

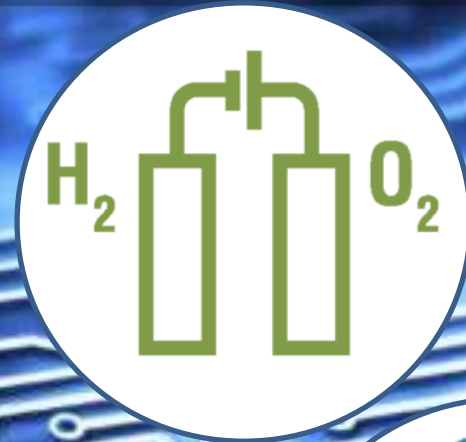
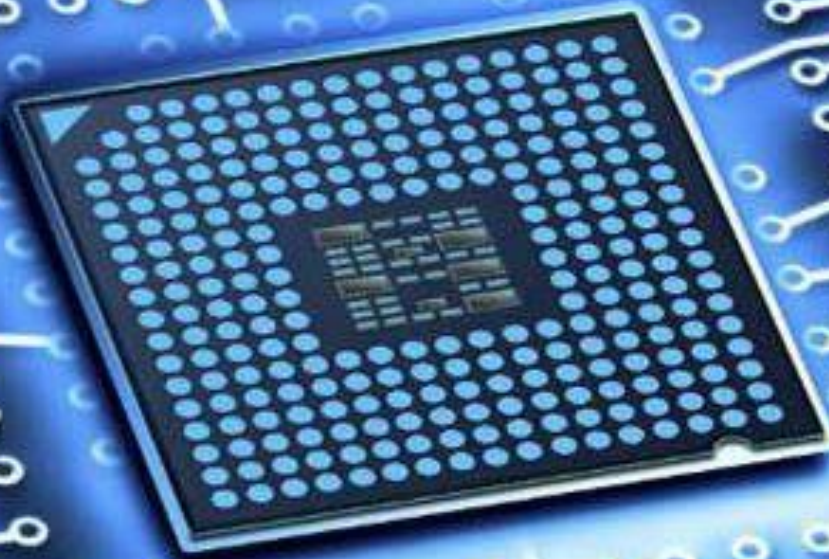


THIN FILM OXIDES FOR SOLID STATE ENERGY DEVICES

F. Chiabrera¹, F. Baiutti¹, V. Siller¹, Y. Tang¹, A. Morata¹, A. TARANCÓN^{1,3}

ICREA PROFESSOR AND HEAD OF THE NANOIONICS AND FUEL CELLS GROUP

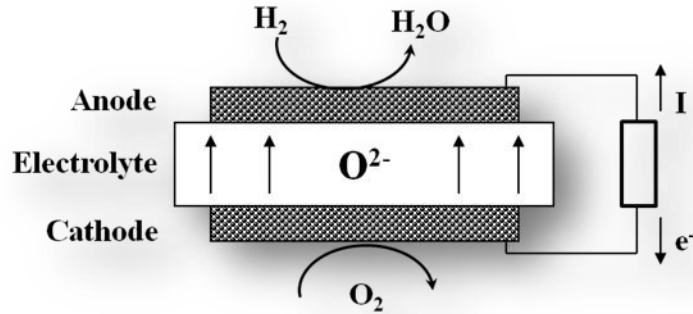
TF-SOLID STATE IONICS DEVICES: A NEW REVOLUTION



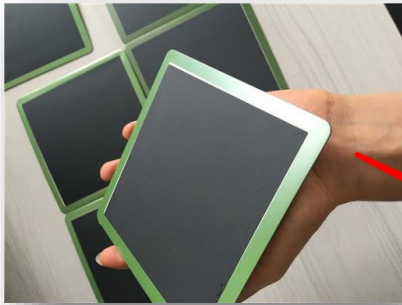
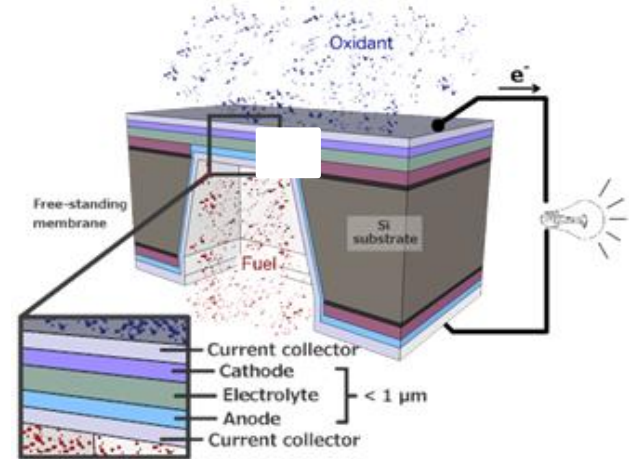
KEEP THE FUNCTIONALITY AFTER MINIATURIZATION



SOLID OXIDE FUEL CELL



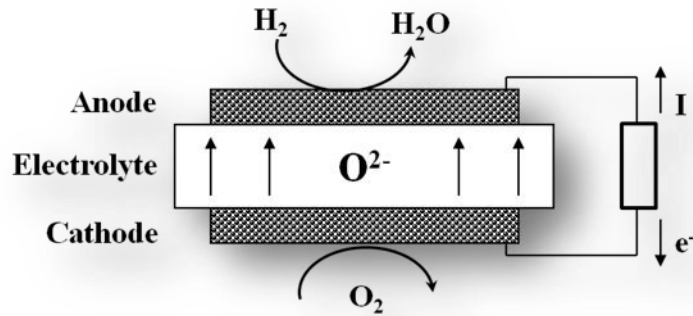
THIN FILM SOLID OXIDE FUEL CELL



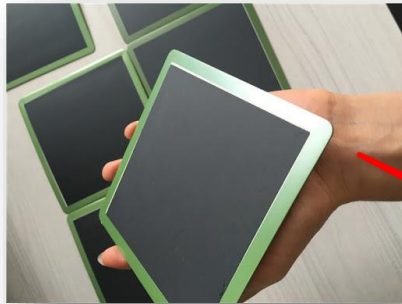
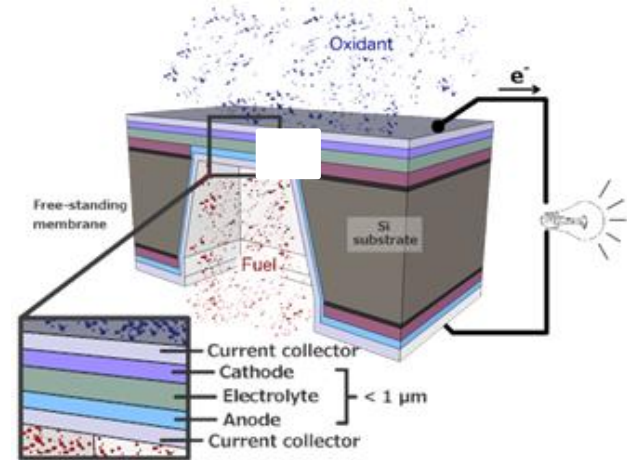
KEEP THE FUNCTIONALITY AFTER MINIATURIZATION



SOLID OXIDE FUEL CELL



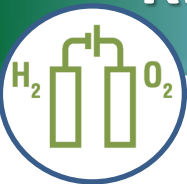
THIN FILM SOLID OXIDE FUEL CELL



THIN FILM DEPOSITION

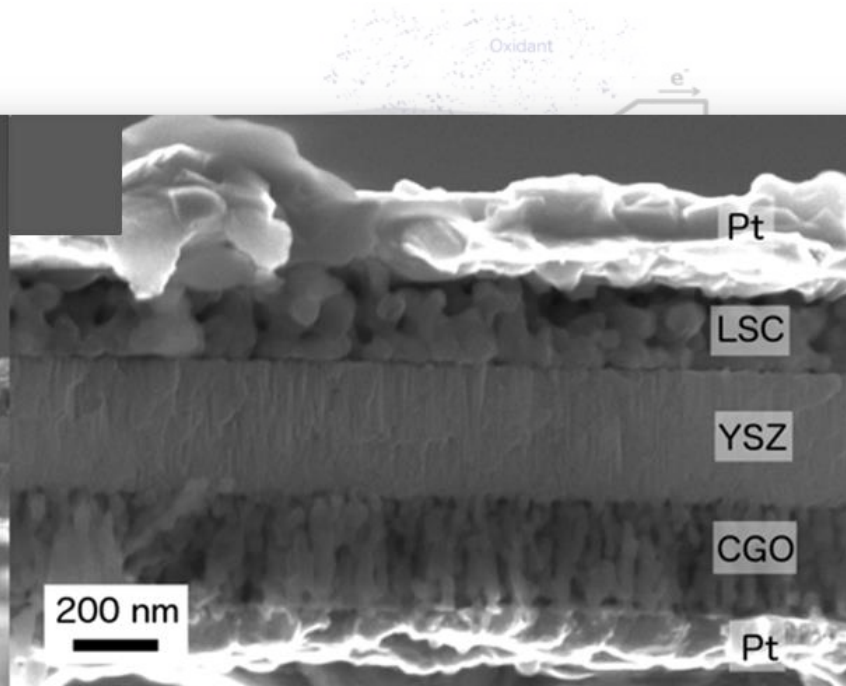
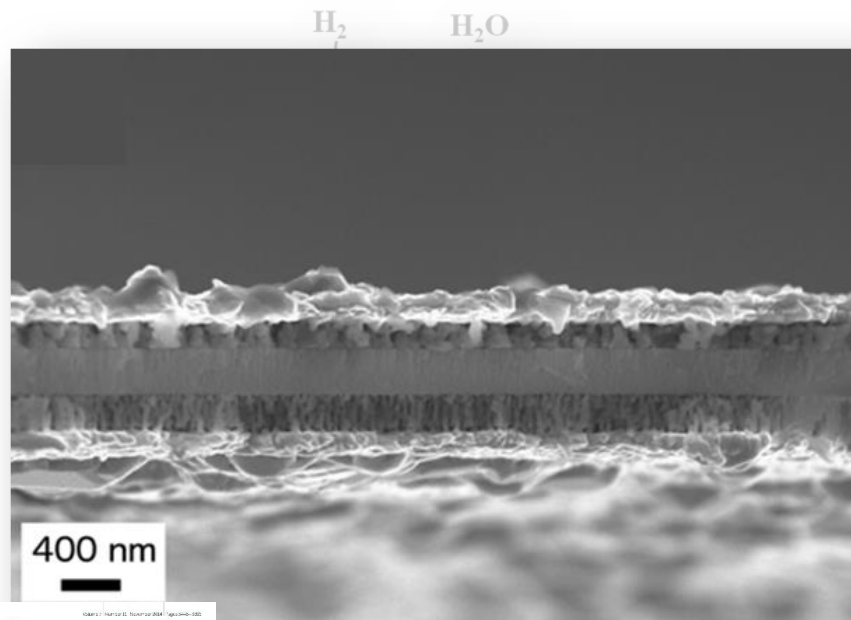


KEEP THE FUNCTIONALITY AFTER MINIATURIZATION



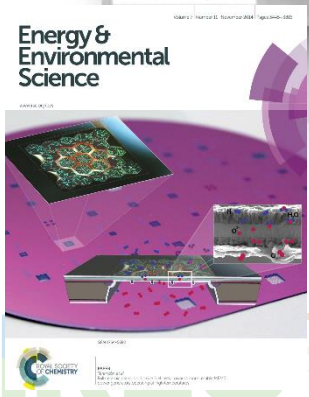
SOLID OXIDE FUEL CELL

THIN FILM SOLID OXIDE FUEL CELL



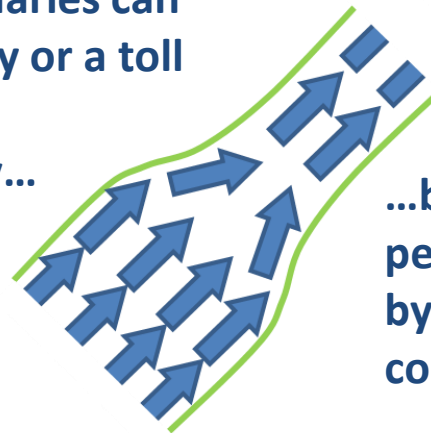
TFs ARE INTERFACE-DOMINATED MATERIALS WITH **NEW FEATURES**

I. Garbayo et al., Energy Environ. Sci., 2014,7, 3617-3629

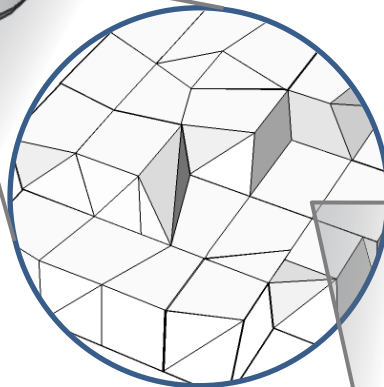
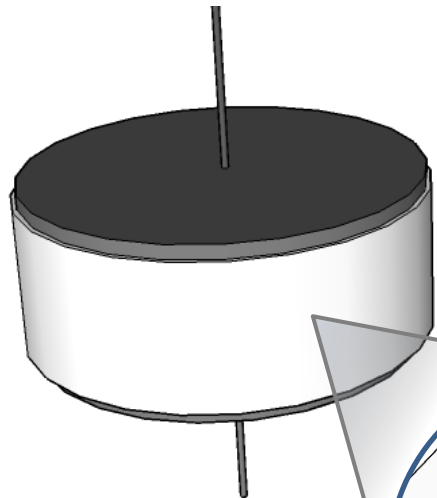


WHY NEW FEATURES?

Grain boundaries can be a highway or a toll for electric conductivity...



