

In situ synthesis of LiCoO_2 to enable better contact with $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$ and investigation of their thermal stability.



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ABSTRACT

This poster presents an investigation into the interface between electrolytes and cathodes in solid-state batteries (SSBs). The study focuses on employing $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$ (Nb-LLZO) as the Li-garnet electrolyte and LiCoO_2 (LCO) as the cathode material. As seen in Fig 1, the most important issues regarding interface of SEs and active materials are related to poor interfacial contact requiring for high temperature sintering. This then also results in issues regarding formation of secondary phases and cation intermixing.

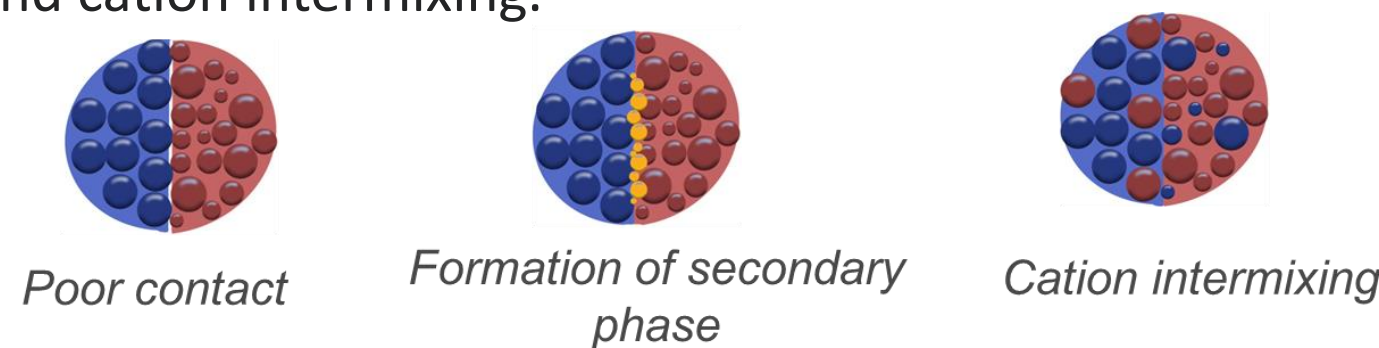


Fig. 1: Issues arising at the interface of garnet – cathode material after heat treatment.

Our previous research showed that heat treatment of the mixtures of SE and LCO at 900 °C results in poor interfacial contact. One method to avoid high temperature sintering is the use of precursor powder of LCO for the in-situ synthesis on the particles of Nb-LLZO.

MOTIVATION

The pursuit of advanced energy storage systems is increasingly vital for modern demands like portable electronics, electric vehicles, and renewable energy. SSBs offer improved safety, energy density, and cycle life over liquid electrolyte-based batteries. To harness these benefits, understanding the electrolyte-cathode interface is crucial. This connection profoundly impacts SSB performance, including conductivity and stability. Thus, investigating these properties is pivotal for optimizing SSB design. This poster delves into the electrolyte-cathode interface in SSBs, utilizing Nb-LLZO as the Li-garnet electrolyte and LCO as the cathode material. Industrial implementation of SSBs is detained due to the poor contact between the electrolyte and cathode material. One method that can improve the contact area of the garnet with the active material without the need of high sintering temperatures is the in-situ synthesis of LiCoO_2 from nitrate precursors, whose decomposition act as a binding agent on the surface.

