Compatibility assessment of solid ceramic electrolytes and active materials based on thermal dilatation for the development of solid-state batteries

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Assembling an all ceramic solid-state battery (ACSSB) using inorganic oxide electrolytes is challenging. The battery must have a continuous layered structure with a thin dense electrolyte separator and interfaces between active material (AM) and ceramic electrolytes (CE) must be optimized within the electrodes to minimize polarization. This is generally achieved using high temperature processing. Selecting suitable AM and CE materials is a complex task that requires a thorough knowledge of the electrochemical behavior of each material in addition to a deep understanding of the thermal and chemical compatibility with other components of the cell. Mismatched thermal expansion coefficients (TECs) of the various layers and materials in the device can lead to cracks during the sintering step and upon cooling that dramatically affect the battery performance. Moreover, it must be certain that no reaction occurs between active materials and electrolytes in the sintering temperature range. These are two key parameters to address for the development of all ceramic solid-state batteries. High temperature x-ray diffraction (HT-XRD) has been used to determine TECs of various well-known oxide AM and CE up to 1000 °C. It is shown that TECs of typical CEs vary between \(-1 \times 10^{-5} \text{ K}^{-1}\) to \(4 \times 10^{-5} \text{ K}^{-1}\) but still remain more stable than that of conventional AMs, which are higher on average. On the basis of TEC, lower mismatch is found for different couples. Chemo-thermal compatibility is then investigated for couples with LiNi\(_0.5\)Mn\(_1.5\)O\(_4\) (LNMO) material. It is determined that mixing Li\(_{0.33}\)La\(_{0.55}\)TiO\(_3\) (LLTO) with LNMO might be an interesting avenue for sintering ACSSB.

Introduction

Lithium ion batteries (LIBs) are the most commonly used batteries for mobile storage because of their high energy density, long cycle life and relatively low cost. Typical LIBs contain organic liquid electrolytes.\(^1\) Despite several advantages of this type of electrolyte (high conductivity and easy formability), solid electrolytes may represent an avenue for future advances in LIB technology, including development for electric vehicles and stationary applications. Safety and energy density are among the main obstacles faced by liquid electrolytes for the most stringent LIB applications. Organic liquid electrolytes are subject to catch fire due to overheating or short-circuiting.\(^2\) Nowadays, the production of LIBs for mobile applications is well controlled and accidents are extremely rare (but not nonexistent). However, the large number of LIBs that are often packed together require higher safety standards as a result of possible chain reactions.\(^3\) Ceramic oxide electrolytes may present a solution for safer and more energy density systems because of their non-flammability and wide potential window. Inorganic oxide electrolytes have relatively good conductivities \((10^{-5} - 10^{-3} \text{ S cm}^{-1})\) at room temperature, high mechanical strength, and high chemical stability.\(^4\) However, assembling an all ceramic solid-state battery with an inorganic oxide electrolyte is challenging as it requires a deep knowledge of the electrochemical, chemical and thermal behavior of each component of the cell.\(^2\)-\(^7\)

The battery must be a continuous layered structure of ceramics with a thin dense electrolyte separator, in order to minimize polarization.\(^8\) Preparing such batteries requires mixing solid electrolytes with active materials and conductive fillers in the electrode part to ensure optimized interfaces between active material and electrolytes. This is often achieved with oxide-based materials via high temperature processing between 600 and 1200 °C.\(^8\)-\(^13\) In the electrolyte part itself, sintering at high temperature allows the ceramic grains to merge, this leads to a reduction of overall porosity. This favors the formation of an efficient lithium ion pathway between the electrolyte particles and the two composite electrodes. It can be noticed than co-sintering of
CE and AM material are not the only way to prepare oxide based ASSB in the literature. For example, infiltration of AM in induced CE porosities or use of additives to allow “cold sintering” are other ways.\(^1\)\(^4\)\(^1\)\(^5\) Besides, most of the works in literature are focused on “solvent assisted” ASSB preparation that consists of the cold mixing of CE and AM with a conducting polymer dissolved in a solvent, conductive fillers to produce composite electrode.\(^1\)\(^6\)\(^1\)\(^7\) Even though the thermal compatibility is not an issue for these systems, the chemical and electrochemical compatibility issue remain and is largely addressed.

