PROJECT DATES: 01/10/2022 – 01/10/2025

LARGE AREA MAGNETRON SPUTTERED ALL-SOLID-STATE BATTERIES WITH ALD BUFFER LAYERS
ARISER

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TURKISH PROJECT PARTNERS:

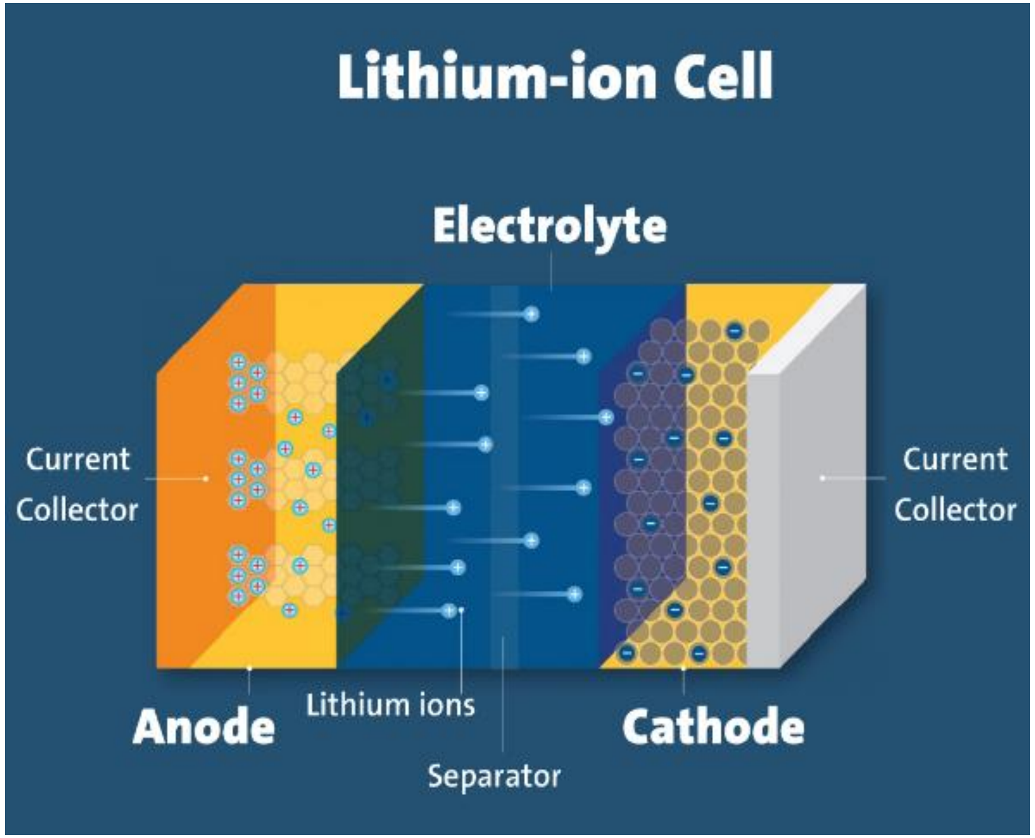
- IZMIR INSTITUTE OF TECHNOLOGY - 122N410
- KOC UNIVERSITY - 122N517
- TEKNOMA - 122N516

POLISH PROJECT PARTNERS:

- ŁUKASIEWICZ-IMIF
- CBRTP

Outline

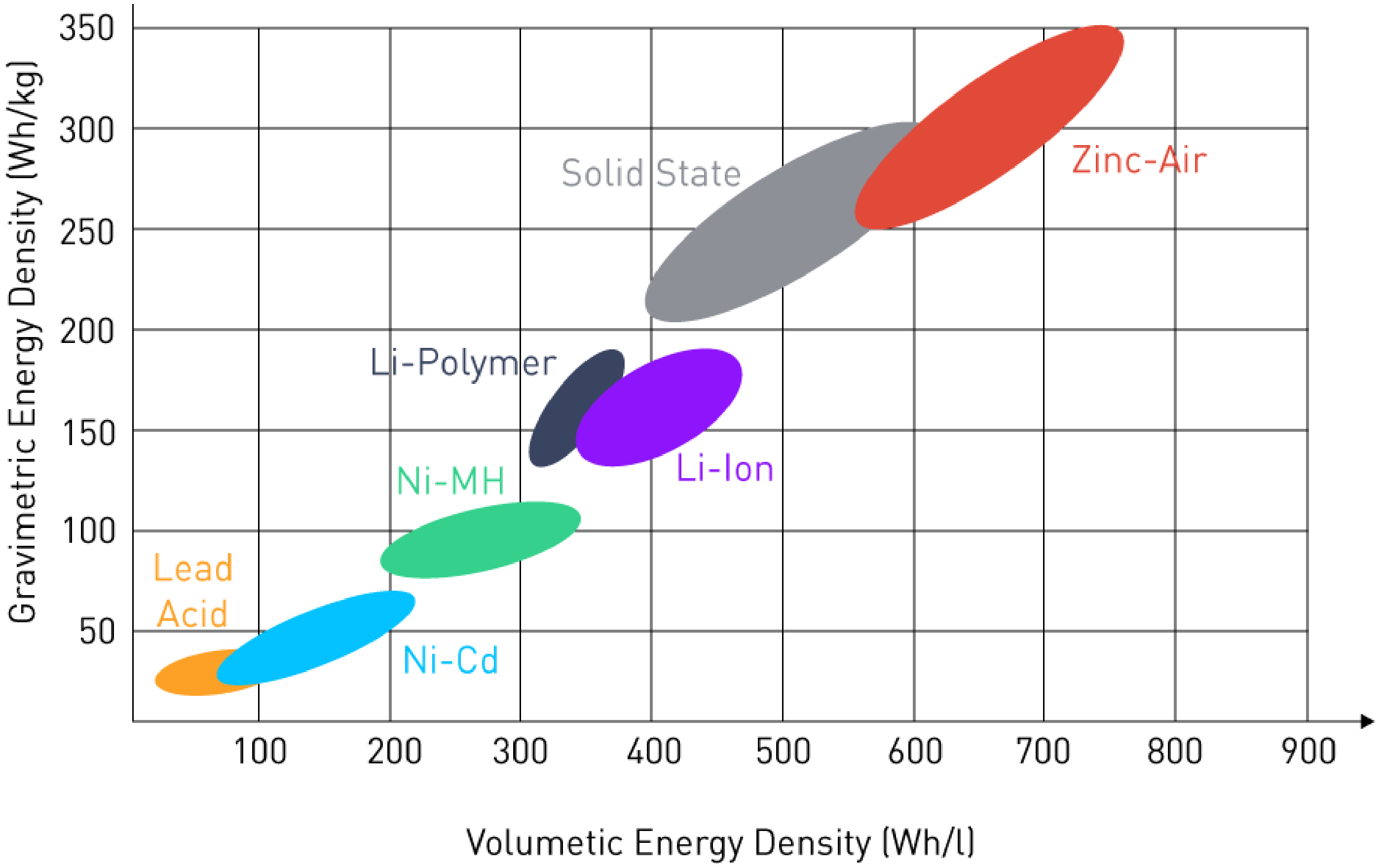
- Introduction
- All Solid State Lithium–ion Batteries
- Advantages of ASSLIBs
- Pert Chart of ARISER
- Experimental Procedure
- Conclusion
- Outcomes within the Scope of the Project
- Acknowledgments



