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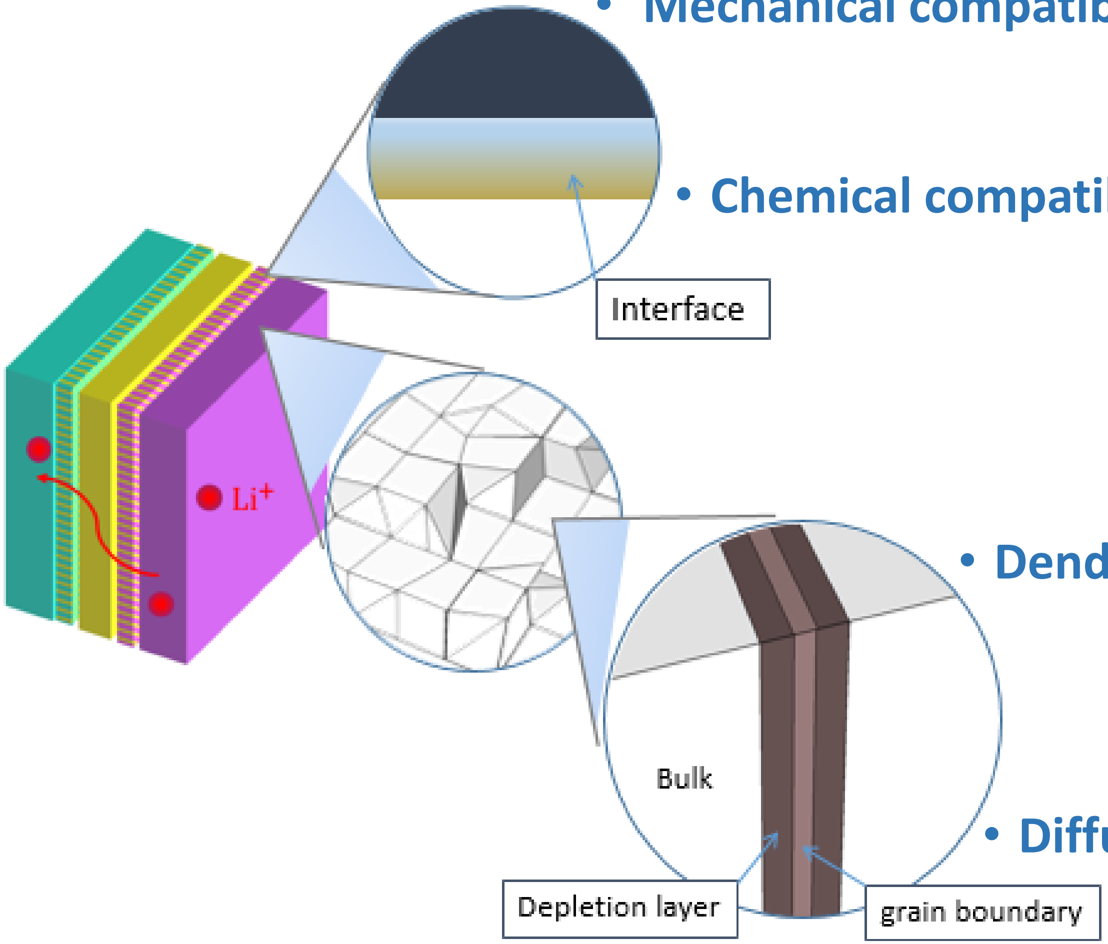
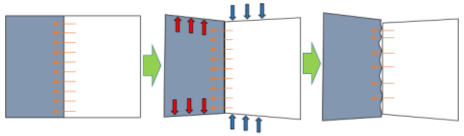
Operando optical techniques for understanding materials and interfaces in energy applications

Alex Morata, Juan Carlos Gonzalez-Rosillo, Valerie Siller, Beatrice Laurenti
Fernanda Monteiro, Francesco Chiabrera, Marc Nuñez, Albert Tarancón

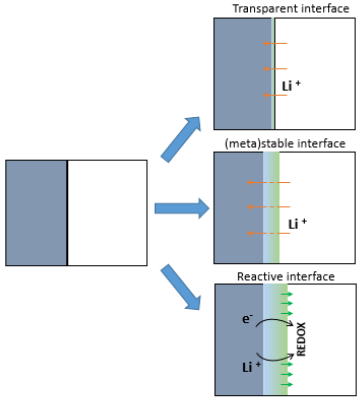
Operando characterization: Interfaces in energy devices



- **Mechanical compatibility**

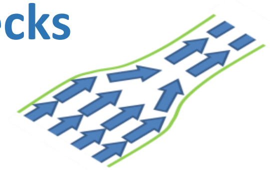


- **Chemical compatibility**



- **Dendrites**

- **Diffusion bottlenecks**



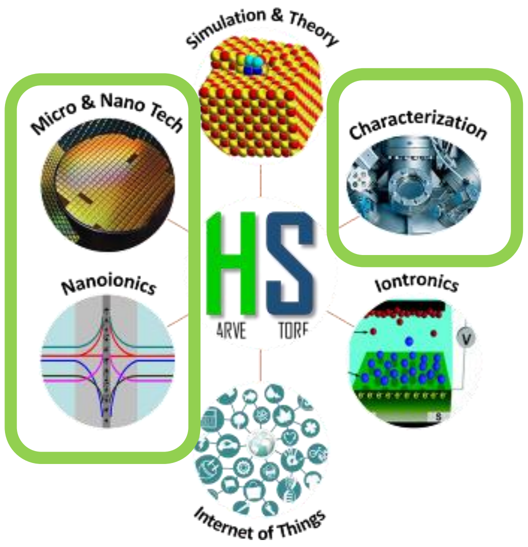
It is crucial to have insight on ***interfaces and track the changes taking place during operation***

Ongoing projects involving operando characterization

HARVESTORE

Future Strategies for Powering the IoT

H2020-FETPROACT



”Disruptive micro-energy and storage technologies”

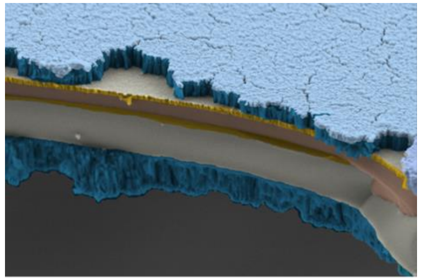
- Thin film Li-ion batteries
- Oxide thermoelectrics
- Micro-Solid Oxide Cells (SOCS)
- HT ceramic photovoltaics

EPISTORE

ENERGY IN THIN LAYERS

Thin Film Reversible Solid Oxide Cells for Ultracompact Electrical Energy Storage

H2020-FETPROACT

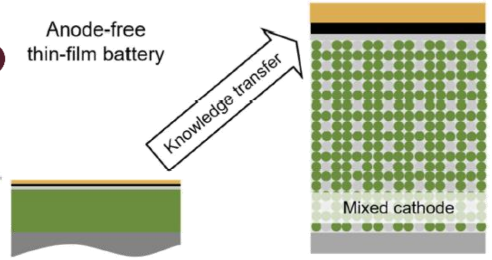


“Pocket-sized stacks based on thin-film reversible solid oxide cells (TF-rSOCs) to efficiently store renewable electricity”

AFREESSB

Anode-Free Solid-State Batteries

M-ERA.NET



“Objectives are: i) To develop anode-free thin-film SSBs, ii) to transfer the anode-free concept to bulk cathodes, iii) to develop operando characterisation methods”

ADVAGEN

Development of ADVAnced next GENeration Solid-State batteries for Electromobility Applications

HORIZON-2021-2025

Develop hybrid oxide-sulfide composite ceramic electrolytes
→ Novel, stable, high performing and up-scalable electrolytes when in contact with a protected thin metallic lithium anode

Develop an optimised Li anode composed of thin lithium metal films
→ Thin lithium metal films deposited by thermal evaporation on top of copper current collector foils, with high stability, along with a protective layer

Develop solid nickel rich NMC-based high performing cathodes
→ Key towards stable, safe and highly performant cells

Demonstrate stable, safe and performant 10Ah pouch cells
→ Stable, safe and performant 10Ah pouch cells using an oxide-sulfide hybrid electrolyte, a Ni-rich cathode and a thin lithium metal anode in a pilot line

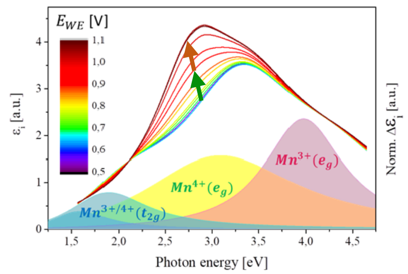
Develop new combined operando characterisation techniques
→ To allow materials and interface optimisation by the in-situ observation of the changes taking place in realistic operation conditions

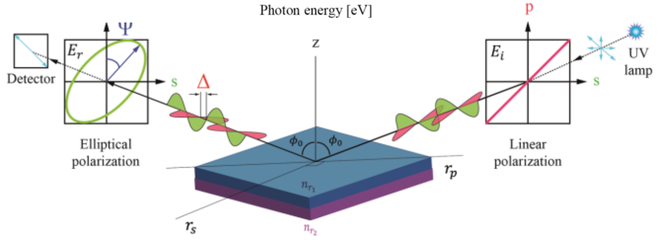
				Combined SE-Raman		
					TERS	
TECHNIQUE / PHENOMENA	XRD	Neutron diffraction	OEMS	Spectroscopic ellipsometry	Raman spectroscopy	AFM
Phase transition/ segregation	X	X	X		X	
Light element characterization		X				
Oxygen stoichiometry		X			X	
Interface reaction (e.g. electrode/electrolyte, oxide/sulfide)				X	X	
Volume expansion	X	X		X		X
Dendrite formation				X		
Nanostructure evolution				X		X

“New lithium metal (LiM) battery cell technology based on a safe, reliable, and high performing hybrid solid-state electrolyte (LLZO-LPS based)”

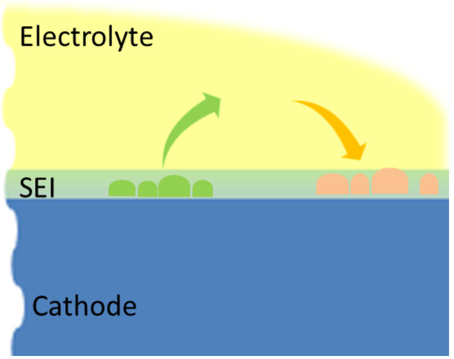
Two operando optical characterization techniques

