



OPEN Chemical compatibility at the interface of garnet-type Ga-LLZO solid electrolyte and high-energy Li-rich layered oxide cathode for all-solid-state batteries

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All-solid-state batteries (ASSBs) with a garnet-type solid electrolyte have been considered promising alternatives to traditional batteries with a liquid organic electrolyte, due to their enhanced safety and ability to accommodate high energy density electrodes. In this study, we conducted a comprehensive investigation of the high-temperature chemical compatibility between the garnet-like $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Ga-LLZO) electrolyte and high-energy-density Li-rich layered $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode (LNM). Our findings suggest that a high temperature reaction between the Li-rich cathode and Ga-LLZO occurs at 700–900°C depending on the form of reactants. This reaction results in the formation of $\text{La}(\text{Ni}, \text{Mn})\text{O}_3$ and Li_2ZrO_3 as the two main products, as confirmed by powder X-ray diffraction and transmission electron microscopy analysis. Li_2ZrO_3 was discovered for the first time as a reaction product, and its formation in the case of Li-rich layered cathode material was rationalized with DFT + *U* calculations. The results were also compared with those obtained for a typical layered high-energy-density cathode material $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811).

The booming electric vehicles industry calls for high-energy-density and safe batteries¹. An attractive approach to boost an electrochemical performance of automotive batteries is the application of high-energy-density electrodes like lithium-metal anode, providing the highest possible theoretical specific capacity of 3860 mA·h·g^{−1}^{2–4}. However, the conventional Li-metal batteries with liquid organic-based electrolytes encounter a number of issues like poor Coulombic efficiency, significant Li-metal anode volume expansion/contraction upon cycling, and Li dendrite formation^{5,6} promoting high risk of short-circuit, electrolyte decomposition and hazardous thermal runaway⁷. In turn, a safe employment of Li metal anode is possible by replacing the liquid organic electrolyte with ceramic Li-ion conducting solid electrolyte, i.e. moving towards all-solid-state batteries (ASSB) that is beneficial not only for energy density but also for safety due to mitigated dendrite formation, albeit not completely⁸. In turn, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), doped with Al or Ga in order to stabilize a highly Li-ion conductive cubic phase (S.G. $I\bar{3}d$), is considered as one of the most promising solid electrolytes for ASSBs due to a high Li-ion conductivity of 10^{-4} – 10^{-3} S/cm^{9–13} and wide electrochemical stability window of 0.05–5 V vs. Li^+/Li ^{14–17}. Unlike other classes of solid electrolytes, such as NASICON-based $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP)¹⁸ and $\text{Li}_{3x}\text{La}_{2/3-1/3x}\text{TiO}_3$ (LLTO) with perovskite structure^{19,20} LLZO is chemically inactive with respect to metallic Li.

Meanwhile, the fabrication of proper cathode-electrolyte interface (CEI) in ASSBs usually requires a high temperature sintering (700–900 °C), and ASSBs may suffer from high interfacial resistance originated from the mutual diffusion of cathode and electrolyte components with the formation of non-conductive interfacial phases and/or cathode/electrolyte crystal structure degradation^{21,22}. Therefore, understanding high temperature treatment impact on the structure and phase composition of CEI is crucial for the development of sustainable ASSBs. For this purpose, numerous studies of the sintering processes of LLZO-based electrolytes and the most widespread commercial cathode materials LiCoO_2 (LCO), LiFePO_4 (LFP), LiMn_2O_4 (LMO), and $\text{LiNi}_x\text{Mn}_y\text{O}_2\text{O}_z$ (NMCXYZ) have been reported over the decade^{23–31} (Supplementary Table S1). Thus, no remarkable chemical reaction was reported between LLZO and LCO at the temperature up to 900°C^{23–25,27} except the transformation

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of LLZO from cubic to tetragonal phase at the LLZO/LCO interface³². For NMC materials ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ - NMC111, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ - NMC622, $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ - NMC811) the reaction with LLZO-based electrolytes was shown to occur at 700–900 °C, which leads to the formation of LaTMO_3 (TM = Ni, Co, or Mn), $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}_4\text{LiNiO}_8$ products regardless the NMCXYZ composition^{23,25–27,30,33}. $\text{LiM}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (rock salt phase) and NMC-like structures with partial replacement of M by Zr were also proposed³³. Higher chemical reactivity with respect to LLZO-based electrolyte was observed for LMO. So, $\text{La}_2\text{Zr}_2\text{O}_7$, Li_2MnO_3 , LaMnO_3 , and $\text{La}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ reaction products were found after Ta-doped LLZO/LMO co-sintering at > 600 °C^{23,27} and even lower temperature 400–500 °C is required to activate the chemical reaction in thin films²⁹. Finally, LFP demonstrated the lowest chemical stability towards LLZO-based electrolytes as far as $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$, Fe_2O_3 , and Li_3PO_4 reaction products were detected when LFP and LLZO were fired at quite moderate temperature of 300–400 °C^{23,24,28}.

Nevertheless, besides all the abovementioned cathode materials, there are also so-called Li-rich layered oxides $\text{Li}_{4/3-x}\text{Ni}^{2+}_x\text{Mn}^{4+}_{2/3-x}\text{Co}^{3+}_x\text{O}_2$ (Li-rich NMCs), which attract particular attention as delivering record electrochemical capacity as high as 270 mA·h·g^{−1} and energy density > 1000 W·h·kg^{−1}³⁴. They are considered as next generation high-energy positive electrode materials, and their outstanding electrochemical performance is provided by joint cationic ($\text{Ni}^{2+} \rightarrow \text{Ni}^{3+/4+}$, $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$) and anionic ($2\text{O}^{2-}/\text{O}_2^{n-}$, $n < 4$) redox activity³⁵. However, partially irreversible O-framework oxidation at high potentials (> 4.5 V vs. Li^+/Li) with subsequent gaseous O_2 release^{36–38} hinders the practical application of Li-rich NMCs in Li-ion batteries with organic-based liquid electrolytes due to safety issues, which is albeit not the problem for ASSBs based on ceramic LLZO electrolyte. Moreover, the stability of LLZO at high potentials (up to 5 V vs. Li^+/Li) makes it a perfect candidate to match with Li-rich layered oxide cathodes, since Li-rich NMCs are high-voltage cathodes and should be cycled up to 4.8 V vs. Li^+/Li . Surprisingly, to the best of our knowledge, there is a lack of information on chemical interaction of the Li-rich layered transition metal oxides and LLZO during high temperature co-sintering.

Herein we report on high-temperature chemical compatibility of $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Ga-doped LLZO) solid electrolyte and $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (LNM) Co-free Li-rich cathode materials with different morphologies. The results were compared with those for the typical and extensively studied Ni-rich NMC cathode (NMC811), taken as a reference material. Combined *ex-situ* scanning and transmission electron microscopy as well as powder X-ray diffraction studies provided the meaningful data on the microstructure, crystal structure, chemical and phase composition of the interface layer formed at various temperatures. In addition, DFT + *U* calculations were carried out in order to understand the difference in the main reaction products observed for Li-rich and Ni-rich layered oxides. Our studies will potentially contribute to the building of ASSBs with high energy density electrodes.

Methods

Solid electrolyte synthesis

Ceramic samples of $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Ga-LLZO) were obtained via solid-state synthesis. Before the synthesis, La_2O_3 (Sigma-Aldrich, ≥ 99.9% purity) and ZrO_2 (Sigma-Aldrich, ≥ 99% purity) were dried at 900 °C and Li_2CO_3 (Sigma-Aldrich, ≥ 99% purity) was dried at 400 °C overnight. To prepare the Ga-LLZO pellets, stoichiometric amounts of La_2O_3 , ZrO_2 , Ga_2O_3 (Sigma-Aldrich, ≥ 99.9% purity) and Li_2CO_3 with 10 wt% excess were mixed in isopropanol using a SPEX ball-mill for 1 h. Then the resulting powder was dried and pressed into 30 mm pellets using a uniaxial press with the load of 2 tones. After pressing, the pellets were placed into corundum crucibles being covered on all sides with the parent powder to prevent reaction with the crucibles and minimize Li losses. Pellets were sintered at 1100 °C for 10 h in air (heating rate 300 °C/h). After sintering, the pellets were crushed into powder again with an agate mortar and pestle and milled in a planetary ball mill (10 min, powder to milling balls mass ratio 1:40, 650 rpm, zirconia jar and 5 mm balls) under acetone. Dried powder was then pressed into pellets of 10 mm in diameter and ~ 1.2 mm in height using uniaxial press with the load of 2 tones followed by isostatic pressing with the load of 300 MPa. Final sintering was performed at 1100 °C for 18 h in air (heating rate 300 °C/h) with parent powder coverage. The obtained Ga-LLZO electrolyte pellets were polished with SiC paper and ethanol (FEPA grit size 800, 1200, 2000 and 4000) and further stored in an Ar-filled glovebox to prevent them from reacting with air and moisture³⁹.

$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (LNM) cathode material synthesis

The $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ carbonate precursor was synthesized via co-precipitation and hydrothermal routes. For co-precipitation, 150 mL of 1 mol/L aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Sigma Aldrich, ≥ 99%) with the molar ratio $\text{Ni}^{2+}:\text{Mn}^{2+} = 0.25:0.75$ along with 150 mL of an aqueous solution containing 1 mol/L Na_2CO_3 as a precipitation agent and 0.5 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ as a complexing agent were simultaneously pumped into a 500 mL continuously stirred batch reactor under Ar atmosphere. The reactor was pre-filled by 20 vol% with distilled water. The feeding rate of both solutions was about 1 mL/min, and the continuous stirring was kept at 800 rpm. The temperature of the reactor was maintained at 56 °C, while pH was fixed at 7.7–7.8. After co-precipitation, the mixture was aged with continuous stirring at 56 °C for 12 h.

