Supporting Information for:

Single-step ball milling synthesis of highly Li+ conductive Li$_{5.3}$PS$_{4.3}$ClBr$_{0.7}$ glass ceramic electrolyte enables low-impedance all-solid-state batteries

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Synthesis of GC-Li$_{5.3}$PS$_{4.3}$ClBr$_{0.7}$

The electrolyte was synthesized by using a high-energy planetary ball mill (Pulverisette 7, Fritsch). A stoichiometric mixture of reagent grade Li$_2$S (99.9%, Alfa Aesar), P$_2$S$_5$ (99%, Merch-Millipore), LiCl (99.9%, Sigma Aldrich), LiBr (99.9%, Sigma Aldrich) powders was filled in a zirconia pot (20 ml volume) with 10 zirconia balls ($\varnothing = 10$ mm) in an Ar-filled glovebox. A rotational speed of 850 rpm for 8.25 hours (5 min milling; 15 min rest; 99 cycles) was used. The resulting powder was ground in an agate mortar.

Ionic conductivity measurements

105 mg of the electrolyte were filled into a CompreDrive Measurements Cell inside an Ar-filled glovebox. The cell was then placed inside the CompreDrive (rhd Instruments), and a fabrication pressure of 400 MPa was applied for 120 seconds. The pressure was released, the cell equipped with a heating case and a pressure of 100 MPa applied. The measurements were carried out using a potentiostat/galvanostat AUTOLAB PGSTAT302N (Metrohm Autolab, Utrecht, Netherlands). The impedance spectra were taken in a frequency range from 10^5-10^1 Hz with an applied rms AC voltage of 10 mV. The temperature was varied in 5°C increments between 30 and 85°C. The sample thickness of the pellet was measured with a micrometer screw gauge (Mitutoyo). The impedance spectra were analyzed with the RelaxIS software package (rhd Instruments).

SEM images

SEM images were taken using a Gemini II (Zeiss, Germany) and an accelerating voltage of 2 kV.

X-ray powder diffraction

X-ray powder diffraction date were collected using an STOE StadiMP diffractometer, equipped with a Mython 1 K silicon strip detector and a Cu Kα X-ray source (λ = 1.54056 Å). The powder was filled inside a quartz vessel and sealed under argon. The data were collected using the Debye-Scherrer geometry. Crystallite sizes L were determined by using the Scherrer equation $L = \frac{K\lambda}{\Delta 2\theta \cdot \cos\theta}$ (wavelength λ; correction factor K = 0.89; $\Delta 2\theta = \frac{Half\ width}{360°} \cdot 2\pi$).

Preparation of electrode composites

The cathode composite powder consisting of $LiNbO_3$@LCO, GC-$Li_{5.3}PS_{4.3}ClBr_{0.7}$ / GC-Li_6PS_5Cl and carbon fibers was prepared by mixing the three powders using a high-energy planetary ball mill (Pulverisette 7, Fritsch) with a weight ration of 70:30:3. A rotational speed of 200 rpm for 1 hour (30 min milling; 5 min rest; 2 cycles) was used.

Electrochemical characterization

For the electrochemical testing, a self-built cell setup ($\varnothing$ = 10 mm) was used. First 80 mg of the electrolyte were filled in the cell and compacted at 200 MPa for 2 minutes. After this 15 mg of the cathode were dispensed onto one side of the electrolyte layer. The cell was compacted at 300 MPa for 2 minutes. Last an indium foil ($\varnothing$ = 10 mm), which was used as an anode, was applied at 300 MPa onto the other side of the electrolyte. The electrochemical measurements were performed using a BioLogic SP-150. The cycling experiments were carried out at 0.1 C, 98 MPa, ambient temperature (25 °C) between 3.7 V and 2.1 V. The impedance spectra were taken in a frequency range from 10^5-10^{-3} Hz with an applied rms AC voltage of 10 mV.
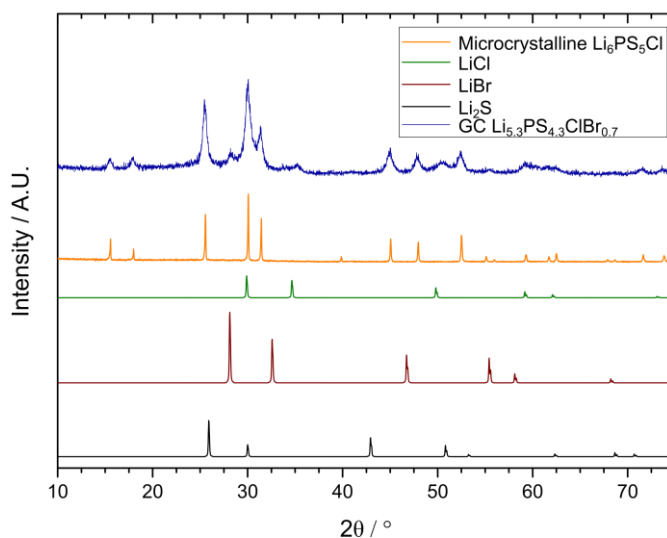
Results

