

Article

Enhanced Interfacial Stability of Mn-Based Cation-Disordered Rocksalt $\text{Li}_{1.2}\text{Cr}_{0.3}\text{Ti}_{0.3}\text{Mn}_{0.3}\text{O}_{1.9}\text{F}_{0.1}$ Cathodes via an Ion-Conductive LAGP Glass Ceramic Coating

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Abstract

Mn-based disordered rock-salt (DRX) cathode materials offer high theoretical capacities and operating voltages, rendering them promising candidates for high-energy-density lithium-ion batteries. However, severe interfacial reactions between Mn-based DRX cathodes and the electrolyte can induce surface degradation and a pronounced increase in interfacial impedance. In this study, a LAGP glass ceramic coating layer was introduced onto the surface of $\text{Li}_{1.2}\text{Cr}_{0.3}\text{Ti}_{0.3}\text{Mn}_{0.3}\text{O}_{1.9}\text{F}_{0.1}$ (LCTMOF) particles to minimize direct contact between the active material and the electrolyte, thereby enhancing the capacity retention over 50 cycles. It delivered an initial discharge capacity of 278.7 mAh g^{-1} and retained 227.3 mAh g^{-1} after 50 cycles. Relative to the pristine uncoated cathode, the LAGP glass ceramic coating material achieved a capacity retention of 81.5% together with improved rate performance, retaining a high specific capacity of 184.5 mAh g^{-1} at a current density of 500 mA g^{-1} . Surface XPS analysis, together with the electrochemical results, suggests that the LAGP glass ceramic coating mitigates cathode interfacial degradation under the investigated cycling conditions.

Keywords: lithium-ion batteries; disordered rock-salt cathodes; surface modification; particle coating



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1. Introduction

The growing demand for sustainable rechargeable batteries with high energy density has accelerated the development and widespread adoption of lithium-ion batteries (LIBs) for electrochemical energy storage. LIBs currently dominate the rechargeable-battery market because of their high energy density and favorable safety characteristics [1–3]. To further increase energy density, high-capacity ternary layered cathodes, including $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ (NMC) [4], $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$ (NCM) [5], and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (NCA) [6], have been extensively developed. These materials can

deliver specific capacities approaching 200 mAh g^{-1} , exceeding those of many conventional commercial cathodes. However, extensive Li extraction during cycling requires substantial transition-metal redox activity and can trigger pronounced structural rearrangement [7–11]. These processes are often accompanied by phase transitions, surface densification, and oxygen loss, resulting in rapid electrochemical degradation and poor cycling stability [12–15].

By contrast, Mn-based disordered rock-salt (DRX) cathodes have emerged as promising candidates for next-generation high-specific-energy lithium-ion batteries (LIBs). Their advantages arise from the natural abundance and low cost of Mn and the reduced dependence on critical metals such as Ni and Co [16–18]. Representative Mn-based DRX compounds include $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$ [19], $\text{Li}_4\text{Mn}_2\text{O}_5$ [20], and $\text{Li}_2\text{MnO}_2\text{F}$ [16,21]. These materials commonly deliver reversible capacities exceeding 200 mAh g^{-1} . Some compositions can achieve $280\text{--}355 \text{ mAh g}^{-1}$, corresponding to material-level specific energies of approximately $700\text{--}1100 \text{ Wh kg}^{-1}$ [22,23]. In conventional layered cathodes, Li^+ migration through intermediate tetrahedral sites is strongly influenced by neighboring transition-metal (TM) cations. In contrast, Li excess and cation disorder in DRX materials promote the formation of 0-TM migration channels. In these channels, the activated tetrahedral site does not face-share with any TM cation, substantially lowering the Li^+ migration barrier [24]. A sufficiently interconnected population of 0-TM channels forms a three-dimensional Li^+ percolation network throughout the DRX structure. This network enables extensive and reversible Li^+ extraction and reinsertion [25]. Mn-based DRX cathodes can utilize conventional $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox for charge compensation. Compositional regulation through F^- substitution and high-valent d^0 cations, such as Ti^{4+} and Nb^{5+} , can further activate $\text{Mn}^{2+}/\text{Mn}^{4+}$ two-electron redox chemistry [26]. This multielectron redox process increases the number of electrochemically accessible electrons and thus enhances the achievable specific capacity. More importantly, Li excess generates abundant Li–O–Li local configurations, which introduce high-energy nonbonding O 2p states. These states allow lattice oxygen to participate in anionic redox during deep delithiation [10]. Consequently, oxygen redox provides additional capacity beyond that available from conventional transition-metal redox alone. For example, charge compensation in $\text{Li}_2\text{MnO}_2\text{F}$ involves coupled Mn and O redox processes. Molecular O_2 species can form during charging and become confined within Li-vacancy clusters [27]. This reversible oxygen-redox mechanism contributes substantially to the high capacity of $\text{Li}_2\text{MnO}_2\text{F}$, which reaches approximately 280 mAh g^{-1} .

However, these high-capacity redox mechanisms are intrinsically associated with substantial structural and interfacial instability [28]. Li^+ transport in DRX cathodes is highly sensitive to local short-range order and the connectivity of the 0-TM network. Their intrinsically low electronic conductivity also requires particle downsizing, intensive mechanical milling, and relatively high conductive-carbon contents to fully access the available capacity [29]. Extensive Li extraction coupled with oxygen redox can induce lattice-oxygen loss, irreversible Mn migration, and surface densification during repeated cycling. Incomplete reversal of Mn migration permanently modifies the local coordination environment of lattice oxygen. This structural evolution can cause substantial irreversible capacity loss. Although particle downsizing improves Li^+ transport kinetics, the increased cathode/electrolyte interfacial area accelerates parasitic reactions at high operating potentials [30]. For $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$ cycled in carbonate-based electrolytes, progressive growth of a LiF-rich cathode-electrolyte interphase (CEI) has been reported. This degradation is accompanied by lattice-oxygen loss, CO_2/O_2 evolution, Mn over-reduction and dissolution, and irreversible surface reconstruction [31]. These processes increase interfacial resistance and accelerate capacity fading. These degradation mechanisms underscore the need for protective electrolyte-based coatings on Mn-based DRX cathodes [32].

A continuous, compact, and chemically stable coating can physically isolate the highly reactive DRX surface from the electrolyte. Such protection can mitigate high-voltage electrolyte oxidation, HF-induced corrosion, and reactions involving reactive oxygen species. It can also suppress lattice-oxygen release, Mn dissolution, surface reconstruction, and continuous CEI growth. Unlike conventional inert oxide coatings with limited ionic conductivity, Li⁺-conductive electrolyte coatings can provide both interfacial protection and efficient Li⁺ transport across the interface [33–35]. This dual functionality minimizes the additional kinetic resistance introduced by the protective layer. For example, a Li⁺-conductive borate coating on Li₂Mn_{2/3}Ti_{1/3}O₂F effectively suppressed Mn dissolution and reduced interfacial resistance [25]. With a 3 wt.% coating, the modified cathode retained approximately 130 mAh g^{−1} after 100 cycles.

Mn-based DRX cathodes typically operate over wide voltage windows and require relatively high conductive-carbon contents. Under these conditions, sulfide solid electrolytes are particularly susceptible to oxidative decomposition at the cathode interface [36]. Solid electrolytes with greater oxidative stability can therefore provide substantially improved cycling stability. Accordingly, coating DRX particles with a thin and conformal electrolyte layer represents a promising strategy for stabilizing the cathode/solid-electrolyte interface. A suitable coating should facilitate Li⁺ transport and limit detrimental interfacial reactions under the intended cycling conditions. Its protective performance should be distinguished from its intrinsic electrochemical stability, because thermodynamic instability does not necessarily result in rapid decomposition [37]. Such a layer can suppress parasitic interfacial reactions, stabilize oxygen-redox chemistry, and improve ionic contact at the cathode/solid-electrolyte interface [37]. Nevertheless, excessive coating should be avoided. An overly thick or abundant coating can lengthen Li⁺ diffusion pathways, reduce the active-material fraction, and increase first-cycle capacity loss. Therefore, the coating composition, thickness, and thermal-treatment conditions should be carefully optimized in a coordinated manner [38].

In this work, Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ (LAGP), a glass ceramic electrolyte with high Li⁺ conductivity, was employed as a functional surface coating for Li_{1.2}Cr_{0.3}Ti_{0.3}Mn_{0.3}O_{1.9}F_{0.1} (LCTMOF). An amorphous LAGP layer was first deposited onto LCTMOF particles via a hydrothermal process and subsequently subjected to thermal treatment to induce partial crystallization, yielding an ionically conductive LAGP glass ceramic coating. Microstructural characterization revealed the formation of a uniform LAGP glass ceramic coating approximately 5 nm thick on the LCTMOF surface, which can reduce direct contact between the active cathode and the liquid electrolyte and thereby mitigate detrimental interfacial reactions. X-ray photoelectron spectroscopy (XPS) analysis further confirmed that the LAGP glass ceramic surface modification effectively stabilized the cathode surface. Electrochemical measurements demonstrated that LCTMOF@LAGP maintained a discharge capacity of 227.3 mAh g^{−1} after 50 cycles, corresponding to a capacity retention of 81.5%, markedly higher than the 56.8% retention of pristine LCTMOF. Even at a high current density of 500 mA g^{−1}, LCTMOF@LAGP delivered a reversible specific capacity of 184.5 mAh g^{−1}, demonstrating its enhanced rate capability. This work demonstrates an effective surface-engineering strategy for enhancing the cycling stability of Mn-based high-capacity cathode materials.