For hydrothermal synthesis, 0.5 mol/L aqueous solution of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (RusKhim, ≥ 99% purity) with the molar ratio $\text{Ni}^{2+}:\text{Mn}^{2+} = 0.25:0.75$ was mixed with an aqueous solution of 0.5 mol/L Na_2CO_3 and ascorbic acid (0.028 mol per 1 mol of TM) with the volume ratio of 1:3. The mixture was placed into a 100 mL Teflon-lined hydrothermal reactor with 70 vol% loading and kept at 235 °C for 4 h under continuous stirring.

The obtained $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ precipitates were filtered, washed with distilled water, and dried under dynamic vacuum at 110 °C overnight. For the lithiation step, the stoichiometric amounts of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ and pre-ground and dried Li_2CO_3 were carefully mixed for 10–20 min in an agate mortar. The resulting mixture was further annealed at 500 °C for 5 h and at 850 °C for 12 h in air with intermediate regrinding. Finally, the

obtained cathode powders were stored in an Ar-filled glovebox. $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode materials obtained via co-precipitation and hydrothermal synthesis are further denoted as LNM_c and LNM_h.

$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) cathode material synthesis

The TM hydroxide precursor $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ was synthesized via co-precipitation method. Aqueous solution of TM sulfates ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, $\geq 99\%$) with the molar ratio $\text{Ni}^{2+}:\text{Mn}^{2+}:\text{Co}^{2+} = 0.8:0.1:0.1$ and total concentration of 2 mol/L ($V = 1300$ mL) was slowly pumped into a 5 L continuously stirred tank reactor, pre-filled with 1250 mL of 0.85 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ under Ar atmosphere. Simultaneously, aqueous solutions ($V = 1300$ mL) of 4 mol/L NaOH (SigmaAldrich, $\geq 99\%$) as a precipitation agent and 300 mL of 4 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ as a complexing agent were pumped into the reactor under Ar. The feeding rate of both solutions was about 5 mL/min, and the continuous stirring was kept at 1000 rpm. The reactor temperature was maintained at 50 °C and pH was fixed to 11.0–11.1. After co-precipitation, the resulting reaction mixture was kept at 50 °C under stirring for about 16–17 h for aging. The obtained precursor was centrifuged, washed with distilled water several times and dried at 90 °C for ~12 h under dynamic vacuum. The dried hydroxide precursor was mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$ (Ruskhim, $\geq 99\%$) in a molar ratio of 1:1.05 and annealed at 750 °C for 12 h in O_2 flow to produce NMC811.

Co-sintering of the cathode material and solid-state electrolyte

The deposition of LNM and NMC811 layers on the Ga-LLZO electrolyte pellets was carried out by screen printing technique. For this purpose, pastes were prepared from the powders of cathode materials together with a terpineol binder (Heraeus V006, Germany) in the 1:1 mass ratio. The pastes were printed through a stencil polymer mesh VS-Monoprint PES HT PW 100/40 (Verseidag-Techfab, Germany) by means of a rubber squeegee blade. The subsequent thermal treatment of Ga-LLZO samples with electrode layers was carried out at 700–900 °C for 3 h in air. Then the samples were transferred and stored in an Ar-filled glovebox.

In order to analyze the reaction products of LNM/NMC811 and Ga-LLZO upon high temperature co-sintering, electrolyte pellets were grinded into fine powder using the ball mill and mixed with the corresponding cathode materials in the ratio of 1:1 by volume. The resulting mixture was pressed again into pellets and sintered at 700, 800–900 °C for 3 h in air. Afterwards, the PXRD studies with subsequent quantitative analysis using the Rietveld method were performed to estimate the mass fraction of each phase in the co-sintered mixture.

Materials characterization

Relative density measurement

The geometric density of the Ga-LLZO samples was determined by dividing the mass by the physical dimensions of the pellets. The relative densities were determined by dividing the geometric density by the theoretical one.

Powder X-ray diffraction (PXRD)

PXRD patterns were collected using a Huber G670 Guinier diffractometer with a $\text{Co K}_{\alpha 1}$ radiation source and Ge (111) monochromator ($\lambda = 1.788996$ Å) and Bruker D8 Advance diffractometer with a Cu K_{α} radiation source ($\lambda_1 = 1.54056$ Å, $\lambda_2 = 1.54439$ Å) and energy-dispersive position-sensitive LYNXEYE XE detector. The LeBail and Rietveld refinements were performed using the Jana2006 software⁴⁰.

Thermogravimetry-differential scanning calorimetry (TG/DSC)

TG/DSC measurements were carried out with a Netzsch STA-449 thermogravimetry – differential scanning calorimeter under artificial air flow. The mixed cathode-electrolyte powders were heated at 3 °C/min rate in the 25–900 °C temperature range. To diminish the influence of heat capacity and processes occurs in individual compounds, the Ga-LLZO and cathode powders in the same ratio as in the studied mixture were placed in the reference crucible.

Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Quantitative chemical element analysis for Ga-LLZO electrolyte was performed with the inductively coupled plasma-optical emission spectroscopy (ICP-OES) using ICP-6810 spectrometer (Shanghai Macy Instrument). Aqueous solutions for analysis were prepared by dissolving ~0.1 (for Ga and Zr element analysis) and 0.22 g (for Li and La measurements) of powder in 10–15 mL of a solution of nitric and hydrochloric acid (1:3 vol. ratio) with subsequent dilution to 200 and 250 mL, respectively, with deionized water. The calibration solutions were prepared by dissolving corresponding amounts of standard solutions containing La, Li, Ga and Zr elements (Inorganic Ventures) in aqueous 0.1 mol/L HNO_3 to obtain solutions with concentrations ranging from 1.0 mg/L to 10.0 mg/L.

Morphology

The morphology and particle size distribution of the cathode powders and Ga-LLZO pellets were analyzed using ThermoFisher Quattro S and Tescan Solaris scanning electron microscopes (SEM). Particle size distribution and mean particle size were calculated with deep-learning analysis of electron microscopy images⁴¹. Intensity profiles were plotted and analyzed with the Gatan Digital Micrograph software. The signal averaging was performed from a 60 micrometers wide region.

Transmission electron microscopy (TEM)

Focused ion beam SEM (FIB-SEM) was used for TEM specimen preparation with a FEI Helios G4 PFIB, equipped with a focused Xe-ion beam system and a Tescan Solaris equipped with a focused Ga-ion beam system. Pt and Pt/C were deposited as a protective layer. Trench milling was performed at 30 keV, 3.2 nA, 52° with the

respect to electron beam using ion beam, U-cut - at 30 keV, 1 nA, -10° . Thinning of the lamella was done in 3 steps: (1) 30 keV; 0.1 nA, $49.5\text{--}54.5^\circ$; (2) 30 keV, 30 pA, $50\text{--}53.5^\circ$; (3) 2 keV, 20 pA, $56\text{--}47^\circ$. Selected area electron diffraction (SAED) patterns, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive X-ray spectra and elemental maps in the STEM mode (STEM-EDX) were acquired on a probe aberration-corrected FEI Titan Themis Z electron microscope supplied with a Super-X system for energy-dispersive X-ray (EDX) analysis at 200 kV.

Automatic slice & view (ASV)

Sample preparation for ASV was performed with FIB-SEM technique using a FEI Helios G4 PFIB, equipped with a focused Xe-ion beam. The volume of the area of interest of the cathode/solid electrolyte was removed slice by slice using FIB (30 kV, 1 nA) and SEM images (5 kV, 0.1 nA) were acquired during the slicing process (slice thickness was 10 nm). The set of SEM images was processed in the Avizo software package including segmentation, final 3D visualization and video of the cutting process.

DFT + *U* calculations

Density functional theory (DFT) calculations were performed using the projected augmented plane wave method, with the Vienna ab initio Simulation Package (VASP)⁴² and facilitated by the high-throughput python-based package SIMAN⁴³. All calculations were conducted within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form⁴⁴ for the exchange–correlation functional. The electron–ion interaction was described with the projector augmented wave (PAW) method⁴⁵. To take into account the strongly correlated nature of the *d*-electrons of manganese, a Hubbard correction is utilized within the Dudarev scheme⁴⁶. Gaussian smearing with a smearing width of 0.1 eV was used for Brillouin-zone integrations. All calculations were performed with spin polarization, assuming ferromagnetic ground state. The plane-wave kinetic energy cutoff was set to 400 eV, and the Gamma-centered *k*-point mesh with a *k*-spacing less than $0.5 \text{ \AA}^{-1}$. This optimization process employed a quasi-Newton algorithm until the maximum force permitted for any vector component was less than $0.05 \text{ eV \AA}^{-1}$. More details on calculations and discussion provided in Supplementary note: DFT + *U* calculations.

Results and discussion

The crystal structure, composition and morphology of the carbonate precursors $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ synthesized via co-precipitation and hydrothermal methods and hydroxide precursor $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ have been analyzed before annealing with the lithium source. PXRD patterns (Supplementary Fig. S1–S2, Table S2) demonstrate that all precursors are single phase materials and exhibit the trigonal MnCO_3 structure (JCPDS #44-1472, S.G. $R\bar{3}c$) or $\beta\text{-Ni}(\text{OH})_2$ structure (JCPDS #74-2075, S.G. $P\bar{3}m1$) for $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ and $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ compounds, respectively.