Source: UL Research Institutes, 2021

All-Solid-State Lithium-ion Batteries (ASSLIB)

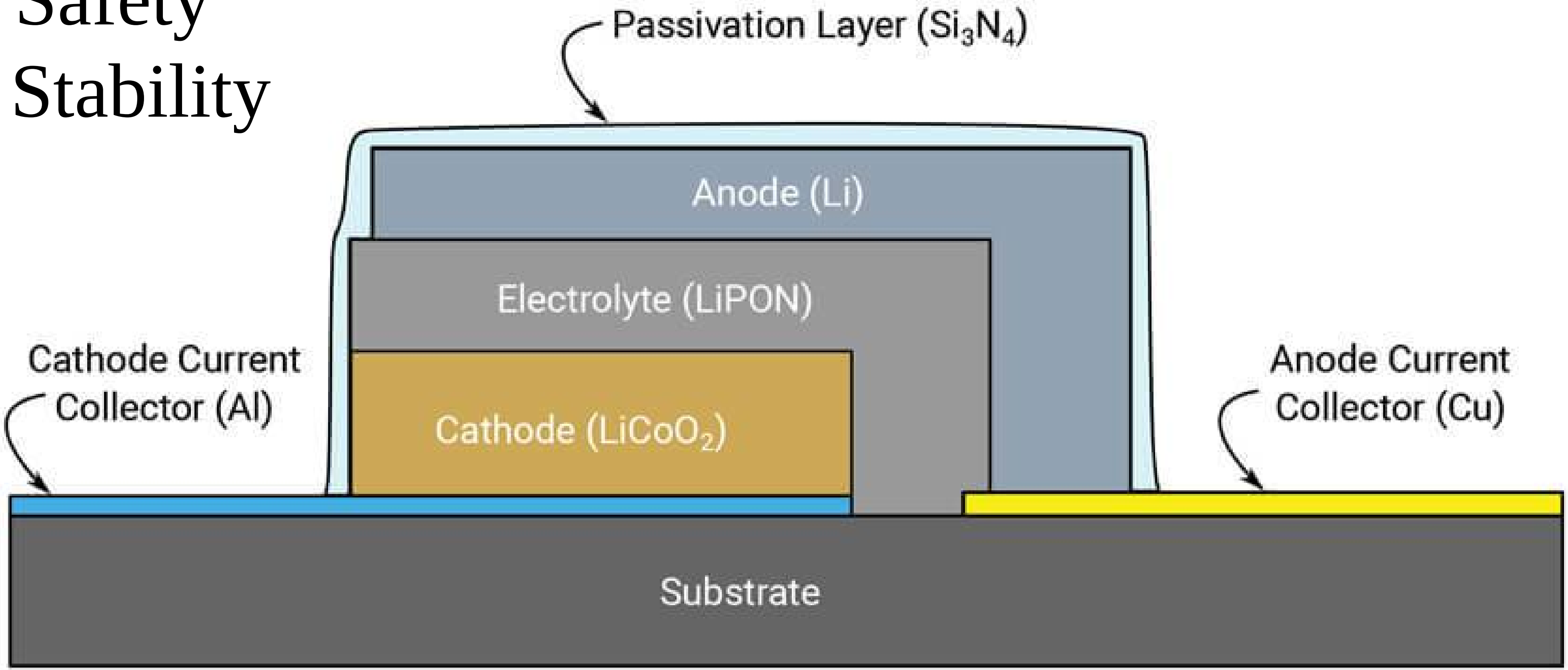
- Energy densities **(both volumetric and gravimetric) increase** from traditional Lead Acid batteries to advanced Zinc-Air batteries.
- Lithium-based batteries (Li-Ion and Li-Polymer) provide a **significant increase** in energy density compared to older technologies like Lead Acid and Ni-Cd.
- Emerging technologies like **Solid State and Zinc-Air** show the highest potential energy densities.



Source: Monolithic Power

Advantages of ASSLIBs

- Wider Operating Temperature Range
- High Energy Density
- Enhanced Safety
- Improved Stability



Project Partners

Gulnur Aygun (Project Leader), Lutfi Ozyuzer - Izmir Institute of Technology-IZTECH
Small area thin film growth by magnetron sputtering technique

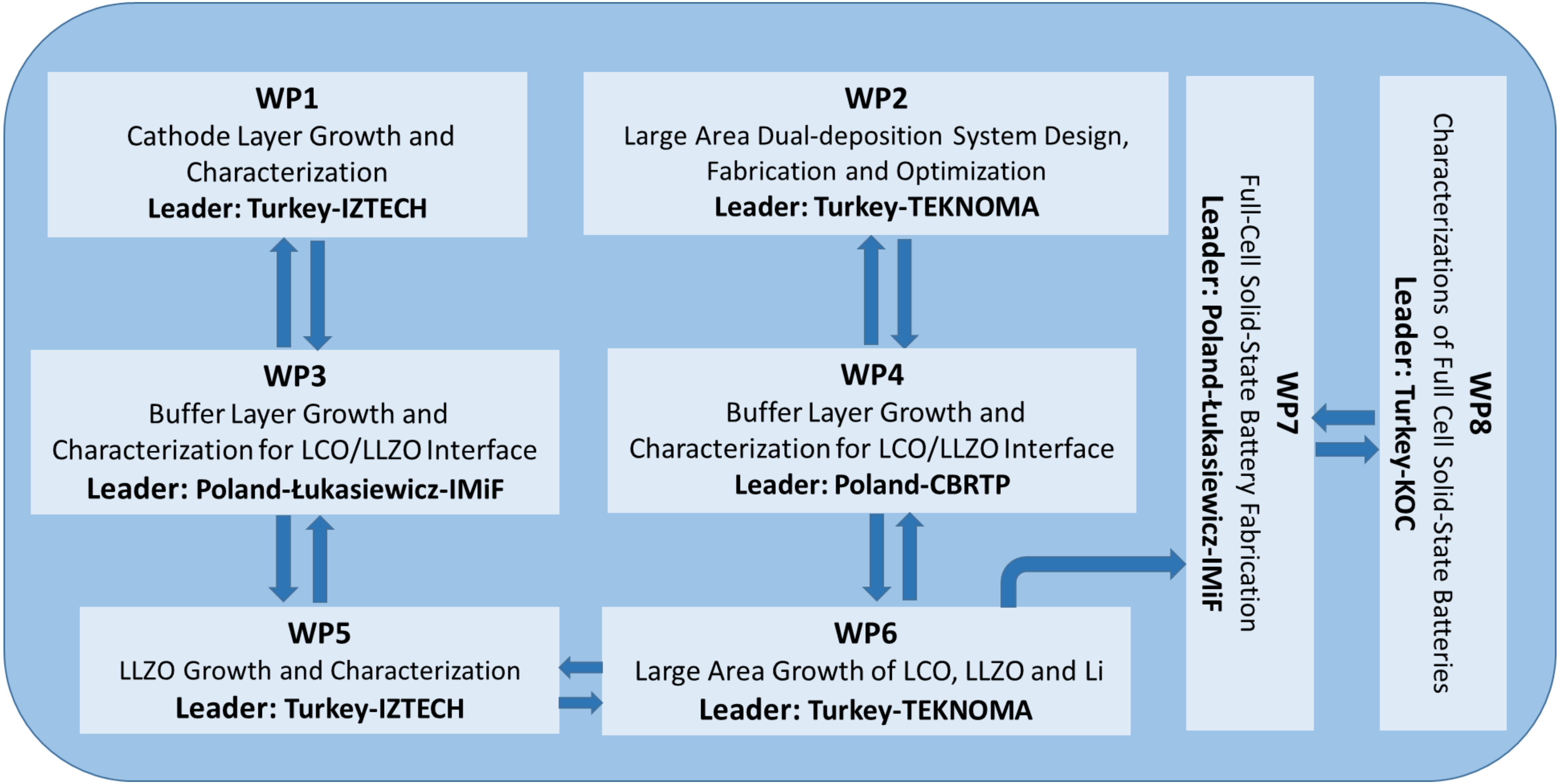
Mehtap Ozdemir Koklu - TEKNOMA Technological Materials Inc.
Large area thin film growth by magnetron sputtering technique.

