

## Electronic Supplementary Information

### 20 mS/cm Li-argyrodite Solid electrolyte produced via facile high-speed-mixing

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## 1. Experimental section

### 1.1 Preparation of $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ powders

To prepare  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ , Lithium sulfide ( $\text{Li}_2\text{S}$ , 99.98%, GanFeng Lithium Co., Ltd.),  $\text{P}_2\text{S}_5$  (99%,  $\text{P} > 24$  wt%, Sinopharm Chemical Reagent Co., Ltd.), and anhydrous  $\text{LiCl}$  (99.98%, dried at  $150\text{ }^\circ\text{C}$ ,  $<200$  ppm, Aladdin) crystalline powders were used as starting materials. Firstly, the raw materials were weighed and proportioned according to the molar ratio of  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ , and then the 500 g raw materials were pulverized at ultra-high speed (25000 rpm) with a powder-mixing machine (DaDeYaoJi). The precursor powder sample with uniform particle sizes can be obtained in 150 s by a total of 6 stirring times (25 s per time), following 1 minute interval each time for heat dissipation of the machine. The obtained precursor powder was semi-sealed in a quartz crucible with ground mouth and then annealed at  $480\text{ }^\circ\text{C}$  for 16 h to obtain the highest  $\text{Li}^+$  conductivity corresponding the optimal phase-pure  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ .

While the precursor samples for comparison were prepared by traditional high-energy ball-milling. The required amounts of raw materials above were ball milled in  $\text{ZrO}_2$  (1L volume per  $\text{ZrO}_2$  tank  $\approx 3.5$  kg) or Agate tanks with 650g YSZ balls and then milled with a planetary ball mill apparatus (MITR Co Ltd, YXQM-8L. Main disk,  $\phi 420$  mm). The total weight of the mixture was almost 50 grams, and the ball-milling speed was fixed at 180 rpm. The milling duration was varied to find the optimal milling time, starting with 2 hours firstly and gradually reducing to 1 hour each time, continuing to 30 minutes per processing, and finally to 10 minutes. The total number of ball-milling was 20-30 times. As with the sintering process described above, the precursor was semi-sealed in a quartz crucible and annealed at  $480^\circ\text{C}$  for 16 hours (NBD-ML1200-10CI with a 1L chamber) to obtain the final  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  solid electrolyte. All the above processes were operated in argon-filled glovebox ( $\text{H}_2\text{O}$ ,  $\text{O}_2 < 1$  ppm) because of the reactivity of the precursors with oxygen and moisture.

### 1.2 Preparation of $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ ceramics

The  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  powder was simply milled at 120 rpm for 1 h inside polyurethane tank, and then was pressed into green pellets ( $\phi 10$  mm) and sintered in a 5 mL  $\text{Al}_2\text{O}_3$  crucible inside sealing  $\phi 50 \times \text{h}76$  mm (110 mL) quartz crucible at  $480\text{ }^\circ\text{C}$  for 4 h. The ceramics was so fragile that it would be cracked at only 6 MPa (effective pressure).

### 1.3 Characterization

Powder X-ray diffraction (PXRD) (Rigaku, Ultima IV, nickel-filtered  $\text{Cu-K}\alpha$  radiation,  $\lambda = 1.542\text{ \AA}$ ) was employed to determine the phase component of precursor and annealed powders and the test conditions were  $2\theta$  range of  $10\text{-}80^\circ$  with the step of  $2.4^\circ/\text{min}$  at room temperature. To prevent the reaction with moisture and oxygen, the powders were sealed in polyimide (PI) film in an argon-filled glovebox.

### 1.4 Electrochemical Testing

The ionic conductivity of the  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  electrolyte material was determined by AC impedance spectroscopy. Samples for the measurement were prepared by pressing 300 mg of  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  powder into a pellet with a 10 mm diameter under a pressure of 1.25 tons. Carbon-coated aluminum foil disks were attached to both faces of the pellet as blocking electrodes. It is worth noting that the soft In foil was applied as the blocking electrodes and continuously pressed at 3–6 MPa for good contact to the LPSC ceramic, while also avoiding ceramic cracking during testing. AC impedance measurements were performed using Ivium electrochemical workstation in the frequency range of 1 Hz to 1 MHz with an applied voltage of 0.2 V. Impedance measurements from