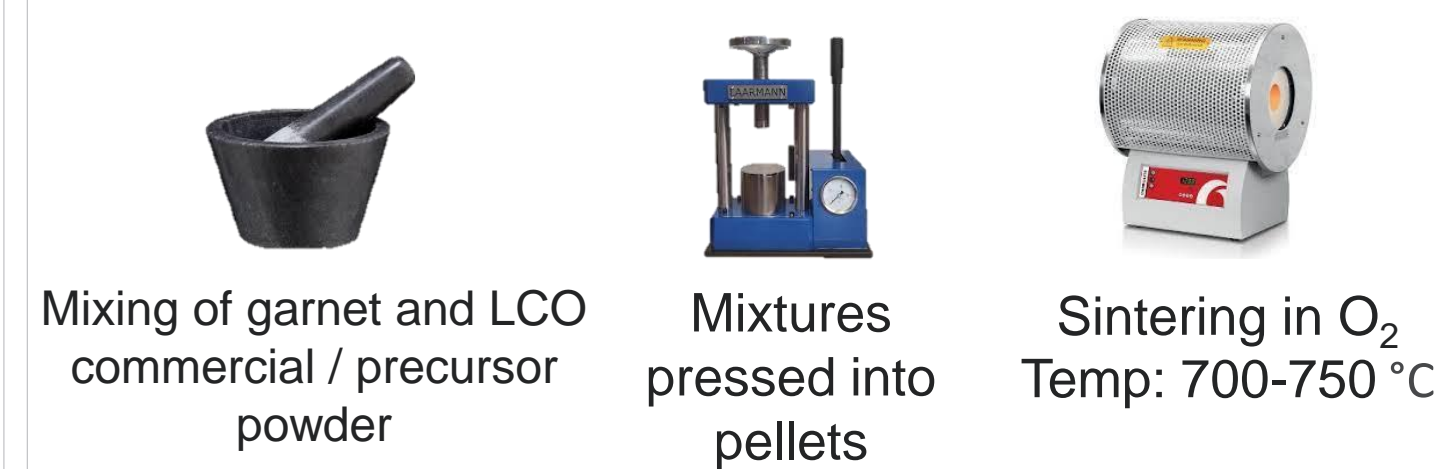
METHODS

Section 1:

- Nb-LLZO precursor was prepared by roll milling stoichiometric amounts of Li_2CO_3 , La_2O_3 , ZrO_2 and Nb_2O_5 . 10 mol% excess Li was added. The mixture after it was dried, was pressed into pellets and heat treated in two heating steps of 2 hours each at 1050 °C in muffle furnace.
- LiCoO_2 precursor solution was prepared from stoichiometric amounts of LiNO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in DI. 10 mol% excess Li was added. The dried gel was crushed into powder and then pressed into pellets and heat treated in a tube furnace under O_2 at 700 °C for 1h.

Section 2:

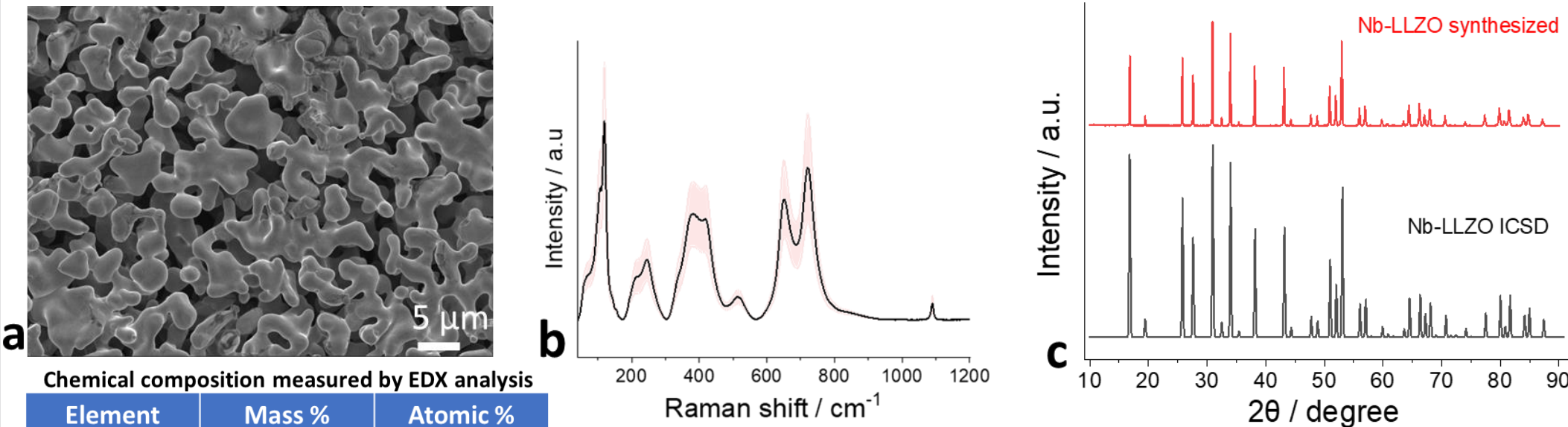
- 50-50 wt% of Nb-LLZO/LCO precursors mixtures were prepared by the following procedure.