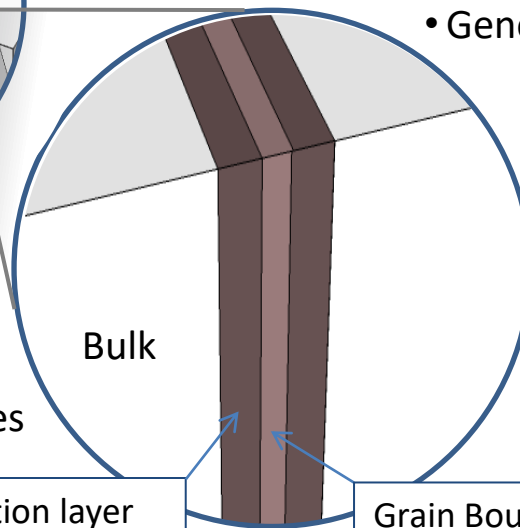
...but the final performance will be given by the worst performing component of the system



• Electric fields

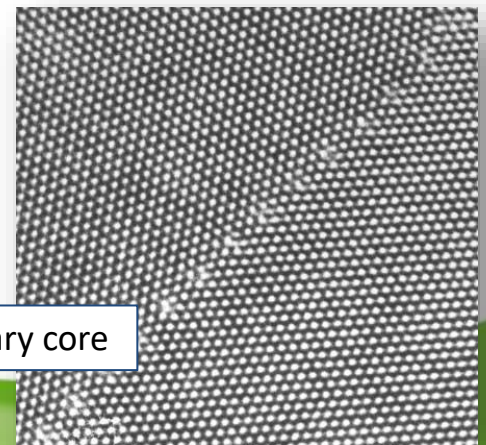
• Accumulation of dopants/charge carriers

• Accumulation of impurities



• Generation of defects/vacancies

• Strains

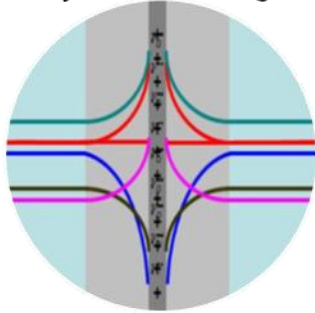


Depletion layer ("Electrical GB")

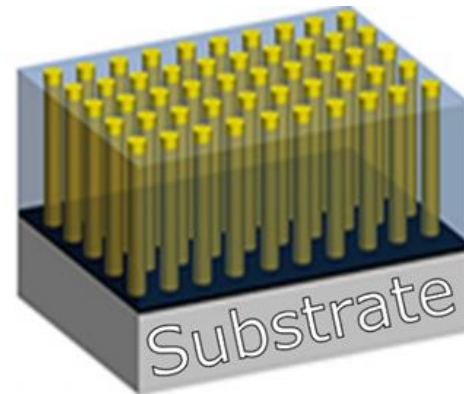
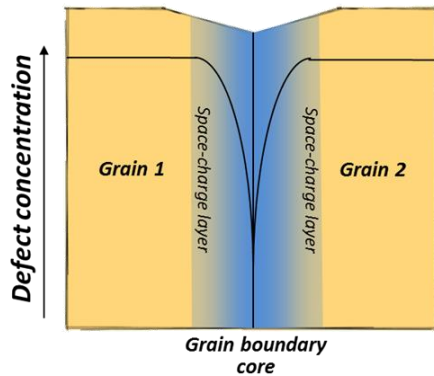
Grain Boundary core

HOW TO CONTROL INTERFACES AND IONS AT NANOSCALE?

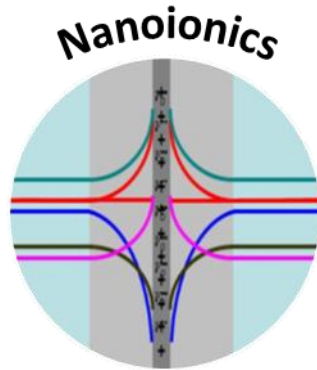
Nanoionics



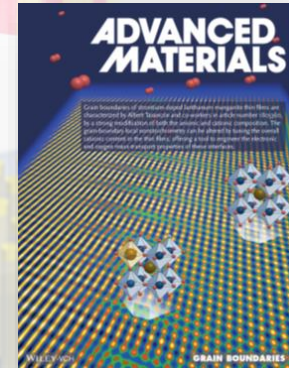
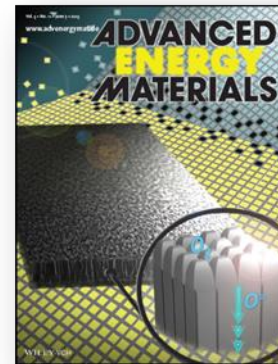
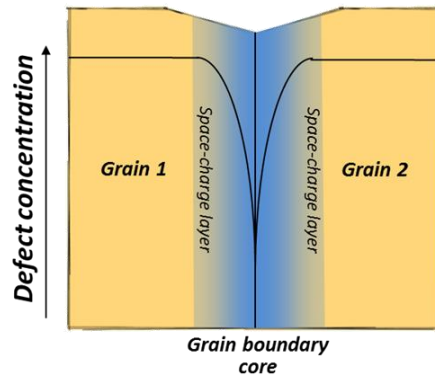
Nanoengineering



HOW TO CONTROL INTERFACES AND IONS AT NANOSCALE?



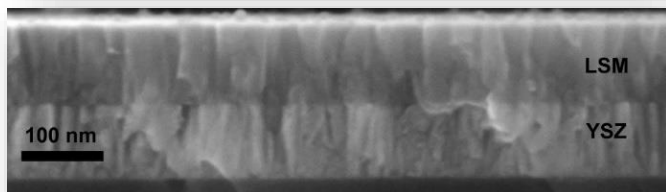
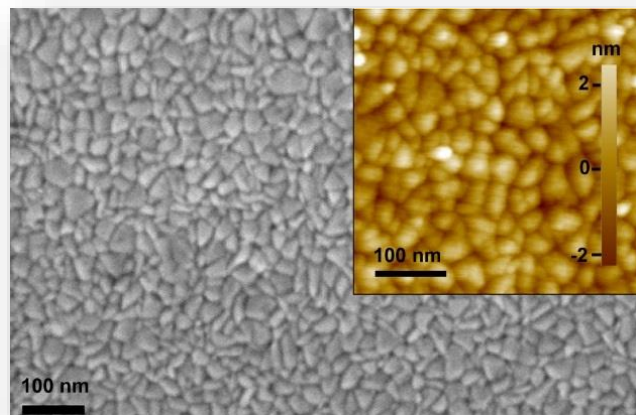
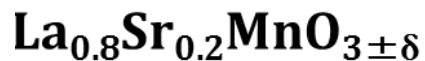
ENHANCEMENT OF IONIC CONDUCTIVITY IN INTERFACE-DOMINATED TF-MIECs



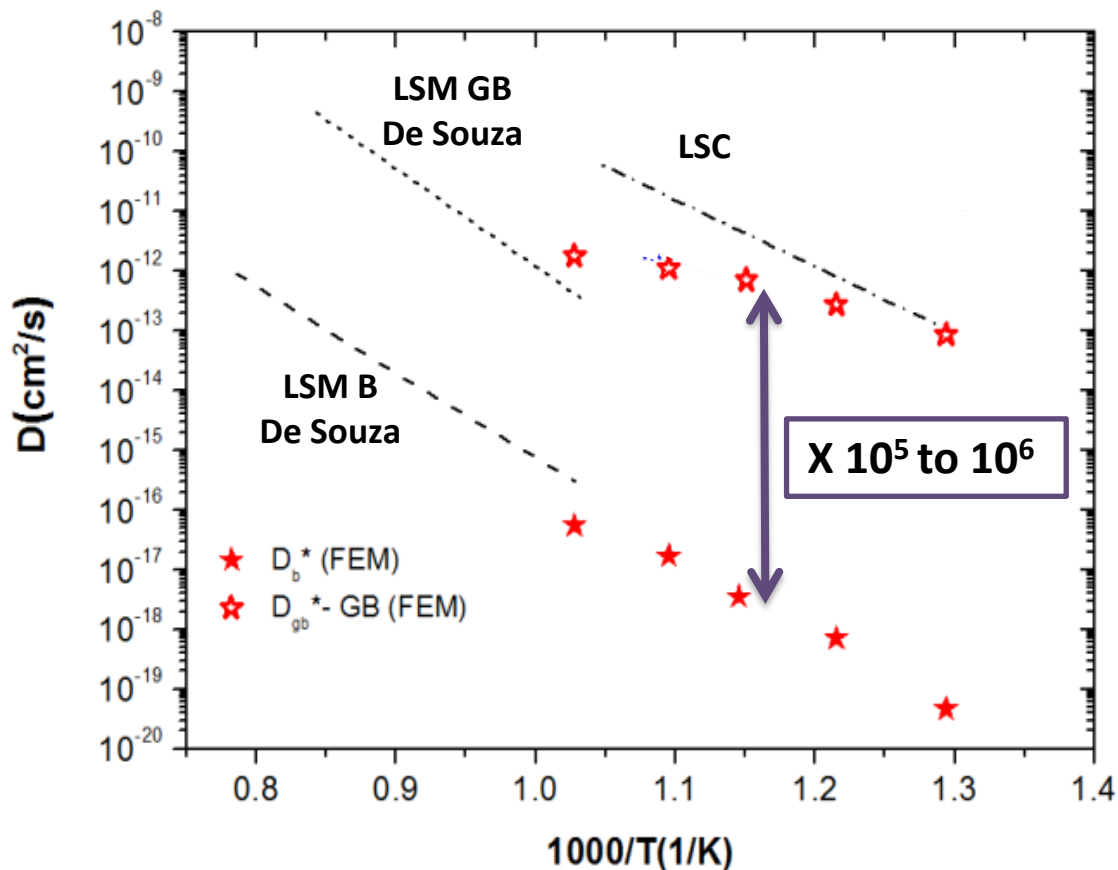
Saranya et al, Adv Energy Mater 5 (2015) 1500377

Chiabrera et al. Adv Mater 31 (2019) 1805360

ENHANCED IONIC CONDUCTIVITY IN TF-MIXED CONDUCTORS



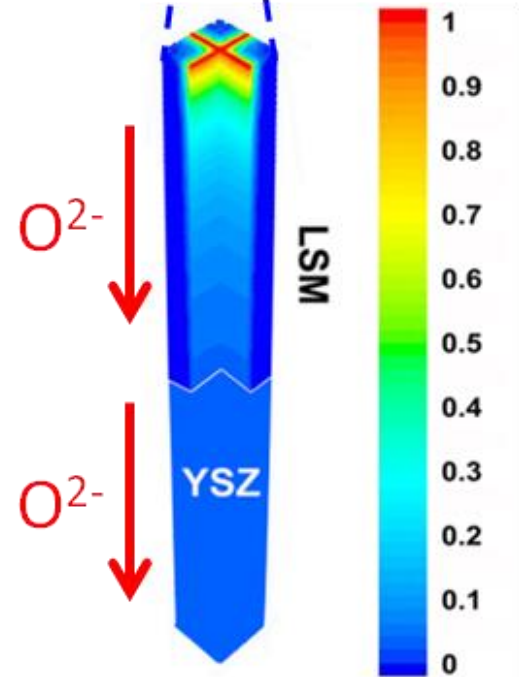
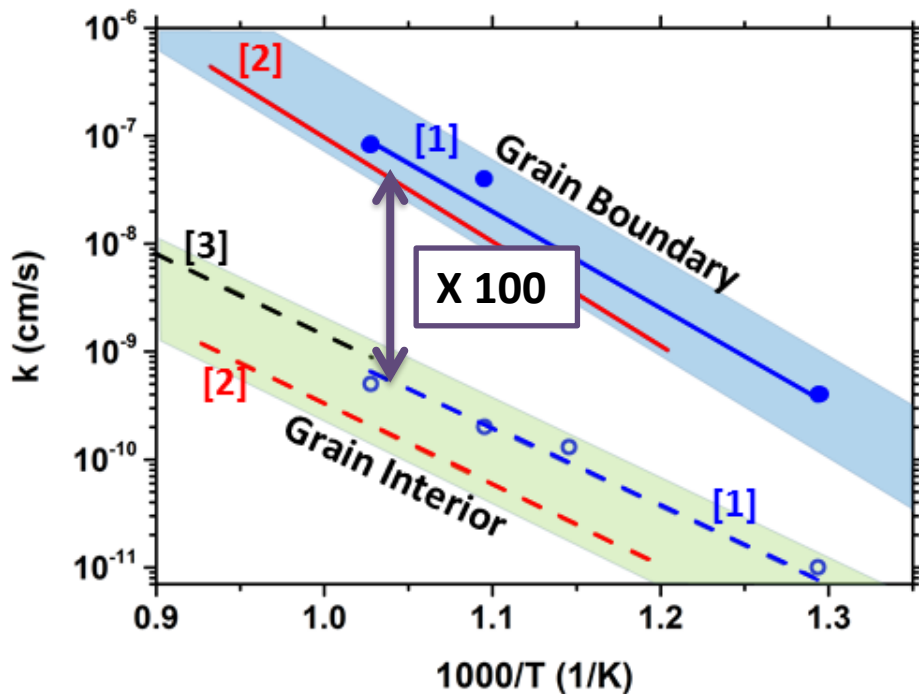
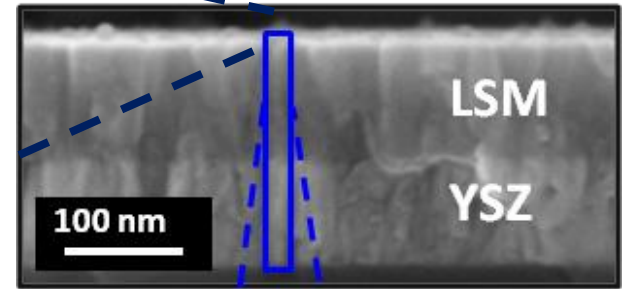
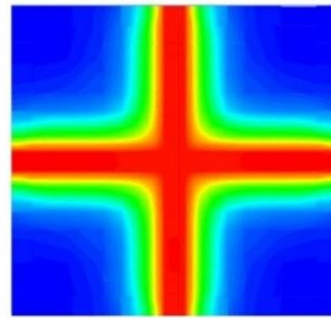
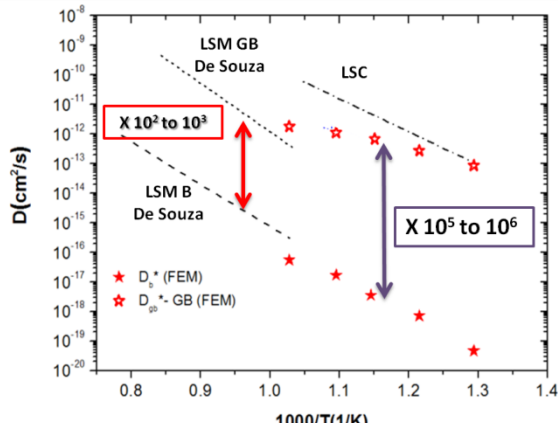
SIMS- ISOTOPE DEPTH PROFILING



