

Supporting Information

Synergistic Activation of Grain Boundaries with Dual Salts Enables Fast Lithium Percolation in LATP-based Solid State Electrolytes

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† # Equal contribution

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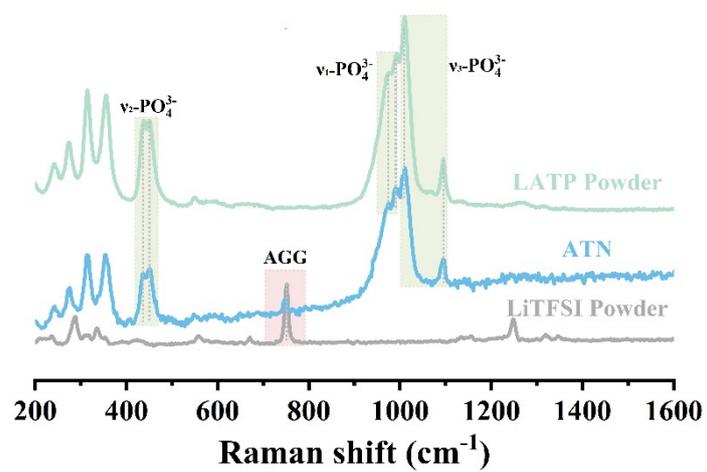


Figure S1. Raman spectra of ATN, LiTFSI powder, and the pristine powder samples.

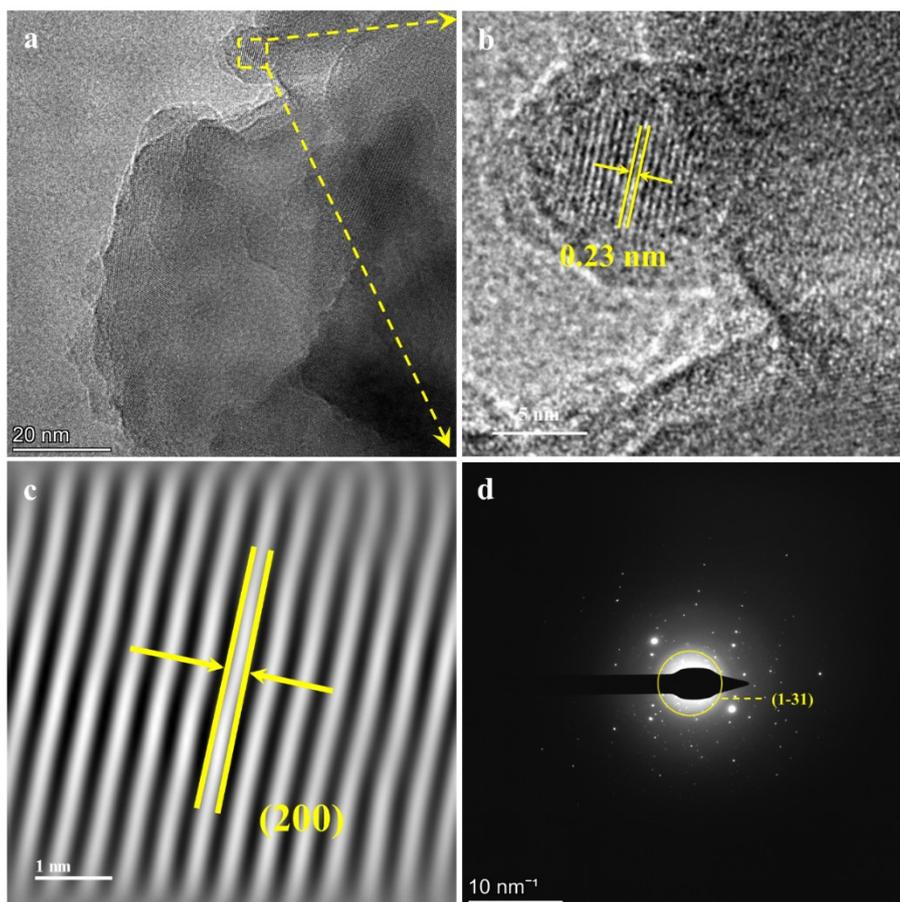


Figure S2. a,b). TEM image of ATN composite solid electrolyte.c) Inverse Fourier transform graph d). SAED image.

