

$\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{1-x}\text{V}_x\text{O}_3$ vanadium doped to improve electrochemical performance as a solid electrolyte in lithium-ion batteries.

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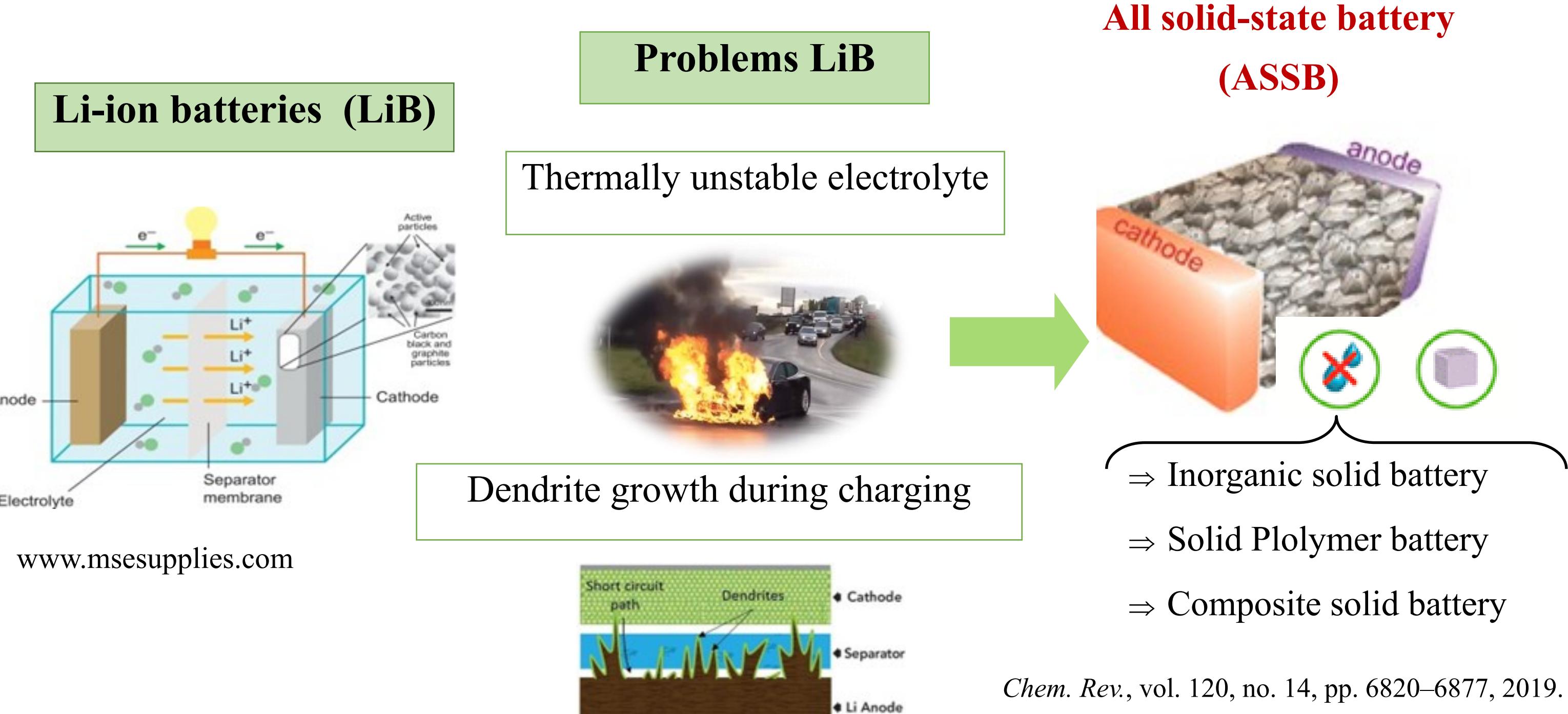
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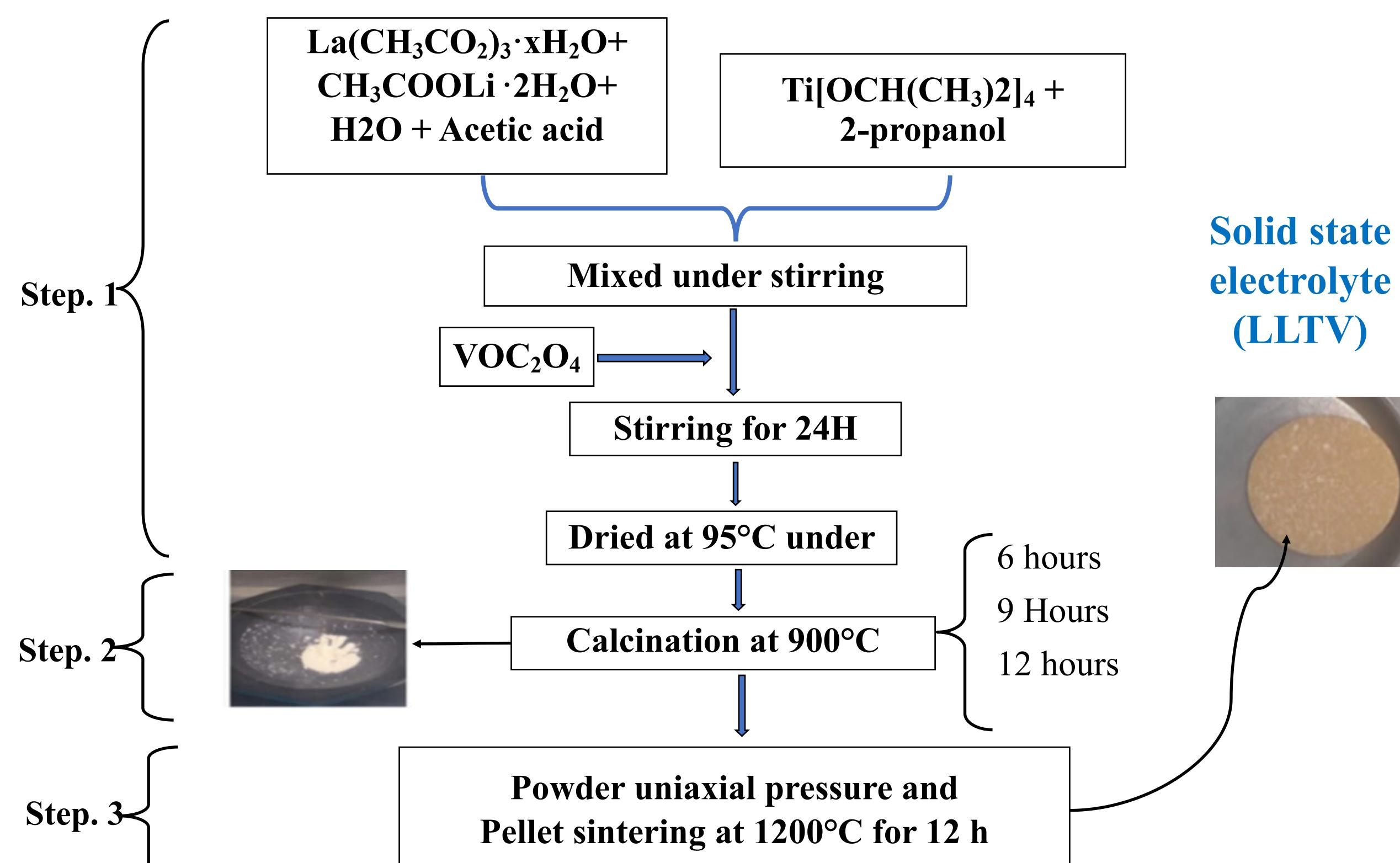
The 4th World Conference on Solid Electrolytes for Advanced Applications: Garnets and Competitors