Saranya et al, Adv Energy Mater 5 (2015) 1500377

OXYGEN EXCHANGE IS ALSO ENHANCED

SIMS- ISOTOPE DEPTH PROFILING

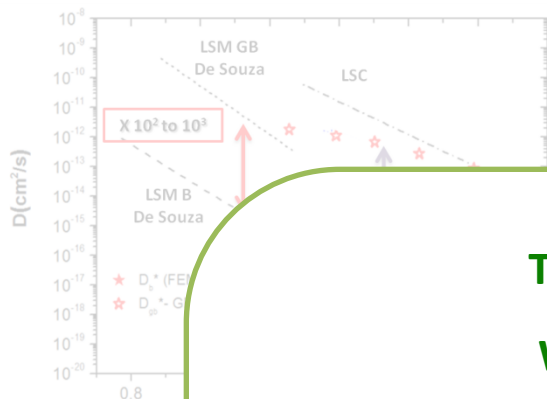


Saranya et al, *Adv Energy Mater* 5 (2015) 1500377

Saranya et al. *Chem. Mater.* 30 (2018) 5621–5629

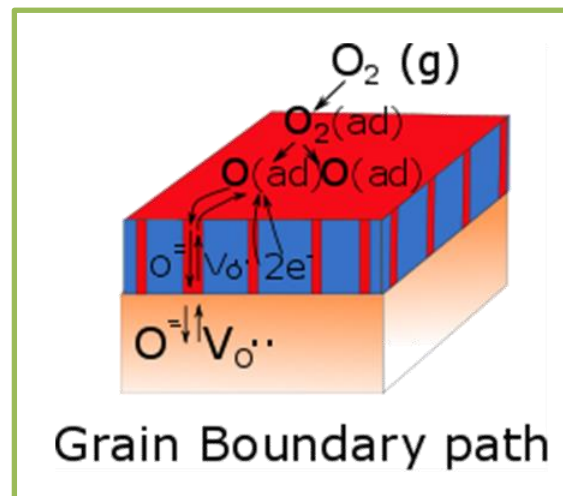
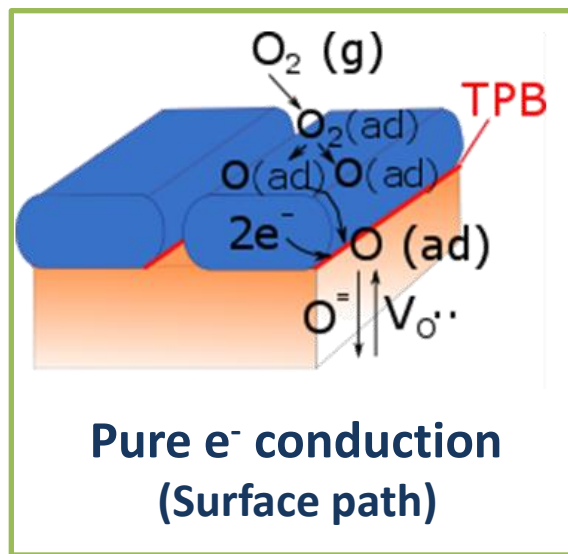
STRONG IMPLICATIONS ON THE OXYGEN INCORPORATION PATHWAY

SIMS- ISOTOPE DEPTH PROFILING

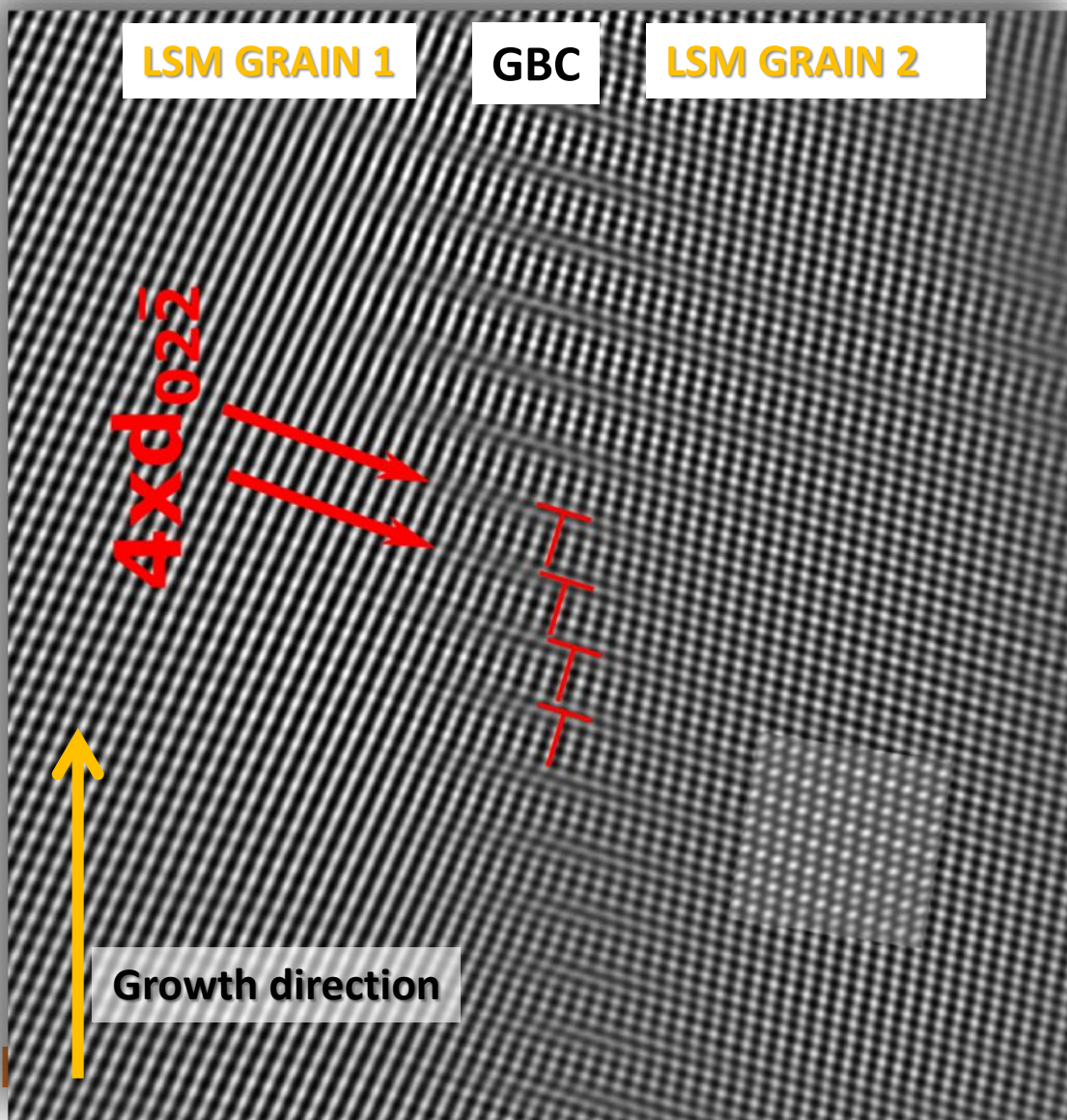


THE GRAIN BOUNDARY PATH IS NOW OPEN:

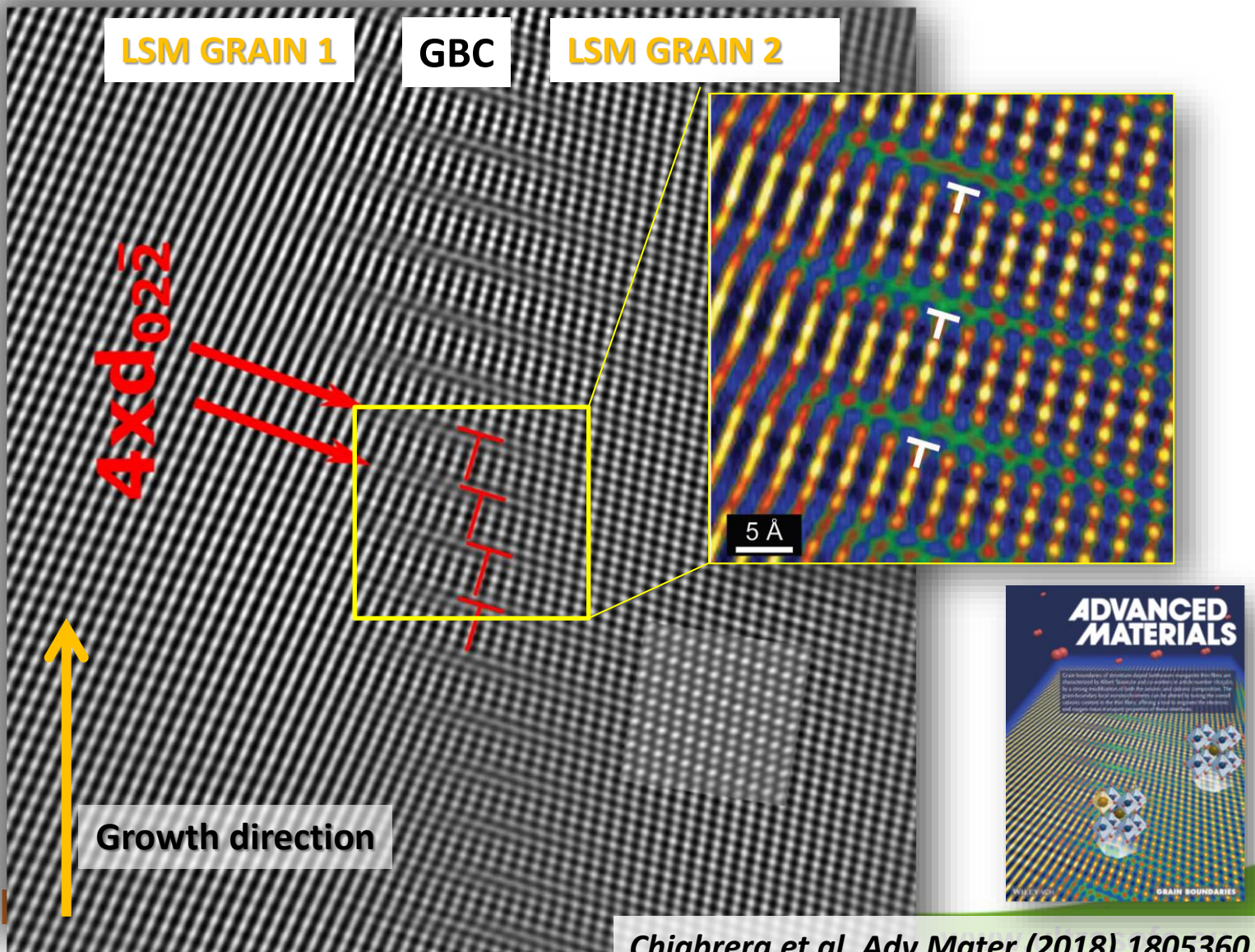
WE CAN CHANGE THE NATURE OF THE LSM



STRAIN AT THE GRAIN BOUNDARY LEVEL GENERATE DEFECTS



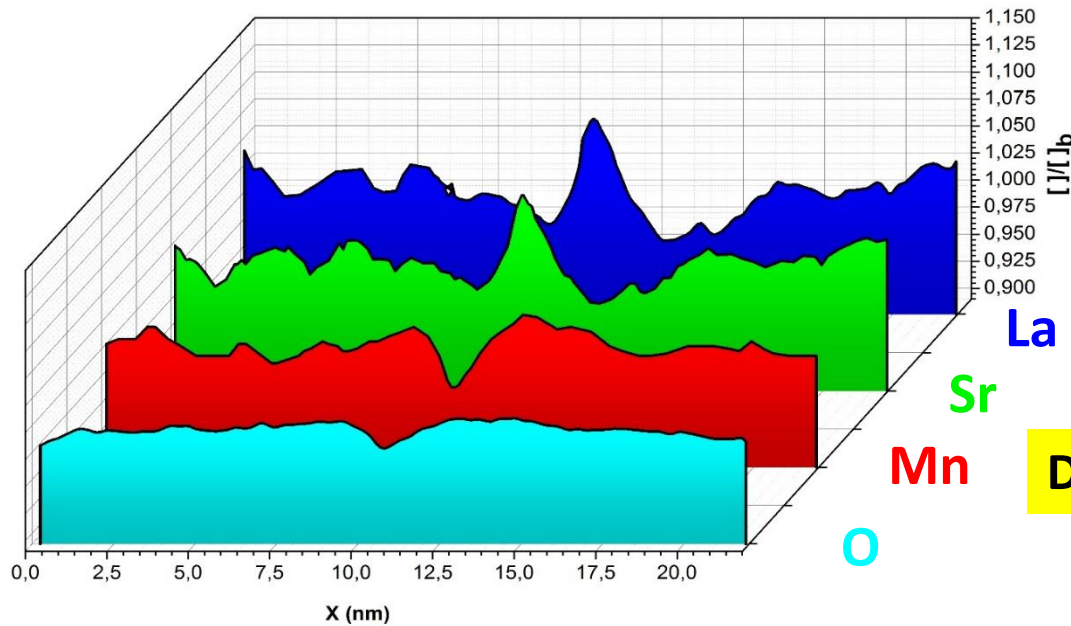
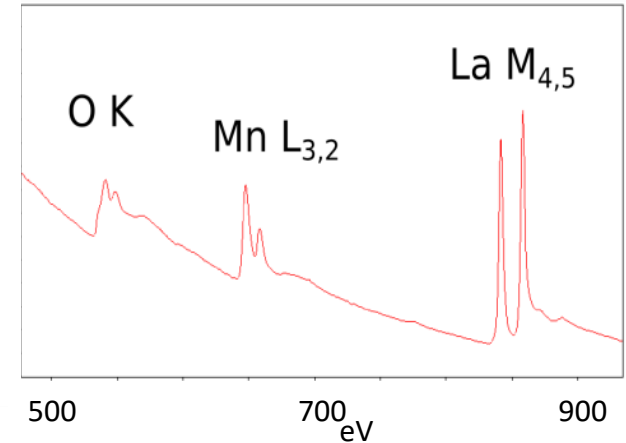
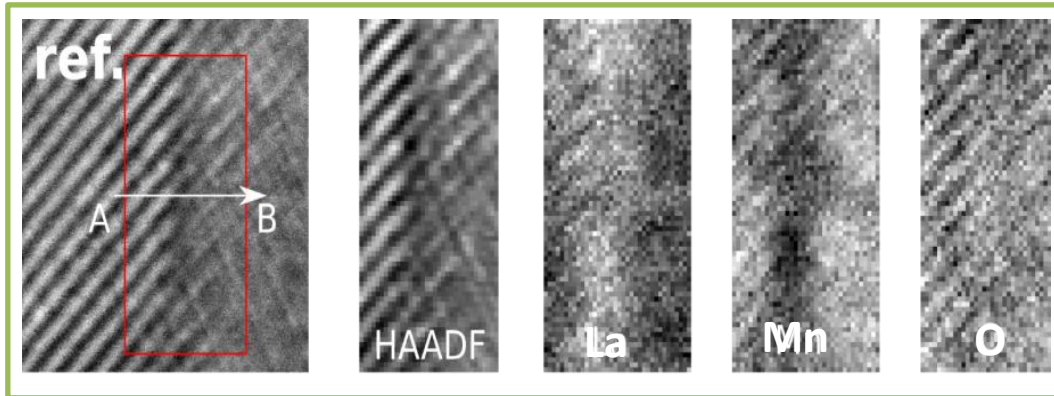
STRAIN AT THE GRAIN BOUNDARY LEVEL GENERATE DEFECTS