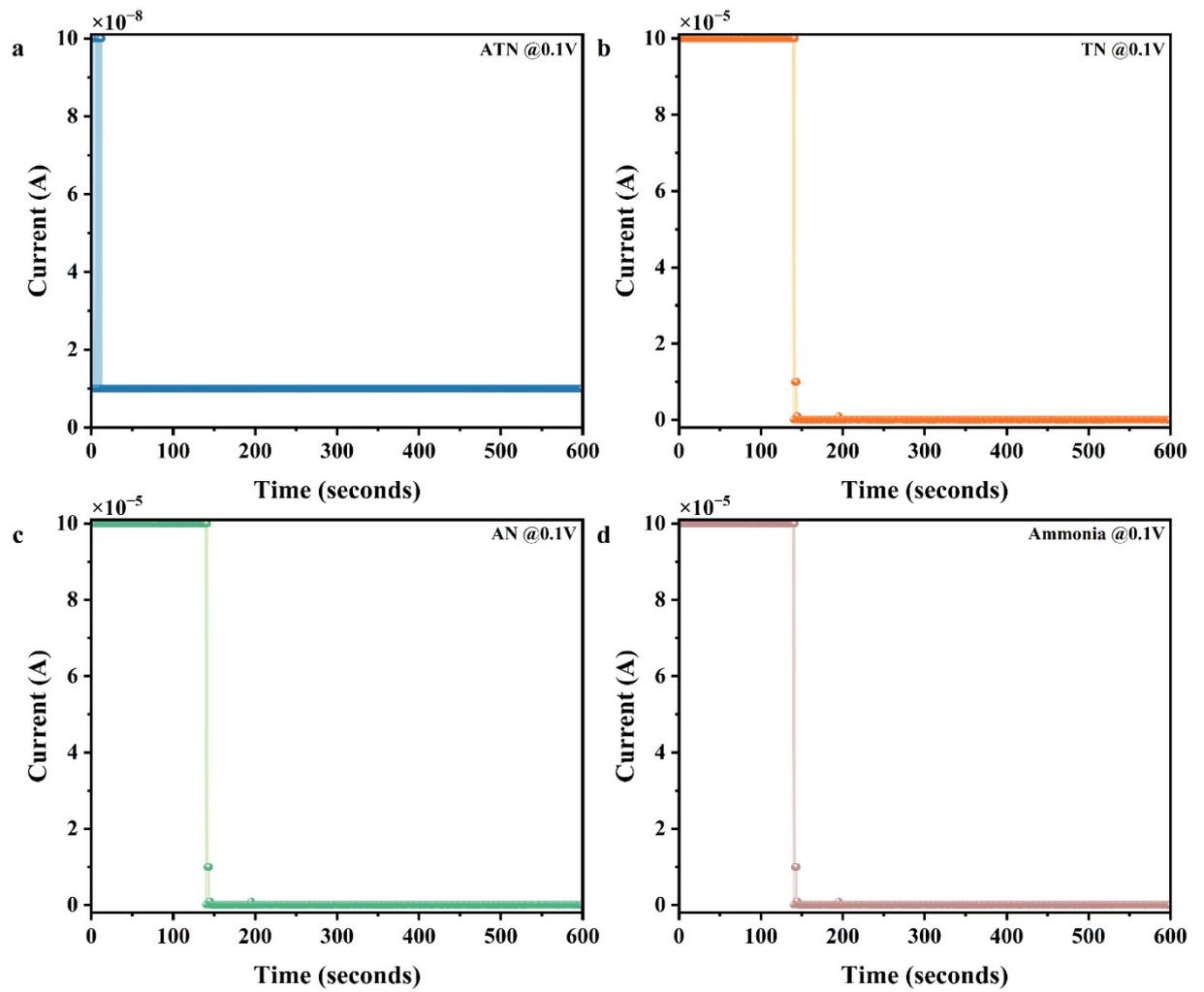


Figure S3. DC polarization diagram of a) ATN, b) TN, c) AN and d) Ammonia at 0.1V.