After the lithiation step, PXRD patterns demonstrate a single-phase Li-rich layered O3-type $C2/m$ structure (Supplementary Fig. S4, Table S4–5) for the LNM_c, LNM_h samples⁴⁷ and O3-type $R\bar{3}m$ structure (Supplementary Fig. S5, Table S4, 6) for NMC811. According to the SEM data (Supplementary Fig. S3, S6 and Table S3), the powders of cathode materials inherit the morphology of the carbonate/hydroxide precursors and consist of spherical particles with an average size of $8.66 \pm 0.07 \text{ }\mu\text{m}$, $0.70 \pm 0.02 \text{ }\mu\text{m}$, and $5.94 \pm 0.08 \text{ }\mu\text{m}$ for the LNM_c, LNM_h, and NMC811 materials, respectively. The Ni: Mn ratio for LNM and the Ni: Mn: Co ratio for NMC811 materials, calculated using quantitative EDX analysis, agree well with the expected 3:1 and 8:1:1 ratios, respectively, within a standard deviation (Supplementary Table S7).

In turn, the obtained Ga-LLZO is also a single phase and crystallizes in cubic garnet-type structure (S.G. $Ia\bar{3}d$) with $a = 12.974(7) \text{ \AA}$ (Supplementary Fig. S7, Table S8). Chemical composition was determined via ICP-OES (Supplementary Table S9) being in a good agreement with the expected $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ stoichiometry. SEM images of the sintered Ga-LLZO pellets (Supplementary Fig. S8) demonstrate high relative density, which achieves 95% of the crystallographic one calculated from Rietveld refinement. The homogeneous distribution of Ga, La, Zr and O throughout the Ga-LLZO sample was validated by STEM-EDX elemental mapping (Supplementary Fig. S9). Quantitative EDX analysis revealed the Ga: La: Zr ratio of 5(1):55(3):40(3), which is close to 4:58:38 expected for stoichiometric $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$.

The results of the Rietveld refinement on the co-sintered LNM/NMC811 and Ga-LLZO powders are summarized in Supplementary Table S10–11 and Fig. 1, while corresponding PXRD patterns are provided in Supplementary Fig. S10–S18. After co-sintering of Ga-LLZO and NMC811 at $700\text{--}800^\circ\text{C}$, the tetragonally distorted Ruddlesden–Popper (RP) phase $\text{La}_4\text{Li}(\text{TM})\text{O}_8$ (S.G. $I4/mmm$, $a \approx 3.77 \text{ \AA}$, $c \approx 12.62 \text{ \AA}$, TM = Ni, Mn, Co) was found to be the reaction product, constituting 9 wt% of the final mixture. After raising the reaction temperature to 900°C , the mass fraction of $\text{La}_4\text{Li}(\text{TM})\text{O}_8$ reached $\approx 15.6 \text{ wt\%}$, and another product Li_2ZrO_3 was observed in a trace amounts ($\approx 2.3 \text{ wt\%}$). To our knowledge, the formation of Li_2ZrO_3 was not reported as a reaction product between Ga-LLZO and Li-stoichiometric NMC cathode materials, although it was detected sometimes in LLZO-based materials as an admixture^{48–51}. Noteworthy, that the noticeable intensity redistribution between the 003 and 104 diffraction maxima of the NMC811 phase takes place after high-temperature annealing with Ga-LLZO (Supplementary Fig. S16–S18), which is a consequence of increasing TM (mainly Ni^{2+}) content at the Li site⁵² amounting to 13.83(9)%, 21.29(8)% and 23.04(8)% after co-sintering at 700, 800 and 900°C , respectively.

In contrast to the reference NMC811, in the case of LNM_c, Li-free cubic $\text{La}_2\text{Zr}_2\text{O}_7$ (S.G. $Fd\bar{3}m$, $a \approx 10.8 \text{ \AA}$) and trigonal $\text{La}(\text{Ni}, \text{Mn})\text{O}_3$ perovskite (S.G. $R\bar{3}c$, $a \approx 5.5 \text{ \AA}$, $c \approx 13.2 \text{ \AA}$) as well as $\text{La}_3\text{Li}(\text{Ni}, \text{Mn})\text{O}_7$ with tetragonal RP structure (S.G. $P4_2/mnm$, $a \approx 5.40 \text{ \AA}$, $c \approx 20.21 \text{ \AA}$) are formed after annealing with Ga-LLZO at 700°C in almost equal amounts. In addition, $<1 \text{ wt\%}$ Li_2ZrO_3 was also detected. The formation of $\text{La}(\text{Ni}, \text{Mn})\text{O}_3$ was frequently observed upon studying the LLZO and NMC co-sintering process^{23,25,27,31,53–55}. After increasing the

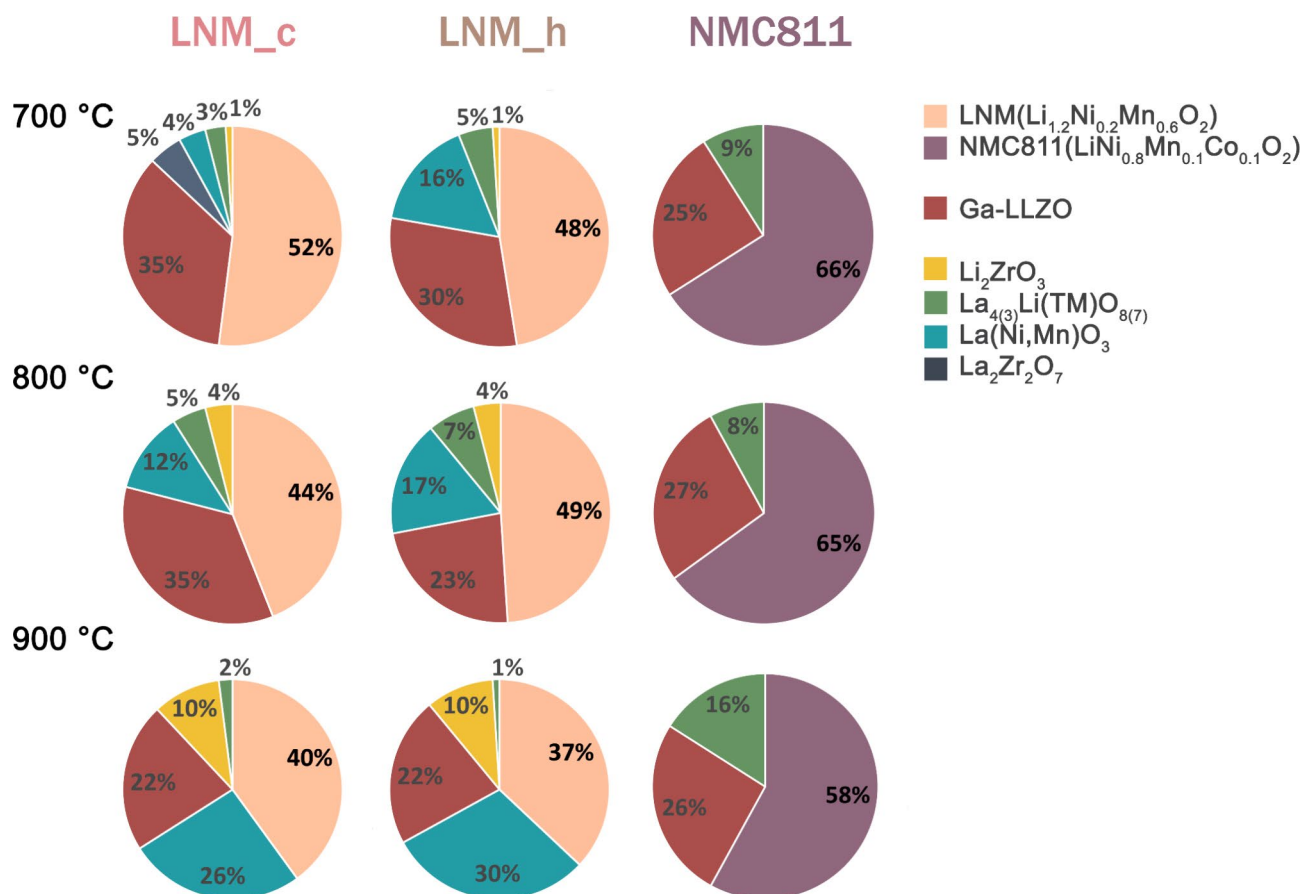


Fig. 1. Phase fractions (wt%) of the resulting products for Ga-LLZO and LNM/NMC811 powders sintered at 700, 800 and 900 °C for 3 h, estimated via quantitative analysis using the Rietveld method.

temperature to 800 and 900 °C, La₂Zr₂O₇ phase disappears, but La(Ni, Mn)O₃ and Li₂ZrO₃ fractions increase significantly and together constitute >1/2 of the resulting mixture, while La₃Li(Ni, Mn)O₈ transforms to La₄Li(Ni, Mn)O₈, and its concentration goes down. The same behavior can be traced for LNM_h material except of two features. First, the concentration of La₂Zr₂O₇ is one order of magnitude lower for LNM_h (≈0.4% wt%) than that for LNM_c (≈5% wt%) after annealing with Ga-LLZO at 700 °C (Fig. 1). Therefore, as far as LNM_h possesses much lower particle size (higher free surface area) than LNM_c and, hence, should have been more active in solid-state reaction with Ga-LLZO, we assume that La₂Zr₂O₇ is not the final, but intermediate product of the reaction between Li-rich layered cathode material and Ga-LLZO, and it can be observed only at moderate temperatures (up to 700 °C). Second, La₄Li(Ni, Mn)O₈ is formed after co-sintering of LNM_h and Ga-LLZO even at 700 °C, and its mass fraction rises upon increasing the annealing temperature.

