

TEM Observation of LaPO₄-Dispersed LATP Lithium-Ion Conductor

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ABSTRACT

We have previously reported that a three-fold increase in lithium-ion conduction can be achieved on LATP (Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃) by dispersing LaPO₄ particles through the co-sintering of LATP with 4 wt% of LLTO (Li_{0.348}La_{0.55}TiO₃). However, the LaPO₄ formation during sintering has been detected only by means of XRD and back-scattered SEM, and precise morphology of LaPO₄ particles as well as LATP/LaPO₄ interface have still been uncertain. In the present study, we carried out TEM experiments on the LaPO₄-dispersed LATP composite to investigate the detailed microstructure and compositions of the dispersed LaPO₄ particles and surrounding LATP matrix. HR-TEM coupled with EDS reveals that LaPO₄ particle attains an intimate contact with the LATP matrix, which would allow the formation of space charge layer at the interface to enhance the conductivity.

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Keywords : HRTEM, Lithium-ion Conductor, LATP, Space Charge Layer

1. Introduction

In the current stage of research on lithium-ion conductors, a primary goal is to improve their ionic conductivities.^{1–5} As one of the modification strategies, it has been reported that dispersion of dielectric particles in the halide-type lithium-ion conductors provide significant improvement of ionic conductivity.^{6–8} The mechanism of conductivity enhancement has been elucidated by Maier's model, where the local ion mobility is increased due to the formation of space charge layer at the ionic conductive matrix/dielectric particle interface.^{9,10} However, this approach has been mostly applied on halide-based lithium-ion conductors,^{6–8,11–15} while very few on the oxide-based systems.^{16–19}

In the previous works, we have reported that 4 wt% addition of LLTO (Li_{0.348}La_{0.55}TiO₃) particles into LATP (Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃) matrix followed by co-sintering resulted in an ionic conductivity enhancement from 0.28 mS cm^{−1} (pristine LATP) to 0.76 mS cm^{−1}.²⁰ Similar experiment on LAGP (Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃) also achieved the conductivity improvement by introducing LLTO, although the amount of increase is smaller than that of LATP-based system.²¹ X-ray diffraction and backscattered-SEM indicated that dielectric LaPO₄ particles have been created by decomposing LLTO during co-sintering, which would induce the space charge layer for the conductivity improvement. However, above experiments only proved the formation of LaPO₄ particles, while precise morphology of dispersed particle as well as the LATP/LaPO₄ interface are still uncertain.

The HR-TEM is widely used technique to study the chemical, crystallographic and microstructural feature of particles and

interfaces.^{22–26} In this work, morphology, chemical composition, and lattice structure of the particles have been investigated through HR-TEM imaging, EDS and SAED characterization. In addition, the morphology of LATP matrix/LaPO₄ particle interface has also been studied.

2. Experimental

2.1 Preparation of LLTO particles

LLTO has been prepared by conventional solid-state reaction method. Stoichiometric amounts of starting materials, Li₂CO₃ (99.0 % Wako Pure Chem., Japan), La₂O₃ (99.5 % Wako Pure Chem.) and TiO₂ (Rutile, 99.9 % Kojundo Chem., Japan) reagents, were mixed in an automatic grinder with an aid of ethanol for 5 h before calcination at 800 °C for 10 h. The calcined product was crushed and isostatically pressed under 392 MPa and sintered at 1300 °C for 10 h. The sintered LLTO pellets were then crushed, and ball-milled at 400 rpm for 10 h using zirconia pot and balls (Pulverisette7 premium line, Fritsch, Germany) with a small amount of ethanol.

2.2 Preparation of LATP precursor

LATP was prepared by mixing stoichiometric amounts of Li₂CO₃ (99.0 % Wako Pure Chem., with a 10 % excess), γ-Al₂O₃ (97.0 % Stream Chemical, USA), TiO₂ (99.99 % Kojundo Chem.) and NH₄H₂PO₄ (99.0 % Wako Pure Chem.) in automatic grinder with an aid of ethanol for 5 h prior to calcination at 700 °C for 2 h. The calcined product was then crushed to form precursor powder.