Ugur Unal KOC University,
Chemical characterizations of thin films.

Kamil Kosiel, Anna Szerling - Łukasiewicz Research Network-
Institute of Microelectronics and Photonics,
Metal oxide buffer layer growth on small area thin film by ALD technique.

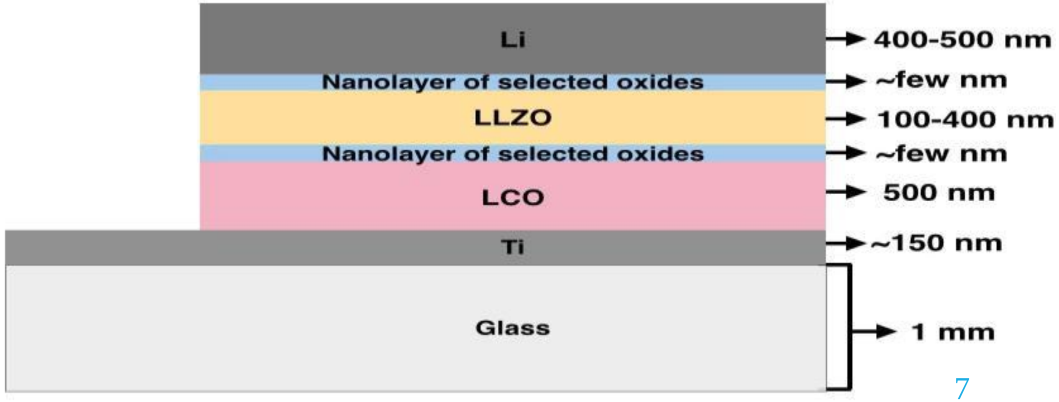
Robert Socha – CBRTP SA Research and Development Center of Technology for Industry,
Metal oxide buffer layer growth on large area thin film by ALD technique.

Pert Chart of ARISER



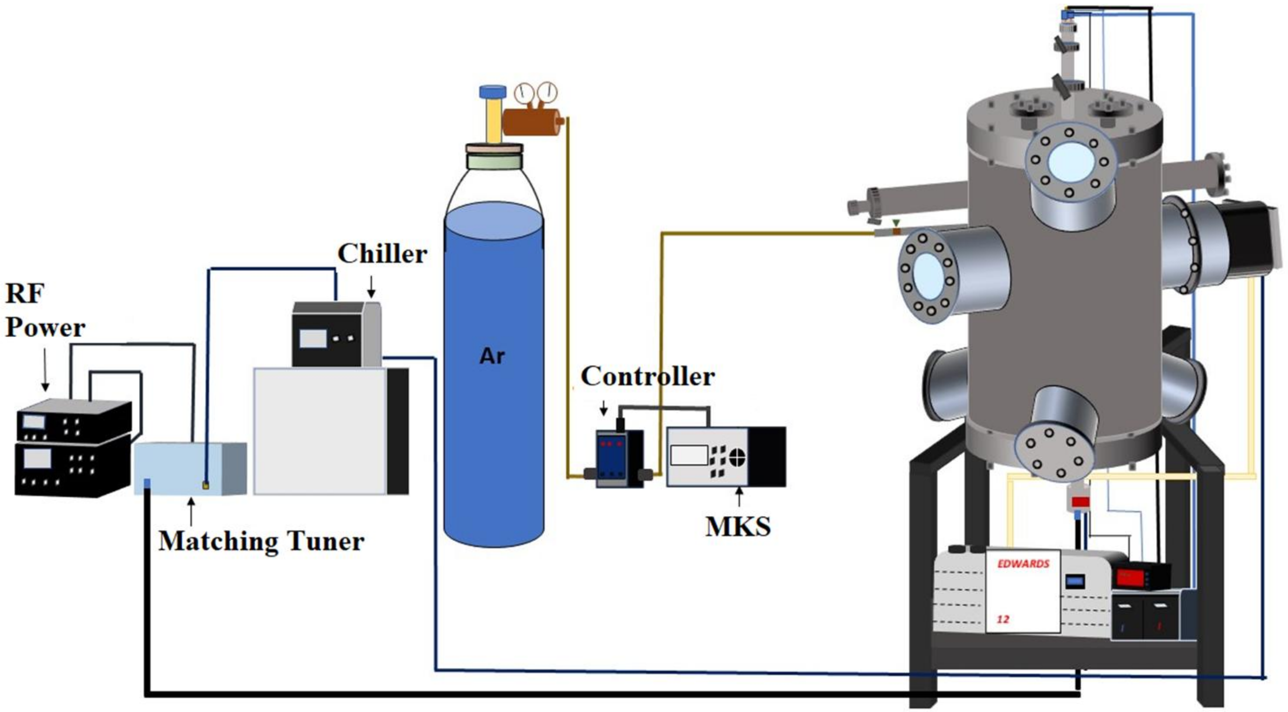
Experimental Procedure-1

Ti growth on SLG substrate by DC magnetron sputtering → LCO growth on SLG/Ti thin film by RF Magnetron sputtering → Metal oxide buffer layer growth with ALD technique on SLG/Ti/LCO thin film → LLZO growth on SLG/Ti/LCO/Metal Oxides by RF magnetron sputtering → Metal oxide buffer layer growth with ALD technique on SLG/Ti/LCO/Metal Oxide/LLZO → Li layer growth with thermal evaporation on SLG/Ti/LCO/MetalOxide/LLZO/ Metal Oxide



