shear and compression.

![Figure 1](image_url)  
Figure 1. Scheme of the formation sequence of LMO@LMP composite cathode particles.
actions of the attrition-type mill. Conversely, the particle shape and size were unchanged after the mechanical coating. The powder properties of the products are summarized in Table 1. The median size of all core-shell LMO@AmMP precursor powders corresponded to 3.4 µm, nearly equal to that of LMO. Subtle changes in the products were evident in their specific surface area. When small amounts of AmMP plates were deposited on LMO spheres, the specific surface area decreased to 1.9 m²/g for LMO@AmMP3 from 2.3 m²/g of LMO. This was due to the coating of the rugged surface with LMO primary particles. Furthermore, the specific surface area increased with increases in the additive amount of AmMP. This increase was caused by an increase in the number of AmMP plates with a higher specific surface area (Sₓ of AmMP about 23 m²/g).

The prepared core-shell LMO@AmMP precursor powders were treated with LiNO₃ vapor in a sealed vessel to convert AmMP into LMP on the shell layer. The hydrothermal vapor treatment of LMO@AmMP samples was conducted at 120°C using 1 M LiNO₃ solution, while that of LMO@AmMP10 was conducted at 160°C to achieve complete conversion. Figure 7 shows XRD patterns of the treated products. The diffraction peaks of AmMP disappeared after treatment with the LiNO₃ vapor. Conversely, tiny peaks that were observed due to LMP appeared distinctly with increases in the additive amount. Changes were not observed in the diffraction pattern of

Figure 2. SEM images of (a) LMO spheres and (b) AmMP plates. (c) XRD patterns of the two starting materials.

Figure 3. SEM image of the cross-sectional surface of an LMO sphere.

Figure 4. XRD patterns of core-shell LMO@AmMP products.
LMO for any samples, and this indicated that LMO is stable upon reaction with the LiNO$_3$ vapor at high pressures and temperatures. Assuming that all the AmMP particles on LMO were converted to LMP particles, the fractions of LMP in the LMO@LMP3, LMO@LMP5, LMO@LMP7, and LMO@LMP10 were calculated to be 2.5%, 4.2%, 5.9%, and 8.5%, respectively. Figure 8 shows SEM and TEM-EDS images of LMO@LMP5. Although the spherical morphology was retained after the hydrothermal treatment, the particle surface was apparently covered with spiny LMP products (Figure 8(a)). The magnified TEM image reveals that rectangular LMP rods were formed on the LMO spheres (Figure 8(b)). A slightly segregated distribution of P (when compared with core-shell LMO@AmMP precursor particles (Figure 5(d)) indicates a particle shape change associated with the conversion reaction to LMP (Figure 8(d)). In the case of the LMO@LMP7 sample, the same particle morphology as

Table 1. Powder properties of LMO@AmMP and LMO@LMP products.

| Additive amount (%) | LMO@AmMP | LMO@LMP |
|---------------------|-----------|----------|
|                     | D$_{50}$ (µm) | S$_{w}$ (m$^2$/g) | D$_{50}$ (µm) | S$_{w}$ (m$^2$/g) |
| 3                   | 3.4       | 1.9      | 3.4         | 2.2          |
| 5                   | 3.4       | 2.1      | 3.4         | 2.2          |
| 7                   | 3.4       | 2.7      | 3.3         | 3.2          |
| 10                  | 3.4       | 2.7      | 3.3         | 3.5          |

D$_{50}$ and S$_{w}$ of LMO spheres are 3.9 µm and 2.3 m$^2$/g, respectively.

LMO for any samples, and this indicated that LMO is stable upon reaction with the LiNO$_3$ vapor at high

Figure 5. (a) SEM image, (b) TEM image, and EDS elemental maps of (c) Mn and (d) P for LMO@AmMP5 particles.

Figure 6. Overlay EDS elemental map of LMO@AmMP5 particles (Mn and P in green and red, respectively).

Figure 7. XRD patterns of LMO@LMP composite products.
that of LMO@LMP5 was obtained through the conversion reaction from LMO@AmMP7. Figure 9 shows TEM-EDS images of LMO@AmMP7 and LMO@LMP7 samples. From these results, we prepared the LMO@LMP composite particles through a two-step process. The formation of LMP rods on LMO spheres led to an increase in the specific surface area (Table 1). The median size was maintained after the hydrothermal vapor treatment, which succeeded in converting only the shell layer of LMO. The hydrothermal vapor conversion of AmMP into LMP led to a particle shape change from plates to rods. The conversion reaction of ammonium metal phosphates to alkaline metal phosphates is topotactic, and a plate precursor can accordingly be transformed into a rod-like product [33]. A structural rearrangement from the edge of the AmMP plates is produced in the LMP rods by the condensation of LiO$_6$ octahedra via an ion exchange reaction of solid-state NH$_4^+$ with LiNO$_3$ vapor. Hydrothermal vapor treatment is a useful method for controlling a crystal surface [34].

Figure 8. (a) SEM image, (b) TEM image, and EDS elemental maps of (c) Mn and (d) P for LMO@LMP5 composite particles.