2.3 Fabrication of LATP – 4 wt% LLTO composite

To prepare LATP – LLTO composite, the LLTO powder (4 wt%) and LATP precursor were mixed by a planetary ball-mill (Pulverisette7 premium line, Fritsch) for 5 h at 400 rpm with a small amount of ethanol followed by drying at 120 °C. The mixed

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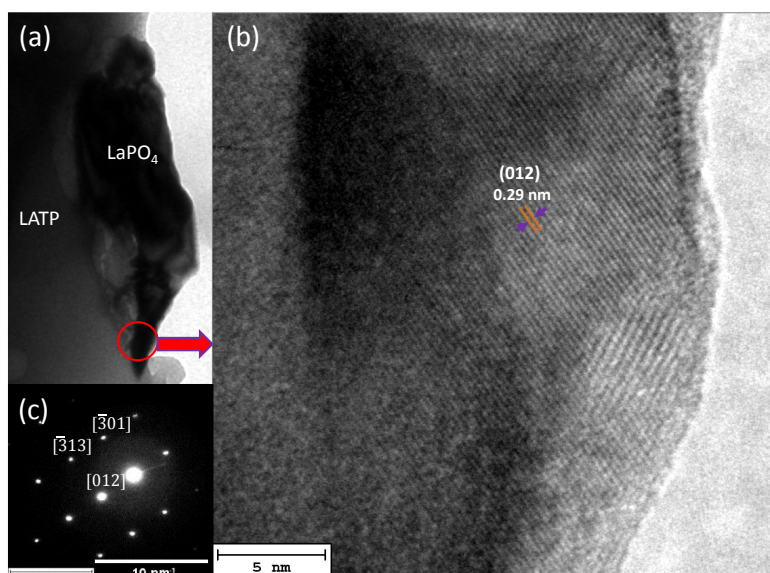


Figure 1. (a) TEM image at matrix/particle boundary region. (b) HR-TEM image at the particle area. (c) SAED pattern at the particle area.

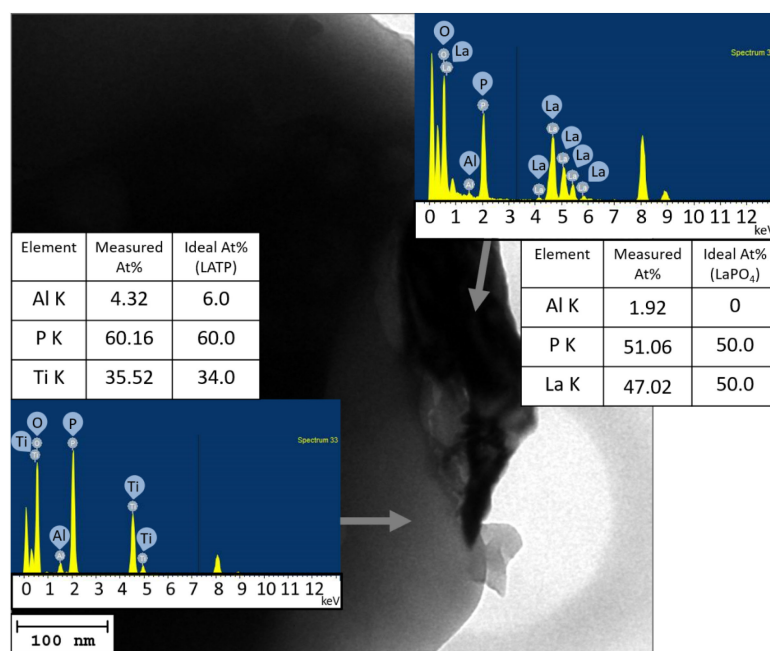


Figure 2. Point EDS results at matrix (lower-left) and particle (upper-right) areas.

powder was then isostatically pressed at 100 MPa and sintered at 1000 °C for 10 h to form LATP-LLTO composite pellets.