When considering continuous layered structure of ceramics, sintering is the most critical step for material compatibility. As processing temperatures are high, the thermodynamic stability of mixed materials can be an issue and it needs to be considered. When instability is expected, the reaction kinetic may help to minimize the chemical reactivity between the electrolyte ceramic and the active material, which will then depend on the sintering technique used and the processing time at high temperature. For example, techniques like Spark Plasma sintering has been preferred due to the fast sintering which requires only few minutes to happen. The products formed are most of the time ion-insulating and electrochemically inactive.\(^1\)\(^8\) In that case, chemical reaction between the active material and the electrolyte should be avoided during thermal processing. Moreover, during cool down, cracks due to thermal dilatation can happen. Cracks decrease the mechanical properties of the battery and are obstacles to Li-ion displacement, so they should also be avoided.\(^1\)\(^9\) Because of that, thermal and chemical compatibility between ceramic electrolytes and active materials must be studied and fully understood.

However, forming multilayer ceramic devices is not new. Ceramic electrolytes are already widely used in solid oxide fuel cells (SOFC). While electrolytes in lithium batteries conduct lithium ions, unlike electrolytes in SOFC which conduct oxygen ions, similar materials can be used in both devices. The preparation of multilayer fuel cell electrolytes has been extensively researched in the past.\(^2\)\(^0\)\(^–\)\(^2\)\(^3\) For example, the effects of stress generated by thermal dilatation have already been addressed in SOFCs as these devices are operated at elevated temperatures. Similarly, to all ceramic battery cells, cracks within the fuel cells are highly detrimental. The primary driving force of crack formation during the fabrication of hybrid ceramics is the stress that is caused by a mismatch in the thermal expansion coefficients \(\alpha\) (TEC) of the various layers/materials.\(^2\)\(^0\) TEC is defined by eqn (1):

\[
\alpha = \frac{1}{L} \frac{dL}{dT}.
\]

Where \(L\) is a length in a direction, such as a cell parameter. Upon cooling, the stress generated \((\sigma)\) between an active and solid electrolyte material can be roughly evaluated by eqn (2) where isotropic elastic behavior of mixed materials is assumed.\(^2\)\(^5\)

\[
\sigma = \frac{\Delta \alpha \Delta T}{E_{a.m} + \frac{1}{E_{c.m}}}
\]

Where \(\Delta \alpha\) is the TEC mismatch between the active material and the solid electrolyte, \(\Delta T\) is the difference between the sintering temperature and the room temperature, \(E_{a.m}\) and \(E_{c.m}\) are the elastic moduli of the active material and the electrolyte material. More accurate methods exist for better prediction of interfacial stresses, such as the Finite Element Analysis which is a model of failure based on the Weibull statistics.\(^2\)\(^6\) Models also depend on the cell geometry (planar or tubular), and on the microstructure of materials.\(^2\)\(^0\)\(^–\)\(^2\)\(^3\) The same methodology used in SOFC research can also be applied for the selection of solid oxide electrolytes and active material for the assembly of all solid-state batteries. However, literature on the TECs for lithium battery materials is scarce. The assessment of the TECs of typical solid electrolytes and active materials is therefore a valuable tool for the careful selection of battery components.

For SOFC devices, the TEC is usually measured using dilatometry.\(^3\)\(^2\) In this work, high temperature X-ray diffractometry (HT-XRD) is chosen such that precise measurements can be directly related to the crystallographic structure of the sample. Moreover, with HT-XRD, the dependence of the TEC on the crystallographic axis can be assessed. It is important to take this parameter into account, because strong anisotropy could result in microcracking when the grain size exceeds a certain critical value during sintering.\(^3\)\(^3\) In-situ XRD also allows structural changes or parasitic reactions that occur with changing temperature to be closely followed.

The aim of this article is to suggest an effective method for the selection of compatible materials for the sintering process of all solid-state ceramic batteries. In the present paper, typical solid electrolytes and active materials for use in lithium ion batteries are studied using HT-XRD with a focus on their respective TECs. Thermal stabilities of three couples are evaluated based on the minimal mismatch of the mean TEC between the AM and the CE. These materials are tested in a classical furnace. The results presented here are intended to be used as a reference guide for battery ceramists.

## Materials and method

### Materials and synthesis

All CE materials were synthesized in the laboratory. Oxide CEs were prepared via solid-state processes while \(\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3\) (LATP) was produced by hydrothermal synthesis.

Prior to synthesizing, \(\text{La}_2\text{O}_3\) was fired at 900 °C overnight to remove carbonate due to its hygroscopic nature.

Phase pure \(\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3\) (LATP) was produced via a hydrothermal process\(^3\)\(^4\) using intermediate product \(\text{Ti}_2\text{O}_5(\text{PO}_4)_2\) obtained from \(\text{TiO}_2\) (99% Sigma Aldrich) stirred in an aqueous solution containing Phosphoric acid (85%) at 160 °C. \(\text{Al(OH)}_3\) (Fisher Scientific) and \(\text{LiOH}\) (98% Sigma Aldrich) were added after cooling at 80 °C. The obtained suspension was dried, ground and finally heated to 900 °C for 6 h.

