Importance of ALD Grown Buffer Layer for Magnetron Sputtered $LiCoO_2/Li_7La_3Zr_2O_{12}$ in All-Solid-State Lithium-ion Batteries

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Abstract

This study advances all-solid-state lithium-ion batteries (ASSLIBs) by focusing on the deposition of $LiCoO_2$ (LCO) as a cathode and $Li_7La_3Zr_2O_{12}$ (LLZO) as a solid electrolyte. A dual-deposition system combining RF magnetron sputtering and thermal evaporation enables the fabrication of uniform, scalable thin films for large-area applications. The project optimizes growth parameters to achieve high energy density (~200 mAh/g) and cycle stability. Special attention is given to the LCO-LLZO interface, where atomic layer deposition (ALD) introduces a nano-layered buffer film to improve adhesion and charge transfer. Extensive characterization techniques, including SEM, XRD, Raman spectroscopy, XPS, and electrochemical measurements, evaluate the structural and electrochemical properties of the films. The project aims to achieve ASSLIBs with over 200 mAh/g capacity and 80% retention after extended cycling, contributing to the development of high-capacity, durable batteries for next-generation energy storage applications.

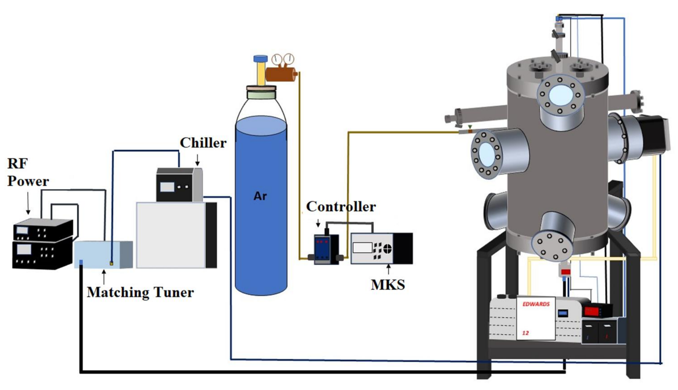
Introduction

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

Layer Flow Chart

- Ti was grown on SLG as a current collector improves the structural integrity and conductivity of the battery and ensures effective electron flow.
- LCO cathode serves as the material for lithium-ion storage.
- A buffer layer made of metal oxide (Al_2O_3, ZrO_2, Al_2O_3-ZrO_2) is located between the cathode and the solid electrolyte to improve interfacial stability.
- LLZO solid electrolyte layer facilitates efficient ion conduction while preventing dendrite growth.
- Lithium metal anode layer provides a source for lithium ions during charging.