Finally, we can conclude that Li-rich LNM exhibits higher reactivity with Ga-LLZO compared to NMC811, although TG/DSC measurements reveal that the reaction between Ga-LLZO and LNM/NMC811 starts at ~400 °C (Supplementary Figure S19). Regardless of the morphology and sintering conditions, the reaction products make up a larger fraction of the final mixture for LNM compared to NMC811. Moreover, annealing of LNM and NMC811 with Ga-LLZO leads to the formation of different major reaction products. Thus, if La₄Li(TM)O₈ is predominantly formed after co-sintering of NMC811 and Ga-LLZO, Li₂ZrO₃ and La(Ni, Mn)O₃ are mainly produced if LNM/Ga-LLZO mixture is fired at the same conditions. In general, our findings are in agreement with A. Bauer et al.³³, who found that Ni-rich NMC cathode materials tend to form La₄Li(TM)O₈ RP phase after annealing with LLZO-based electrolytes, while Mn-rich cathode materials are prone to form La(TM)O₃ trigonal perovskite at the same conditions, albeit La₄Li(TM)O₈ can also be sometimes found in trace amounts. However, Li₂ZrO₃ as a reaction product of the Ga-LLZO and Li-rich layered oxide was never detected in a noticeable amount in the annealed mixture of LLZO-based electrolytes and conventional NMC-based cathode materials. LNM and NMC811 cathode materials were additionally co-sintered with Ga-LLZO at 900 °C in Ar flow (20 ml/min), and PXRD results are given in Supplementary Figure S20. In this case, for both LNM and NMC811 materials a significant fraction of the tetragonal Ga-LLZO phase were found. The formation of tetragonal LLZO from cubic LLZO after annealing in inert N₂ flow was earlier reported by Paoletta et al.³⁹

Further, aiming to investigate how the different high-temperature reaction pathways for LNM and NMC811 materials affect the microstructure of the cathode/Ga-LLZO electrolyte interface (CEI), cathode powders were applied on the top surface of Ga-LLZO solid electrolyte pellets by screen printing technique as described in the experimental part. Then, the Ga-LLZO pellets with cathode layers were annealed at 700, 800 and 900 °C for 3 h

in air. An overview and high-magnification cross-section SEM images of CEI in the annealed samples are given in Figs. 2 and 3, respectively. Despite the reaction between LNM/NMC811 and Ga-LLZO was proven to occur at 700 °C in the case of intermixed and pressed powder materials, no visible interaction between the LNM/NMC811 layers and Ga-LLZO pellet was observed in the samples annealed up to 800 °C. This difference can be attributed to a much higher contact area between Ga-LLZO and the cathode material in pressed powder samples

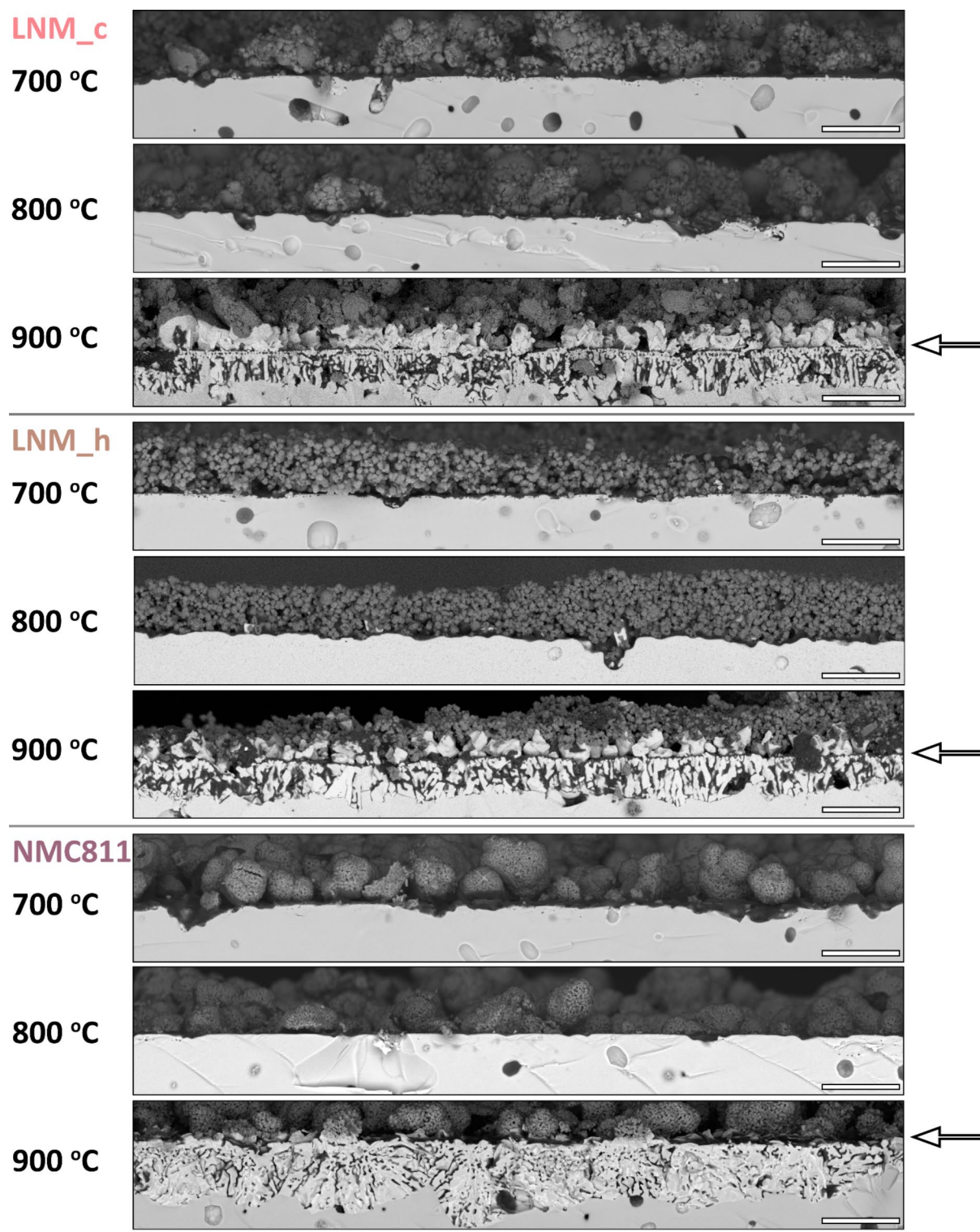


Fig. 2. Overview cross-section SEM images of the CEI between the Ga-LLZO membranes and LNM_c (top), LNM_h (middle), and LNM811 (bottom) cathode layers co-sintered at 700, 800 and 900 °C. Arrows indicate the position of the CEI before annealing. Scale bar is equal to 10 μm .