Polycrystalline \(\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_3\) (LLTO) was prepared by solid state reaction. In order to synthesize 10 g of product, stoichiometric amounts of \(\text{La}_2\text{O}_3\) and \(\text{TiO}_2\) and 10 mol% excess of Li_2CO_3 (to prevent lithium vaporization from occurring during thermal treatments) were mixed in isopropyl alcohol via ball
milling for 24 h at 700 rpm with 12 balls of ZrO₂ (10 mm diameter) in a Fritsch planetary mill Pulverisette. After solvent evaporation, the powder was calcined in an alumina crucible at 1100 °C for 1 h (rate of 20 °C min⁻¹, heating and cooling). The resultant powder was ground using a high energy ball mill (SPEX Mill) using 3.15 g of ZrO₂ ball per gram of powder with 2 wt% of stearic acid. Powder sieved below 45 μm is used in order to press a pellet (diameter = 10 mm) under a pressure of 600 MPa for 30 minutes. The pellet was sintered at 1200 °C for 5 h (heating rate of 10 °C min⁻¹ and cooling rate of 30 °C min⁻¹) using the powder bed technique.

Al-doped Li₉₋₂.₅Al₂.₅₂La₂.₅₂Zr₁₂O₄₂ (AL-LLZO) was prepared via a solid-state process. First, stoichiometric amounts of Al(NO₃)₃·9H₂O, ZrO₂ and La₂O₃ and 10 mol% excess of LiOH·H₂O were ground in a high energy ball mill before being degassed for 12 h at 600 °C. The degassed mixture was then milled for a second time. Part of the resulting powder was pelletized and then placed in a ZrO₂ crucible using the powder bed technique at 900 °C for 10 h.

Three grades of AM layered oxides LiNiₓMn₁₋ₓO₂ were provided by Targray, Canada: LiNi₀.₃₃Mn₀.₆₆Co₀.₆₆O₂ (NMC111), and LiNi₀.₃₃Mn₀.₆₆Co₀.₆₆O₂ (NMC532), and LiNi₀.₃₃Mn₀.₆₆Co₀.₆₆O₂ (NCA). Spinel LiNi₀.₃₃Mn₁₋ₓO₄ (LNO) from Sigma Aldrich was also investigated. LiFePO₄ (LFP, P2) was supplied by Johnson Matthey. LiFe₀.₂₅Mn₀.₇₅PO₄ (LFMP) was synthetized by melt process. Fe₂O₃ metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atomet 1001HP from Rio Tinto-Quebec Metal Powder (QMP)), LiPO₃ made from the dehydration of LiH₂PO₄ (from metal (Atome...
Disorder transition of La$^{3+}$ ions occurs at 1000 °C to the cubic one than to that of the initial material with the high temperature phase is preserved with a structure closer to the impurities are recovered after cooling. The LLTO cell parameters (Fig. 2a) at 30 °C are $a = 7.753(1)$ Å, $b = 7.803(1)$ and $c = 7.706(1)$ Å. These values are in agreement with literature values.\textsuperscript{47,48} Parameters increase linearly to $a = 7.818(1)$ Å, $b = 7.864(1)$ and $c = 7.778(1)$ Å at 900 °C. An order–disorder transition of La$^{3+}$ ions occurs at 1000 °C where the $b$ and $c$ parameters tend to be closer to the $a$ parameter with $a = 7.827(1)$ Å, $b = 7.840(1)$ Å and $c = 7.821(1)$ Å.\textsuperscript{49} After cooling, the high temperature phase is preserved with a structure closer to the cubic one than to that of the initial material with $a = 7.742(1)$ Å, $b = 7.768(1)$ Å and $c = 7.756(1)$ Å which demonstrates the importance of cooling rate to conserve the more conductive disordered phase as well as the good reversibility of the LLTO unit cell (volume of the unit cell is conserved).

XRD was used to determine the TEC of LLTO as shown in Fig. 2b. The TEC was found to remain relatively constant at about $1 \times 10^{-5}$ K$^{-1}$ until 900 °C. There is no evidence of differences between the evolution of the TEC along the $a$, $b$ and $c$ directions which is consistent with the fact that the only difference between the axes is the ordering of La atoms and the rotation of the TiO$_6$ octahedra. At 1000 °C the order–disorder phase transition is responsible for the huge anisotropy of TECs along the $b$ and $c$ directions; these become $-3 \times 10^{-5}$ K$^{-1}$ and $5.5 \times 10^{-5}$ K$^{-1}$ respectively.

