

Research Article

High Li^+ Conductivity of $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$ with Hybrid Solid Electrolytes for Solid-State Lithium Batteries

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Solid-state electrolytes (SSEs) are promising future power sources for electronic vehicles (EVs) and devices due to their enhanced safety features, high energy density, and nonflammability. The NASICON structure has emerged as a frontrunner in oxide-based electrolytes, boasting high Li-ion conductivity and air stability. Nevertheless, developing high-performance oxide-based electrolytes remains challenging due to their inherently hard and brittle nature, presenting obstacles to achieving an optimal interface between the cathode and anode. In this study, to overcome this issue and enhance electrochemical stability and Li-ion conductivity, a new approach employing a hybrid solid electrolyte amalgamating polymer electrolytes with inorganic $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$ powder ($x = 0, 0.015, 0.030, 0.045, \text{ and } 0.060$) was investigated. Notably, employing nanosized $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) synthesized via the sol-gel method led to a remarkable increase in ionic conductivity to $7.29 \times 10^{-4} \text{ S cm}^{-1}$, which was attributed to enhanced pellet density. Electrochemical analysis revealed that $\text{Li}_{1.345}\text{Al}_{0.255}\text{Mg}_{0.045}\text{Ti}_{1.7}(\text{PO}_4)_3$ exhibited superior specific capacity, stable high current density performance, and capacity recoverability compared to LATP. This pioneering study highlights the potential of hybrid solid electrolytes incorporating Mg-doped LATP as a promising material for practical solid-state lithium batteries.

1. Introduction

Lithium-ion batteries (LIBs) are commonly utilized in electric and hybrid cars, as well as portable electronic devices, owing to their environmentally friendliness and adequate energy storage capacity [1, 2, 3]. However, serious safety problems are associated with using highly flammable liquid electrolytes in conventional LIBs. These risks include electrolyte contamination, burning risk factors, and electrode surface damage [4, 5, 6, 7, 8, 9]. All-solid-state batteries (ASSBs) have been developed to replace flammable organic electrolyte compounds with solid-state components to address these challenges. ASSBs are a feasible alternative to battery technology owing to their increased safety and energy density. Three types of solid electrolytes, the fundamental components of ASSBs, are available: inorganic,

polymer, and inorganic-organic hybrid solid electrolytes. Solid electrolytes provide unique opportunities for improved performance [10, 11]. Since the 1950s, when Li_3N was discovered, inorganic solid-state electrolytes (SSEs) have played a crucial role in the development of LIBs. Li_3N gave excellent ionic conductivity ($10^{-3} \text{ S cm}^{-1}$ at ambient temperature) but low breakdown voltage (0.445 V). A thin-film Li phosphorus oxynitride (LiPON) was first presented by Oak Ridge National Laboratory in 1992. The Li-ion motion in perovskite-type $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (LLTO) was shown by Inaguma et al., a year later. At room temperature, LLTO showed more than $2 \times 10^{-5} \text{ S cm}^{-1}$. Fu [12, 13] created NASICON-type SSEs having conductivities of 10^{-4} and $1.3 \times 10^{-3} \text{ S cm}^{-1}$, namely $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP) and $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP). All-solid-state Li batteries (ASSLBs) have great promise thanks to the garnet-type

rapid ionic conductor $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), which was described by Murugan et al. [14]. It has high thermal and chemical stability and outstanding ionic conductivity ($3 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperature) [12, 13, 14, 15, 16, 17, 18].

Inorganic oxide electrolytes have received increasing attention because of their remarkable qualities, including high ionic conductivity, low electronic conductivity, outstanding chemical stability, extensive electrochemical windows, and robust safety features [19]. Many studies have focused on NASICON-structured $\text{LiMe}_2(\text{PO}_4)_3$ ($\text{Me} = \text{Ti}^{4+}$, Ge^{4+} , Zr^{4+} , etc.) LATP in this area of inorganic oxide electrolytes [20]. The strong ionic conductivity of LATP, which is generally between 10^{-4} and $10^{-5} \text{ S cm}^{-1}$ at room temperature; its exceptional chemical stability, even in the presence of ambient air or humidity, and the financial sustainability of the manufacturing technique are the reasons for this increased research focus. Despite the several benefits of LATP, its application is limited by its stiffness and poor interfacial interaction functionality, among other issues. Nevertheless, a more urgent issue is using LATP material, as its inability to contact lithium metal directly presents a significant barrier. This problem is particularly apparent when using LATP in LIBs because the addition of lithium metal causes Ti^{4+} to be reduced to Ti^{3+} . As a result of this reduction, a redox reaction arises at 2.5 V vs. Li/Li^+ , hindering the significant ionic conductivity shown by LATP [21, 22, 23]. The ability to interact the material with other lower potential anode materials, such as lithium, is restricted. A battery short circuit might result from lithium or C_6Li reducing LATP which could induce electrical conductivity in the solid electrolyte. This results in a significant interface impedance between the electrode and solid electrolyte, ultimately hindering practical application performance and operational efficiency [7, 21, 24]. Nikodimos et al. [25, 26] reported that the diffusion channel size significantly increased when two dopants, Al^{3+} and Sc^{3+} , were used with an ion with a larger ionic radius than those of Ge^{4+} and Al^{3+} . This enhancement in ion mobility results in increased ionic conductivity. Therefore, it is anticipated that adding a divalent-cation dopant will increase the amount of mobile Li^+ in the LATP electrolyte and improve the material's crystal structure, ultimately resulting in increased Li^+ conductivity [25, 26].

In this study, a solid electrolyte material based on LATP exhibited great potential for use in solid-state batteries. Employing Mg^{2+} , a more affordable and readily available divalent cation, led to a significant increase in Li^+ concentration and an expansion of diffusion channels because of its higher ionic radius (0.72 Å) than those of Ge^{4+} and Al^{3+} [26]. Herein, two approaches to address these perennial issues are introduced, both utilizing the doping of Mg^{2+} in a hybrid solid electrolyte. $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$ (or Mg-doped LATP, where $x = 0, 0.015, 0.030, 0.045, 0.060$) was created by synthesizing a hybrid solid electrolyte composed of polymer electrolytes and various amounts of inorganic powders doped with Mg^{2+} . The effects of Mg^{2+} addition on Li^+ conductivity and energy barrier were carefully examined. The most attractive solution was experimentally verified after computational modeling was used to predict the ideal dopant composition for favorable LATP characteristics [7, 27, 28]. Several Mg precursors were subjected to

intensive testing to determine which would work best for homogenized and efficient interactions with additional precursors. These results are expected to advance garnet solid electrolyte-based solid-state batteries by highlighting the importance of a comprehensive approach in designing both the bulk and grain boundaries of the solid electrolyte for long-term battery stability.

2. Materials and Methods

2.1. Material Synthesis. The synthesis of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) and $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$ (Mg-doped LATP) involved utilizing specific precursors. In the sol-gel process, precise amounts of lithium acetate dehydrate ($\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich, 98%), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 99%), magnesium acetate tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 99\%$), titanium (IV) butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, Sigma-Aldrich, 97%), phosphoric acid (Sigma-Aldrich, 85 wt.% in H_2O), 2-methoxyethanol (Alfa Aesar, 99%), and poly (ethylene glycol) (PEG, Sigma-Aldrich, Mw 200) were employed to synthesize LATP and Mg-doped LATP nanoparticles. The mixture solution was heated in a hydrothermal Teflon liner at 200°C for 6 hr, then gradually cooled to room temperature. Ivory-colored powders were collected after drying in a vacuum oven. Subsequently, the nanoparticles were annealed in a furnace at 525°C for 5 hr under a 5% H_2/Ar mixed gas atmosphere. For the solid-state reaction, lithium carbonate (Li_2CO_3 , Sigma-Aldrich, $\geq 99\%$), aluminum oxide (Al_2O_3 , gamma-phase, Alfa Aesar, 99.97%), magnesium oxide (MgO , Sigma-Aldrich, 97%), titanium (IV) oxide (TiO_2 , Sigma-Aldrich, $\geq 99.5\%$), and ammonium phosphate dibasic ($(\text{NH}_4)_2\text{HPO}_4$, Sigma-Aldrich, 98%) were utilized [29, 30, 31, 32, 33]. The resulting powder was then calcined for 2 hr at 850°C in a hot furnace.

2.2. Fabrication of Hybrid Solid Electrolytes and Cathode Electrodes. The synthesis of a solid polymer electrolyte and the addition of inorganic powder were used to create hybrid solid electrolytes using the sol-gel process [34]. When bisphenol A ethoxylate diacrylate (Mn ~688, Hannong Chemicals) and lithium bis (trifluoromethyl sulfonyl) imide (LiTFSI , Alfa Aesar, $\geq 98\%$) are combined in an 8:2 ratio, the former becomes dispersed in poly (ethylene glycol) dimethyl ether (PEGDME, Hannong Chemicals). Bisphenol A ethoxylate diacrylate mixed solution and tert-butyl peroxyneodecanoate solution (Luperox 10A, Arkema), which is utilized as a radical chain reaction initiator, were mixed at a ratio of 100:1. Ten percent LATP and 10% Mg-doped LATP powders were blended into a well-mixed solution and compared to the total amounts of PEGDME and bisphenol A. The mixture was poured into a container, and the solution was evaporated for 3 hr using a hot plate to solidify the electrolytes [20]. This simple procedure allowed the hybrid solid electrolytes to be punched into discs with diameters of 16 mm. LiFePO_4 (LFP) powder was employed as an active material, conductive agent, binder, and solvent in fabricating the cathode electrode slurry. Other components were conductive acetylene black, polyvinylidene fluoride (PVDF), and *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, 99.5%). The slurry was combined with poly (ethylene glycol), dimethyl

ether, and LiTFSI in a THINKY mixer. Using a doctor blade with a 25 μm thickness, the homogeneously mixed slurry was coated over Al foil and vacuum-dried at 120°C. The electrode was punched into 14 mm-diameter discs to serve as a working electrode.

