Supplementary Information

Quasi-solid electrolytes using a single-cation ionic liquid

Yuta Ito, Keigo Kubota, Yuta Maeyoshi, Toyoki Okumura and Kazuki Yoshii**

Research Institute of Electrochemical Energy, Department of Energy and Environment,

National Institute of Advanced Industrial Science and Technology (AIST),

1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

CORRESPONDING AUTHORS

* Yuta Ito − orcid.org/0000-0002-8494-9381; Email: ito.yuta@aist.go.jp

* Kazuki Yoshii − orcid.org/0000-0001-8904-6790; Email: k.yoshii@aist.go.jp

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S1. Materials and Methods

Materials

A Li-based single-cation ionic liquid (SCIL) was prepared using lithium bis(fluorosulfonyl)amide (Li[F–SO_2–N–SO_2–F], LiFSA; Kanto Chemical Co., Inc.) and lithium (fluorosulfonyl)(trifluoromethylsulfonyl)amide (Li[F–SO_2–N–SO_2–CF_3], LiFTA; Angene International Ltd.). LiFSA and LiFTA were each dried at 80 °C for 10 h before mixing. $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ (LATP, LiCGC, PW-01, Ohara Inc.) was obtained from Ohara Inc. and dried at 120 °C for 12 h.

Preparation of $Li[FSA]_{0.35}[FTA]_{0.65}$

LiFSA and LiFTA were weighed at a molar ratio of 0.35:0.65 in an Ar-filled glove box and sealed in a 45 ml pot with 30 g of Φ4 mm zirconia balls. Planetary ball milling (Pulverisette 7 Premium Line, Fritche Japan, Co., Ltd.) was performed at 150 rpm for 10 h. The milled sample was vacuum dried at 40 °C for 17 h.

Preparation of quasi-solid electrolytes (QSEs)

The preparation process of QSEs, pelleting, and cell assembly were all performed in an Ar-filled glove box. LATP was mixed with $Li[FSA]_{0.35}[FTA]_{0.65}$ at x wt% Li-SCIL (x = 0, 1, 5, 10, 17, 25, 33, and 50) using a mortar, followed by vortex mixing for 3 min (Lab

Dancer, IKA Co., Ltd.). The blends remained free-flowing powders without slurry- or mud-like behavior. Similarly, QSEs containing SiO_2 were prepared by compositing SiO_2 (TECHNAN, Lot Si-CIL.42.1/071302000) with SCIL using the same procedure. Assuming a SiO_2 density of 2.2 g cm^{-3}, SCIL was incorporated at 18 wt% (corresponding to 21 vol%).

Approximately 80 mg of the QSE powder was loaded into a pelletizing die, heated with a ring heater (Sansho Industry Co., Ltd.) to 90 °C, and pressed in the following sequence:

- Applying 200 MPa while ramping the temperature from 25 °C to 90 °C at 10 °C min^{-1};
- Holding for 60 min at 20 MPa and 90 °C;
- Increasing the pressure to 400 MPa and then holding for 5 min at 90 °C;
- Releasing the pressure and cooling to 25 °C.

The pellet thickness was measured at 25 °C immediately after demolding.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS)

Solid-state battery evaluation cells (Osaka Shoko Ltd.) were used to measure the QSEs with x wt% Li-SCIL (x = 0, 1, 5, 10, 17, 25, and 33). Au foil current collectors (Nilaco;

0.05–0.1 mm thickness, 10 mm diameter) were placed on both faces of each pellet. A pair of SKD tool steel rods (JIS tool steel grade) were positioned above and below the pellet, and a polycarbonate cylinder was used to maintain alignment. The cell stack was sandwiched by stainless-steel plates and secured with four screws.

