Electronic Supplementary Information

Effect of synthesis process on the Li-ion conductivity of $LiTa_2PO_8$ solid electrolyte materials for all-solid-state batteries

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Table S1. Identified crystals in samples A and D after heating for 30 min at 750, 850, 950, 1050, and 1100 ℃.

Heating temperature / ° C	Sample A	Sample D
750	Ta2O5, TaPO5	Ta2O5, TaPO5
850	Ta2O5, TaPO5	Ta2O5, TaPO5
950	Ta2O5, PrecursorLTPO	Ta2O5, PrecursorLTPO
1050	PrecursorLTPO, LTPO	PrecursorLTPO
1100	LTPO, PrecursorLTPO	PrecursorLTPO, LTPO

Table S2-1. Structural information of the samples determined via Rietveld analysis of the X-ray powder diffraction data.

	sample A	sample B	sample C	sample D
R_{wp}	6.148	5.683	6.325	7.013
R_p	4.484	4.155	4.66	5.146
mass ratio of $LiTa_2PO_8$	0.9805	0.9671	0.9792	0.978
mass ratio of $LiTa_3O_8$	0.0195	0.0329	0.0208	0.022
Lattice parameters:				
$LiTa_2PO_8$ in C2/C				
a /Å	9.7067(1)	9.7152(1)	9.7089(1)	9.7039(2)
b /Å	11.5295(2)	11.5379(1)	11.5311(2)	11.5252(2)
c /Å	10.700(2)	10.7078(1)	10.702(2)	10.6977(2)
α /°	90	90	90	90
β /°	90.05	90.05	90.0499	90.0499
γ /°	90	90	90	90
unit -cell volume/Å^2	1197.45(3)	1200.28(2)	1198.11(3)	1196.43(4)
$LiTa_3O_8$ in C2/C				
a /Å	9.417(3)	9.419(1)	9.410(2)	9.404(2)
b /Å	11.508(4)	11.524(2)	11.516(2)	11.498(3)
c /Å	5.045(2)	5.0502(9)	5.046(1)2	5.042(2)
α /°	90	90	90	90
β /°	91.0493	91.0506	91.0486	91.047
γ /°	90	90	90	90
unit -cell volume/Å^2	546.7(3)	548.1(1)	546.8(2)	545.1(3)

Table S2-2. Atomic parameters for sample A.

$LiTa_2PO_8$ in C2/C						
label/atm	site	site occupncy	x	y	z	B/Å^2
Li1	8f	0.72	0.26078	0.14395	0.40256	1
Li2	8f	0.21	-0.08379	0.14159	0.08445	1
Li3	4a	0.14	0	0	0	1
Ta1	8f	1	0.24771	0.40352	0.24419	0.443
Ta2	4e	1	0	0.15299	0.25	0.769
Ta3	4b	1	0	0.5	0	0.385
P1	8f	1	0.50953	0.29176	0.05905	0.497
O1	8f	1	0.04744	0.15965	0.44828	1
O2	8f	1	0.3815	0.34798	0.0855	1
O3	8f	1	0.35871	0.00324	0.37803	1

$LiTa_3O_8$ in C2/C						
label/atm	Site	site occupncy	x	y	z	B/Å^2
Ta1	8f	1	0.25001	0.43998	0.25033	-
Ta2	4e	1	0	0.16097	0.25	-
O1	8f	1	0.36966	-0.06268	0.3546	1
O2	8f	1	-0.07425	0.23323	0.52044	1
O3	8f	1	0.14244	0.0621	-0.04378	1
O4	8f	1	0.0828	0.34071	0.23175	1
Li1	4e	1	0	0.62(7)	0.25	1

O4	8f	1	0.45627	0.17584	0.06131	1
O5	8f	1	0.15714	0.26425	0.20111	1
O6	8f	1	0.15138	0.44397	0.39099	1
O7	8f	1	0.39305	0.29161	0.35666	1
O8	8f	1	0.12921	0.03025	0.21319	1

Table S2-3. Atomic parameters for sample B.