Chiabrera et al. Adv Mater (2018) 1805360

atarancon@irec.cat

CATION NON-STOICHIOMETRY AT THE GRAIN BOUNDARY

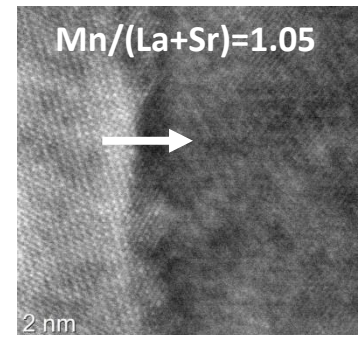
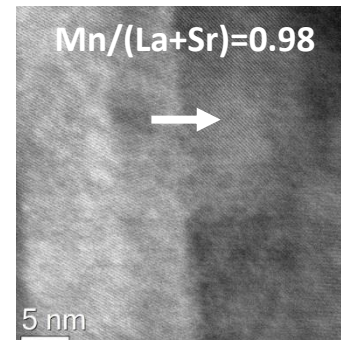
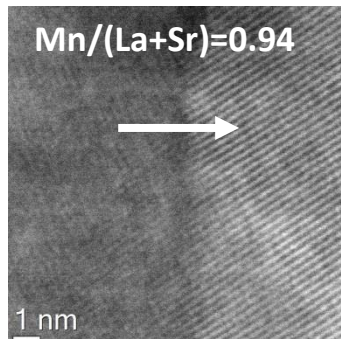
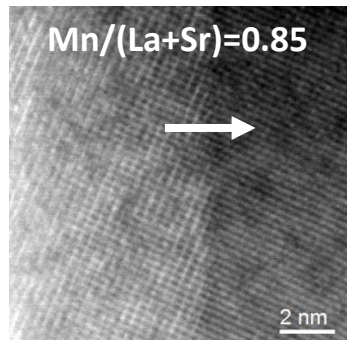


Non-stoichiometry at GB:

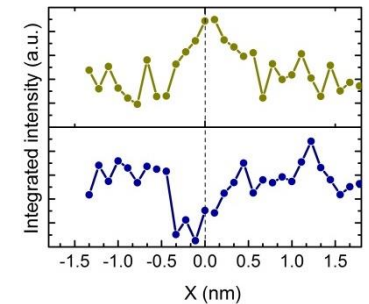
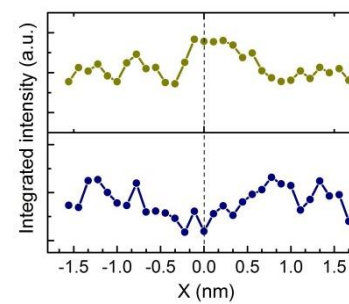
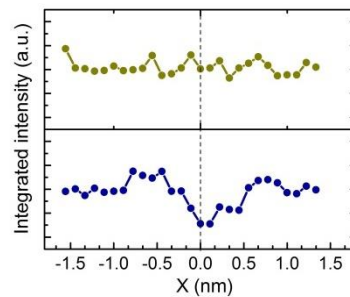
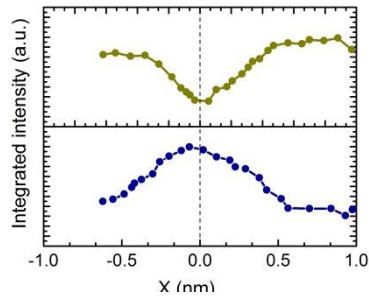
- La and Sr excess
- Mn deficiency
- O depletion => $[V_{O}^{\bullet\bullet}]$ ↑

DISLOCATIONS & SOMETHING ELSE

TUNING OF PROPERTIES BY GB ENGINEERING

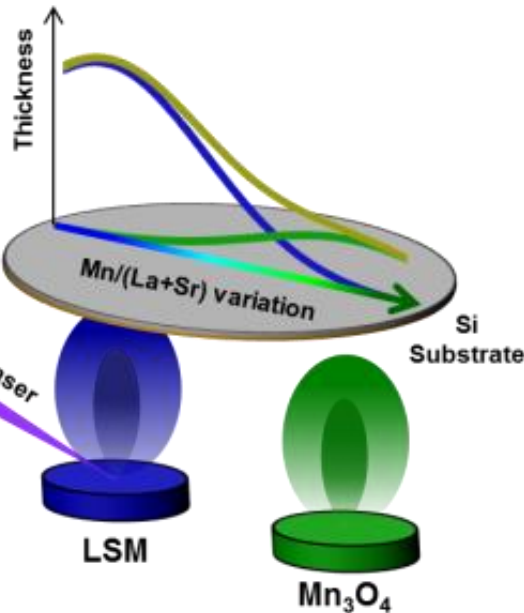


Mn

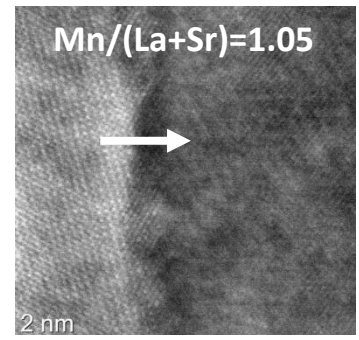
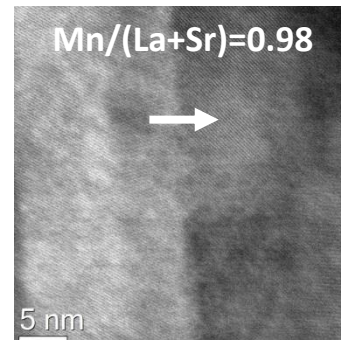
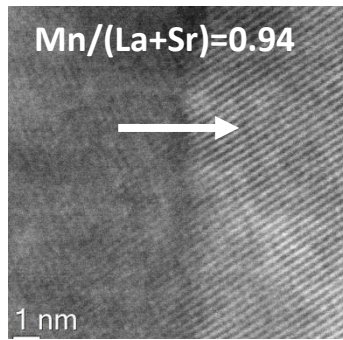
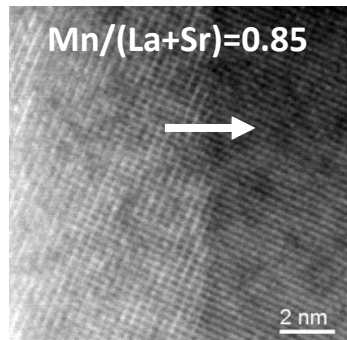


Mn

La

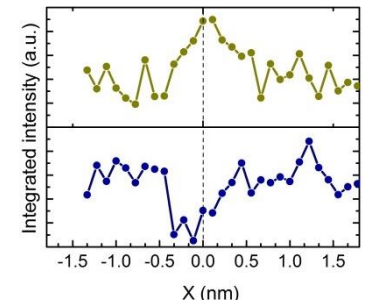
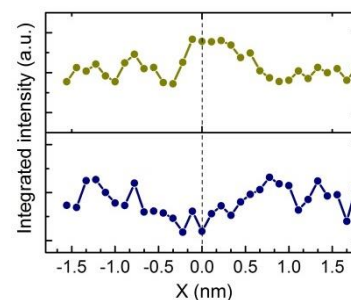
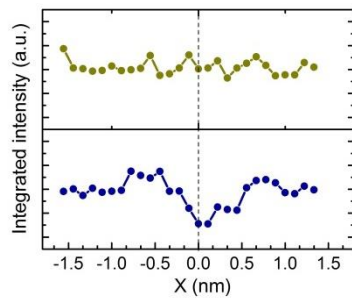
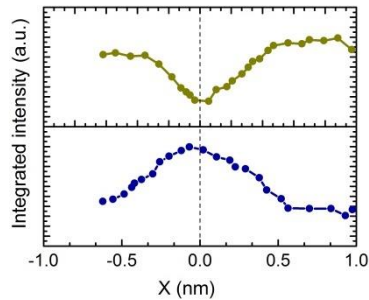


TUNING OF PROPERTIES BY GB ENGINEERING



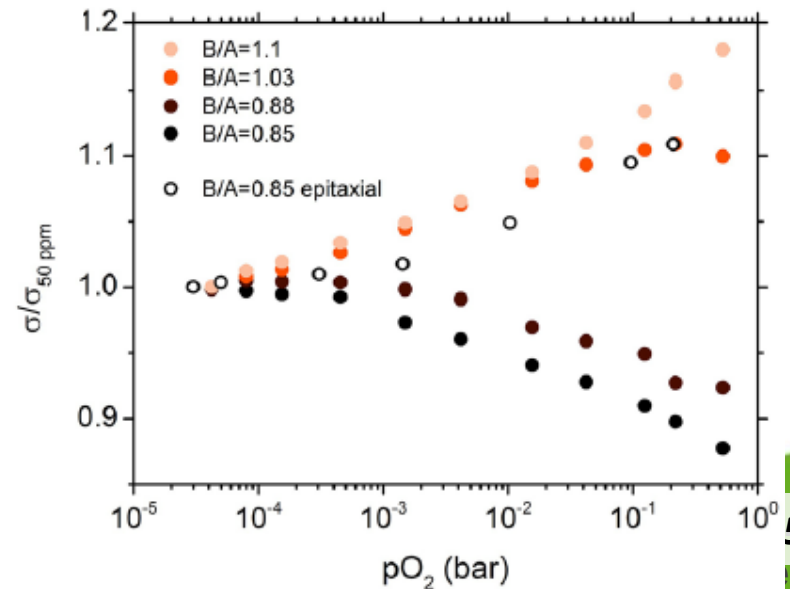
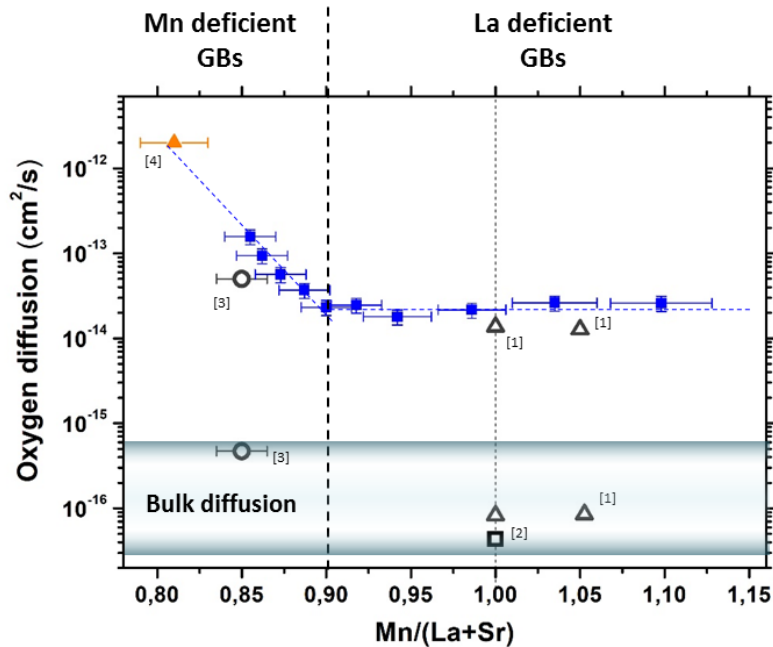
Mn

La

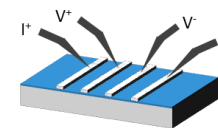
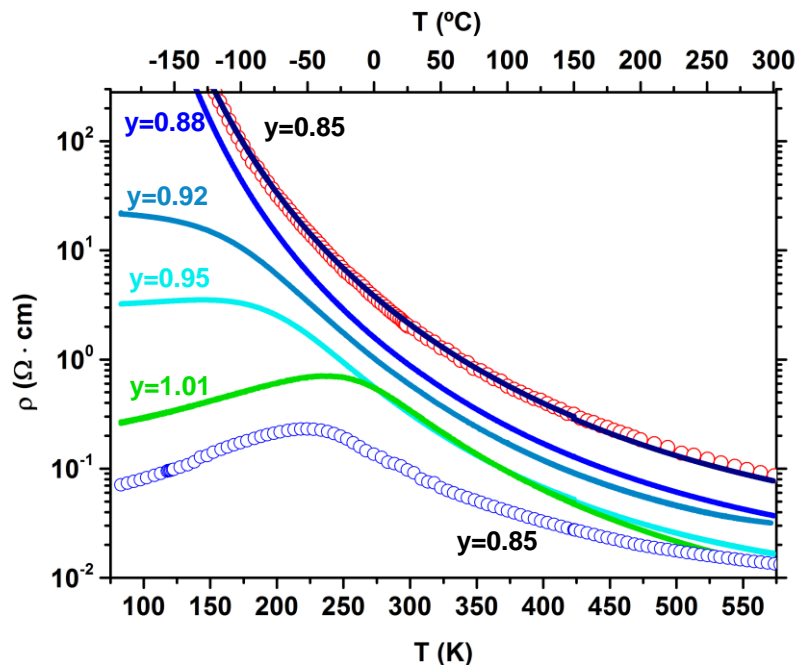
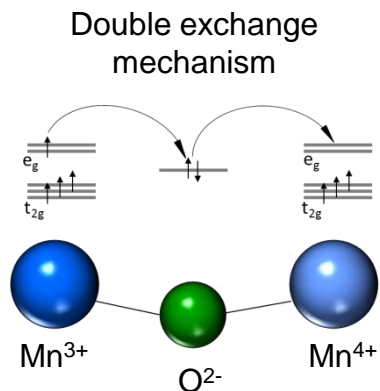


