# LITHIUM-TITANATE THIN FILMS BY SOLID STATE REACTION AS ELECTRODE MATERIAL FOR LITHIUM-ION BATTERIES

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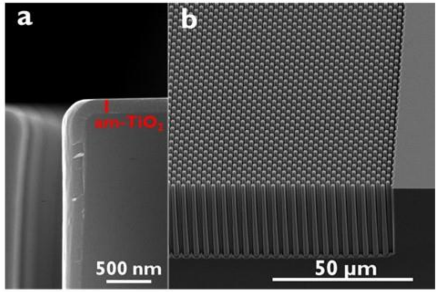
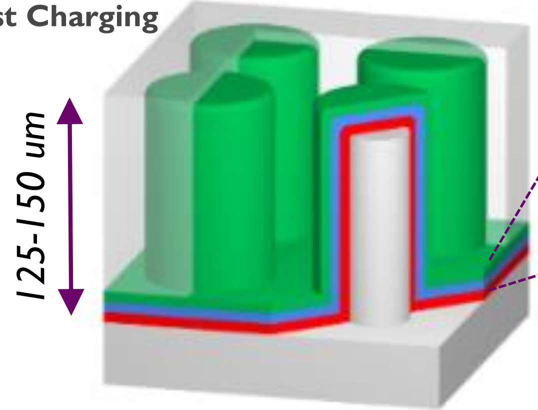
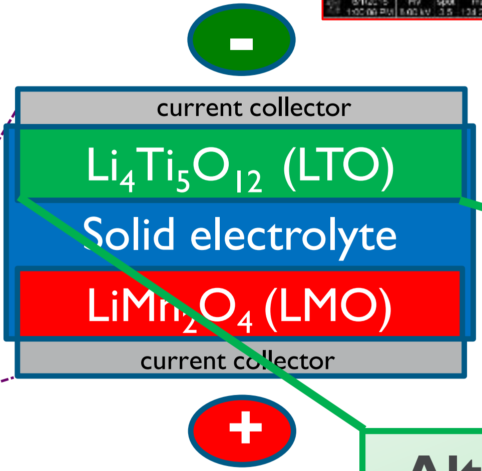
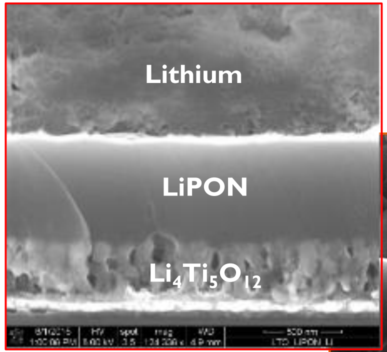
# THIN-FILM BATTERIES

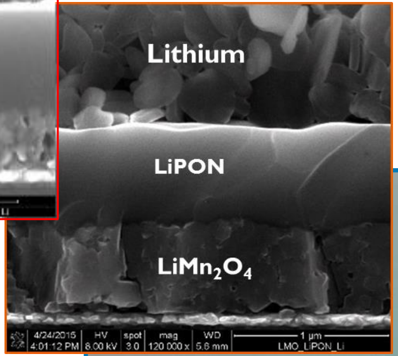


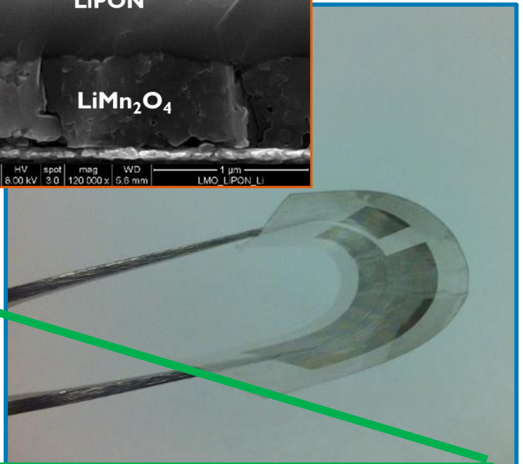

Fast Charging



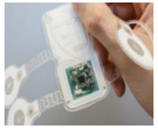



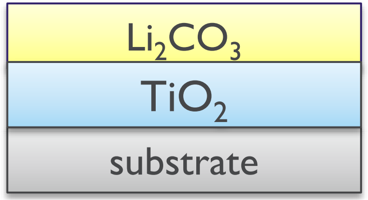
**Alternative $Li_4Ti_5O_{12}$ thin films fabrication method that can be used for making thin-film batteries on planar and 3D microstructured substrates**