Nasicon material LATP. Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (LATP), a part of the NASICON-type structure family and it crystallizes as LiTi$_6$(PO$_4$)$_3$ in the R$3c$ space group. Diffractogram in the range of temperatures between 30 °C and 1000 °C and result of the fit at 30 °C using Le Bail refinement are shown in Fig. 3a (ESI1). The densification of LATP occurs at least at 700 °C.\textsuperscript{50} Small amount of LiTiPO$_5$ are identified in the diffractometer pattern of LATP. LATP is stable up to 800 °C where intensities drop and full width at half maximum (FWHM) increase as a result of a decrease in the measured crystallite size from 250 to 120 nm. XRD analysis allows the evolution of the crystallite size to be followed when it is inferior to 200 nm, even if absolute values must be taken carefully, this evolution is significant and explained below.

LATP cell parameters in air, reported in (Fig. 3a), vary from $a = 8.505(1)$ Å and $c = 20.800(1)$ Å at 30 °C to 8.505(1) Å and 21.430(1) Å at 1000 °C, respectively using the hexagonal unit cell. Cell parameter $a$ remains constant over the temperature range contrary to $c$ which varies significantly. These cell parameters are in good agreement with the experiment conducted under vacuum by Monchak et al. up to 800 °C: this means that LATP is stable and does not release oxygen at high temperatures.\textsuperscript{51} After cooling, the cell parameters are recovered with $a = 8.507(2)$ Å and $c = 20.800(3)$ Å. The different evolutions of the lattice parameters with temperature are likely to lead to significant anisotropy which can be quantified by calculating the TEC.

A strong anisotropy between $a$ and $c$ axis is visible for the TEC of the LATP material in Fig. 3b: $3.1 \times 10^{-5}$ K$^{-1}$ along the $c$ axis and about $1 \times 10^{-6}$ K$^{-1}$ along the $a$ axis up to 1000 °C. Critical grain size due to mismatch of the TEC was estimated to be about 1 μm.\textsuperscript{50} Because of this high anisotropy, the reduction

\[ \text{Relative Intensity} \]

\[ \text{Temperature (°C)} \]

\[ \text{Intensity} \]

\[ \text{Temperature (°C)} \]

\[ \text{Intensity} \]

\[ \text{Temperature (°C)} \]
of crystallite size observed above 800 °C can be attributed to cracks within grains leading to pulverization. As cracks are not suitable for ionic conductivity, the sintering of materials containing LATP should be performed carefully. Data reported by Monchak et al. were used to calculate the TEC of LATP under vacuum and are compared to the present analysis performed in air. The results from experiments performed in air or vacuum are very similar and confirm the non-influence of the atmosphere on LATP.

**Garnet material Al–LLZO.** In its cubic phase (space group Ia3d), Al–LLZO exhibits high ionic bulk conductivity of 10⁻⁴ to 10⁻³ S cm⁻¹ at ambient temperature and a wide potential window, and it is chemically stable versus metallic lithium. Nevertheless, Al–LLZO has interfacial issues: it is unstable in air and it reacts with H₂O and CO₂, consequently Li₂CO₃ is easily formed on the surface, reducing the total conductivity.  

Moreover, Al–LLZO must be sintered at high temperature (about 1200 °C). Diffractogram in the range of temperatures between 30 °C and 1000 °C and result of the fit at 30 °C using Le Bail refinement are shown in Fig. S2 (ESI†). After synthesis, the cubic phase of Li₆.₅Al₀.₂₅La₂.₉₂Zr₂O₁₂ is identified with two small unknown peaks at around 2θ = 40° and 54°. A visible peak associated with La₂Zr₂O₇ appears at 500 °C: this was attributed to a loss of lithium caused by exposure to humidity. Proton and lithium are exchanged and LiOH is formed and at higher temperature this lack of lithium causes the formation of La₂Zr₂O₇ from Al–LLZO main phase. Nevertheless, the cubic space group of the main phase is conserved, and no other impurities are detected at higher temperatures. The structural changes occurring in the phase as a function of temperature are detailed below. As La₂Zr₂O₇ amount is not negligible (approximatively 12 wt% based on the ratio of main peak intensity of the two phases), diffractograms were analyzed as a two-phase mixture of Li₆.₅Al₀.₂₅La₂.₉₂Zr₂O₁₂ and La₂Zr₂O₇.