Metal oxides buffer layer: Al_2O_3, ZrO_2, Al_2O_3-ZrO_2,

Experimental Procedure-2



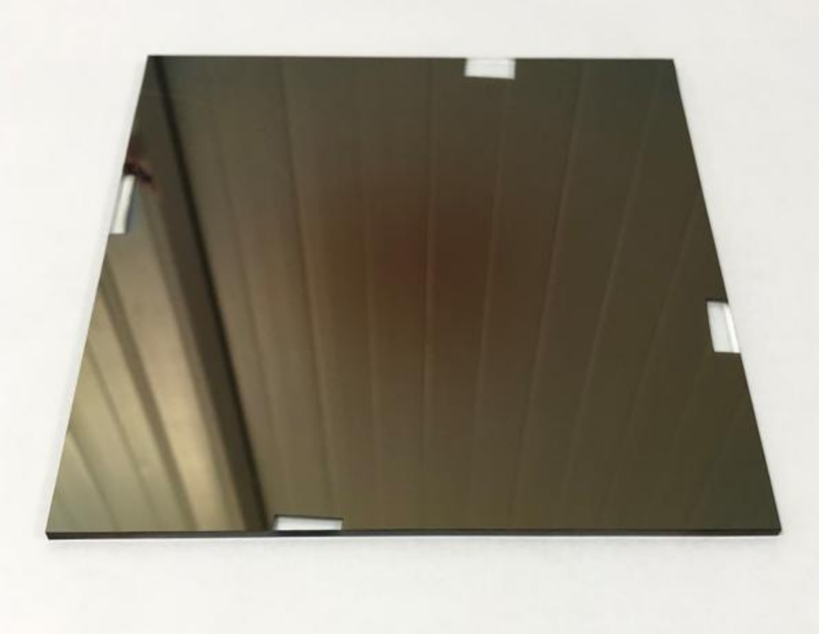
Schematic of magnetron sputtering vacuum chamber

Glovebox system

Growth of LCO Cathode Layer

Ti thin film growth → LCO thin film growth → Characterization of SLG/Ti/LCO thin film

Growth Parameters	Ti Thin Film	LCO Thin Film
Power	120 W	65 W
Power Supply	DC	RF
Pressure	10^{-2} Torr	10^{-3} Torr
Gas Flow	25 sccm	70 sccm

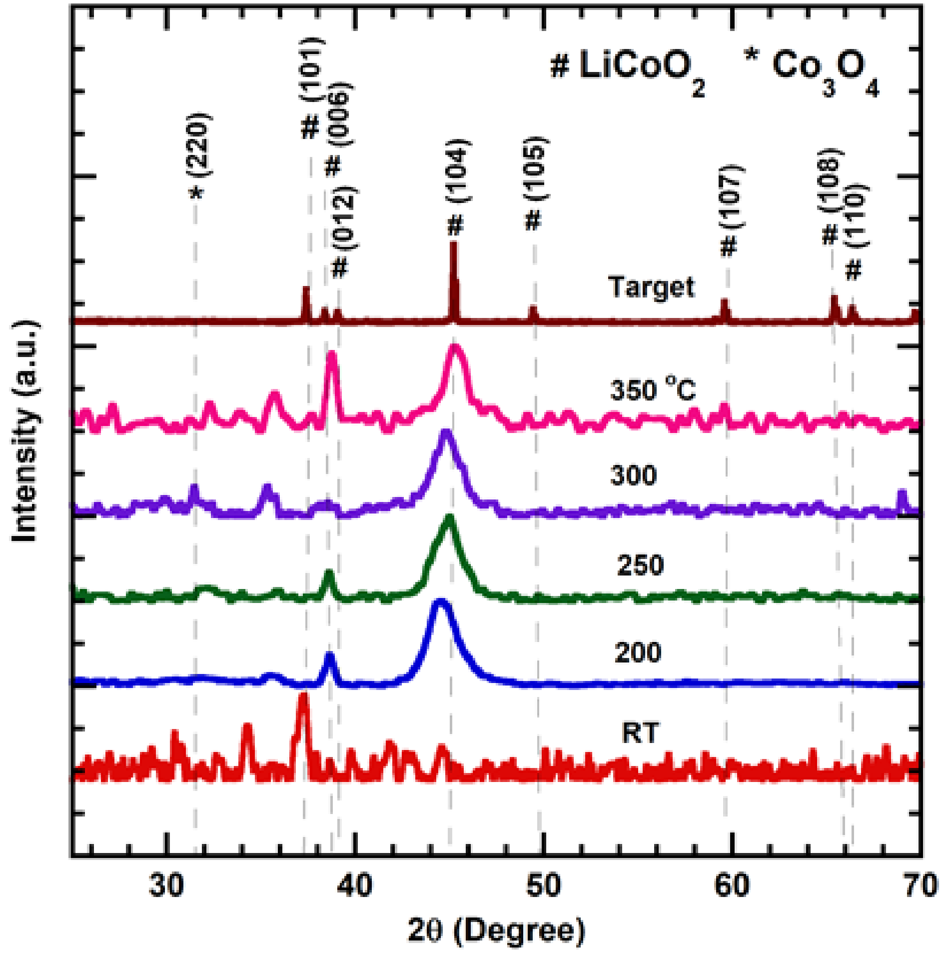


SLG/Ti/LCO thin film deposited on 15 cm x 15 cm glass substrate

Characterization of LCO Cathode Layer-1

- In XRD graph, (104) orientation, correspond to is critical for lithium-ion transport. This is an important finding that confirms the LCO thin film's potential to achieve optimal perfomance.

- (006) and (104) peaks play a significant role in calculating the lattice parameters and volume of LCO target and thin films, where (006) corresponds to the c-axis and (104) corresponds to the a-axis



XRD results of LCO target and LCO thin films grown at different substrate temperatures.

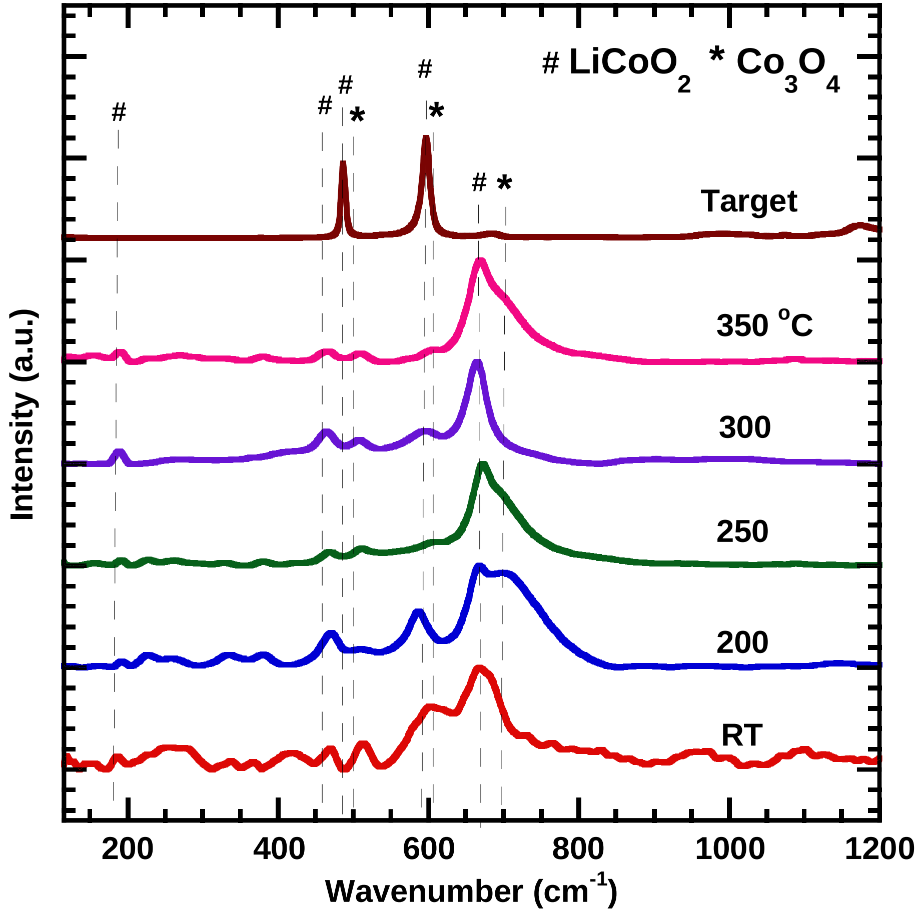
Characterization of LCO Cathode Layer-2

Sample Name	a (Å)	c (Å)	c/a	d_{006} (Å)	d_{104} (Å)	V ($Å^3$)
LCO Target	2.81	14.04	5.00	2.34	2.00	96.01
LCO Thin Film (for 250 °C Substrate Temperature)	2.90	13.44	4.62	2.24	2.01	97.89

Lattice parameters and unit cell volumes of LCO target and thin film grown 250 ^{o}C.