***Smart carts, patches, wearables and flexible electronics…***

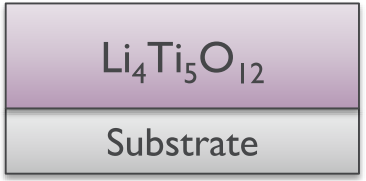
# PROPOSED FABRICATION PROCESS: $Li_4Ti_5O_{12}$ THIN FILMS BY SOLID STATE REACTION

**The fabrication by solid state reaction is a very known technique for making powder material**
**→ Apply this fabrication method to make thin films**



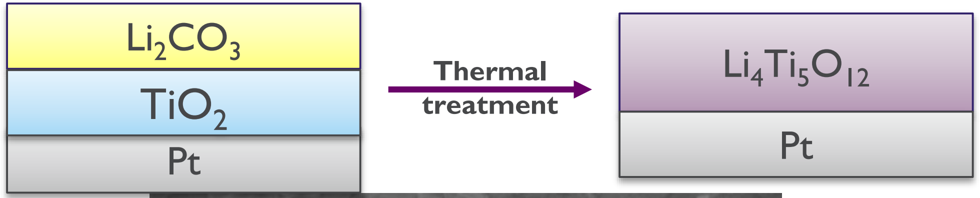

$$Li_2CO_3 + 5/2TiO_2 \rightarrow 1/2Li_4Ti_5O_{12} + CO_2$$

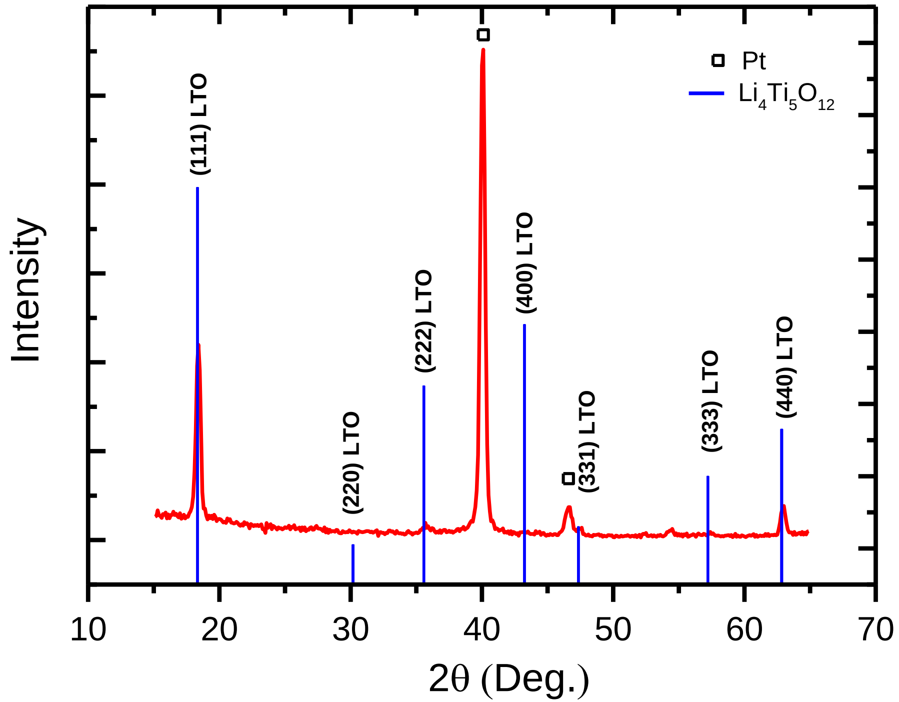
**Thermal treatment**

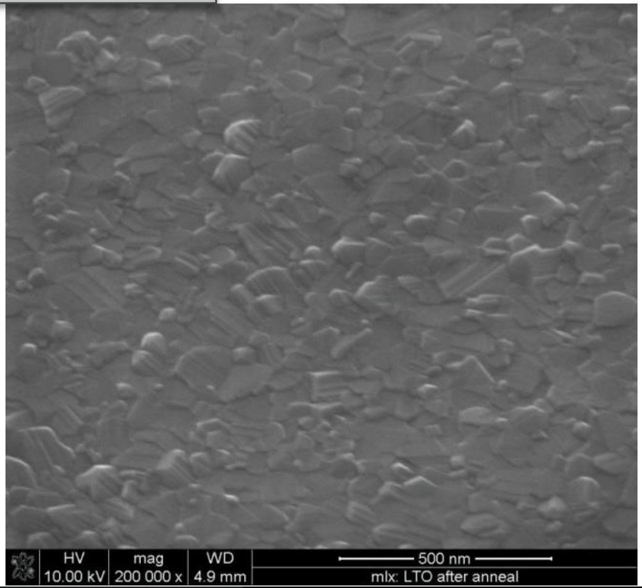


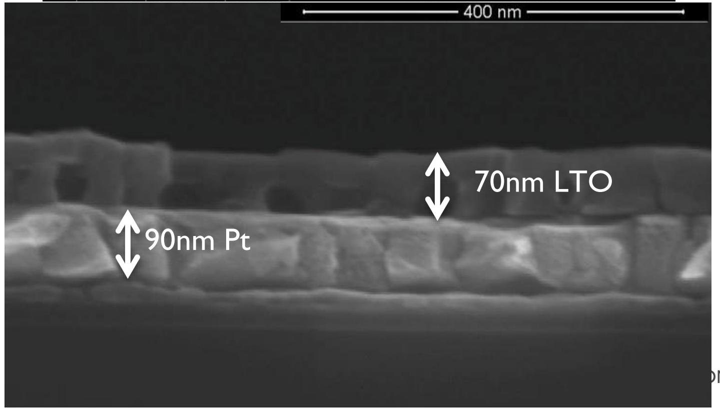

The $TiO_2$ layer is deposited by sputtering or atomic layer deposition (ALD)
The $Li_2CO_3$ layer is deposited by spincoating

# PHASE AND MORPHOLOGY



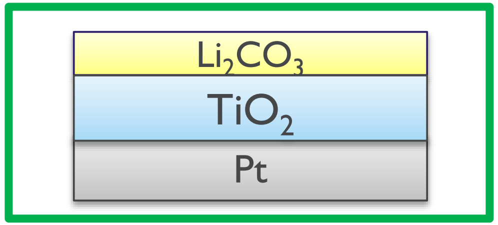




- Characteristic diffraction peaks of spinel $Li_4Ti_5O_{12}$
- Continuous 70 nm thick film with a crystalline morphology