- **Operando spectroscopic ellipsometry**
  - Tracking Li content in electrodes (LMO, LFP cathodes)
  - Studying diffusion limitations (LMO cathode)
  - Studying stability at low voltages (LTO anode)





- **Tip-Enhanced Raman Spectroscopy (TERS)**
  - Electrolyte-electrode interfaces in Li-ion batteries (LMO cathode)
  - Operando experiments: electrochemical TERS (LMO cathode)



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Two operando optical characterization techniques

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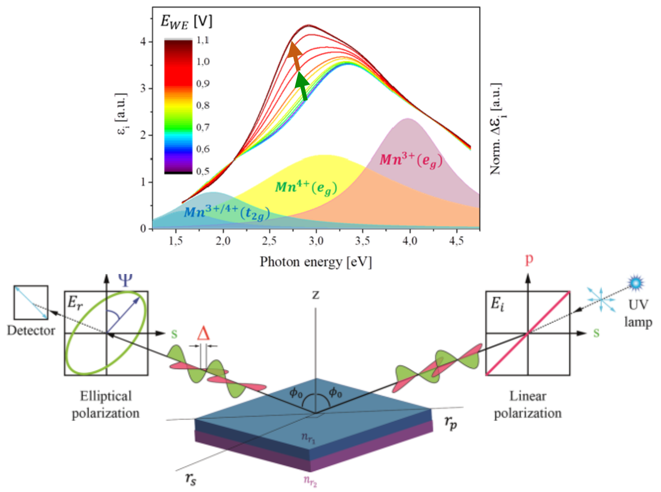

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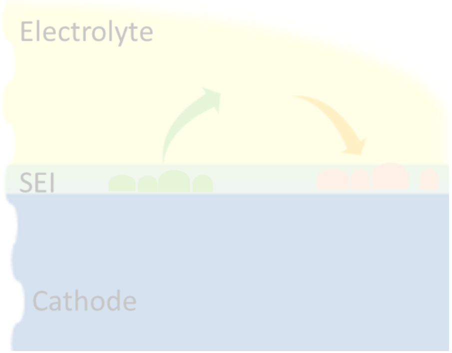

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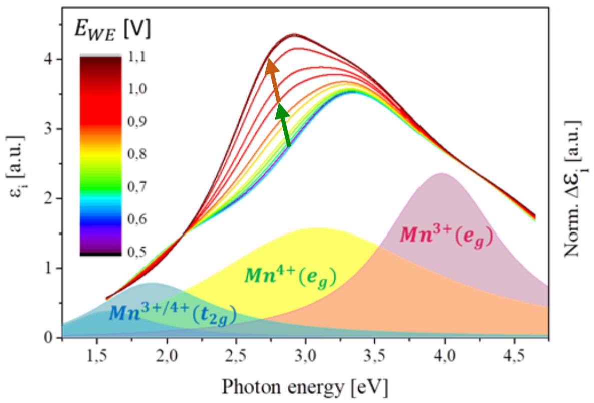
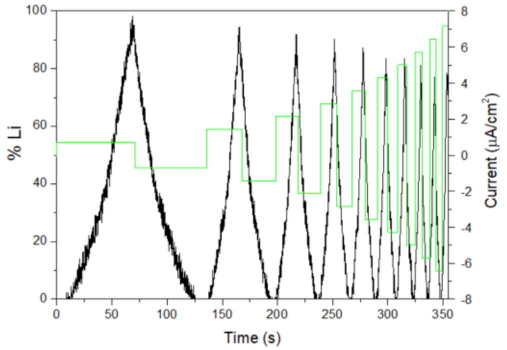
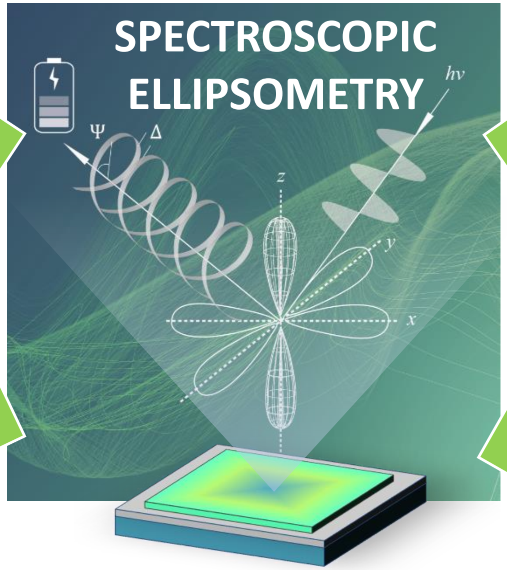
Introduction - Spectroscopic Ellipsometry

Li CONTENT

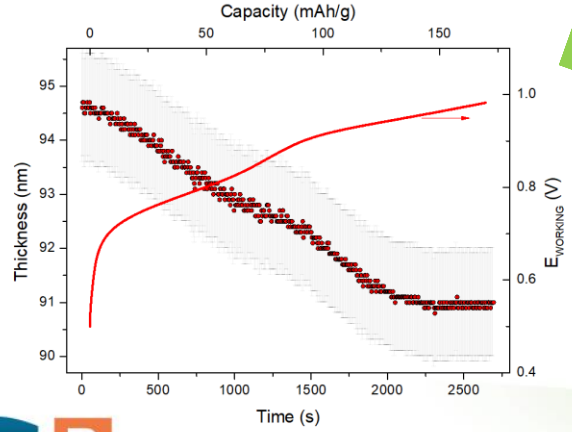


DIFFUSION LIMITATIONS



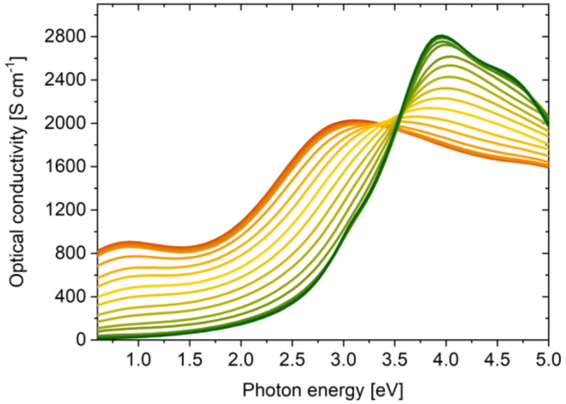


VOLUME CHANGES



- ***Non destructive***
- ***Accessible***
- ***Fast rate***

DEFECTS CONCENTRATION



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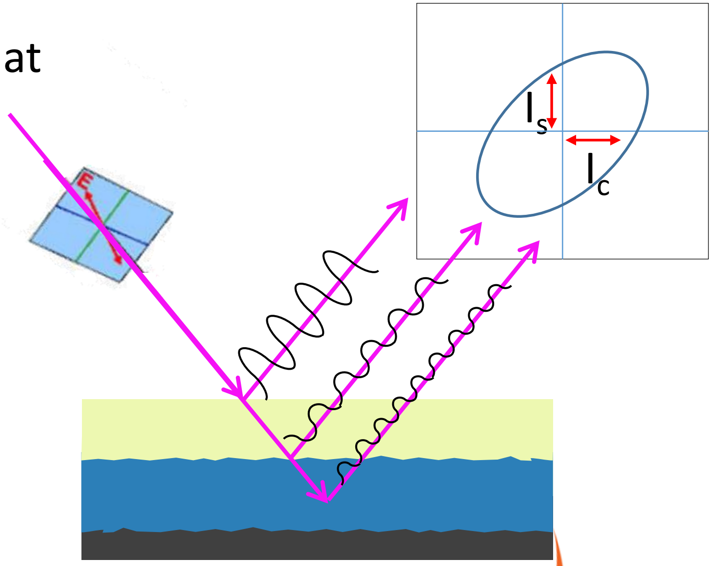
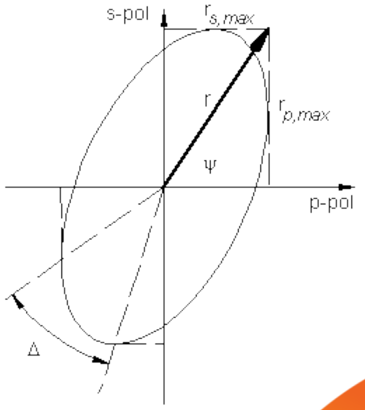
Introduction - Spectroscopic Ellipsometry

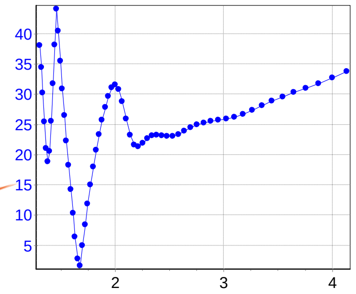
Highly accurate ***non-destructive*** technique that uses polarized light to provide the ***thickness and the optical properties*** of a thin film.