2.4 High resolution TEM observation

The synthesized LATP – LLTO composite was roughly crushed and dispersed on a copper grid to serve the TEM experiments. A field-emission TEM (JEM-F200, JEOL, Japan) operated at 200 kV equipped with an EDS detector (Oxford Instruments, UK) in STEM mode has been employed for investigating the morphology, chemical composition, and crystal structure of the prepared composite.

3. Results and Discussion

Figure 1(a) shows the TEM image at matrix/particle boundary area, where the rod-shaped particle can be distinguished from the matrix due to the darker contrast. This particle possesses a

dimension below 500 nm with an intimate contact with the LATP matrix. The HR-TEM image and the electron diffraction pattern at the particle are shown in Figs. 1(b) and 1(c). The indexed SAED pattern and the corresponding *d*-spacing of the lattice image confirm that the particle is consistent with the monoclinic structured LaPO₄ (*a* = 0.684 nm, *b* = 0.708 nm, *c* = 0.651 nm and β = 103.24°).²⁷ In terms of the chemical composition, EDS point analysis was conducted at both matrix and particle areas, the results of which are shown in Fig. 2. The EDS result from the particle area (upper-right inset) shows that the atomic percentages of cations are approximately coincide with the ideal values of LaPO₄, within uncertainties in the EDS detection. The EDS result at the matrix (lower-left inset) also agrees with the nominal composition of LATP ignoring lithium. Therefore, present TEM data undoubtedly confirm the previous XRD and SEM results that LLTO particles reacted with LATP matrix upon sintering to form LaPO₄ phase while the LATP phase was preserved.²⁰ Recent work has also achieved LaPO₄

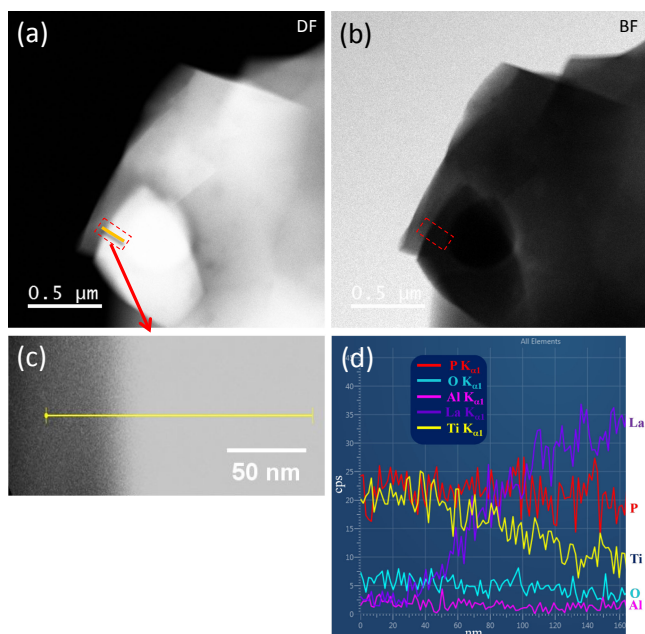


Figure 3. (a) and (b) dark field and bright field TEM image at matrix/particle boundary area. (c) Enlarged image at matrix/particle boundary and EDS scanning trace. (d) EDS scanning result.

dispersion through the co-sintering of LATP with La_2O_3 nano powder, which discovered that LiTiPO_5 phase (PDF# 44-0083) is also formed as a by-product during the formation of the LaPO_4 particles.²⁸ Further verification on XRD patterns of LATP – 4 wt% LLTO also identified the LiTiPO_5 phase. However, since such phase and other impurities are not detected by the TEM observation in this work, the LaPO_4 formation reaction ignoring the mass ratio can be written as: $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3 + \text{Li}_{0.348}\text{La}_{0.55}\text{TiO}_3 \rightarrow \text{LaPO}_4 + \alpha$, where the α denotes the other residual phases of the reaction containing LiTiPO_5 .