2.3. Material Characterization. The X-ray diffraction (XRD) analysis of the powder samples was conducted using a MiniFlex 600 Rigaku instrument equipped with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) in the 2θ range of 10°–100°, with a step size of 0.0025° and scan speed of 0.3° min^{−1}. To study the crystal structure, Rietveld refinement was performed using the General Structure Analysis System (GSAS) software. To visualize the unit cells in detail, the structural parameters of the synthesized powders were determined using a three-dimensional visualization system for electronic and structural analysis (VESTA). Field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping images were obtained using a Nova NanoSEM 450. High-resolution transmission electron microscopy (HR-TEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEOL JEM-2100F microscope. X-ray photoelectron spectroscopy (XPS, K α) data, collected for chemical analysis, were analyzed by fitting the spectral results using Origin software with X-ray photoemission spectrum special baseline mode and the Shirley method. The binding energies were calibrated based on the C1s peak (284.6 eV). The Raman spectra were recorded using an NRS-3100 laser at an excitation wavelength of 532 nm.

2.4. Electrochemical Measurements. The ionic conductivities of the LATP and Mg-doped LATP pellets were assessed through EIS, employing a 5 mV AC amplitude within a frequency range of 1 Hz–1 MHz using an Autolab/M101 system. Before EIS measurement, the synthesized powders were subjected to cold isostatic pressing (YLJ-CIP, MTI Korea) at 300 MPa to form disc-shaped pellets with a diameter of approximately 12 mm and a thickness of approximately 1.2 mm. The pellets were then sintered at 950°C for 6 hr in an air environment and gradually cooled to prevent thermal shock. To facilitate the EIS measurements of the Li⁺ conductivities, the samples were meticulously polished to remove any traces of water, using 320–5,000 SiC grinding papers. Subsequently, gold (Au) was sputtered onto both sides of the pellets to form Au/pellet/Au configurations, which served as blocking electrodes. The relative density of the pellets was determined using Archimedes method with a density determination kit. Geometric shrinkage, potentially influenced by cracks or porosities, was assessed by measuring the weight of the sample in both auxiliary liquid and air. To prepare the cathode for full cell evaluation, a slurry comprising 80% LiFePO₄ cathode (purchased from MTI Corp.), 10% carbon black (Super P), and 10% PVDF-HFP by weight was formed in *N*-methyl-2-pyrrolidone (NMP, Sigma–Aldrich, 99.5%). This slurry was then coated onto aluminum foil, compressed, and vacuum-dried at 120°C for 12 hr to fabricate an electrode. The electrode was subsequently cut into discs with a diameter of 14 mm, achieving a mass loading of ~4 mg cm^{−2}. The composite solid electrolyte

was immersed in 0.2 mL electrolyte for 10 min. The electrolyte consisted of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a 50 : 50, v/v ratio. A coin cell (CR2032) was assembled in an argon-filled glove box (maintaining the oxygen and moisture levels below 0.3 ppm) using a Celgard 2400 polypropylene separator. Galvanostatic charge–discharge experiments were conducted using a WonA-Tech (WBCS 3000) battery charger at a constant current density ranging from 0.1 C to 1.0 C (where 1 C corresponds to 160 mAh g^{−1} concerning the active material) within a voltage range of 2.5–4.2 V versus Li/Li⁺.

2.5. Calculation Methods. In this study, we conducted all the density functional theory (DFT) calculations with the Vienna ab initio simulation package (VASP) [35]. These analyses employed the projector-augmented wave method [36], and the exchange–correlation potential was described by the generalized gradient approximation (GGA) [37] within the Perdew–Burke–Ernzerhof (PBE) parametrization. Key computational parameters included a plane-wave cutoff energy set at 520 eV. For the cell relaxation process, k-point meshes were configured to a 3 × 3 × 1 grid, while a reduced 1 × 1 × 1 grid was used during ab initio molecular dynamics (AIMD) simulations. The atomic structures of LATP and Mg-doped LATP were derived from the LiTi₂(PO₄)₃ structure by randomly substituting Ti with Al or Mg. To satisfy the stoichiometry, extra Li atoms were randomly inserted into the 18e site [38].

3. Results and Discussion

XRD was utilized to investigate the crystal structures of LiTi₂(PO₄)₃ (LTP), Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP), and Li_{1.345}Al_{0.255}Mg_{0.045}Ti_{1.7}(PO₄)₃ (Mg-doped LATP-15%) synthesized via sol–gel method. Rietveld refinement of the freshly prepared samples was performed using synchrotron diffraction data. The Rietveld refinement and XRD patterns of the doped samples are presented in Figures 1(a), 1(b), 1(c), and 1(d) [39]. The pristine NASICON structured LiTi₂(PO₄)₃ (JCPDS, 35-0754) compound exhibited a good fit with the XRD patterns, and the crystal structure model of the Mg-doped LATP showed a rhombohedral phase with a space group of *R* $\bar{3}c$, consisting of octahedral TiO₆ and tetrahedral PO₄ units (Figures 1(e) and 1(f)) [39, 40]. In the case of the specific NASICON compounds, the relatively broad diffraction peaks suggest the formation of a crystalline structure postannealing at 525°C, displaying a notably lower thermal threshold compared to conventional solid-state routes due to impurity phases like AlPO₄ and Li₂TiO₃ [41, 42]. The presence of an impurity phase was evidenced by the XRD profiles of Mg-doped LATP, which manifested as an expansion of the XRD pattern within the range of 21.8°–24.3°. The synthesis of Mg-doped LATP involved incrementally replacing Al³⁺ with Mg²⁺ at 10% intervals, up to 50%. For instance, in Mg-doped 10% LATP (Mg-doped LATP-10%), 10% of 0.3 mol Al³⁺ was substituted with 0.03 mol Mg²⁺, resulting in the chemical formula Li_{1.33}Al_{0.27}Mg_{0.03}Ti_{1.7}(PO₄)₃. The impurity phase, magnesium tetrakisphosphate (MgP₄O₁₁), was detected in trace amounts beyond 40% Mg concentration. The chemical formulas at 40% and 50% Mg-doping were determined as Li_{1.42}Al_{0.18}Mg_{0.12}Ti_{1.7}(PO₄)₃ and

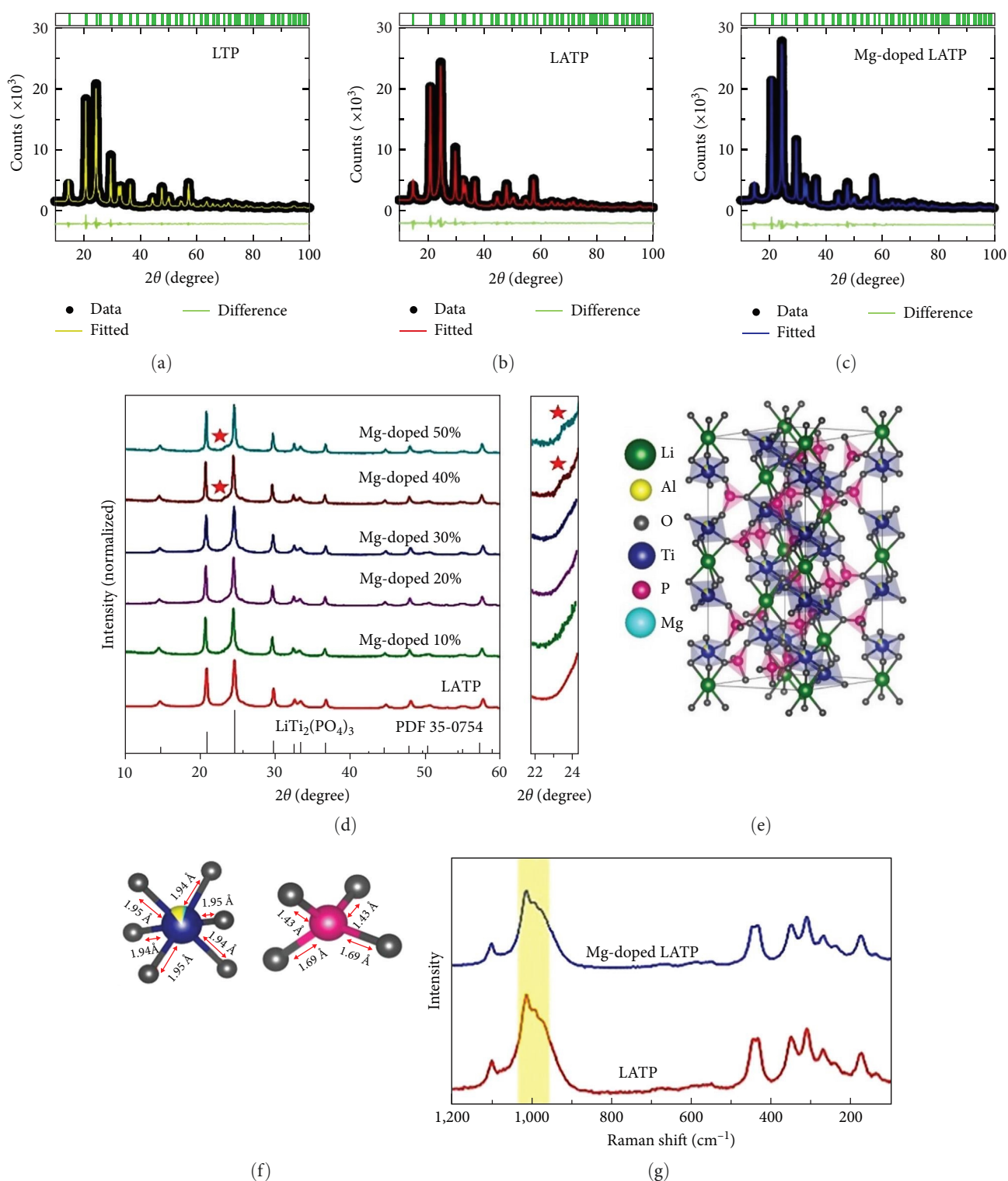


FIGURE 1: Rietveld refinement results based on HR-XRD of (a) $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), (b) $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP), and (c) $\text{Li}_{1.345}\text{Al}_{0.255}\text{Mg}_{0.045}\text{Ti}_{1.7}(\text{PO}_4)_3$ (Mg-doped LATP-15%). (d) XRD pattern of $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$ ($x = 0, 0.03, 0.06, 0.09, 0.12, 0.15$). (e) Crystal structure model of Mg-doped LATP with 15% dopant. (f) Octahedra of TiO_6 , where Al and Mg occupancy are represented by yellow and light blue contribution, respectively, and tetrahedra of PO_4 . (g) Raman spectra of LATP and Mg-doped LATP-15% powders.