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1. Introduction



Synthesis: The coprecipitation Method was used to obtain the solid electrolytes (SE) $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{1-x}\text{V}_x\text{O}_3$.



Solid electrolytes

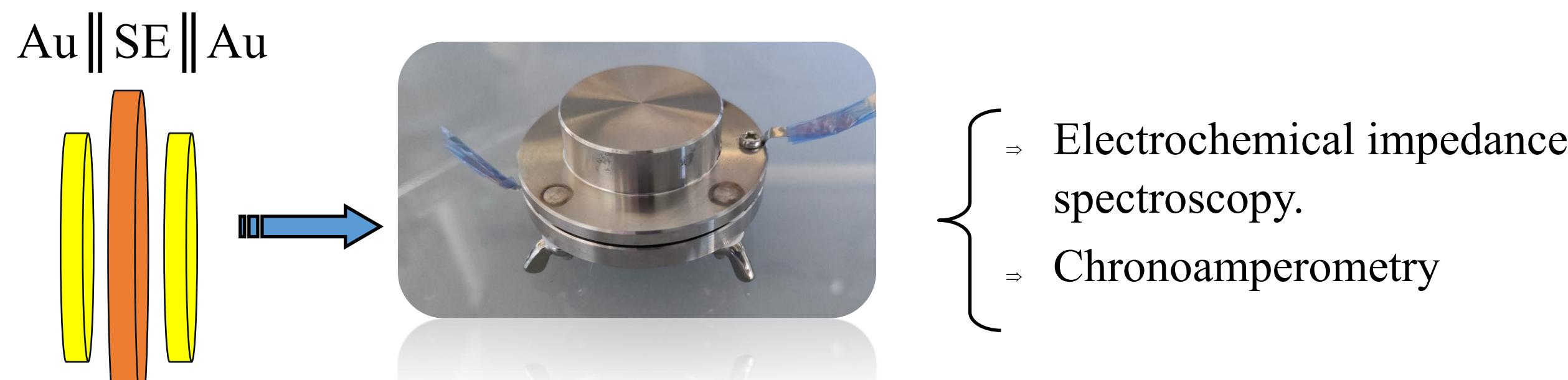
- Perovskite-type oxides and sulfide-type are promising solid electrolytes for all-solid-state batteries. Although the $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$ perovskite (ABO_3) shows high chemical stability, high bulk ionic conductivity ($1.0 \times 10^{-3} \text{ S/cm}$), the total ionic conductivity is lower ($1.96 \times 10^{-5} \text{ S/cm}$) because of the grain boundary resistance, which reduces the transport.
- To reduce the grain-boundary resistance it has been proposed the reduction the activation energy. Doping the B site of the perovskite structure with cations of smaller ionic radius is an alternative to decrease the interatomic bonding forces and improve the lithium conductivity [1][2].

Objective

To explore the synthesis of the material $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{1-x}\text{V}_x\text{O}_3$ (LLTV; $x = 0, 0.01, 0.02$ and 0.03) through the coprecipitation method, the effect of the calcination time of the powders and the sintering at high temperature (1200°C) to obtain a solid electrolyte, with potential use in Li-ion batteries.