Figure 3 presents the result of a line scanning of EDS across the matrix/particle boundary. Dark (a) and bright (b) field images exhibit distinct contrasts at the boundary. The enlarged image in (c) indicates an intimate contact between the particle and the matrix. EDS scanning has been conducted along the yellow line in (c),

where left and right areas correspond to the matrix and particle, respectively. It is shown in (d) that titanium signal decreases toward right hand while lanthanum increases, which also supports that the matrix and particle are consist of LATP and LaPO_4 , respectively. Gradual changes in titanium and lanthanum signals might be caused by the spot size of incident electron beam or the contribution of the backward part due to the small particle thickness. The intimate contact observed in Figs. 1(a) and 3 should be essential for the space charge layer model which can explain the conductivity improvement in dielectric particle-dispersed ionic conductors.^{9,10} The HR-TEM image at bulk area of the matrix is shown in Fig. 4, where the indexed FFT pattern is consistent with the structure of LATP with hexagonal lattice ($a = 0.850 \text{ nm}$, $c = 2.08 \text{ nm}$).²⁹

In summary, the present work confirms the dispersion of LaPO_4 particles and their morphology through HR-TEM experiment on the LaPO_4 -dispersed LATP prepared by co-sintering LATP with LLTO. While the space charge layer at the LaPO_4 particle/LATP matrix interface is not directly observed, the intimate contact between the LaPO_4 particle and the LATP matrix is revealed, which should be a key microstructural feature to form the space charge layer at the particle/matrix interface. In future studies, ^7Li NMR should be employed to characterize the diffusion of lithium ions focusing on the bulk and particle/matrix boundary regions, and to study the diffusion behavior of lithium ions at the space charge layer.³⁰

4. Conclusion

In this work, the LaPO_4 -dispersed LATP lithium-ion conductor has been investigated by HR-TEM accompanied by EDS characterization. It was confirmed that the LaPO_4 particles are dispersed in the LATP matrix. TEM images at the LATP matrix/ LaPO_4 particle interfaces show an intimate contact, which can be attributed to the reaction between LATP and LLTO during the sintering. It is believed that this microstructural feature is an essential condition for the formation of space charge layer at the LATP matrix/ LaPO_4 particle interface, which enables the three-fold conductivity enhancement as the previous report.

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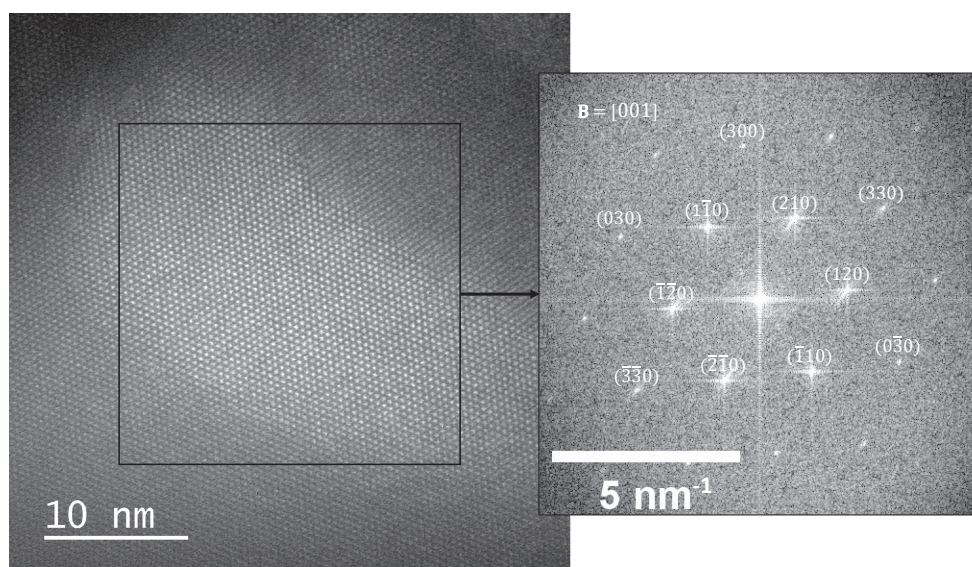


Figure 4. HR-TEM image at bulk of LATP matrix and indexed FFT pattern.

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