$\text{Li}_{1.45}\text{Al}_{0.15}\text{Mg}_{0.15}\text{Ti}_{1.7}(\text{PO}_4)_3$, respectively. Using the GSAS program, the goodness-of-fit (χ^2) and weighted profile factor (R_{wp}) were lower than 4% and 5% across all samples, respectively.

A comprehensive summary of the lattice parameters and crystal structure is provided in Tables S1, S2, and S3. Notably, the lattice parameters of Mg-doped LATP-15% were observed to be larger than those of LATP, rendering it more conducive to Li^+ diffusion. This enlargement is attributed to the larger ionic radius of Mg^{2+} than those of Ti^{4+} and Al^{3+} . Specifically, the a , b , and c values and the unit cell volume of Mg-doped LATP-15%, exhibited slight increases due to the larger ionic radius of Mg^{2+} . Given the radii Al^{3+} (0.505 Å) and P^{5+} (0.17 Å), the replacement of Mg^{2+} ions at the 12c site, rather than the 18e site is favorable. Additionally, varying amounts of Li were incorporated into the Mg-doped LATP to facilitate charge compensation for Al^{3+} and Mg^{2+} , enhancing the diffusion channel size and Li^+ ionic mobility. The Mg occupancy was determined to be 0.0225, while the Al and Ti occupancies were found to be 0.1275 and 0.8500, respectively. Notably, when Mg was doped into the Al or Ti sites, the Wyckoff position remained the same, i.e., 12c (refer to Table S4). Raman spectroscopy was employed for further structural investigation, as illustrated in Figure 1(g) [39]. The region surrounding the highest peak at a Raman shift of 960–1,020 cm^{-1} corresponds to the symmetric stretching vibration area of $(\text{PO}_4)^{3-}$. Comparing LATP and Mg-doped LATP, the Raman mode of Mg-doped LATP appeared wider due to lattice distortion and atomic disorder within the tetrahedral and octahedral structures [43].

XPS was utilized to investigate the chemical properties of the solid electrolyte/liquid electrolyte interface (SELEI). XPS measurements were performed on the LATP and Mg-doped LATP surfaces that were in contact with the Li metal anode, and an Mg 1s peak was observed for Mg-doped LATP. Following cycling, the XPS full survey spectra of the LATP and Mg-doped LATP pellets are shown in Figure 2 [39]. The binding energy range of the detected peaks in the Mg 1s spectra was 1,300–1,310 eV, with the peak at 1,305 eV. However, the Mg 1s peak was not observed in the LATP spectrum. Furthermore, at 465.82 and 460.61 eV, the Ti 2p spectra split into Ti 2p_{3/2} and Ti 2p_{1/2}, respectively. The formation of a peak around 134 eV, resulting from PF_6^- , appeared in the high-resolution P 2p spectra obtained after cycling. The Ti 2p, P 2p, and Al 2p XPS data show no changes during cycling, suggesting that Li metal did not reduce them, which may be avoided because of the development of a SELEI layer. All elemental binding energies of LATP and Mg-doped LATP were identical, except for Mg.

Among the investigated materials, Mg-doped LATP-15% exhibited the highest ionic conductivity. SEM was employed to capture the morphologies of the LATP and Mg-doped LATP-15% samples. Figures 3(a) and 3(b) show LATP and Mg-doped LATP-15% synthesized via solid-state reaction, each exhibiting sizes exceeding 1 μm . Notably, Mg-doped LATP-15% displayed an uneven grain size distribution, larger than LATP's, attributable to lattice distortion and volume expansion phenomena. Similarly, Figures 3(c) and 3(d) show the morphologies of the powders synthesized via the sol–gel method. While LATP displayed irregular characteristics, as observed previously, Mg-doped LATP exhibited even more pronounced unevenness,

manifesting as nanoparticle sizes ranging from approximately 50 to 300 nm. This disparity in morphology between LATP and Mg-doped LATP underscores the influence of the synthesis method and composition on the resulting structures, potentially affecting their respective electrochemical properties. Furthermore, TEM images (Figures 3(e) and 3(f)) provide a more detailed examination of the nanoparticle powders synthesized via the sol–gel method, offering more precise insights into their morphologies. The expansion observed in the Mg-doped samples may be explained by fluctuations in the surface energy or lattice strain [44, 45].

EDS mapping analyses (as depicted in Figure 4(a)) were conducted on the Mg-doped LATP powder, revealing a homogeneous dispersion of elements (Al, Mg, Ti, P, and O) within the grains. Despite the uniform Mg doping in LATP, the SAED pattern (Figure 4(b)) illustrates distinct dots arranged within the matrix, confirming the preservation of the NASICON structure in Mg-doped LATP [38]. Additionally, Figure 4(c) highlights the (113) phase, a prominent LTP peak observed by HR-TEM, with a measured d-spacing of 0.36 nm. This characterization underscores the structural integrity and elemental distribution within Mg-doped LATP, suggesting its potential suitability for various applications, particularly in electrochemical devices where such features are critical to performance and stability [39]. Figure S1 shows sintered pellets prepared at 950°C using LATP and Mg-doped LATP powders under two distinct synthesis conditions. In the case of solid-state reactions, the grain sizes of LATP and Mg-doped LATP (Figure S1) were approximately ten-fold larger compared to those synthesized via the sol–gel method, as seen in the sintered pellets of the as-prepared LATP and Mg-doped LATP nanoparticles (Figure S1), respectively [46].

The grains came into contact throughout the sintering process and began merging, leading to grain growth. Particles synthesized via solid-state reactions exhibited larger pores between grains, resulting in the formation of numerous grain boundaries [47]. In contrast, the sol–gel method produced much smaller particles, allowing for denser packing between the particles within the sintered pellet [48]. Consequently, after sintering, smaller pores were present between the grains, with fewer grain boundaries, as shown in Figure S2. This comparison highlights the impact of the synthesis method on grain size, pore distribution, and grain boundary formation in the resulting sintered pellets, influencing their overall properties and performance in various applications.

EIS was performed on the synthesized samples to understand further how the dopants affected the ionic conductivity of the electrolytes. Figure 5(a) shows Nyquist plots of the LATP and Mg-doped LATP pellets at room temperature [39]. The initial semicircle observed at high frequencies indicates the bulk resistance region, while the subsequent semicircle corresponds to the grain boundary resistance region. The total resistance (R_t), comprising bulk resistance (R_b) and grain boundary resistance (R_{gb}), was determined from a semicircle fitted using the eissal software. The inset in Figure 5(a) illustrates the equivalent circuit model, where R_1 denotes bulk resistance, R_2 denotes grain boundary resistance, and CPE represents grain boundary capacitance. This equivalent circuit model aids in understanding the electrical