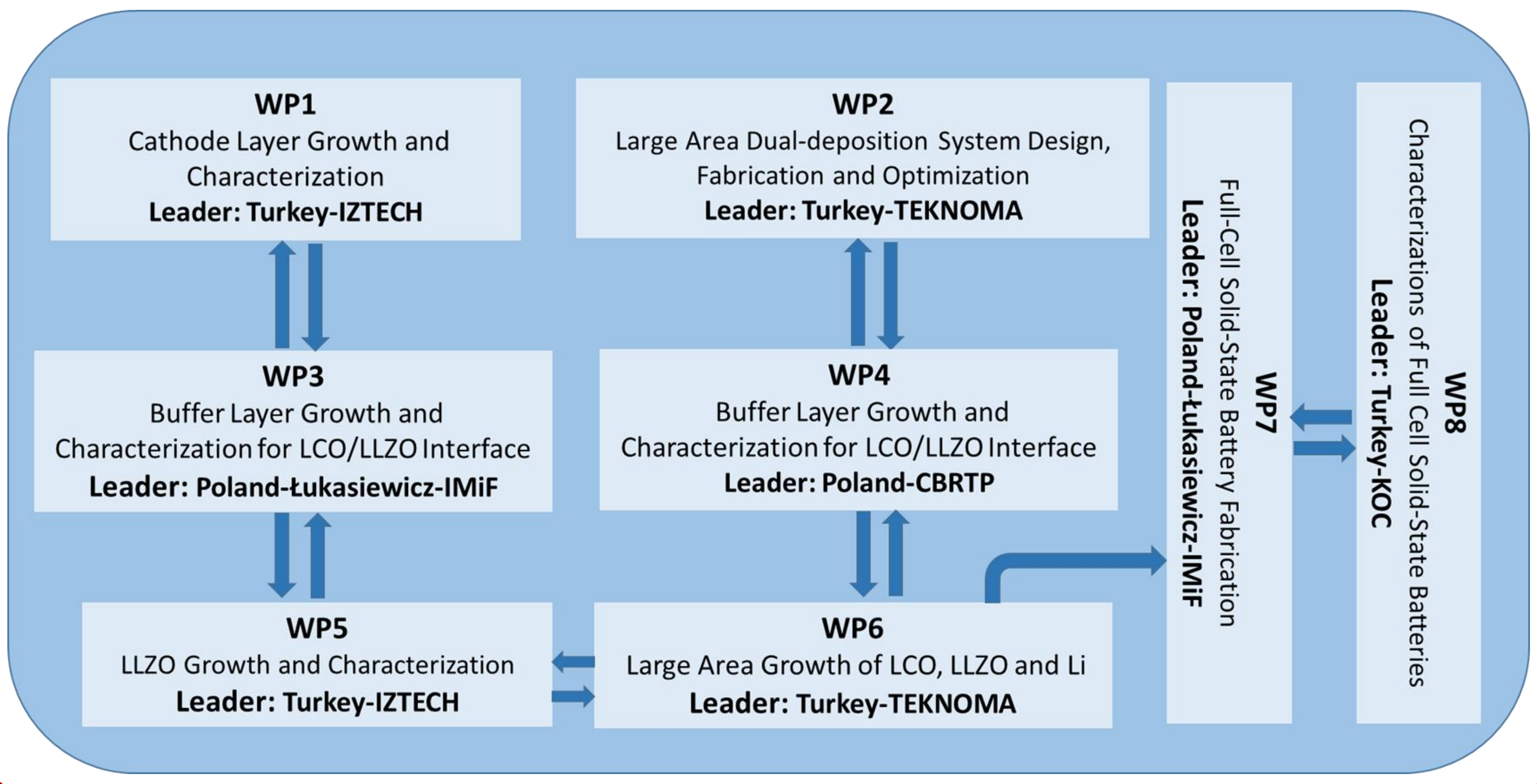
Thin film battery structure



Schematic of magnetron sputtering vacuum chamber


Image of the glovebox system

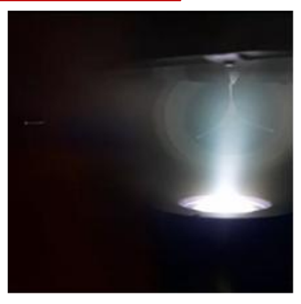
Pert Chart of ARISER



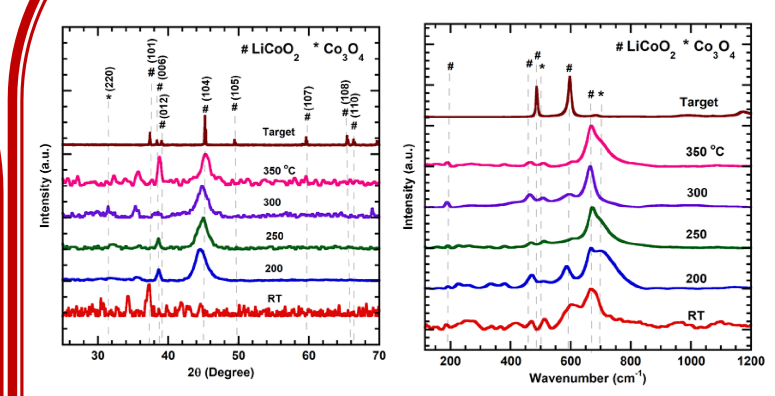
LCO

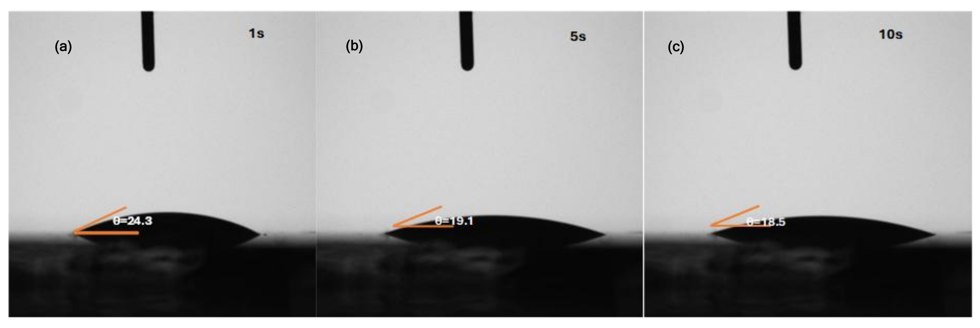
Thin film deposition → Characterization

- About 100 nm Ti thin film was deposited onto SLG using DC power supply of 120 W.
- LCO was grown on SLG/Ti by RF magnetron sputtering at a power of 65 W.