2. Materials and Methods

2.1. Materials Synthesis

Li_{1.2}Cr_{0.3}Ti_{0.3}Mn_{0.3}O_{1.9}F_{0.1} (LCTMOF) was synthesized via a conventional high-temperature solid-state reaction. As illustrated in Figure 1a, stoichiometric amounts of Li₂CO₃ (99%, Aladdin, Shanghai, China), LiF (99%, Aladdin, Shanghai, China), MnO

(99%, Aladdin, Shanghai, China), TiO_2 (99%, Aladdin, Shanghai, China), and Cr_2O_3 (99%, Aladdin, Shanghai, China) were mixed in isopropanol and ball-milled at 250 rpm for 12 h to ensure homogeneous mixing, followed by drying in an oven for 12 h. The resulting homogeneous precursor mixture was sintered at 950°C for 10 h under an Ar atmosphere, followed by furnace cooling to room temperature. The as-synthesized LCTMOF particles were subsequently pulverized using a planetary ball mill operated at 500 rpm for 8 h.

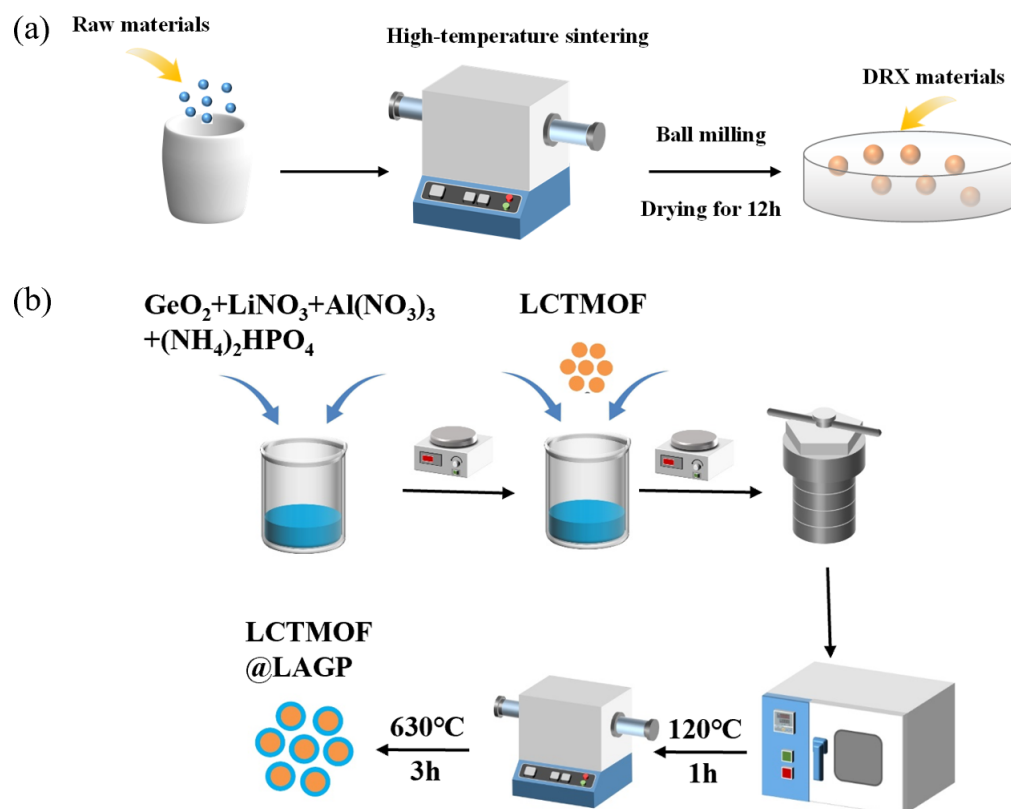


Figure 1. Scheme of synthesis procedure of (a) LCTMOF and (b) LCTMOF@LAGP.

Glass $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ (LAGP)-coated LCTMOF cathode powders were prepared via a hydrothermal route, as schematically illustrated in Figure 1b. GeO_2 was mixed with citric acid, after which a 20 wt.% LiNO_3 aqueous solution, a 20 wt.% $\text{Al}(\text{NO}_3)_3$ aqueous solution, and $(\text{NH}_4)_2\text{HPO}_4$ powder were sequentially added in the required stoichiometric proportions under continuous stirring to obtain a homogeneous solution. Subsequently, an appropriate amount of ethylene glycol was introduced and the solution was magnetically stirred for 30 min, after which LCTMOF powders were added in amounts corresponding to nominal LAGP coating layer contents of 3, 5, and 7 wt.%; The precursor amounts were adjusted to target nominal LAGP contents of 3, 5, and 7 wt.%, defined as $m_{\text{LAGP}} / (m_{\text{LCTMOF}} + m_{\text{LAGP}}) \times 100\%$. Here, m_{LAGP} denotes the theoretical LAGP mass calculated from the precursor stoichiometry, assuming complete conversion and retention. The resulting samples were designated LCTMOF@LAGP3, LCTMOF@LAGP5, and LCTMOF@LAGP7, respectively.

Following the hydrothermal treatment, the precursor was dried in a muffle furnace at 120°C for 1 h. The dried precursor was subsequently heat-treated at 630°C for 3 h in a tube furnace under an Ar atmosphere. Before heating, the furnace tube was evacuated using a vacuum pump and then purged with Ar at a high flow rate to displace residual air. During heat treatment, a continuous Ar flow of 0.1 L/min was maintained to keep the furnace tube under positive pressure relative to the surroundings and minimize air ingress.

2.2. Characterization

The crystal structure of LCTMOF was characterized by X-ray diffraction (XRD, Philips X'Pert, Almelo, The Netherlands) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over a 2θ range of $10\text{--}90^\circ$. The morphology, microstructure, and elemental distribution of LCTMOF were investigated by scanning electron microscopy (SEM, Quanta 200FEG, FEI Co., Ltd., Hillsboro, CA, USA), energy-dispersive X-ray spectroscopy (EDS), and field-emission transmission electron microscopy (TEM, Talos F200X, FEI Co., Ltd., Hillsboro, Hillsboro, CA, USA). The surface chemical states and valence states of representative elements in the cathode materials were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Waltham, MA, USA).

2.3. Electrochemical Tests

The cathode slurry was prepared by mixing the active material, carbon black, and poly(vinylidene fluoride) (PVDF, Aladdin, Shanghai, China) in a weight ratio of 80:10:10 using N-methyl-2-pyrrolidone (NMP, Aladdin, Shanghai, China) as the solvent. The resulting homogeneous slurry was uniformly coated onto Al foil, vacuum-dried at 120°C for 12 h, and subsequently punched into circular electrodes. A solution of 1 mol/L LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 by volume, Aladdin, Shanghai, China) was used as the electrolyte, the active material loading was maintained about $4.5 \text{ mg}\cdot\text{cm}^{-2}$. A polypropylene membrane (Celgard 2500, Charlotte, NC, USA) was employed as the separator, and Li metal foil served as the counter electrode. The electrodes were assembled into CR2032-type coin cells. Galvanostatic charge–discharge measurements were conducted at room temperature within a voltage window of 1.5–4.8 V versus Li/Li⁺. Specific capacities were calculated based on the total mass of the LCTMOF@LAGP composite powder. Electrochemical impedance spectroscopy (EIS, Autolab, Utrecht, Netherlands) measurements were carried out at the open-circuit voltage (OCV, CH Instruments, Shanghai, China) over a frequency range of 0.01 Hz to 1 MHz. Cyclic voltammetry (CV, CH Instruments, Shanghai, China) measurements were conducted over a potential range of 1.5–4.8 V versus Li/Li⁺. EIS measurements were performed at the fully discharged state after resting for 3 h to ensure comparable states of charge. CV measurements were performed at a scan rate of 0.5 mV/s. EIS measurements were conducted with an AC perturbation amplitude of 5 mV.

3. Results

As shown in Figure 2a, the XRD pattern of LAGP glass powder exhibits a broad amorphous halo without discernible crystalline diffraction peaks. This feature confirms the predominantly amorphous nature of the LAGP powder. The room-temperature ionic conductivity of separately prepared LAGP glass ceramics was evaluated by electrochemical impedance spectroscopy after heat treatment at 630°C for different durations. The impedance spectra and calculated conductivities are presented in Figure S4 and Table S1, respectively. The sample heat-treated for 3 h, corresponding to the thermal-treatment conditions used to prepare the coated cathodes, exhibited an ionic conductivity of $4.2 \times 10^{-4} \text{ S/cm}$, excluding carbon black, PVDF, and the Al current collector.

Figure 2b shows the XRD patterns of the LCTMOF@LAGP samples prepared via the hydrothermal coating process. All major diffraction peaks can be indexed to the disordered rock-salt phase (PDF No. 81-0095, cubic Fm-3m space group). This result indicates that the DRX structure of LCTMOF is well preserved after LAGP glass ceramic coating. No detectable reflections from crystalline impurity phases are observed in the coated samples. No characteristic reflections attributable to LAGP glass ceramic are detected after surface modification.