SECTION 1: Synthesis of materials

Synthesis of Nb-LLZO

LLZO can take either the tetragonal or cubic structure.^[1] Nb as dopant in Zr sites, can achieve cubic structure stable at room temperature. Raman and XRD analysis (Fig. 2b,c) both show the cubic structure of Nb-LLZO, agreeing with literature.



Cubic structure is the most favorable due to its higher ionic conductivity. EDX analysis also shows that the right chemical composition of Nb-LLZO is achieved.

Fig. 2 SEM image and EDX analysis (a), Raman spectrum (b) and XRD pattern (c) of synthesized Nb-LLZO

Synthesis of LiCoO_2

LiCoO_2 was synthesized from nitrate precursors. XRD and Raman analysis (Fig. 3b,c) show that at these conditions layered material was produced, ideal for Li cycling in a battery. Low temperature LiCoO_2 also exist in spinel structure which is detrimental for battery cycling and unwanted.

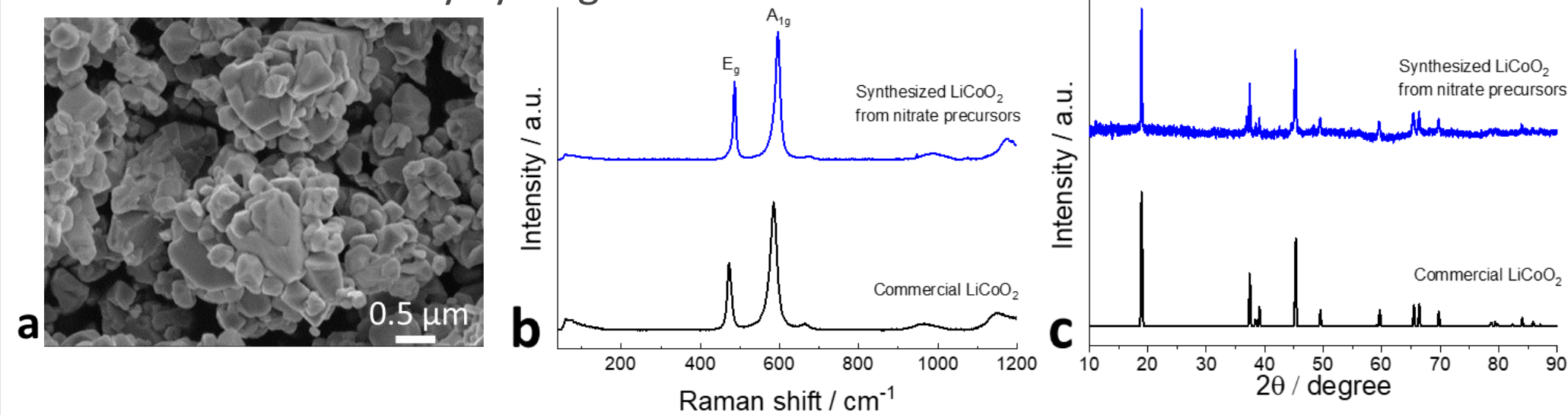


Fig. 3 SEM image and EDX analysis (a), Raman spectrum (b) and XRD pattern (c) of synthesized LiCoO_2 from nitrate precursors at 700 °C for 1h. Refined unit cell parameters are also given (blue) and compared with literature values for a- NaFeO_2 structure.

