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Article

Improving the Stability of Lithium Aluminum Germanium Phosphate with Lithium Metal by Interface Engineering

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Abstract: Lithium aluminum germanium phosphate (LAGP) solid electrolyte is receiving increasing attention due to its high ionic conductivity and low air sensitivity. However, the poor interface compatibility between lithium (Li) metal and LAGP remains the main challenge in developing all-solid-state lithium batteries (ASSLB) with a long cycle life. Herein, this work introduces a thin aluminum oxide (Al₂O₃) film on the surface of the LAGP pellet as a physical barrier to Li/LAGP interface by the atomic layer deposition technique. It is found that this layer induces the formation of stable solid electrolyte interphase, which significantly improves the structural and electrochemical stability of LAGP toward metallic Li. As a result, the optimized symmetrical cell exhibits a long lifetime of 360 h with an areal capacity of 0.2 mAh cm⁻² and a current density of 0.2 mA cm⁻². This strategy provides new insights into the stabilization of the solid electrolyte/Li interface to boost the development of ASSLB.

Keywords: lithium aluminum germanium phosphate; lithium metal anode; interface modification; atomic layer deposition



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1. Introduction

Lithium metal is a promising anode candidate for constructing high-energy-density lithium batteries due to its high specific capacity (3860 mAh g⁻¹) and low redox potential (−3.05 V vs. standard hydrogen electrode) [1,2]. Currently, its development is plagued by the intrinsic safety issues of liquid electrolytes because of the flammability of organic solvents used [3,4]. Replacing organic liquid electrolytes with non-flammable and highly conductive solid electrolytes (SEs) is an effective approach to improving battery safety [5,6]. With respect to this, there is growing research interest in the development of all-solid-state lithium-ion batteries (ASSLBs), and significant progress has been made over the past few years [7–9]. Critical characteristics of SEs include high lithium-ion conductivity, excellent chemical stability, and good mechanical properties [10]. Various SEs have been well developed, such as polymer-based SEs, garnet-type Li₇La₃Zr₂O₁₂ [11], sulfide [12], and NASICON-type LiM₂(PO₄)₃ (M = Ti, Ge, Hf, Zr, Sn) [13], as well as composite SEs [14–16]. Aluminum (Al)-doped NASICON-type Li_{1+x}Al_xGe_{2-x}(PO₄)₃ (LAGP) oxides have received tremendous attention due to their high chemical and electrochemical stability in the air, high ionic conductivity (>10⁻⁴ S cm⁻¹), and good mechanical strength [10]. The fast Li-ion conduction in the LAGP system benefits from the main Li-ion diffusion pathway along 36f and M₂ interstitial sites resulting from Al³⁺ to Ge⁴⁺ substitution [17]. LAGP SEs have been synthesized by various routes, from melt-quenching [18], sintering [19], sol-gel [20], to hot-press [21], etc. Controlling key parameters such as crystallization and sintering temperature or pressure is critical in tailoring desirable highly-conductive LAGP pellets [21–23].

Li/LAGP interfacial incompatibility remains the main challenge for the further development of ASSLBs. Due to the high Fermi energy level of Li metal, germanium (Ge) in

LAGP would be irreversibly degraded upon being contacted with Li metal at the Li/LAGP interface, resulting in an increased impedance versus time [24]. When an electrical current is applied to the Li metal anode, part of Li ions can be reduced at the LAGP side, leading to a local volume expansion which triggers cracks in the LAGP SE [25]. These cracks could cause the pulverization of SEs, mechanical deterioration, or even cell failure (short circuit) [26]. Consequently, the unstable Li/LAGP interface causes inferior cell capacity and lifetime, which need to be mitigated using effective interfacial stabilization strategies.

Li et al. [27] introduced a succinonitrile-based plastic interlayer between Li metal and LAGP by in situ solidification. This interlayer isolated the direct contact between Li and LAGP and regulated uniform Li-ion distribution, which enabled a 240-h cycle life in symmetrical Li cells. Zhou et al. [28] sputtered an amorphous Ge thin film on the LAGP surface, which ensured intimate Li/LAGP contact and suppressed the unexpected Ge reduction, thus contributing to a superior symmetrical cell over 100 cycles at 0.1 mA cm^{-2} . Xiong et al. [29] created a quasi-solid-state paste interlayer composed of LAGP nanoparticles and ionic liquid, which enabled fast Li-ion conduction and improved chemical stability toward metallic Li, and suppressed thermal runaway. Sun et al. [30] adopted the atomic layer deposition (ALD) technique to coat ultrathin aluminum oxide (Al_2O_3) on the surface of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP), and the Li/LATP interface was significantly stabilized at 0.01 mA cm^{-2} . Currently, most Li/LAGP/Li symmetrical cells show a long cycle time at a low current density of 0.1 mA cm^{-2} [1,3,25,26,28,31–37], making it hard to meet the demand for practical applications. Improving the electrochemical stability of LAGP at higher current densities is an urgent task in the development of high-energy-density ASSLBs [38].

