Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY INFORMATION

Reducing the environmental footprint of solid-electrolytes - a green synthesis route for LATP

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Table S1 Overview of energy input for all major synthesis steps.

Process step	Energy in kWh		
	Literature standard (19)	LATP-c	LATP-e
Preparation aluminiumacetate solution	0.218	-	-
Gravimetry	8.949		
Mixing solution	0.143	0.143	0.143
Drying	13.878	13.878	13.878
Milling		0.095	0.095
Calcination	11.208	11.208	
Sintering	12.791	12.791	12.791
Total	47.187	38.115	26.907

CO_2 output during synthesis was calculated based on the energy input of the synthesis and the CO_2 output of the German energy mix in Feb. 2023 of 420 g/W.

Table S2 Reduced synthesis materials.

Educt	LATP standard	Proposed synthesis
LiOH	82.03 g/kg	82.03 g/kg
$Ti[OCH(CH_3)_2]_4$	555.29 g/kg	555.29 g/kg
H_3PO_4	383.40 g/kg	319.50 g/kg
$Al[OOCH_3(OH)_2]$	70.41 g/kg	-
$AlPO_4$	-	79.54 g/kg

Amount of synthesis material needed for the standard LATP synthesis and the proposed, optimized route. An additional CO_2 reduction by 28.69 g/kg LATP is achieved by substituting Aluminium acetate for Aluminium phosphate.

Cost reduction was calculated based on the amounts and prices taken from Sigma Aldrich in Feb. 2023.

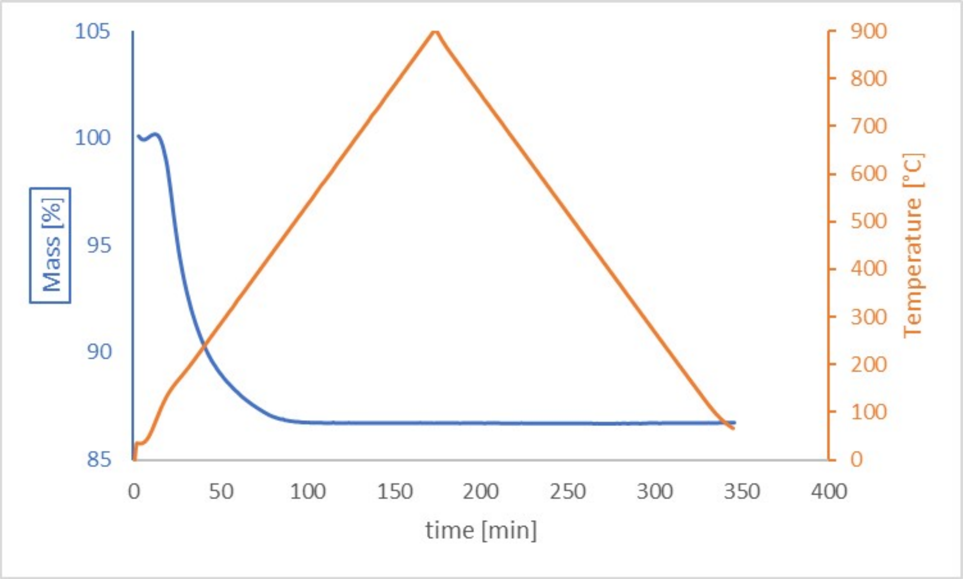

Figure S1 TGA data of the calcination reaction of LATP-c.

The reaction is finished at 530°C. The calcination temperature is therefore set to 600°C.