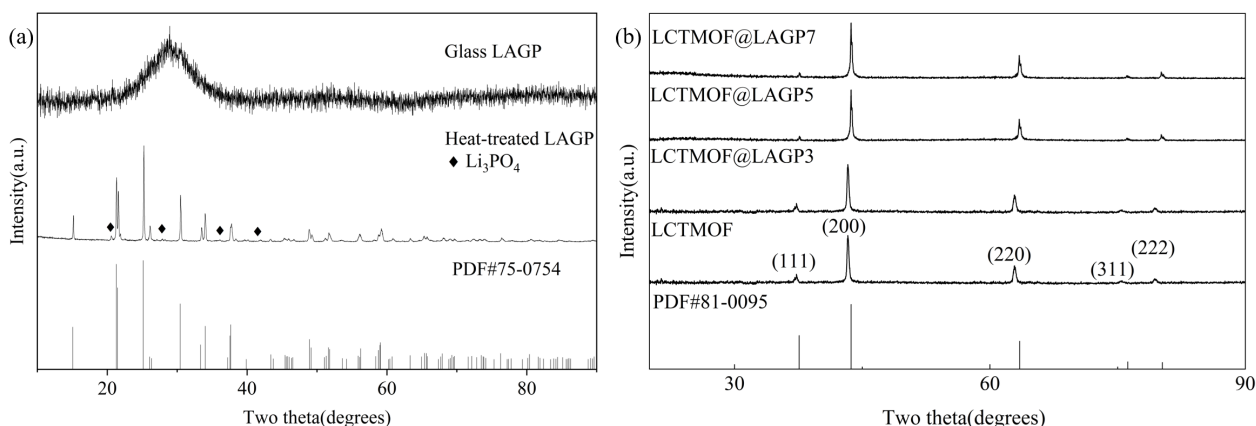


Figure 2. XRD patterns of (a) LAGP samples and (b) LCTMOF@LAGP samples.

Figure 2a compares the XRD patterns of the separately prepared LAGP precursor before and after heat treatment. Before heating, the broad diffuse halo is consistent with a predominantly amorphous structure. After heat treatment at 630 °C, crystalline reflections emerge, including those associated with the NASICON-type phase and additional reflections assigned to Li_3PO_4 , indicating crystallization accompanied by secondary-phase formation. The principal reflections of the LCTMOF@LAGP composites in Figure 2b remain indexable to the cubic DRX structure. No separate reflections attributable to the coating-related crystalline phases are clearly resolved under the present measurement conditions. This observation does not establish that the heat-treated coating is wholly amorphous. The low coating fraction limits its contribution to the overall diffraction pattern, while small crystalline domains, if present, may further broaden and weaken the corresponding reflections.

The local TEM observations provide complementary structural information: the coating before heat treatment exhibits amorphous features, whereas the heat-treated sample contains both locally crystalline regions and regions without discernible lattice fringes. These observations are consistent with partial crystallization of the coating. However, its crystalline fraction and phase composition cannot be quantified from the present data, and minor coating-related phases, including Li_3PO_4 , cannot be excluded solely because their reflections are not resolved in the composite XRD patterns.

The crystallite size of the DRX particles can be calculated by the Scherrer equation (Equation (1)), where K represents the Scherrer constant ($K = 0.9$), λ represents the wave length of Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), β represents the peak width of X-ray diffraction peaks. The peak parameters and corresponding size estimates are summarized in Table 1.

The arithmetic means of the estimates from the three reflections are 27.37, 27.50, 25.98, and 31.16 nm for LCTMOF, LCTMOF@LAGP3, LCTMOF@LAGP5, and LCTMOF@LAGP7, respectively. All four samples therefore exhibit apparent coherent diffraction domain sizes in the order of tens of nanometers. The estimates vary among the selected reflections. Such variation may reflect contributions from microstrain, defects, anisotropic domain dimensions, and instrumental broadening, in addition to finite crystallite size. Accordingly, these values are interpreted as approximate apparent crystallite sizes rather than physical particle sizes. The arithmetic means to summarize the three reflection-specific estimates and do not represent a measured particle-size distribution.

$$D = K\lambda/\beta\cos\theta \quad (1)$$

The coated samples exhibit reflections at higher 2θ than pristine LCTMOF, but the shift is not monotonic with nominal LAGP content. For example, the (200) positions are 43.337° , 43.679° , 43.820° , and 43.709° . These shifts are consistent with smaller average

interplanar spacings, although instrumental and specimen-position effects have not been excluded. Possible contributions from stress, defect chemistry, or compositional changes cannot be distinguished by the present data.

Table 1. XRD peak parameters and Scherrer estimates of the crystallite sizes of the LCTMOF phase in pristine and LAGP-coated samples.

Samples	(hkl)	2 θ /°	FWHM°	Crystallite Sizes/nm
LCTMOF	(200)	43.337	0.261	32.812
	(220)	62.912	0.364	25.574
	(222)	79.405	0.435	23.738
LCTMOF@LAGP3	(200)	43.679	0.257	33.366
	(220)	63.469	0.344	27.154
	(222)	80.241	0.473	21.994
LCTMOF@LAGP5	(200)	43.820	0.252	34.051
	(220)	63.630	0.390	24.001
	(222)	80.393	0.523	19.900
LCTMOF@LAGP7	(200)	43.709	0.223	38.401
	(220)	63.490	0.319	29.345
	(222)	80.217	0.404	25.724

Figure 3 presents the TEM characterization of pristine LCTMOF. Pronounced particle agglomeration and nanosized crystallites can be observed in the TEM images. The EDS elemental maps in Figure 3b show a homogeneous distribution of Cr, Ti, and Mn throughout the LCTMOF particles (Table 2). The HRTEM image in Figure 3f reveals well-defined lattice fringes with an interplanar spacing of approximately 2.07 Å. This spacing can be indexed to the (200) plane of the disordered rock-salt structure and agrees well with PDF No. 81-0095. The corresponding SAED pattern in Figure 3g exhibits diffraction reflections characteristic of the DRX phase, including those associated with the (111) plane. These results further support the assignment of LCTMOF to the cubic Fm-3m structure.

Table 2. STEM-EDS composition of region B in Figure 3e (at. %).

Samples	Cr	Ti	Mn	O	F
LCTMOF	10.89	8.52	9.77	67.78	3.04

To directly visualize the LAGP glass coating formed on hydrothermally prepared LCTMOF@LAGP particles, TEM characterization was performed, as shown in Figure 4. The TEM image in Figure 4a reveals numerous nanoparticles agglomerated into larger secondary particles with sizes of approximately 100 nm. The elemental distribution of the modified cathode was further examined by scanning transmission electron microscopy (STEM), as shown in Figure 4b,c,e,f. Ti and Mn are predominantly distributed within the particle interior, consistent with the spatial distribution of the LCTMOF phase. In contrast, P is enriched at the particle surface and serves as a characteristic marker of the LAGP glass phase. This distribution confirms the successful formation of an LAGP glass coating on the LCTMOF particles through the hydrothermal process. As shown in Figure 4d,h, a dense and continuous coating layer approximately 5 nm thick is clearly observed on the DRX particle surface. Well-defined lattice fringes are visible within the LCTMOF particles, whereas no discernible lattice fringes are observed in the LAGP glass coating layer. The coating region also exhibits diffuse diffraction features characteristic of an amorphous phase. These observations confirm that the LAGP coating predominantly retains its glassy state before heat treatment.

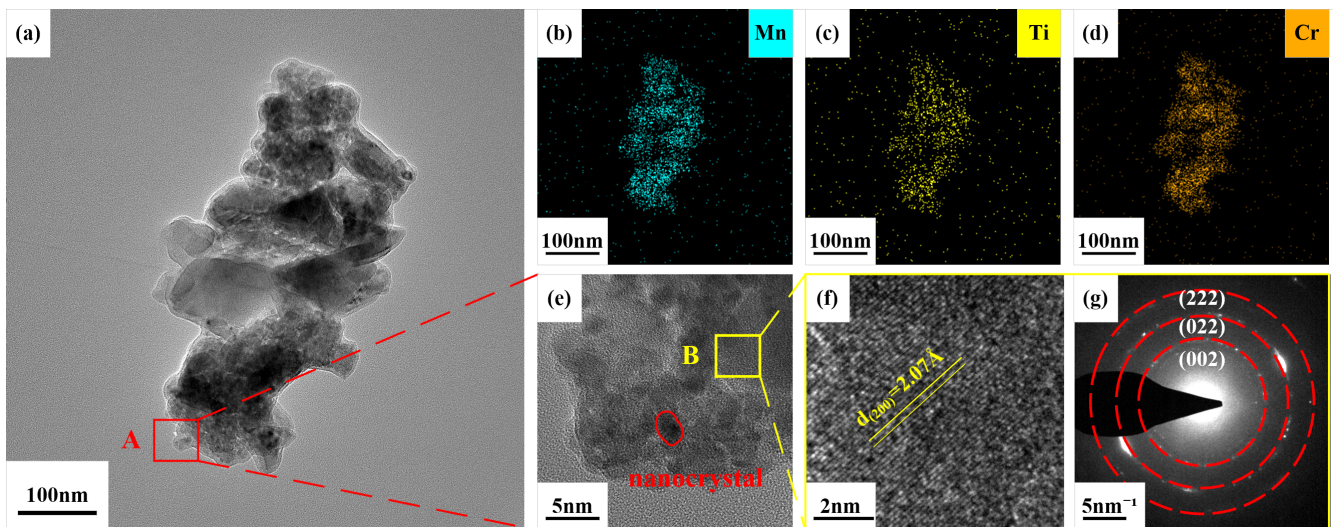


Figure 3. TEM Images of uncoated LCTMOF. (a) TEM image; (b–d) EDS elemental maps of Mn, Ti, and Cr, respectively; (e) magnified TEM image; (f) HRTEM image; and (g) SAED pattern.