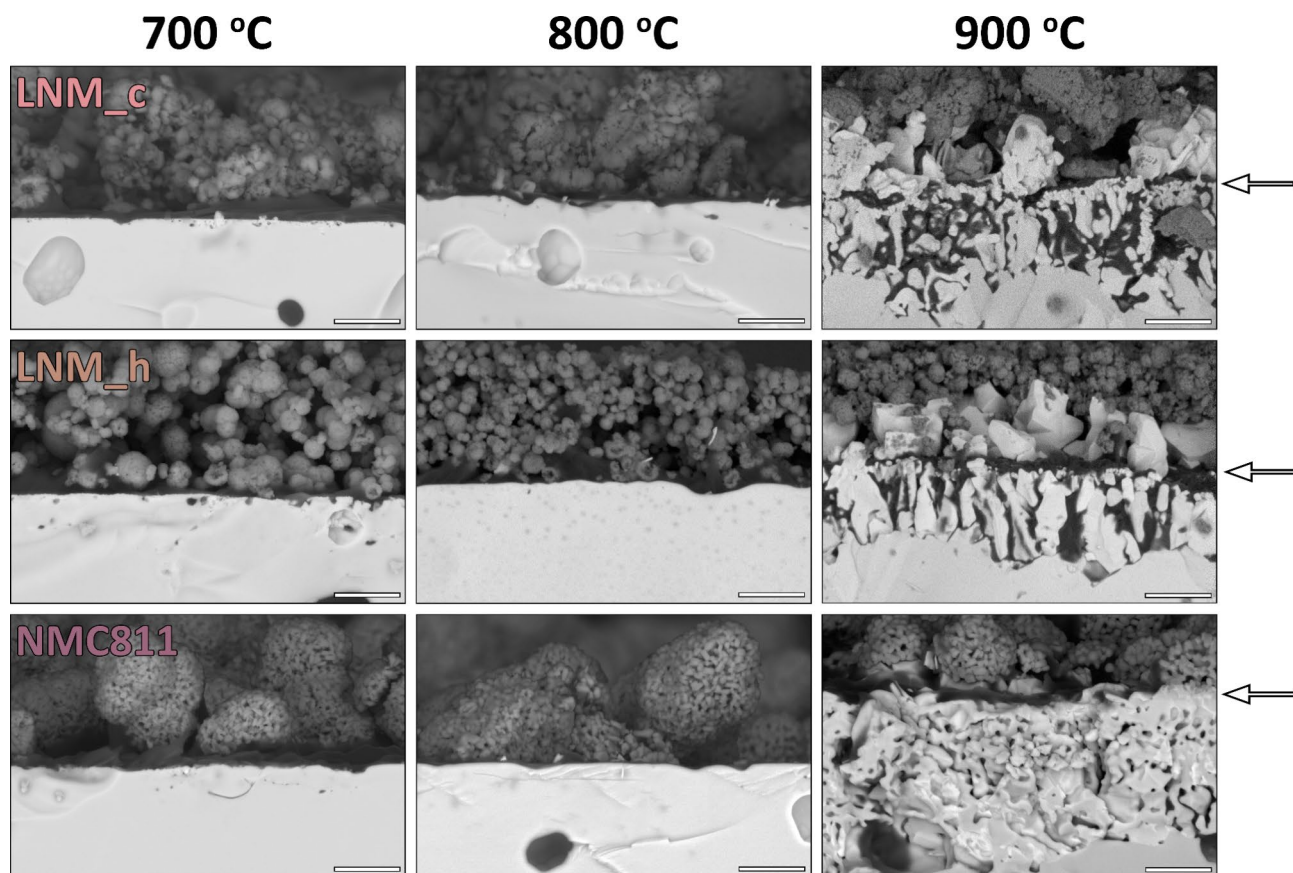


Fig. 3. High magnification cross-section SEM images of the CEI between the Ga-LLZO membranes and LNM_c (top), LNM_h (middle), and LNM811 (bottom) cathode layers co-sintered at 700, 800 and 900 °C. Arrows indicate the position of the CEI before annealing. Scale bar is equal to 5 μm .

that promotes the solid-state reaction. Meanwhile, the formation of a very defective layer at the CEI for both LNM and NMC811 materials was detected at 900 °C (Figs. 2 and 3). For the LNM_c and LNM_h materials two distinct reaction zones can be identified in the interface region. The first one (at the electrolyte side below the arrows indicating the CEI position before annealing in Figs. 2 and 3) appears as oblong columns perpendicular to the cathode/electrolyte interface plane. These columns are surrounded by a second phase that appears darker in the backscattered electrons (BSE) in SEM imaging. The second zone (at the cathode side, above the arrows in Figs. 2 and 3) is represented by chunks that envelope the cathode material. The boundaries of the reaction zones are generally parallel to the original CEI. However, in the case of NMC811 only the first type of reaction zone is present, which extends only into the solid electrolyte and does not noticeably affect the cathode layer. Furthermore, the propagation of the reaction zone over the electrolyte pellet is no longer uniform and has a rather radial character. In the cross-section SEM image, this looks like semicircles.

The thickness of the reaction zone at the interface between the cathode and Ga-LLZO electrolyte at 900 °C was estimated from cross-section SEM images by plotting the intensity profile averaged over the region of 60 μm across the CEI (Fig. 4). The left and right sides in the intensity profiles (Fig. 4) represent the solid electrolyte (lower part of the SEM images) and the cathode regions (upper part of the SEM images), respectively. For the LNM cathode materials, the dark-brown and light-brown rectangles represent the two reaction zones at the electrolyte and cathode sides, respectively. As the particle size of the cathode material decreases on going from LNM_c to LNM_h, the thickness of the reaction zone at 900 °C increases due to an increased number of point contacts. Surprisingly, the thickest reaction zone was found in NMC811/Ga-LLZO annealed at 900 °C, even though NMC811 demonstrated the least reactivity towards Ga-LLZO in powder form.

Automatic slice-and-view (ASV) procedure was performed in order to make the 3D reconstruction of the reaction zones formed after co-sintering Ga-LLZO with LNM_c, LNM_h and NMC811. SEM images of the area of interest before ion milling are given in Supplementary Fig. S21. Figure 5 shows the reconstruction results for the reaction zones at the solid electrolyte side. The pore space in the reaction zone constitutes approx. 19, 22, and 13 vol% of the whole CEI for LNM_c, LNM_h, and NMC811 samples, respectively. Pore's spatial distribution pattern is different for these three samples. For LNM_c, pores are segregated at the top part, near the initial LNM_c/Ga-LLZO interface before annealing, while for LNM_h and NMC811 the branched filaments are formed, which penetrate the whole CEI layer, although for NMC811 the distribution of pore filaments exhibits rather radial character. Meanwhile, the average thickness of the reaction zone at the solid electrolyte side was calculated from ASV as 4.7 μm for LNM_c, 5.4 μm for LNM_h and 6.8 μm for NMC811, which agrees with the

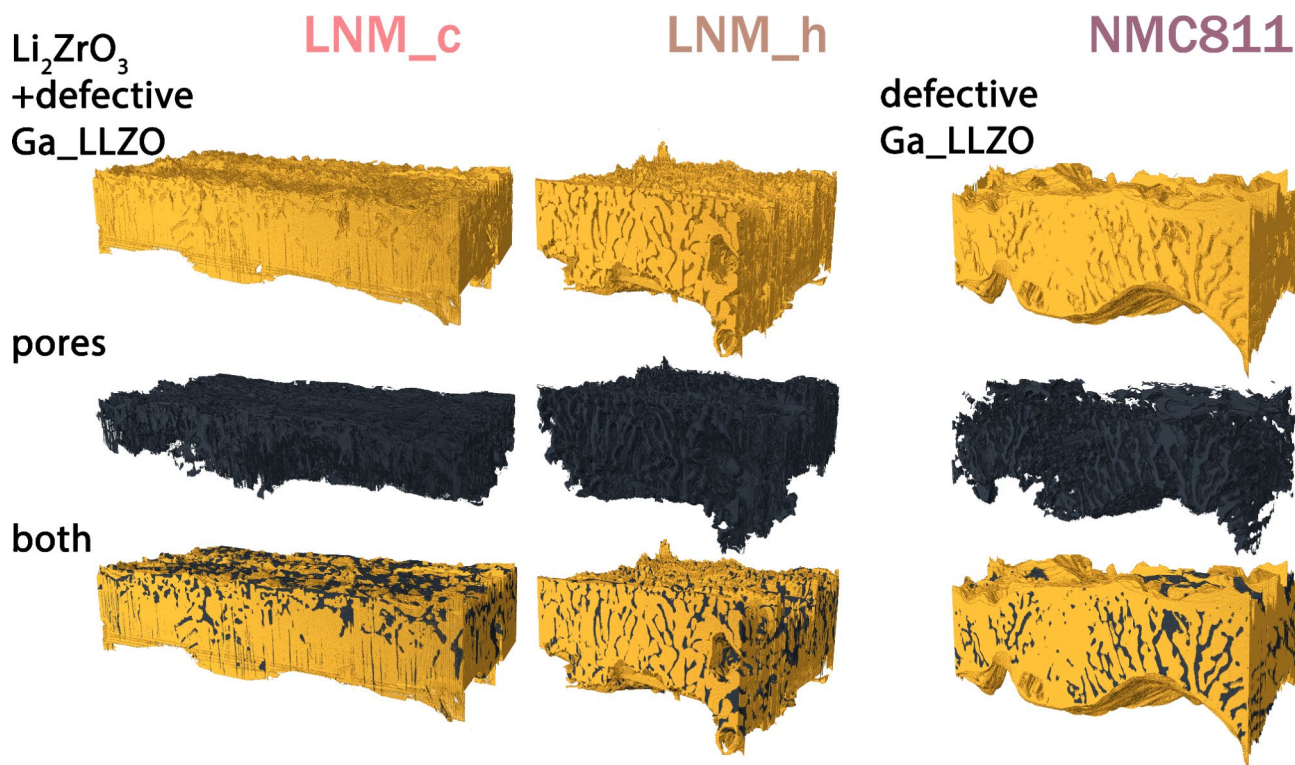
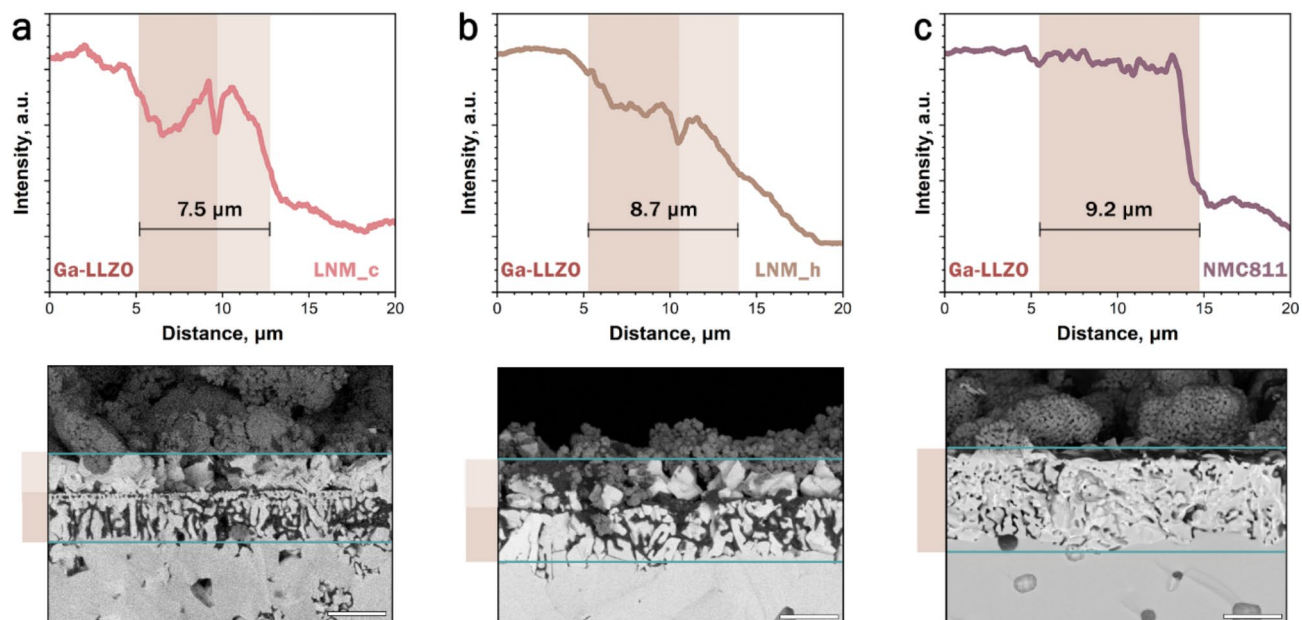