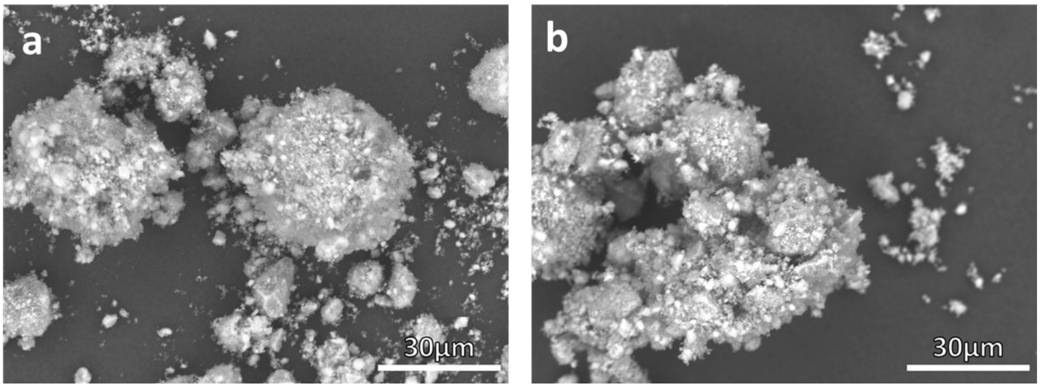

Figure S2 c: SEM picture of the calcined LATP-c powder after wet milling and drying; d: SEM picture of the dried LATP-e powder after wet-milling and drying.

Table S3 Elemental Distribution of the sintered pellets, normalized for P=3.

	Li [mol]	Al[mol]	Ti [mol]	P [mol]
LATP-c	1.5	0.49	1.5	3
LATP-e	1.55	0.47	1.59	3

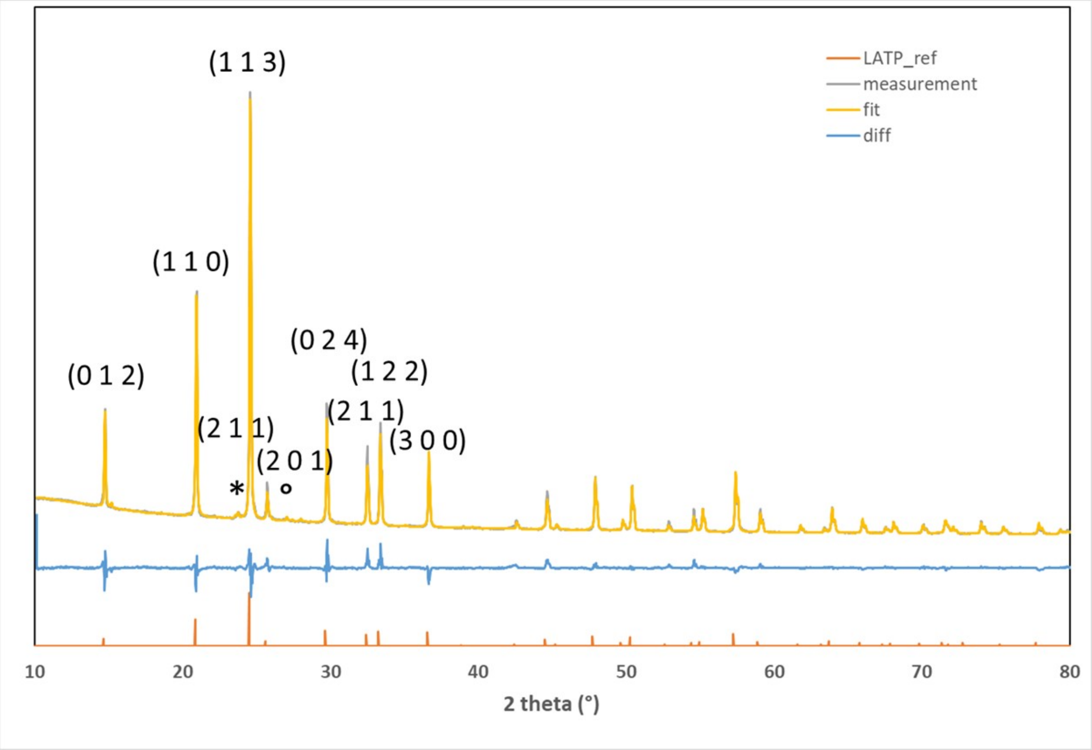

Figure S3 Rietveld refinement of a sintered LATP Pellet from LATP-c powder.