2. Methodology

Electrochemical Characterization

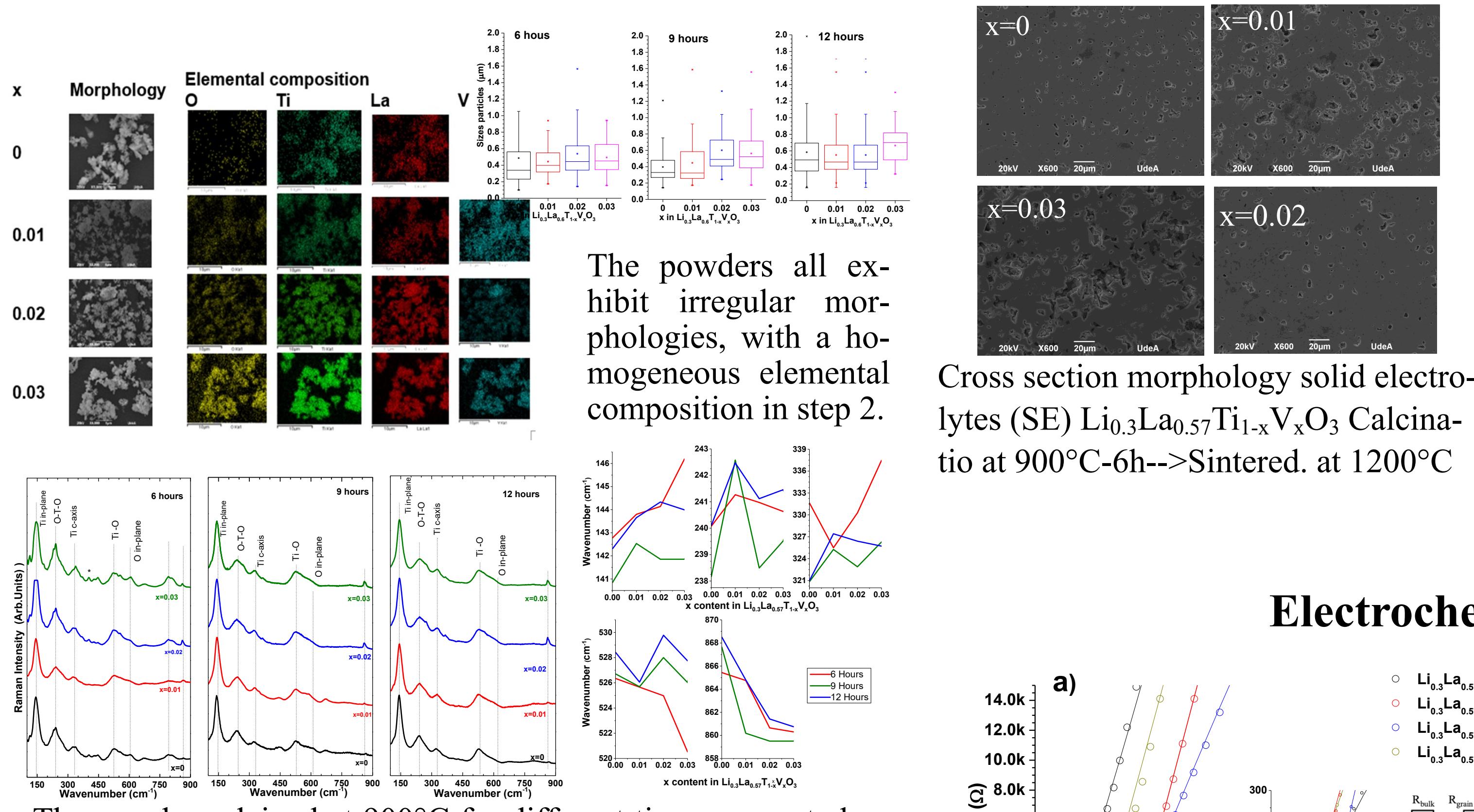


Eq. 1 was used to calculate the ionic and electronic conductivity, and the Arrhenius relation (Eq. 2) for the activation energy.

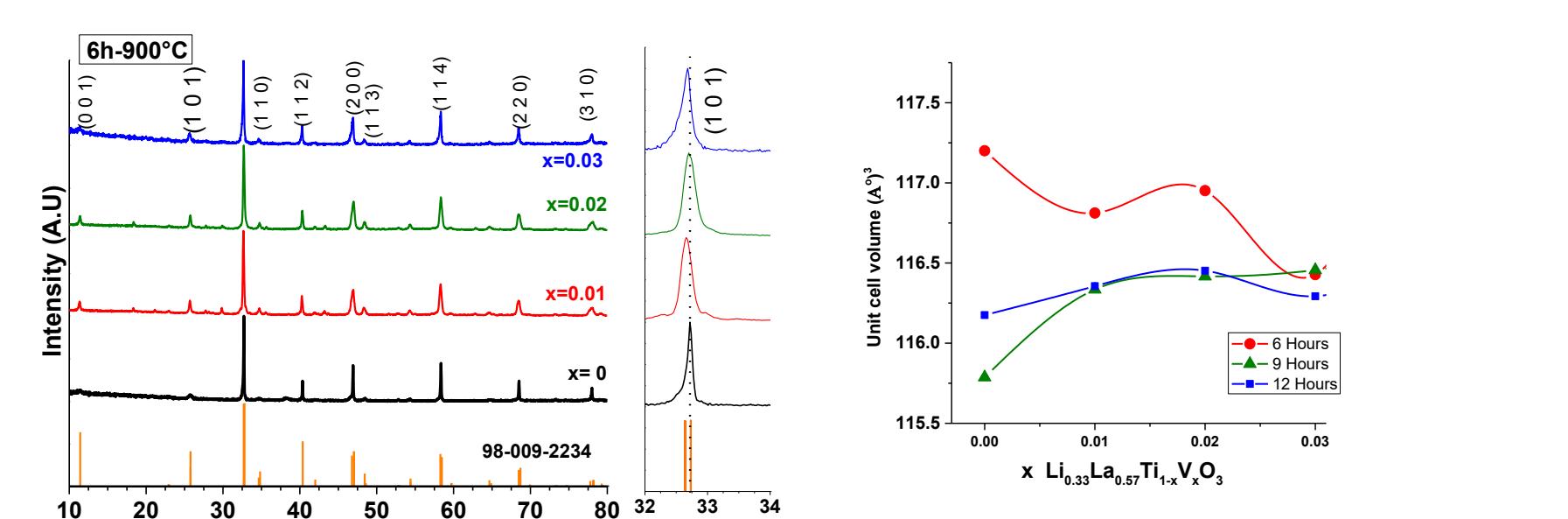
$$\sigma = \frac{L}{RA} \quad \text{Equ. 1} \quad \sigma(T) = \sigma_0 e^{-\frac{Ea}{k_B T}} \quad \text{Equ. 2}$$