Mn

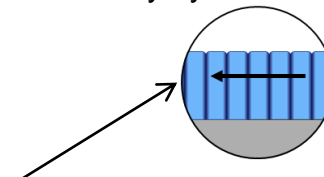
La



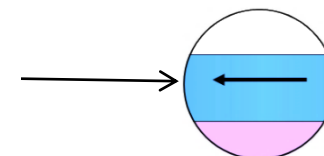
TUNING OF PROPERTIES BY GB ENGINEERING: ELECTRICAL



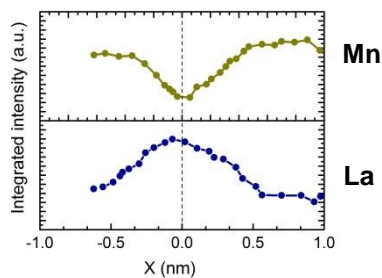
Polycrystalline thin films



Epitaxial thin films on NdGaO₃(110)

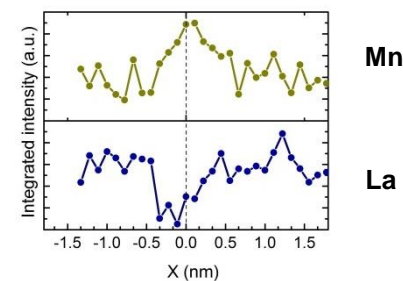


Mn/(La+Sr) < 0.92



Insulating behaviour

Mn/(La+Sr) > 0.92



Double exchange mechanism

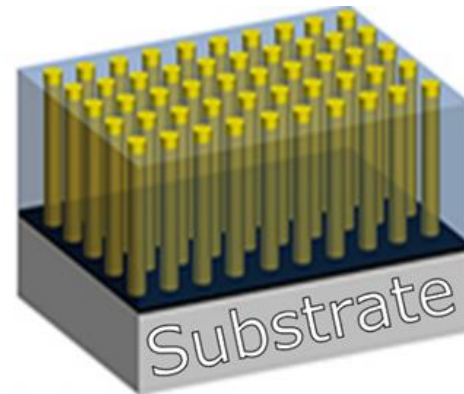
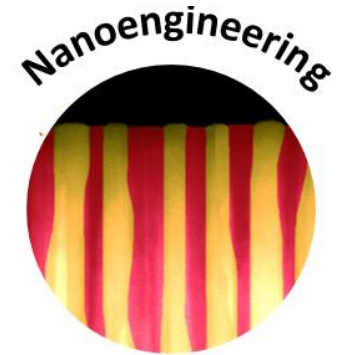
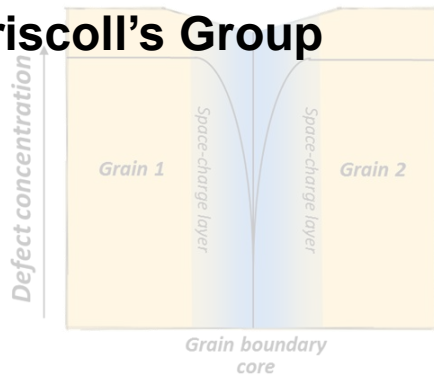
HOW TO CONTROL INTERFACES AND IONS AT NANOSCALE?

VERTICALLY ALIGNED NANOCOMPOSITES



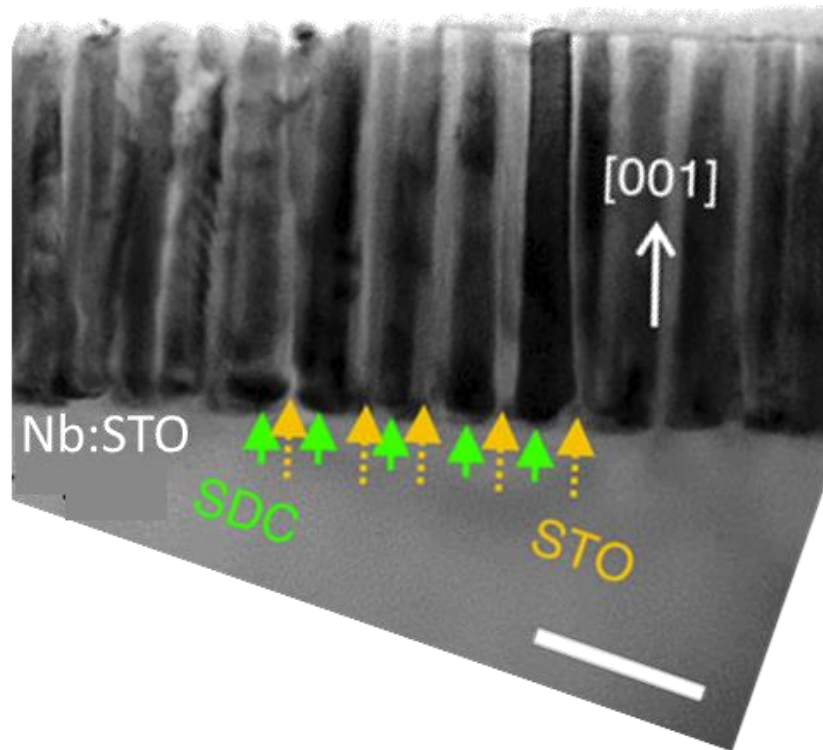
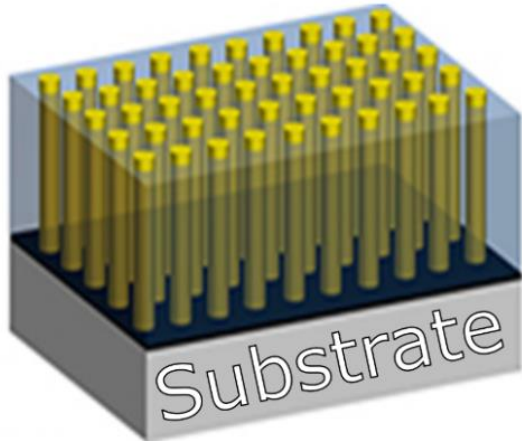
UNIVERSITY OF CAMBRIDGE

Driscoll's Group



VERTICALLY ALIGNED NANOSTRUCTURES (VANs) FOR SOCs

Matrix Nanopillars



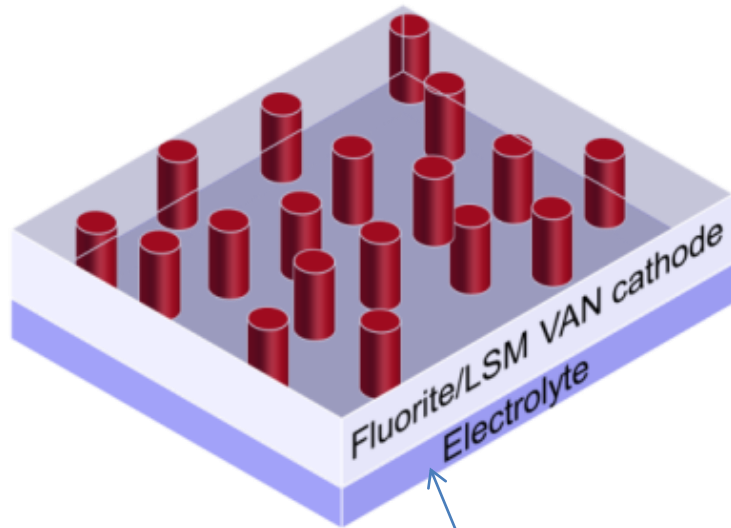
Nature Materials **7**, 314–320 (2008)
Nature Communications, **6**, 8588 (2015)
Nature Communications, **7**, 12373 (2016)
APL Materials, **Vol.5**. (2017)

- ✓ Self-assembled by PLD
- ✓ Well-controlled and tunable
- ✓ Large interfacial area (nm pillars)

Time for SOCs' VANs

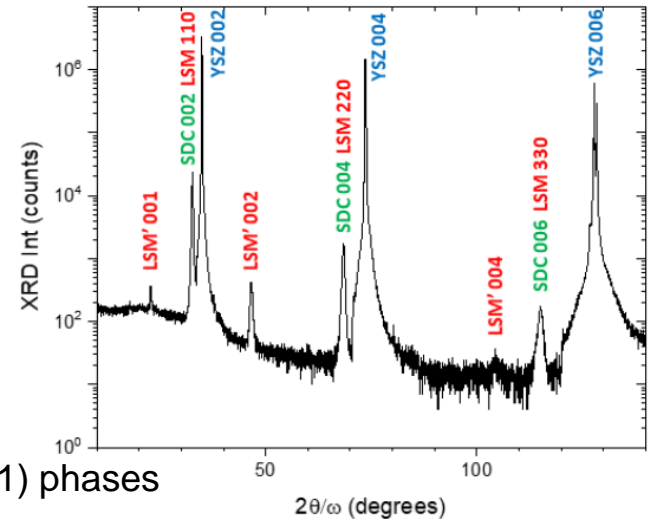
- LSM/fluorites
- LSCF (mesoporous)

LSM/FLUORITE VAN

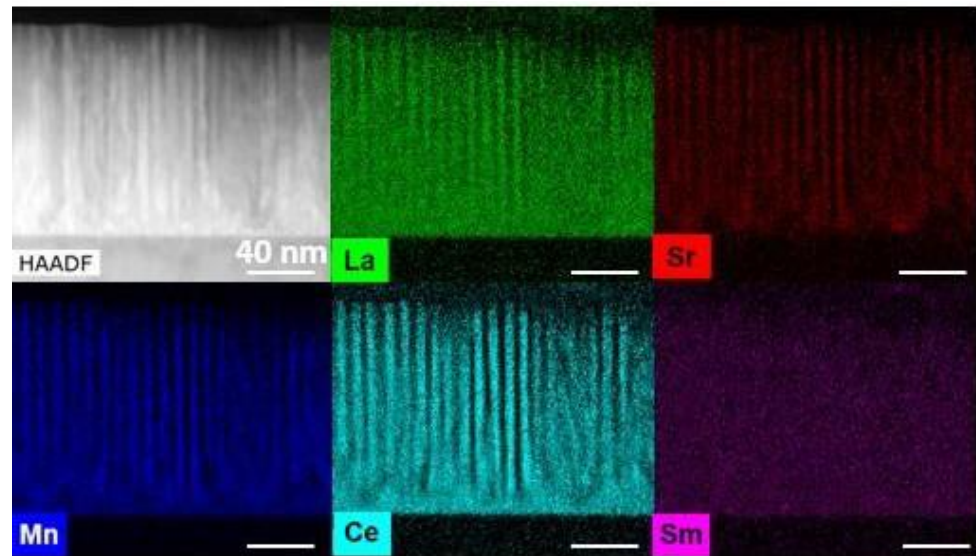


YSZ substrate

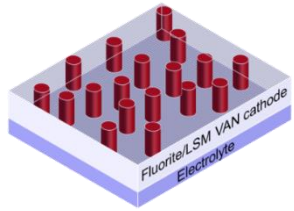
- LSM provides the electronic path
- Fluorite brings oxygen to the TPBs
- Tested fluorites → Sm:CeO₂, Pr:CeO₂, YSZ