Fig. 5. Slice-and-view reconstruction of the reaction zone at the electrolyte side between the Ga-LLZO membranes and LNM_c (left), LNM_h (middle), and LNM811 (right) cathode layers co-sintered at 900 °C.

results obtained from SEM intensity profiles. Thus, with a decrease in the particle size (i.e. an increase in the number of contact points between cathode and electrolyte particles), the reaction proceeds more intensively, forming a thicker reacted layer at the interface. Unfortunately, the reaction zone at the cathode side is difficult to separate from the cathode itself due to poor contrast, which hinders the segmentation process.

The local crystal structure and composition of the CEI formed at 900 °C was investigated for LNM_c, LNM_h and NMC811 via transmission electron microscopy on lamellar samples. The STEM-EDX compositional maps for all the samples are given in Figs. 6, 7 and 8. It should be mentioned that FIB-SEM with a focused Ga-ion beam was used for the sample preparation. The Ga ions tend to incorporate into the thin cross-section samples disabling assessment of Ga distribution via STEM-EDX. Four phases can be distinguished at the LNM_c/Ga-LLZO interface (Fig. 6). The bottom part of the lamella consists of pure Ga-LLZO. Then, moving upward, Zr-rich cyan areas are found. This phase is present as elongated areas surrounded by Ga-LLZO. Taking into account the PRXD data, it can be assigned to Li_2ZrO_3 . Next, the top part of the image is occupied by the phase enriched with La and TM, which fits well with $\text{La}(\text{Ni}, \text{Mn})\text{O}_3$. Noteworthy that despite the La:TM ratio for $\text{La}(\text{Ni}, \text{Mn})\text{O}_3$ is close to 1:1 from STEM-EDX data, the Ni:Mn ratio varies in a wide range from 1:4 to 1:1 in this compound.

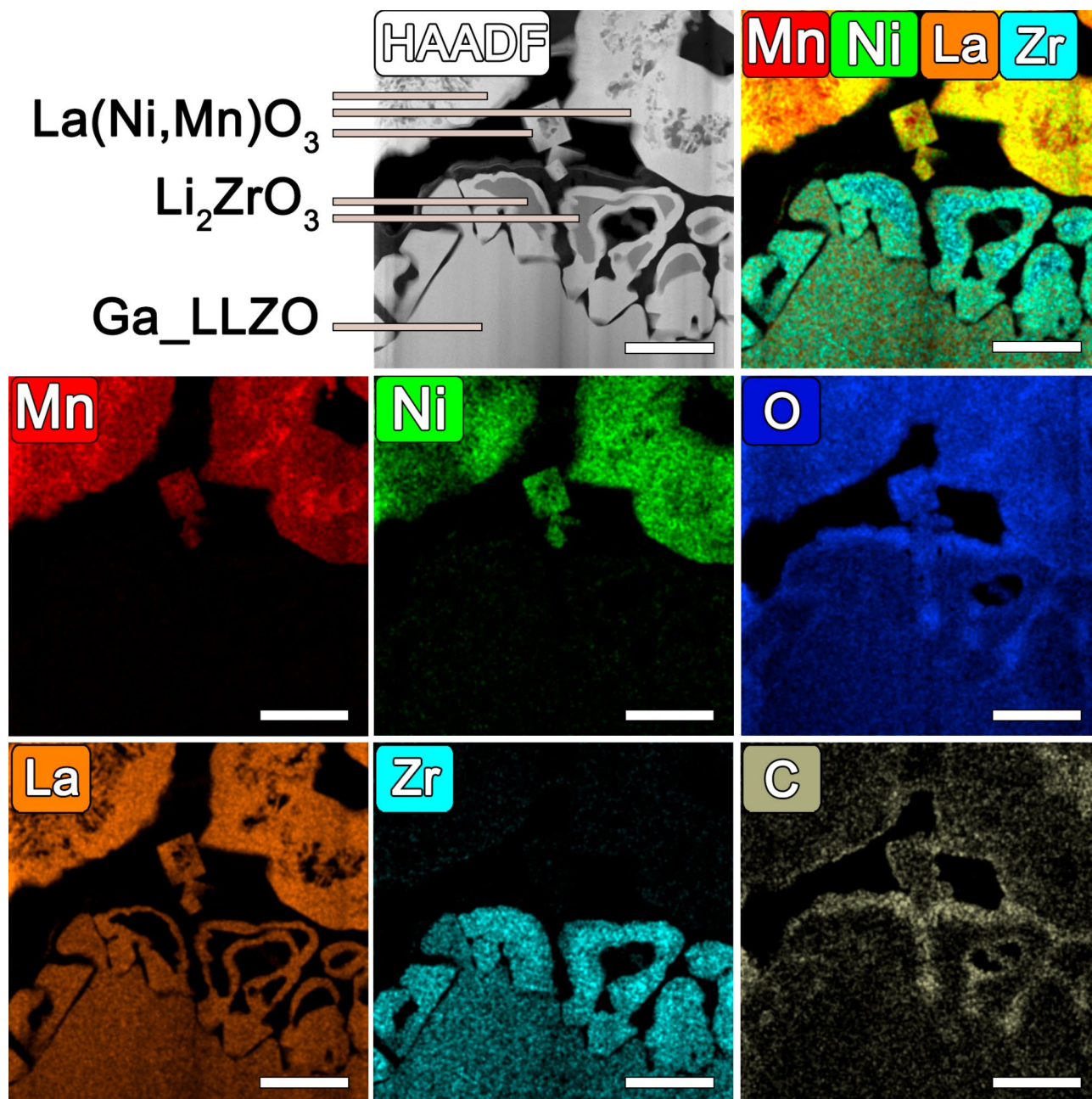


Fig. 6. HAADF-STEM image of the LNM_c/Ga-LLZO interface co-sintered at 900 °C with corresponding color-coded STEM-EDX compositional map and individual elemental maps of Ni, Mn, La, Zr, O, and C. Scale bar is equal to 2 μm.

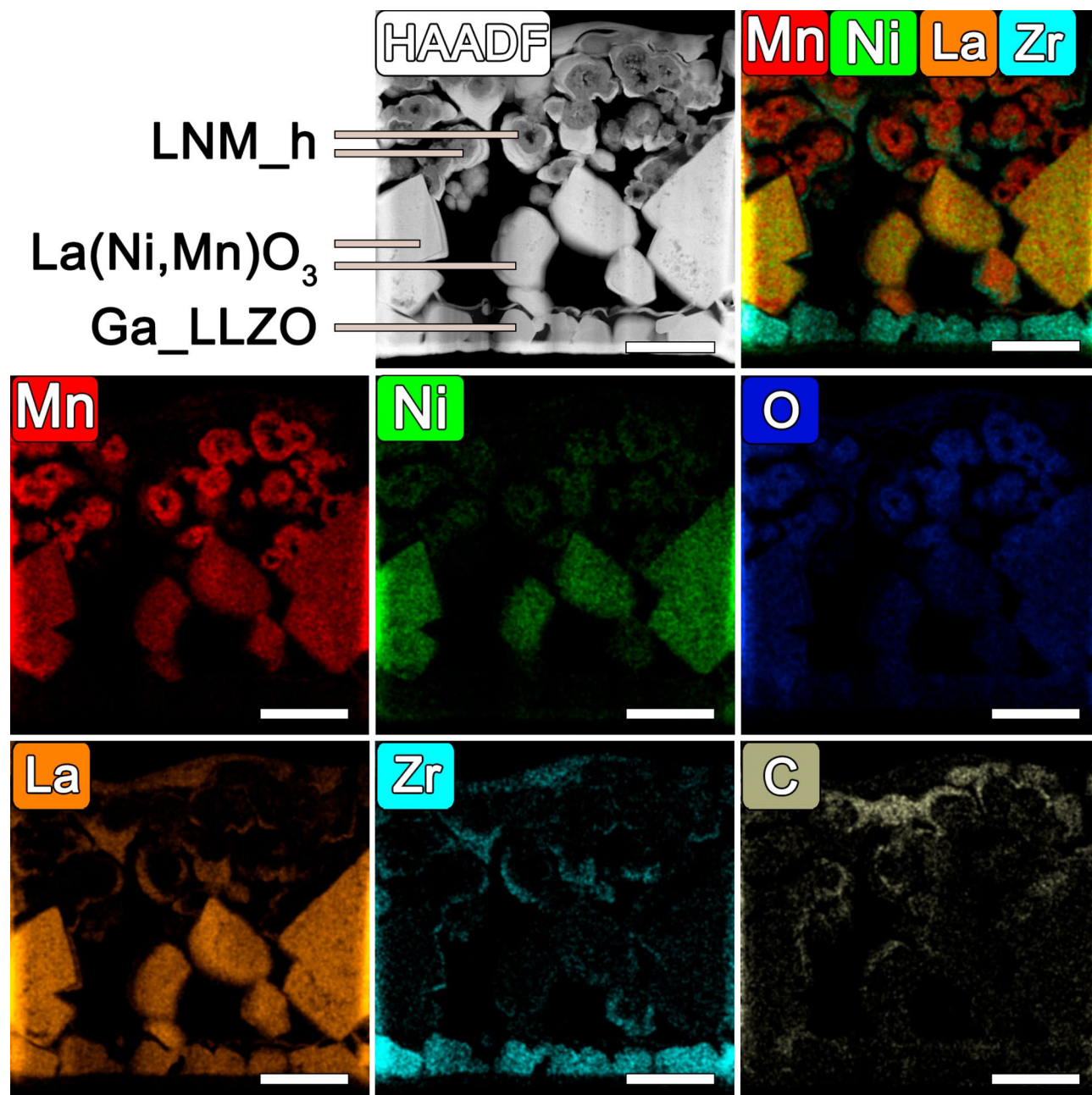


Fig. 7. HAADF-STEM image of the LNM_h/Ga-LLZO interface co-sintered at 900 °C with corresponding color-coded STEM-EDX compositional map and individual elemental maps of Ni, Mn, La, Zr, O, and C. Scale bar is equal to 2 μm.