3. Results.

Physic-Chemistry Characterization Step 2

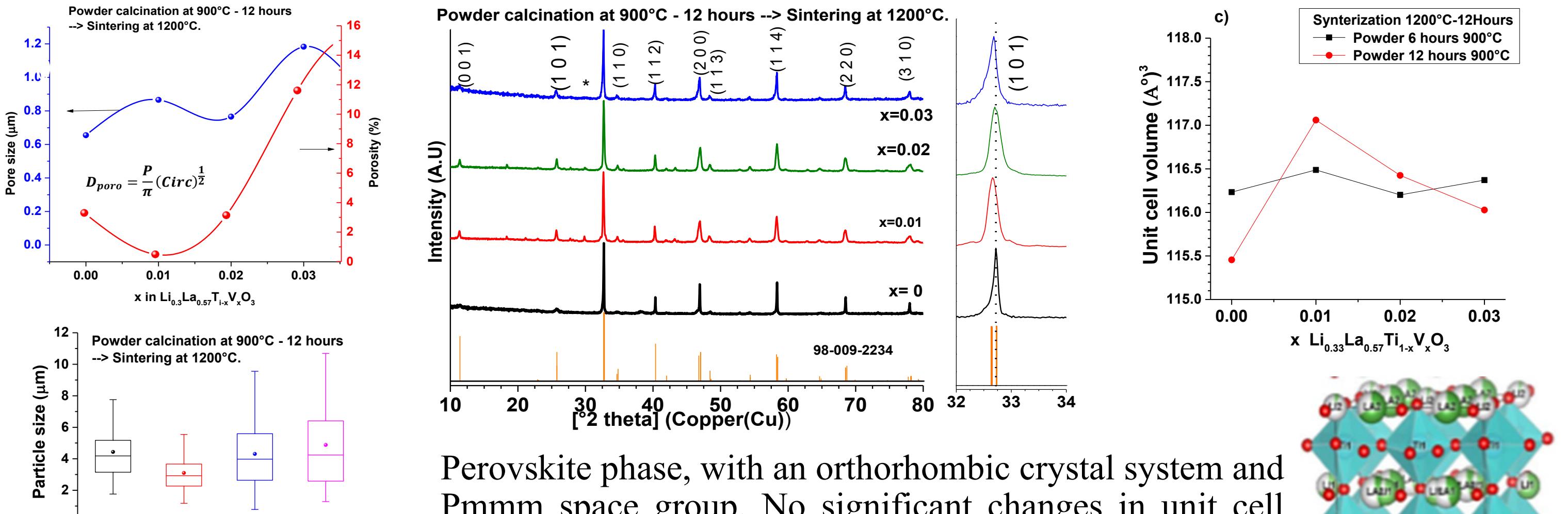


The powder calcined at 900°C for different times present characteristic vibration bands of perovskite-type structures [5][6].



The powders calcined at 6, 9, and 12 hours exhibit a perovskite phase and can be indexed with an orthorhombic crystal system and Pmmm space group.