Rietveld refinement of the XRD data of a sintered pellet from LATP-c powder. * marks the orthorhombic LATP phase, ° marks the LTP secondary phase.

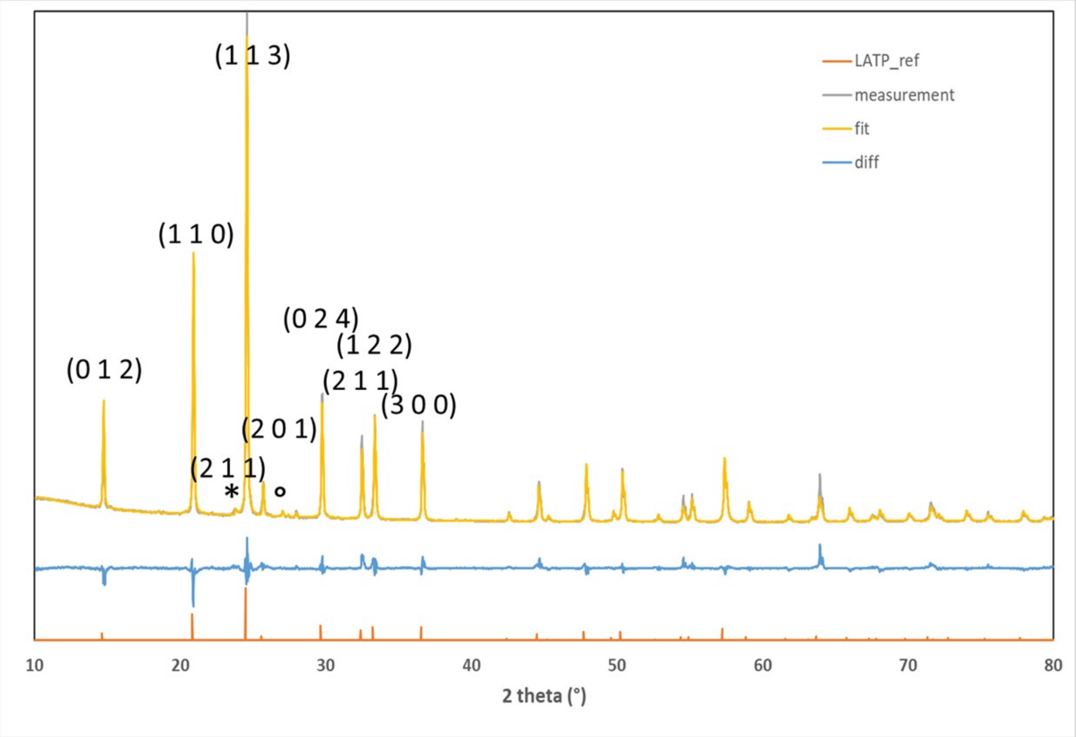

Figure S4 Rietveld refinement of a sintered LATP pellet from LATP-e powder.

Rietveld refinement of the XRD data of a sintered pellet from LATP-e powder. * marks the orthorhombic LATP phase, ° marks the LTP secondary phase.