$LiTa_2PO_8$ in C2/C							$LiTa_3O_8$ in C2/C						
label/atm	site	site occupncy	x	y	z	B/Å²	label/atm	Site	site occupncy	x	y	z	B/Å²
Li1	8f	0.72	0.30083	0.14342	0.32849	1	Ta1	8f	1	0.25026	0.43855	0.24983	-
Li2	8f	0.21	-0.08242	0.14241	0.08198	1	Ta2	4e	1	0	0.15961	0.25	-
Li3	4a	0.14	0	0	0	1	O1	8f	1	0.38217	-0.30265	0.43925	1
Ta1	8f	1	0.24747	0.40352	0.24446	0.41	O2	8f	1	0.00063	0.17594	0.58927	1
Ta2	4e	1	0	0.15303	0.25	0.892	O3	8f	1	0.13885	0.0403	-0.00734	1
Ta3	4b	1	0	0.5	0	0.388	O4	8f	1	0.11901	0.36786	0.20252	1
P1	8f	1	0.50804	0.29073	0.05823	0.424	Li1	4e	1	0	0.62 (4)	0.25	1
O1	8f	1	0.04366	0.16042	0.44506	1							
O2	8f	1	0.37827	0.35199	0.08547	1							
O3	8f	1	0.36505	0.00529	0.37814	1							
O4	8f	1	0.4532	0.17601	0.06024	1							
O5	8f	1	0.15957	0.26793	0.19287	1							
O6	8f	1	0.15253	0.44418	0.3913	1							
O7	8f	1	0.39413	0.29198	0.35607	1							
O8	8f	1	0.13129	0.0276	0.21544	1							

Table S2-4. Atomic parameters for sample C.

$LiTa_2PO_8$ in C2/C							$LiTa_3O_8$ in C2/C						
label/atm	site	site occupncy	x	y	z	B/Å²	label/atm	Site	site occupncy	x	y	z	B/Å²
Li1	8f	0.72	0.29295	0.14556	0.3507	1	Ta1	8f	8	0.2502	0.43971	0.22956	-
Li2	8f	0.21	0.06658	0.14424	0.08256	1	Ta2	4e	8	0	0.15974	0.25	-
Li3	4a	0.14	0.06658	0.14424	0.08256	1	O1	8f	8	0.36445	-0.26571	0.4895	1
Ta1	8f	1	0.24772	0.40353	0.24372	0.421	O2	8f	8	-0.06397	0.30575	0.64236	1
Ta2	4e	1	0	0.15309	0.25	0.898	O3	8f	8	0.14513	0.04802	0.09913	1
Ta3	4b	1	0	0.5	0	0.47	O4	8f	8	0.07564	0.3218	-0.33305	1
P1	8f	1	0.50779	0.29185	0.05716	0.599	Li1	4e	8	0	0.62 (6)	0.25	1
O1	8f	1	0.0415	0.15921	0.44516	1							
O2	8f	1	0.37917	0.35119	0.08407	1							
O3	8f	1	0.36525	0.00824	0.37729	1							
O4	8f	1	0.45387	0.17879	0.06195	1							
O5	8f	1	0.16	0.26684	0.19207	1							
O6	8f	1	0.15498	0.44302	0.39142	1							
O7	8f	1	0.39579	0.29138	0.35751	1							
O8	8f	1	0.12942	0.02605	0.21407	1							

Table S2-5. Atomic parameters for sample D.

$LiTa_2PO_8$ in C2/C							$LiTa_3O_8$ in C2/C						
label/atm	site	site occupncy	x	y	z	B/Å²	label/atm	Site	site occupncy	x	y	z	B/Å²
Li1	8f	0.72	0.09105	0.13784	0.41975	1	Ta1	8f	1	0.25014	0.43596	0.20715	-
Li2	8f	0.21	0.08705	0.13901	0.08453	1	Ta2	4e	1	0	0.16229	0.25	-
Li3	4a	0.14	0	0	0	1	O1	8f	1	0.36042	-0.08405	0.30657	1
Ta1	8f	1	0.24775	0.40358	0.24319	0.42	O2	8f	1	-0.08927	0.28952	0.62075	1
Ta2	4e	1	0	0.15301	0.25	0.838	O3	8f	1	0.14098	0.07238	0.06068	1
Ta3	4b	1	0	0.5	0	0.422	O4	8f	1	0.07822	0.33123	0.21726	1
P1	8f	1	0.50771	0.29308	0.05796	0.402	Li1	4e	1	0	0.62 (7)	0.25	1
O1	8f	1	0.03987	0.15845	0.44348	1							
O2	8f	1	0.37914	0.35084	0.08532	1							
O3	8f	1	0.36592	0.00393	0.37673	1							
O4	8f	1	0.45569	0.1776	0.06235	1							
O5	8f	1	0.16005	0.26872	0.19835	1							
O6	8f	1	0.15561	0.44413	0.39302	1							
O7	8f	1	0.39568	0.29282	0.35685	1							
O8	8f	1	0.12984	0.02793	0.21363	1							

Table S3. Atomic concentration of the samples after the 2nd heating.