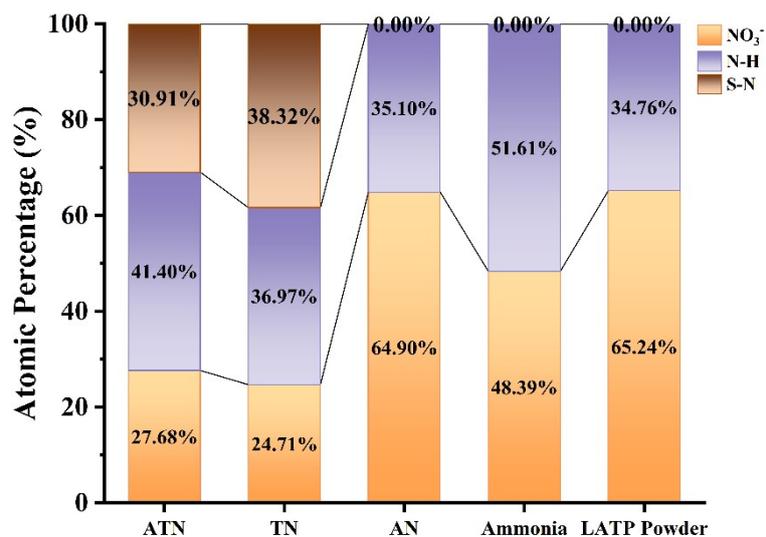


Figure S4. Corresponding atomic ratios in N1s spectra for the ATN, TN, Ammonia, AN, and the pristine LAMP powder.