SECTION 2.: Interfacial contact and thermal stability of mixtures Improvement of contact area

As shown in Fig. 4, the interfacial contact between commercial LCO and Nb-LLZO is very poor after heat treatment at 700 °C for 1h. In comparison, the use of LCO precursor powder dispersed in IPA results in better contact. The decomposition of the nitrates precursors act as binding agent on the surface of the electrolyte.

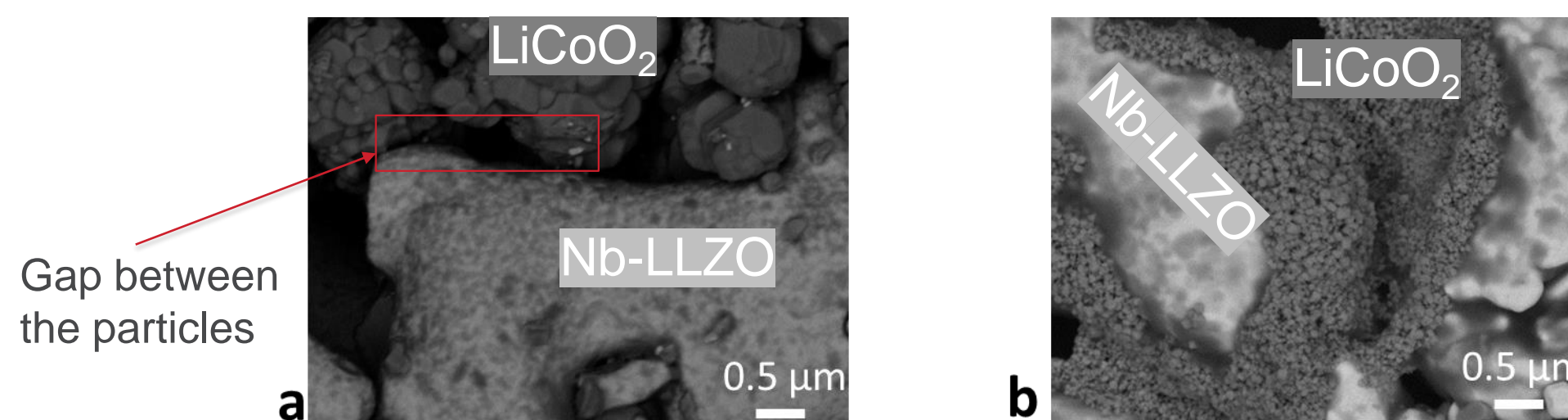


Fig. 4 SEM images of heat-treated mixtures of Nb-LLZO with (a) commercial LCO and (b) LCO precursors

Reactivity with Nb-LLZO

- When in contact with Nb-LLZO at 700 °C spinel LCO is produced. Increasing the temperature to 720 °C seems to result in layered structure (Fig 5a).
- In addition, Nb-LLZO is known to react with LCO to produce LaCoO_3 at temperatures > 750 °C.^[2] During the in-situ synthesis of LCO, the reactivity increases, as shown from Figs 5a and 5b, where the peak at 690 cm^{-1} related to LaCoO_3 is shown and secondary phase is observed in back scattered electron image.