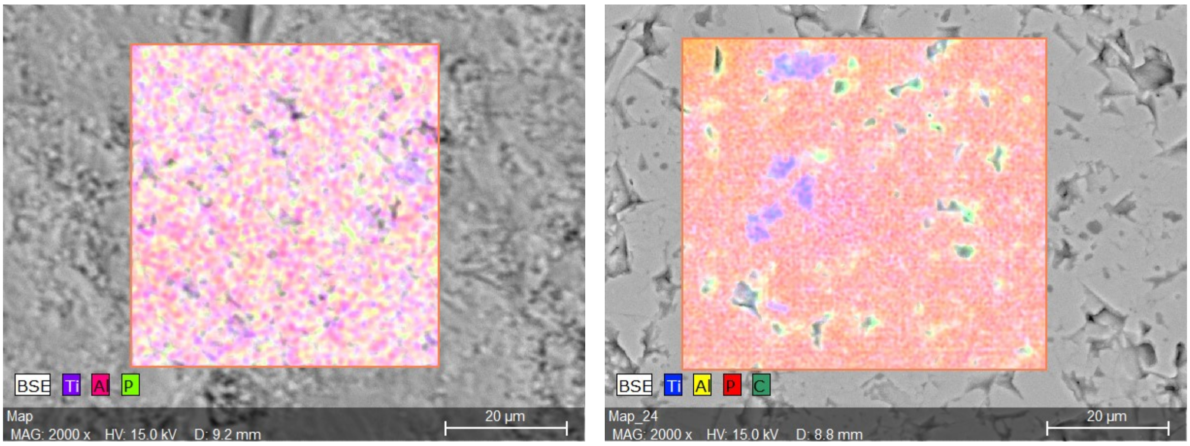

Figure S5 left: EDX mapping of a sintered LATP-c pellet cross-section; right: EDX mapping of a sintered LATP-e pellet cross-section.

Both samples show a uniform distribution of elements in the bulk material. A secondary phase with lowered Al-content is visible in distinct grains.