	Atomic concentration		
	Li	P	Ta
Sample A	1	1.2	2
Sample B	1.1	1.2	2
Sample C	1.2	1.2	2
Sample D	1.2	1.1	2

Table S4. Relative density of the sintered pellet samples.

Sample	A	B	C	D
Relative density /%	95.48	88.21	94.38	90.6

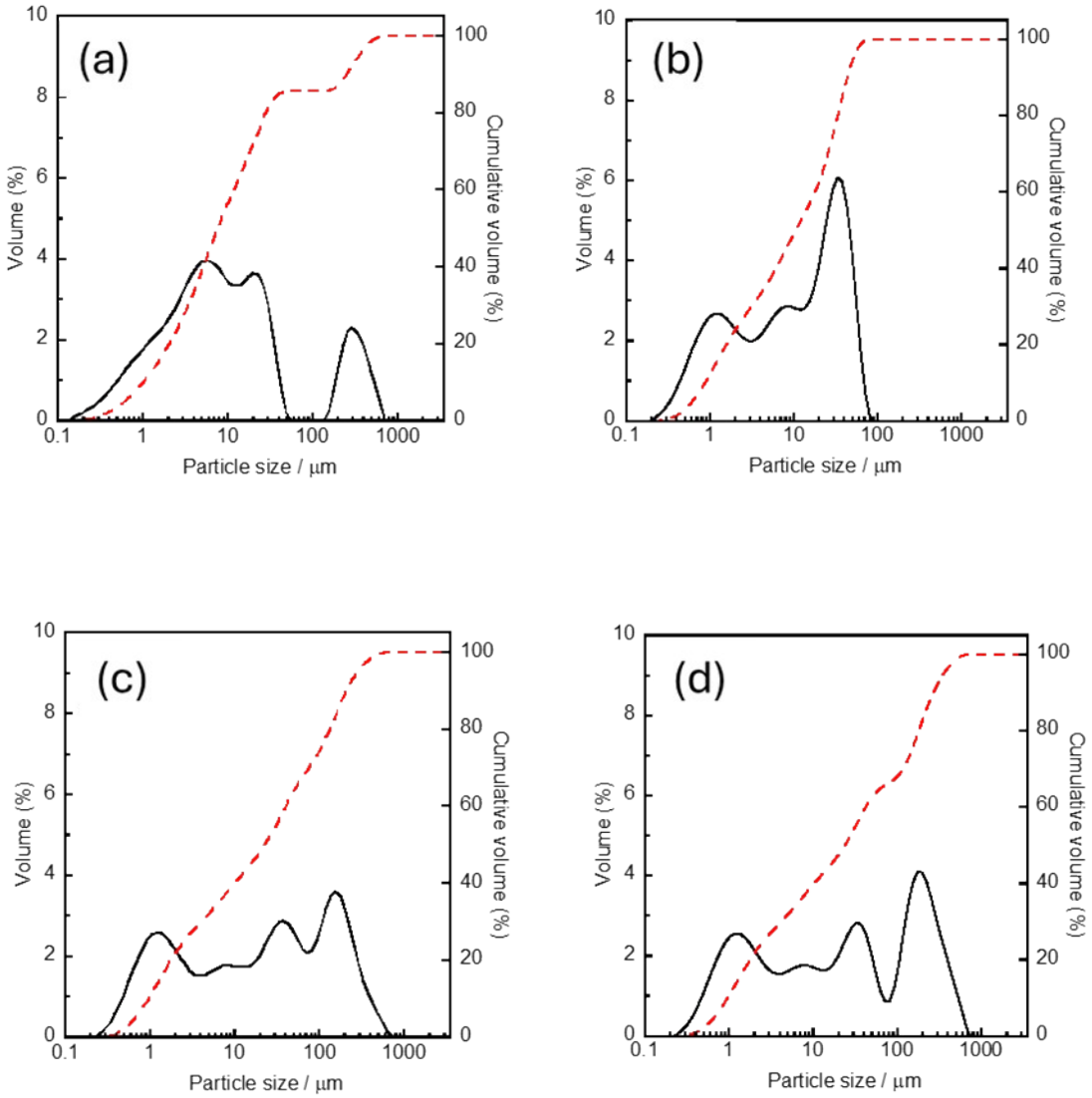

Fig. S1. Particle size distribution of the precursor particles for (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