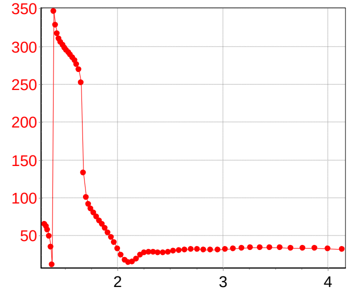
Ideal technique for studying thin-film **materials and systems**





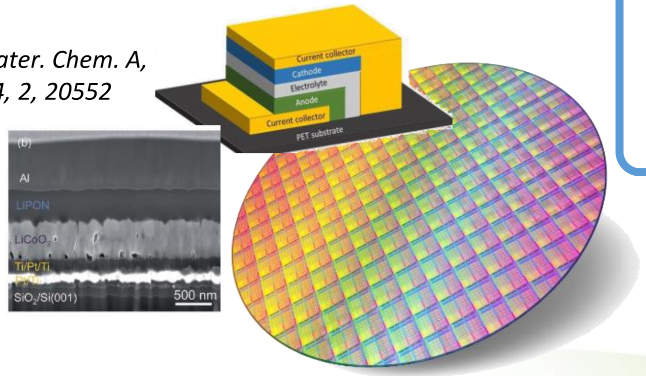
$$\rho = \tan(\Psi)e^{i\Delta}$$





DEVICES PERFORMANCE

J. Mater. Chem. A, 2014, 2, 20552



Multi-layers

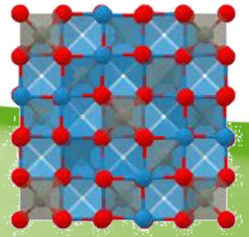
- Depth profiles
- Interfaces
- Thickness

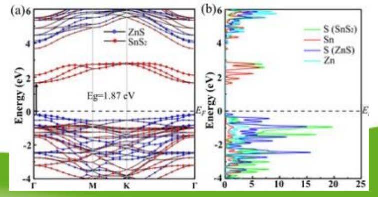
Optical properties

$$\varepsilon = \varepsilon_r + i\varepsilon_i$$

- Composition
- Crystallinity

MATERIALS PROPERTIES





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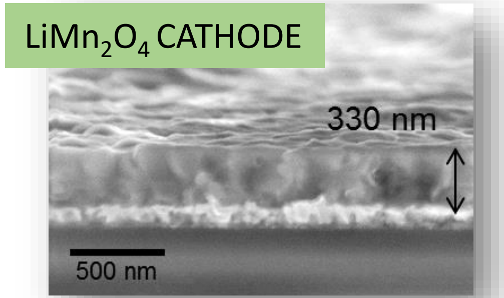
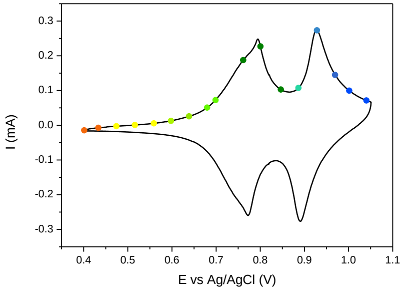
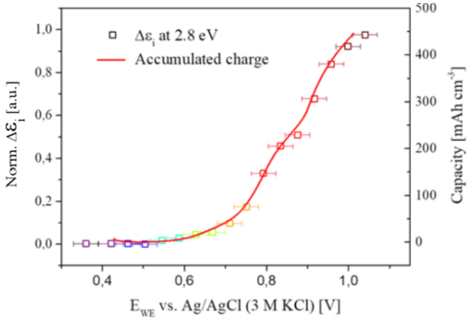
Operando ellipsometry - energy materials

Electrochemical Energy Storage





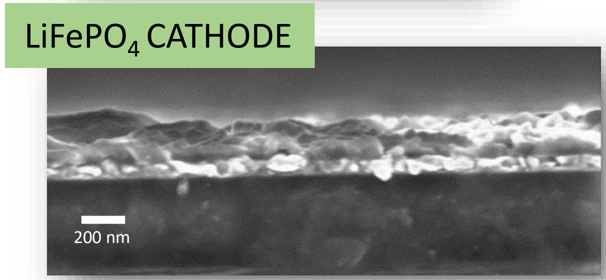


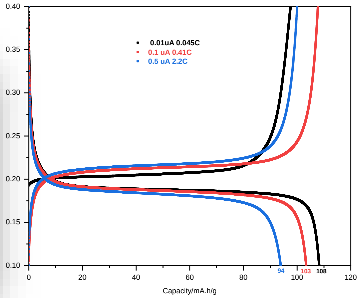
- **Li-CONTENT-DIFFUSION RATE**

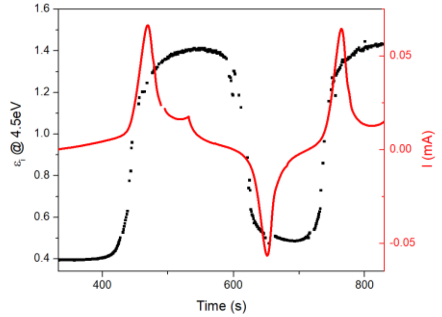
*A. Morata et al., J. Mater. Chem. A, 2020, **8**, 11538.*

- **OPERATION IN EXTENDED RANGE**

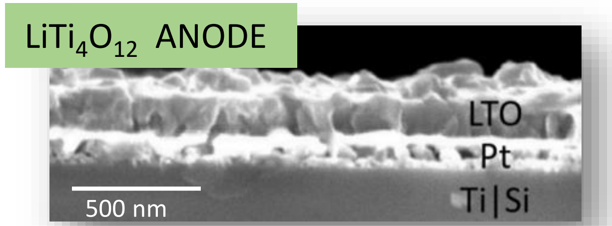
*V. Siller et al., ACS Appl. Mater. Interfaces, **14** (2022), 33438*

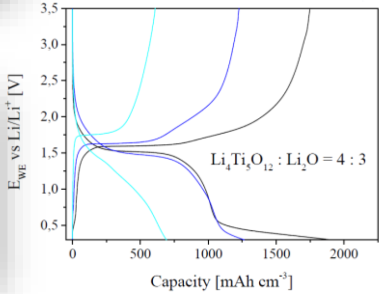


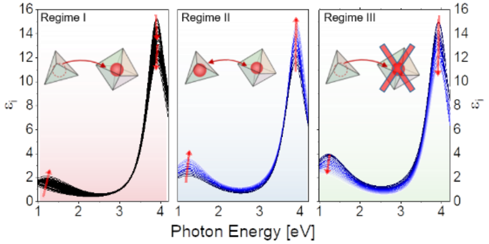




- **Li-CONTENT-DIFFUSION MECHANISMS**



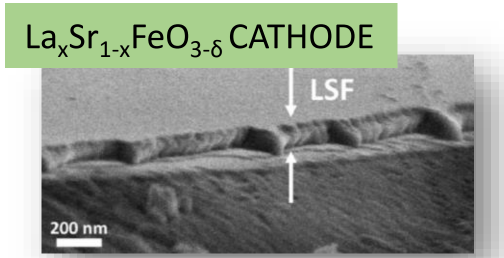


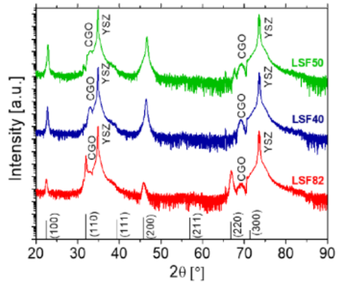


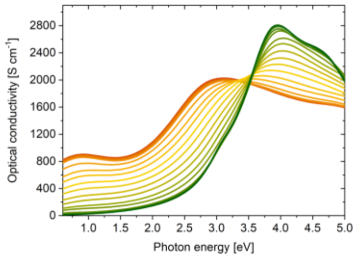
- **STABILITY UNDER DEEP LITHIATION REGIME**

V. Siller, et al. Materials Today Energy 25 (2022) 100979

Solid Oxide Cells

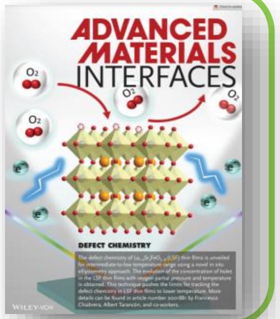






- **DEFECT CHEMISTRY**

Y. Tang, et al. Advanced Materials Interfaces 8 (6), 2170031



Operando ellipsometry - energy materials

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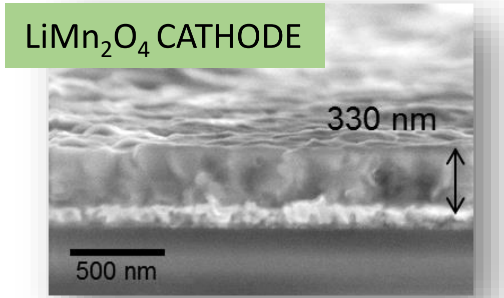

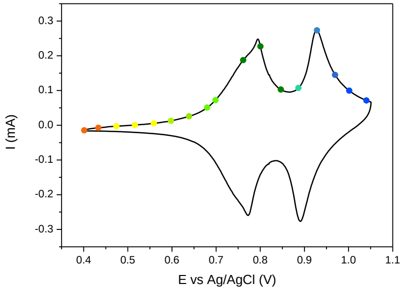

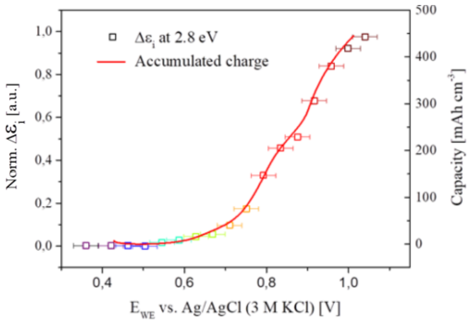

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*A. Morata et al., J. Mater. Chem. A, 2020, **8**, 11538.*

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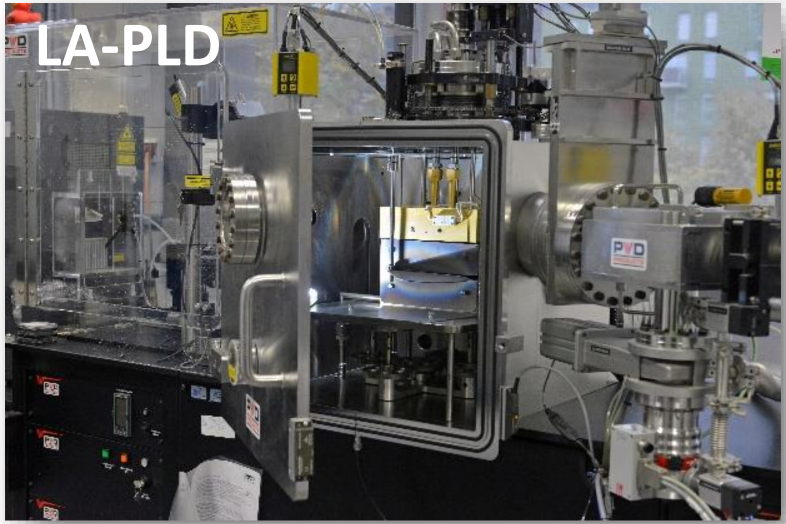
V. Siller, et al. Materials Today Energy 25 (2022) 100979