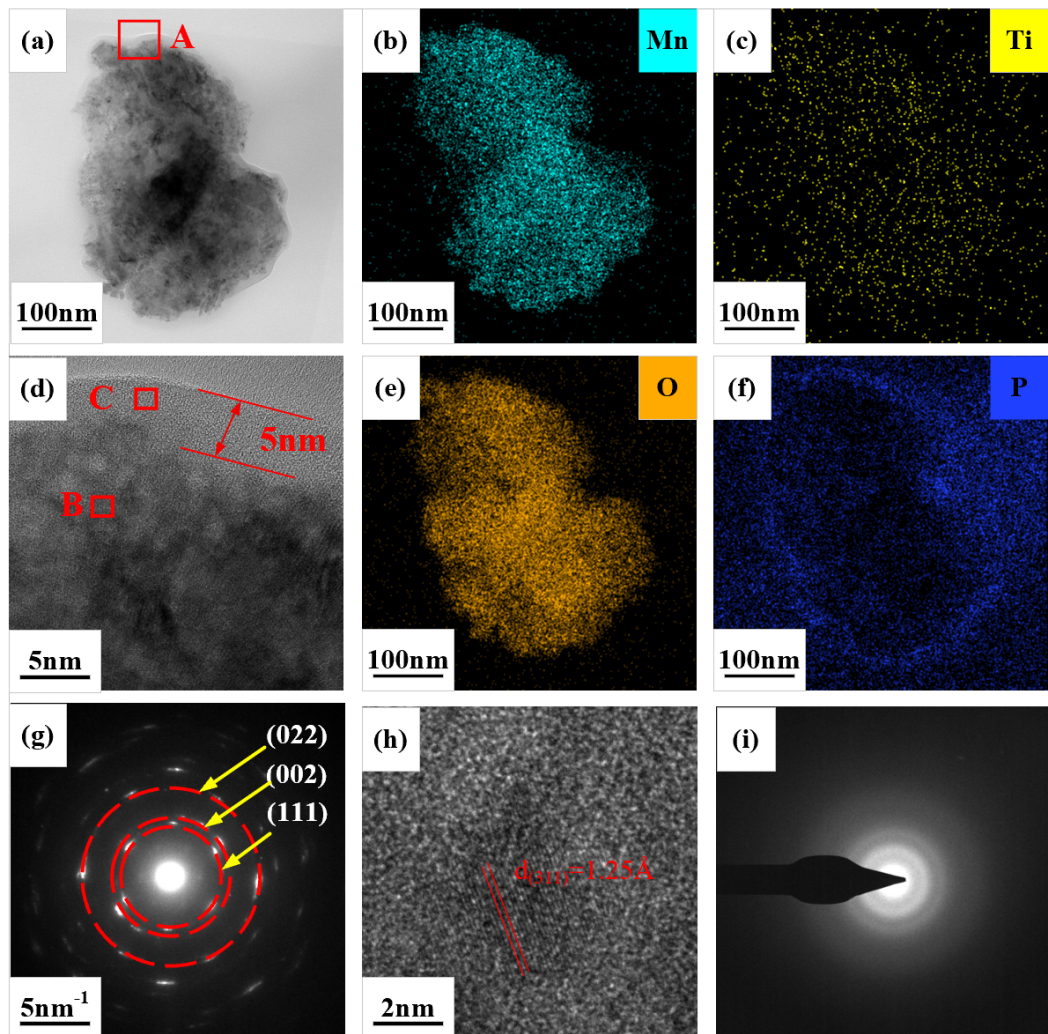


Figure 4. TEM characterization of the as-prepared LCTMOF@LAGP5 sample synthesized via the hydrothermal method without subsequent heat treatment. (a) TEM image; (b,c,e,f) EDS elemental maps of Mn, Ti, Cr, and P, respectively; (d) magnified TEM image of region A in (a); (g) selected-area electron diffraction (SAED) pattern of region B in (d); (h) HRTEM image of region B in (d); and (i) SAED pattern of region C in (d).

As shown in the TEM image of the heat-treated LCTMOF@LAGP sample in Figure 5a, three structurally distinct regions can be identified. The outermost coating layer shows no discernible lattice fringes, indicating an amorphous structure. Combined with the preceding results and STEM elemental mapping, this surface layer can be assigned to amorphous LAGP. Beneath the amorphous LAGP layer, two crystalline regions with distinct lattice-fringe arrangements are observed. STEM elemental mapping shows that the region outlined in red contains P, whereas the region outlined in yellow is enriched in Mn, Ti, and Cr. To further determine the phase composition, selected-area electron diffraction (SAED) analysis was performed, as shown in Figure 5e. The P-containing region outlined in red can be assigned to crystalline LAGP. It exhibits an interplanar spacing of 3.54 Å corresponding to the (113) plane, consistent with PDF No. 75-0754. In contrast, the Mn-rich, Ti-rich, and Cr-rich region outlined in yellow is assigned to the disordered rock-salt LCTMOF phase. This region exhibits an interplanar spacing of 1.46 Å corresponding to the (220) plane, in good agreement with PDF No. 81-0095.

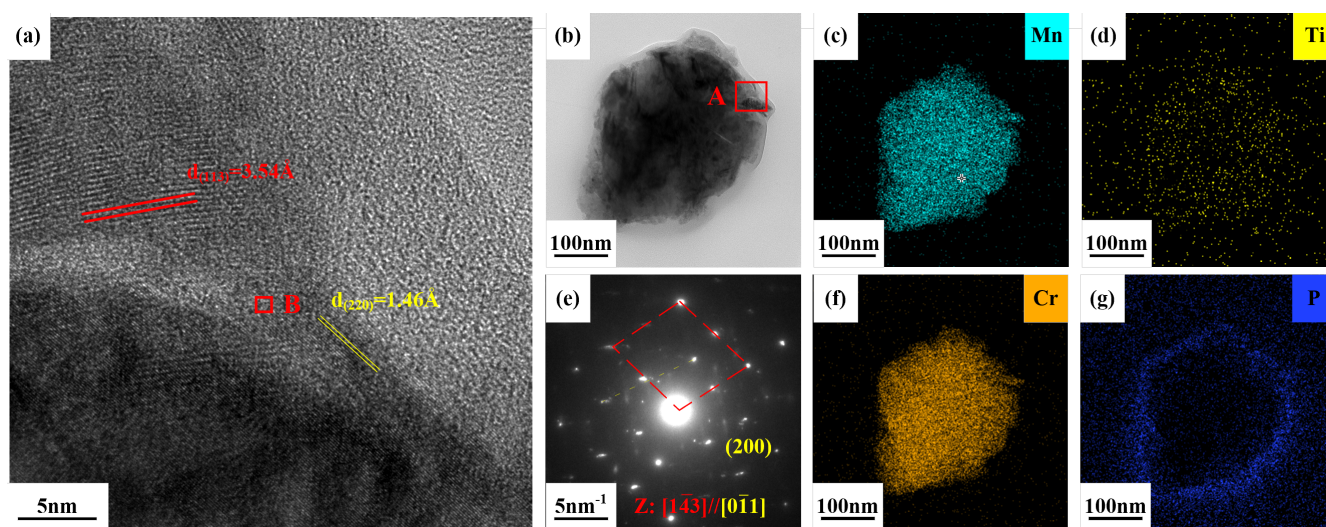


Figure 5. TEM images of heat-treated LCTMOF@LAGP5 samples. (a) HRTEM image of region A in (b); (b) TEM image; (c,d,f,g) EDS elemental maps of Mn, Ti, Cr, and P, respectively; and (e) selected-area electron diffraction (SAED) pattern of region B in (a).

The structural characterization should be interpreted within its spatial and analytical limits. XRD indicates retention of the dominant DRX phase, whereas local electron diffraction and elemental mapping provide evidence consistent with a partially crystallized LAGP-containing coating. These observations do not establish a chemically abrupt or reaction-free LAGP/LCTMOF interface. In particular, minor phosphate-containing reaction products, amorphous interfacial phases, and limited interdiffusion may remain unresolved. The improved electrochemical performance demonstrates a beneficial effect of the surface modification but does not independently establish that there are no other reaction phase after heat treatment.

When cycled at 10 mA g^{−1} within 1.5–4.8 V versus Li/Li⁺, Figure 6a,b show the galvanostatic charge–discharge profiles of pristine LCTMOF and LAGP glass ceramic-coated electrodes at 10 mA g^{−1}. The profiles correspond to the first and 50th cycles, respectively. As shown in Figure 6a, all samples exhibit similar first-cycle profiles without a distinct voltage plateau near the upper cutoff voltage of 4.8 V. This similarity indicates that LAGP glass ceramic coating does not substantially alter the intrinsic electrochemical reaction characteristics of LCTMOF. The coated samples also exhibit comparable initial discharge capacities and Coulombic efficiencies. Thus, the investigated LAGP glass ceramic contents have only a minor effect on the initial capacity utilization. After 50 cycles, pristine

LCTMOF shows pronounced discharge-voltage decay and substantially greater capacity loss than the coated electrodes, as shown in Figure 6b. In contrast, the LAGP glass ceramic-coated electrodes maintain higher discharge voltages and capacities after prolonged cycling. These results indicate that LAGP glass ceramic surface modification effectively improves the long-term electrochemical stability of LCTMOF. Galvanostatic cycling was further performed to evaluate the effect of LAGP coating content.