The Al–LLZO cell parameter presented in Fig. 4a does not vary linearly: three temperature ranges can be observed [30–200], [200–500] and [500–1000] °C. At 30 °C, the cell parameter a = 12.970(1) Å is in good agreement with the literature value. Then, it increases to 13.036(1) Å, 13.057(1) Å and 13.165(1) Å at 200, 500 and 1000 °C respectively. The formation of La₂Zr₂O₇ is suspected to be responsible for this behavior: the formation of La₂Zr₂O₇ may change the phase composition, which may also affect the cell parameters. Hubaud et al. reported the same trend for values without further indication on the formation of La₂Zr₂O₇. From 500 °C to the end of the experiment, amount of La₂Zr₂O₇ phase seems to be constant, which indicate that there is no further formation. Interestingly, cell parameter of PHASE seems to be constant around 10.90(1) Å between 500 and 1000 °C. Although La₂Zr₂O₇ formation is irreversible and the relative intensity is not fully recovered after cooling, the cell parameter of the main phase remains almost the same as a = 12.962(1) Å.

Three specific different linear TEC evolutions associated with the three temperature ranges of Al–LLZO [30–200], [200–500] and [500–1000] °C can be observed in Fig. 4b. In the [30–200] °C range, the TEC decreases from 3.6 × 10⁻⁵ to 1.8 × 10⁻⁶ K⁻¹ which correspond to the Al–LLZO TEC phase before pyrochlore formation. Then the TEC increases to 1.6 × 10⁻⁵ K⁻¹ at 500 °C due to pyrochlore formation: Al–LLZO composition might be different at each temperature and so would be the TEC. Finally, after complete formation of the pyrochlore phase, the TEC of Al–LLZO stays almost constant with further increases in temperature. Mean TEC of La₂Zr₂O₇ calculated with its cell parameters is 3 × 10⁻⁶ K⁻¹. Robert Vassen et al. measured its TEC at 9.1 × 10⁻⁶ K⁻¹. Inferior value and negative TEC measured at 800 °C might be due to incertitude as La₂Zr₂O₇ is a minor phase and analysis has been done with only 2 peaks at low angle.

**Active materials.**

**Lamellar oxide material.** Lamellar oxides LiNi₁/₃Mn₁/₃Co₁/₃O₂ (NMC111) and LiNi₀.₅Mn₀.₃Co₀.₂O₂ (NMC532) are among the most common oxide-based positive electrode materials. In the discharge state (fully lithiated), NMC111 has all Ni and Co atoms in oxidation states +2 and +3 respectively and NMC532...
has a mix of $+2/+3$ for Ni and $+3/+4$ for Co atoms. As electronic density is different, dilatation and the resulting evolution of cell parameters might be affected. Like NMC, the NCA material has the space group R3m. Diffractogram in the range of temperatures between 30 °C and 1000 °C and result of the fit at 30 °C using Rietveld and Le Bail refinement are shown in Fig. S3–S5 (ESI) for NMC111, NMC532 and NCA respectively. No impurities appear for NMC111 in the studied temperature range. NCA and NMC532 show no impurities until 800 °C and 1000 °C respectively. At these temperatures, the irreversible apparition of other weak intensity peaks attributed to LiAlO$_2$ is observed. However, for the main phase, relative intensities are stable throughout the temperature range. A reaction with the alumina crucible is the main hypothesis for the formation of these impurities. Segregation of phases such as LiAlO$_2$ in alumina doped nickel rich oxide has already been reported. 58

NCA has a smaller $c$ and a similar $a$ lattice parameter compared to NMC materials at 30 °C with $a = 2.886(1)$ Å and $c = 14.190(1)$ Å which is consistent with literature 59 (Fig. 5a). Lattice parameters of NCA increase to $a = 2.917(1)$ Å and $c = 14.450(1)$ Å at 900 °C. After cooling, cell parameter $a$ is slightly bigger with 2.873(1) Å and $c$ is recovered with almost no difference (14.192(1) Å).