In this work, the effect of sintering temperature on the structure and ionic conductivity of LAGP is investigated, and $850 \text{ }^\circ\text{C}$ is found as the optimal sintering temperature to reach an ionic conductivity of $2.4 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. Furthermore, an ultrathin Al_2O_3 coating layer is deposited in the LAGP pellet surface via the ALD technique, which physically isolates the contact between Li metal and LAGP SE and enhances the electrochemical stability of LAGP toward metallic Li. The Li symmetrical cell with Al_2O_3 -coated LAGP SE showed an excellent lifetime of 360 h at a current density of 0.2 mA cm^{-2} and capacity density of 0.2 mAh cm^{-2} , which is higher than most previously reported Li/LAGP/Li cells with interlayer modification.

2. Materials and Methods

2.1. Materials

LAGP powders with a stoichiometric formula of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ were purchased from the Shanghai Institute of Ceramics (Shanghai, China). The precursors for ALD were trimethylaluminium (TMA) and deionized water (H_2O). Lithium hexafluorophosphate (LiPF_6 , Gotion, CAS: 21324-40-3), ethylene carbonate (EC, Gotion, CAS: 96-49-1), and diethyl carbonate (DEC, Gotion, CAS: 105-58-8) were used as received for coin cell assembly.

2.2. Preparation of LAGP Pellets

LAGP pellets were made by a conventional dry-pressing method (15T Compact Hydraulic Pellet Press, MTI Corporation, Richmond, CA, USA). To begin, 0.2 g LAGP of powder was placed into a stainless-steel die with 12 mm diameter and pressed at 200 MPa uniaxial pressure at room temperature for 2 min. The obtained pellets were then transferred into a ceramic crucible. The sintering process was conducted at $800\text{--}900 \text{ }^\circ\text{C}$ in the air for 6 h at a heating rate of 2° min^{-1} in a tube furnace. The thickness of the as-prepared LAGP pellets was about 0.8 mm.

2.3. Atomic Layer Deposition of Al_2O_3 on LAGP

The Al_2O_3 layer was coated on LAGP in a commercial ALD reactor (GEMStar™ XT Atomic Layer Deposition Systems, Singapore). The coating process was carried out at $100 \text{ }^\circ\text{C}$ by following a TMA pulse/TMA purge/ H_2O pulse/ H_2O purge sequence in each cycle. After 50 cycles, Al_2O_3 films were deposited on LAGP noted as LAGP@ Al_2O_3 50.

2.4. Materials Characterizations

The morphologies and microstructures of LAGP powder and pellets were observed and analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) was used to analyze the crystal structure of LAGP. Surface elemental analysis was investigated by X-ray photoelectron spectroscopy (XPS).

Electrochemical impedance spectroscopy EIS measurements were carried out at 25 °C and elevated temperatures (30–60 °C). The LAGP pellets were Au-coated on both sides as electrodes and clamped for conduction. The ionic conductivity (σ) of LAGP was measured by Equation (1):

$$\sigma = \frac{L}{RA} \quad (1)$$

where L and A are the thickness and effective area of LAGP, respectively, and R is the resistance obtained by EIS testing within a frequency range of 0.01–10⁶ Hz with an AC amplitude of 5 mV.

2.5. Electrochemical Measurements

CR2032 cells were assembled in an argon-filled glovebox workstation with H₂O and O₂ less than 0.1 ppm. First, 10 μ L electrolyte (1 M LiPF₆ in EC: DEC) were added to each Li/LAGP/Li cell. Symmetrical Li/LAGP/Li cells were tested in NEWARE battery cycler (CT-4008T-5V50mA-164, Shenzhen, China) at room temperature and 40 °C with current densities ranging from 0.02 to 0.2 mA cm⁻² with a plating-stripping time of 1 h. The cycled Li/LAGP batteries were disassembled in the argon-filled glove box and then characterized by SEM and XPS to collect surface composition information.

3. Results and Discussion

Figure 1 presents the SEM images of LAGP pellets sintered at 800, 850, and 900 °C, respectively. Most LAGP particles have small sizes of less than 1 μ m, as shown in Figure S1. After being pressed and sintered at high temperatures (800–900 °C), LAGP particles were closely stacked to form a dense surface, and no pores were found in higher-magnification images, ensuring continuous Li-ion pathways to achieve high ionic conductivity. The ionic conductivity of LAGP solid electrolyte relies on the Li-ion conduction in both bulk (σ_{bulk}) and along the grain boundary (σ_{gb}). With the sintering temperature increasing, unit cell volumes would grow to form wider Li-ion migration channels, thus leading to higher bulk conductivity σ_{bulk} [23,39]. The Li-ion conduction along the grain boundary (σ_{gb}) mainly depends on grain-grain ceramics contact and density. High sintering temperatures above 850 °C would possibly induce cracks due to grain strain, decrease ceramics density, and slow down Li-ion transport at the grain boundary [23,40,41]. Consequently, LAGP sintered at 850 °C showed the highest ionic conductivity.