Remnants of unreacted cathode material can be seen in the upper part of the lamella, although they are strongly overlapped with La(Ni, Mn)O₃ and difficult to distinguish. The STEM-EDX compositional maps for the LNM_h/Ga-LLZO sample (Fig. 7) follow the same pattern as those for LNM_c/Ga-LLZO, although Li₂ZrO₃ was not found here, probably due to the limited area of the lamella. Nevertheless, the faceted La(Ni, Mn)O₃ chunks are well defined as the La and TM rich areas. Particles of the cathode material are visible at the top part of the image. The crystalline nature of the phases and the phase composition was validated via the atomic resolution HAADF-STEM imaging and SAED studies (Supplementary Fig. S22, the detailed description is provided in the caption). La₄Li(TM)O₈ was not found via TEM, most probably due to its low concentration in the LNM/Ga-LLZO samples (<2.5 wt%).

However, the 500 nm layer of La₄Li(TM)O₈ was detected at the NMC811/Ga-LLZO interface (Fig. 8) in the reaction zone at the cathode side. HAADF-STEM image and SAED pattern of this area with detailed description are presented at Supplementary Fig. S23. To the best of our knowledge, for the first time the formation of La₄Li(TM)O₈ was directly evidenced by atomic-resolution imaging for co-sintered LLZO-based electrolyte with Ni-rich NMC cathode (Supplementary Fig. S23). The agglomerated NMC811 particles are visible at the top of the

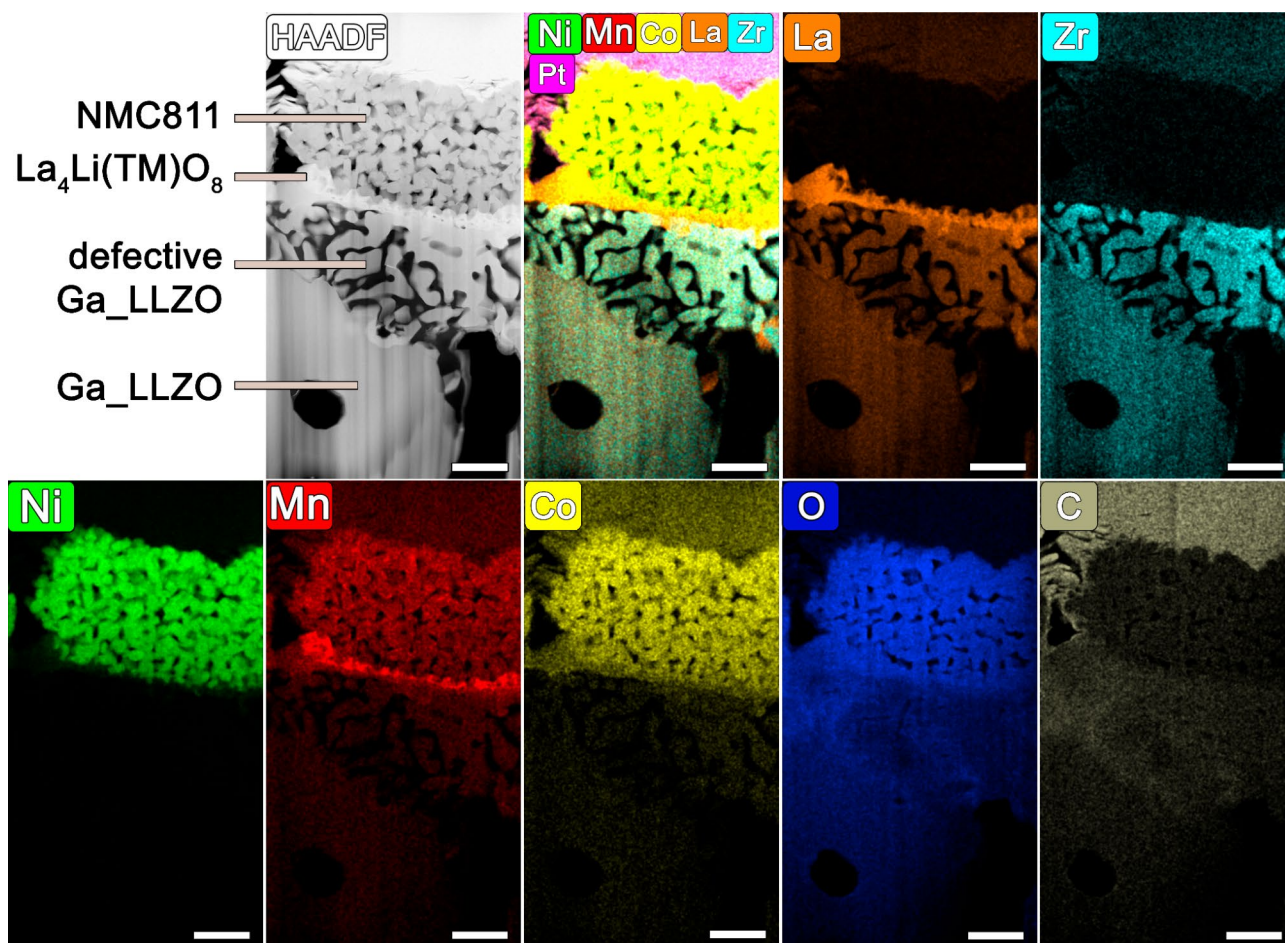


Fig. 8. HAADF-STEM image of the NMC811/Ga-LLZO interface co-sintered at 900 °C with corresponding color-coded STEM-EDX compositional map and individual elemental maps of La, Zr, Ni, Mn, Co, O, and C. The Pt and C signals originate from lamella sample preparation procedure. Scale bar is equal to 2 μm .

image (see also Supplementary Fig. S24). HAADF-STEM images confirm the PXRD results that a pronounced Ni migration to the Li sites takes place in NMC811 upon high-temperature treatment with Ga-LLZO.

To sum up, LNM reacts more intensively with Ga-LLZO than NMC811, albeit the reasons for such behavior are still not fully understood. The only difference between the Li-rich and Li-stoichiometric layered oxides in terms of their reaction with Ga-LLZO is the formation of Li_2ZrO_3 in the case of LNM, which was not reported for NMCXYZ. So, another main product of the reaction between LNM and Ga-LLZO - LaTMO_3 is not unique for Li-rich materials and was also previously observed for NMC111 and NMC622^{23,54}. Therefore, we suspect that it is the formation of Li_2ZrO_3 that is responsible for the high reactivity of Li-rich layered oxides toward LLZO-based solid electrolytes.

In this regard, to elucidate why Li_2ZrO_3 forms in the case of the LNM/Ga-LLZO system, while it is practically absent for the NMC811/Ga-LLZO, we performed DFT + U calculations. For that, we calculated Li_2ZrO_3 formation energies using thermodynamic conditions derived from the equilibrium of phases formed after co-sintering of Ga-LLZO with the cathode materials (see Supplementary Table S11). The considered phases and their calculated total energies are provided in Supplementary Table S12. Chemical potentials for the species were calculated using Eq. (S2) and Eq. (S3) (refer to Supplementary note: DFT + U calculations) and were used to determine the Li_2ZrO_3 formation energies. Here, we considered co-sintering of Ga-LLZO with either LNM or NMC811 cathodes in the ambient atmosphere ($P(\text{O}_2) = 0.21 \text{ atm}$) at $T = 700\text{--}900 \text{ }^\circ\text{C}$ (Fig. 9). Across the entire temperature range, the formation energies of Li_2ZrO_3 for the NMC811/Ga-LLZO system were positive and significantly higher than those for the LNM/Ga-LLZO system, which were negative.