The average TEC of NMC111 was already measured by dilatometry and was found to be about 1.2–1.3 × 10⁻⁵ K⁻¹. 71 Here, the TEC depending on the crystallographic orientation is plotted as a function of temperature in Fig. 5b and is compared to that of LiNi$_{0.6}$Mn$_{0.4}$Co$_{0.1}$Al$_{0.5}$O$_2$ (NCA), which has the same structure as NMC532, in order to determine the impact on the TECs of different atomic amounts with different states of oxidation. The results are displayed in Fig. 5b. Lamellar oxides NMC111 and NMC532 show similar results: a linear increase in the TEC along the $a$ direction from 1 × 10⁻⁵ to 2 × 10⁻⁵ K⁻¹ at 700 °C, and then a steeper slope, increasing to 4.6 × 10⁻⁵ K⁻¹ for NMC111 and 3.9 × 10⁻⁵ K⁻¹ for NMC532 at 1000 °C. Interestingly, at 700 °C, impurities appear for NMC532. For NCA, the TEC along $a$ direction increases linearly from 8 × 10⁻⁶ K⁻¹ to 1.7 × 10⁻⁵ K⁻¹ at 600 °C. A slope break appears, and the TEC raises to 4.6 × 10⁻⁵ K⁻¹ at 900 °C. The TEC along the $c$ direction increase linearly from 1.8 × 10⁻⁵ K⁻¹ to 2.8 × 10⁻⁵ K⁻¹ at 1000 °C for NMC111 whereas it seems to stay constant around 2 × 10⁻⁵ K⁻¹ for NMC532. Along the $c$ direction, the TEC is constant around 2.2 × 10⁻⁵ K⁻¹ until 700 °C after which it decreases to 1.7 × 10⁻⁵ K⁻¹ at 900 °C. Fig. S6 (ESI) shows the mean TECs of NMC111, NMC532 and NCA: interestingly, All NMC-type materials have the same TEC and exhibit similar behaviour with slope breaks around 700 °C. The effect of substitution seems to change the TEC anisotropy. At the beginning of the transition, a loss of oxygen or reactivity with the crucible might be associated with the slope breaks. 72,73 This further emphasizes the importance of sintering conditions. Sintering tools or dies and atmospheric conditions must be chosen with caution as contamination and low partial pressure of oxygen (in air, vacuum or strongly reducing graphic environment) change the TEC and therefore may be responsible for undesired chemical reactions.

### Spinel material LNMO

The spinel LiNi$_{0.6}$Mn$_{0.4}$Co$_{0.1}$O$_2$ (LNMO) (space group $Fd\bar{3}m$) is a high potential positive electrode (flat discharge curve at 4.7 V). 74

Diffractogram in the range of temperatures between 30 °C and 1000 °C and result of the fit at 30 °C using Le Bail refinement are shown in Fig. S7 (ESI). The spinel LMNO shows small impurities which have been identified as the NiMnO$_2$ phase. The crystallographic intensities are stable until 600 °C. At 700 °C, the FWHM decreased due to increases in crystallite size from

**Fig. 5** (a) Lattice parameters of NMC1:1, NMC5:3:2 and NCA in air depending on the temperature and (b) thermal expansion coefficient (TEC) as a function of temperature and the crystallographic axis of NMC1:1, NMC5:3:2 and NCA.
Integration of the NiMnO$_3$ impurity is a plausible explanation as the recovery with a bigger cell parameter range. At 1000°C, the spinel phase cell parameter in this temperature range increases upon insertion and its disinsertion of lithium makes the material after chemical delithiation of LFP using acetic acid a non-reversible phase transition occurs at 600°C with Fe$_2$(PO$_4$)$_3$ formation due to the partial reduction of Fe$^{3+}$ to Fe$^{2+}$. As the experiment is performed under argon atmosphere, the carbon coating on the particles is likely responsible for this reduction. To increase the thermal stability of FP, using a more oxidizing environment (air) increases the hetrosite phase stability to 600°C but a trigonal structure (space group P3$_2$1) starts to irreversibly grow even if heterosite remains the main phase.

Cell parameters of LFP (Fig. 7a) are $a = 10.321(1)$ Å, $b = 6.001(1)$ Å and $c = 4.693(1)$ Å and those of LFMP are $a = 10.414(1)$ Å, $b = 6.074(1)$ Å and $c = 4.728(1)$ Å at 30°C. The cell parameters are in good agreement with the literature and the difference between LFP and LFMP can be explained by the

Fig. 6 (a) Lattice parameters of LNMO depending on the temperature and (b) thermal expansion coefficient (TEC) as a function of temperature and the crystallographic axis of LNMO. (*) Calculated from data of Zeng et al. 76

Fig. 7 (a) Lattice parameters of LFP, LFMP and FP in argon atmosphere depending on the temperature and (b) thermal expansion coefficient (TEC) as a function of temperature and the crystallographic axis of LFP, LFMP and FP.
substitution of Fe by Mn which has a bigger ionic radius, 0.75 Å vs. 0.8 Å. In both cases, the cell parameters increase by approximately 0.11, 0.09 and 0.08 Å for a, b and c respectively. The cell parameters of FP are \( a = 9.818(1) \text{ Å}, b = 5.790(1) \text{ Å} \) and \( c = 4.781(1) \text{ Å} \) at 30 °C and are also in good agreement with Yamada et al. They increase to \( a = 9.840(1) \text{ Å}, b = 5.841(1) \text{ Å} \) and \( c = 4.807(1) \text{ Å} \) at 500 °C and follow a smoother trend than LFP and LFMP. After cooling, LFP presents almost the same cell parameters while \( b \) increases slightly: \( a = 10.346(1) \text{ Å}, b = 6.003(1) \text{ Å}, c = 4.693(1) \text{ Å} \). LFMP presents the same cell parameters with \( a = 10.412(1) \text{ Å}, b = 6.073(1) \text{ Å} \) and \( c = 4.727(1) \text{ Å} \).