XRD patterns of LAGP pellets sintered at 800–900 °C are shown in Figure 2a. All the characteristic peaks of LAGP pellets match well with the LAGP powders and can be indexed as LiGe₂(PO₄)₃ (JCPDS PDF No. 80-1924). Figure 2b gives the Nyquist plot of LAGP pellets sintered at 800–900 °C measured in a frequency range of 0.01–1 \times 10⁶ Hz at room temperature. LAGP T850 possesses a smaller electrochemical impedance (283 Ω) than LAGP T800 (390 Ω) and T900 (392 Ω), thus leading to higher ionic conductivity of 2.4 \times 10⁻⁴ S cm⁻¹ (vs. 2.0 \times 10⁻⁴ and 1.8 \times 10⁻⁴ S cm⁻¹ for T800 and T900, respectively) as illustrated in Figure 2c. Further, the relationship between impedance and temperature for LAGP T850 is plotted in Figure 2d. It could be found that the impedance markedly decreases from 260 to 92 Ω with temperature increasing from 30 to 60 °C, corresponding to the ionic conductivity from 2.6 \times 10⁻⁴ to 7.3 \times 10⁻⁴ S cm⁻¹. LAGP T850 will be selected as a reference for further electrochemical stability tests with Li metal due to its highest ionic conductivity.

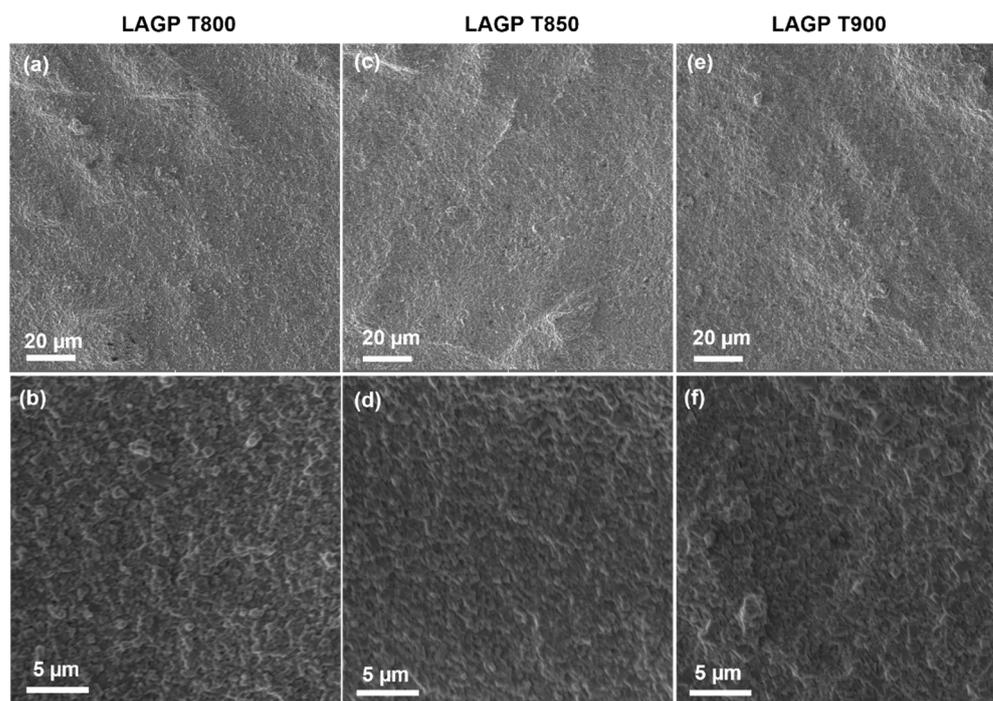


Figure 1. SEM images of LAGP pellets sintered at (a,b) 800 °C, (c,d) 850 °C, and (e,f) 900 °C.