The cells and silica gel desiccant (FUJIFILM Wako Pure Chemical Corp.) were sealed in airtight containers (EC Frontier Co., Ltd.) in an Ar atmosphere. The following temperature cycling was performed in a thermostatic chamber (SU-222, ESPEC Co.): 25 °C → 90 °C → −10 °C → 25 °C, with 2 h holds after every 5 °C change. EIS spectra were recorded at each temperature plateau using HZ-Pro (Meiden Hokuto Co., Ltd.) with an AC amplitude of 50 mV. The frequency range was 1 MHz to 0.1 Hz, and 20 points were sampled per decade. EIS of Li-SCIL was measured in four-electrode configuration as described in our previous work.[1]

Chronoamperometry (CA)

For CA, symmetric cells were assembled with the QSE containing 17 wt% Li-SCIL (or the general IL) using Li metal foils (Honjo Metal Co., Ltd.; 0.2 mm thickness, 9 mm diameter). To suppress the reduction of LATP by Li metal, separators impregnated with Li-SCIL were placed between the Li electrodes and QSE, resulting in a stack of Li/separator/QSE/separator/Li.

Material characterization

Scanning electron microscopy (SEM) observation and energy dispersive X-ray (EDX) analysis

Surface and cross-sectional morphology and elemental distributions of the samples were examined by SEM/EDX (JSM-6700F series, JEOL Ltd.). The samples were mounted in a argon-filled glovebox and transferred using sealed holders to minimize exposure.

X-ray diffraction

XRD patterns were collected on a MiniFlex (Rigaku Corp.) at a scan rate of 2° min^{-1} with a tube current of 20 mA and voltage of 40 kV.

Density measurement of SCIL

The density of $Li[FSA]_{0.35}[FTA]_{0.65}$ was determined by measuring the volume of the melted and vacuum-degassed liquid in a graduated cylinder at 50 °C, 100 °C, and 150 °C. A linear fit yielded the equation d (g cm^{-3}) = −0.0003 T (K) + 1.935 (R^2 = 1), which corresponds to a density of 1.85 g cm^{-3} at 25 °C by extrapolation.

Differential scanning calorimetry (DSC)

DSC (TA7020, Hitachi High-Tech) measurements were performed under a nitrogen atmosphere. Approximately 6.9 mg of the QSE powder was sealed in an aluminum pan and heated from room temperature to 120 °C at a rate of 2 °C min^{-1}. The melting point of SCIL and thermal stability of QSEs were evaluated from the obtained thermograms.

S2. Supplementary Table

Supplementary Table S1. Structural information of QSEs comprising LATP and various Li-SCIL contents ($Li[FSA]_{0.35}[FTA]_{0.65}$) calculated using the densities of 2.94 g cm^{-3} for LATP[2] and 1.85 g cm^{-3} for SCIL at 25 °C.

Weight of QSE (mg)	Weight fraction of SCIL (wt%)	Volume fraction of SCIL (vol%)	Measured thickness of QSE (mm)	Volume of QSE (cm^3)[a]	Volume fraction excluding LATP in QSE (vol%)[b]	Pore filling fraction (vol%)[c]	Porosity of QSE (%)[d]
80.24	0	0.000	0.546	0.0429	36.4	0.000	36.4
80.29	1	1.00	0.569	0.0447	39.5	2.50	38.5
80.42	5	5.30	0.535	0.0420	38.1	13.9	32.8
80.28	10	11.0	0.515	0.0404	39.2	27.9	28.3
80.33	16.7	20.4	0.462	0.0363	37.3	54.7	16.9
80.22	25	32.5	0.435	0.0341	40.0	81.1	7.56
80.00	33.3	44.2	0.418	0.0328	44.7	98.1	0.84

[a] Volume of QSE: disk area (10 mm diameter) × measured thickness.