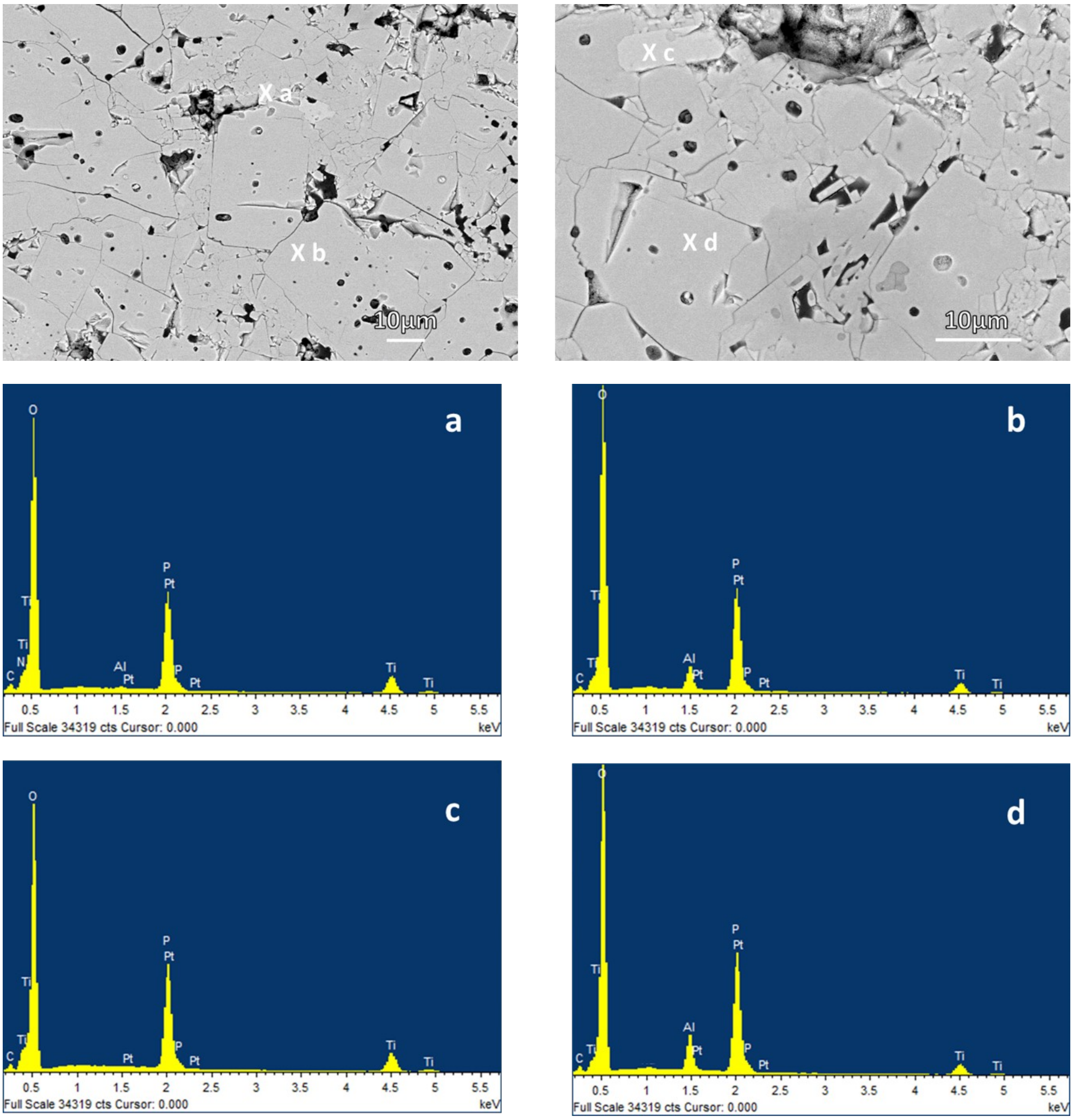

Figure S6 EDX spectra of a) LATP-c secondary phase; b) LATP-c main phase; c) LATP-e secondary phase; d) LATP-e main phase.

EDX spectra of both the LATP-c material (point a and b) and the LATP-e material (point c and d) were taken on the secondary phase and the main phase. The secondary phase shows a significant reduction in Al-signal.

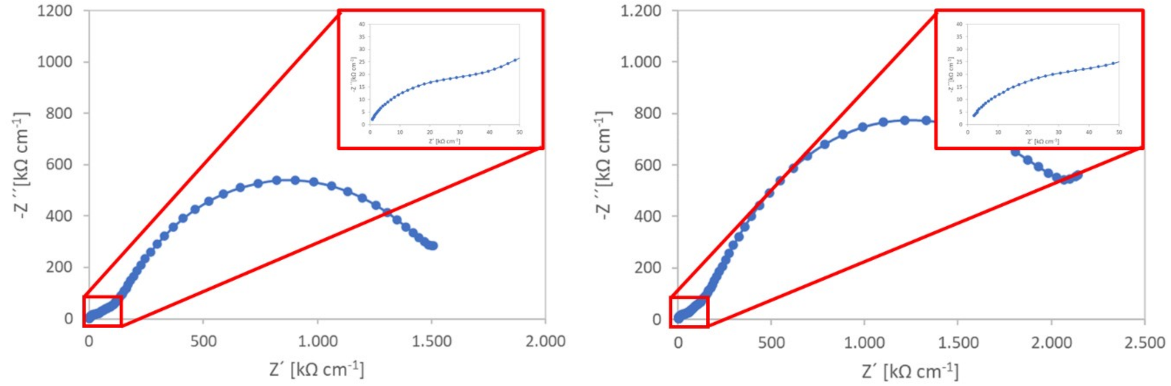

Figure S7 left: Impedance measurement of the LATP-c sample at -100°C, right: Impedance measurement of the LATP-e sample at -100°C.

At lowered temperatures, the semi-circle corresponding to the grain boundary resistance can be seen in the low frequency range. The corresponding the capacitance is $2.4 \cdot 10^{-9}$ F for LATP-c and $2.13 \cdot 10^{-9}$ F for LATP-e.

The semi-circle corresponding to the bulk resistance can be seen in the high frequency range (magnified inset). The capacitance is $5.3 \cdot 10^{-12}$ F for LATP-c and $5.9 \cdot 10^{-12}$ F for LATP-e.