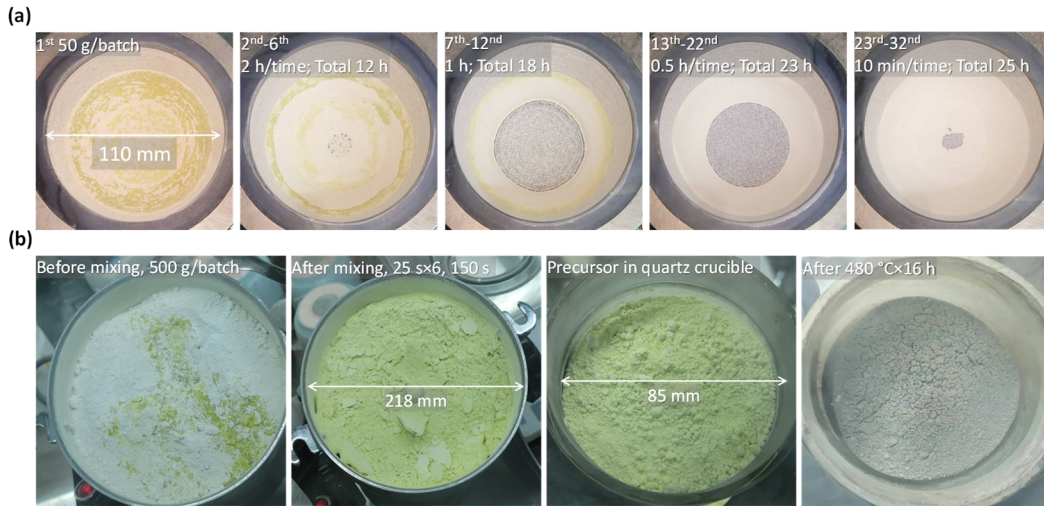
100 MHz to 1 Hz at  $-70\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$  for LPSC pellets including ceramics with Indium foils as the blocking electrodes were conducted using Toyo Co. Ltd. LN-Z2-HF ultra-high frequency impedance test system.

Commercial-loading all solid-state NCM622/Li<sub>5.4</sub>PS<sub>4.4</sub>Cl<sub>1.6</sub>/graphite primary mould battery were prepared as follow. Commercially available NCM622 was mixed with Li<sub>5.4</sub>PS<sub>4.4</sub>Cl<sub>1.6</sub> prepared at different methods with a weight ratio of 7:3 used a mixer (Thinky mixer ARE310) at a speed of 1000 rpm for 150 s to obtain the final composite cathode. The preparation of the composite anode was similar to that of the cathode: commercial graphite heated with  $500\text{ }^{\circ}\text{C}$  for 3 h was mixed with Li<sub>5.4</sub>PS<sub>4.4</sub>Cl<sub>1.6</sub> with a weight ratio of 6:4 using the above equipment at a speed of 1000 rpm for 600 s. It was worth noting that the Li<sub>5.4</sub>PS<sub>4.4</sub>Cl<sub>1.6</sub> used in the positive and negative electrodes of the full solid-state battery were further wet-milled by isobutyrate to reduce the particle sizes to 1-3  $\mu\text{m}$  [35]. 22.5 mg of the above-mentioned cathode was used in combination with 120 mg of Li<sub>5.4</sub>PS<sub>4.4</sub>Cl<sub>1.6</sub> electrolyte to make a 10 mm two-layer pellet by a pressure of 1.9 tons. Finally, a pressure of 2.5 tons was applied to make the three-layer pellet followed by attaching 15 mg anode mixture on the other side. All the electrochemical properties measurements for solid-state lithium batteries in this work are performed at room temperature ( $25\text{-}30\text{ }^{\circ}\text{C}$ )