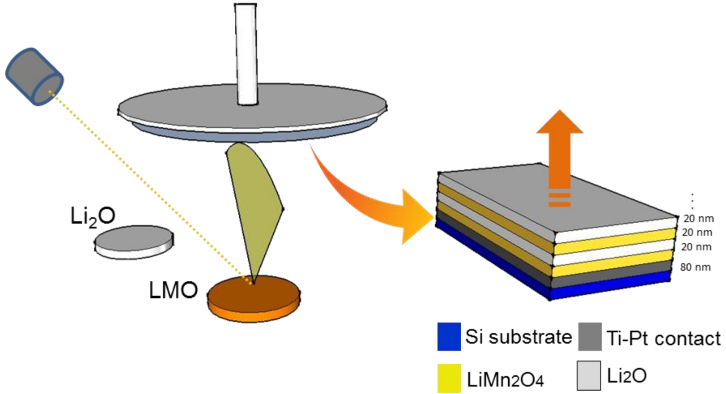
Solid Oxide Cells

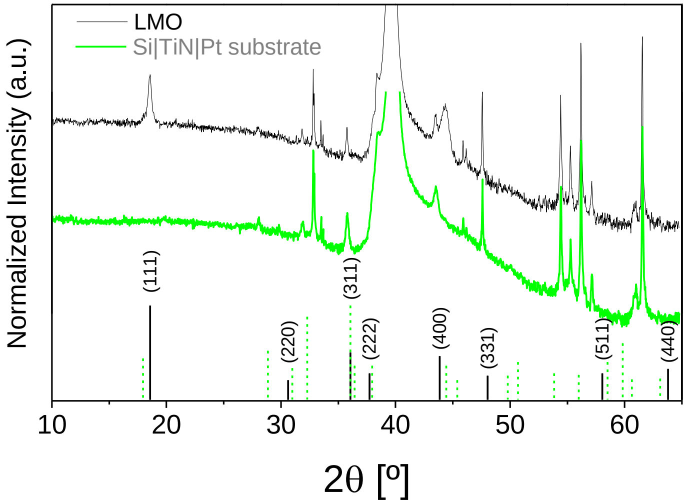
- **DEFECT CHEMISTRY**

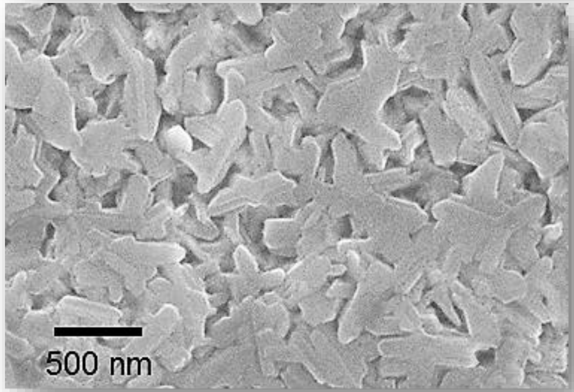
Y. Tang, et al. Advanced Materials Interfaces 8 (6), 2170031

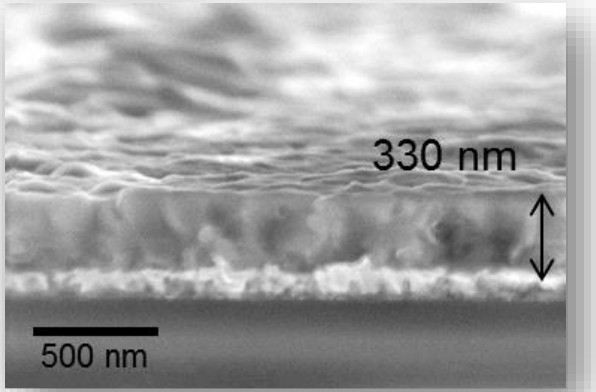
Thin film Li-ion battery cathode: $LiMn_2O_4$

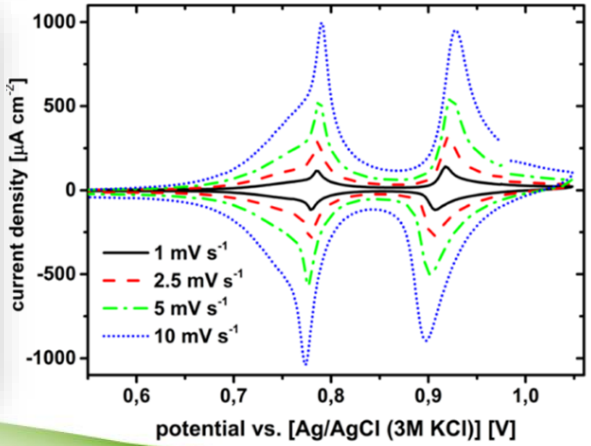


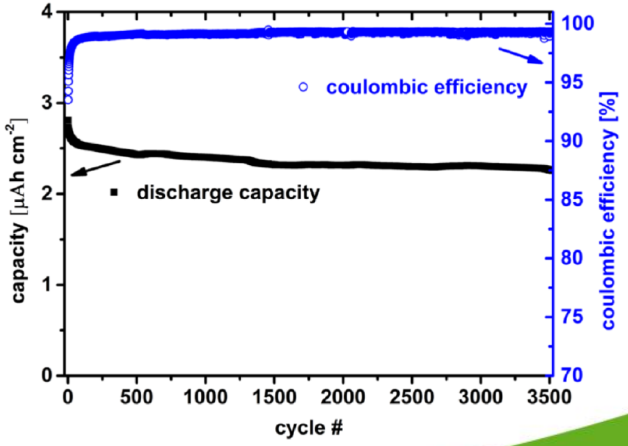












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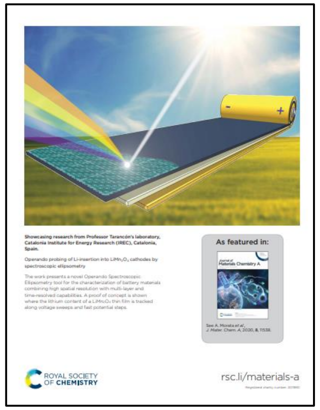
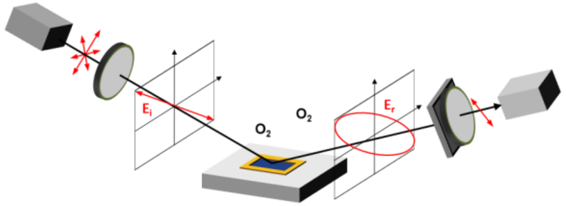
M. Fehse et al., Thin Solid Films 648 (2018) 108–112

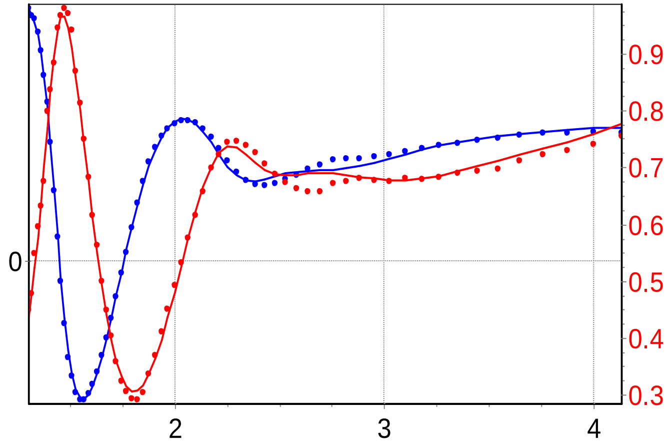
M. Fehse et al., ACS Appl. Mater. Interface, 9 (2017) 5295–5301

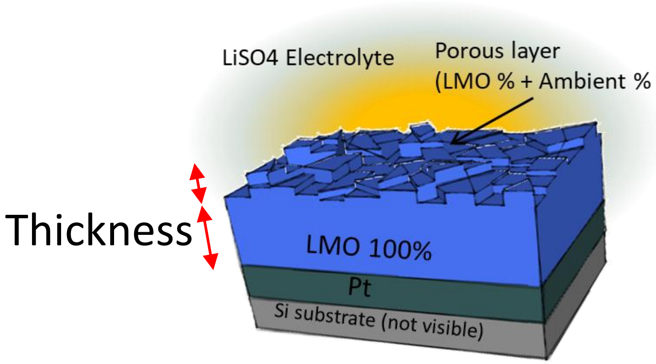
Spectroscopic ellipsometry – model construction

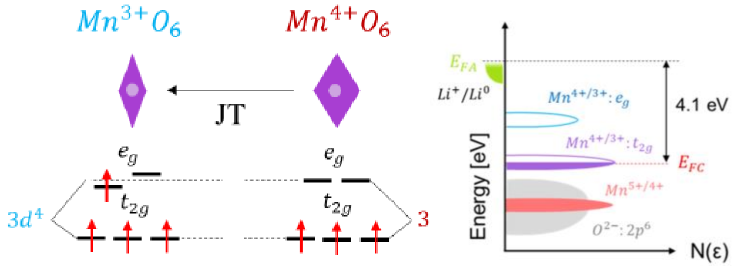
A. Morata et al., J. Mater. Chem. A, 2020, 8, 11538.