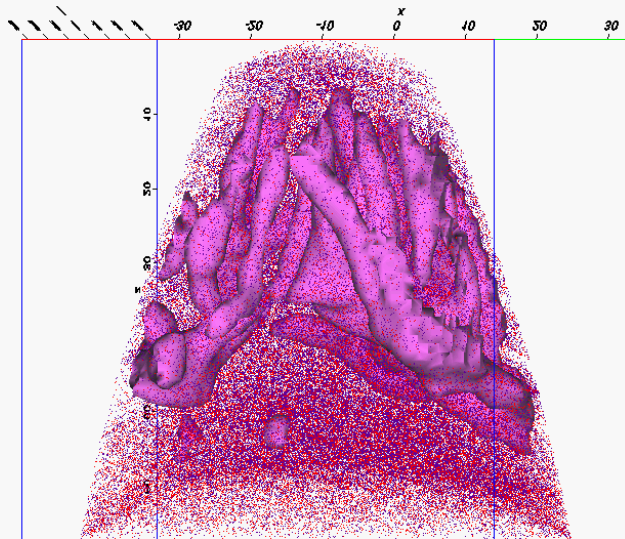
Highly oriented (001) phases



LSM/FLUORITE VAN: FUNCTIONAL PROPERTIES

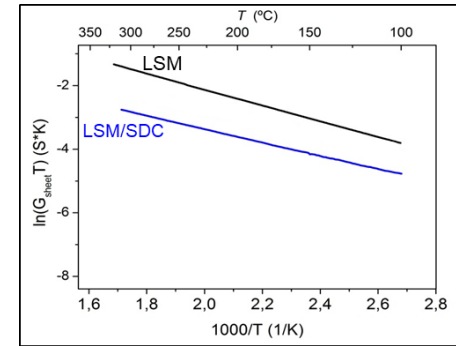


Atom-Probe tomography

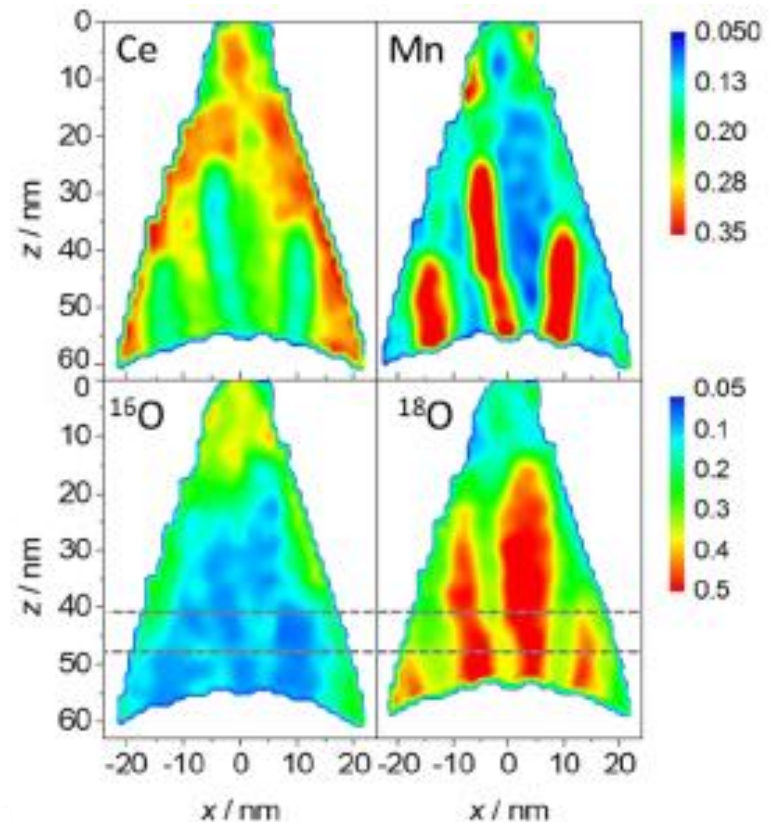


APT by D. Diercks, Colorado School of Mines

In-plane conductivity

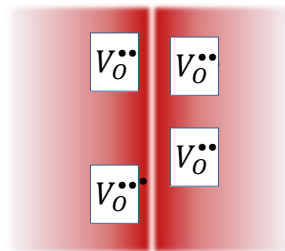
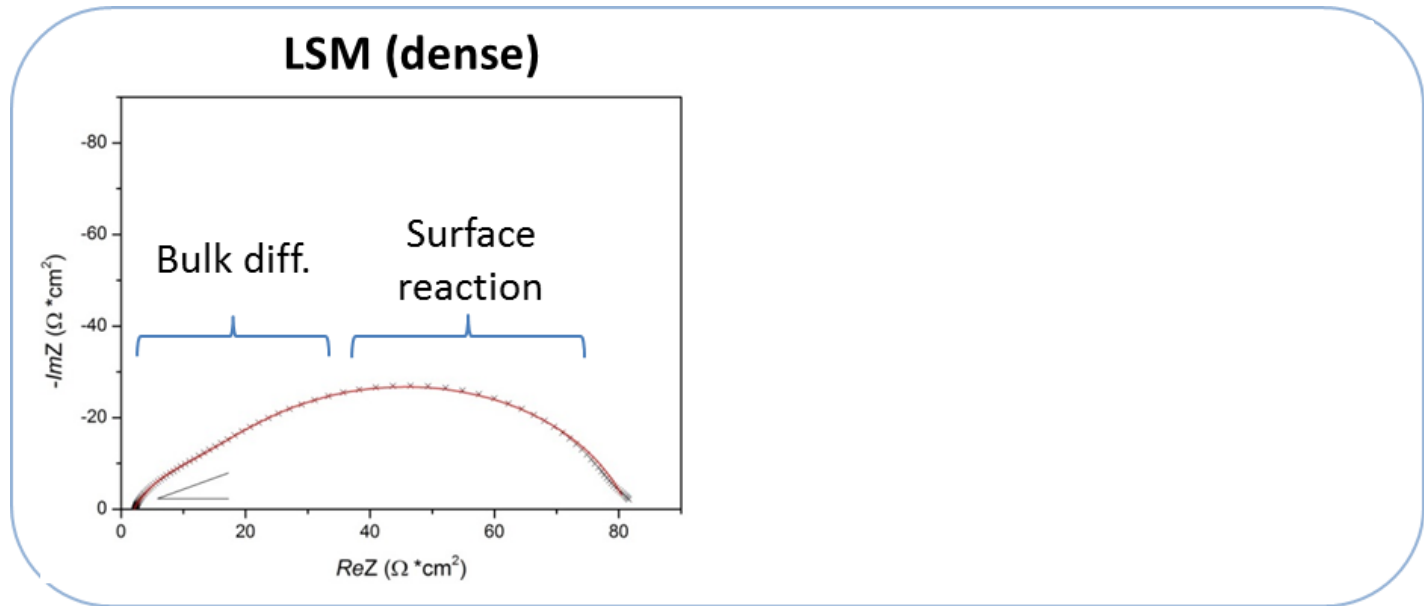
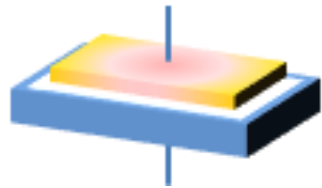


Synergistic role in O²⁻ incorporation



LSM/FLUORITE VAN: ELECTROCHEMICAL BEHAVIOUR

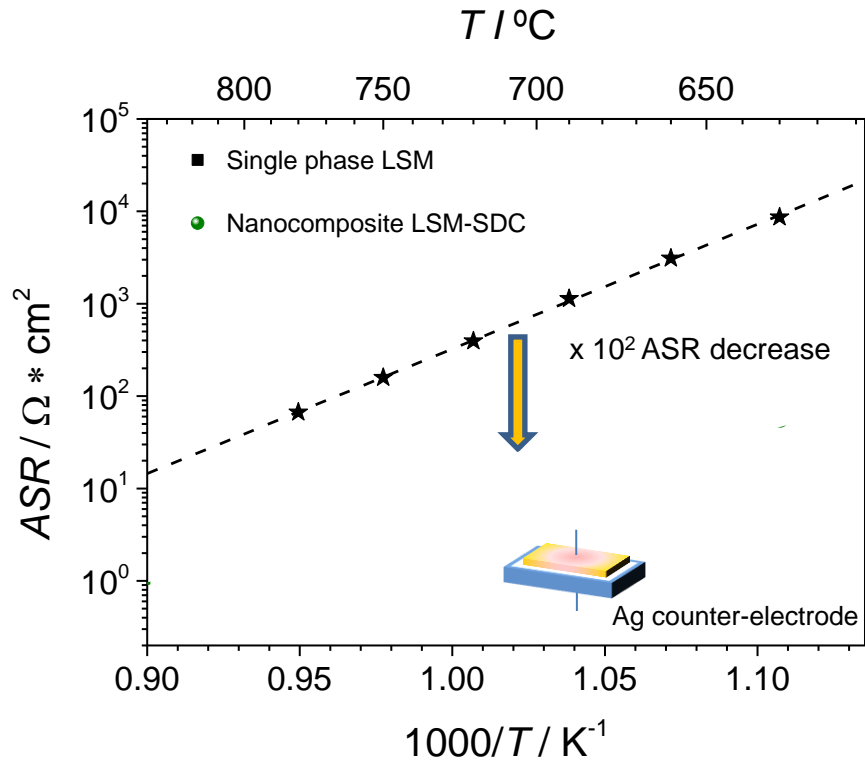
Out-of-plane polarization



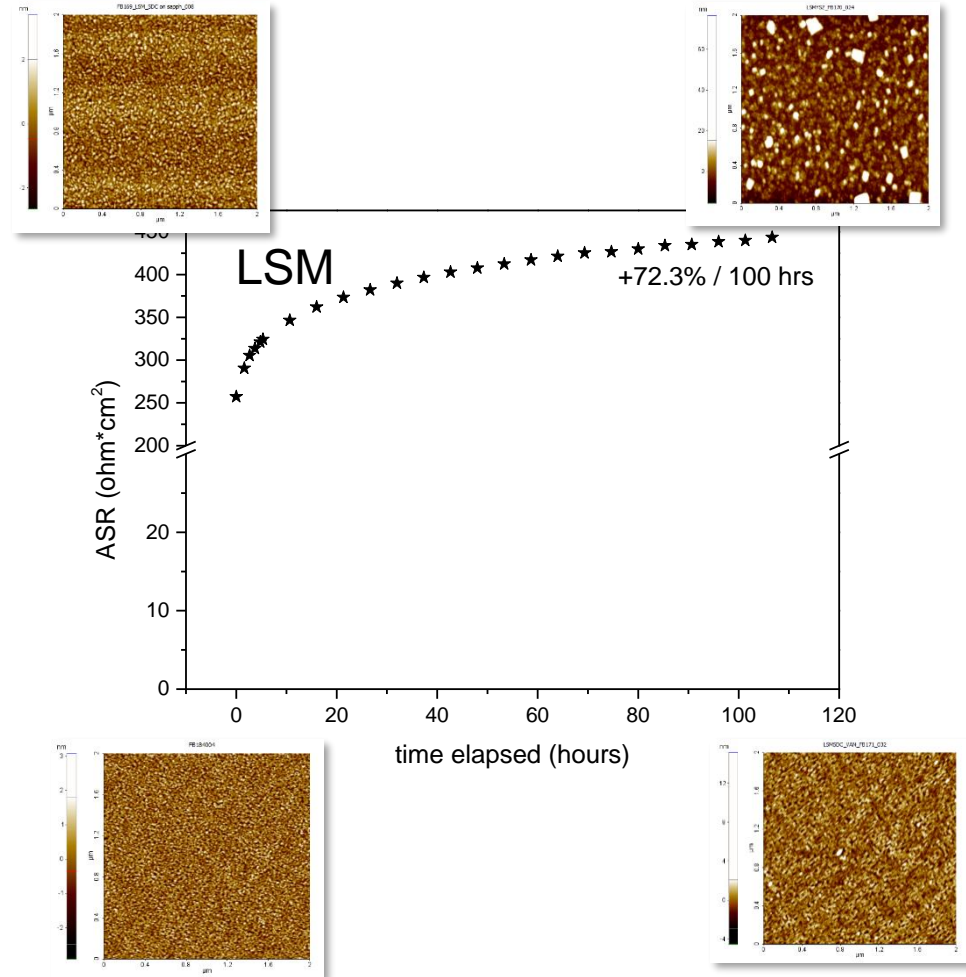
LSM GB

LSM/FLUORITE VAN: ELECTROCHEMICAL BEHAVIOUR

Electrochemical performance: ASR



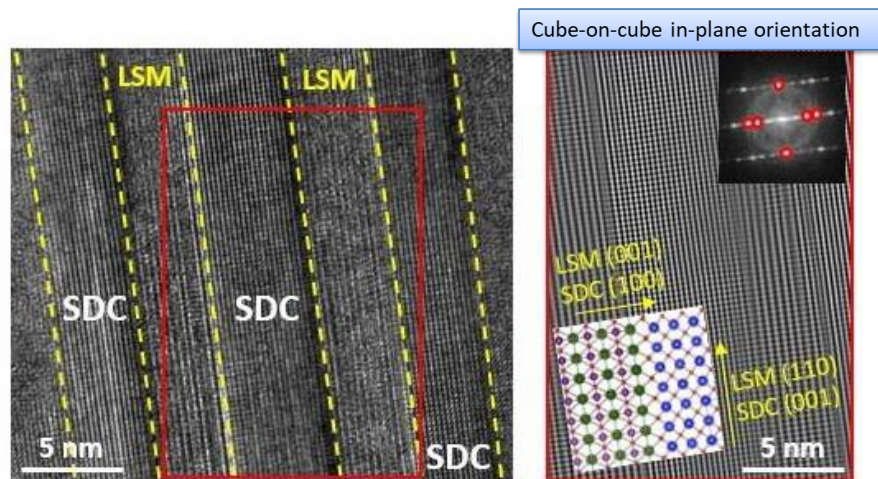
Long-term thermal stability



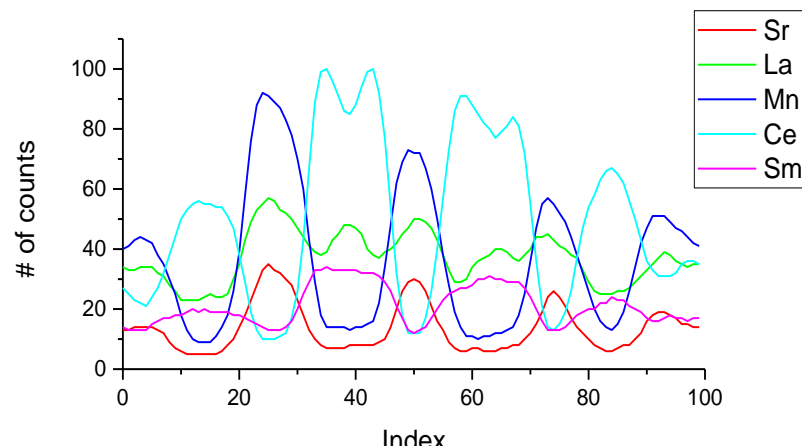
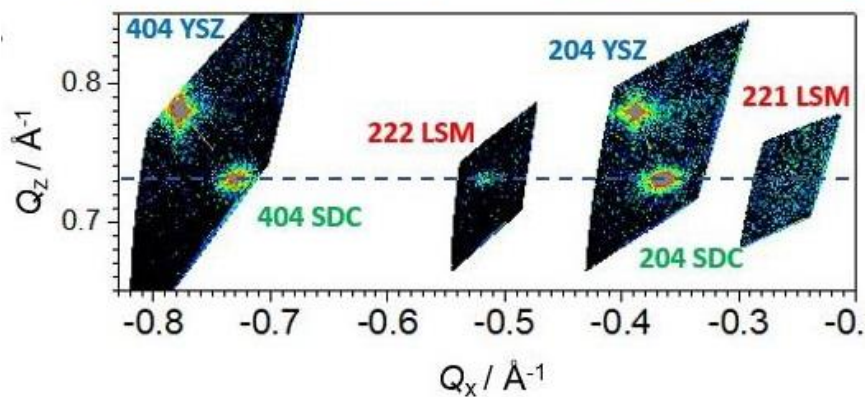
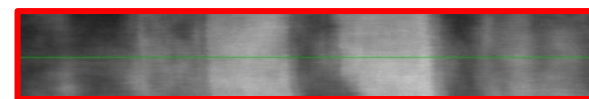
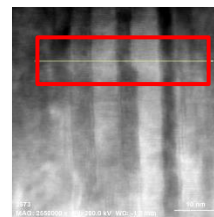
LSM/FLUORITE VAN: ORIGIN OF THE LONG TERM STABILITY

Sr segregation less favorable under in-plane compressive strain

Observed isotropic compressive strain (-0.8%)