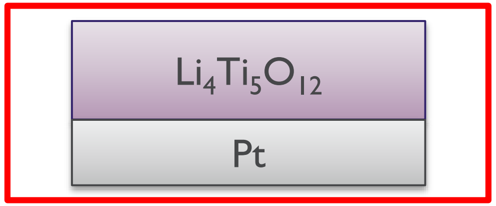
# XPS SURFACE SPECTRA BEFORE AND AFTER ANNEALING

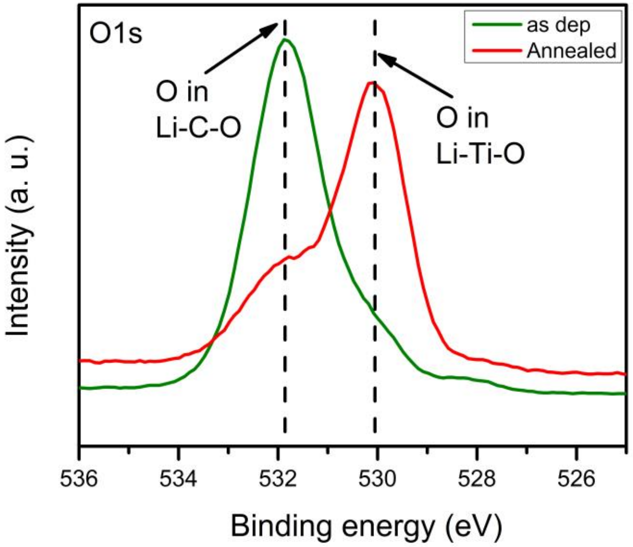
**As deposited**



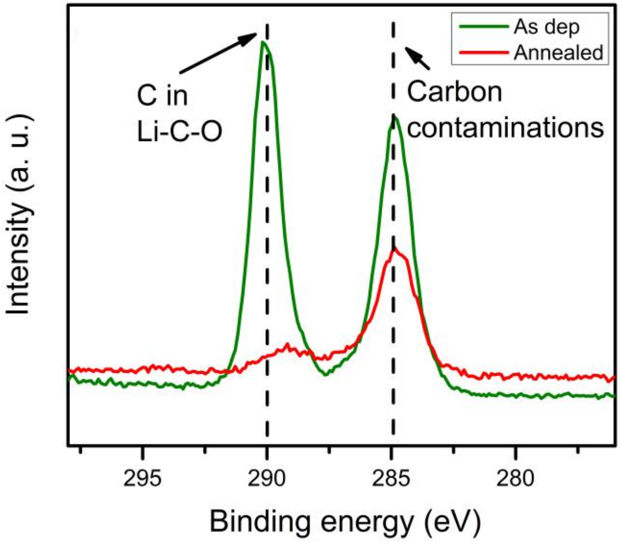

**Thermal treatment**

**After annealing**

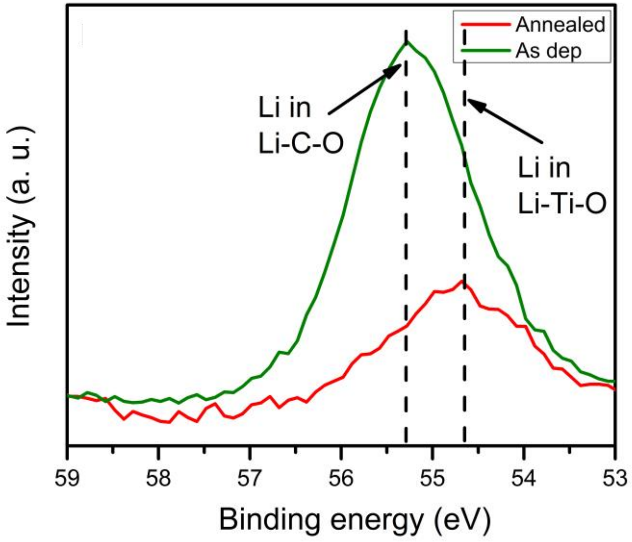