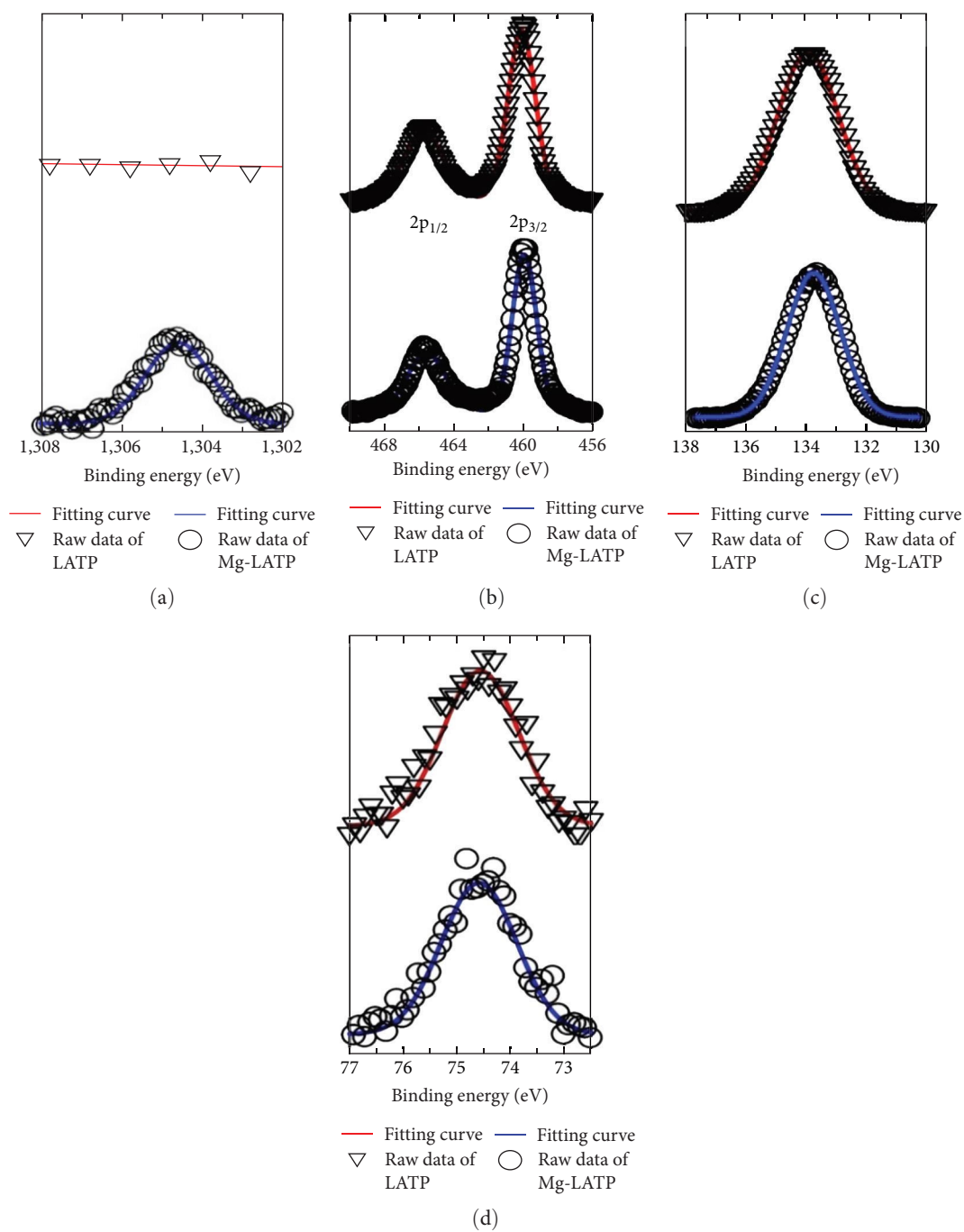


FIGURE 2: Continued.

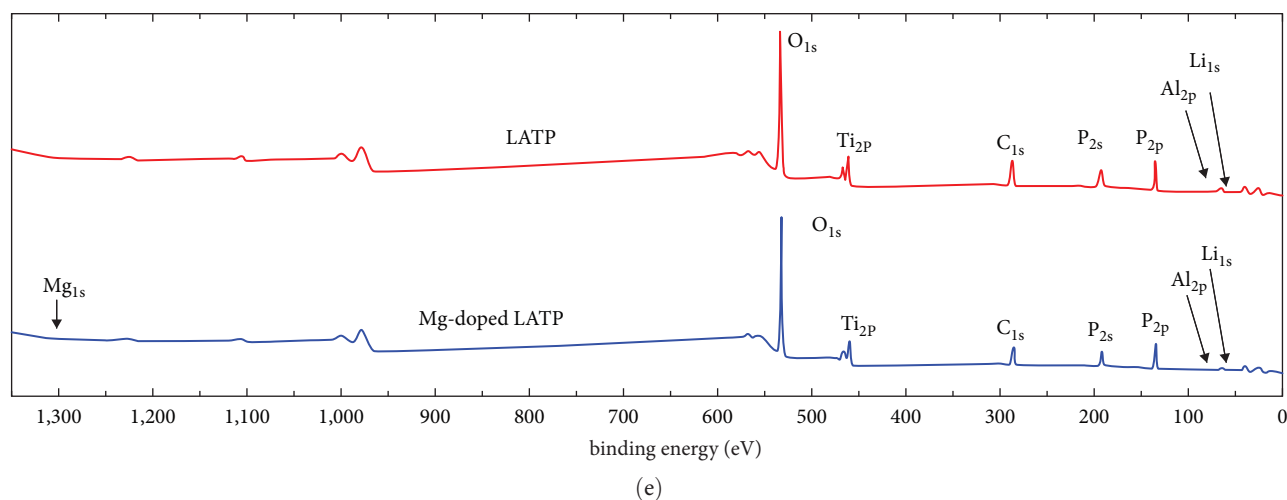


FIGURE 2: XPS spectra of (a) Mg 1s, (b) Ti 2p, (c) P 2p, and (d) Al 2p. (e) XPS total survey spectra.

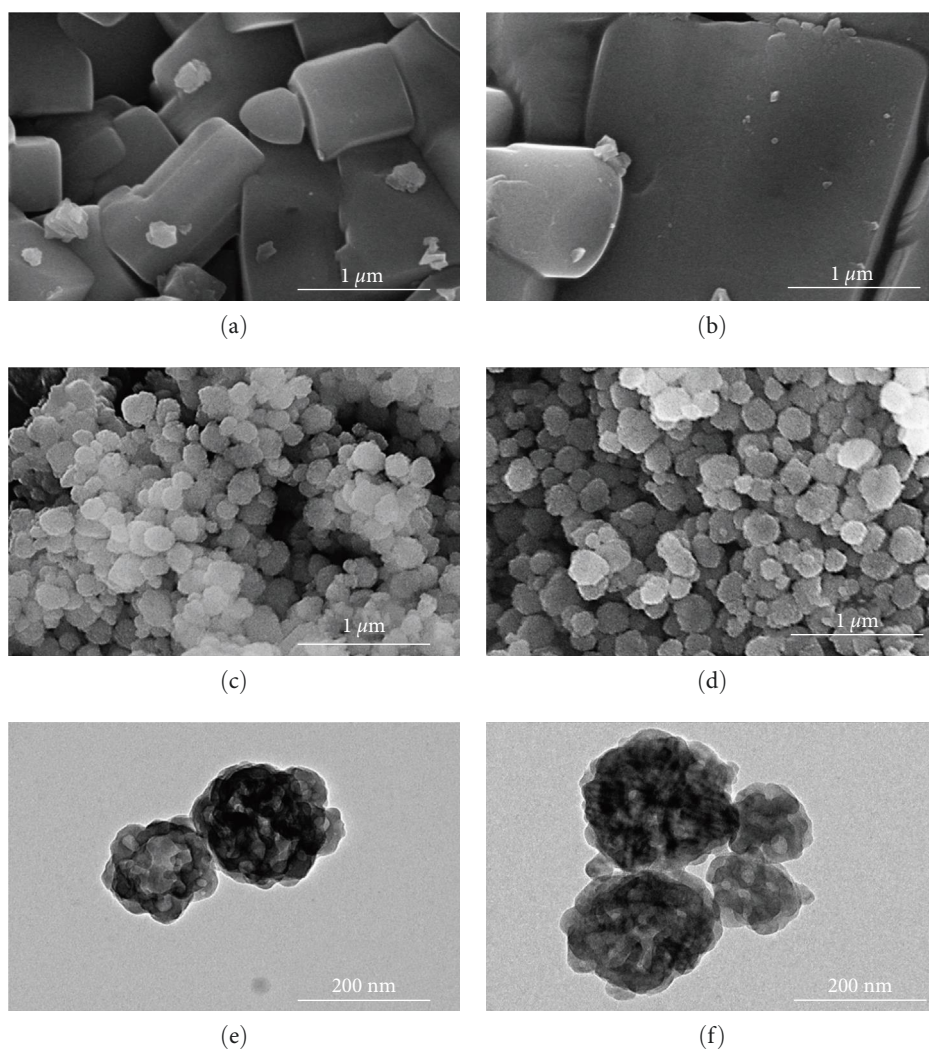


FIGURE 3: SEM images of (a) LATP and (b) Mg-doped LATP synthesized by solid-state reaction. SEM images of (c) LATP and (d) Mg-doped LATP nanoparticles synthesized by sol-gel method. TEM image of (e) LATP and (f) Mg-doped LATP nanoparticles.