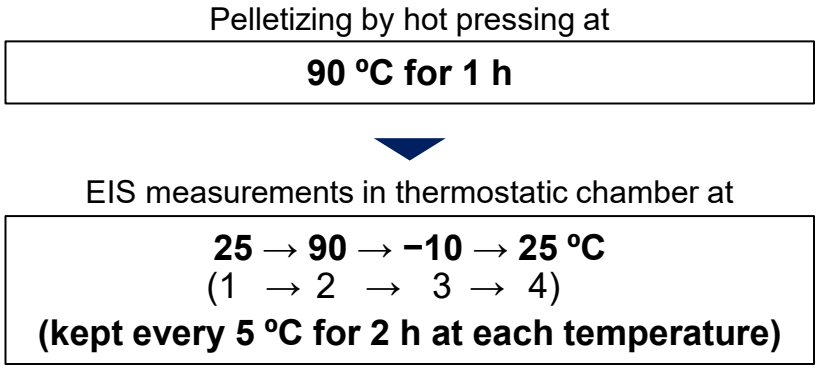
[b] Volume fraction excluding LATP in QSE (%): [(Volume of QSE − Calculated volume of LATP) ÷ Volume of QSE] × 100.

[c] Pore filling fraction (vol%): [Calculated volume of SCIL÷ (Volume of QSE × Volume fraction excluding LATP (%) ÷ 100)] × 100.

[d] Porosity of QSE: (Volume of QSE – calculated volume of LATP − calculated volume of SCIL) ÷ Volume of QSE × 100.

Supplementary Table S2. Ionic conductivity of quasi-solid electrolytes (QSEs) as a function of temperature (25–90 °C). The values represent the average of three independent measurements (N = 3). For LATP alone (0 wt%) and SCIL (100 wt%), ionic conductivity is reported only at 90 °C. For QSEs with 1 and 5 wt% SCIL, values are reported at 40, 60, and 90 °C due to limitations in reliable measurement at lower temperatures.

Weight fraction of SCIL in QSEs wt(%)	25 °C	40 °C	60 °C	90 °C
0	-	-	-	2.5×10^{-8}
1	-	1.1×10^{-9}	5.3×10^{-9}	5.2×10^{-8}
5	-	2.7×10^{-9}	2.2×10^{-8}	9.6×10^{-7}
10	2.3×10^{-9}	1.9×10^{-8}	1.6×10^{-7}	4.5×10^{-6}
17	1.5×10^{-8}	1.3×10^{-7}	1.1×10^{-6}	1.8×10^{-5}
25	1.5×10^{-8}	1.2×10^{-7}	1.1×10^{-6}	2.5×10^{-5}
33	1.2×10^{-8}	$1.2 \times 10^{-}7$	1.3×10^{-6}	3.5×10^{-5}
100	-	-	-	3.4×10^{-5}



S3. Supplementary Figures

Fig. S1 Temperature programs during pelletizing and temperature-dependent EIS measurement at 25 °C → 90 °C → −10 °C → 25 °C (1 → 2 → 3 → 4).