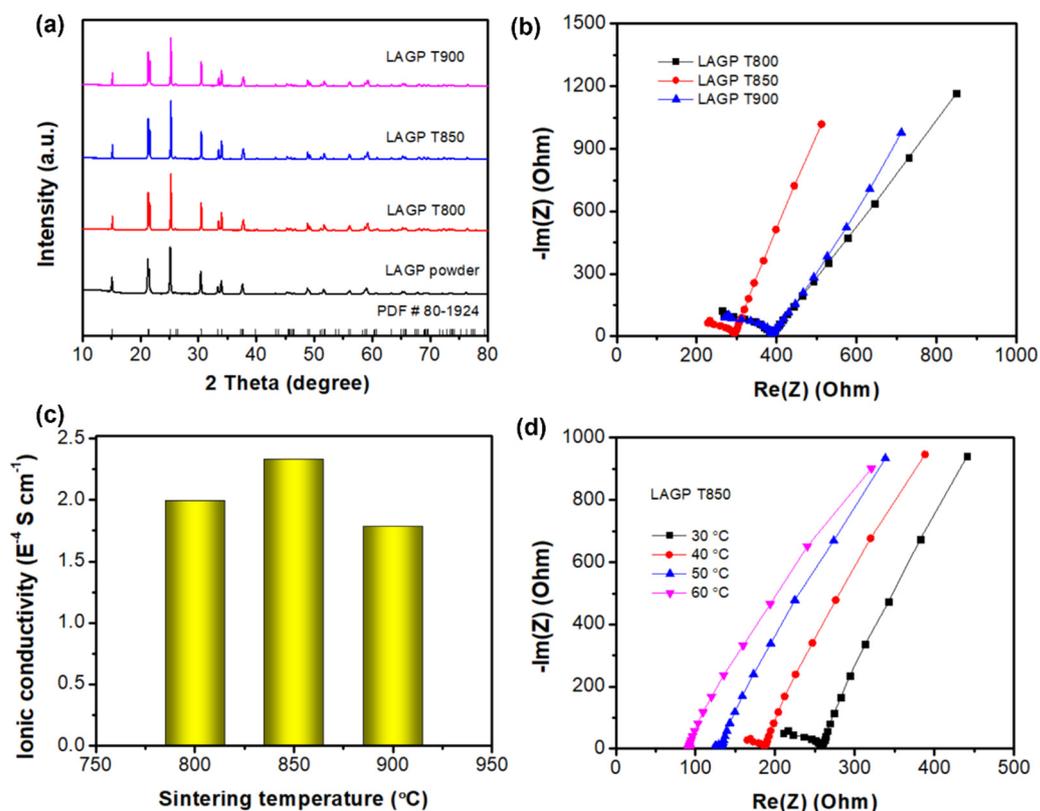


Figure 2. (a) XRD patterns, (b) Nyquist plots, (c) ionic conductivities of LAGP T800, LAGP T850, and LAGP T900 pellets, (d) Nyquist plots of LAGP T850 at 30–60 °C.

Figure S2 shows a voltage-time profile of Li/LAGP/Li symmetrical cell at room temperature. It could be found that the voltage hysteresis is gradually increasing at a low current density of 0.02 mA cm^{-2} and rapidly rises to 3 V at only 0.04 mA cm^{-2} . The

large overpotential can be attributed to the unstable Li/LAGP interface and Li dendritic deposition [26]. Herein, the Al_2O_3 layer is deposited on the surface of LAGP, as illustrated in Figure 3a, which can separate LAGP from the Li metal to prevent side reactions. The thickness of the Al_2O_3 layer is controlled at 5 nm based on our previous study on the $\text{P2-Na}_{0.66}(\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13})\text{O}_2$ cathode [42]. Figure 3b–g displays the SEM images of LAGP and $\text{LAGP@Al}_2\text{O}_3$ 50 from the top view and cross-section. Both demonstrate a compact and flat surface without pores. There is no noticeable change found in the surface and cross-section morphology.

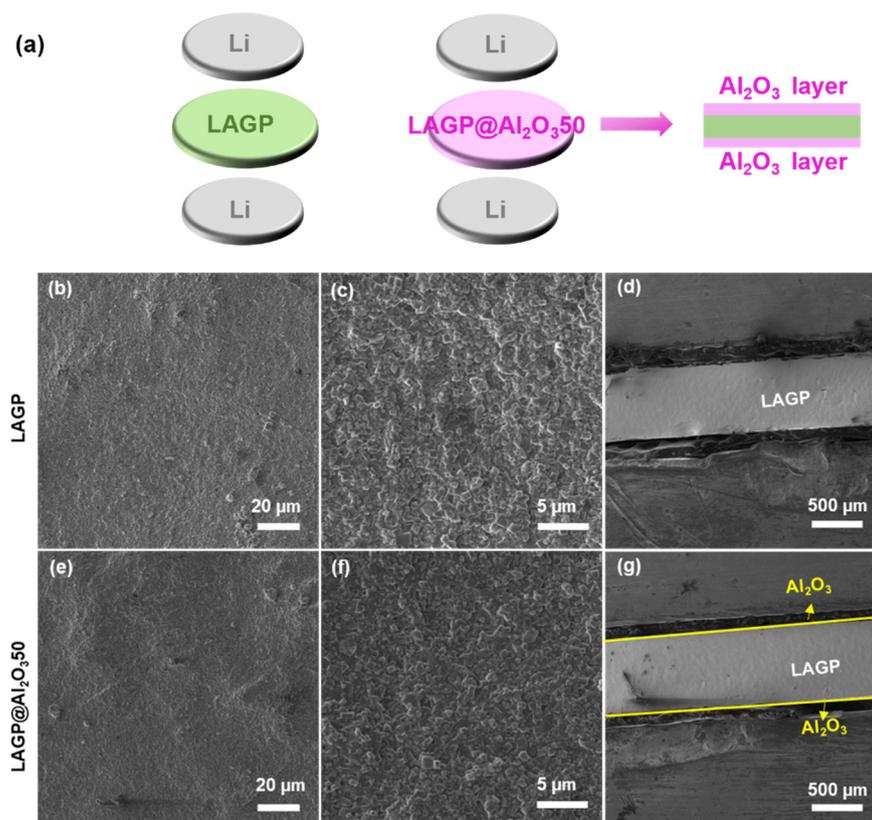


Figure 3. (a) Schematic illustration of Li/LAGP/Li and Li/LAGP@Al₂O₃/Li cell configurations, top-view and cross-sectional SEM images of (b–d) LAGP and (e–g) LAGP@Al₂O₃50.

XPS characterization was carried out to investigate the surface chemistry of LAGP with and without the Al_2O_3 layer. As shown in Figure S3 and Table S1, Ge, P, and Li elements are only detected on bare LAGP surface and absent for LAGP@Al₂O₃50, suggesting the successful deposition of Al_2O_3 film on the LAGP surface. The prominent peak in Li 1s XPS spectra (Figure 4a) is assigned to Li oxide of LAGP [43], while it is not detectable in LAGP@Al₂O₃50 (Figure 4b). Al 2p peaks can be resolved into 2p_{1/2} and 2p_{3/2} peaks corresponding to the existence of Al in LAGP and ALD- Al_2O_3 (Figure 4c,d). Similarly, P is only observed in bare LAGP (Figure 4e) and is absent for Al_2O_3 -coated LAGP (Figure 4f). Therefore, it can be concluded that the thin Al_2O_3 layer by ALD is successfully deposited on the surface of LAGP without significant morphology change. The Al_2O_3 layer is expected to induce a stable interface between Li and LAGP, suppress side reactions, and enhance the electrochemical stability of LAGP toward metallic Li.