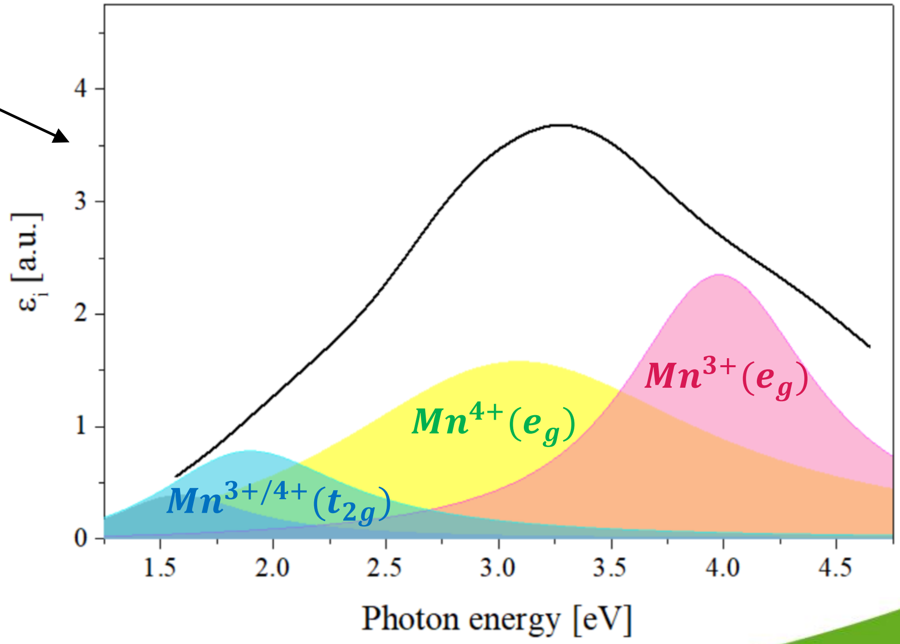












- Delta Psi2 software (Horiba Scientific)

IREC
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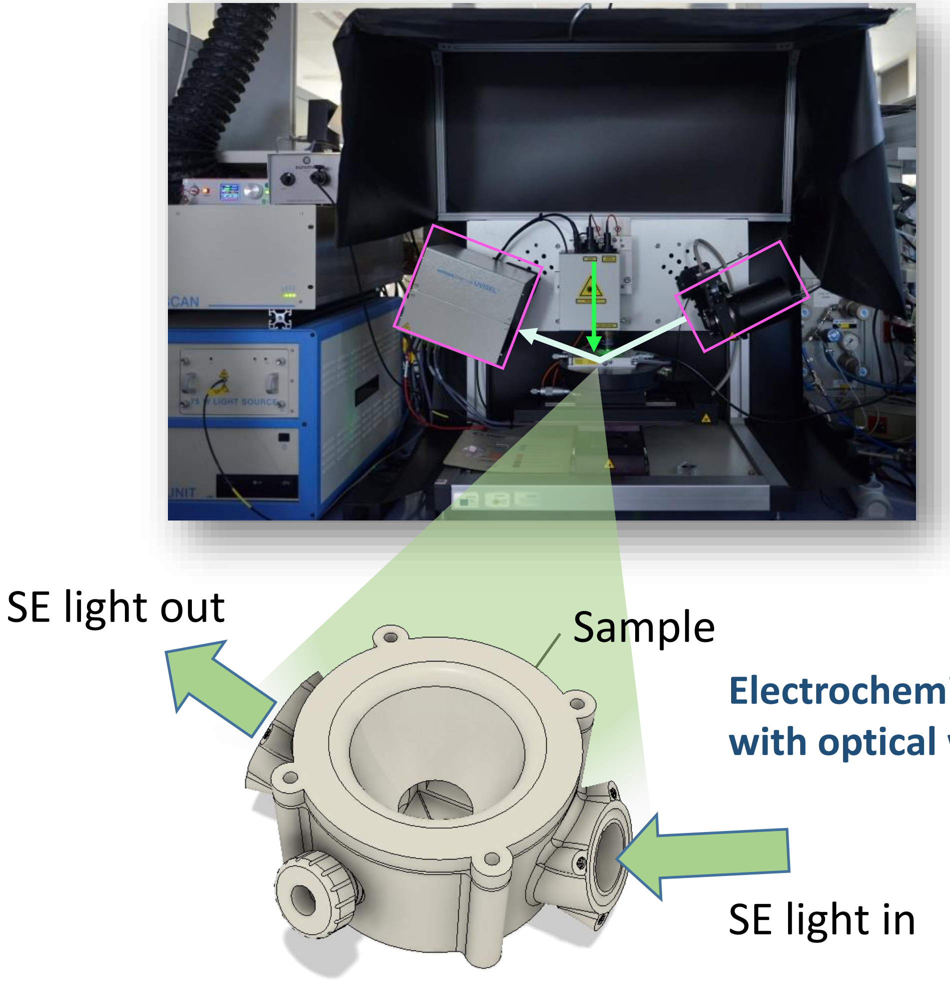
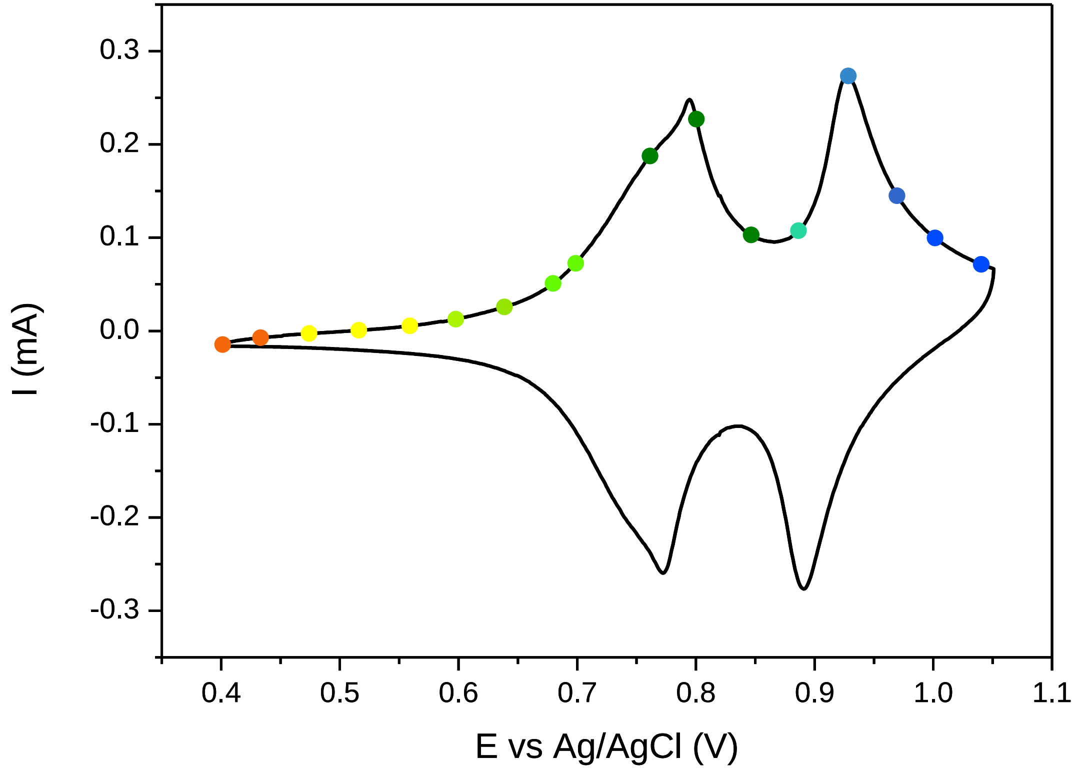
Operando Spectroscopic Ellipsometry



Electrochemical chamber with optical windows

$LiMn_2O_4 \rightarrow MnO_2 + Li^+ + e^-$



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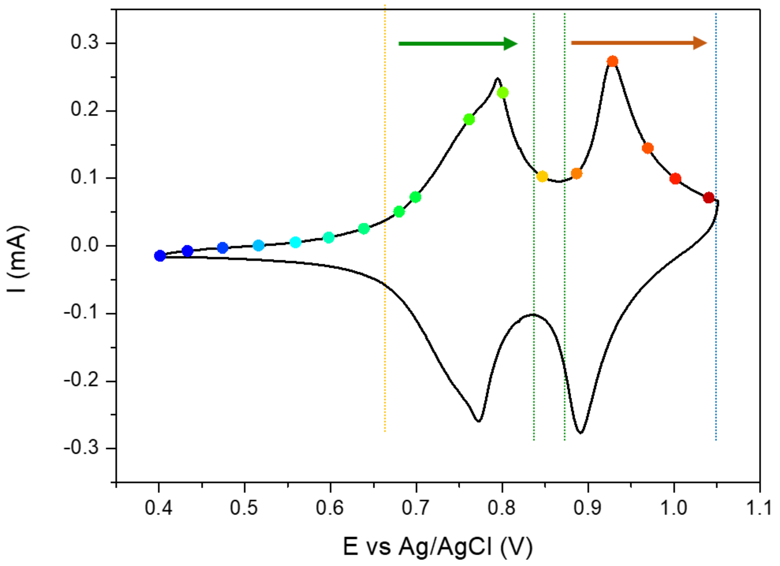
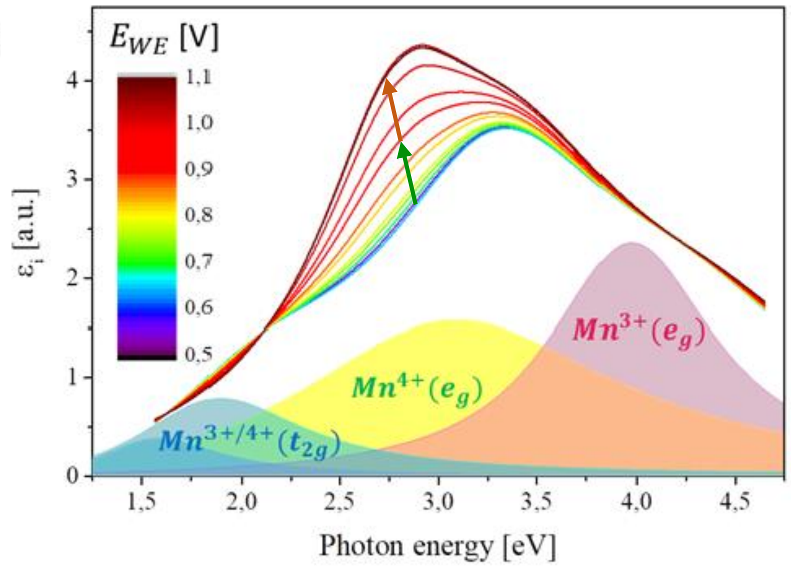
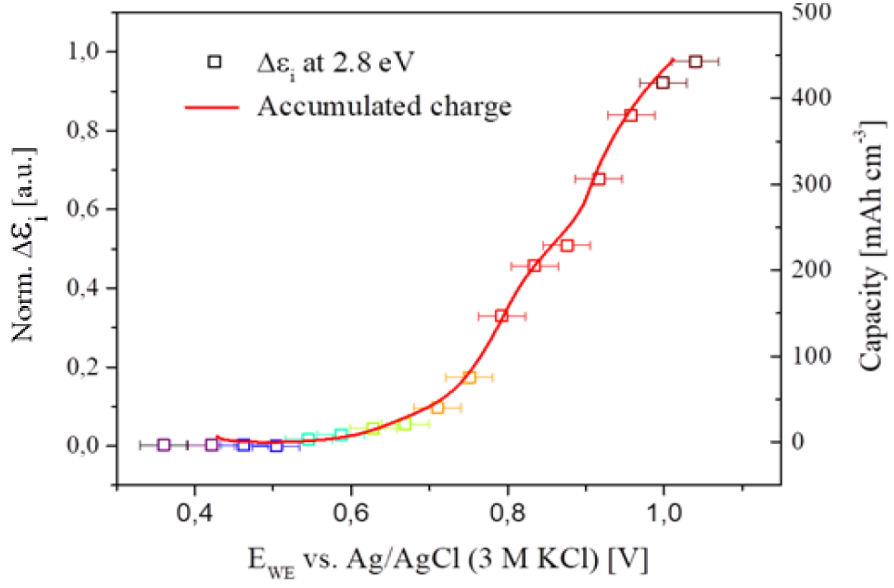
Tracking Li content