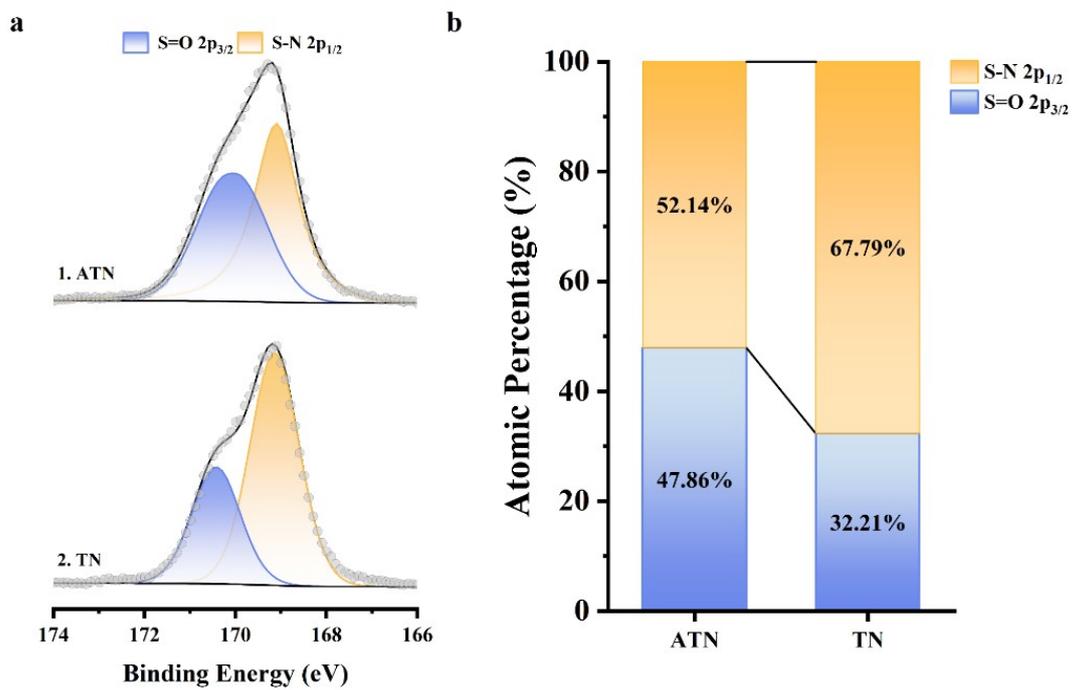


Figure S5. XPS spectra of CSP composite solid electrolytes. a) S2p spectra for the ATN and TN. Corresponding atomic ratios in b) S2p spectra for the ATN and TN.

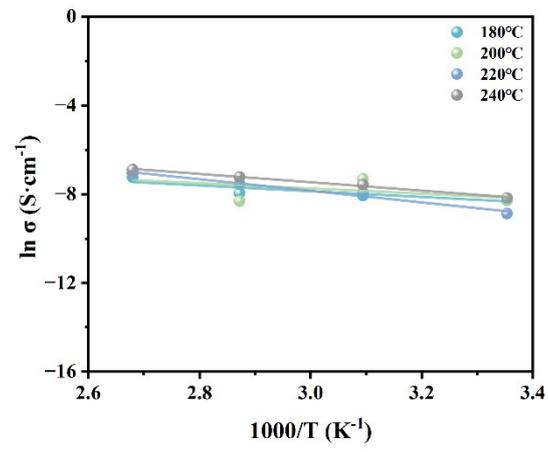


Figure S6. Arrhenius plot of ATN sintered at different temperatures.