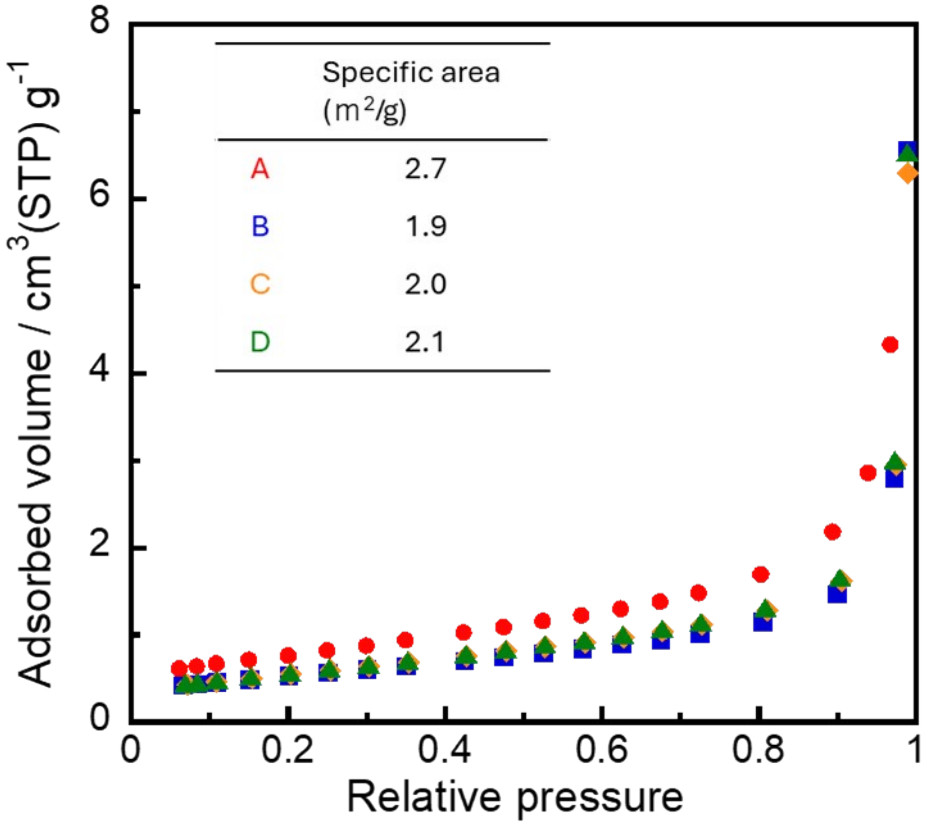

Fig. S2 Nitrogen gas adsorption curves of the adjusted samples A-D.