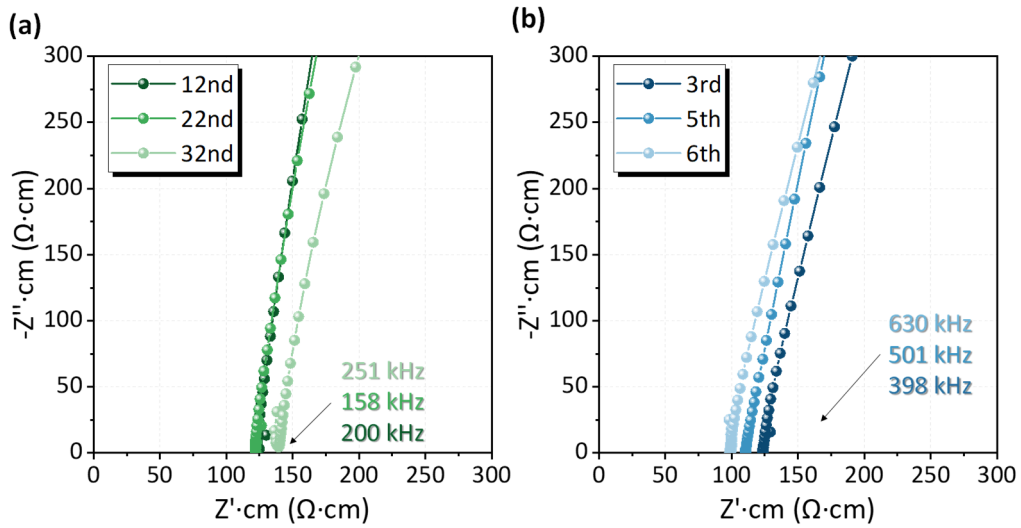
## 2. Supplementary Data

**Table S1** A comparison of the process parameters of the ball mill and the high-speed mixing synthesis paths.

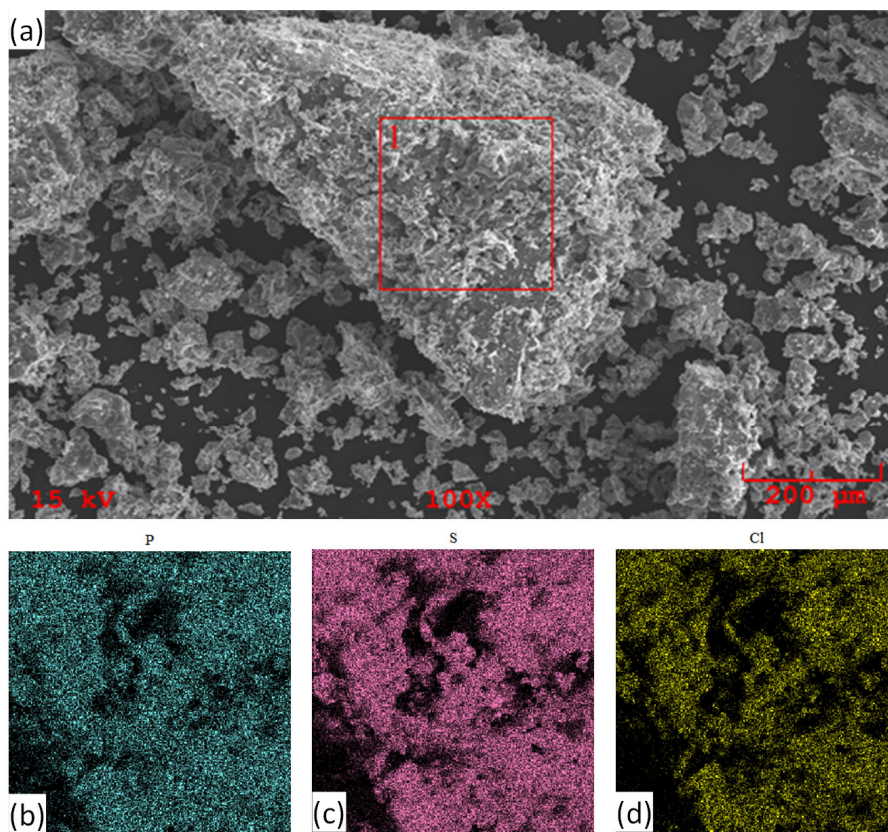
Parameters	Conventional ball-milling	High-speed mixing
Equipment	Planetary miller, ZrO <sub>2</sub> or Agate tank, YSZ balls	High speed mixer
Tank/chamber dimensions	$\phi 110 \times h100\text{ mm}$	$\Phi 218 \times h151\text{ mm}$
Grinding/mixing media	Yttrium stabilized zirconia, $\phi 10\text{ mm}$ , 650 g	Stainless steel (No. 316) blades
<b>Max weight per batch</b>	<b>50 g</b>	<b>500 g</b>
Grinding/mixing speed	180/360 rpm (revolution/rotation)	Power 2000 W, 10000-25000 rpm
<b>Treating duration/repeat times</b>	<b>1-2 h, 10-20 times</b>	<b>25 s, 6 times</b>
Sintering condition	10-20 g sealed in Quartz tube, $460\text{-}550\text{ }^{\circ}\text{C} \times 16\text{ h}$	100-300 g in Al <sub>2</sub> O <sub>3</sub> crucible, $460\text{-}510\text{ }^{\circ}\text{C} \times 16\text{ h}$