Fig S1. XRD pattern of GC $Li_{5.3}PS_{4.3}ClBr_{0.7}$ and reference patterns of Li_6PS_5Cl, LiCl, LiBr and Li_2S.
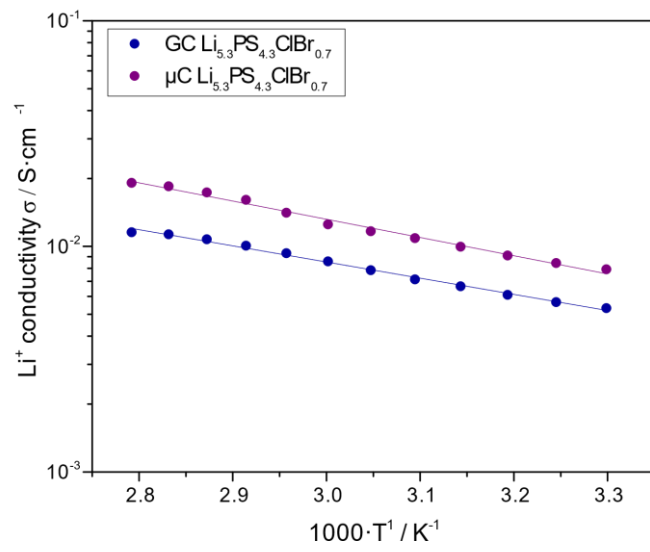
Fig S2. Arrhenius plot of the ionic conductivity of GC $Li_{5.3}PS_{4.3}ClBr_{0.7}$ and µC $Li_{5.3}PS_{4.3}ClBr_{0.7}$.
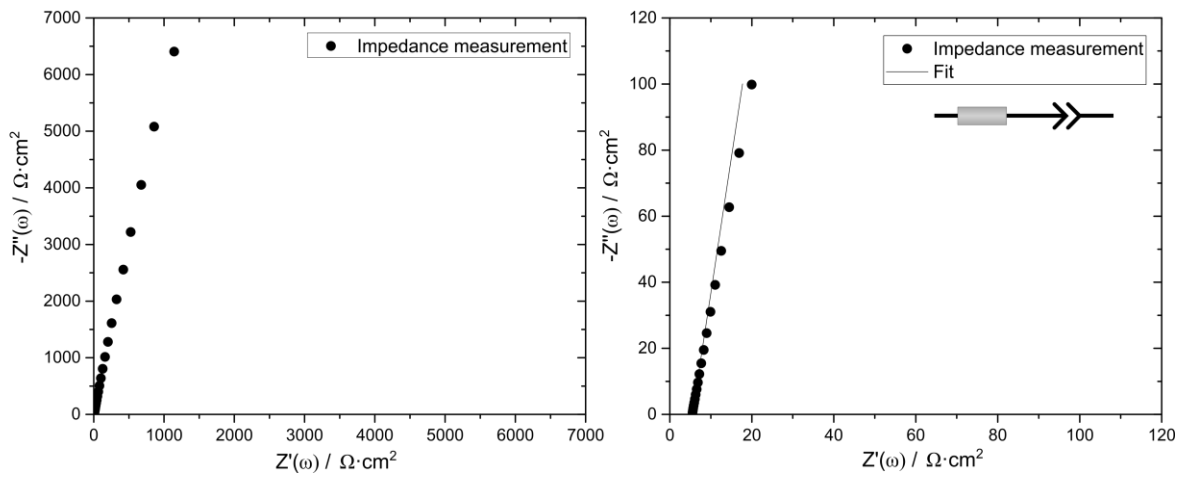

Fig S3. Exemplary impedance Nyquist plot of µC $Li_{5.3}PS_{4.3}ClBr_{0.7}$ at 30°C (left)

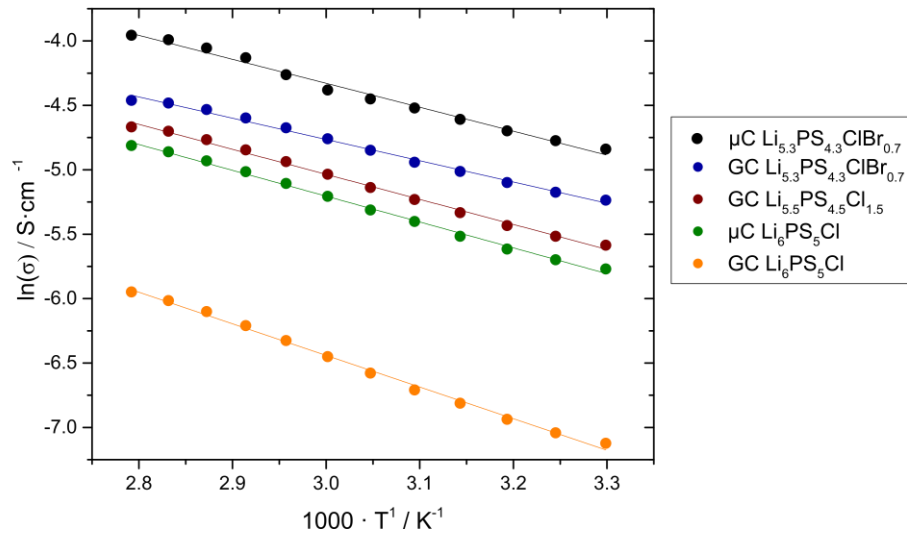and zoom into the high-frequency regime (right)

Fig S4. Arrhenius plots of the ionic conductivity of the solid electrolytes.

Table S1: Activation energies and ionic conductivities of the different solid electrolytes at 25°C and at 20°C, respectively.

Sample	E_A / eV	$\sigma_{25°C}$ / mS $\cdot$ cm^{-1}	$\sigma_{20°C}$ / mS $\cdot$ cm^{-1}
GC Li$_{5.5}$PS$_{4.5}$Cl$_{1.5}$	0.16	3.2	2.9
GC Li$_6$PS$_5$Cl	0.20	0.67	0.58
µC Li$_6$PS$_5$Cl	0.16	2.7	2.4
GC Li$_{5.3}$PS$_{4.3}$ClBr$_{0.7}$	0.13	4.8	4.3
µC Li$_{5.3}$PS$_{4.3}$ClBr$_{0.7}$	0.15	6.8	6.1