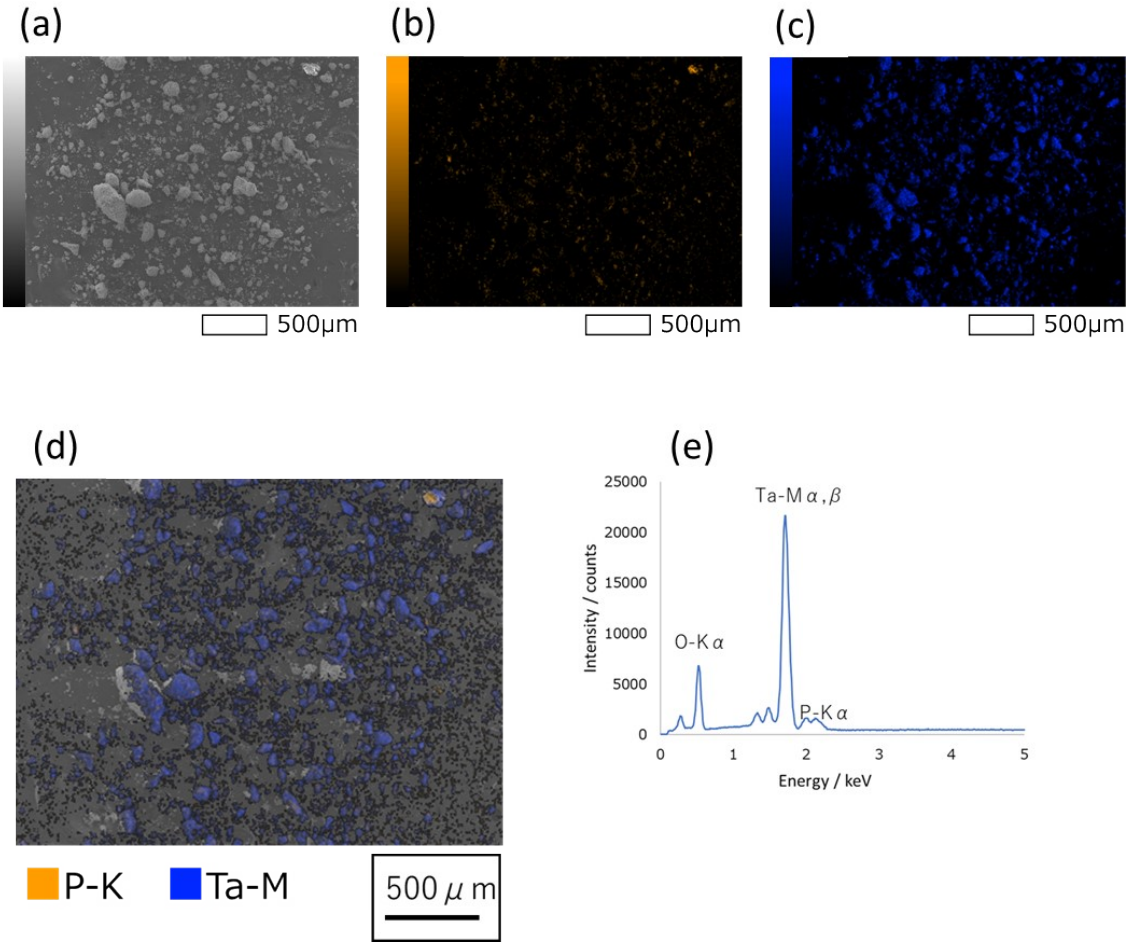

Fig. S3 SEM-EDS analysis results of the mixed starting powder materials for sample D. (a) SEM image, (b) P, (c) Ta, (d) P and Ta elemental distributions, and (e) EDS spectra.

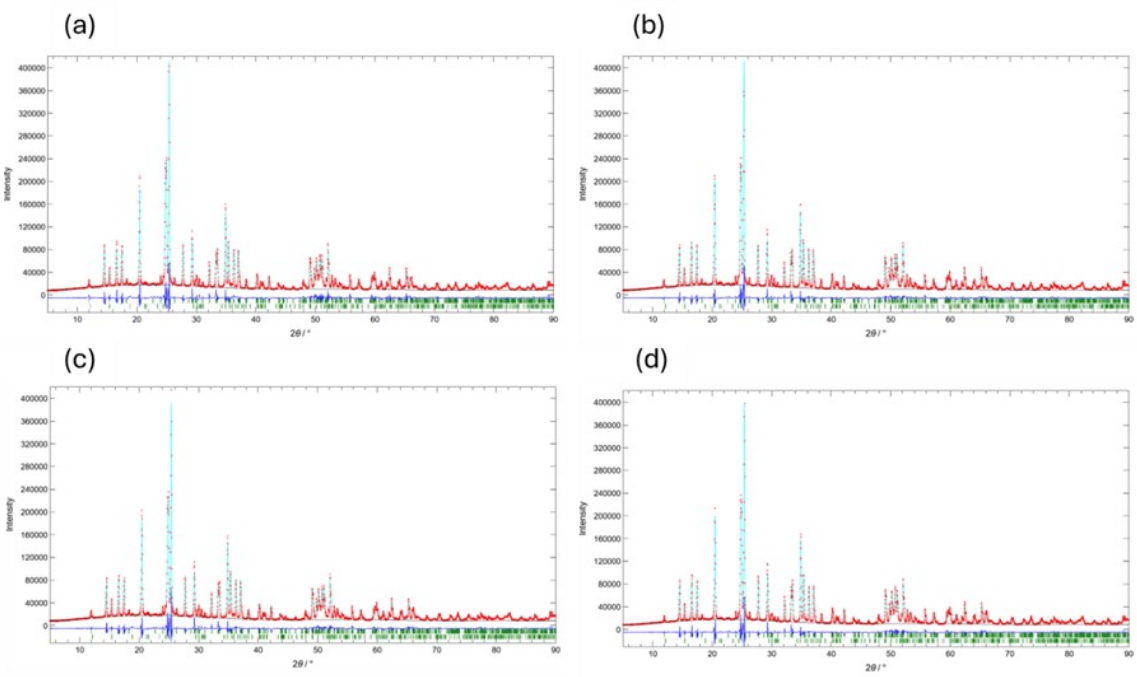

Fig. S4 Rietveld refinement of the XRD patterns for the (a) sample A, (b) sample B, (c) sample C, and (d) sample D. Observed (red plus marks), calculated (light blue solid line), and differences between the observed and calculated patterns. The short vertical lines below the profile indicate the peak positions of all the possible Bragg reflections of $LiTa_2PO_8$ and $LiTa_3O_8$.