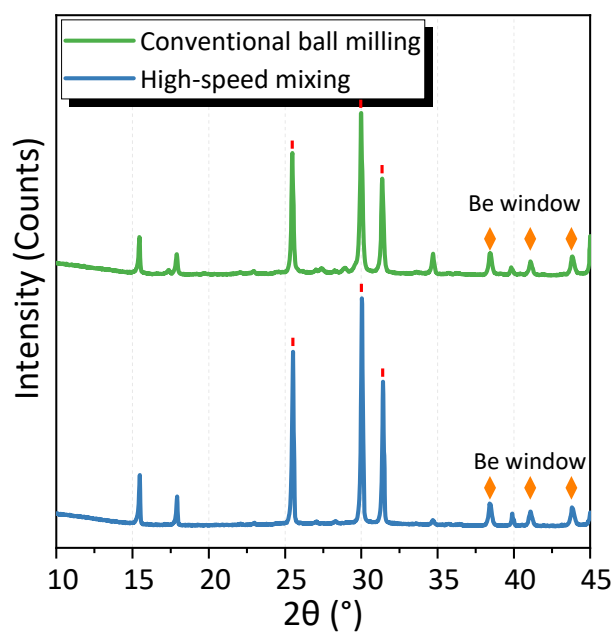
**Fig. S1** (a) The actual flow chart showing the 1<sup>st</sup>, 6<sup>th</sup>, 12<sup>th</sup>, 22<sup>nd</sup>, 32<sup>nd</sup> in the traditional ball-milling and (b) the innovative high-speed mixing synthesis route for lithium argyrodite  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ .



**Fig. S2** Nyquist plots of sintered  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  produced by ball-milling path at 12<sup>th</sup>, 22<sup>nd</sup>, 32<sup>nd</sup> times (a) and high speeds mixing path at 3<sup>rd</sup>, 5<sup>th</sup>, 6<sup>th</sup> times (b).



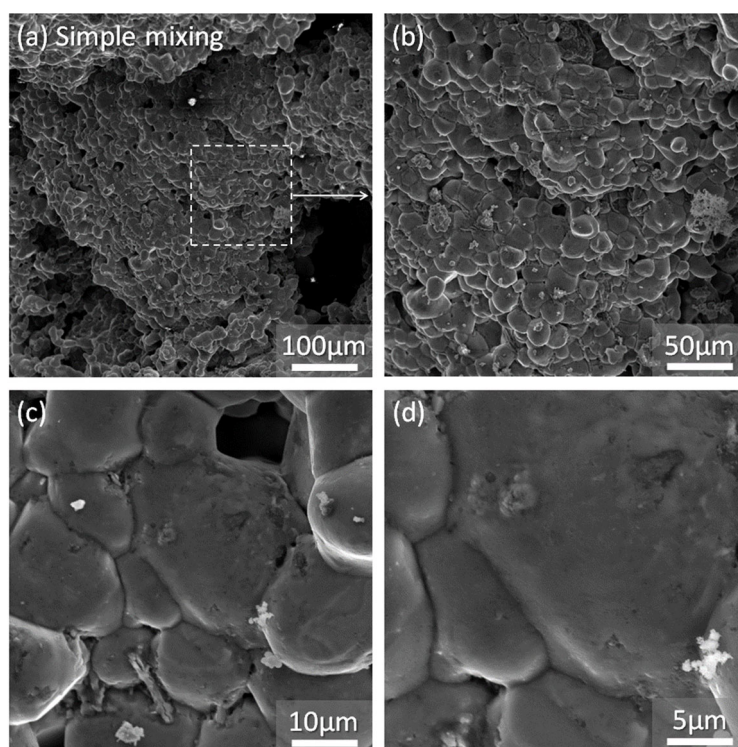
**Fig. S3** (a) SEM images, (b) Phosphorus, (c) Sulfur and (d) Chlorine EDX mapping of the sintered  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ .



