**Microstructure and ionic conductivities of NASICON-type Li1.3Al0.3Ti1.7(PO4)3 solid electrolytes produced by cold sintering assisted process**

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Table S1. Calculated room-temperature bulk (*σ*b), grain boundary (*σ*gb), and total (*σ*t) conductivities for LATP electrolytes produced by CSP / dry-pressing and subsequently annealing at different temperatures

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Processing condition | | *σ*b (S/cm) | *σg*b (S/cm) | *σ*t (S/cm) |
| CSP + post-annealing | As-CSPed | 6.40 × 10-4 | 2.02 × 10-6 | 2.01 × 10-6 |
| 700 ℃ | 5.85 × 10-4 | 3.89 × 10-6 | 3.86 × 10-6 |
| 800 ℃ | 3.61 × 10-4 | 3.10 × 10-5 | 2.86 × 10-5 |
| 900 ℃ | 1.14 × 10-3 | 6.86 × 10-4 | 4.29 × 10-4 |
| 1000 ℃ | 6.66 × 10-4 | 1.87 × 10-4 | 1.46 × 10-4 |
| 1100 ℃ | 6.99 × 10-4 | 2.30 × 10-5 | 2.23 × 10-5 |
| Dry-pressing + annealing | 700 ℃ | 5.11 × 10-4 | 2.19 × 10-5 | 2.10 × 10-5 |
| 800 ℃ | 9.72 × 10-4 | 4.97 × 10-5 | 4.73 × 10-5 |
| 900 ℃ | 1.36 × 10-3 | 6.58 × 10-5 | 6.28 × 10-5 |
| 1000 ℃ | 1.24 × 10-3 | 9.14 × 10-5 | 8.51 × 10-5 |
| 1100 ℃ | 1.21 × 10-3 | 6.56 × 10-5 | 6.22 × 10-5 |

Table S2. Summary of relative density (ρ) and conductivity (σ) versus sintering temperature of LATP ceramics produced by various sintering routes from earlier and current work

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Composition  Li1+xAlxTi2-x(PO4)3 | Powder synthesis route | Sintering method | Sintering temperature (ºC) | Sintering time | ρ (%) | σ (S/cm) | Ref |
| *x* = 0.3 | Solid-state reaction | CS | 1000 | 2 h | × | 3.35×10-4 | [1] |
| *x* = 0.3 | Solid-state reaction | CS | 1000 | 12 h | 97.3 | 4.81×10-4 | [2] |
| *x* = 0.3 | Sol-gel | CS | 1100 | × | 94.2 | 1.88×10-4 | [3] |
| *x* = 0.3 | Hydrothermal | CS | 1200 | 3 h | 98.06 | 2.44×10-4 | [4] |
| *x* = 0.3 | Sol-gel | CS | 1100 | 8 h | 94.2 | 1.0×10-4 | [5] |
| *x* = 0.3 | Sol-gel | CS | 1000 | 1 h | 86-90 | 3-4×10-4 | [6] |
| *x* = 0.3 | Solid-state reaction | CS | 1200 | 2 h | 91.8 | 1.34×10-6 | [7] |
| *x* = 0.3 | Sol-gel | CS | 1000 | 12 h | 71 | 7.3×10-5 | [8] |
| *x* = 0.3 | Solid-state reaction | CS | 1200 | 2 h | 95.9 | 7×10-4 | [9] |
| *x* = 0.3 | Solid-state reaction | UHS | 960 | 100 s | 90.2 | 4.67×10-4 | [10] |
| *x* = 0.3 | Solid-state reaction | UHS | 1200 | 60 s | > 90 | × | [11] |
| *x* = 0.3 | Sol-gel | SPS | 900 | 0 | 99 | 6.8×10-5 | [8] |
| *x* = 0.3 | Melt quenching | SPS | 1000 | 5 min | 96.7 | 1.2×10-4 | [12] |
| *x* = 0.4 | Sol-gel | SPS | 650 | 8 min | 100 | 1.12×10-3 | [13] |
| *x* = 0.3 | Melt quenching | SPS | 1000 | 5 min | 99.4 | 1×10-3 | [14] |
| *x* = 0.3 | Coprecipitation | SPS | 900 | 5 min | 97 | 1.6×10-4 | [15] |
| *x* = 0.4 | Sol-gel | SPS | 900 | 1 min | 97 | 5×10-4 | [16] |
| *x* = 0 | Solid-state reaction | SPS | 1100 | 10 min | ~ 94 | 1.4×10-5 | [17] |
| *x* = 0.3 | Solid-state reaction | SPS | 1100 | 10 min | ~ 96 | ~ 1×10-4 | [17] |
| *x* = 0.3 | Melt quenching | SPS | 1000 | 5 min | 98.9 | 4×10-4 | [18] |
| *x* = 0.3 | Sol-gel | SPS | 1100 | 15 min | 98 | 1×10-3 | [19] |
| *x* = 0.4 | Melt quenching | MW | 1000 | 30 s | × | 5.33×10-4 | [20] |
| *x* = 0.3 | Solid-state reaction | MW | 890 | 10 min | 90 | 3.15×10-4 | [21] |
| *x* = 0.3 | Solid-state reaction | FAST | 900 | 3 h | 86 | 4.76×10-4 | [22] |
| *x* = 0.3 | Sol-gel | HP | 1100 | × | 96.7 | 1.83×10-4 | [23] |
| *x* = 0 | × | HP | 1050 | 1 h | 88 | 2×10-7 | [24] |
| *x* = 0.3 | Solid-state reaction | CSP | 200 | 30 min | × | 3.0×10-4 | [25] |
| *x* = 0.3 | Sol-gel | CSP | 200 | 1 h | 94 | 1.26×10-5 | [26] |
| Annealed @ 800 | 1 h | 95 | 1.55×10-4 |
| *x* = 0.3 | Sol-gel | CSP | 120 | 1 h | × | × | [27] |
| Annealed @ 650 | 2 h | 93 | 8.04×10-5 |
| *x* = 0.3 | Solid-state reaction | CSP-assisted process | 250 | 1 h | 83.0 | 2.01×10-6 | This work |
| Annealed @ 900 | 1 h | 87.4 | 4.29×10-4 |
| Annealed @ 1000 | 1 h | 96.0 | 1.46×10-4 |

CS = conventional sintering; CSP = cold sintering process; FAST = field-assisted sintering technique; HP = hot pressing; MW = microwave sintering; SPS = spark plasma sintering; UHS = ultrafast high-temperature sintering; × = no reported data.

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Figure S1. XRD patterns of the starting LATP powders for CSP and pellets produced by CSP at different temperatures, along with the reference LiTi2(PO4)3 pattern (JCPDS card: 35-0754).

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Figure S2. The relationship between relative density and CSP temperature for LATPsamples produced by CSP under 250 MPa for 1 h.

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