Figure 5a shows voltage profiles of symmetrical Li cells with bare and Al_2O_3 -coated LAGP SEs at 0.02–0.2 mA cm⁻² at 40 °C. Li/LAGP/Li cell has a lower overpotential at the initial current density of 0.02 mA cm⁻², which becomes larger with the increase in current density and finally fails at 0.12 mA cm⁻². In comparison, the Li/LAGP@Al₂O₃50/Li cell exhibits a stable voltage hysteresis after initial cycles and undergoes a repeated Li

plating/stripping process at a much higher current density of 0.2 mA cm^{-2} . The steady voltage profiles of LAGP@Al₂O₃50 (Figure 5b,c) indicate the formation of a stable solid electrolyte interphase (SEI) between Li and LAGP. Long-term cycling performance is evaluated for the Li/LAGP@Al₂O₃50/Li cell, which exhibits a long lifetime of 320 h at the areal capacity of 0.2 mAh cm^{-2} and current density of 0.2 mA cm^{-2} (Figure 5d). The voltage hysteresis is mostly stabilized at 0.3 V until 250 h and then shows a slight increase, as illustrated in Figure 5e. It should be noted that the rate test is performed following the cycling test from the same Li/LAGP@Al₂O₃50/Li cell. Consequently, this cell has a 360-h Li plating/stripping duration at 0.2 mAh cm^{-2} .

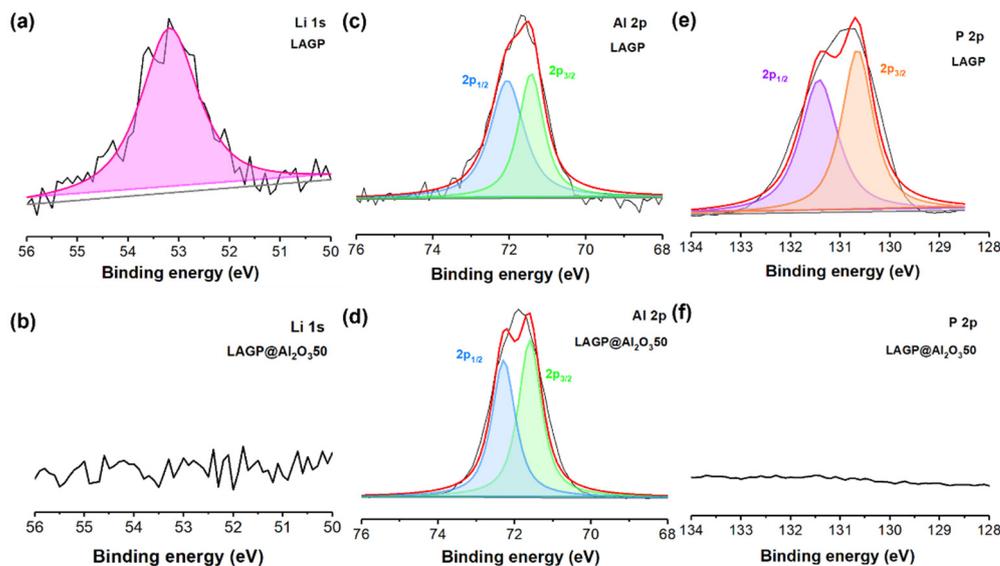


Figure 4. XPS spectra of (a,b) Li 1s, (c,d) Al 2p, and (e,f) P 2p of LAGP and LAGP@Al₂O₃50.