To study the origin of the different Li_2ZrO_3 formation energies for the two types of cathode materials, we calculated chemical potentials ($\Delta\mu_i$) at the average co-sintering temperature and the intermediate U value ($T = 1073 \text{ K}$ and $U = 3 \text{ eV}$). The results are provided in Supplementary Table S13. Since μ_{O} is the same for both cathodes, the difference in formation energies is attributed to the μ_{Li} and μ_{Zr} chemical potentials. Surprisingly, the calculated μ_{Li} value turned out to be lower in the LNM/Ga-LLZO system ($\Delta\mu_{\text{Li}} = -5.81 \text{ eV}$) compared to that in the NMC811/Ga-LLZO system ($\Delta\mu_{\text{Li}} = -5.02 \text{ eV}$). This suggests that Li extraction from LNM is more difficult than from NMC811, making Li_2ZrO_3 formation less favorable in the LNM/Ga-LLZO system (the lower the μ_p , the stronger the element is bound in the structure). However, Zr atoms appeared to be much more reactive

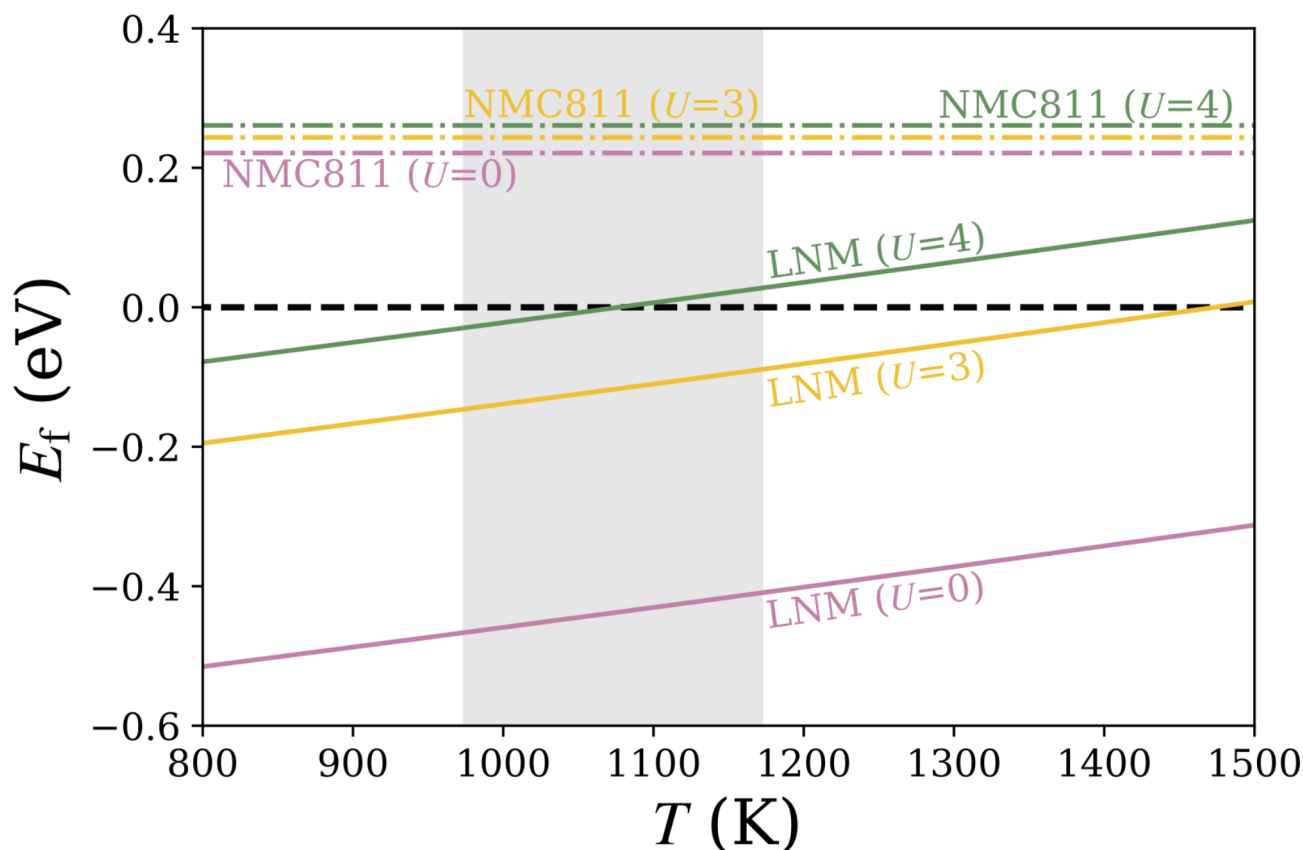


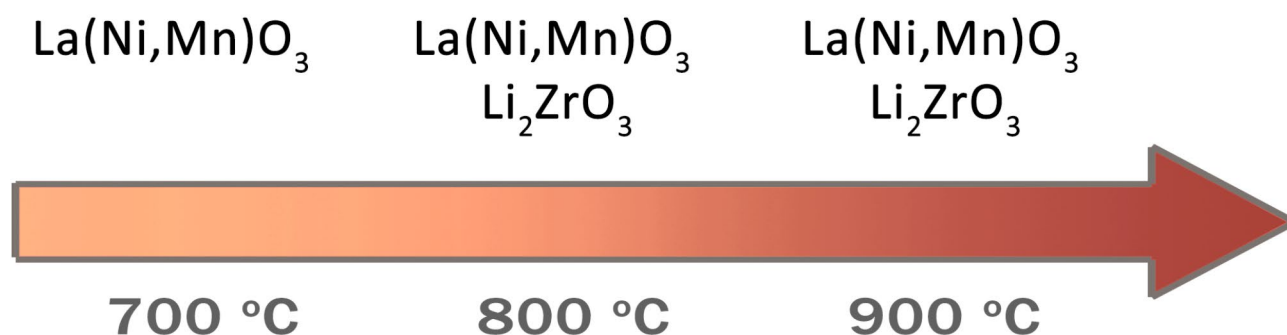
Fig. 9. Formation energies of Li_2ZrO_3 for $P(\text{O}_2)=0.21$ atm in the case of Ga-LLZO co-sintering with LNM and NMC811 cathode materials. The gray shaded area corresponds to the typical co-sintering temperatures of 973–1173 K for the electrode/solid electrolyte interface.

in the LNM/Ga-LLZO system ($\Delta\mu_{\text{Zr}} = -8.64$ eV) rather than NMC811/Ga-LLZO ($\Delta\mu_{\text{Zr}} = -9.80$ eV) at the co-sintering conditions. As a result, the formation of Li_2ZrO_3 is promoted instead of retention of Zr in the LLZO phase. These findings explain why the Li_2ZrO_3 phase is observed at the LNM/Ga-LLZO interface, but not at the NMC811/Ga-LLZO interface.

Conclusions

In this work, we performed a comprehensive investigation of the chemical compatibility between Ga-LLZO solid garnet-type electrolyte and Li-rich $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (LNM) cathode material with different morphologies at high sintering temperatures, which is necessary to ensure a tight contact between the electrolyte membrane and the cathode layer. The main reaction products of LNM/Ga-LLZO co-sintering at different temperatures are compared with that for the NMC811/Ga-LLZO system in Fig. 10. We established that Li-rich layered oxide reacts much more intensively with Ga-LLZO than conventional NMC811 layered cathode material, producing two compounds - $\text{La}(\text{Ni}, \text{Mn})\text{O}_3$ and Li_2ZrO_3 . Presumably, it is the formation of Li_2ZrO_3 that is at the origin of the increased Li-rich layered oxides reactivity toward Ga-LLZO as far as it is the unique product of LNM/Ga-LLZO reaction detected for the first time, while $\text{La}(\text{Ni}, \text{Mn})\text{O}_3$ has been found previously multiple times as the reaction product of Ga-LLZO and NMCXYZ cathodes at high temperatures. The reasons for Li_2ZrO_3 formation in the case of LNM/Ga-LLZO co-sintering were revealed by DFT + U calculations. The formation of Li_2ZrO_3 is promoted by higher Zr reactivity at elevated temperatures as soon as the Li-rich cathode is applied. To conclude, it is clear from our study that building sustainable ASSBs based on an LLZO electrolyte and Li-rich high-energy-density cathode requires using additional buffer layers (such as LiNbO_3 and LiTaO_3 frequently used in ASSB research)^{56–61} at the CEI to prevent the mutual diffusion of the elements and deterioration of the phase composition at CEI that could compromise the battery performance.

LNLM



NMC811

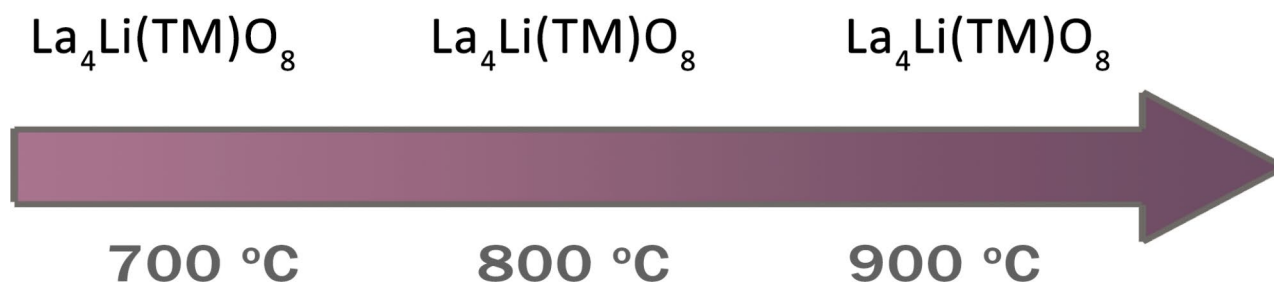


Fig. 10. Schematic representation of the main reaction products (> 5 wt%) between Ga-LLZO and corresponding cathode materials at different co-sintering temperatures.

Data availability

Data sets generated during the current study are available from the corresponding author on reasonable request.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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