- The insertion at c.a. 0,7 V and 0,85V, is reflected in the variation of the absorbance at 2,8-3 eV
- The value of the ε_i can track the Mn^{3+} Mn^{4+} transition taking place during Li intercalation

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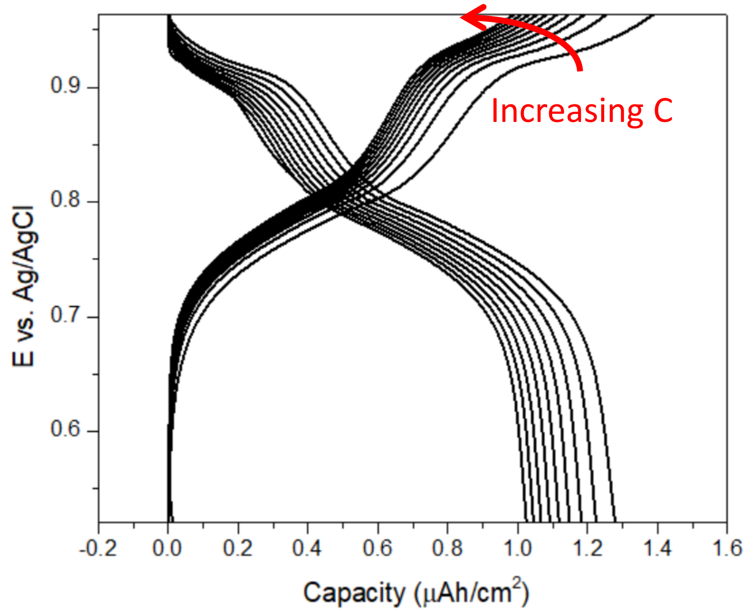
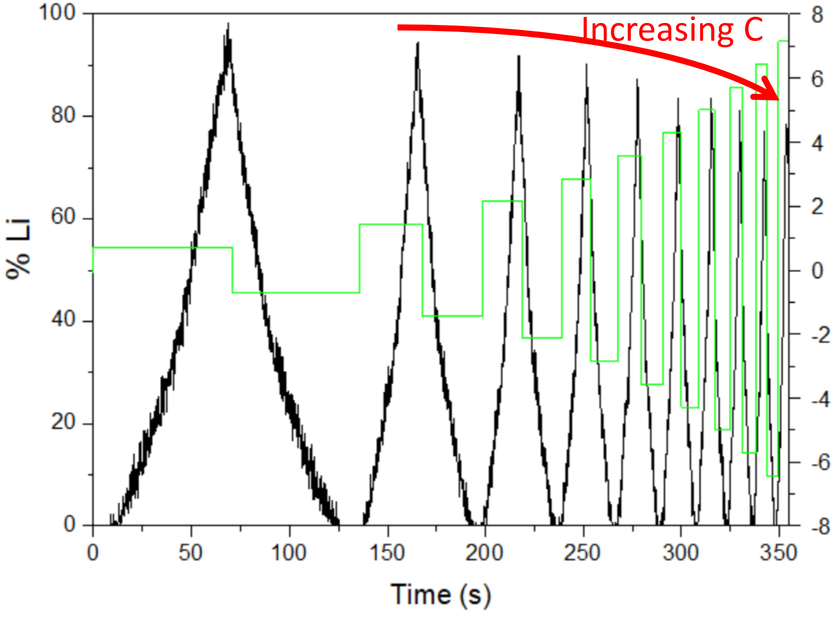
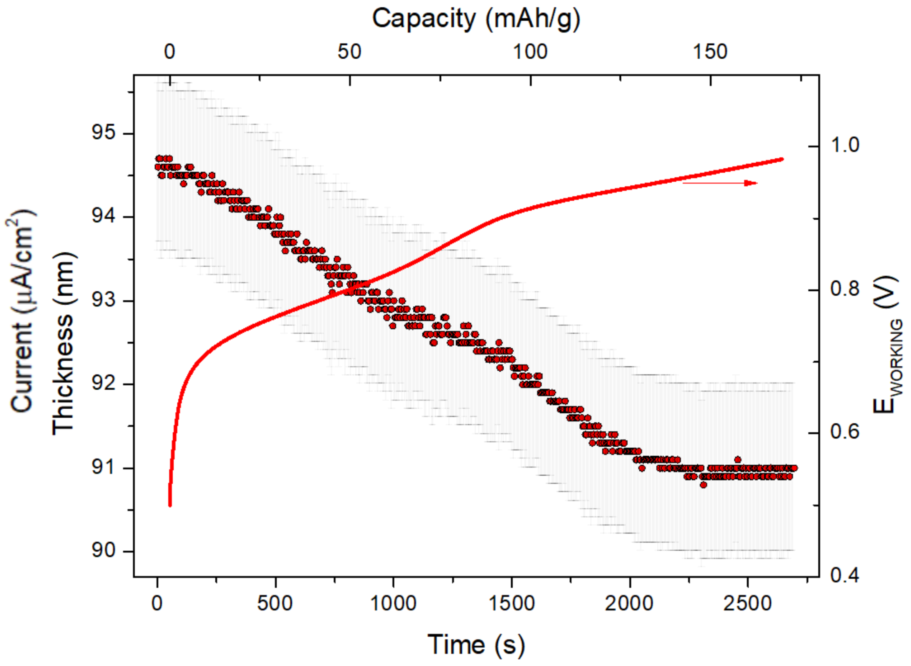
A. Morata et al., J. Mater. Chem. A, 2020, 8, 11538.

Tracking Li content and volume expansion







- It is possible to track the Li content in the layer during charging-discharging cycles
- The limitations due to fast charging are clearly observed
- Volume changes of the layer due to Li insertion can be detected

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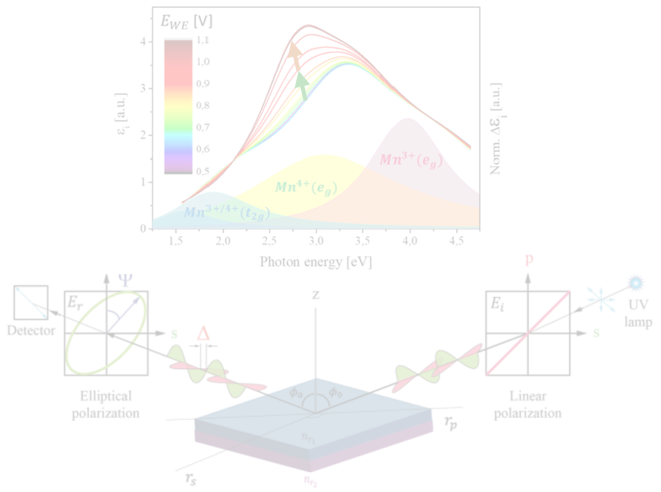
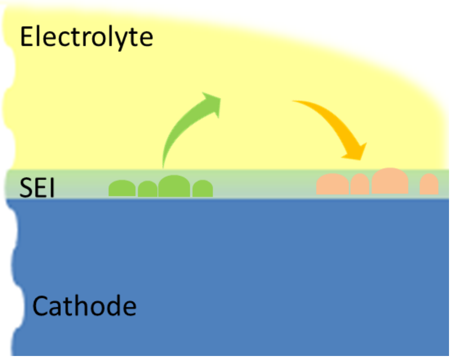
Two operando optical characterization techniques

- **Operando spectroscopic ellipsometry**
  - Tracking Li content in electrodes (LMO, LFP cathodes)
  - Studying diffusion limitations (LMO cathode)
  - Studying stability at low voltages (LTO anode)



- **Tip-Enhanced Raman Spectroscopy (TERS)**
  - Electrolyte-electrode interfaces in Li-ion batteries (LMO cathode)
  - Operando experiments: electrochemical TERS (LMO cathode)



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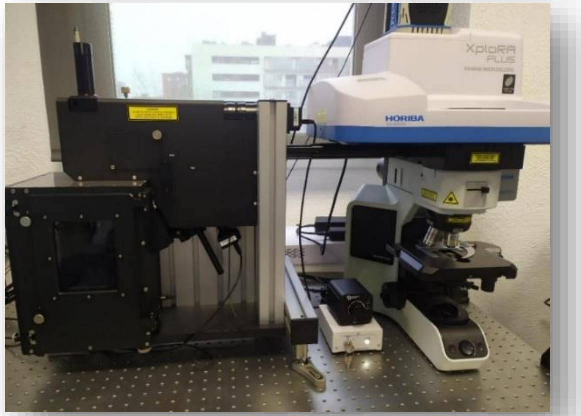
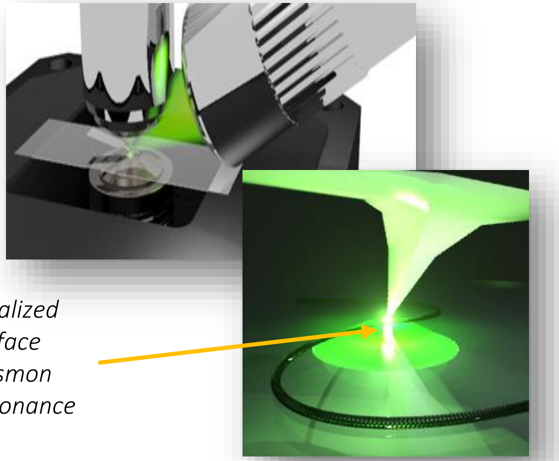
Tip-Enhanced Raman Spectroscopy



AFM (AIST-NT SPM) coupled with Horiba XploRA Raman Spectrometer

TERS **combines the chemical sensitivity of** Raman spectroscopy **with high spatial resolution** of scanning probe microscopy (**SPM**) and enables chemical imaging of surfaces at the nanometer length-scale.