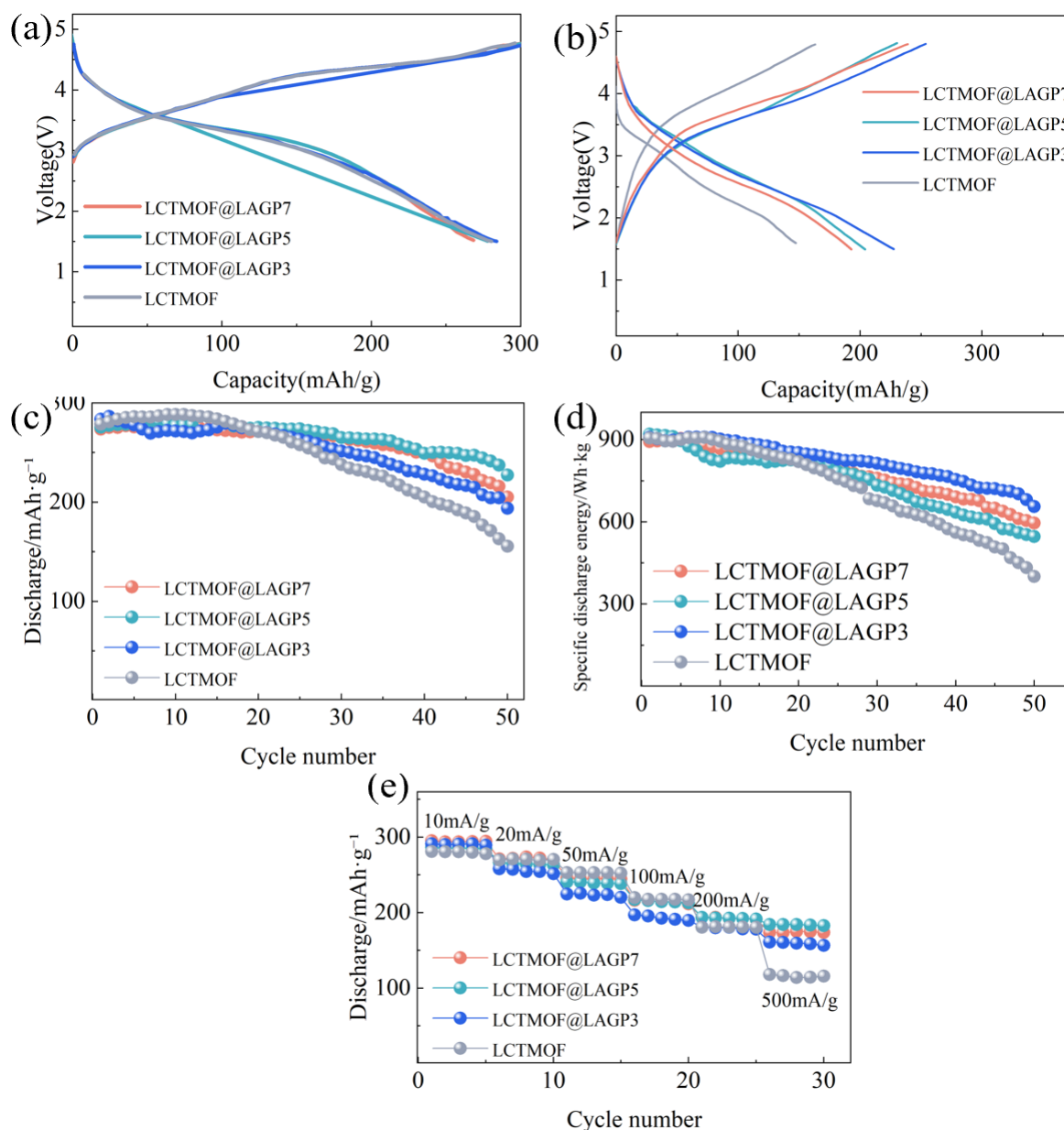


Figure 6. Electrochemical performance of LCTMOF@LAGP cathodes. (a) Galvanostatic charge-discharge profiles for the first cycle and (b) the 50th cycle; (c) cycling performance in terms of specific capacity; (d) evolution of specific energy during cycling; and (e) rate capability, the measurements in panels (a–d) were performed at 10 mA g⁻¹ within 1.5–4.8 V versus Li/Li⁺. The rate-performance measurements in panel (e) used the same voltage window at the indicated current densities.

As shown in Figure 6c, Pristine LCTMOF delivered an initial discharge capacity of 298.1 mAh g⁻¹, which decreased to 169.3 mAh g⁻¹ after 50 cycles. This corresponds to a capacity retention of only 56.8%, indicating severe degradation during prolonged cycling. In comparison, LAGP surface modification markedly improved the cycling stability of LCTMOF. LCTMOF@LAGP3 delivered an initial discharge capacity of 283.7 mAh g⁻¹

and retained 193.6 mAh g^{-1} after 50 cycles. The corresponding capacity retention is 68.2%. Increasing the LAGP content to 5 wt.% yields the best cycling performance. LCTMOF@LAGP5 delivered 278.7 mAh g^{-1} initially and retained 227.3 mAh g^{-1} after 50 cycles. Its capacity retention reaches 81.5%, which is 24.7 percentage points higher than that of pristine LCTMOF. These results suggest that an optimized LAGP glass ceramic coating effectively mitigates interfacial degradation and improves capacity retention during cycling [39]. Further increasing the LAGP content to 7 wt.% results in inferior electrochemical performance. LCTMOF@LAGP7 retains 205.1 mAh g^{-1} after 50 cycles, corresponding to a capacity retention of 72.3%.

The initial discharge capacity decreases from 298.1 mAh g^{-1} for pristine LCTMOF to 278.7 mAh g^{-1} for LCTMOF@LAGP5, corresponding to a reduction of approximately 6.5%. Because the capacities are normalized to the total composite-powder mass, this decrease partly reflects dilution by the LAGP coating. Assuming a coating fraction of 5 wt.% of the composite and negligible direct capacity contribution from LAGP, the capacity expected from mass dilution alone is 283.2 mAh g^{-1} . The measured capacity is approximately 4.5 mAh g^{-1} below this estimate. The additional difference may reflect reduced accessibility of some surface reaction sites, additional transport resistance, or changes in electronic contact caused by the coating. Experimental variability may also contribute. These effects cannot be quantitatively separated using the present measurements. Accordingly, the lower initial capacity is attributed primarily to the expected mass-dilution effect, with possible additional limitations in active-material utilization. The capacity increase observed during subsequent early cycles is consistent with progressive electrochemical activation but does not exclude partial blocking of surface reaction sites.

The dependence of electrochemical performance on nominal LAGP glass ceramic content suggests a balance between surface protection and coating-associated penalties. LCTMOF@LAGP5 exhibits the highest capacity retention after 50 cycles (81.5%), compared with 68.2% and 72.3% for LCTMOF@LAGP3 and LCTMOF@LAGP7, respectively. It also delivers the highest capacity at 500 mA g^{-1} among the coated samples, indicating the most favorable overall performance within the investigated composition range. At 3 wt.%, the coating may provide insufficient protection of the reactive LCTMOF surface. Increasing the nominal content to 5 wt.% may improve protection while preserving adequate transport and electronic contact. At 7 wt.%, the increased fraction of coating material dilutes the specific capacity on a composite-mass basis and may additionally introduce local transport limitations or reduce active-material accessibility. However, mass dilution alone does not account for the lower capacity retention, which is referenced to each sample's initial capacity. These interpretations remain tentative because coating coverage, thickness distributions, and impedance were not systematically compared across all three coating contents. Nominal coating content should therefore not be equated directly with coating thickness. The results identify 5 wt.% as the best-performing nominal content among the samples tested.

Figure 6d shows the evolution of specific energy calculated based on the mass of the active cathode material during cycling. Pristine LCTMOF exhibits pronounced specific-energy decay from an initial 906.3 Wh kg^{-1} to 401.2 Wh kg^{-1} after 50 cycles. In contrast, the LAGP-coated electrodes exhibit substantially slower specific-energy decay. This improvement results from the combined enhancement of capacity retention and discharge-voltage stability during cycling. LCTMOF@LAGP3 retains a specific energy of 646.5 Wh kg^{-1} after 50 cycles, substantially exceeding that of pristine LCTMOF. Overall, an optimized LAGP glass ceramic coating enhances electrochemical stability of LCTMOF after 50 cycles, whereas excessive coating can adversely affect interfacial transport.

Figure 6e compares the rate capabilities of pristine LCTMOF and electrodes with different LAGP coating contents. The discharge capacity decreases with increasing current density for all electrodes, with pristine LCTMOF showing the most pronounced decline. At high current densities, limited reaction time and increased polarization restrict Li^+ transport and reduce utilization of the electrochemically active material. At relatively low current densities of $\leq 100 \text{ mA g}^{-1}$, all electrodes exhibit comparable discharge capacities. This result indicates that LAGP glass ceramic coating has little influence on capacity utilization under low-rate conditions. At higher current densities, however, the performance differences become increasingly pronounced, and all LAGP glass ceramic-coated electrodes outperform pristine LCTMOF. At 500 mA g^{-1} , LCTMOF@LAGP3, LCTMOF@LAGP5, and LCTMOF@LAGP7 deliver 161.2 , 184.5 , and 173.8 mAh g^{-1} , respectively. These values substantially exceed the 118.0 mAh g^{-1} delivered by pristine LCTMOF. The improved high-rate performance suggests that the LAGP coating alleviates interfacial kinetic limitations and promotes efficient Li^+ transport. At 500 mA g^{-1} , LCTMOF@LAGP5 delivered the highest discharge capacity among the tested samples.

To evaluate cycling behavior beyond the initial 50-cycle comparison, the original complete 100-cycle records are now provided in Figure S5 to show the subsequent capacity evolution. (Figure S5). LCTMOF@LAGP5 delivered a discharge capacity of 185.5 mAh g^{-1} after 100 cycles, corresponding to a capacity retention of 66.5%. Under the same conditions, pristine LCTMOF delivers 71.4 mAh g^{-1} with a capacity retention of 24.0%. The specific capacity fading trend is consistent with that observed after 50 cycles. These measurements extend the cycling assessment beyond the interval used for the main early-cycle analysis.