## C1s




## Li1s




**The thermal treatment causes elements intermixing and the LTO material formation**

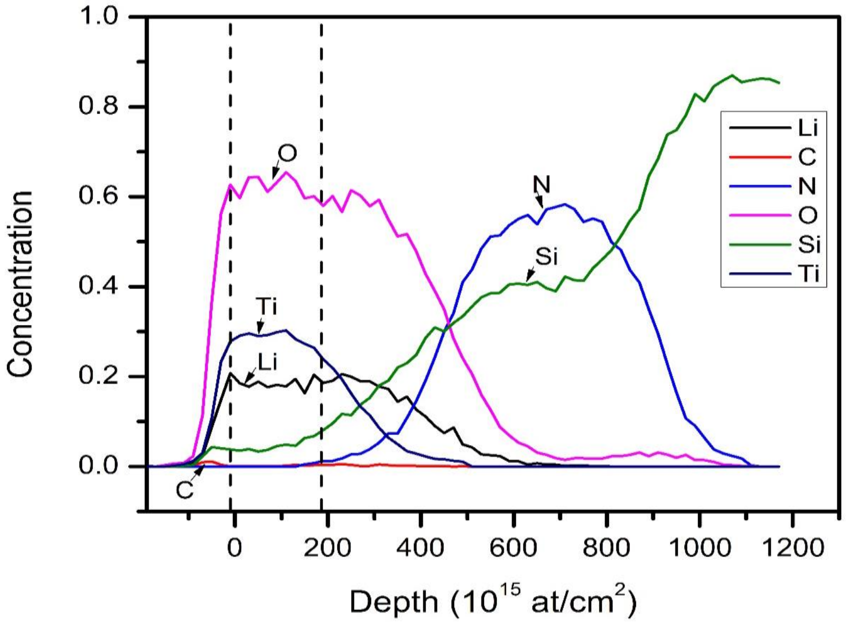
**Excess of $Li_2CO_3$ is detected after annealing**

# STOICHIOMETRY AND ELEMENTS DISTRIBUTION

$Li_4Ti_5O_{12}$

$Si_3Ni_4$

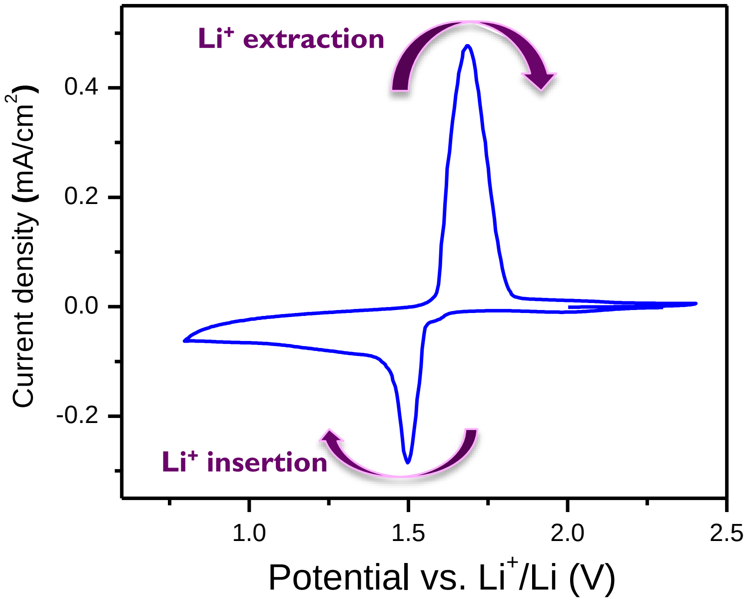
## ERDA (ELASTIC RECOIL DETECTION ANALYSIS)