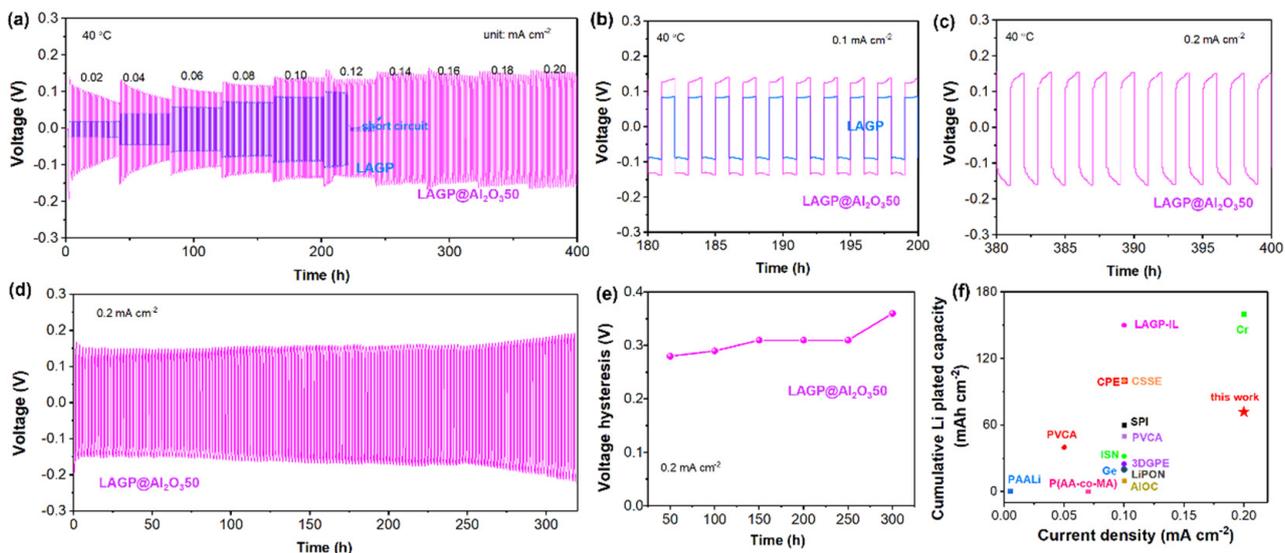


Figure 5. (a) Rate performance of symmetrical Li cells with bare and Al₂O₃-coated LAGPs as SEs at $0.02\text{--}0.2 \text{ mA cm}^{-2}$ at $40 \text{ }^\circ\text{C}$, voltage profiles at (b) 0.1 and (c) 0.2 mA cm^{-2} , (d) long-term cycling performance of the Li/LAGP@Al₂O₃50/Li cell at 0.2 mA cm^{-2} (areal capacity: 0.2 mAh cm^{-2}) and (e) corresponding voltage hysteresis, (f) comparison of cumulative Li plated capacity from this work and literatures.

Moreover, Table 1 and Figure 5f compare cumulative Li plated capacity of previous Li/LAGP/Li cells and this work in the cycling test. It can be seen that most of the previous studies proposed polymer interlayer to modify Li/LAGP interface and assessed the cycling performance at 0.1 mA cm^{-2} , which demonstrated smaller cumulative Li plated capacity below 60 mAh cm^{-2} . Although the Li/Cr-LAGP-Cr/Li [3] cell showed a high Li plated capacity of 160 mAh cm^{-2} , the overpotential is as large as 1.2 V upon Li plating/stripping behaviors. In comparison, this work employs an inorganic Al_2O_3 layer to stabilize Li/LAGP interface, and the cell possesses a much smaller overpotential of 0.3 V at 0.2 mA cm^{-2} .

Table 1. Comparison of Li/LAGP/Li cells with interface modification.

Cell Configuration	Interface Modification Layer	Cycling Performance	Cumulative Li Plated Capacity (mAh cm^{-2})	References
Li/PP-LAGP-PP/Li *	PP	500s @0.25 mA	-	[31]
Li/SPI-LAGP-SPI/Li *	SPI, by in situ solidification, 10 μm	600 h @0.1 mA cm^{-2}	60	[1]
PAALi/LAGP/PAALi *	PAALi + LAGP	100 h @0.005 mA cm^{-2}	0.5	[32]
Li/P(AA-co-MA)-LAGP-P(AA-co-MA)/Li	P(AA-co-MA), by spray-coating, 1.5 μm	20,000 s @0.07 mA cm^{-2}	0.39	[25]
Li/PVCA-LAGP-PVCA/Li *	LiTFSI/PVCA,	500 h @0.1 mA cm^{-2}	50	[33]
Li/AIOC-LAGP-AIOC/Li	AIOC, by spin coating, 11 μm	100 h @0.1 mA cm^{-2}	10	[34]
Li/CPE-LAGP-CPE/Li	CPE, by spin coating	1000 h @0.1 mA cm^{-2}	100	[36]
Li/ISN-LAGP-ISN/Li *	SN + LLZAO + FEC + LiTFSI, by in situ solidification	320 h @0.1 mA cm^{-2}	32	[27]
Li/Ge-LAGP-Ge/Li	Ge, by puttering, 60 nm	200 h @0.1 mA cm^{-2}	20	[28]
Li/Cr-LAGP-Cr/Li	Cr, by sputtering, 30 nm	800 h @0.2 mA cm^{-2}	160 (overpotential: 1.2 V)	[3]
Li/LAGP-IL-LAGP-LAGP-IL/Li	LAGP-IL	1500 h @0.1 mA cm^{-2}	150	[29]
Li/3DGPE-LAGP-3DGPE/Li *	PVDF-HFP + PEGDE + DPPO, 100 μm	250 h @0.1 mA cm^{-2}	25	[44]
Li/CSSE-LAGP-CSSE/Li	PVC + TPU + LiTFSI, 50 μm	1000 h @0.1 mA cm^{-2}	100	[45]
Li/PVCA-LAGP-PVCA/Li	PVCA + FEC	800 h @0.05 mA cm^{-2}	40	[37]
Li/LiPON-LAGP-LiPON/Li	LiPON, by sputtering, 3 μm	200 h @0.1 mA cm^{-2}	20	[26]
Li/ Al_2O_3 -LAGP- Al_2O_3 /Li *	Al_2O_3 , by ALD, 5 nm	360 h @0.2 mA cm^{-2}	72 (overpotential: 0.3 V)	This work

*: 10 μL liquid electrolyte was used, or the interlayer was immersed in liquid electrolyte.