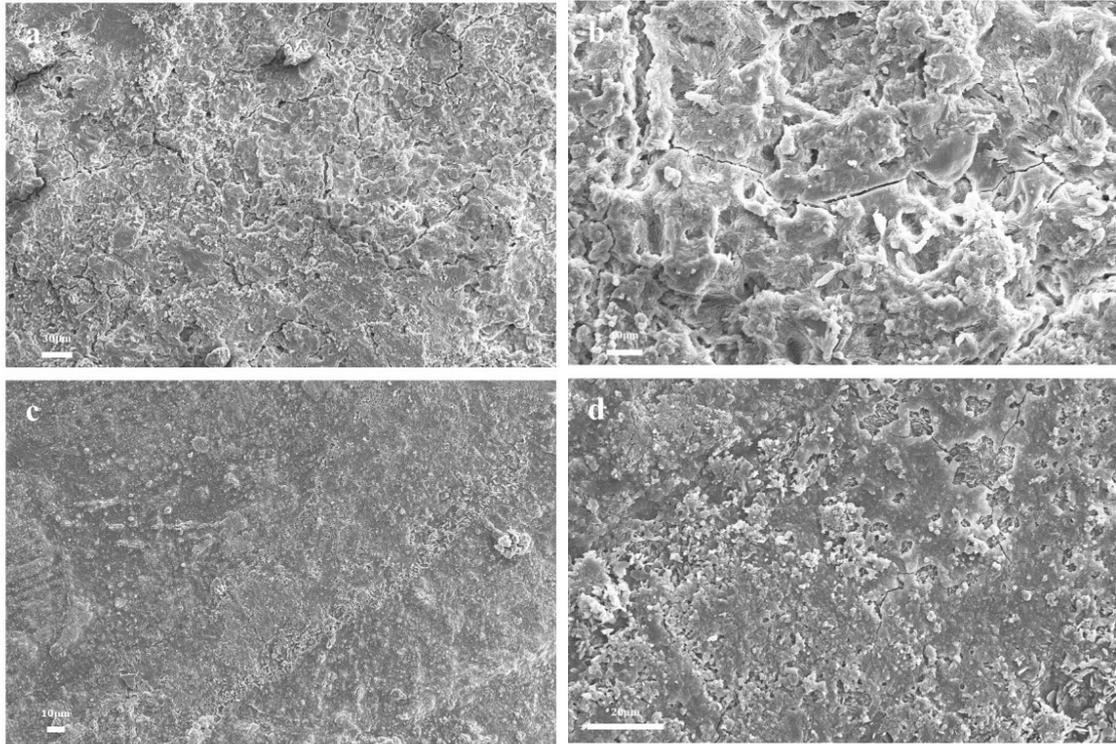


Figure S7. SEM images of the LMA surface a,b) before cycling and c,d) after cycling.

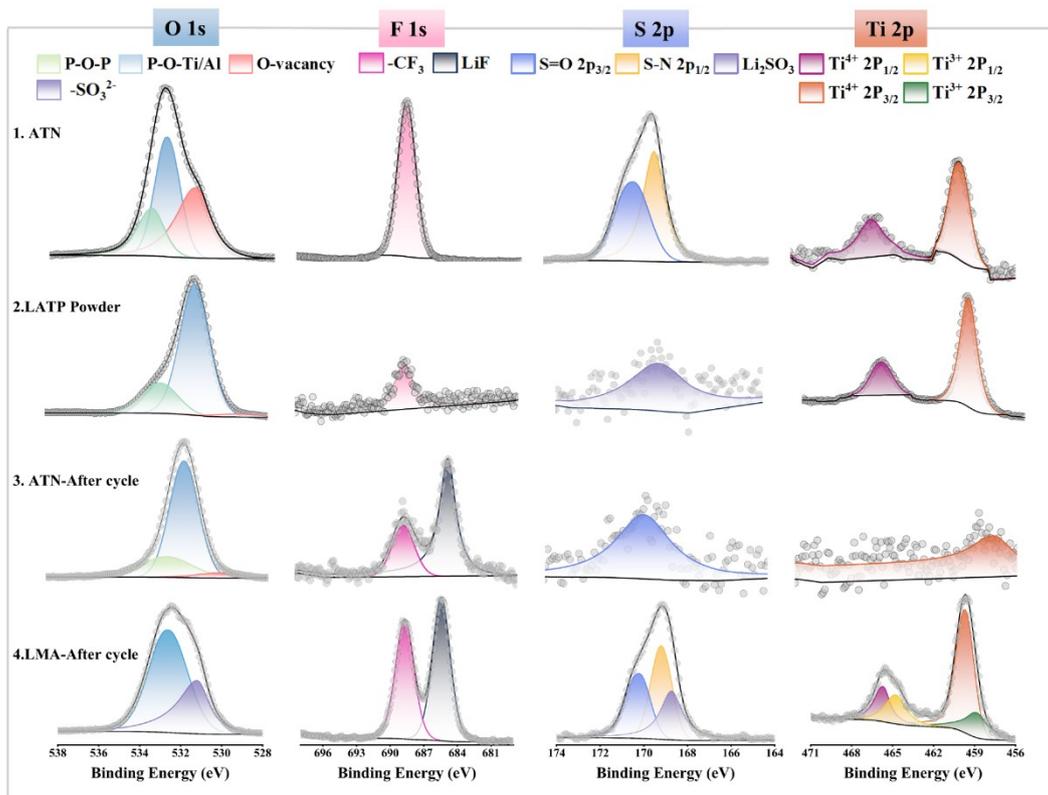


Figure S8. XPS spectra of ATN and LMA surface after cycling O 1s spectra, F 1s spectra, S 2p spectra. and Ti 2p spectra.