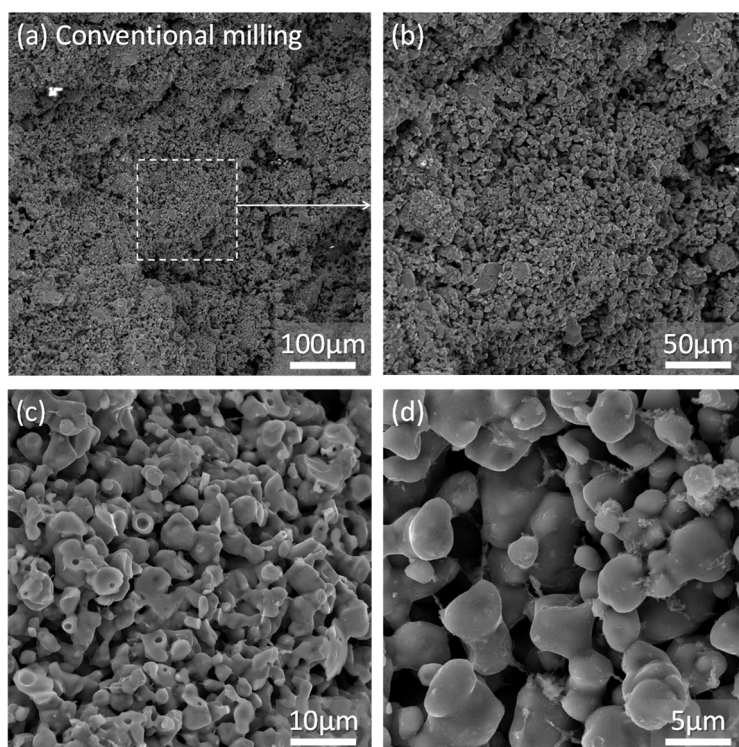
**Fig. S4** XRD data for annealed  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  prepared via the high-speed mixing and traditional ball-milling methods.

**Table S2** The XRD data of center position, FWHM, and area of the three main peaks of resulting from cubic  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  prepared via the high-speed mixing and conventional ball-milling methods.

Sample No.	Center Position	FWHM	Area
High-speed mixing	25.52	0.12141	6351.26
	30.04	0.12553	9313.05
	31.42	0.13351	5646.01
Conventional ball-milling	25.48	0.14583	5212.36
	30.00	0.19359	9209.93
	31.36	0.18229	4923.85