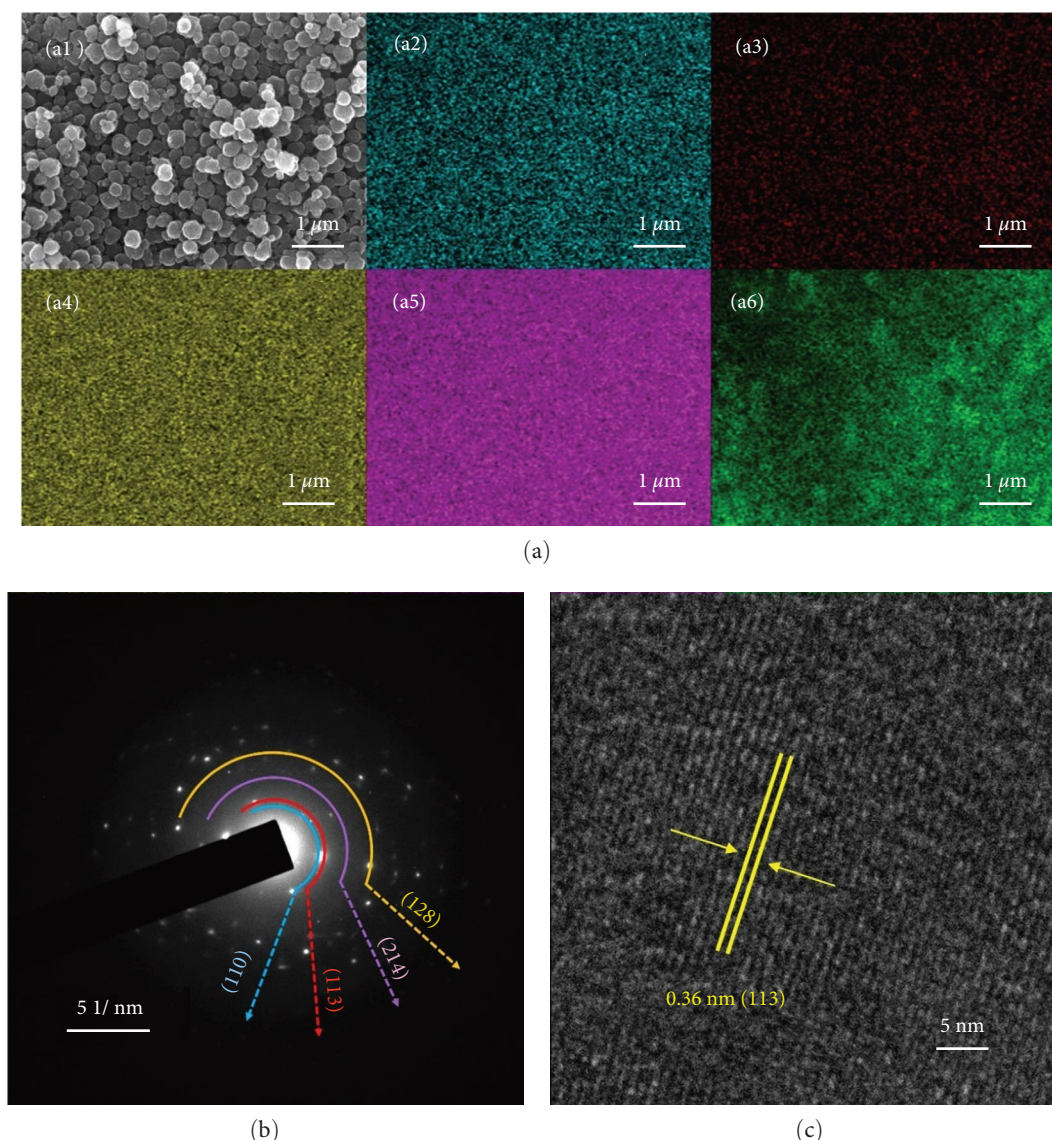


FIGURE 4: (a) (a1) SEM images and EDS mapping area for elements (a2) Al, (a3) Mg, (a4) Ti, (a5) P, and (a6) O. (b) SAED pattern and (c) HR-TEM image of Mg-doped LATP.

behavior of the pellets by delineating the contributions of the bulk and grain boundary components to the overall impedance, which is essential for analyzing their electrochemical performance and conductivity characteristics. The ionic conductivity (σ) of LATP and Mg-doped LATP can be calculated as follows:

$$\sigma = \frac{l}{AR}, \quad (1)$$

where l represents the thickness of the electrolyte pellet, A denotes the area of the electrolyte disc, and R signifies the resistance. Figure 5(a) illustrates that Mg-doped LATP exhibited a lower resistance than LATP, enabling the determination of the high ionic conductivity of Mg-doped LATP. Nyquist plots in Figure 5(b), measured at temperatures ranging from 25 to 60°C for LATP electrolytes, reveal a consistent

semicircle representing the grain boundary and a tail indicative of electrode polarization across all temperatures [39]. These results demonstrate a decrease in resistance with increasing temperature and a corresponding increase in frequencies for bulk conduction. At room temperature, the calculated ionic conductivities were 0.116 mS cm^{-1} for LATP and 0.385 mS cm^{-1} for Mg-doped LATP. The introduction of Mg ions increased the Li-ion concentration owing to charge neutrality and affected the lattice parameters, thus expanding the Li-ion channels as pathways [49]. As the temperature increased, the resistance of sintered LATP gradually decreased, leading to an increase in ionic conductivity from 0.116 mS cm^{-1} at 25°C to 1.042 mS cm^{-1} at 60°C. Figure 5(c) shows the bulk ionic conductivity with a green line (y -axis on the right) and the grain boundary ionic conductivity with a black line (y -axis on the left). Impedance data at various temperatures were fitted using the same equivalent circuit,

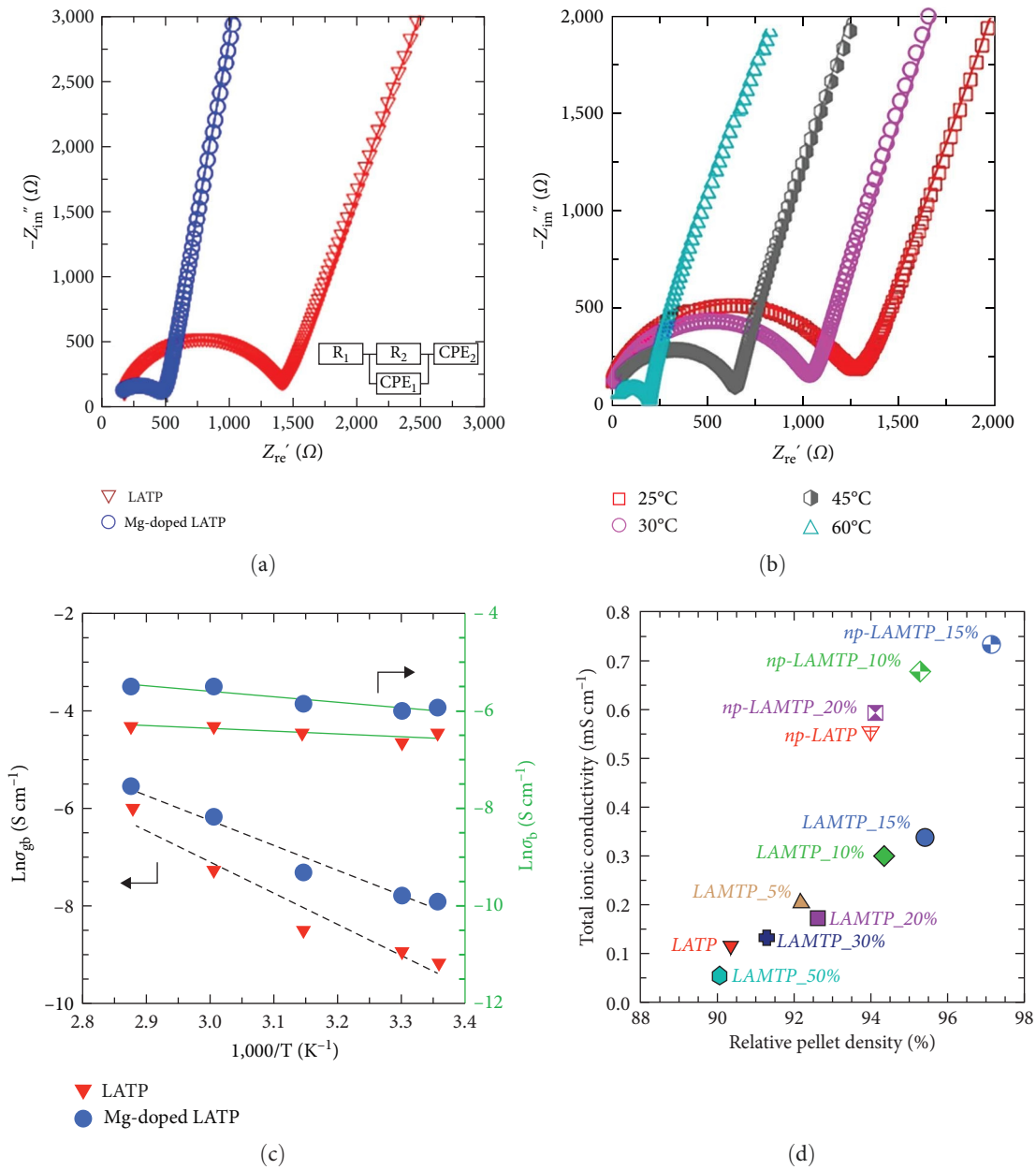


FIGURE 5: (a) Nyquist plot of SS//LATP//SS and SS//Mg-doped LATP//SS at RT. (b) Nyquist plot of LATP at different temperatures. (c) Bulk and grain boundary ionic conductivities of LATP and Mg-doped LATP at various temperatures and fitting curves. (d) Total ionic conductivity and relative pellet density values of LATP and Mg-doped LATP.

enabling the determination of the conductivity of the LATP and Mg-doped LATP electrolytes at different temperatures to calculate the activation energy. Ionic conductivity follows the Arrhenius law as follows:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_b T}\right), \quad (2)$$

where E_a is the activation energy, k_b is the Boltzmann constant, and σ_0 is the pre-exponential factor.

$$E_a = \frac{k_b T_1 T_2}{(T_1 - T_2)} - \ln \frac{\sigma_1}{\sigma_2}. \quad (3)$$

According to Equation (3), the activation energy (E_a) values for LATP, Mg-doped LATP-10%, and Mg-doped LATP-15% were determined as 0.43, 0.355, and 0.305 eV, respectively. Notably, Mg-doped LATP-15% exhibited a lower E_a than LATP, indicating faster migration of Li-ions within Mg-doped LATP electrolytes. Mg-doped LATP nanoparticles, synthesized via the sol-gel method, demonstrated an enhanced ionic conductivity of 0.729 mS cm^{-1} , surpassing

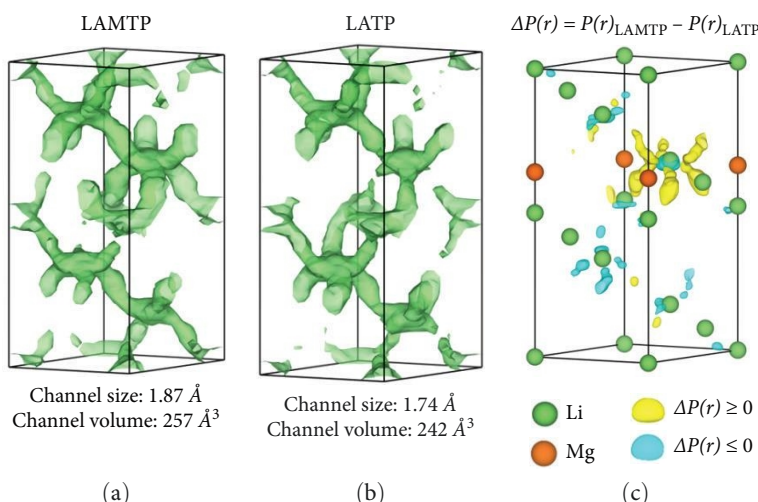


FIGURE 6: (a) Li⁺ probability density isosurfaces of Mg-doped LATP and (b) LATP. (c) Atomic position of Li and Mg, and probability density differences between Mg-doped LATP and LATP.