The TEC of LFP (Fig. 7b) along the c direction presents a relatively constant increase from \( 1.6 \times 10^{-5} \text{ K}^{-1} \) to \( 2.4 \times 10^{-5} \text{ K}^{-1} \) at 600 °C, whereas that of the \( b \) direction also increases from \( 1.2 \times 10^{-5} \text{ K}^{-1} \) to \( 2.3 \times 10^{-5} \text{ K}^{-1} \). The TEC along the \( a \) direction, which is equal to \( 1.4 \times 10^{-5} \text{ K}^{-1} \), is almost constant throughout the temperature range. Except for LFMP at \( T = 800 \text{ °C} \), which shows a bigger increase, the TECs are very similar, meaning that Fe substitution by Mn has almost no influence on the thermal expansion of the phase. The delithiated FP material has lower \( a \) and \( b \) cell parameters and a higher \( c \) parameter which is in agreement with literature. Compared to LFP, FP presents lower TECs. The TEC along the \( c \) axis is the most impressive, decreasing from \( 1.5-2.5 \times 10^{-5} \text{ K}^{-1} \) to \( 0-5 \times 10^{-6} \text{ K}^{-1} \). However, the slope of the TECs begins to invert at 500 °C which might be due to the formation of \( \text{Fe}_2\text{PO}_4\text{Fe}_3 \). Fig. S6 (ESI) shows the mean TECs of LFP, LFMP and FP: LFP and LFMP are almost identical while the TEC of the delithiated sample clearly reduces the mean.

**Mixed material based on TEC analysis.** The probability of the formation of cracks at the solid electrolyte/active material interface is minimized by reducing the mechanical stress due to thermal dilatation between both materials. According to eqn (2), \( \Delta\text{TEC} = |\text{TEC(CE)} - \text{TEC(AM)}| \) must be as low as possible. Fig. 8 displays \( \Delta\text{TEC} \) between each AM and CE depending on the temperature. The mean TEC calculated based on the three axes, disregarding anisotropic dilatation, is used for this calculation. This approximation allows the selection of compatible materials from HT-XRD results. As NMC111, MMC532 and NCA have similar Mean TEC as shown in Fig. S6 (ESI), only MMC532 is represented. For the same reason in Fig. S6 (ESI) between LFP and LFMP, only LFP is represented. On fig. 8, a red line is drawn at \( 5.0 \times 10^{-6} \text{ K}^{-1} \) corresponding to \( \Delta\text{TEC} \) targeted value generally used for SOFC. Most of the Al–LLZO–AM couples do not comply with the target value as the \( \Delta\text{TEC} \) is varying close to one order of magnitude above \( 5.0 \times 10^{-6} \text{ K}^{-1} \) all along the temperature range. Solely based on the \( \Delta\text{TEC} \) and the threshold determined here, no AM would be compatible with Al–LLZO material. This is because the volume expansion of Al–LLZO is somewhat erratic with temperature. This is contrasting with the results found for LLTO and LATP. As the Mean TEC for LLTO and LATP is more regular, variations of \( \Delta\text{TEC} \) displayed on Fig. S1 (ESI) are more linear. Most of the \( \Delta\text{TEC} \) of CE–AM fall slightly above the threshold up to 600 °C. It is particularly true for phosphate-based and layered oxides AM. The case of LNMO is more complex as it reversibly splits into two phases above 600 °C; a huge increase of \( \Delta\text{TEC} \) is observed beyond that temperature. Still, among all the couples studied here, four CE/AM couples have a \( \Delta\text{TEC} \) below the target up to 500 °C: FP and LNMO mixed with LLTO or LATP. 500 °C remains a relatively low temperature though that may not allow for efficient sintering. With a higher threshold (\( \approx 1.0 \times 10^{-5} \text{ K}^{-1} \)), more couples would become compatible up to 800 °C with a more sensible temperature. However, the use of high sintering temperature also implies that the chemical stability between the materials must be guaranteed.