To reveal the internal structural change after repeated cycles, the cycled Li/LAGP/Li and Li/LAGP@ Al_2O_3 50/Li were disassembled for further analysis. Figure 6 shows the SEM images and digital photos of cycled LAGP and LAGP@ Al_2O_3 50. Abundant pores and cracks are observed in cycled-bare LAGP at different magnifications, and the cycled LAGP surface turns yellow, implying possible Ge^{4+} reduction after being in contact with Li metal [25]. The pores and cracks may originate from continuous Li dendrite deposition at the unstable Li/LAGP interface and ultimately cause a short circuit failure [25,26]. On the contrary, Al_2O_3 -coated LAGP illustrates a flat and dense surface after cycling, indicating the generation of stable SEI. This Al_2O_3 -induced SEI regulates Li dendrites and induces a reliable symmetrical Li cell. Therefore, the deposited thin Al_2O_3 film is beneficial for stabilizing the Li/LAGP interface and regulating Li dendrites.

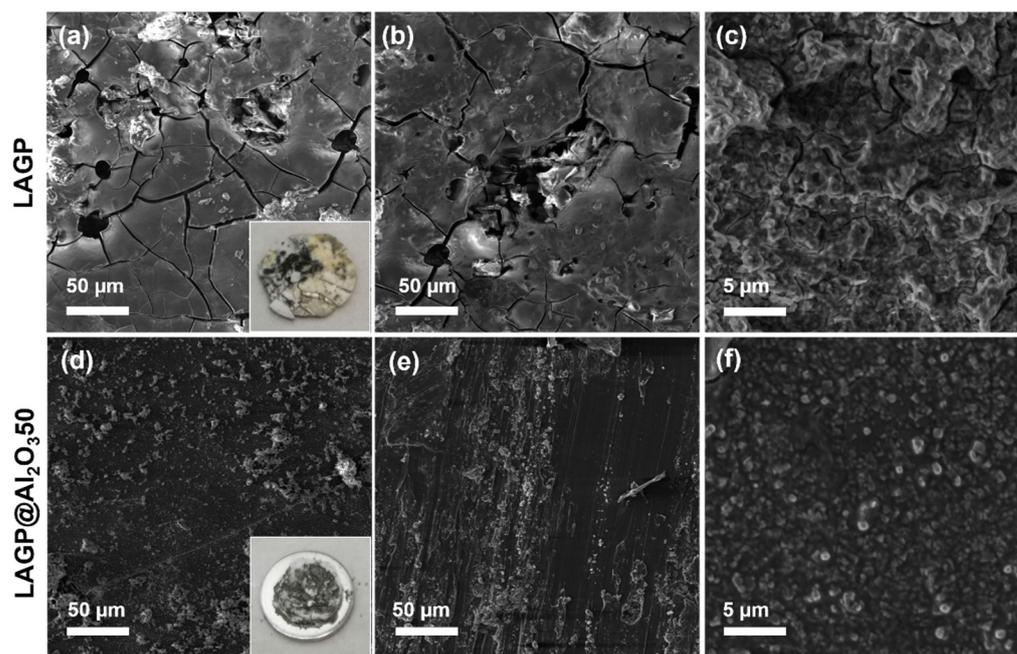


Figure 6. Top-view SEM images of cycled (a–c) LAGP and (d–f) LAGP@Al₂O_{3.50}. The insets of (a,d) show the photos of cycled LAGP and LAGP@Al₂O_{3.50}.

Meanwhile, a XPS test was performed to collect surface elemental information of cycled LAGP and LAGP@Al₂O_{3.50}. As shown in Figures S4 and 7a, and Table S2, the Al signal is absent in bare LAGP, implying the formation of an Al-deficient SEI layer. Al 2p spectra in Figure 7b can be assigned to two peaks at 72.2 and 71.5 eV, respectively, which slightly shift to 72.7 and 72.0 eV with 1060 s etching (corresponding to about 8.8 nm depth from the top of the surface). Since the SEI layers are usually ~70 nm or thicker [46,47], both the 0 s and 1060 s etching spectra should come from the SEI layer instead of the LAGP SE. Meanwhile, the absence of Al signal from the cycled bare LAGP sample also indicates that the 1060 s etching does not reach the bulk LAGP SE. The peak shift of Al 2p spectra reveals the compositional variation in the SEI layer along the vertical direction of cycled LAGP@Al₂O_{3.50}. The surface Li 1s spectrum (0 s etching) of cycled bare LAGP (Figure 7c) can be decomposed into two peaks located at 53.1 and 52.3 eV, respectively, corresponding to LiF and Li₂O₂ in the SEI layer. The surface Li 1s spectrum (0 s etching) obtained from LAGP@Al₂O_{3.50} shows higher binding energies of 53.5 and 53.0 eV for LiF and Li₂O₂ (Figure 7d). It should be noted that the Li 1s spectrum from cycled LAGP@Al₂O_{3.50} surface has a smaller LiF/Li₂O₂ ratio than cycled bare LAGP, suggesting the different SEI compositions from the coated and uncoated LAGPs. A higher LiF/Li₂O₂ ratio is observed in the Li 1s spectrum of cycled LAGP@Al₂O_{3.50} after 1060 s etching, implying a gradient distribution of LiF/Li₂O₂ in the SEI layer. F 1s spectra in Figure 7e,f originate from Li_xPF_y and LiF, which could be ascribed to the decomposition of the small addition of liquid electrolyte (LiPF₆ in EC:DEC) [37]. The LiF/Li_xPF_y ratio becomes larger for the LAGP@Al₂O_{3.50} after 1060s etching, which also indicates the compositional variation in the SEI layer along with the depth. The XPS results suggest that the SEI layers formed on the bared LAGP and Al₂O₃ coated LAGP possess different compositions. The Al₂O₃ coating induces an Al-containing SEI layer [48,49], formed on the surface of LAGP after repeated Li plating/stripping cycles. This unique SEI layer enhances the electrochemical stability of LAGP SE and extends the lifetime of Li/LAGP/Li symmetrical cells.