Figure 7a,b show the cyclic voltammetry (CV) profiles of LCTMOF and LCTMOF@LAGP5 during the first three cycles. During the anodic scan, pristine LCTMOF exhibits two prominent oxidation peaks, as shown in Figure 7a. The peak at approximately 3.7 V is attributed to Mn oxidation, primarily involving the $\text{Mn}^{2+}/\text{Mn}^{4+}$ redox couple. The second oxidation peak near 4.6 V is associated with anionic oxygen oxidation. The high-voltage oxidation feature is commonly associated with anionic redox involving lattice oxygen, although the exact nature of the oxidized oxygen species cannot be determined from the present electrochemical data alone [27,40]. During the subsequent cathodic scan, the reduction peak near 3.2 V is mainly associated with Mn^{4+} reduction toward lower oxidation states. Compared with pristine LCTMOF, LCTMOF@LAGP5 exhibits substantially better overlap of the cathodic peaks during the first three cycles. This improved overlap indicates enhanced electrochemical reversibility after LAGP coating.

To further clarify the origin of the improved electrochemical performance, charge-discharge profiles and differential-capacity (dQ/dV) curves were systematically analyzed. Figure 7c,d show the charge-discharge profiles of LCTMOF and LCTMOF@LAGP5 at different cycle numbers. Both electrodes initially exhibit an increase in discharge capacity, followed by gradual capacity fading and progressive voltage decay. However, LCTMOF@LAGP5 shows substantially less polarization growth and voltage decay than pristine LCTMOF. These results suggest that LAGP coating mitigates the progressive deterioration of electrode kinetics during cycling.

Figure 7e presents the dQ/dV profiles of pristine LCTMOF. The oxidation peak labeled P1 is attributed to the $\text{Mn}^{2+}/\text{Mn}^{4+}$ redox process, whereas the oxidation peak at P2 corresponds to the oxidation of lattice O^{2-} to oxidized oxygen species O_n^- [37]. During charging, the oxidation peak near 3.4 V is mainly associated with Mn^{2+} oxidation. With continued cycling, this peak becomes more pronounced and gradually shifts toward lower potentials. The high-voltage oxidation peak near 4.3 V is attributed to oxygen-redox activity. Its progressive attenuation and eventual disappearance indicate increasing irreversibility of the high-voltage oxygen-redox process. During the first discharge, a reduction peak appears

near 3.4 V and is mainly associated with reduction in oxidized Mn species. With increasing cycle numbers, this peak gradually weakens and shifts toward lower potentials. This evolution is consistent with increasing polarization and progressive changes in the local redox environment. A new low-voltage reduction feature appears near 2.7 V after 10 cycles. By the 20th cycle, this feature shifts to approximately 2.4 V and becomes more pronounced. Such low-voltage redox activity has been associated with the development of spinel-like local environments in Mn-based cathodes. Its emergence therefore suggests progressive structural rearrangement toward a spinel-related configuration during prolonged cycling.

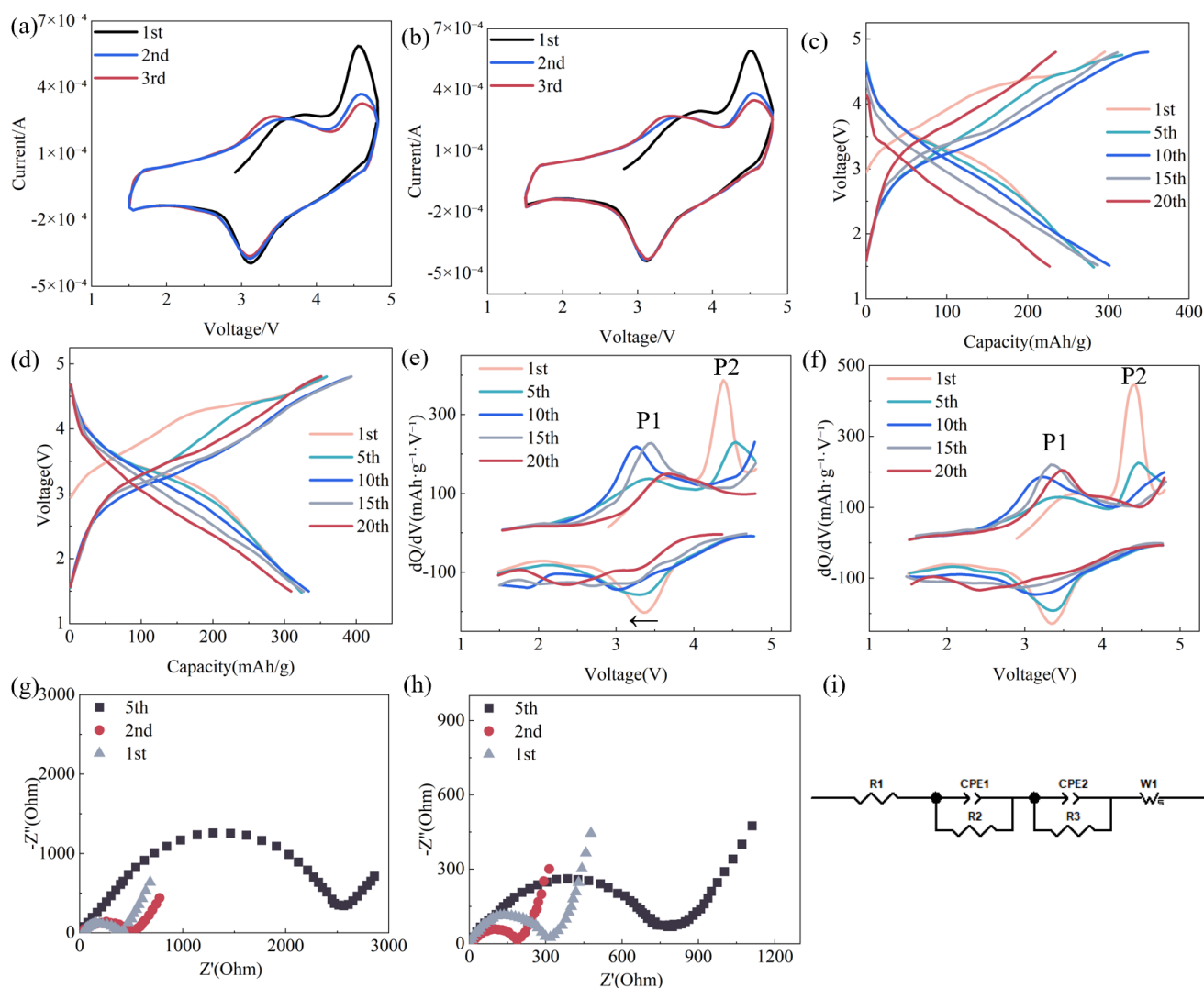


Figure 7. Electrochemical characterization of LCTMOF and LCTMOF@LAGP5 cathodes. (a,b) Cyclic voltammetry (CV) profiles of LCTMOF and LCTMOF@LAGP5, respectively; (c,d) galvanostatic charge-discharge profiles of LCTMOF and LCTMOF@LAGP5, respectively; (e,f) differential-capacity (dQ/dV) profiles of LCTMOF and LCTMOF@LAGP5, respectively; and (g,h) electrochemical impedance spectroscopy (EIS) spectra of LCTMOF and LCTMOF@LAGP5, respectively; (i) Equivalent circuit diagram.

Figure 7f shows the dQ/dV profiles of LCTMOF@LAGP5. The coated electrode exhibits redox features similar to those of pristine LCTMOF but shows markedly slower peak attenuation. The peak remains clearly detectable through the fifth cycle and gradually disappears only after approximately 10 cycles. This delayed attenuation suggests improved reversibility of the high-voltage oxygen-redox process after LAGP coating. Meanwhile, the peak does not emerge until approximately the 20th cycle and remains relatively weak there-

after. The delayed appearance of this low-voltage feature suggests slower development of spinel-like structural environments in LCTMOF@LAGP5. Overall, the dQ/dV results indicate that LAGP coating suppresses polarization growth and delays irreversible redox and structural evolution during cycling.

Electrochemical impedance spectroscopy (EIS) was further employed to evaluate the influence of LAGP coating on interfacial kinetics, as shown in Figure 7g,h. In the equivalent circuit, R_1 represents the ohmic resistance of the cell. The high-to-medium-frequency semicircle is assigned to CEI resistance R_2 coupled with the constant-phase element CPE1. The medium-to-low-frequency semicircle corresponds to charge-transfer resistance R_3 coupled with CPE2. The inclined low-frequency tail is represented by the Warburg element W_s and reflects Li^+ diffusion within the electrode [26,41,42]. The fitted impedance parameters are summarized in Table 3.

Table 3. Fitted EIS parameters of LCTMOF and LCTMOF@LAGP5 (Ω).

Samples	R1 1st	R1 5th	R2 1st	R2 5th	R3 1st	R3 5th
LCTMOF	5.1	6.8		407.6	804.9	2754
LCTMOF@LAGP5	9.5	12.7		/	328.7	794.8

Both electrodes exhibit comparable R_1 values, indicating that LAGP coating has little influence on the overall ohmic resistance of the cell. Although these impedance results indicate slower interfacial degradation in the coated electrode, they do not independently establish the electrochemical stability of the LAGP glass ceramic coating or exclude its partial transformation during cycling.