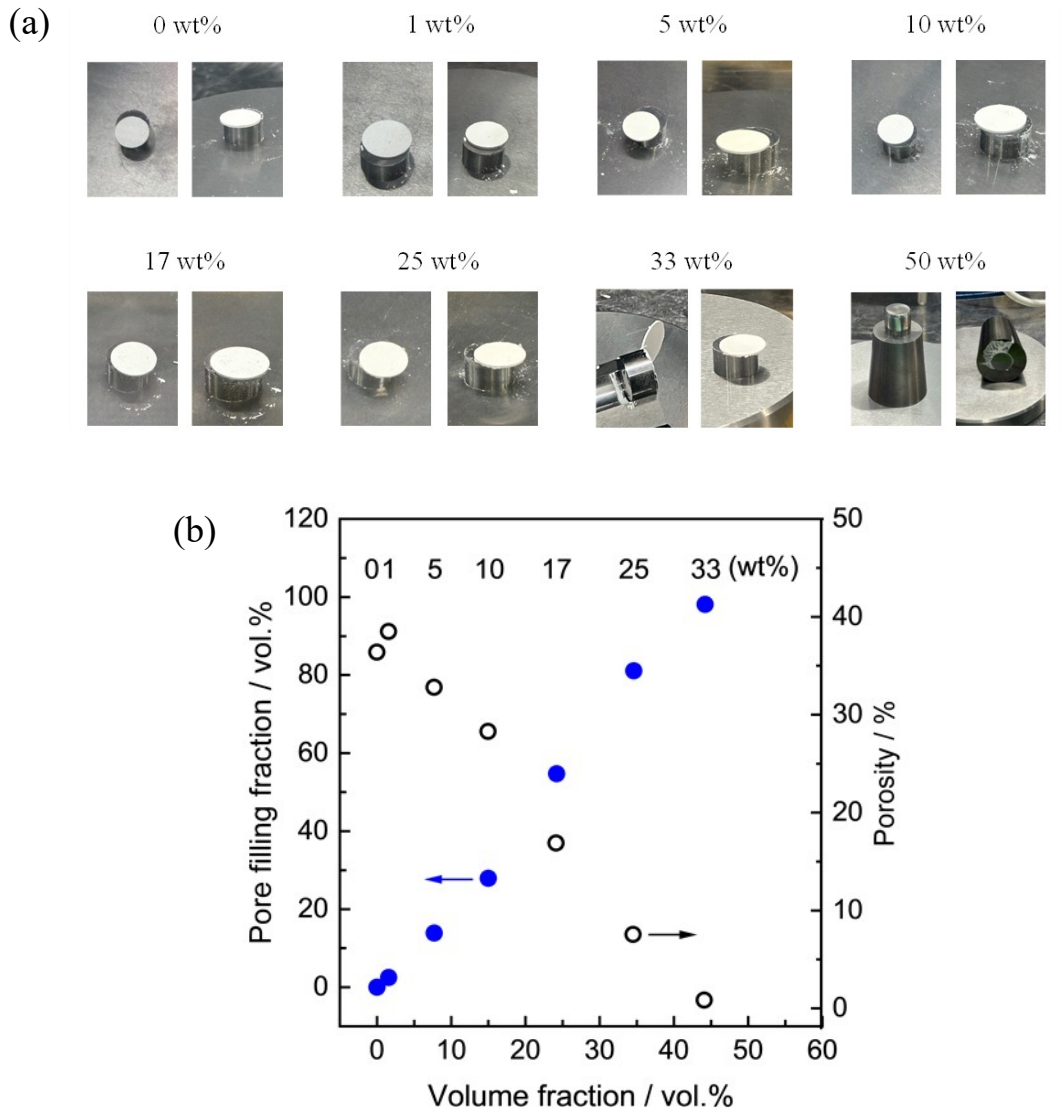


Fig. S2 (a) Photographs of QSE pellets containing *x* wt% SCIL (*x* = 0, 1, 5, 10, 17, 25, 33, and 50) prepared by hot pressing at 90 °C. The pellet with 50 wt% SCIL was fused to the molding die and could not be removed; therefore, this composition was excluded from further evaluation. (b) Pore filling fraction and porosity as functions of the SCIL volume or weight fraction.