that of LATP at 0.554 mS cm^{-1} (Figure 5(d)) [39]. However, when the magnesium concentration exceeded 50%, the ionic conductivity of Mg-doped LATP decreased due to the production of impurities by magnesium, leading to a decrease in pellet density [50]. Utilizing the Archimedes method to determine the relative density of the pellets revealed a proportional relationship between ionic conductivity and relative density. Theoretical density values for LATP (2.92 g cm^{-3}) were employed to calculate relative density. The kinetics of charge diffusion are significantly influenced by the interfacial interaction between ceramics and polymers when polymer phases are used as the electrolyte. The reason for this discovery is that pure ceramics have certain intrinsic properties, such as strong ionic or covalent bonding and noticeable brittleness, which naturally obstruct heat and charge transmission as well as diffusion processes. In contrast, incorporating metals, polymers, or other phases with ceramic matrices in hybrid composites results in a significant decrease in activation energy and interfacial resistance. The secondary phases are responsible for this improvement because they provide increased toughness, flexibility, and the creation of more effective ion or electron transport pathways. For this reason, hybrid composites outperform pure ceramics, especially where high conductivity and quick diffusion are required [51]. Table S5 provides data on the bulk density, total density, and ionic conductivity for various Mg concentrations, including nanoparticle $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$. The smaller particle size facilitated larger interfacial contact areas and expanded the cross-sections for Li⁺ diffusion channels. Consequently, incorporating divalent Mg as a doping element, replacing Al and Ti, increased Li-ion concentrations and enhanced ionic conductivity. Figure S3 shows an inorganic polymer hybrid-type solid electrolyte prepared using the solution casting technique. By introducing a polymer, the electrolyte can be formulated in such a way as to facilitate better wetting and adhesion to the electrode surfaces, mechanical properties, flexibility, and stability. This enhanced contact minimizes interfacial resistance, thereby improving overall cell efficiency and reducing losses during charge-discharge cycles. Therefore, while the ionic

conductivity of bulk Mg-doped LATP may indeed be satisfactory. The introduction of a polymer in the electrolyte formulation is likely aimed at optimizing electrode-electrode contact, improving mechanical properties, enhancing chemical stability, or a combination of these factors to ultimately enhance the overall performance and reliability of the solid-state battery system.

To investigate the enhancement of ionic conductivity by Mg²⁺ doping, we conducted theoretical calculations using AIMD for a comprehensive qualitative and quantitative analysis. In this process, we aimed to ascertain whether the Li⁺ channels underwent expansion or contraction by calculating the probability density [52], $P(r)$, at a temperature of 800 K. The isosurfaces representing the probability densities for Mg-doped LATP and LATP are depicted in Figures 6(a) and 6(b). For a direct comparison between Mg-doped LATP and LATP, we calculated the difference in probability density after normalizing P to ensure that $\int_{\Omega} P dr = 1$, where Ω represents the volume of the unit cell. As illustrated in Figure 6(c), near Mg²⁺, the probability density differences are positive indicating that the Li⁺ transport channel in Mg-doped LATP was broader than that in LATP.

Using the open-source Zeo++ software [53], we measured the size and volume of the Li⁺ transport channel following the removal of Li atoms from the relaxed crystal structures. The channel size was defined as the largest radius of the free sphere that could pass through the framework structures remaining after Li atoms were removed. The channel volume is defined as the occupiable volume of the Li⁺-sized sphere through the transport channel. As shown in Figures 6(a) and 6(b), substituting Al³⁺ with Mg²⁺ resulted in a 7% increase in channel size and a 6% increase in channel volume. As expected, doping with Mg²⁺, which has a larger ionic radius than Ti⁴⁺ and Al³⁺, offers two distinct benefits. First, the introduction of a large radius dopant like Mg²⁺ results in the expansion of both the lattice parameters and Li⁺ transport channels. Second, to maintain charge neutrality after Mg²⁺ is introduced, adding extra Li⁺ ions increase the concentration of mobile carriers for ionic

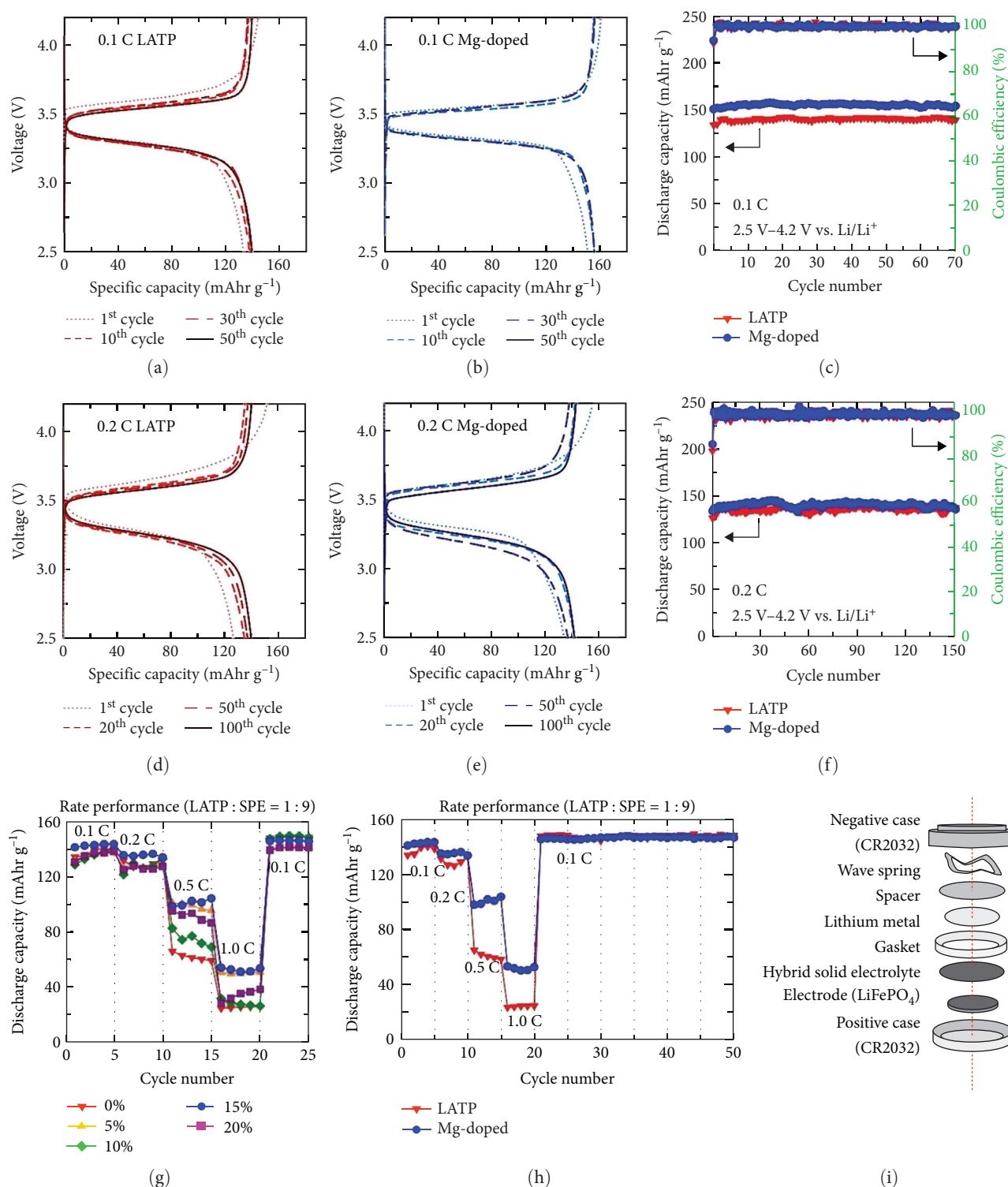


FIGURE 7: Galvanostatic charge/discharge profile of hybrid solid electrolyte using (a) LATP and (b) Mg-doped LATP with LiFePO_4 (LFP) as a cathode material at 0.1 C. (c) Cycling performance of LATP and Mg-doped LATP for 70 cycles at 0.1 C. Galvanostatic charge/discharge profile of hybrid solid electrolyte using (d) LATP and (e) Mg-doped LATP with LFP as a cathode material at 0.2 C. (f) Cycling performance of LATP and Mg-doped LATP for 150 cycles at 0.2 C. (g, h) C-rate performance profile of LATP ($\blacktriangledown$), Mg-doped LATP-5% ($\blacktriangle$), 10% ($\blacklozenge$), 15% ($\bullet$), and 20% ($\blacksquare$). (i) Illustration of a CR2032 coin cell assembly with a hybrid solid electrolyte.

conduction. These synergistic effects lower the activation energy (E_a) of the electrolyte and enhance its ionic conductivity.