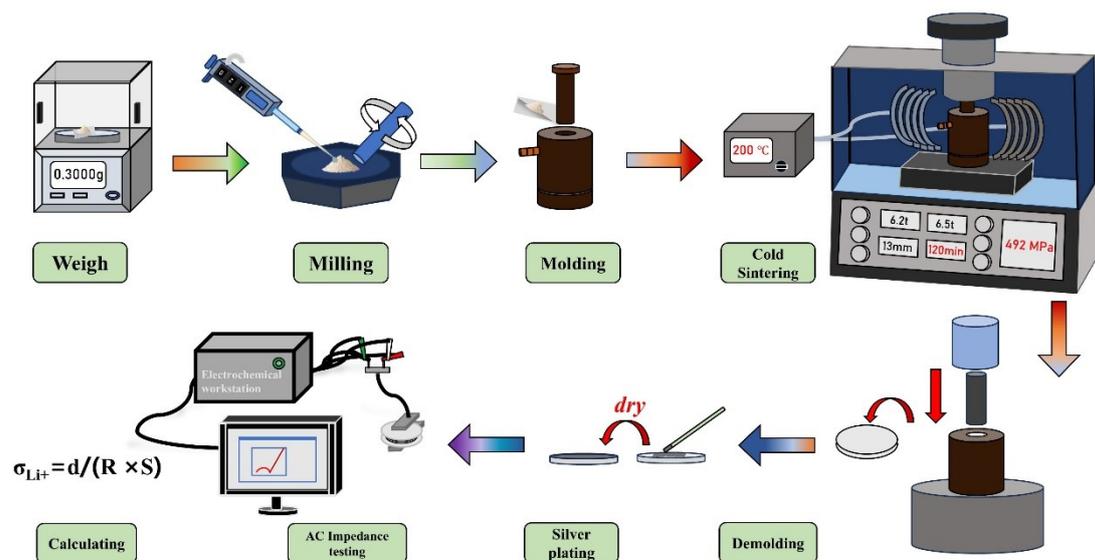


Figure S9. Schematic illustration of one-step cold sintering to produce the composite solid electrolyte.

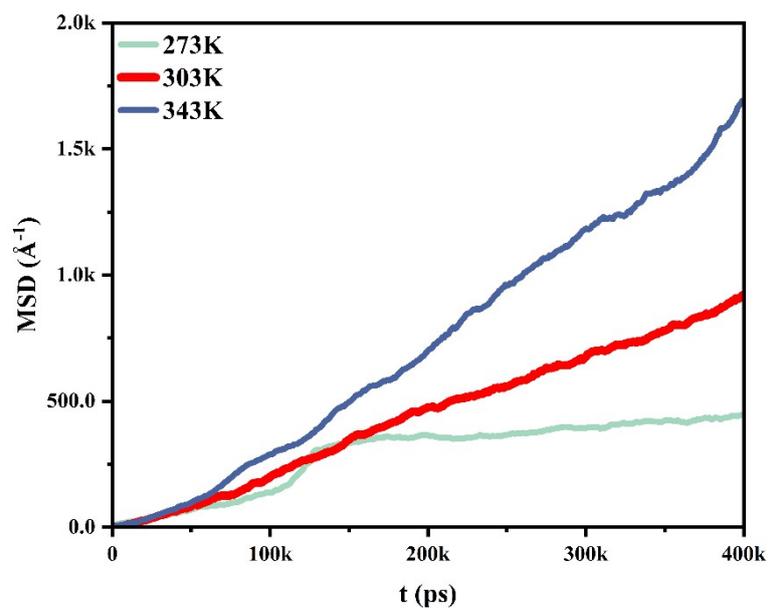


Figure S10. MSD spectra of simulated grain boundary Li⁺ diffusion in ATN at temperature of 273K,303K and 343K.