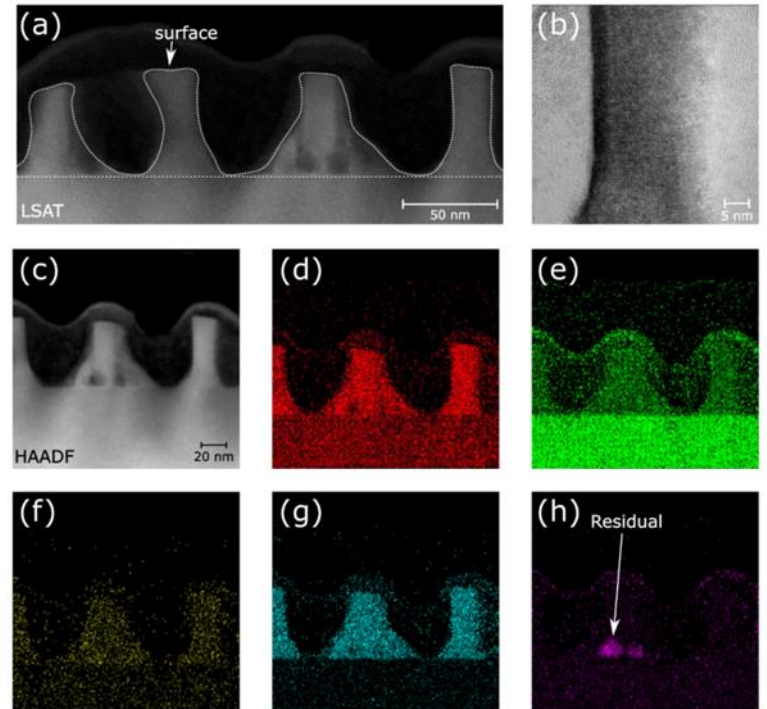
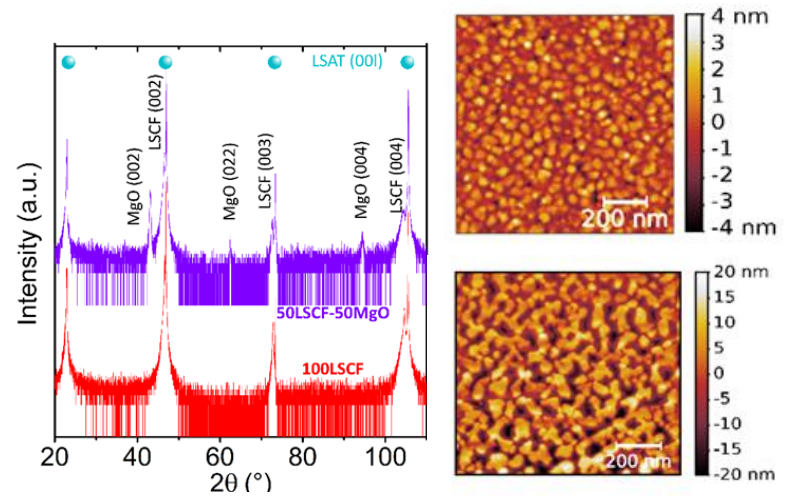
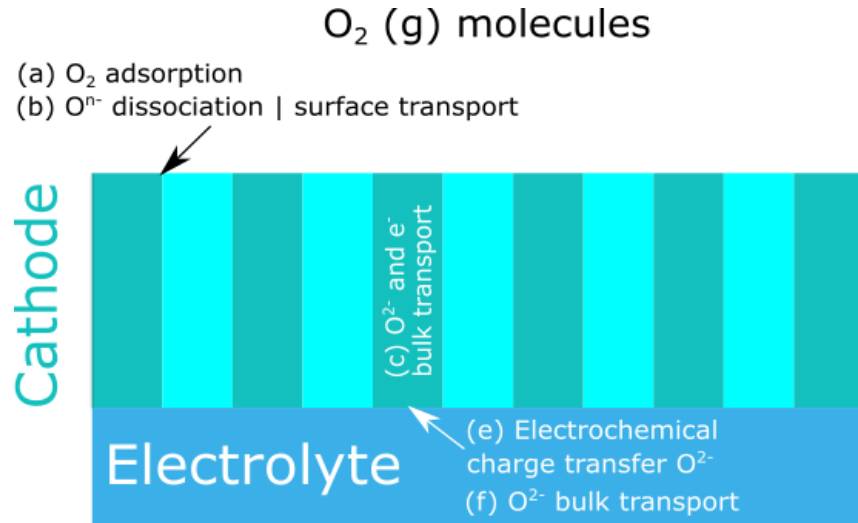


Strain induced by local disorder

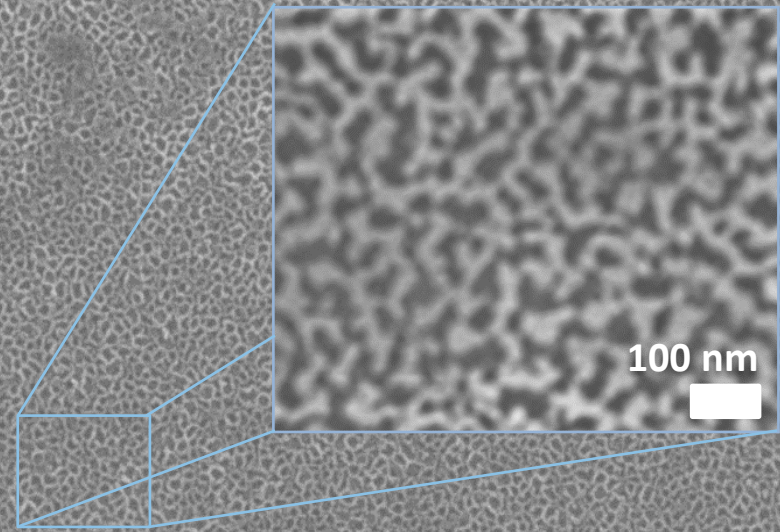
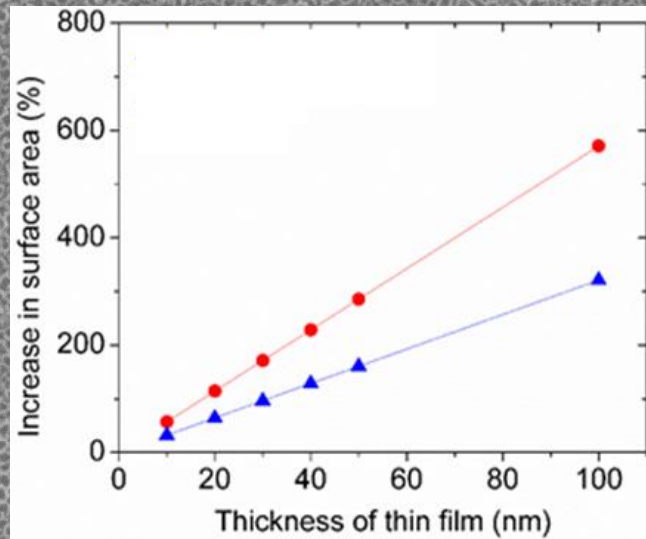


LSCF/SACRIFICIAL PHASE VAN

Porous Mixed Ionic Electronic Conductor

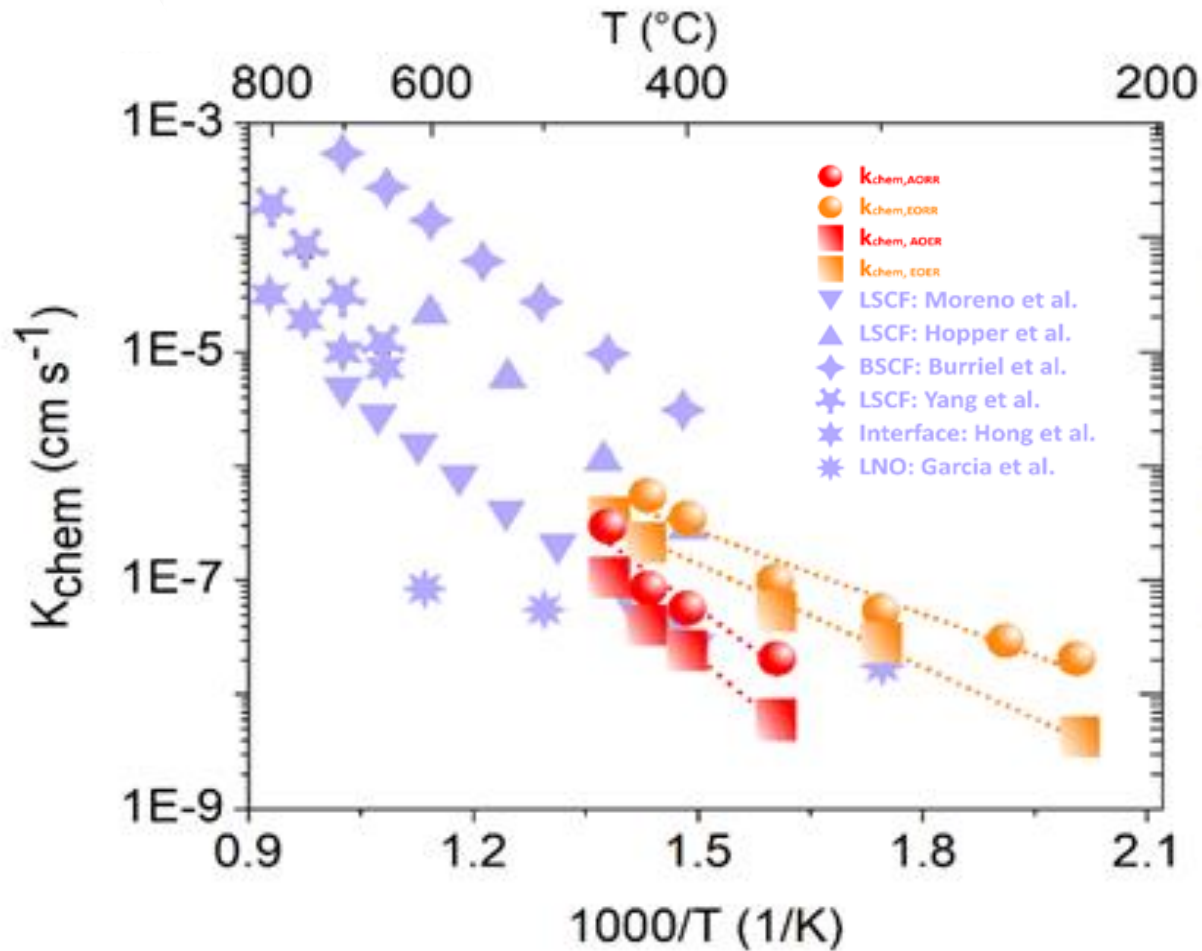


GREAT INCREASE OF SURFACE AREA

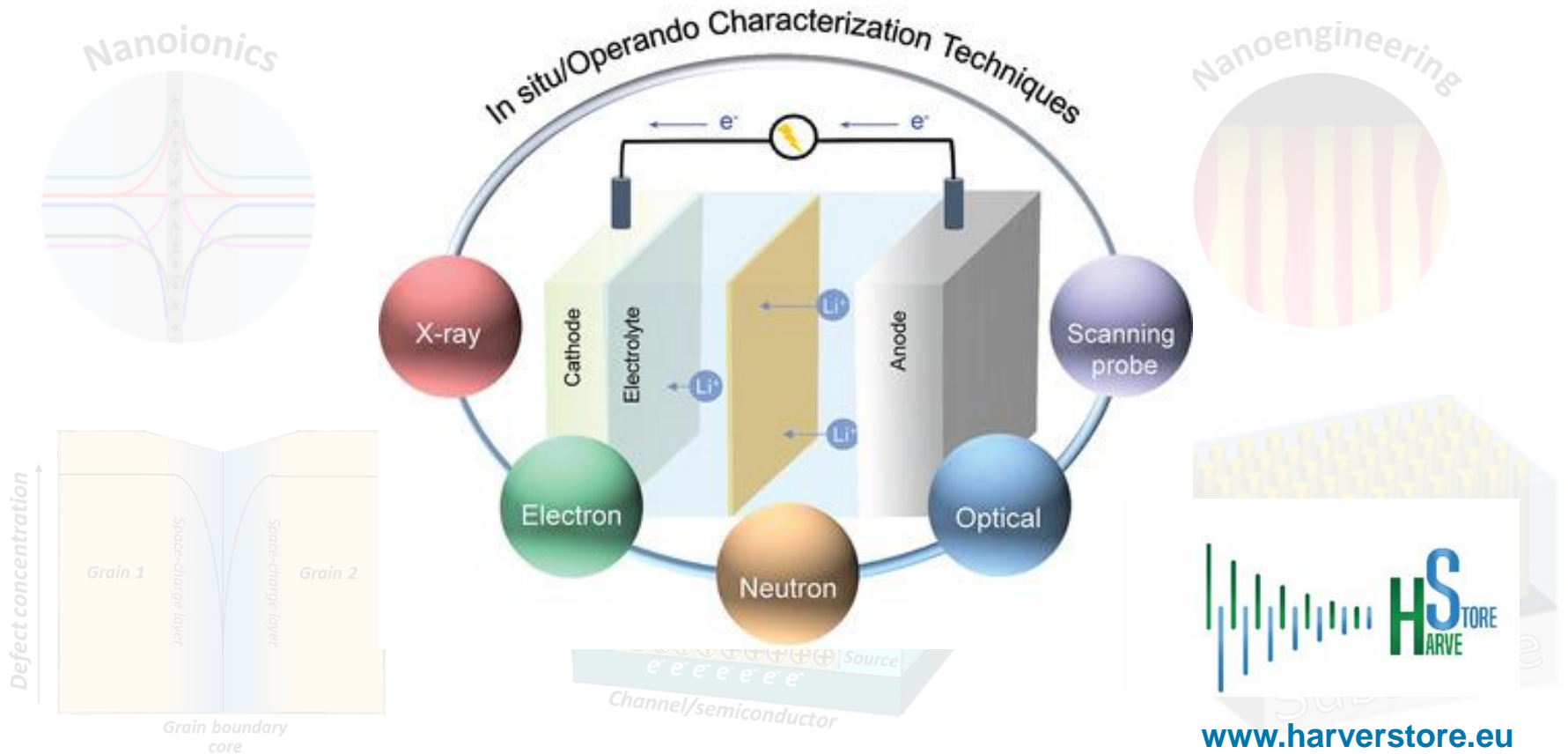


52 %

MESOPOROUS LSCF: ELECTROCHEMICAL PROPERTIES



NEW DISCIPLINES TO CONTROL INTERFACES AND IONS AT NANOSCALE



INTERPLAY OF IONS-ELECTRONS AT THE INTERFACE

SPECTROSCOPIC ELLIPSOMETRY - INTRODUCTION

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

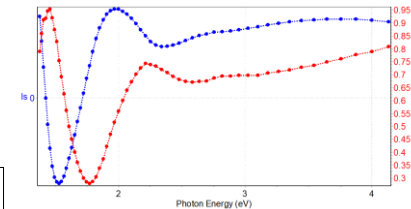
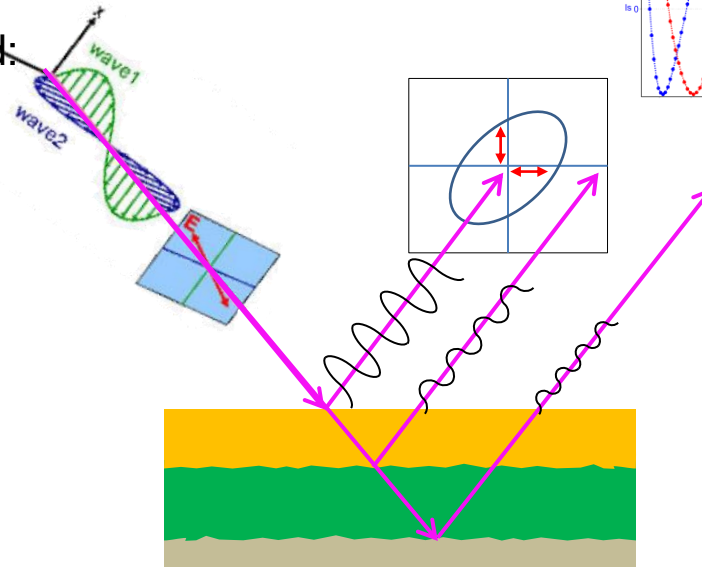
A **change on the polarization of light** when being reflected from the sample is directly related with the **material's optical constants** (complex dielectric constants).