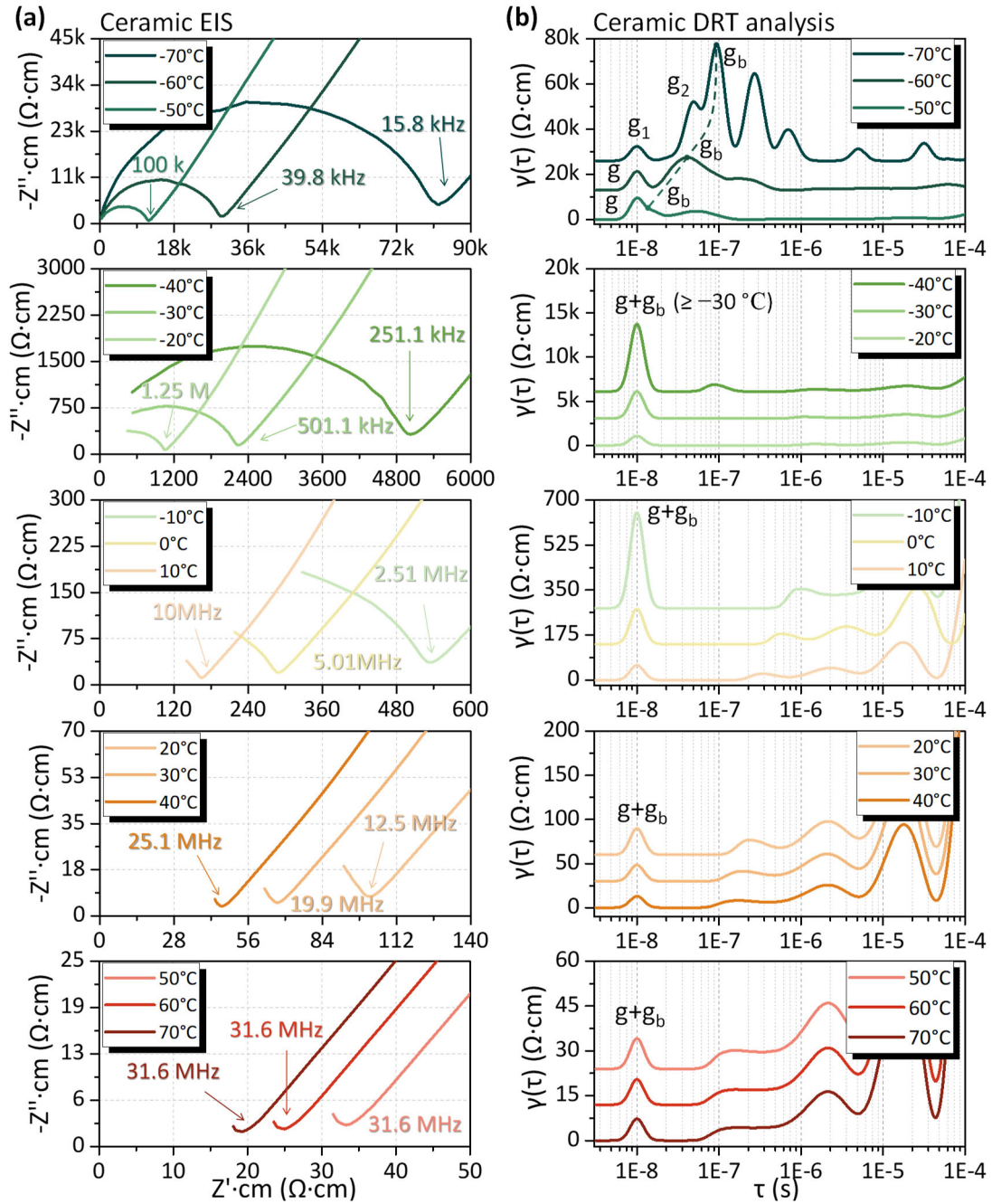
**Fig. S5** SEM image of annealed  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  prepared via the high-speed mixing method at 100  $\mu\text{m}$ , 50  $\mu\text{m}$ , 10  $\mu\text{m}$  and 5  $\mu\text{m}$  microscales.



**Fig. S6** SEM image of annealed  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  prepared via the conventional milling method at 100, 50, 10 and 5  $\mu\text{m}$  microscales.