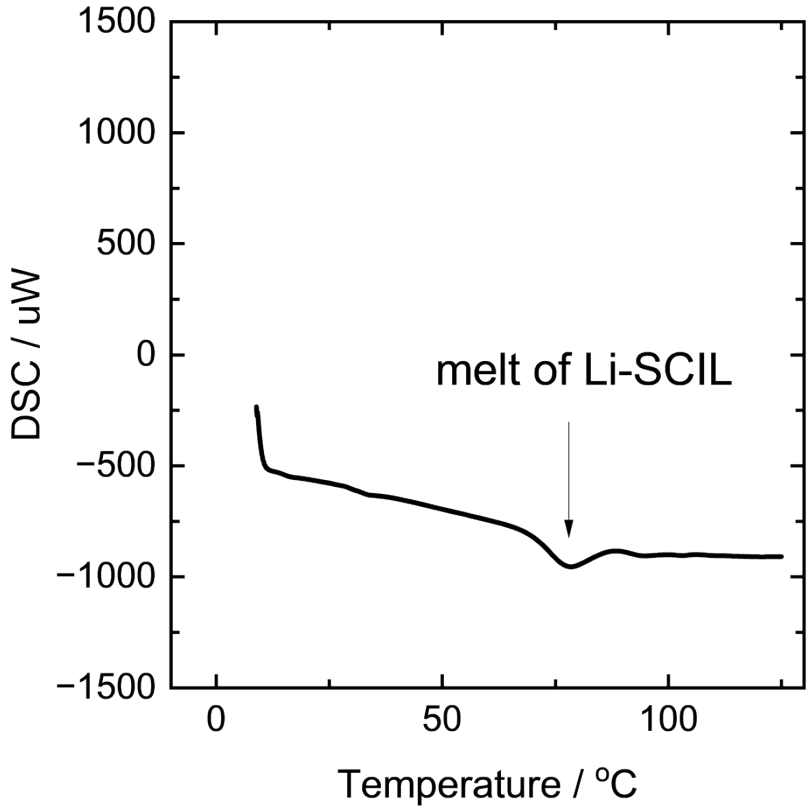


Fig. S3 DSC curve of QSE powder containing 17 wt% SCIL measured at a heating rate of 2 °C min^{-1}.

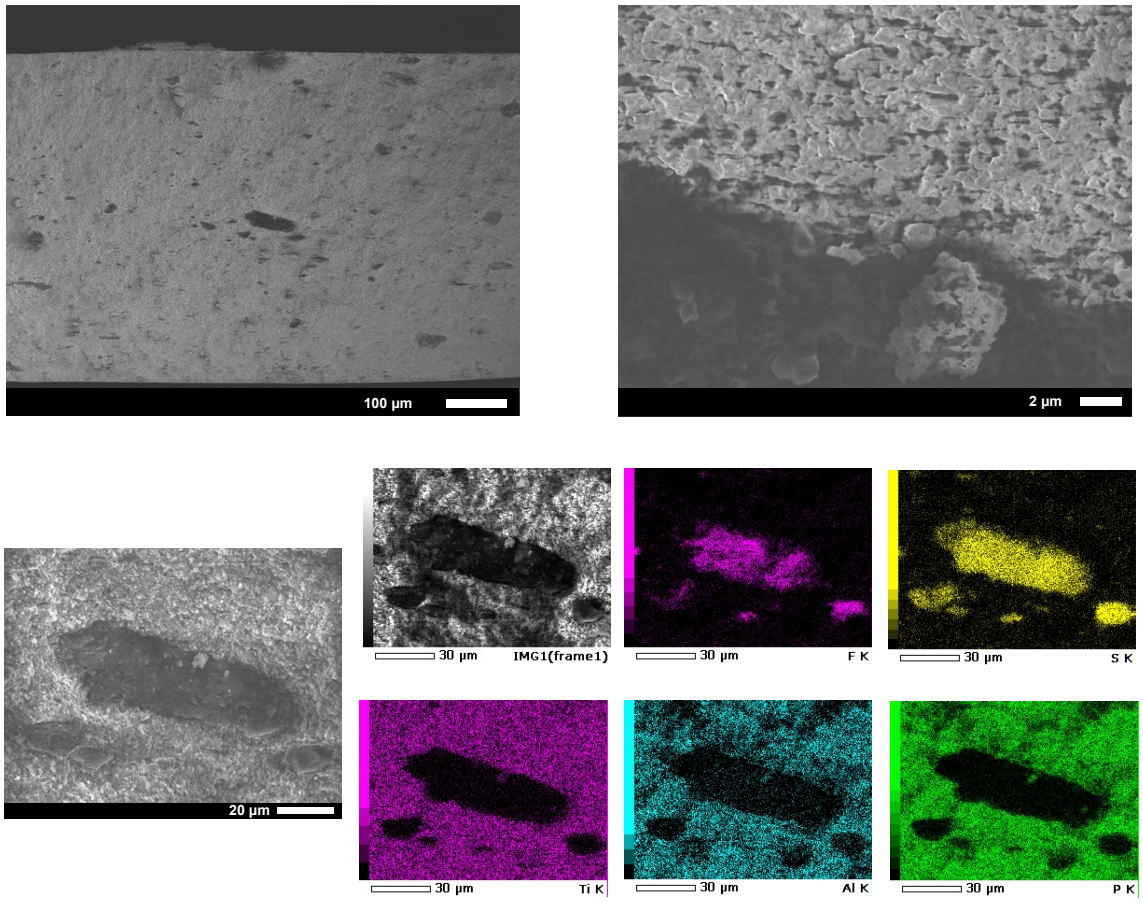


Fig. S4 SEM images and EDX results of QSE pellet containing 17 wt% SCIL prepared by pressing at 25 °C.