Figure 9. TEM-EDS elemental maps of (a-c) LMO@AmMP7 and (d-f) LMO@LMP7 samples; (a,d) Mn, (b,e) P, and (c,f) overlay images of Mn and P. Scale bar: 500 nm.
Charge–discharge tests were conducted up to 30 cycles to compare the cathode performances of LMO and LMO@LMP composites at 60°C. Figure 10 summarizes the electrochemical performances of LMO and LMO@LMP composite cathodes. The first charge–discharge curves of LMO and LMO@LMP7 cathodes exhibited almost the same plateaus at 4.0 and 4.1 V (Figure 10(a)). The presence of the two plateaus was attributed to the different reaction modes of LMO, namely two-phase and one-phase reaction modes based on Li content [35]. The theoretical potential of LMP is identical to that of LMO at approximately 4.1 V (vs. Li⁺/Li). Furthermore, the additive amount of LMP is low relative to that of LMO, and it is thus difficult to determine the charge–discharge potential of LMP. Given the same charge–discharge potential of LMO and LMP, a nearly equal first discharge capacity of 125–130 mAh/g was observed. The core-shell and composite cathodes consisted of two types of active materials with different potentials, which typically results in restriction of the practical discharge capacity due to the limited working potential window [22,23]. Conversely, the composite cathode of LMO and LMP with the same potential windows did not exhibit a restriction in the initial charge–discharge step.

Surprisingly, it was noted that the bare LMP cathode, prepared by the same hydrothermal vapor treatment from the AmMP powder, exhibited poor electrochemical performances: a discharge capacity of only ~8 mAh/g and a large polarization between the charge and discharge steps. This indicates that LMP surface particles do not interfere with the intrinsic cathode performance of LMO. After 30 cycles at 60°C, the discharge capacities of LMO and LMO@LMP7 decreased to 79 and 93 mAh/g, respectively (Figure 10(b)). However, the capacity degradation was suppressed for the LMO@LMP7 composite cathode. A comparison of the charge and discharge plateaus indicated that the LMO@LMP7 cathode exhibited lower polarization in comparison with that of the LMO cathode, a result indicating a decrease in the internal resistance.

The effect of the additive amount of LMP on cathode performance was evaluated for the discharge capacity retention for 30 cycles (Figure 10(c)). The capacity retention of LMO was 63%, which was identical to that of LMO@LMP3. Increasing the amount of LMP increased capacity retention, and the LMO@LMP7 cathode exhibited a maximum value of 72%. Nevertheless, a further increase in the LMP ratio led to a decrease in capacity retention corresponding to 68% for LMO@LMP10. At 60°C, all the cathodes exhibited a gradual decline, although LMP was deposited. This was due to the intrinsic cathode performance of LMO spheres. As shown in Figures 8(a) and 9(f), the converted LMP rods did not fully coat the LMO spheres. Therefore, the electrolyte reached the surface of LMO, and this caused Mn dissolution at high temperatures. Conversely, a larger amount of LMP (which is a thick deposition) exacerbated the disadvantages of

Figure 10. Electrochemical performances of LMO and LMO@LMP composite cathodes; (a) 1st and (b) 30th charge–discharge curves of LMO and LMO@LMP7 cathodes recorded at 15 mA/g at 60°C, (c) discharge capacity retention during 30 cycles, and (d) Nyquist plots at open-circuit potential at an AC voltage of 5 mV at room temperature.
the olivine material including poor ionic and electric conductivities. Performance degradation due to thick LMP coating was reported by Zhang et al [27]. Improvements in the cycling performance of LMO at high temperatures were attained by depositing optimal LMP contents, and the LMO@LMP7 cathode exhibited better cathode performances as a result.

The electrode/electrolyte interfacial compatibility was investigated using electrochemical impedance spectroscopy at room temperature (Figure 10(d)). The semicircle in the Nyquist plot corresponds to the charge-transfer resistance at the electrolyte/active particle interfaces. With respect to fresh cells, the interfacial resistance of the LMO@LMP7 cathode was significantly lower than that of the LMO cathode. While the exact reason for this low resistance can be realized by performing more detailed electrochemical tests, a potential reason is an increase in both the specific surface area and the number of ionic and electronic conduction pathways caused by the formation of LMP rods. On the composite particle surface, interspaces existing between the LMP rods enable the liquid electrolyte to penetrate toward the LMO core, thereby allowing easy access to the Li$^+$ ions [36,37]. Electrons move longitudinally on the LMP rods and subsequently reach the LMO core. Therefore, the decrease in interfacial resistance is due to the construction of ionic and electronic conduction pathways at the LMO surface. The role of LMP is not to achieve synergistic enhancement of the cathode performance of LMO, but to contribute to both addition of thermal stability to LMO and improvement of Li$^+$ conductivity on the particle surface. Cathode performance can be further improved if the converted LMP rods crystallize in a direction orientated to the superior Li$^+$ diffusion pathways [38,39].

4. Conclusions

In this study, we developed a new particle structure for LMO@LMP composite cathodes. These cathodes possess a rod-like surface layer, which is formed by reacting the plate precursors with LiNO$_3$ vapor. The fabrication strategy consists of a two-step process, including mechanical coating and subsequent hydrothermal conversion. Specifically, AmMP plates (as the shell precursor) coated with LMO spheres were converted into LMP rod particles via hydrothermal vapor treatment with LiNO$_3$. Compared with uncoated LMO cathodes, the existence of the optimal LMP contents caused the LMO@LMP composite cathodes to exhibit improved electrochemical performance at 60°C. The capacity retentions of LMO@LMP7 and LMO cathodes after 30 cycles were 72% and 63%, respectively. Further structural arrangement of the LMP surface particles, including their crystal orientation, aspect ratio, and contact points with the LMO core, can lead to development of an LMO cathode suitable for large-scale applications of LIBs.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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