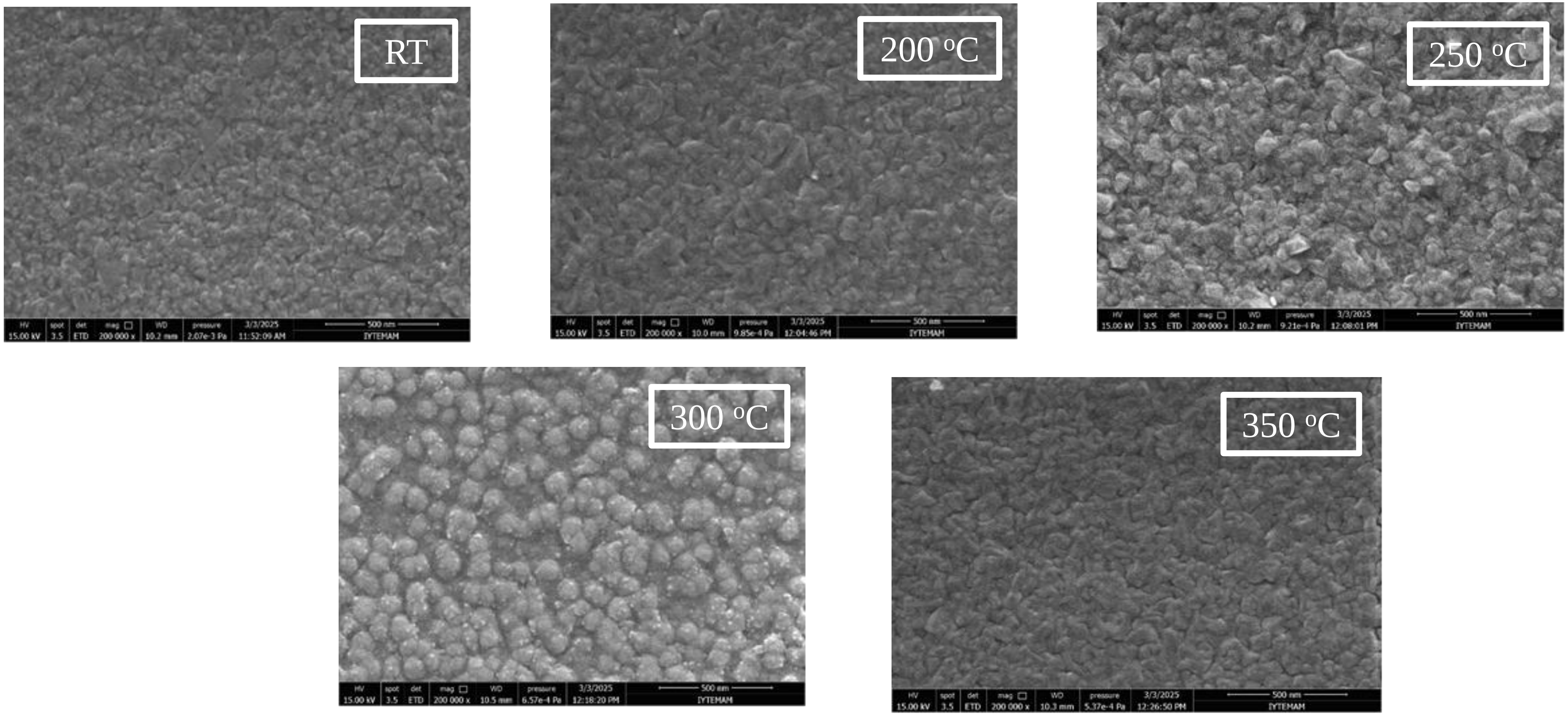
Characterization of LCO Cathode Layer-3

- Raman results confirmed the crystal structure of the LCO target and thin films, showing characteristic E_g and A_{1g} modes.
- LCO thin films exhibited Raman peaks indicating crystallinity, while some peaks suggested the presence of Co_3O_4 secondary phases.



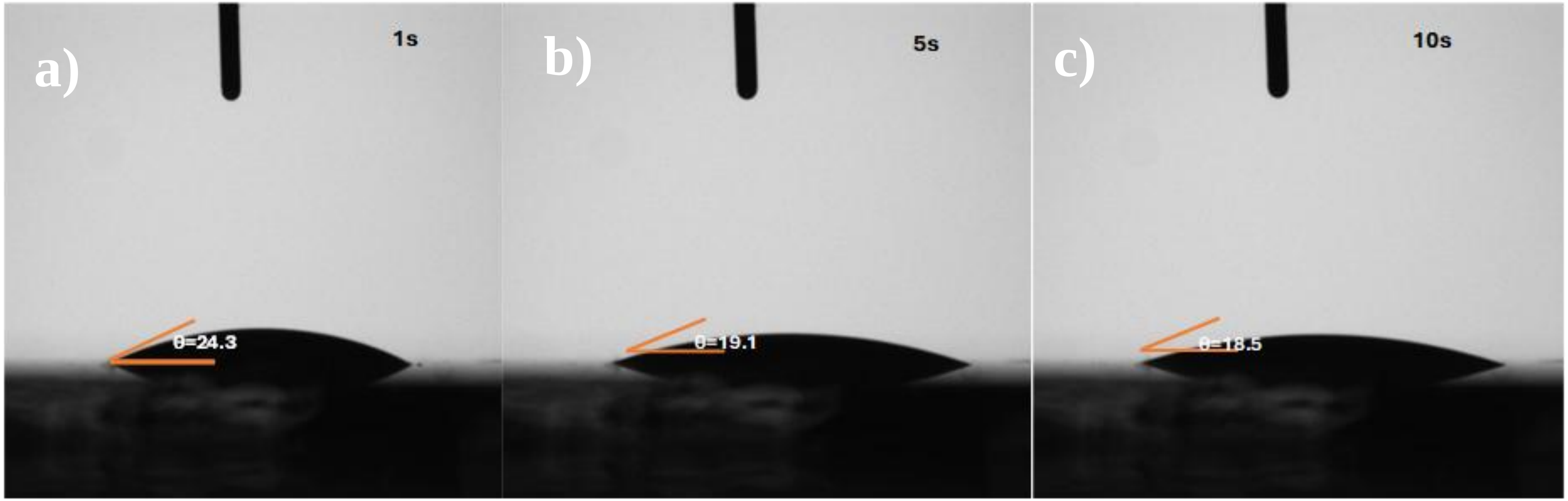
Raman results of LCO target and LCO thin films grown at different substrate temperatures.