To explore the practical viability of LATP and Mg-doped LATP solid electrolytes in solid-state lithium batteries, we conducted experiments by assembling full cells with a Li-metal anode and LFP cathode (see Figure 7) [39]. The galvanostatic charge–discharge curves of LATP and Mg-doped LATP at a current density of 0.1 C are depicted in Figures 7(a) and 7(b), respectively. The capacities of subsequent cycles exceeded those of the first cycle. Initially, Mg-doped LATP exhibited a relatively low initial Coulombic efficiency of 93.7%. This is attributed to the inactivity of solid electrolyte during the first cycle, particularly during the discharge step, leading to incomplete contact with the electrode (Figure 7(c)). However, with Li-ion migration during the initial cycle, the interface contacts between the LFP electrode and hybrid-type solid electrolyte improved, thereby enhancing the cycling stability. Over 70 cycles at 0.1 C current density, Mg-doped LATP demonstrated a higher specific capacity of 155.2 mAh g⁻¹ compared to LATP's 140.5 mAh g⁻¹, with a high Coulombic efficiency exceeding 99.1%. Furthermore, galvanostatic charge–discharge tests were conducted at a higher current density of 0.2 C (Figures 7(d) and 7(e)). Even at double the current density, Mg-doped LATP maintained a slightly higher specific capacity of 140.6 mAh g⁻¹ compared to LATP's 136.1 mAh g⁻¹, with stable Coulombic efficiency over 98.4% (Figure 7(f)). The results suggest that stability between the lithium anode and the hybrid solid electrolyte is achieved through meticulous interface engineering. This process involves introducing a protective interlayer to prevent direct contact and mitigate side reactions. The hybrid solid electrolytes are designed for chemical and electrochemical compatibility with lithium metal, minimizing undesirable reactions. Enhanced mechanical properties help accommodate volume changes and stress at the interface, preventing cracks or voids. Additionally, improved ion conductivity, achieved through additives or secondary phases, ensures efficient lithium-ion transport, reducing high-resistance interfacial layers and promoting stable cycling performance.

Rate performances of LATP and Mg-doped LATP-5%, 10%, 15%, and 20% were evaluated at specific current densities of 0.1 C, 0.2 C, 0.5 C, and 1.0 C (Figure 7(g)). Mg-doped LATP-15% demonstrated significant specific capacities of 143.7, 136.5, 102.5, and 53.7 mAh g⁻¹, respectively, with increasing current density, outperforming LATP. At 1.0 C current density, Mg-doped LATP-15% exhibited the highest specific capacity compared to Mg-doped LATP-5%, 10%, and 20%. Notably, Mg-doped LATP-15% displayed superior stability and higher energy density at high current densities compared to LATP. Upon reverting to the initial 0.1 C current density, LATP and Mg-doped LATP-15% maintained a stable capacity of 149.3 mAh g⁻¹ for 50 cycles (Figure 7(h)). Figure 7(i) illustrates the coin cell assembly of a half-cell with a hybrid solid electrolyte containing LFP and Li metal as the cathode and counter electrode, respectively. Rate performances revealed Mg-doped LATP-15% as optimal, offering superior specific capacities and energy densities at high current densities. Both materials maintained a stable capacity

upon returning to their initial conditions, showing potential for practical use in solid-state lithium batteries. Overall, Mg-doped LATP enhanced battery performance, highlighting its suitability for advanced energy storage applications.

4. Conclusions

In conclusion, our study introduced a new Mg-doped LATP oxide material synthesized through a sol–gel method and solid-state reaction and integrated it into a hybrid-type solid electrolyte for lithium battery applications. Through rigorous analysis, including Rietveld refinement, we demonstrated that Mg-doped LATP offers wider diffusion channels for Li-ions, leading to an enhanced ionic conductivity of $7.29 \times 10^{-4} \text{ S cm}^{-1}$. The slight increase in unit cell volume of Mg-doped LATP compared to that of LATP contributes to reduced grain resistance, further improving its performance. Notably, our findings reveal that nanoparticle LATP, synthesized via the sol–gel method, exhibits superior ionic conductivity compared to bulk powder obtained through a solid-state reaction, attributed to its higher pellet density. Using a hybrid solid electrolyte composed of polymers and inorganic materials addresses the challenge of insufficient surface contact with the electrode, thereby enhancing overall performance. Through galvanostatic charge and discharge analyses, Mg-doped LATP demonstrated a higher specific capacity than LATP while exhibiting stable high current density performance and capacity recoverability, as evidenced by the rate performance analysis. This enhancement, coupled with favorable surface properties and stability at high current densities, suggests that the hybrid solid electrolyte incorporating Mg-doped LATP is a promising candidate for Li metal batteries, with the potential to suppress lithium dendrite formation in the foreseeable future.

Data Availability

The data that support the findings of this study are available upon request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Conflicts of Interest

The authors declare that they have no competing financial interests or personal relationships that may have influenced the work reported in this study.

Authors' Contributions

Haena Kim contributed to writing—original draft, conceptualization, formal analysis, and investigation. Mahammad Rafi Shaik contributed to writing—original draft, review and editing, conceptualization, formal analysis, and investigation. Sukju Kim and Yong Min Park contributed to formal analysis. Dong Won Jeon and Sung Beom Cho contributed to DFT calculation and formal analysis. Sungho Choi contributed to conceptualization and data curation. Won Bin Im contributed to writing—review and editing, supervision, and funding acquisition. Haena Kim, Mahammad Rafi Shaik, and Sukju Kim contributed equally to this work.

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Supplementary Materials

Figure S1: SEM images of the fracture surfaces in the sintered pellets at 950°C. (a) LATP and (b) LAMTP synthesized by solid-state reaction, (c) LATP and (d) LAMTP synthesized by sol-gel method. Figure S2: illustration of sintering process of pellets and grain growth of powders in different synthesized method. Figure S3: fabrication of hybrid solid electrolytes by solution casting method. Table S1: the refinement XRD information of LATP. Table S2: the refinement XRD information of LATP. Table S3: the refinement XRD information of LAMTP. Table S4: structural parameters of LAMTP as obtained from the combined Rietveld refinement of X-ray. Table S5: bulk density and ionic conductivity (at 25°C) of $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$. (*Supplementary Materials*)

References

- [1] Z. Cheng, T. Liu, B. Zhao, F. Shen, H. Jin, and X. Han, "Recent advances in organic-inorganic composite solid electrolytes for all-solid-state lithium batteries," *Energy Storage Materials*, vol. 34, pp. 388–416, 2021.
- [2] M. J. Lee, J. Han, K. Lee et al., "Elastomeric electrolytes for high-energy solid-state lithium batteries," *Nature*, vol. 601, no. 7892, pp. 217–222, 2022.
- [3] K. Pan, L. Zhang, W. Qian et al., "A flexible ceramic/polymer hybrid solid electrolyte for solid-state lithium metal batteries," *Advanced Materials*, vol. 32, no. 17, Article ID 2000399, 2020.
- [4] Y. Fu, K. Yang, S. Xue et al., "Surface defects reinforced polymer-ceramic interfacial anchoring for high-rate flexible solid-state batteries," *Advanced Functional Materials*, vol. 33, no. 10, Article ID 2210845, 2023.
- [5] M. R. Shaik, M. Bissannagari, Y. M. Kwon, K. Y. Cho, J. Kim, and S. Yoon, "Soft, robust, Li-ion friendly halloysite-based hybrid protective layer for dendrite-free Li metal anode," *Chemical Engineering Journal*, vol. 424, Article ID 130326, 2021.
- [6] M. R. Shaik, M. J. Yeo, K. Y. Cho, and S. Yoon, "Robust artificial HfO_2 /PEDOT:PSS polarity layer for increasing stability of Li metal anodes," *Journal of Alloys and Compounds*, vol. 939, Article ID 168703, 2023.
- [7] F. Zheng, M. Kotobuki, S. Song, M. O. Lai, and L. Lu, "Review on solid electrolytes for all-solid-state lithium-ion batteries," *Journal of Power Sources*, vol. 389, pp. 198–213, 2018.
- [8] S. Kim, J.-S. Kim, L. Miara et al., "High-energy and durable lithium metal batteries using garnet-type solid electrolytes with tailored lithium-metal compatibility," *Nature Communications*, vol. 13, no. 1, Article ID 1833, 2022.
- [9] M. R. Shaik, Y. Park, Y.-K. Jung, and W. B. Im, "Interfacial modulation of bifunctional electrolyte additive engineering for dendrite-free and robust lithium metal anode," *Journal of Energy Chemistry*, vol. 97, pp. 120–127, 2024.
- [10] Y. Zheng, Y. Yao, J. Ou et al., "A review of composite solid-state electrolytes for lithium batteries: fundamentals, key materials and advanced structures," *Chemical Society Reviews*, vol. 49, no. 23, pp. 8790–8839, 2020.
- [11] Q. Liu, X. Zhao, Q. Yang et al., "The progress in the electrolytes for solid state sodium-ion battery," *Advanced Materials Technologies*, vol. 8, no. 7, Article ID 2200822, 2023.
- [12] J. Fu, "Fast Li^+ ion conducting glass-ceramics in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{GeO}_2-\text{P}_2\text{O}_5$," *Solid State Ionics*, vol. 104, no. 3–4, pp. 191–194, 1997.
- [13] J. Fu, "Superionic conductivity of glass-ceramics in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$," *Solid State Ionics*, vol. 96, no. 3–4, pp. 195–200, 1997.
- [14] R. Murugan, V. Thangadurai, and W. Weppner, "Fast lithium ion conduction in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$," *Angewandte Chemie International Edition*, vol. 46, no. 41, pp. 7778–7781, 2007.
- [15] S. Xia, X. Wu, Z. Zhang, Y. Cui, and W. Liu, "Practical challenges and future perspectives of all-solid-state lithium-metal batteries," *Chem*, vol. 5, no. 4, pp. 753–785, 2019.
- [16] J. B. Bates, N. J. Dudney, G. R. Gruzalski et al., "Electrical properties of amorphous lithium electrolyte thin films," *Solid State Ionics*, vol. 53–56, pp. 647–654, 1992.
- [17] N. J. Dudney, J. B. Bates, R. A. Zuhr, C. F. Luck, and J. D. Robertson, "Sputtering of lithium compounds for preparation of electrolyte thin films," *Solid State Ionics*, vol. 53–56, pp. 655–661, 1992.
- [18] Y. Inaguma, C. Liquan, M. Itoh et al., "High ionic conductivity in lithium lanthanum titanate," *Solid State Communications*, vol. 86, no. 10, pp. 689–693, 1993.
- [19] Q. Liu, L. Jiang, P. Zheng et al., "Recent advances in stability issues of inorganic solid electrolytes and composite solid electrolytes for all-solid-state batteries," *The Chemical Record*, vol. 22, no. 10, Article ID e202200116, 2022.
- [20] H. Park, S. Choi, E. G. Lee et al., "Comparative electrochemical property of solvent-free ceramic/polymer hybrid electrolytes incorporating sol-gel prepared Li-phosphates, $\text{Li}(\text{Al},\text{Ge})(\text{PO}_4)_3$ and $\text{Li}(\text{Al},\text{Ti})(\text{PO}_4)_3$," *Journal of Alloys and Compounds*, vol. 843, Article ID 155878, 2020.
- [21] Y. Ren, K. Chen, R. Chen et al., "Oxide electrolytes for lithium batteries," *Journal of the American Ceramic Society*, vol. 98, no. 12, pp. 3603–3623, 2015.
- [22] C. Delmas, A. Nadiri, and J. L. Soubeyroux, "The nasicon-type titanium phosphates $\text{Ati}_2(\text{PO}_4)_3$ ($\text{A} = \text{Li}, \text{Na}$) as electrode materials," *Solid State Ionics*, vol. 28–30, pp. 419–423, 1988.
- [23] G. Courbaron, R. B. Nuernberg, J. S. Seviliano et al., "Multi-scale characterization of submicronic NASICON-type solid electrolyte $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ degraded by spark plasma sintering," *Journal of Alloys and Compounds*, vol. 985, Article ID 174062, 2024.
- [24] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, and G.-Y. Adachi, "Ionic conductivity of solid electrolytes based on lithium titanium phosphate," *Journal of The Electrochemical Society*, vol. 137, no. 4, pp. 1023–1027, 1990.
- [25] Y. Nikodimos, M.-C. Tsai, L. H. Abrha et al., "Al-Sc dual-doped $\text{LiGe}_2(\text{PO}_4)_3$ —a NASICON-type solid electrolyte with improved ionic conductivity," *Journal of Materials Chemistry A*, vol. 8, no. 22, pp. 11302–11313, 2020.
- [26] Y. Nikodimos, L. H. Abrha, H. H. Weldeyohannes et al., "A new high- Li^+ -conductivity Mg-doped $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$