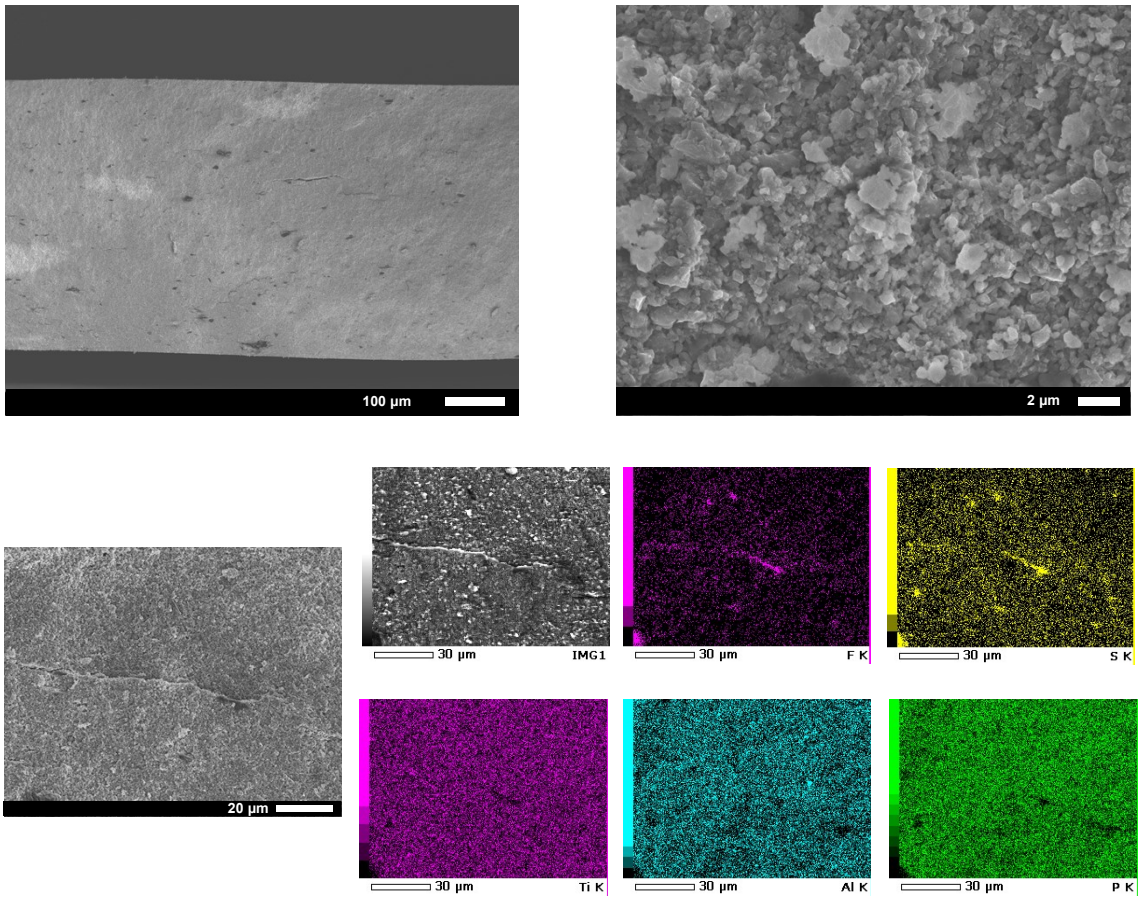


Fig. S5 SEM images and EDX results of QSE pellet containing 17 wt% SCIL prepared by pressing at 90 °C.