Characterization of LCO Cathode Layer-4



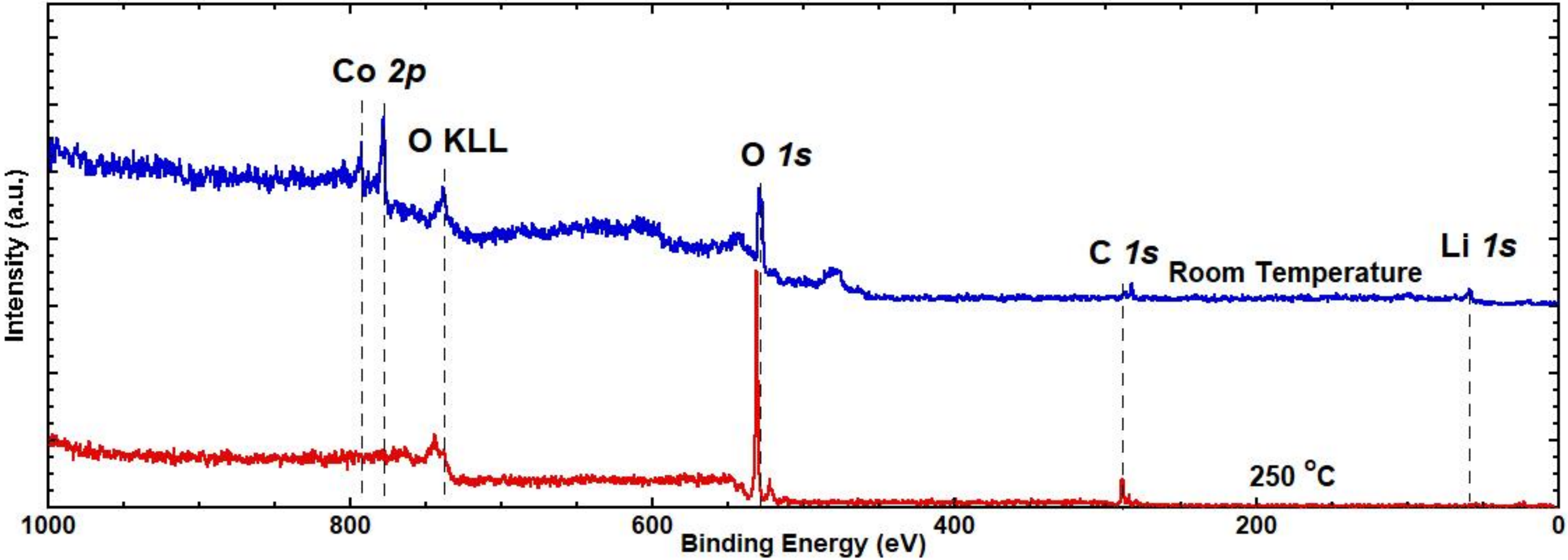
SEM images of LCO thin films grown at different substrate temperatures

Characterization of LCO Cathode Layer-5



Contact angle images of Ti/LCO thin film samples **a)** θ = 24.3°, **b)** θ = 19.1°, **c)** θ =18.5°

Characterization of LCO Cathode Layer-6



XPS Survey spectrum of LCO Layer

Growth of LLZO Solid Electrolyte Layer

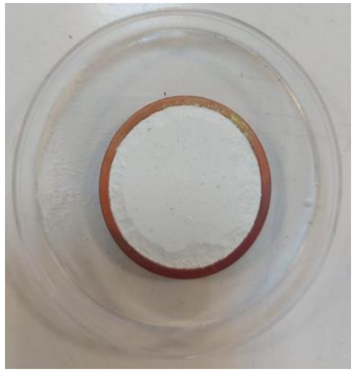
LLZO target preparation → LLZO thin film growth → Characterization of LLZO thin film

LLZO powder was milled in a mortar for 6 hours.

LLZO powder mixture was calcined at 1100°C.

Calcined LLZO powder was milled again for 6 hours.

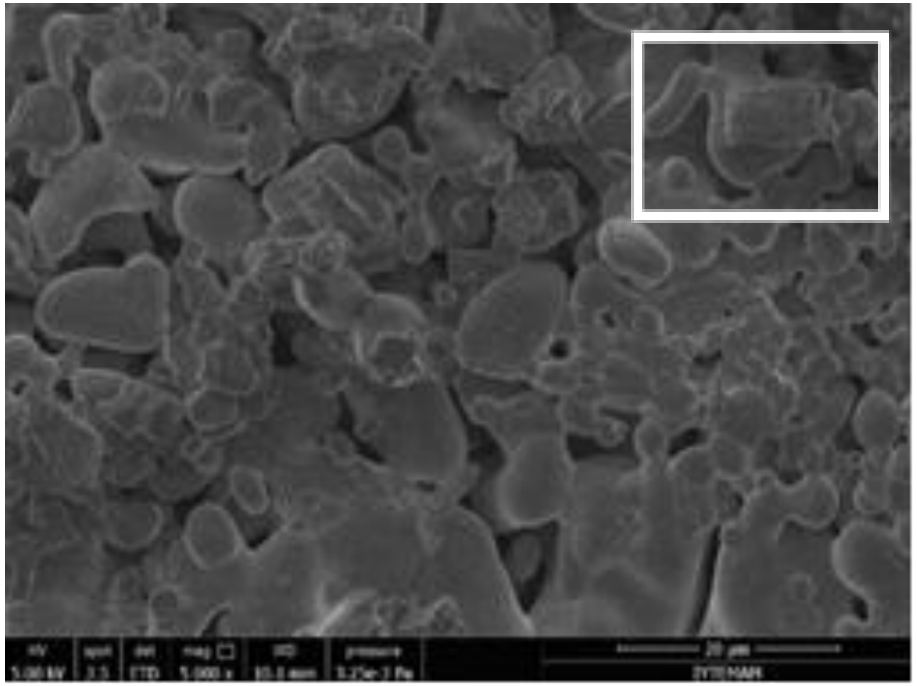
LLZO powder was pressed onto a copper plate under 80 bar pressure.