- LCO serves as a cathode layer for ASSLIBs.

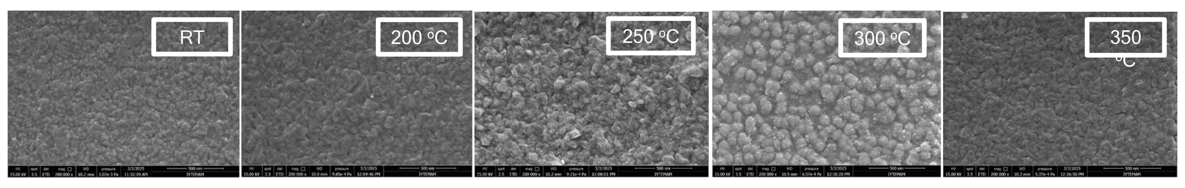

Excentric rotation of the sample holder

Characterization of Ti-LCO thin films

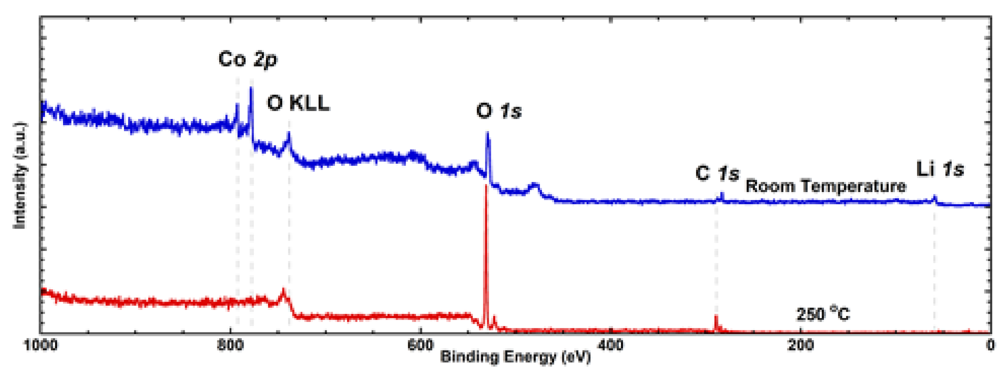

XRD and Raman results of LCO target and LCO thin films



Contact angle of Ti-LCO sample (a) θ=24.3° (b) θ=19.1° (c) θ=18.5°



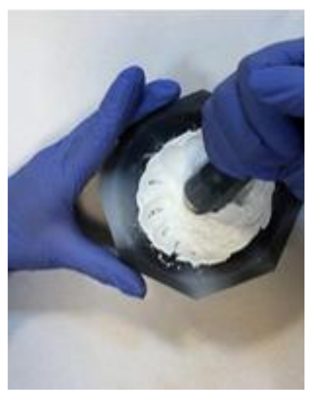
SEM images of LCO thin films grown at different substrate temperatures