Diverse features can be indirectly obtained:

- Composition
- Crystallinity
- Alloy ratio-porosity
- Depth profiles
- Roughness

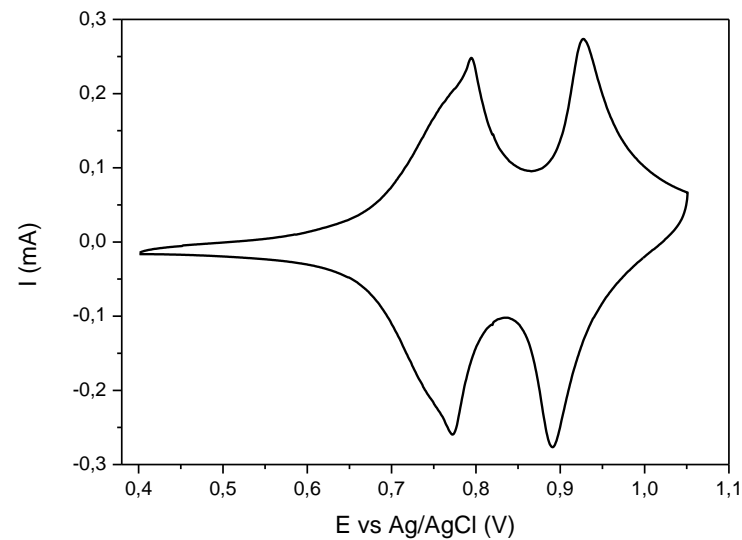
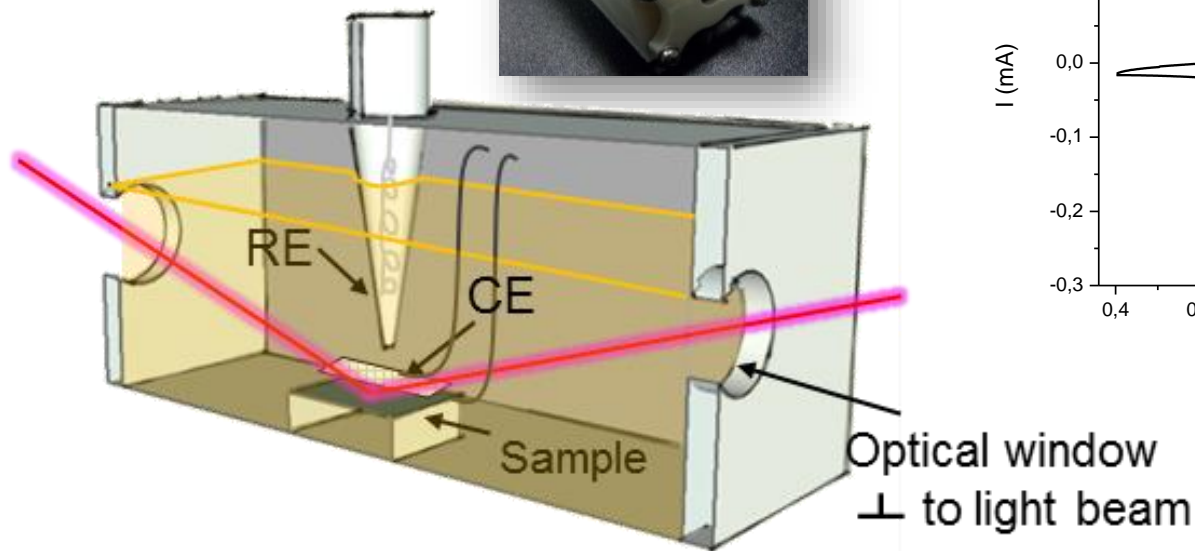
Specially sensitive to:

- **Multilayers**
- **Interfaces**
- **Electronic band configuration**

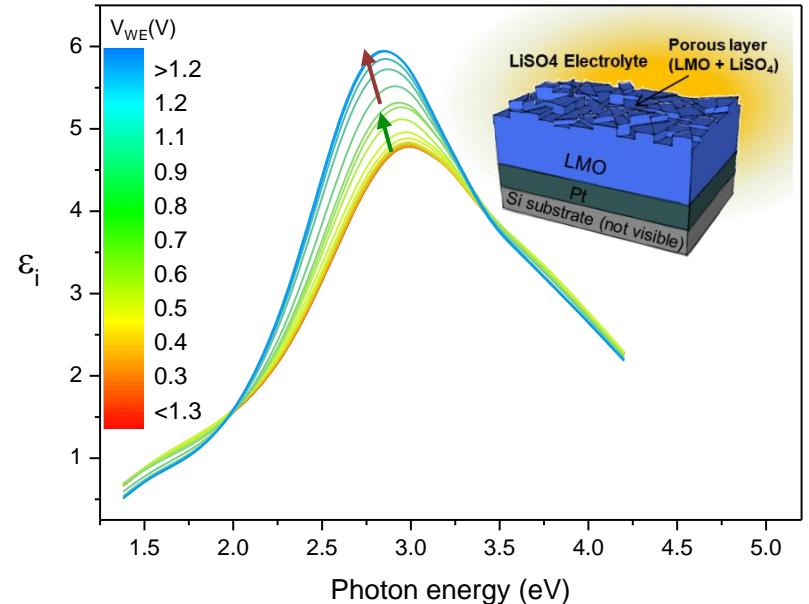
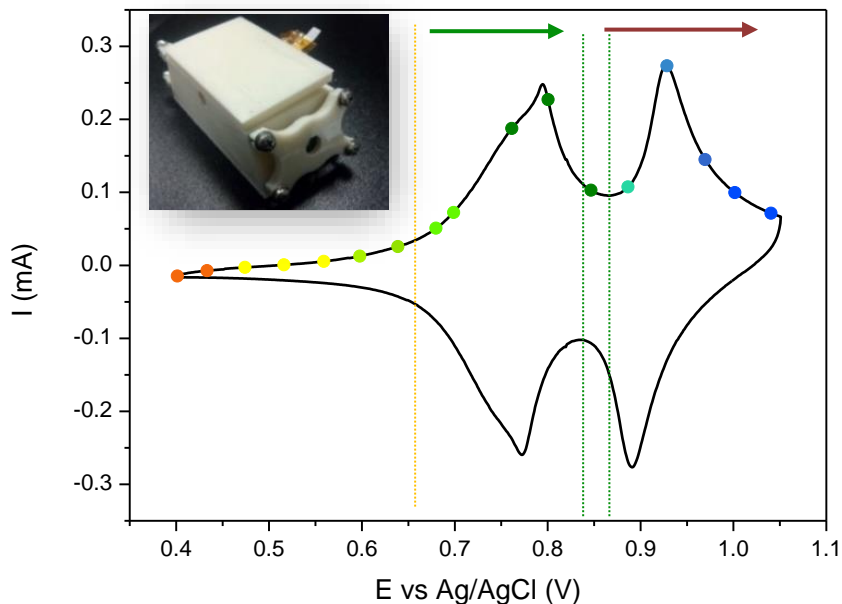


Ideal technique for studying thin-film battery materials and systems

OPERANDO SPECTROSCOPIC ELLIPSOMETRY -ELECTROCHEMICAL CHAMBER

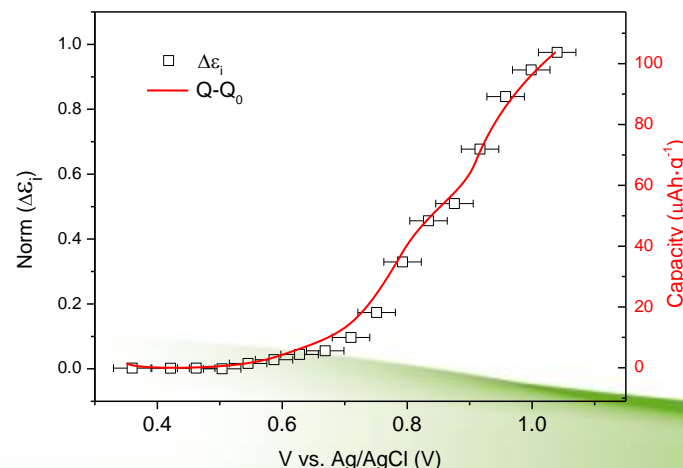


OPERANDO SPECTROSCOPIC ELLIPSOMETRY - RESULTS



CV cycle on the LiMn_2O_4 film inside the electrochemical chamber. The dots represent a the moments at which an SE measurement is acquired.

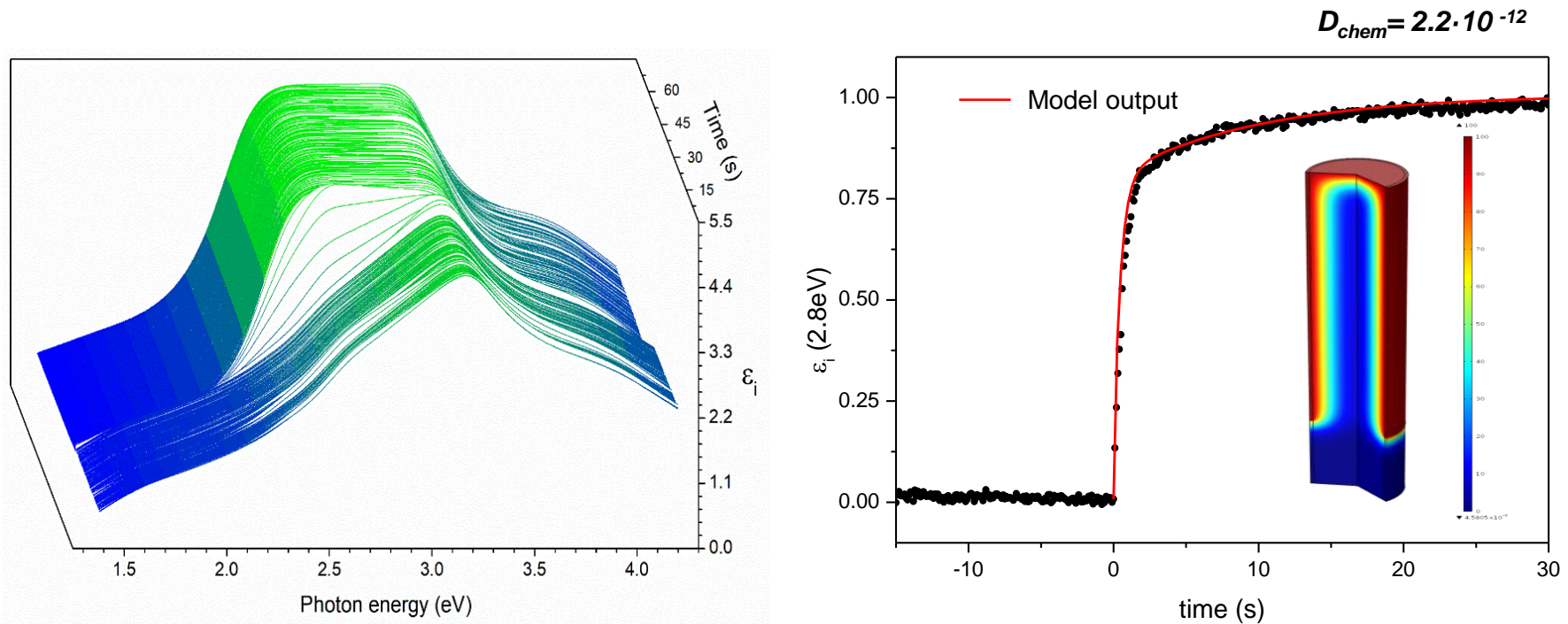
Imaginary part of the dielectric constant (ϵ_i) obtained from the fitting of the measured spectra.



Evolution of ϵ_i and charge accumulated in the layer during the voltage sweep.

OPERANDO SPECTROSCOPIC ELLIPSOMETRY— FAST TRANSIENT CHARACTERIZATION

- Sampling rate can be reduced to some 100 ms
- The tracking of the optical constants gives information on the lithiation of the layer
- The diffusion coefficient of the material can be obtained

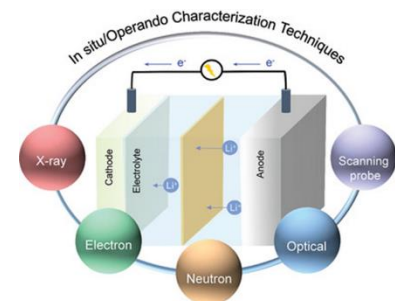
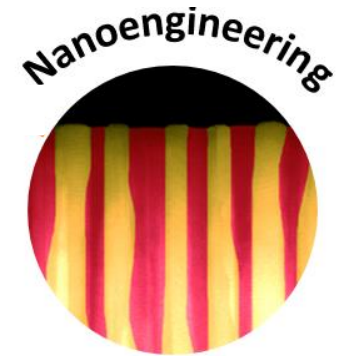
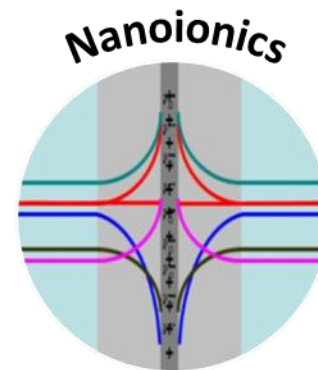


ϵ_1 variation during a sudden potential step from 350 to 1050 mV vs Ag/AgCl (left) and evolution of ϵ_1 at 2.8 eV during this voltage step. The red line corresponds to the normalized current values over time arising from the insertion of lithium in a cylindrical grain obtained from a FDM model. The modeled system is represented in the sketch figure of the inset.

CONCLUSIONS

TF- Solid State Ionics devices for energy:

- Revolution in the energy sector
- Thin Films enable this revolution
- New disciplines and phenomena
- Innovative devices
- New operando characterization techniques



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