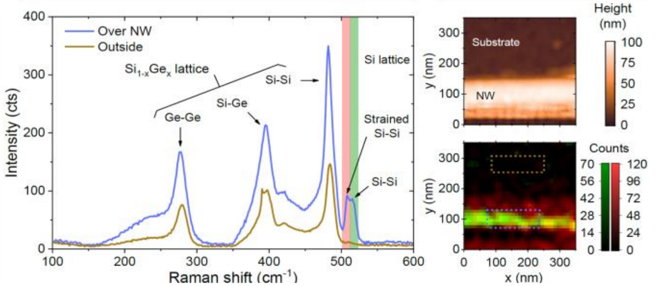
Localized Surface Plasmon Resonance

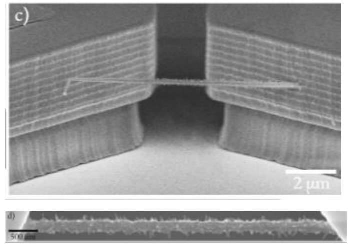
Confinement of the electromagnetic field in the vicinity of the plasmonic tip apex

➔ Enhancement up to 10^7
➔ Detection sensitivity down to the single-molecule level
➔ Spatial resolution at several nanometers or even on a sub-nanometer scale

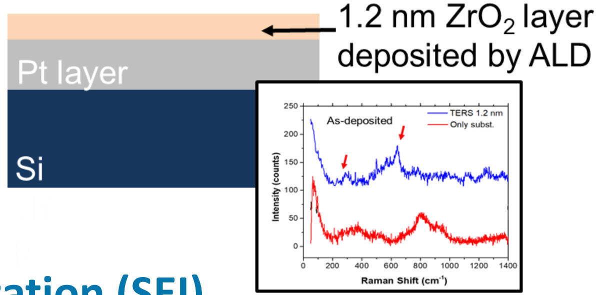
- **Semiconductor nanowires**

J. M. Sojo et al., Small. In-press

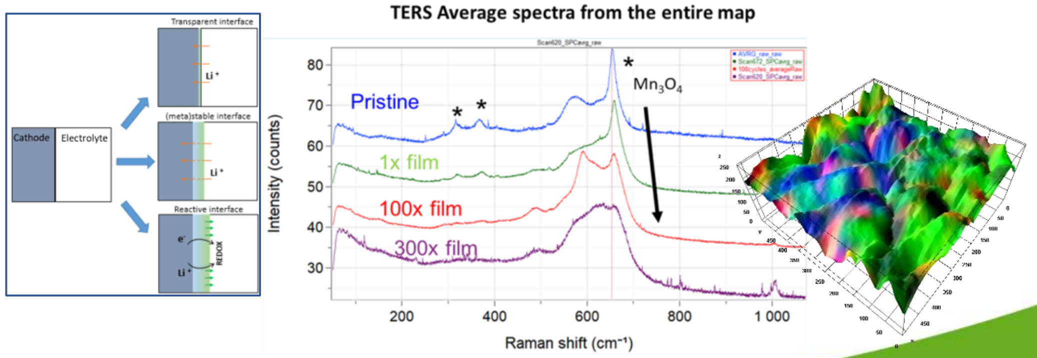




- **Ultra-thin films**



- **Surface characterization (SEI)**



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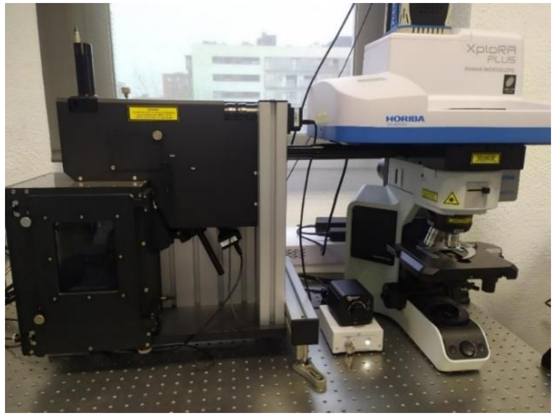
Tip-Enhanced Raman Spectroscopy



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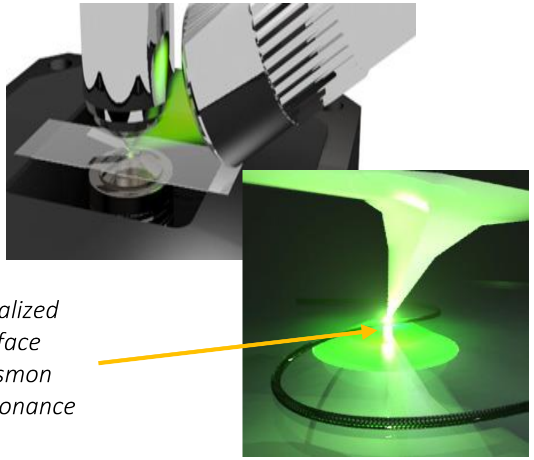

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J. M. Sojo et al., Small. In-press

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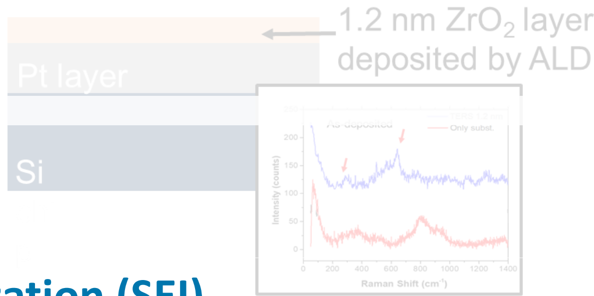

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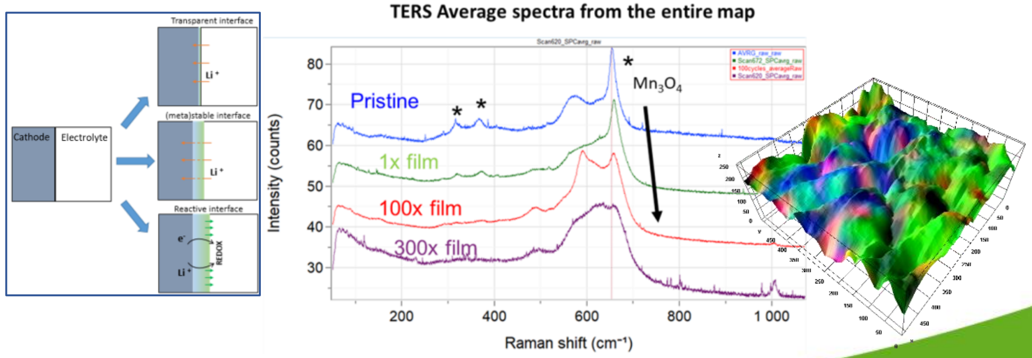

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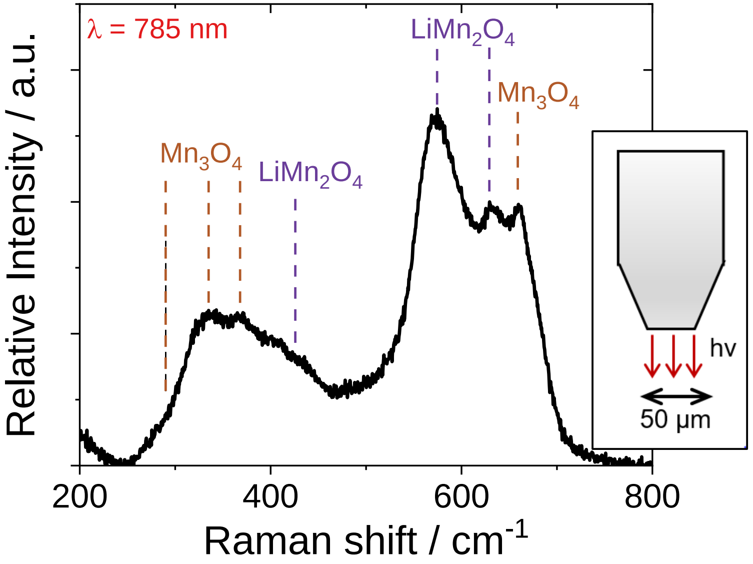
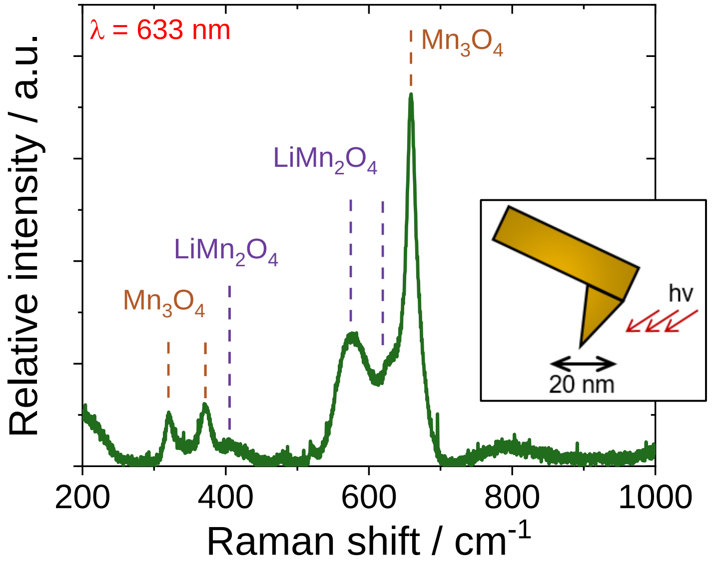
TERS study of the electrolyte-electrode interfaces