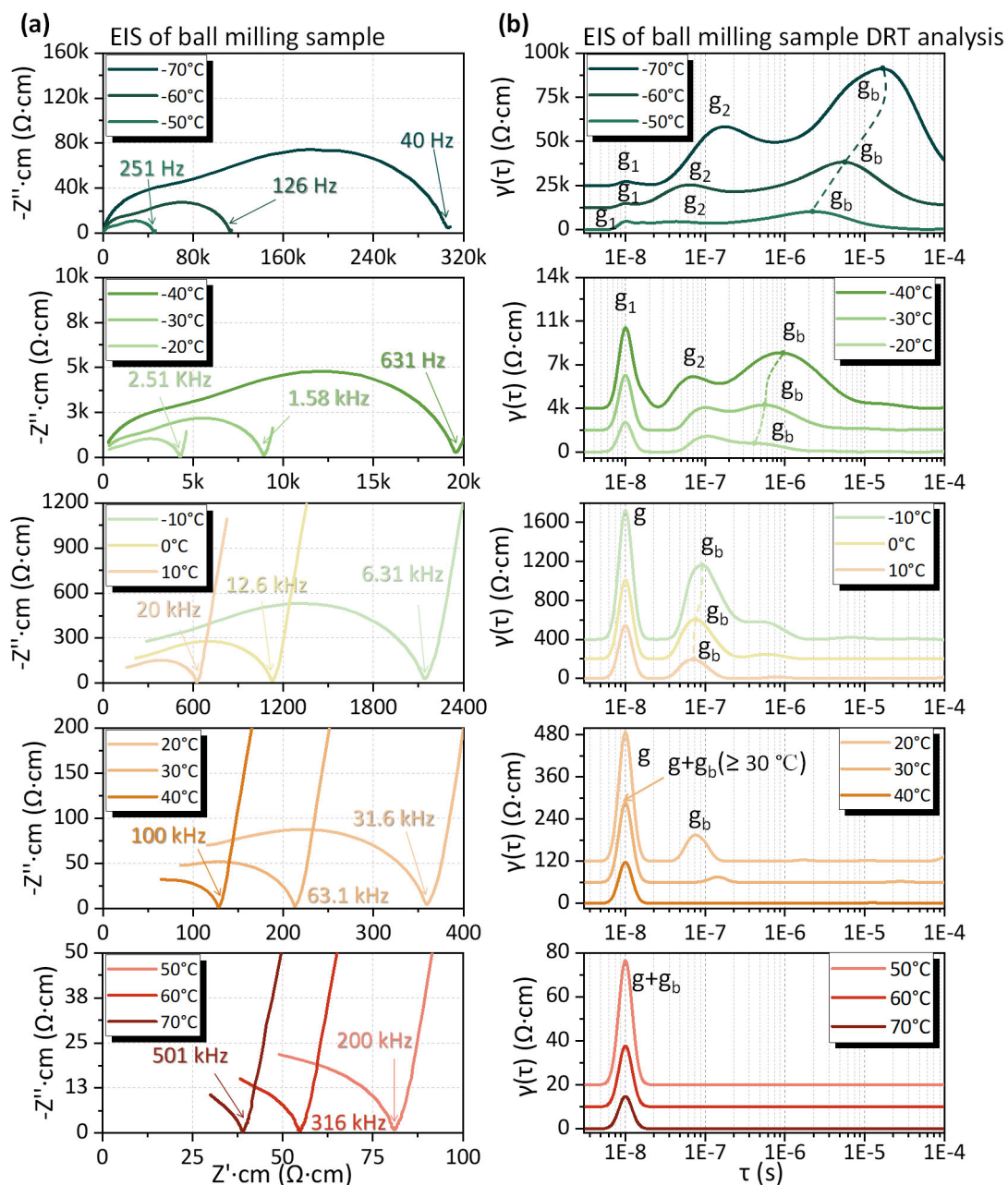
**Table S3** The ionic conductivity of all ceramic samples sintered at 480 °C for 4 h from powder annealed at 480 °C.

Sample No.	Ionic conductivity ( $\text{mS cm}^{-1}$ )	Testing temperature (°C)
Ceramic-1	19.1	28 °C
Ceramic-2	19.6	28 °C
Ceramic-3	20.2	28 °C
Ceramic-4	19.5	28 °C
Ceramic-5	20.6	28 °C
Ceramic-6	19.3	28 °C

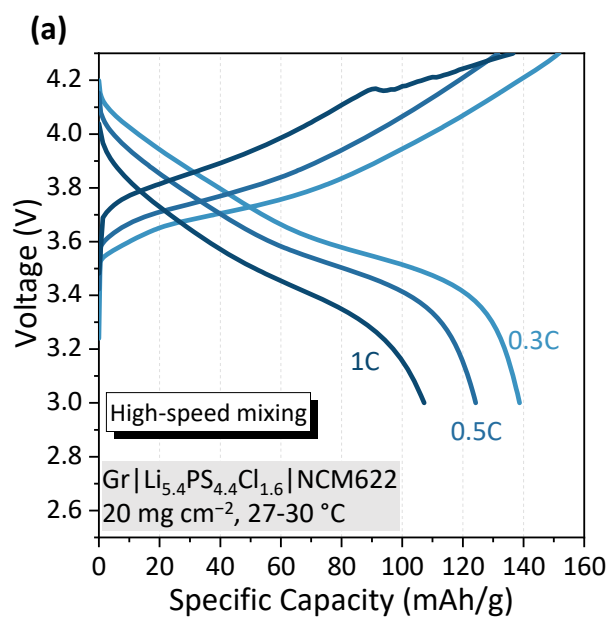


**Fig. S7** Normalized Nyquist plots of (a) ceramic sintered by  $\text{Li}_{5.4}\text{P}_{4.4}\text{S}\text{Cl}_{1.6}$  powder at  $-70$ - $70^\circ\text{C}$  measured by Toyo L -Z2-HF (1 MHz) and (b) relaxation times distributions calculated from normalized EIS data measured of  $\text{Li}_{5.4}\text{P}_{4.4}\text{S}\text{Cl}_{1.6}$  ceramics ( $g$  represents the grain,  $g_b$  represents the grain boundary).