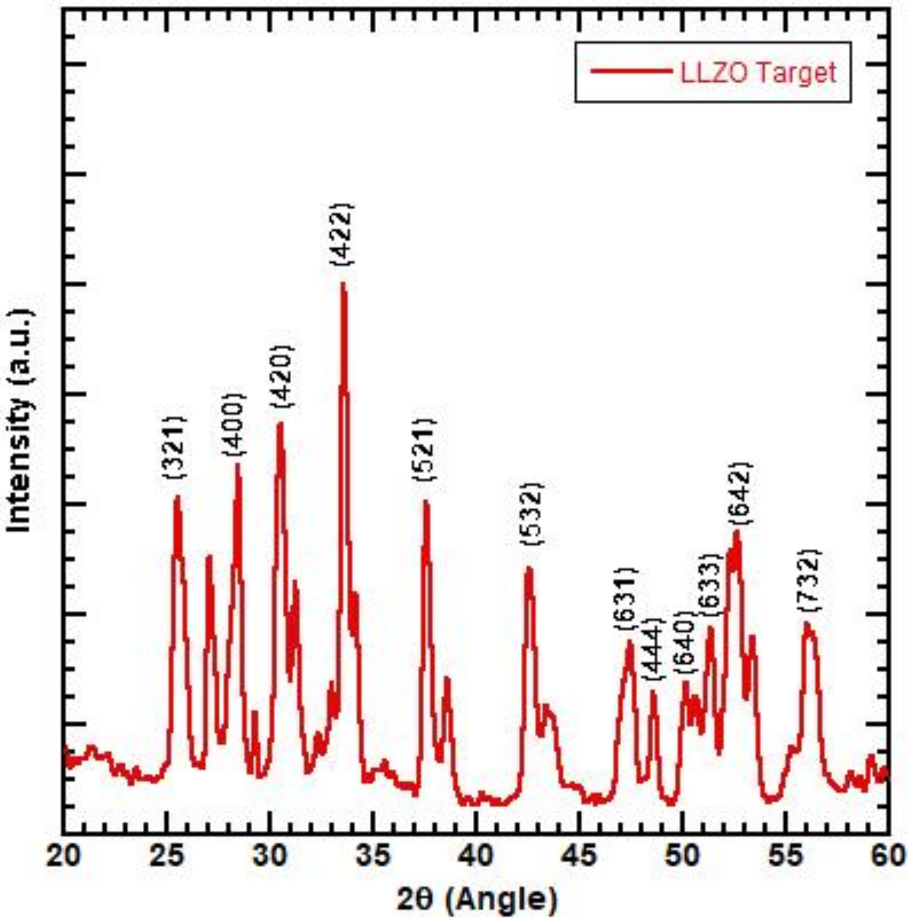
LLZO target was obtained.

LLZO powder pressed onto the copper plate was annealed at 600°C.

LLZO Target Characterization

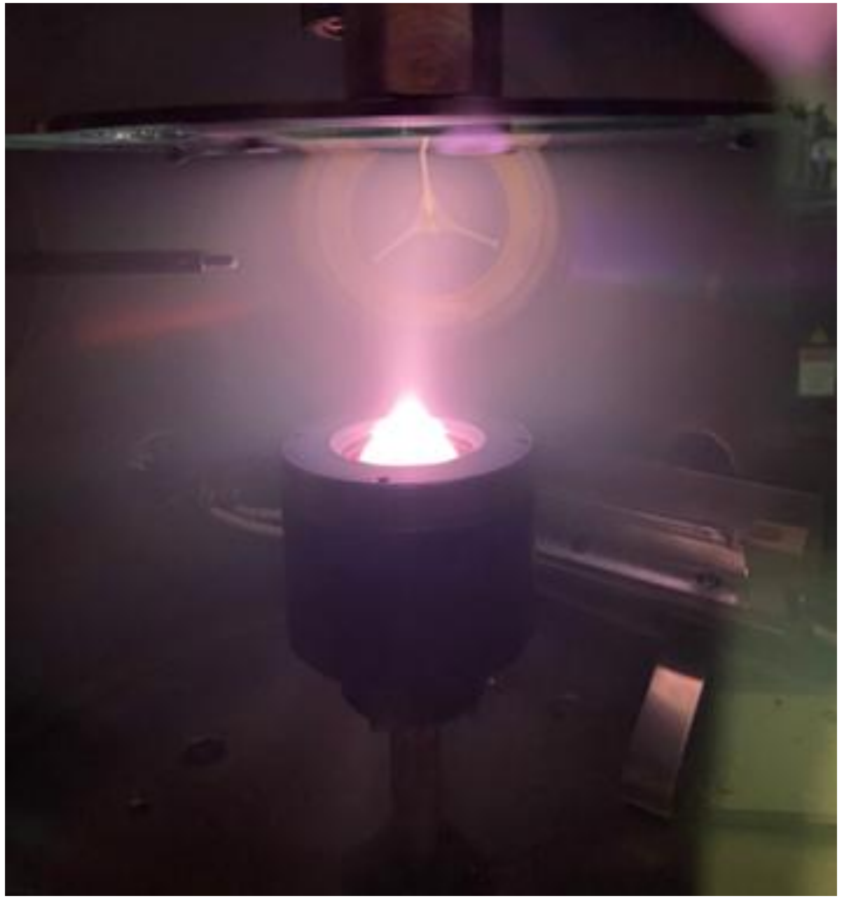


Deformed fragments observed in the SEM image of the LLZO target with size of 20 µm.



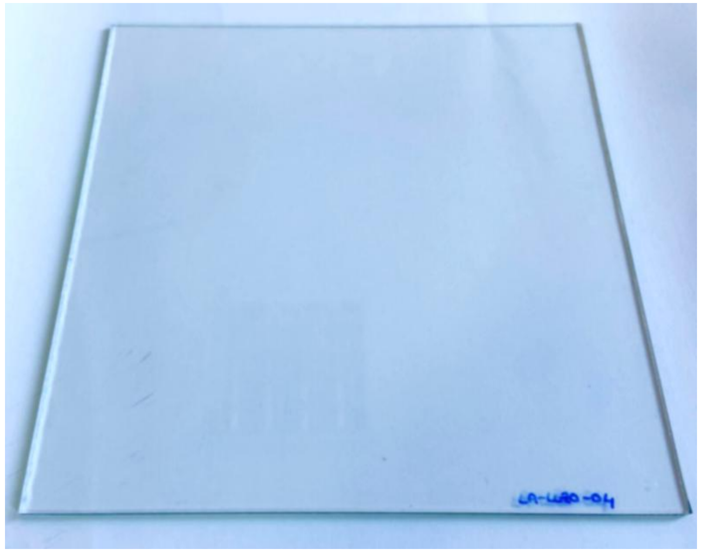
Padarti et al., Journal of Taiwan Institute of Chemical Engineers, (2018), 90.

LLZO Thin Film Electrolyte Layer’s Growth



Plasma during LLZO deposition.

Growth Parameters	LLZO Thin Film
Power	75 W
Power Supply	RF
Pressure	10^{-4} Torr
Gas Flow	70 sccm



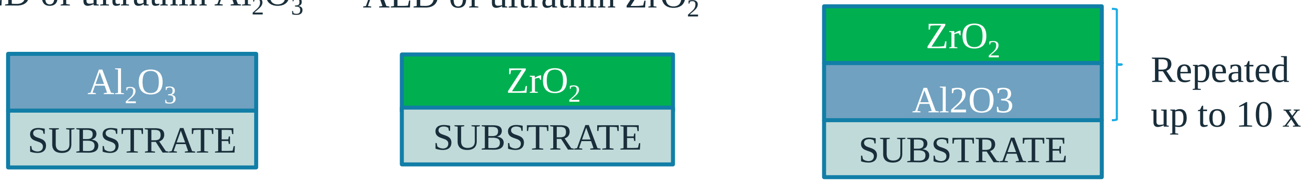
LLZO was deposited
on top of the 15 cm x 15 cm SLG substrate.