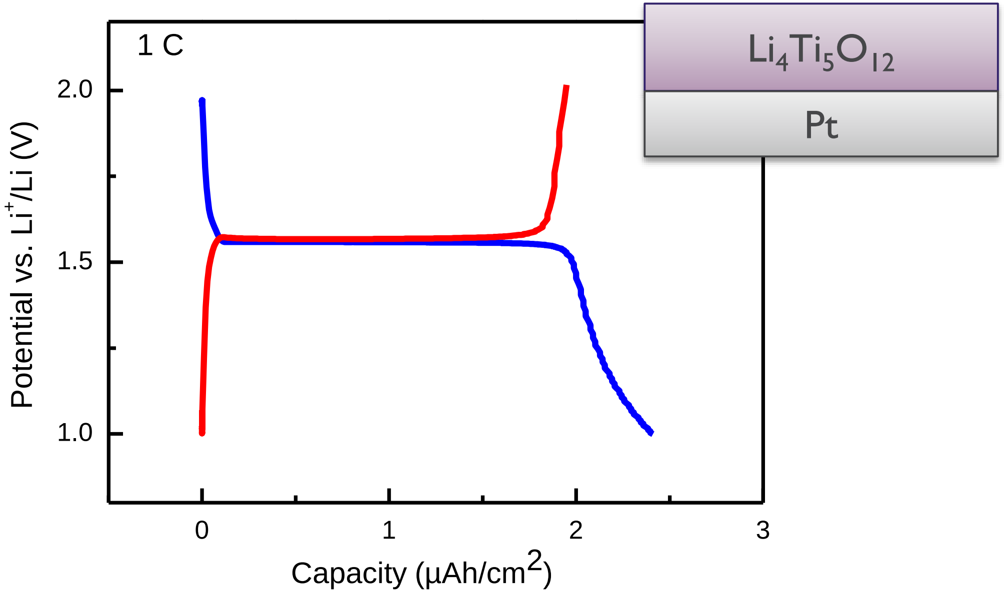


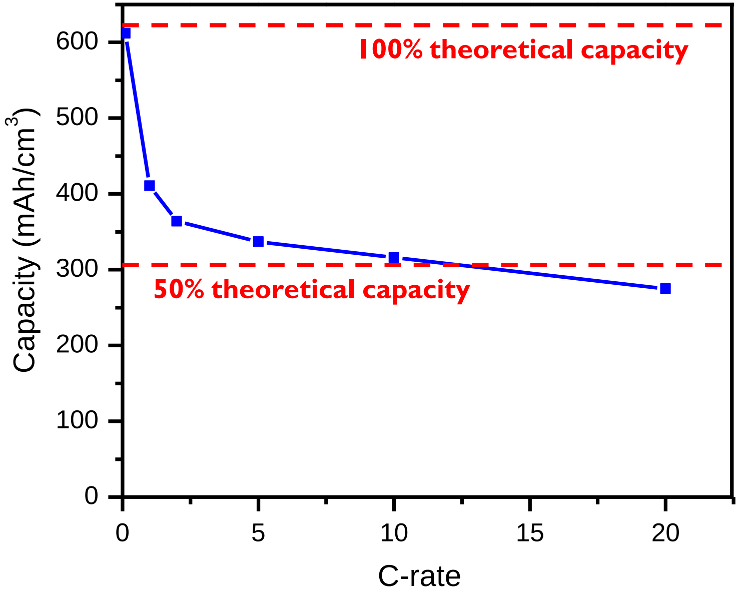

| | Elements ratio of the prepared film (ERDA) | Theoretical elements ratio in LTO |
|---|---|---|
| **Li** | 18 % | 19 % |
| **Ti** | 26 % | 24 % |
| **O** | 56 % | 57 % |

- Homogeneous elements distribution through the LTO layer
- Stoichiometry close to the theoretical stoichiometry of $Li_4Ti_5O_{12}$