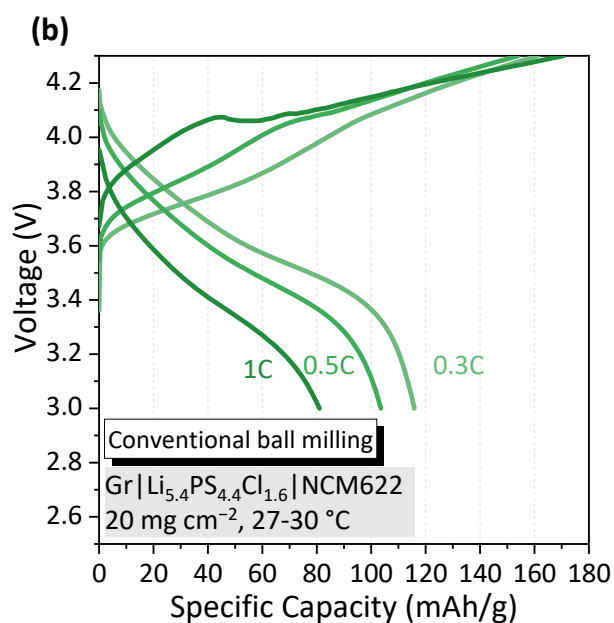




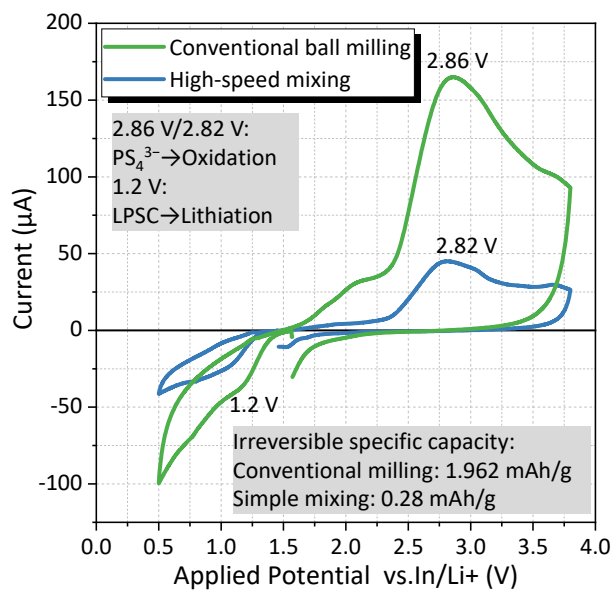
**Fig. S8** Normalized Nyquist plots (a) at  $-70$ – $70^\circ\text{C}$  measured by Toyo L -Z2-HF (1 MHz) and (b) relaxation times distributions calculated from normalized EIS data obtained from  $\text{Li}_{5.4}\text{P}_{4.4}\text{S}\text{Cl}_{1.6}$  powder prepared by conventional ball-milling method (g represents the grain,  $g_b$  represents the grain boundary).



**Fig. S9** Charge/discharge curves of the NCM622/  $\text{Li}_{5.4}\text{P}_{4.4}\text{S}\text{Cl}_{1.6}$ -mixing/graphite all solid-state batteries under 0.3C, 0.5C and 1C rate current densities ( $0.9\text{mA}/\text{cm}^2$ ,  $1.42\text{mA}/\text{cm}^2$  and  $3\text{mA}/\text{cm}^2$ ).



**Fig. S10** Charge/discharge curves of the NCM622/  $\text{Li}_{5.4}\text{P}_{4.4}\text{S}\text{Cl}_{1.6}$ -ball-milling/graphite all solid-state batteries under 0.3C, 0.5C and 1C rate current densities ( $0.9\text{mA}/\text{cm}^2$ ,  $1.42\text{mA}/\text{cm}^2$  and  $3\text{mA}/\text{cm}^2$ ).



**Fig. S11** The first scan profile of the electrolyte tested by cyclic voltammetry (CV) for two different preparation methods.