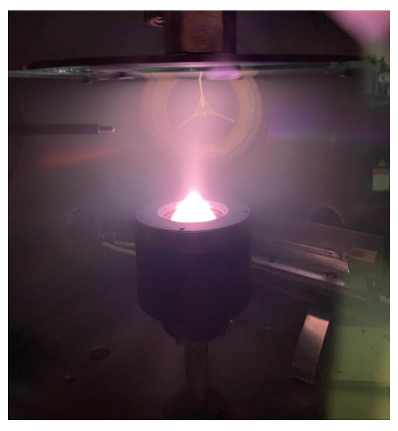
XPS survey spectra of LCO thin films grown at room temperature and 250 °C

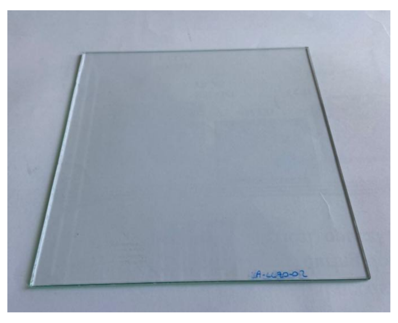
- The XPS analysis of the LCO thin film revealed the observation of key peaks corresponding to Li 1s, Co 2p, O 1s, and C 1s.

LLZO



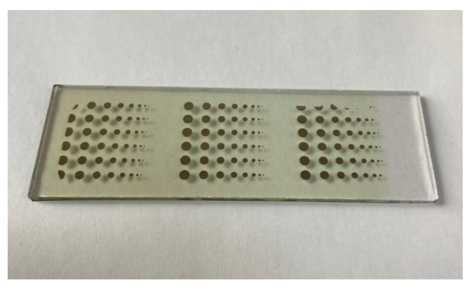
The LLZO powder was mixed by grinding in an agate mortar and then pressed into a pellet.


Plasma during deposition of LLZO


LLZO thin film deposited on 15cm x 15cm glass substrate


LLZO thin film deposited using 83 W RF Power for 60 minutes

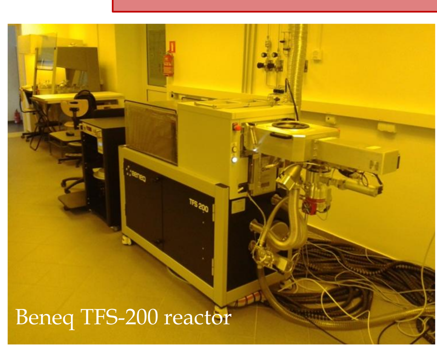

Sample of LLZO grown on ITO coated (contact layer) substrate and the mask


Aluminum contacts of various diameters applied on a SLG/LLZO thin film

Target Preparation → Thin film deposition → Characterization

Optimization studies for LLZO are ongoing.

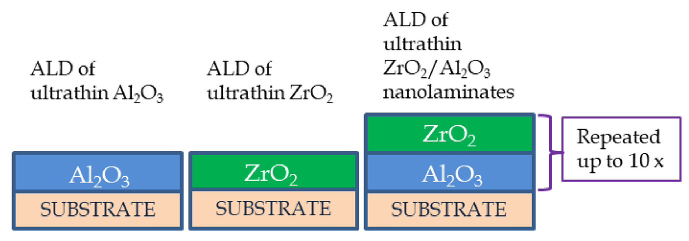
Metal Oxide Buffer Layer




Coated glass in this vacuum case


SLG/Ti/LCO sample in the reaction chamber

- Al_2O_3 and ZrO_2 layers were optimized for < ±2% homogeneity.
- The best Al_2O_3 growth was achieved at 150 °C with a 1:3 TMA-O_2 pulse ratio.
- ZrO_2 growth was performed at 100 °C using TDMAZr and water in 1000 cycles.



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

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

Conclusion

- Ti and LCO layers grown on SLG substrates successfully.
- In-situ heat treatment significantly improved phase purity and crystallinity for LCO.
- Enhanced crystallinity after heat treatment at 250°C.
- Revealed notable changes in chemical states and the emergence of secondary phases.
- LLZO will be grown as a solid electrolyte layer.
- The parameters for optimizing the growth of the LLZO solid electrolyte layer are still being studied.

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