# ELECTROCHEMICAL ACTIVITY

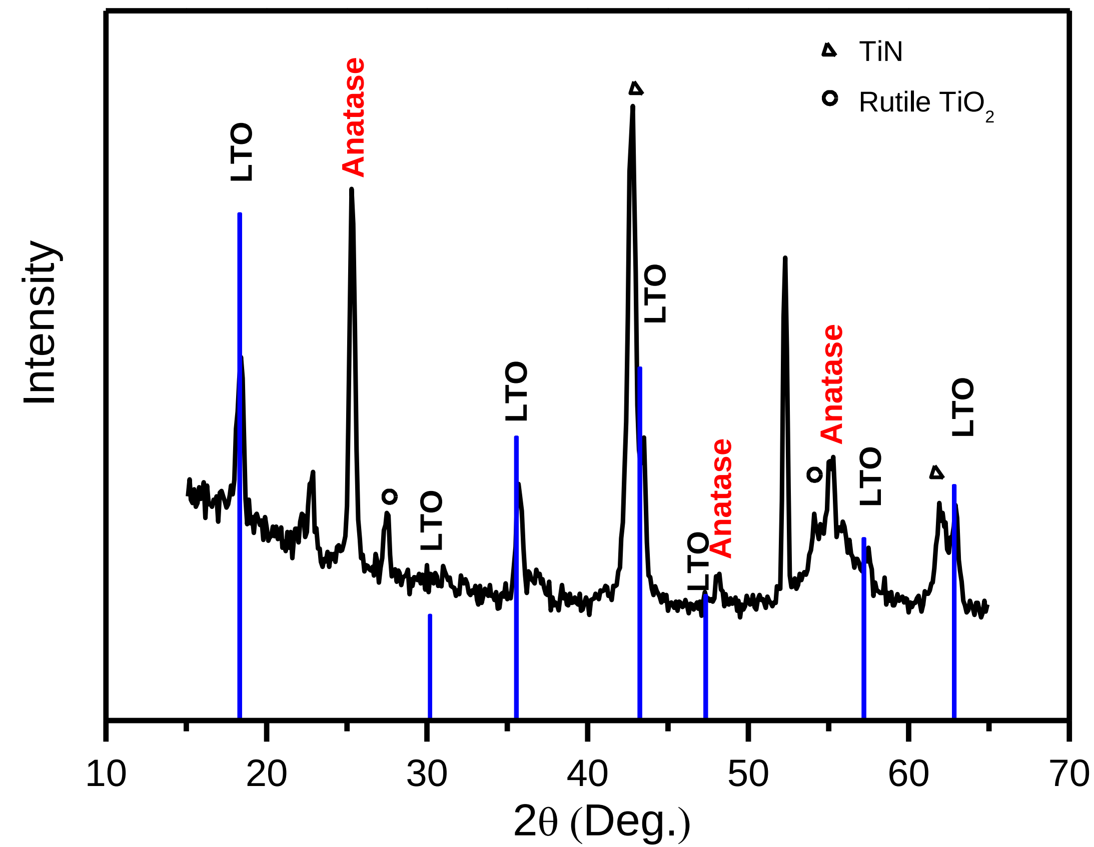


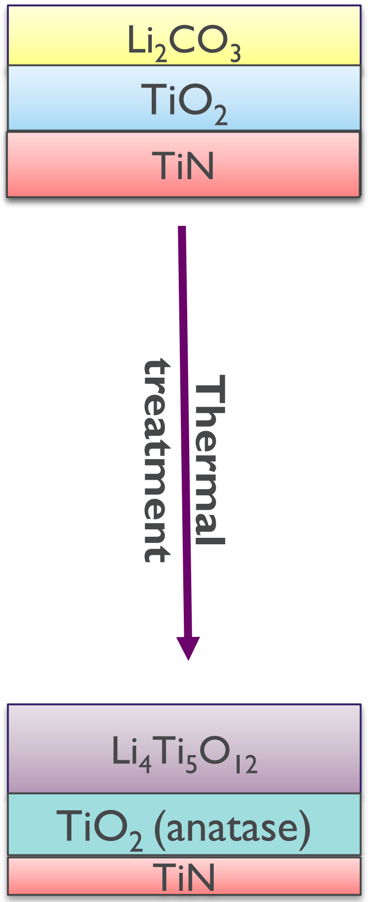




- Redox peak attributed to $Li^+$ insertion/extraction in/from LTO
- Flat potential plateaus at 1.55 V vs. $Li^+/Li$ typical for $Li_4Ti_5O_{12}$
- Theoretical capacity reached at 0.1C
- 45% of the theoretical capacity at 20C