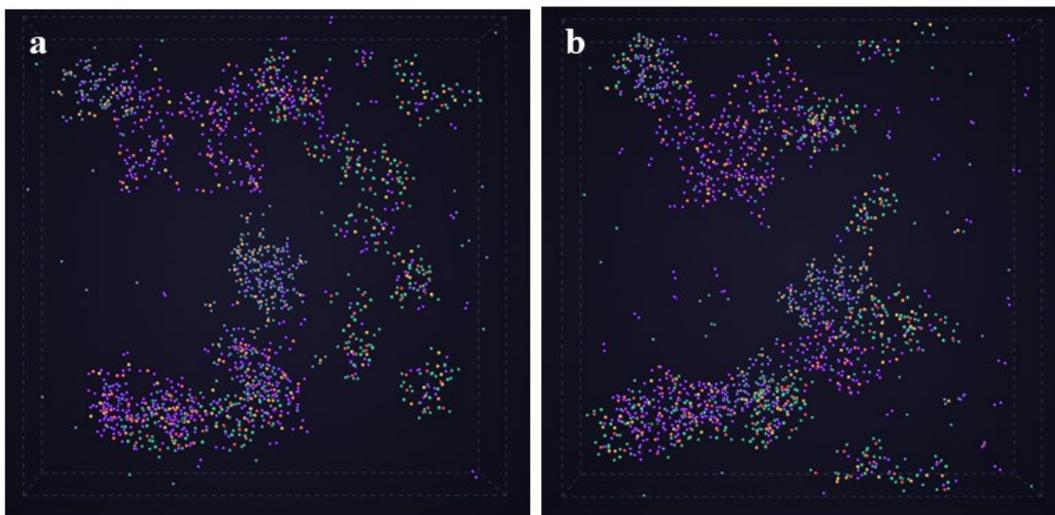


Figure S11. Structural snapshots of the atomic structure model simulated by molecular dynamics calculations after a)5ps and b)40ps.

Table 1. The impedance values fitted from the AC Impedance spectra of ATNs at different temperatures.

CSP temperature (°C)	R (Ω)
140	277
160	227
180	55
200	52
220	93
240	72

Table 2. The MSD lithium-ion diffusion rate values at grain boundaries at different simulated temperatures.

Simulated temperature (K)	D ($\times 10^{-9} \text{cm}^2/\text{s}$)
273	31.6
303	39.6
343	72.8

Table 3. The coordination values of the RDF function Li at grain boundaries at different simulated temperatures. (The first coordination number is abbreviated as n1, and the total coordination number is abbreviated as n)

Simulated temperature (K)	n1	n
273	2.150	8.381
303	3.962	10.056
343	2.707	8.612
373	2.603	8.250

Equation

1. Formula for calculating relative density

Since the SSEs absorb water, the volume method is used to calculate the sample volume. The surface area of the samples is calculated by Imagine J software, and the thickness is calculated by vernier caliper., and the mass is obtained by balance.

$$\rho = \frac{m}{V} \quad \backslash *$$

MERGEFORMAT (1.1)

$$V = d \times S \quad \backslash *$$

MERGEFORMAT (1.2)

$$V_R = \frac{V}{V_T} \times 100\% \quad \backslash *$$

MERGEFORMAT (1.3)

Among them, ρ represents density, m represents the mass of the sample, V represents the volume of the sample, d represents the thickness of the sample, S represents the surface area of the sample, V_R represents the relative density of the sample, and V_T represents the theoretical density of the sample (the theoretical density of LATP is 2.98g/cm³).

2. Formula for calculating ionic conductivity

$$\sigma = \frac{d}{R \times S} \quad (2.1)$$

Among them, σ represents the ionic conductivity of the sample, d is the thickness of the sample, S is the surface area of the sample, and R is the resistance value of the sample.

3. Formula for calculating the diffusion coefficient based on the MSD results

$$D = \frac{l}{6N_a} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_a} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (3.1)$$

4. Formula for calculating the coordination number based on the RDF results

$$n(r) = 4\pi\rho \int_0^r g(r)r^2 dr \quad (4.1)$$