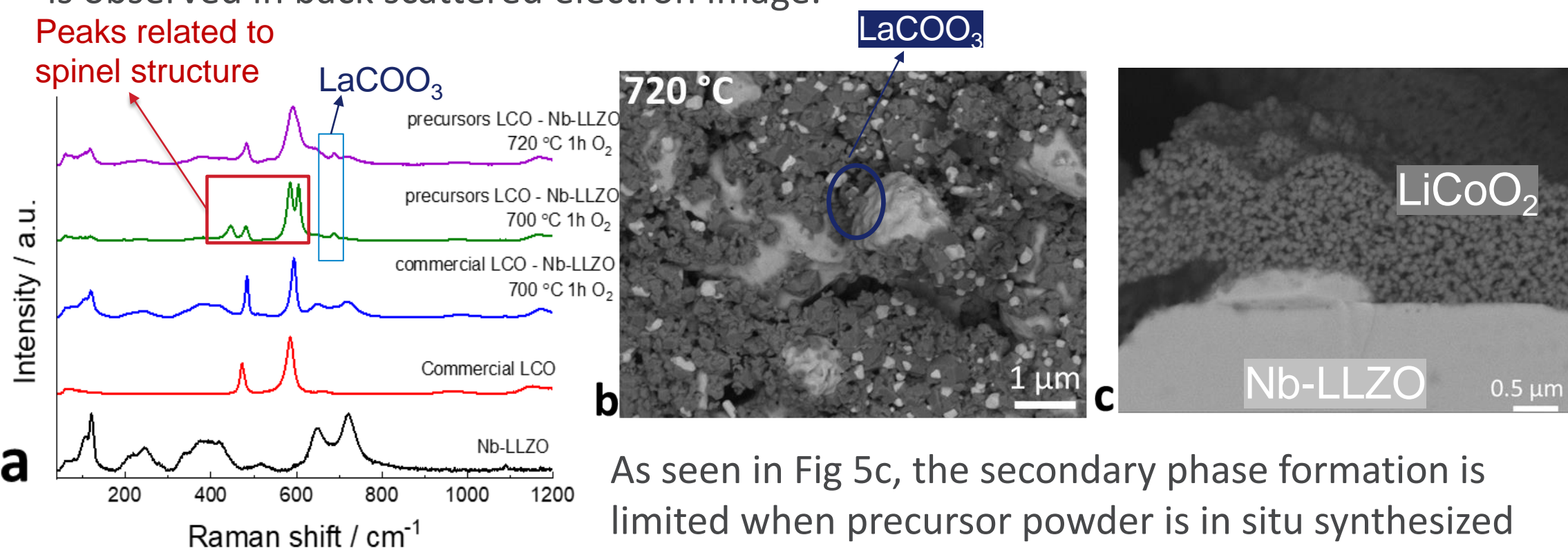


Fig. 5 Raman spectra of mixtures after different conditions of heat treatment (a), SEM image of mixture of 50-50 wt% Nb-LLZO and nitrate precursor powder after heating at 720 °C for 1h, SEM image of in situ synthesized LCO from precursors on Nb-LLZO pellet at 720 °C for 1h (c)

As seen in Fig 5c, the secondary phase formation is limited when precursor powder is in situ synthesized on Nb-LLZO pellet.

CONCLUSIONS

- Successful synthesis of cubic Nb-LLZO at 1050 °C with two heating steps.
- Successful synthesis of layered LiCoO_2 from nitrate precursors at 700 °C for 1h.
- Interfacial contact between SE and active material is improved during in situ synthesis of LCO on Nb-LLZO particles.
- When in contact with Nb-LLZO at 700 °C, spinel LCO is produced instead of layered. Slight increase to 720 °C seems to result in layered structure.
- LaCoO_3 is the side product of the heat treatment of Nb-LLZO with LiCoO_2 .

NEXT STEPS

- Infiltration of precursor solution in Nb-LLZO scaffold to improve interfacial contact.
- Impedance measurements of symmetrical cells consisted of in situ synthesized LCO and sintered pellets of Nb-LLZO.
- Construction of full cell with Li anode.

REFERENCES

- [1] R. Murugan, V. Thangadurai, W. Weppner, *Angewandte Chemie*, 2007, **46**(41), 7778-7781
- [2] Y. Ren, T. Liu, Y. Shen, Y. Lin, CW Nan, *Journal of Materiomics*, 2016, 2(3), 256-284

INTERN BIO

Alhussain is a Penultimate year chemical engineering studying at University College London. He's a dedicated student with a broad range of interests, from engineering and finance to research and development.