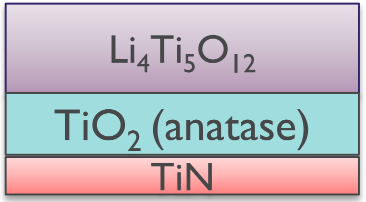
# $Li_4Ti_5O_{12}$ ON TiN

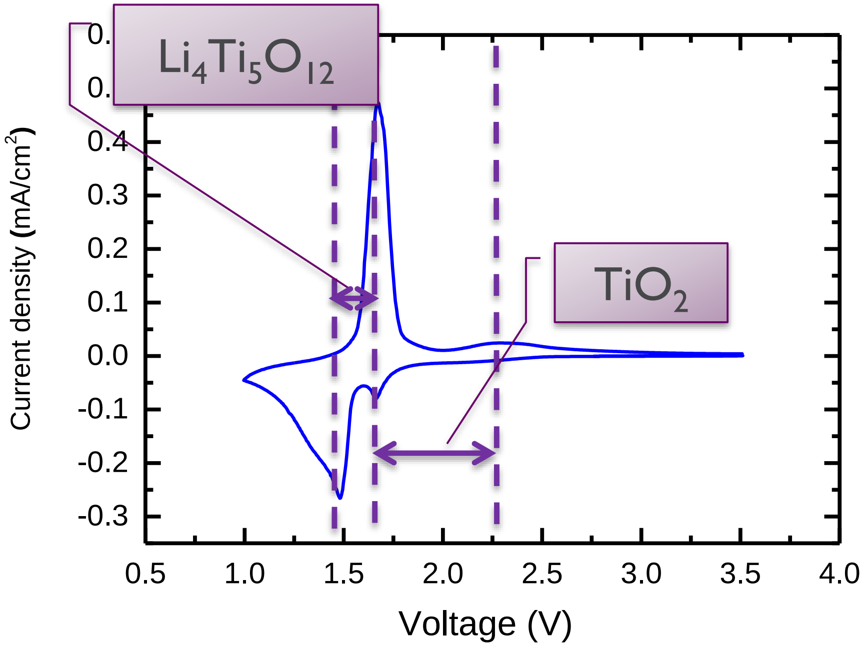


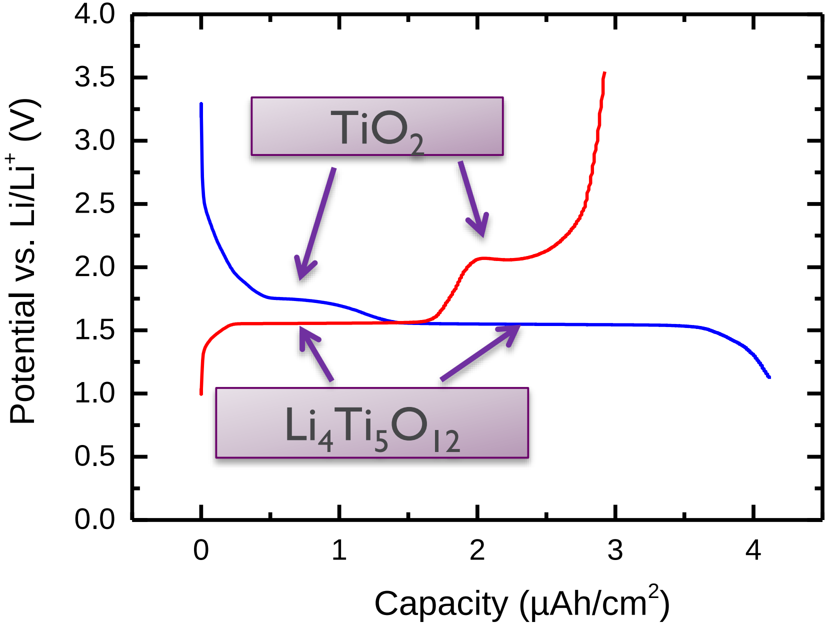




Characteristic spinel LTO diffraction peaks together with $TiO_2$ (mainly anatase and some rutile) and TiN current collector peaks.