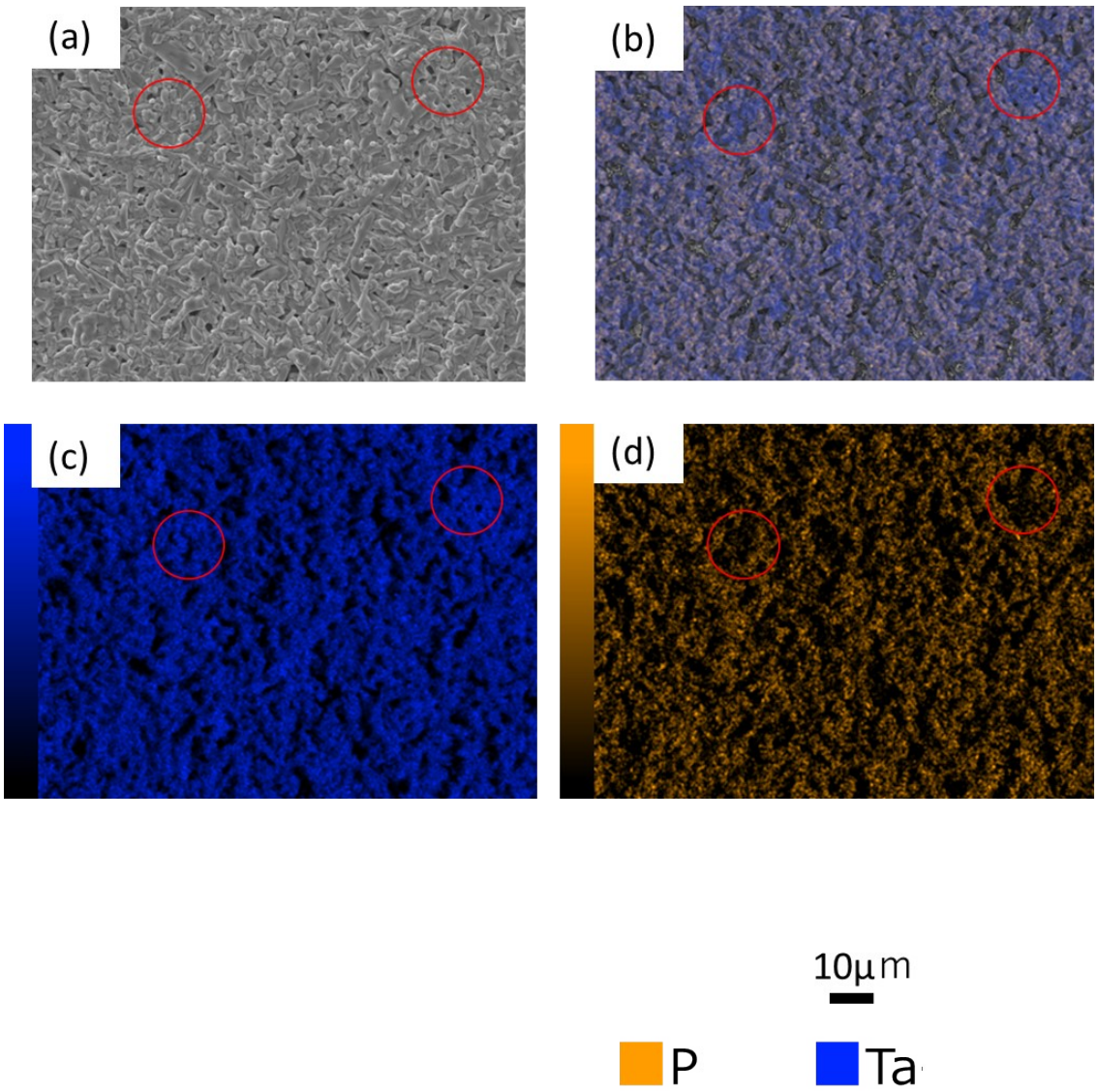

Fig. S5 (a) SEM image, (b) P and Ta, (c) P, and (d) Ta elemental distributions on the surface of the sintered sample B.