For LCTMOF@LAGP5, After the first cycle, the fitted charge-transfer resistance of LCTMOF@LAGP5 was 328.7 Ω and increased to 794.8 Ω after five cycles, whereas that of pristine LCTMOF increased from 804.9 to 2754 Ω . This evolution indicates a relatively moderate deterioration of charge-transfer kinetics. In contrast, pristine LCTMOF exhibits a much larger increase in R_3 . The resistance increases from 804.9 Ω after the first cycle to 2754 Ω after five cycles. These results indicate substantially greater deterioration of interfacial charge-transfer kinetics in pristine LCTMOF. After five cycles, an additional semicircle appears in the Nyquist plot of pristine LCTMOF and is assigned to CEI-related resistance R_2 . The fitted R_2 value is approximately 407.6 Ω . The appearance of this additional interfacial contribution suggests progressive formation of a resistive surface layer during cycling. In contrast, no distinct CEI-related semicircle is resolved for LCTMOF@LAGP5 under the same conditions. This result suggests that the LAGP coating mitigates interfacial side reactions and suppresses the growth of resistive interfacial species [43]. Consequently, the coated electrode exhibits substantially slower impedance growth during cycling. Taken together, the CV, dQ/dV , and EIS results demonstrate that an optimized LAGP coating improves the electrochemical reversibility and interfacial kinetics of LCTMOF. The coating also delays irreversible structural evolution and limits impedance growth, thereby contributing to improved long-term cycling stability.

Figure 8 presents the XPS spectra of LCTMOF and LCTMOF@LAGP5 after different numbers of charge–discharge cycles. As shown in Figure 8a, two Cr species with different oxidation states are identified in the Cr 2p spectrum of the cycled samples. The peaks centered at binding energies of 576.4 eV and 582.8 eV are attributed to Cr^{3+} species, whereas the peaks located at 577.1 and 583.4 eV are assigned to Cr^{5+} species [44]. After 5 and 20 charge–discharge cycles, the Cr^{5+} peak area in LCTMOF@LAGP5 is significantly smaller than that in pristine LCTMOF, indicating that the LAGP coating effectively suppresses the formation or accumulation of highly oxidized Cr species during cycling. As shown in

Figure 8b, owing to the multiple possible oxidation states of Mn, the exact Mn valence state cannot be accurately determined solely from the Mn 2p spectra. To further examine changes in the surface Mn electronic environment, Mn 3s XPS spectra were analyzed (Figure S1). The separation between the two principal Mn 3s features decreases from approximately 6.1 eV after 5 cycles to approximately 5.5 eV after 20 cycles. For commonly studied high-spin manganese oxides, a smaller Mn 3s exchange splitting generally corresponds to a higher Mn oxidation state. A literature-derived relationship reported by Beyreuther, illustrates this inverse correlation [45]. On this basis, the observed decrease is consistent with a trend toward a higher average surface Mn oxidation state. This interpretation is qualitative. The applicability of the reference relationship to the mixed-anion LCTMOF system has not been established, and Mn 3s splitting can also be affected by changes in local bonding and electronic structure [46]. Consequently, the values of 6.1 and 5.5 eV are not used to assign precise average oxidation states or establish the predominance of Mn^{2+} , Mn^{3+} , or Mn^{4+} . The Mn 3s results indicate evolution of the surface Mn electronic environment during cycling but do not independently identify its underlying mechanism. The Mn 2p spectra provides complementary information on the surface Mn chemical environment. However, overlapping binding energies and multiplet structures complicate the assignment and quantification of individual Mn oxidation states [47,48]. The fitted Mn 2p components and the Mn 3s splitting are therefore interpreted cautiously, without treating either as independent proof of a dominant Mn species. The improved cycling performance and slower impedance growth of LCTMOF@LAGP5 support a beneficial coating effect, but the Mn XPS results alone do not establish stabilization of a specific Mn oxidation state.

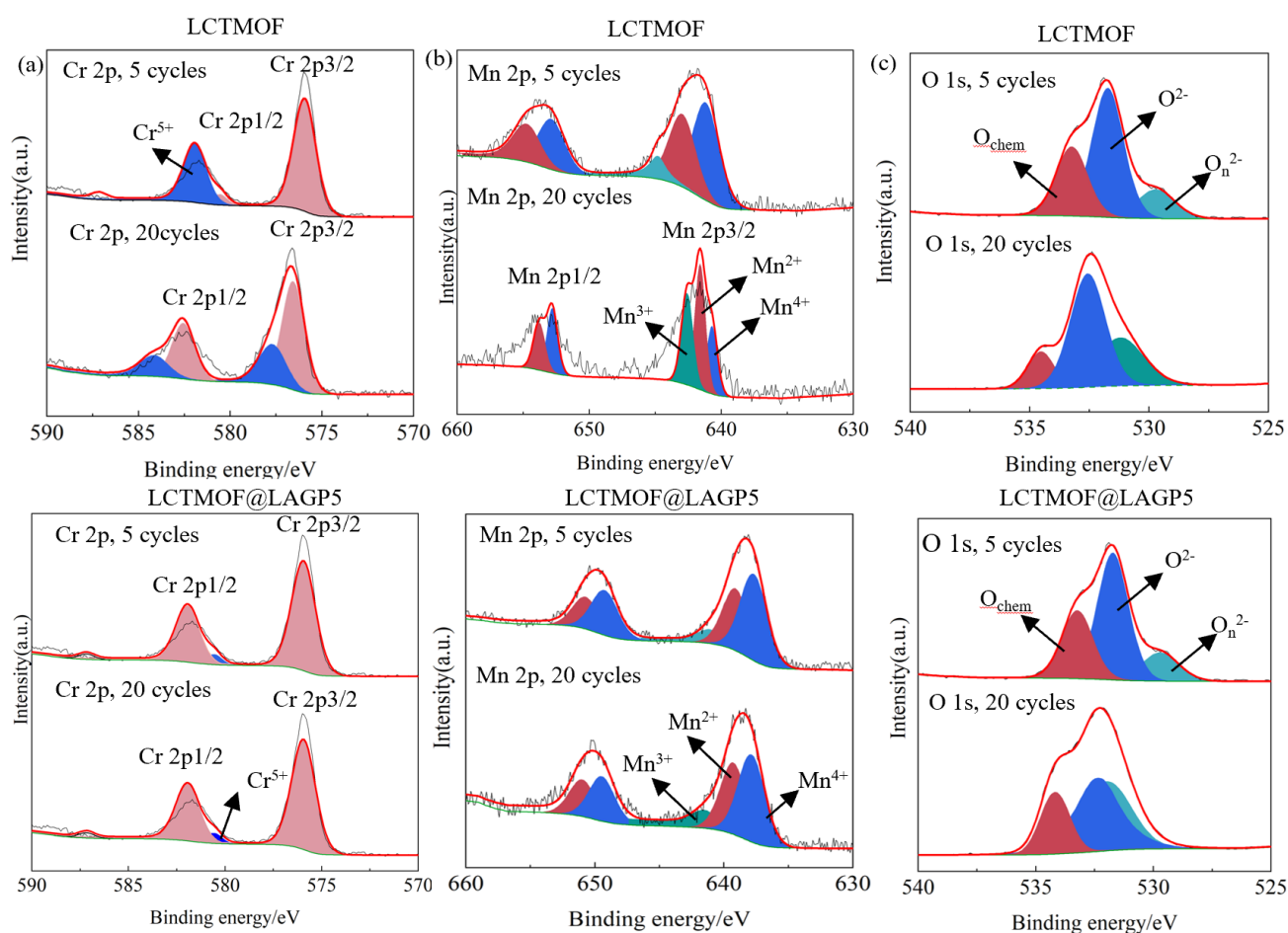


Figure 8. XPS spectra of LCTMOF and LCTMOF@LAGP5 after 5 and 20 cycles. (a) Cr 2p, (b) Mn 2p, and (c) O 1s spectra.

Additional XPS spectra reveal P and Ge signals at the surface of the LAGP-modified material (Figure S3). Together with the TEM observations and elemental mapping, these results support the presence of a LAGP-derived surface layer. However, the P and Ge signals alone do not establish the phase purity, stoichiometry, or uniform coverage of the coating. The Mn and Cr signal intensities in Figure 8 are not used to quantify coating thickness or coverage. Although a nanometer-scale overlayer can substantially attenuate substrate photoelectrons, the substrate signals may remain detectable because the XPS information depth is not a sharp cutoff. The attenuation depends on the effective attenuation length, emission geometry, and overlayer morphology. Moreover, the approximately 5 nm thickness coating layer observed locally before heat treatment does not necessarily represent the surface configuration of the cycled electrodes. Contributions from the cathode–electrolyte interphase and surface heterogeneity further complicate the interpretation of absolute signal intensities. Consequently, the discussion of Figure 8 focuses on the spectral features and surface chemical evolution rather than using intensity differences as direct evidence of partial coverage. The O 1s spectra in Figure 8c exhibit progressive changes in the surface oxygen environment during cycling. In particular, the relative intensity of the high-binding-energy oxygen component near 533.4 eV evolves with increasing cycle number. This feature may originate from surface oxygen-containing species formed through electrolyte decomposition and interfacial reactions [28,40,49]. Changes in the lattice-oxygen-related components further suggest progressive modification of the local oxygen environment during cycling. Combined with the Mn XPS results and electrochemical analysis, these observations indicate more pronounced surface chemical evolution in pristine LCTMOF. In comparison, the LAGP-coated cathode exhibits a more stable surface redox environment, consistent with reduced interfacial degradation during prolonged cycling.