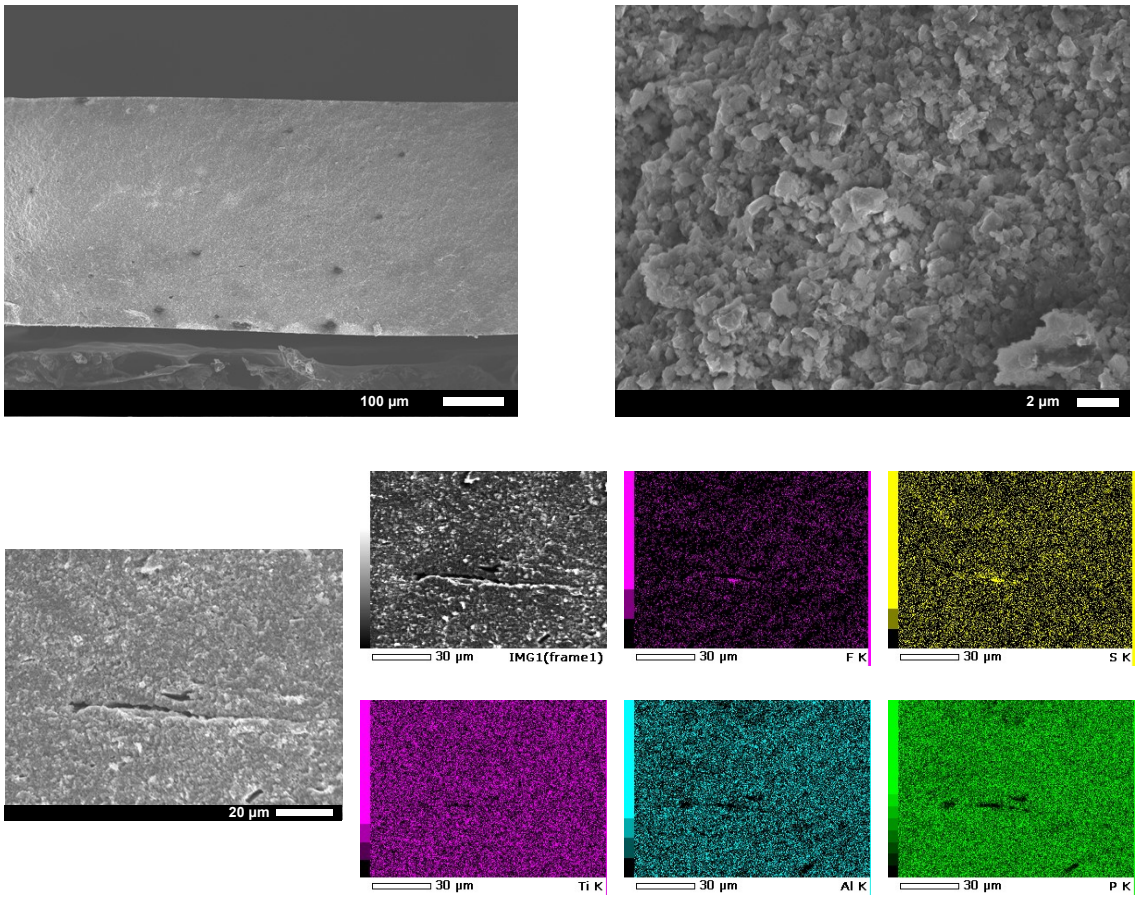


Fig. S6 SEM images and EDX results of QSE pellet containing 17 wt% SCIL prepared by pressing at 90 °C and heating in step 1→2.

References

1. Y. Ito, K. Kubota, Y. Maeyoshi, T. Okumura and K. Yoshii, *J. Phys. Chem. C*, 2025, **129**, 9656-9661.

2. S. Duluard, A. Paillassa, L. Puech, P. Vinatier, V. Turq, P. Rozier, P. Lenormand, P.-L. Taberna, P. Simon and F. Ansart, *J. Eur. Ceram. Soc.*, 2013, **33**, 1145-1153.