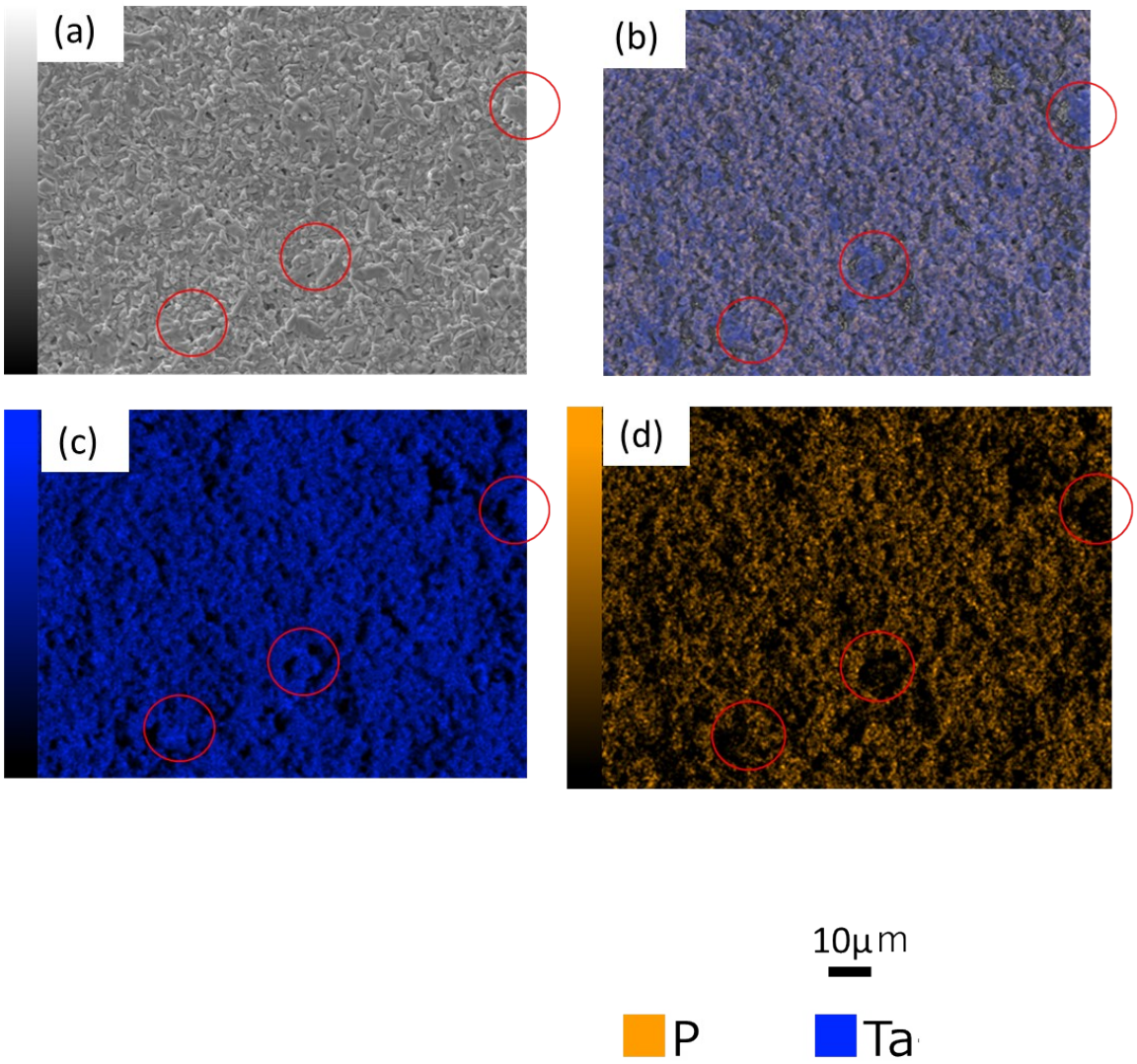

Fig. S6 (a) SEM image, (b) P and Ta, (c) P, and (d) Ta elemental distributions on the surface of the sintered sample C.