- solid electrolyte with enhanced electrochemical performance for solid-state lithium metal batteries,” *Journal of Materials Chemistry A*, vol. 8, no. 48, pp. 26055–26065, 2020.
- [27] F. Lv, Z. Wang, L. Shi et al., “Challenges and development of composite solid-state electrolytes for high-performance lithium ion batteries,” *Journal of Power Sources*, vol. 441, Article ID 227175, 2019.
- [28] H. Aono, N. Imanaka, and G.-Y. Adachi, “High Li^+ conducting ceramics,” *Accounts of Chemical Research*, vol. 27, no. 9, pp. 265–270, 1994.
- [29] J.-I. Moon, H.-C. Cho, and J.-H. Song, “Synthesis and conductive properties of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0, 0.3, 0.5$) by sol-gel method,” *Korean Journal of Materials Research*, vol. 22, no. 7, pp. 346–351, 2012.
- [30] S. Duluard, A. Paillassa, L. Puech et al., “Lithium conducting solid electrolyte $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ obtained via solution chemistry,” *Journal of the European Ceramic Society*, vol. 33, no. 6, pp. 1145–1153, 2013.
- [31] H. Park, E. G. Lee, S.-Y. Kim et al., “Free-standing, robust, and stable Li^+ conductive $\text{Li}(\text{Sr,Zr})_2(\text{PO}_4)_3/\text{PEO}$ composite electrolytes for solid-state batteries,” *ACS Applied Energy Materials*, vol. 4, no. 12, pp. 13974–13982, 2021.
- [32] X. Xu, Z. Wen, J. Wu, and X. Yang, “Preparation and electrical properties of NASICON-type structured $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ glass-ceramics by the citric acid-assisted sol-gel method,” *Solid State Ionics*, vol. 178, no. 1–2, pp. 29–34, 2007.
- [33] E. Zhao, F. Ma, Y. Guo, and Y. Jin, “Stable LATP/LAGP double-layer solid electrolyte prepared via a simple dry-pressing method for solid state lithium ion batteries,” *RSC Advances*, vol. 6, no. 95, pp. 92579–92585, 2016.
- [34] W. Wang, E. Yi, A. J. Fici, R. M. Laine, and J. Kieffer, “Lithium Ion conducting poly(ethylene oxide)-based solid electrolytes containing active or passive ceramic nanoparticles,” *The Journal of Physical Chemistry C*, vol. 121, no. 5, pp. 2563–2573, 2017.
- [35] G. Kresse and J. Furthmüller, “Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set,” *Physical Review B*, vol. 54, no. 16, pp. 11169–11186, 1996.
- [36] P. E. Blöchl, “Projector augmented-wave method,” *Physical Review B*, vol. 50, no. 24, pp. 17953–17979, 1994.
- [37] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Physical Review Letters*, vol. 77, no. 18, pp. 3865–3868, 1996.
- [38] D. Pfalzgraf, D. Mutter, and D. F. Urban, “Atomistic analysis of Li migration in $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) solid electrolytes,” *Solid State Ionics*, vol. 359, Article ID 115521, 2021.
- [39] H. Kim and W. B. Im, *High ionic conductivity of $\text{Li}_{1.3+x}\text{Al}_{0.3-x}\text{Mg}_x\text{Ti}_{1.7}(\text{PO}_4)_3$ with enhanced electrochemical performance by applying hybrid solid electrolytes*, Master’s Dissertation Hanyang University, 2023.
- [40] C. V. Chandran, S. Pristat, E. Witt, F. Tietz, and P. Heitjans, “Solid-state NMR investigations on the structure and dynamics of the ionic conductor $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($0.0 \leq x \leq 1.0$),” *The Journal of Physical Chemistry C*, vol. 120, no. 16, pp. 8436–8442, 2016.
- [41] J. K. Feng, B. G. Yan, J. C. Liu, M. O. Lai, and L. Li, “All solid state lithium ion rechargeable batteries using NASICON structured electrolyte,” *Materials Technology*, vol. 28, no. 5, pp. 276–279, 2013.
- [42] E. C. Bucharsky, K. G. Schell, A. Hintennach, and M. J. Hoffmann, “Preparation and characterization of sol-gel derived high lithium ion conductive NZP-type ceramics $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$,” *Solid State Ionics*, vol. 274, pp. 77–82, 2015.
- [43] J. Luo, Y. Zhong, and G. Chen, “Preparation, microstructure and electrical conductivity of LATP/LB glass ceramic solid electrolytes,” *Journal of Physics: Conference Series*, vol. 2101, no. 1, Article ID 012081, 2021.
- [44] R. Bose, G. Manna, and N. Pradhan, “Surface doping for hindrance of crystal growth and structural transformation in semiconductor nanocrystals,” *The Journal of Physical Chemistry C*, vol. 117, no. 40, pp. 20991–20997, 2013.
- [45] H. T. Huu, N. H. Vu, H. Ha, J. Moon, H. Y. Kim, and W. B. Im, “Sub-micro droplet reactors for green synthesis of Li_3VO_4 anode materials in lithium ion batteries,” *Nature Communications*, vol. 12, no. 1, Article ID 3081, 2021.
- [46] L. Dai, J. Wang, Z. Shi, L. Yu, and J. Shi, “Influence of LiBF_4 sintering aid on the microstructure and conductivity of LATP solid electrolyte,” *Ceramics International*, vol. 47, no. 8, pp. 11662–11667, 2021.
- [47] X. Liu, J. Tan, J. Fu, R. Yuan, H. Wen, and C. Zhang, “Facile synthesis of nanosized lithium-ion-conducting solid electrolyte $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ and its mechanical nanocomposites with LiMn_2O_4 for enhanced cyclic performance in lithium ion batteries,” *ACS Applied Materials & Interfaces*, vol. 9, no. 13, pp. 11696–11703, 2017.
- [48] K. Waetzig, A. Rost, C. Heubner et al., “Synthesis and sintering of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) electrolyte for ceramics with improved Li^+ conductivity,” *Journal of Alloys and Compounds*, vol. 818, Article ID 153237, 2020.
- [49] J. Liu, T. Liu, Y. Pu et al., “Facile synthesis of NASICON-type $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ solid electrolyte and its application for enhanced cyclic performance in lithium ion batteries through the introduction of an artificial Li_3PO_4 SEI layer,” *RSC Advances*, vol. 7, no. 74, pp. 46545–46552, 2017.
- [50] Q. Wang, L. Liu, B. Zhao et al., “Transport and interface characteristics of Te-doped NASICON solid electrolyte $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$,” *Electrochimica Acta*, vol. 399, Article ID 139367, 2021.
- [51] L. Wu, Y. Wang, X. Guo, P. Ding, Z. Lin, and H. Yu, “Interface science in polymer-based composite solid electrolytes in lithium metal batteries,” *SusMat*, vol. 2, no. 3, pp. 264–292, 2022.
- [52] Z. Zhu, I.-H. Chu, Z. Deng, and S. P. Ong, “Role of Na^+ interstitials and dopants in enhancing the Na^+ conductivity of the cubic Na_3PS_4 superionic conductor,” *Chemistry of Materials*, vol. 27, no. 24, pp. 8318–8325, 2015.
- [53] T. F. Willems, C. H. Rycroft, M. Kazi, J. C. Meza, and M. Haranczyk, “Algorithms and tools for high-throughput geometry-based analysis of crystalline porous materials,” *Microporous and Mesoporous Materials*, vol. 149, no. 1, pp. 134–141, 2012.