The XPS spectra reveal changes in the surface chemical environments during cycling, the high-binding-energy O 1s contribution may include electrolyte-derived oxygen-containing species. Consequently, changes in this spectral region cannot be directly converted into changes in CEI amount or thickness. Similarly, attenuation of the Mn and Cr signals is not a unique indicator of interfacial degradation because both the coating and cycling-generated surface layers affect substrate photoelectron intensities. The EIS results provide complementary evidence of a smaller increase in fitted charge-transfer resistance for LCTMOF@LAGP5 than for pristine LCTMOF during the first five cycles. Together with the improved capacity retention, these observations are consistent with mitigated interfacial deterioration after surface modification.

4. Discussion

Based on these results, Figure 9 illustrates the proposed protective role of the LAGP glass ceramic coating at the LCTMOF/liquid-electrolyte interface. The coating reduces direct contact between the active cathode surface and the liquid electrolyte, which can mitigate interfacial side reactions. However, this protective role does not establish intrinsic electrochemical stability throughout the applied voltage window. First-principles calculations predict an oxidative stability limit of approximately 4.3 V versus Li/Li⁺ for LAGP, while decomposition kinetics can delay experimentally observable oxidation [37,50]. Benabed et al. measured an oxidation onset near 4.9 V using PITT with a LAGP/Au composite electrode at 60 °C [51]. This result cannot be directly transferred to the present glass ceramic coating because the material state and electrochemical environment differ. Nevertheless, LAGP-coated LiCoO₂ electrodes have also been reported with an upper charging voltage of 4.8 V [52], showing that high-voltage coating applications are feasible without establishing complete chemical inertness.

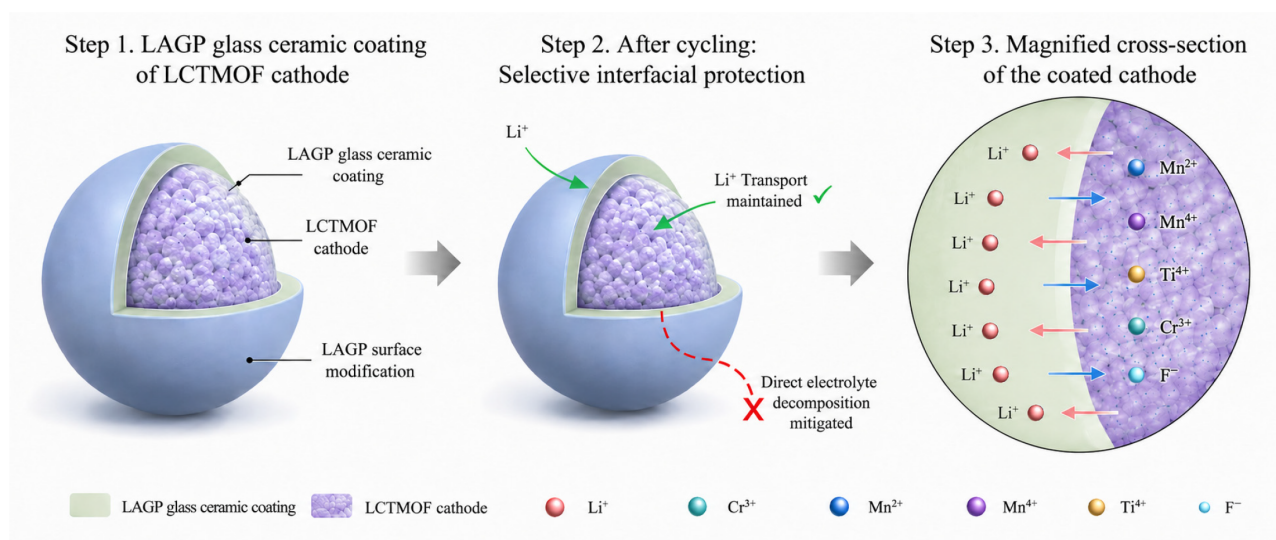


Figure 9. Schematic illustration of the protective mechanism of the LAGP glass ceramic coating layer on the LCTMOF cathode surface.

In the present study, LCTMOF@LAGP5 retains 227.3 mAh g^{-1} after 50 cycles, corresponding to a capacity retention of 81.5%, compared with 56.8% for pristine LCTMOF. The fitted charge-transfer resistance increases from 328.7 to 794.8Ω between the first and fifth cycles for LCTMOF@LAGP5, whereas it increases from 804.9 to 2754Ω for pristine LCTMOF. These results indicate a net improvement in cycling behavior and slower interfacial impedance growth following coating. A plausible interpretation is that reduced direct cathode–electrolyte contact, together with kinetically limited coating degradation, allows the modified interface to remain beneficial during cycling. Reaction-product passivation may also contribute, but neither its occurrence nor its composition has been established here.

The effectiveness of the approximately 5 nm coating depends on its continuity and coverage as well as its thickness. The TEM observations show continuous coverage in the examined regions, and the surface enrichment of P supports the formation of a LAGP-containing surface layer. These features are consistent with reduced direct contact between LCTMOF and the liquid electrolyte. However, local microscopy cannot establish complete, pinhole-free coverage of all particles; therefore, the protective effect is described as a reduction in direct interfacial contact rather than complete isolation.

The ionic conductivity of the LAGP glass ceramic determined by EIS is $4.2 \times 10^{-4} \text{ S cm}^{-1}$, as summarized in Table S1. Given the high ionic conductivity of the LAGP glass ceramic and the short ion transport distance of 5 nm, the additional LAGP glass ceramic coating is not expected to introduce substantial interfacial resistance. Consistent with this interpretation, LCTMOF@LAGP5 exhibits lower fitted charge-transfer resistance than pristine LCTMOF after both the first and fifth cycles, together with improved rate performance. These electrode-level results indicate a favorable balance between interfacial protection and ion transport under the investigated conditions, although they do not separately quantify the resistance of the coating itself.

The available measurements do not demonstrate that the LAGP glass ceramic coating remains chemically unchanged at 4.8 V. In particular, the reported Cr, Mn, and O XPS spectra probe changes in the cathode surface environment but do not directly resolve LAGP decomposition. Similarly, the absence of a separately resolved CEI-related semicircle does not exclude interphase formation. Possible coating reduction near the 1.5 V lower cutoff also cannot be ruled out [46,51]. Therefore, the improved performance is interpreted as evidence of a beneficial coating effect under the tested conditions, rather than proof of a

decomposition-free stability window of 1.5–4.8 V. Table S2 summarizes representative DRX cathodes together with their reported cycling conditions. LCTMOF@LAGP5 delivered an initial discharge capacity of 278.7 mAh g^{-1} and retained 227.3 mAh g^{-1} after 50 cycles, corresponding to a capacity retention of 81.5%, when cycled between 1.5 and 4.8 V at 10 mA g^{-1} . Although several literature studies employed the same voltage window and current density, differences in cycling duration, electrode loading, electrode formulation, and electrolyte composition limit quantitative cross-study comparisons. Therefore, the literature data are used to contextualize the present results, LCTMOF@LAGP5 developed in this work delivers a comparatively high initial discharge capacity together with excellent capacity retention after 50 cycles.

5. Conclusions

In this work, LAGP glass ceramic-coated disordered rock-salt LCTMOF@LAGP cathodes were fabricated via a hydrothermal route, and their microstructural characteristics and electrochemical properties were systematically investigated to clarify the role of the LAGP surface layer and elucidate the mechanism underlying the enhanced cycling stability. The main conclusions are summarized as follows:

1. A uniform glass LAGP coating layer approximately 5 nm thick was successfully formed on the surface of the DRX LCTMOF particles via the hydrothermal process, and subsequent heat treatment induced partial crystallization of the glass layer to form an ionically conductive LAGP glass ceramic coating.
2. The LAGP glass ceramic coating improves the interfacial performance of LCTMOF, as reflected by slower charge-transfer resistance growth and enhanced cycling and rate performance. These results are consistent with reduced detrimental interactions between the cathode and the liquid electrolyte. However, partial transformation of the coating during cycling cannot be excluded, and the observed performance improvement does not establish intrinsic LAGP stability throughout the 1.5–4.8 V window.
3. LAGP glass ceramic surface modification markedly improved the electrochemical performance of LCTMOF, with LCTMOF@LAGP5 exhibiting the optimal overall cycling behavior. It delivered an initial discharge capacity of 278.7 mAh g^{-1} . After 50 cycles, LCTMOF@LAGP5 retained a high discharge capacity of 227.3 mAh g^{-1} with a capacity retention of 81.5%, representing an improvement of 24.7 percentage points over pristine LCTMOF. LCTMOF@LAGP5 also delivered the best rate capability, maintaining a high specific capacity of 184.5 mAh g^{-1} even at a current density of 500 mA g^{-1} .

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings16101160/s1>, Figure S1: XPS spectra of LCTMOF (a) 5 cycles, (b) 20 cycles; Figure S2: XPS spectra of LCTMOF@LAGP5 (a) 5 cycles, (b) 20 cycles; Figure S3. XPS spectra of pristine LCTMOF and LCTMOF@LAGP5 (a) P 2p and Ge 3p, (b) Ge 3d; Figure S4. EIS spectra of LAGP glass ceramics heat-treated for different durations; Figure S5. Cycling performance of LCTMOF@LAGP over 100 cycles; Table S1. Table of conductivity of LAGP glass ceramics under different heat treatment parameters in 630°C ; Table S2. Comparison of the electrochemical performance of selected previously reported surface-coated cathode materials [53–59].

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