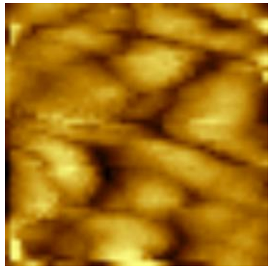
Low power – macro spot Raman



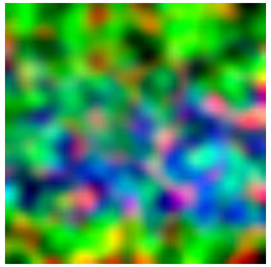
Average TERS spectra

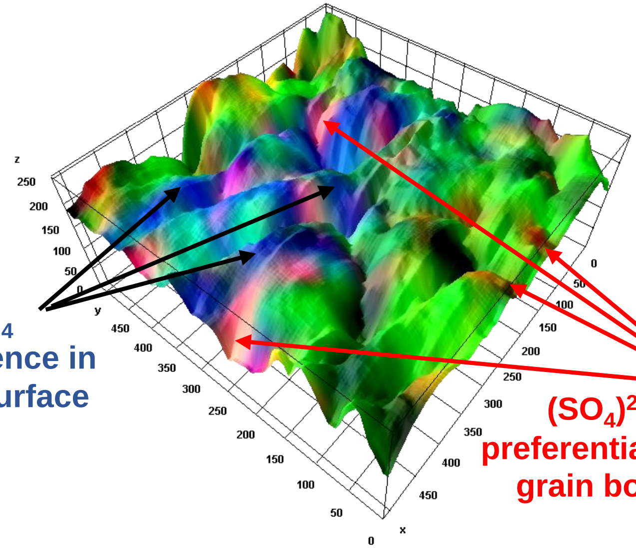


Topography



Raman signals





- Sensitive to phase changes at the surface
- Capable to locate different species with high precision

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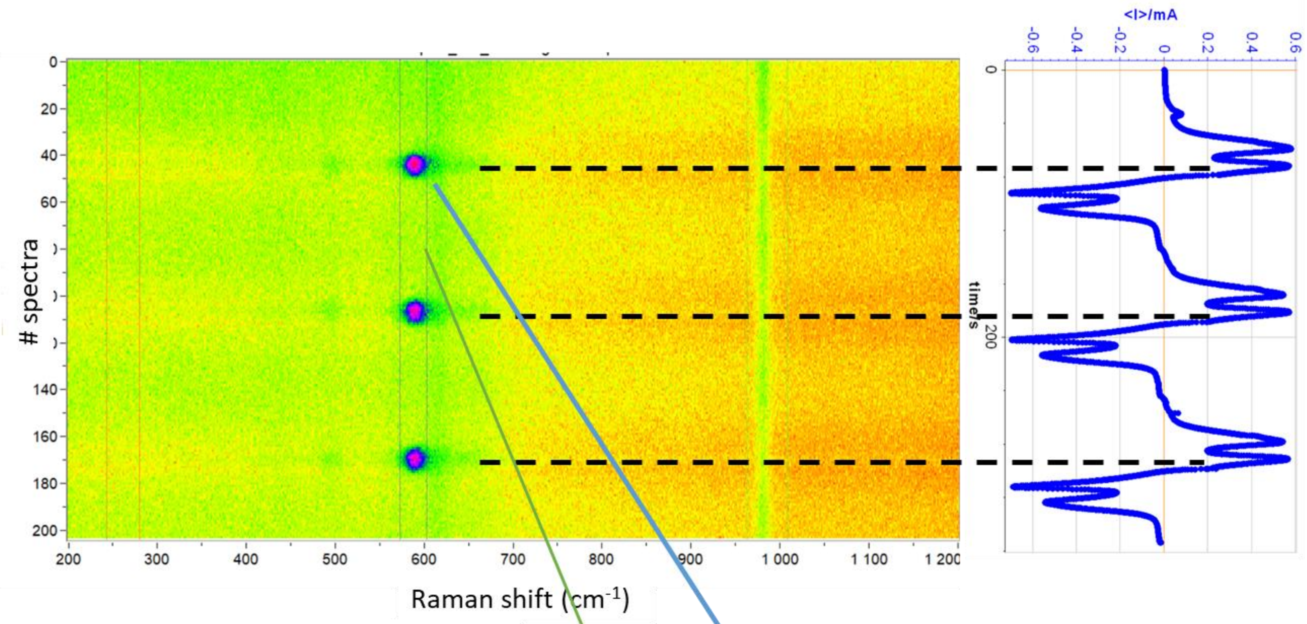
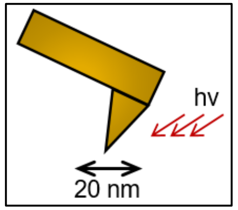
Operando TERS

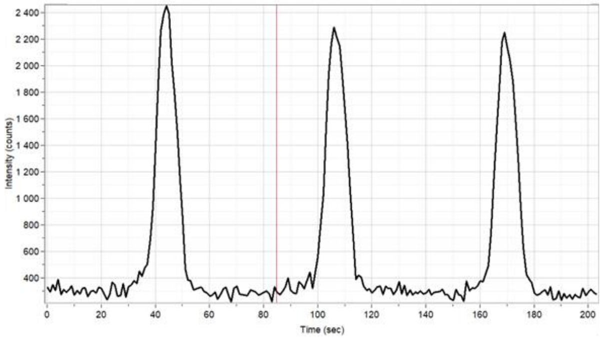




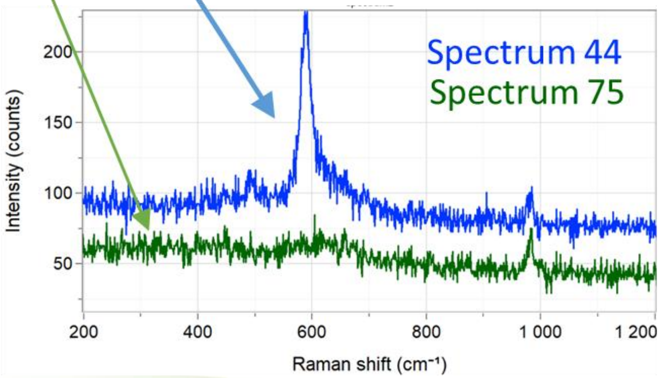
Marc Chaigneau

Alice Fiocco

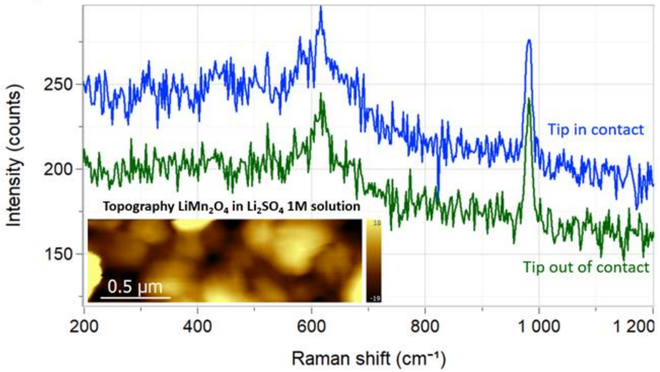
Tracking λ-MnO_2 peak intensity



spectra



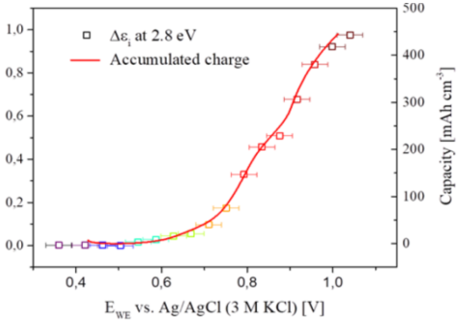
TERS effect demonstrated in aq. electrolyte



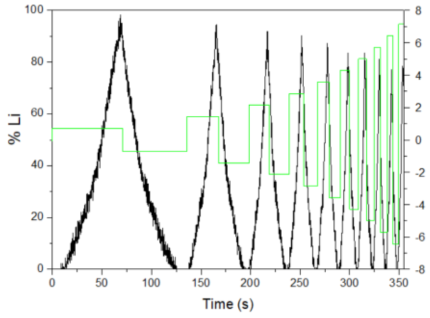
CONCLUSIONS

Operando spectroscopic ellipsometry

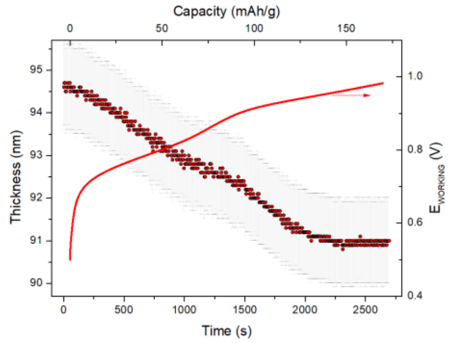
Tracking Li content



Ion diffusion



Thickness evolution

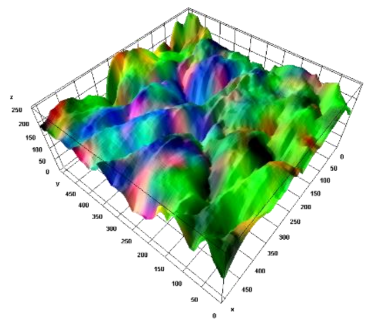


Spectroscopy ellipsometry as a promising tool for:

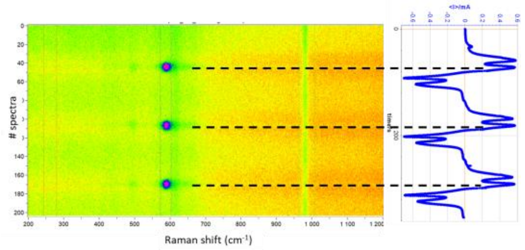
- **Tracking Li content in Li-battery cathodes**
- **Studying ion diffusion in mixed ionic-electronic conductors**
- **Observing volume changes during cycling**

Tip-enhanced raman spectroscopy (TERS)

Spatial distribution of SEI



Operando TERS



TERS has been applied for the detection of surface SEI formation:

- **Surface compounds are visible and distinguishable from the bulk**
- **Knowledge on the spatial distribution of species allow to understand the evolution of SOI over cycling**
- **Preliminary measurements of operando TERS**

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Thank you!

Acknowledgments

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