Metal Oxide Buffer Layer Growth by ALD

Beneq TFS-200 ALD reactor

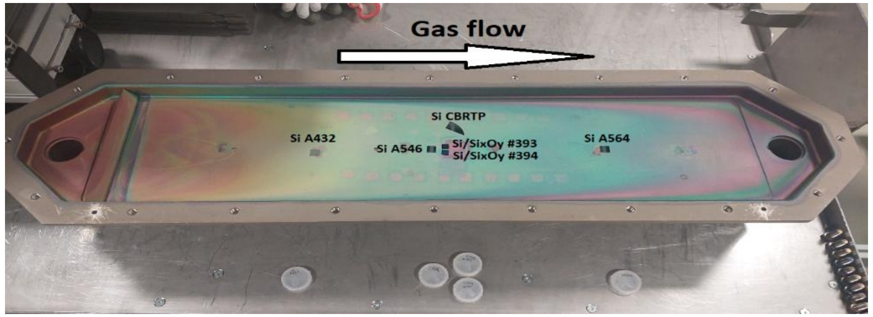
Controlled thickness of the ALD layers – nominally in the range of 2-20 nm

ALD of ultrathin Al_2O_3 | ALD of ultrathin ZrO_2 | ALD of ultrathin ZrO_2/Al_2O_3 nanolaminates



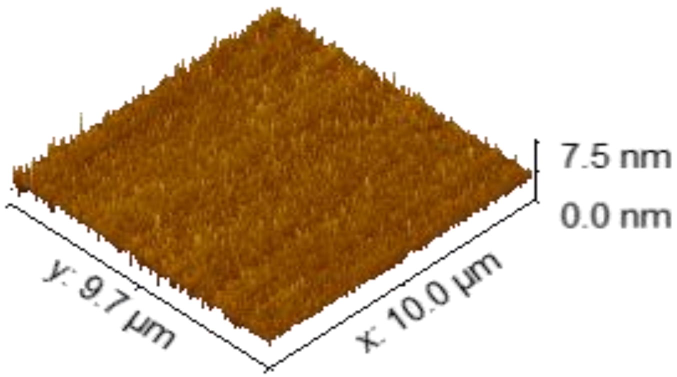
ALD precursors: for ALD of Al_2O_3 - TMAl, H_2O and TMAl, O_3
for ALD of ZrO_2 - TEMAZr, H_2O

- Al_2O_3, ZrO_2, and Al_2O_3-ZrO_2 layers were grown as buffer layer using the ALD technique.
- Suitable precursors and process parameters were optimized for each material.

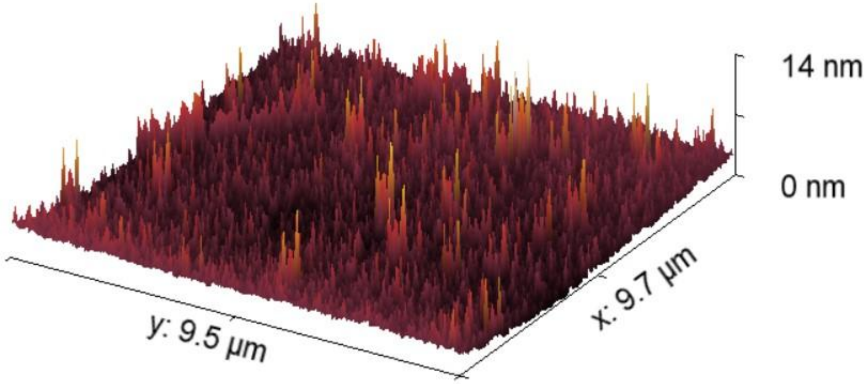


Large-area ALD reaction chamber

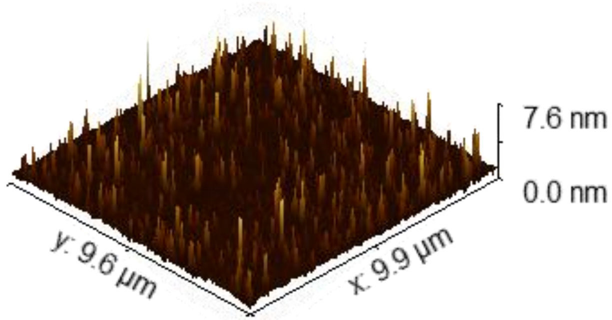
Metal Oxide Buffer Layer Growth by ALD



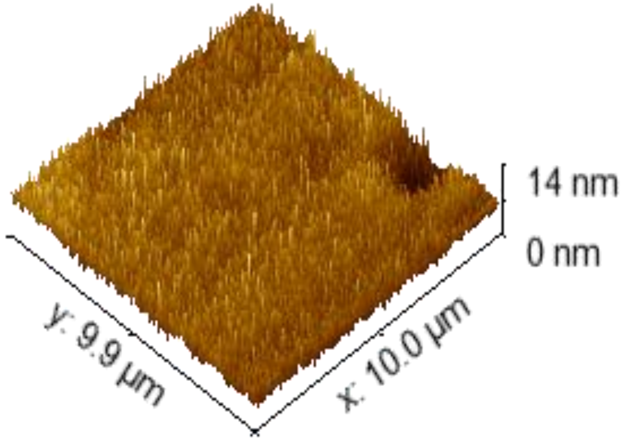
Si - RMS roughness (Sq) = 0.535 nm



2 nm Al_2O_3/Si



2 nm ZrO_2/Si - RMS roughness (Sq) = 436.9 pm



10 x (2 nm ZrO_2/2 nm Al_2O_3) / Si
- RMS roughness (Sq) 1.267 nm

Conclusion

- LCO thin film were grown at 250 °C RF magnetron sputtering, and XRD analysis confirmed that they maintained the (104) crystal orientation critical for lithium-ion transport.
- Raman spectroscopy confirmed the crsytal structure, SEM revealed temperature effect on surface morphology, and XPS analysis identified chemical bonding states of the elements.
- LLZO target was calcined at 1100°C, followed by the growth of LLZO thin films using RF magnetron sputtering. Optimization studies are ongoing.
- Al_2O_3, ZrO_2, and Al_2O_3-ZrO_2 buffer layers were grown using ALD technique.

Outcomes within the Scope of the Project

- PhD Thesis by **Nurcin KARADENIZ** " Low Temperature Magnetron Sputter Growth of Cubic $Li_7La_3Zr_2O_{12}$ Ion Conducting Films for All-Solid State Batteries."

- M.Sc. Thesis by **Nazlıcan ESEN** " Lithium Dependence of Ionic Conductivity in LLZO ($Li_xLa_3Zr_2O_{12}$) Thin Films Grown by Magnetron Sputtering for Lithium Ion Batteries."

- M.Sc.Thesis by **Serra KARPUZ** "Interfacial Characterization Between LLZO and LCO Layers for All Solid State Batteries."

- M.Sc. Thesis by **Polatkan OZCAN** "Growth and Characterization of LiCoO2 Thin Films by Magnetron Sputtering for Lithium Ion Batteries."

- Ozcan, P., Esen, N., Cantas, A., Ozyuzer, L., Ozdemir, M., Kosiel, K., Szerling, A., & Aygun, G. Invesitagiton of $LiCoO_2$ Thin Films Grown under Relatievly Low Substrate Temperature for All Solid State Lithium Ion Batteries *V*acuum, Submitted in December 2024 (*In Progress*).

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THANK YOU

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