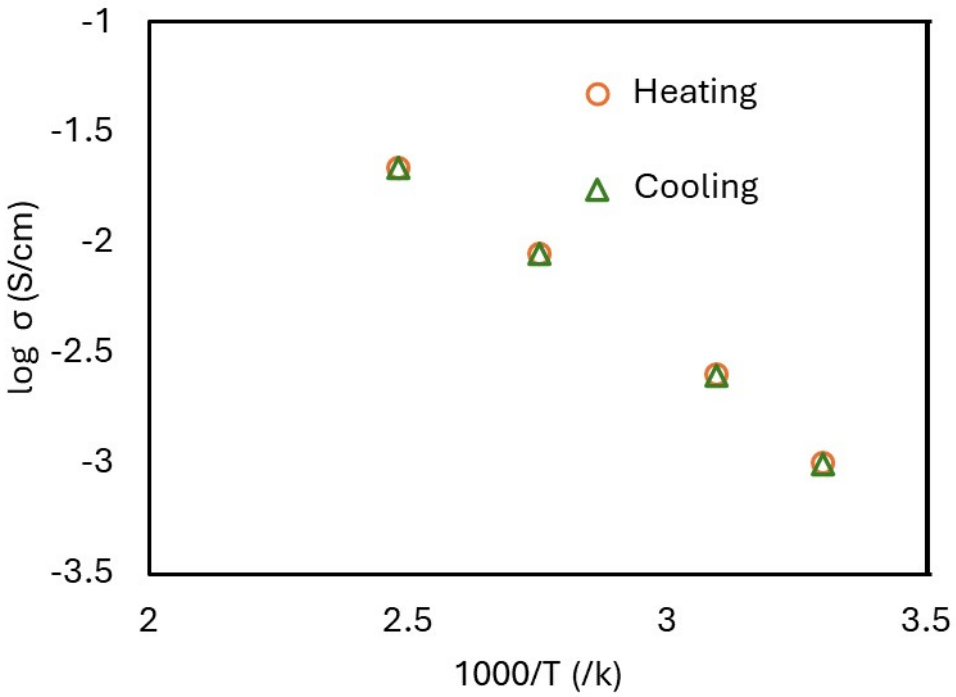

Fig.S7 The Arrhenius plots of the total ionic conductivity of the sample D before and after heating at 200 ˚C. Orange circles and green triangles corresponds to heating (before the heat treatment) and cooling (after the heat treatment) processes, respectively.

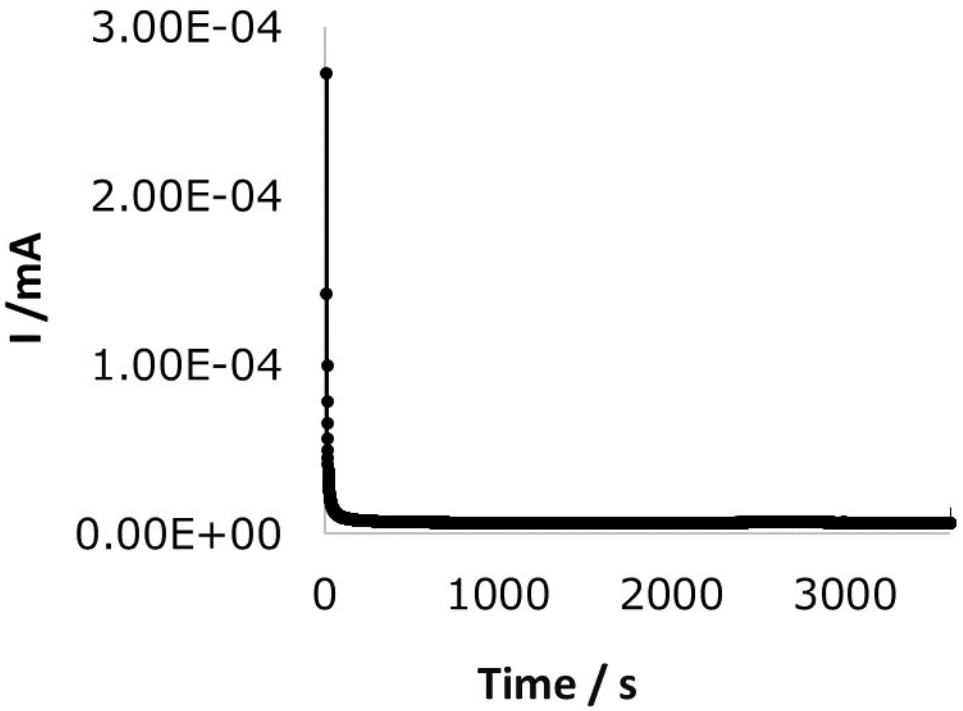

Fig. S8 Direct-current polarisation curves of the sintered sample D, measured at 30 ℃ with 100 mV voltage using blocking Au electrodes.