# ELECTROCHEMICAL ACTIVITY



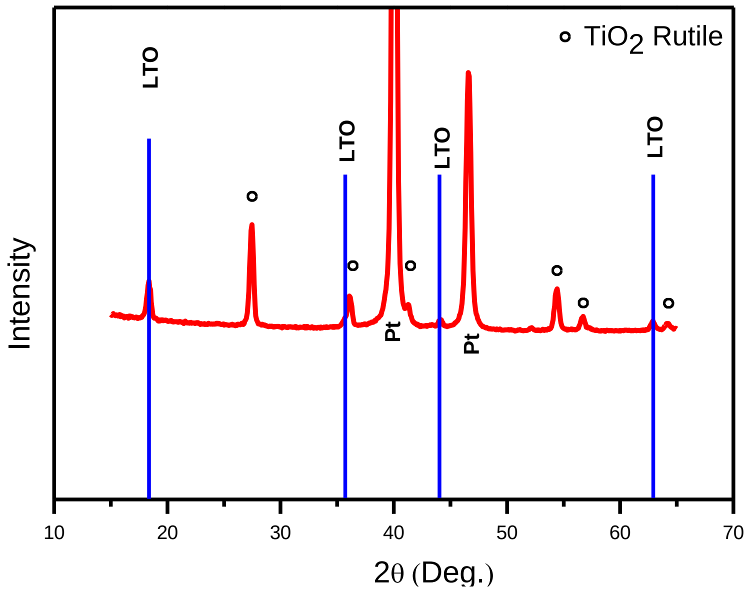



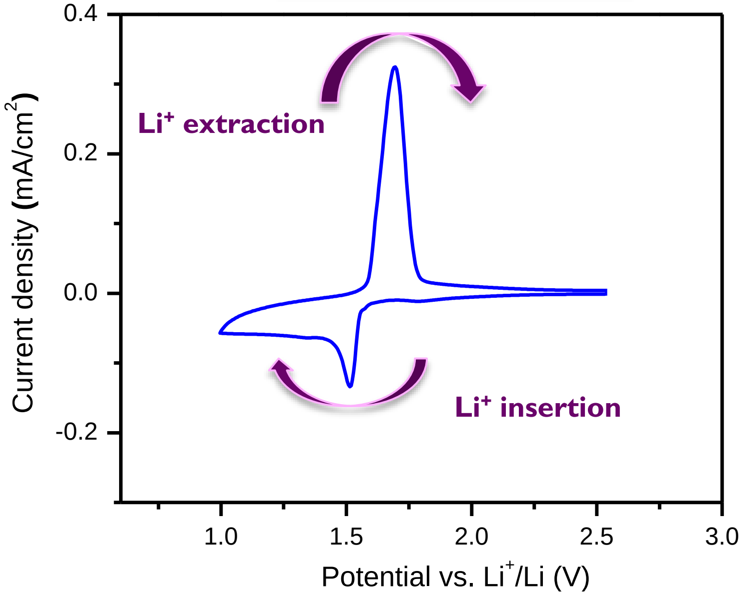




Redox peaks attributed to $Li_4Ti_5O_{12}$ and $TiO_2$

2 operational plateaus for $Li_4Ti_5O_{12}$ and $TiO_2$

# $Li_4Ti_5O_{12}$ WITH RUTILE IMPURITIES


Spinel LTO diffraction peaks together with rutile $TiO_2$ and Pt substrate peaks

Only LTO redox peaks → the rutile $TiO_2$ in not electrochemically active

# ELECTROCHEMICAL ANALYSIS OF THE DIFFERENT STACKS

| | | Cyclic voltammetry (10 mV/s) | |
|---|---|---|---|
| Sample stack | impurities | LTO normalized thickness | $TiO_2$ thickness (nm) |
| **LTO/PT** | -- | 81% | N.A |
| **LTO/Anatase $TiO_2$/TiN** | Anatase | 100 % | 16 nm |
| **LTO/Rutile $TiO_2$/PT** | Rutile | 22 % | N.A |

The sample with LTO and anatase $TiO_2$ on TiN shows the best electrochemical performance: →The anatase $TiO_2$ contributes to the $Li^+$ insertion/extraction process

→ LTO/Anatase$TiO_2$/TiN has better interfaces than LTO/Pt

The rutile $TiO_2$ is not electrochemically active and inhibits the LTO kinetics

# SUMMARY AND CONCLUSION

- $Li_4Ti_5O_{12}$ thin films can be formed by solid state reaction with homogenous element distribution and stoichiometry close to the theoretical LTO stoichiometry
- The $Li_4Ti_5O_{12}$ films formed by solid state reaction are electrochemically active
- The theoretical capacity can be reached at 0.1 C and 45% of it is reached at 20 C
- The presence of rutile $TiO_2$ impurities blocks the LTO kinetics while the anatase $TiO_2$ contributes to the Li-ion insertion/extraction process leading to a better electrochemical performance of the film

# ACKNOWLEDGEMENT

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SEVENTH FRAMEWORK PROGRAMME

The Estore team at imec

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# Thank you for your kind attention!
# Question?