Physic-Chemistry Characterization Step 3



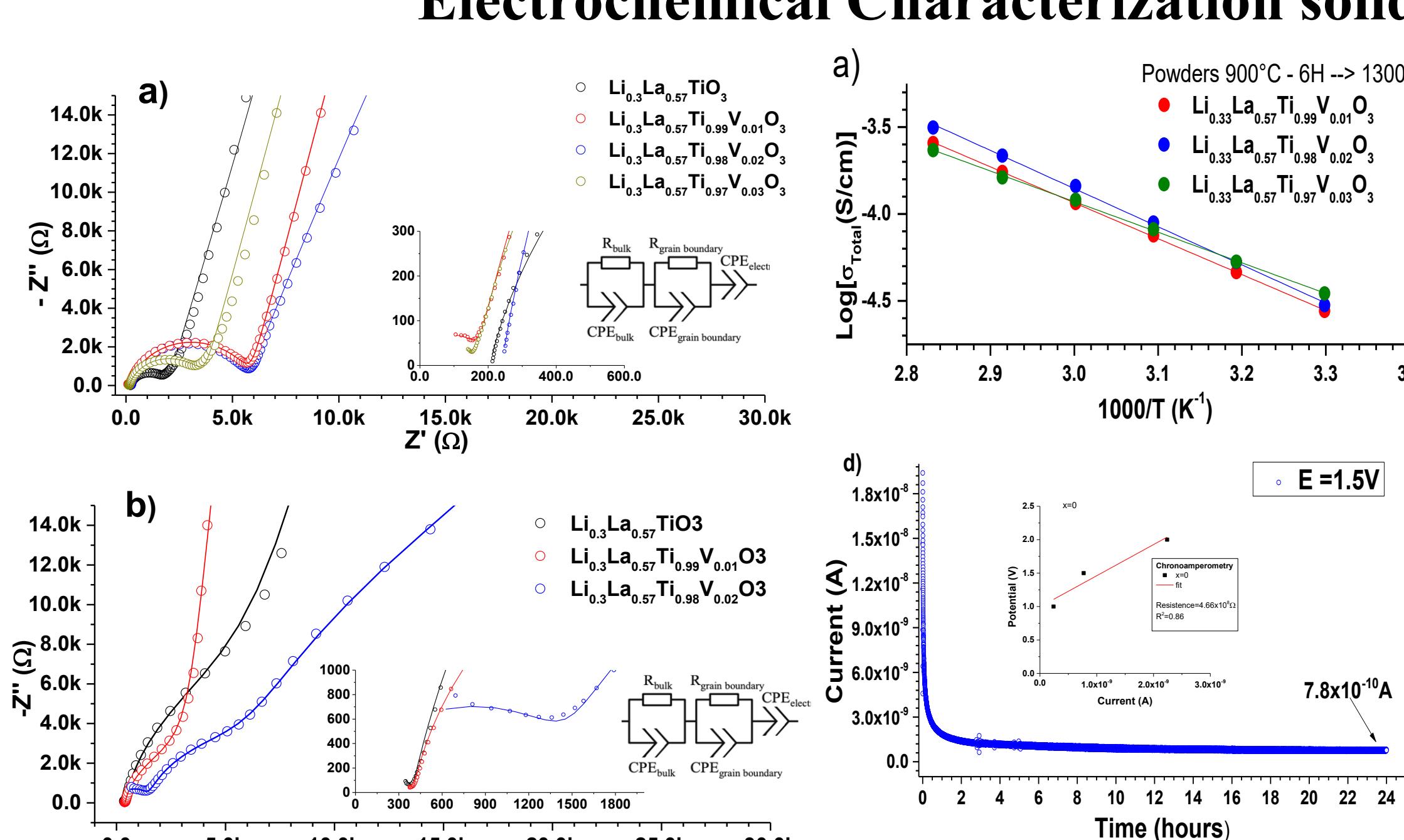
Perovskite phase, with an orthorhombic crystal system and Pmmm space group. No significant changes in unit cell volumes are observed for samples calcined at 900°C for 6 hours and sintered at 1200°C.

4. Conclusions

The solid electrolyte $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ without vanadium exhibits the highest total ionic conductivity $4.54 \times 10^{-5} \text{ S/cm}$, and the $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{0.98}\text{V}_{0.02}\text{O}_3$ exhibits the best grain conductivity ($7.43 \times 10^{-4} \text{ S/cm}$).

A remarkable result was obtained for the solid electrolyte $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{0.99}\text{V}_{0.01}\text{O}_3$, calcined at 900°C for 6 hours and sintered at 1300°C, which exhibited the highest ionic conductivity in grain boundaries, reaching a value of $6.853 \times 10^{-5} \text{ S/cm}$. The electronic conductivity values were lower than 10^{-8} S/cm .

Electrochemical Characterization solid electrolyte LLTV (step 3)



Samples $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{1-x}\text{V}_x\text{O}_3$	σ_g (10^{-3} S/cm)	σ_{bg} (10^{-5} S/cm)	σ_{Total} (10^{-5} S/cm)	Ea (eV)
Calcination 6 hours at 900°C (1200°C)	$x=0$: 4.83	3.88	3.59	0.36
$x=0.01$: 8.9	0.44	0.44	0.44	
$x=0.02$: 1.54	1.40	1.28	0.16	
$x=0$: 4.38	5.07	4.54	0.45	
$x=0.01$: 6.17	3.75	3.53	0.41	
$x=0.02$: 7.43	2.25	2.18	0.44	
$x=0.03$: 5.73	2.63	2.51	0.35	
Calculation 6 hours at 900°C (1300°C)	$x=0.01$: 7.34	8.53	7.6	-
$\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$, Solid state reaction (1300°C) [3]	10	2	1.96	-
$\text{Li}_{0.5}\text{La}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ sol-gel (1300°C) [4]	-	-	5.63	0.47

Where, σ_g , σ_{bg} and σ_{Total} are the ionic conductivity of grain, in boundary grain limits and Total respectively, Ea is the activation energy.

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5. Acknowledgements and References.

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