Using a threshold of \( 5.0 \times 10^{-6} \text{ K}^{-1} \), chemical stability of mixed CE/AM (CE = LLTO or LATP, AM = LNMO) was investigated by performing XRD after heat treatment. As explained above, FP in heterosite structure is not stable under air at 600 °C and FP-related impurities start to irreversibly grow even if heterosite remains the main phase at 600 °C. This maximum temperature is relatively low for allowing the efficient sintering of both LATP and LLTO ceramic electrolyte with FP. In that sense, mixture of FP with ceramic electrolytes was not further addressed. The case of LNMO is more interesting. The results are reported in Fig. 9 in the case of LATP and LLTO with LNMO. From XRD, LATP and LNMO are compatible up to 600 °C. If heat treatment is short (1H),
no impurity is detected but after 10H, a new phase similar to LiMnPO₄ appears with small peaks. It means that LATP and LNMO are not thermodynamically stable at this temperature but kinetic is low which allows short treatment. In that sense Flash sintering using Spark Plasma Sintering (SPS) might be a solution to avoid these reactions as it decreases temperature and time for sintering. Above this temperature, i.e. above the temperature of reversible splitting into spinel plus rock-salt phases, they drastically react together into LiMnPO₄ and other phases.

If the heat treatment is performed for only 1H, LLTO and LNMO show no reaction neither up to at least 900 °C, meaning both materials are compatible up to that temperature in those conditions. After longer thermal treatment (10H) at 900 °C phases similar to Li₂La₂Ti₃O₁₀ starts to grow. Similarly to the preceding mix, this means that LLTO and LNMO are not thermodynamically stable at 900 °C but kinetic is low which allows short thermal treatment. Though, the phase splitting of LNMO due to loss of oxygen occurring above 700 °C might not allow the sintering at higher temperature. This still needs to be clarified experimentally. As oxygen release happens at higher temperature with O₂ pure atmosphere, increasing partial pressure of O₂ might enhance the TEC stability of the spinel phase.

Further experiments in O₂ rich atmosphere are required to confirm our assumption. Moreover, determination of the Young’s modulus of the phases might become mandatory at this point.

The thermal compatibility of active material mixed with electrolyte is discussed above without considering other components. However, the need of electronic additives such as carbon or metals and sintering aid (to favor the sintering) may change these conclusions. Additives used to decrease the sintering temperature might act as a buffer regarding constrains with plastic deformation and allow minimal cracks during cooldown after sintering. For example use of plastic behavior sealant material in SOFC (metal or glass-ceramics) improves the resistance toward constrains as brittle fractures are more damaging than plastic deformation. In the same idea, use of glass-ceramic as sintering additives or metal in the electrode part may help absorbing constrains in ASSBs. Moreover, electronic additive such as carbon in electrode layers might influence the mechanical properties of the layer increasing the flexural strength or fracture toughness by suppression of crack propagation. On the other hand, they may also prevent ideal sintering as they can act as lubricant.

Conclusions

In this work, we used HT-XRD in order to reference the TEC depending on crystallographic axis and temperature of various electrolyte and active materials. Minimal mismatch of TEC between materials is required to decrease stress during heat treatment because excess of stress can generate cracks that have disastrous effect on electrochemical performance. All active materials have really similar TEC, in the same range of values (1–2 × 10⁻⁵ K⁻¹). Delithiated material FP shows smaller TECs under argon compared to LFP up to 500 °C where a non-reversible transition occurs which can be increase to 600 °C under air atmosphere. Use of delithiated active material in solid state batteries during sintering might be a way to reduce TECs mismatch but their lower thermal chemical stability is challenging regarding the densification temperature making it more complicated the assembly of charged solid state batteries for lithium metal application. Solid electrolytes have more diversified TEC and are often more constant. Nevertheless, strong anisotropy of LATP material must be taken in account when sintering as cracks occur above a critical grain size > 0.2 µm. In order to highlight compatible materials with minimal mismatch of the TEC, ATEC between typical AM have been calculated. The lowest mismatch was found for the couples LATP/FP, LATP/LNMO, LLTO/FP and LLTO/LNMO which are below 5.0 × 10⁻⁶ K⁻¹ until 500 °C. On top of the low TEC mismatch up to 500 °C, no thermal degradation of LLTO mixed with LNMO up to 900 °C during short treatment (1H) was reported, which is one of the highest reported to our knowledge. Thermal stability of LNMO might be increased by controlling partial pressure of O₂ which might stabilize its TEC and improve thermal compatibility with LLTO at higher temperatures. Even if thermal degradation of mixes is often under the sintering temperature of CE, sintering additives might be used in order to densify composite material.

We encourage others to reference TEC of other components (active materials, solid electrolytes, conductive fillers and eventually sintering aid) in order to choose and select compatible materials efficiently. Referencing the Young’s modulus is another important thing to predict cracks and use more complex model depending on the architecture of the cell. Beyond that, it will be necessary to consider the stress generated by dilatation of electrodes AM during cycling as it will be critical for the lifetime of the battery.

Conflicts of interest

There are no conflicts to declare.

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