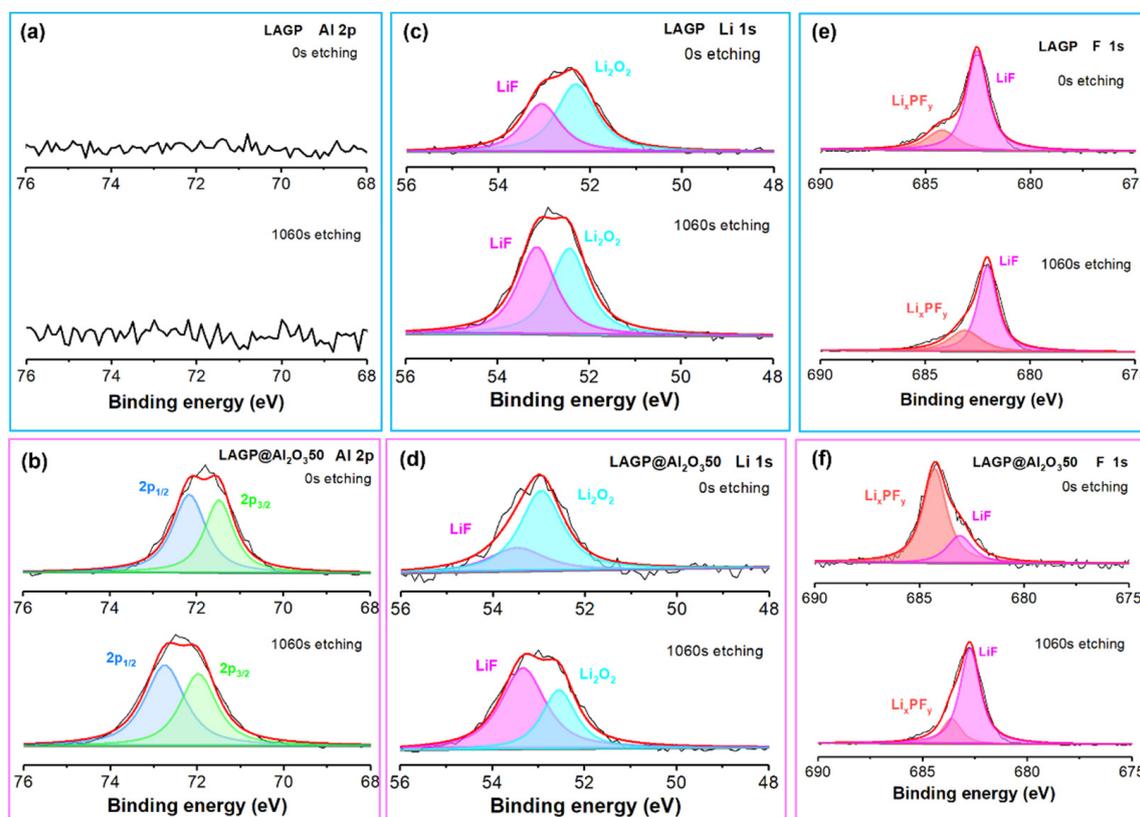


Figure 7. XPS spectra of (a,b) Al 2p, (c,d) Li 1s, (e,f) F 1s of the surface of LAGP and LAGP@Al₂O₃50 after cycling test.

4. Conclusions

In summary, a thin Al₂O₃ film was deposited on the surface of LAGP pellet by the ALD method to address the issue of Li/LAGP interface incompatibility. The optimized Li/LAGP@Al₂O₃50/Li cell maintained a stable voltage profile up to 0.2 mA cm⁻² and exhibited a 360-h cycling duration at the capacity density of 0.2 mAh cm⁻². Remarkably, this cell showed a superior cumulative Li plated capacity of 72 mAh cm⁻² at 0.2 mA cm⁻² current density. SEM and XPS characterizations suggest that Al₂O₃ film induced the formation of an Al-rich SEI layer to regulate Li dendrite deposition and contributes to a uniform and dense interface after long Li plating/stripping cycles.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12111912/s1>. Figure S1: SEM image of LAGP powder, Figure S2: Voltage-time profile of the Li/LAGP/Li cell tested at 25 °C, Figure S3: XPS survey spectra of LAGP and LAGP@Al₂O₃ before the cycling test, Figure S4: XPS survey spectra of LAGP and LAGP@Al₂O₃ after the cycling test, Table S1: Elemental composition of LAGP and LAGP@Al₂O₃50 from XPS before battery tests, Table S2: Elemental composition of LAGP and LAGP@Al₂O₃50 from XPS after cycling tests.

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