CAM-IES kick off meeting

26 January 2017, Cambridge

Judith Driscoll, WP1 leader

WP1

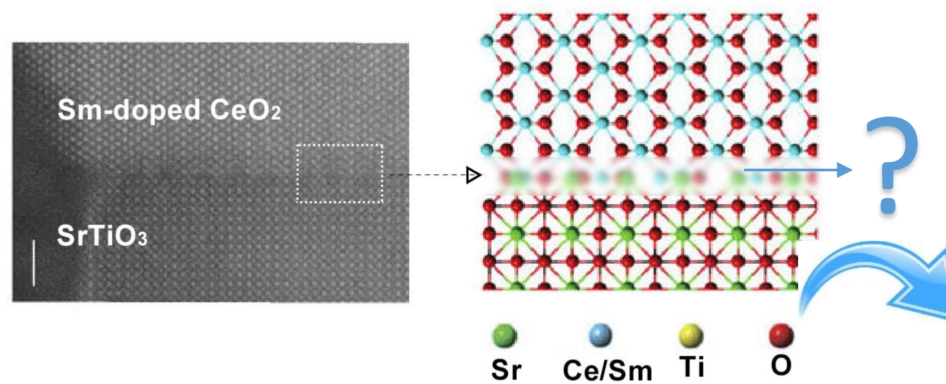
Better understand and improve solid electrolytes and electrolye/cathode *interfaces* for batteries, SOFC and gas separation membranes.

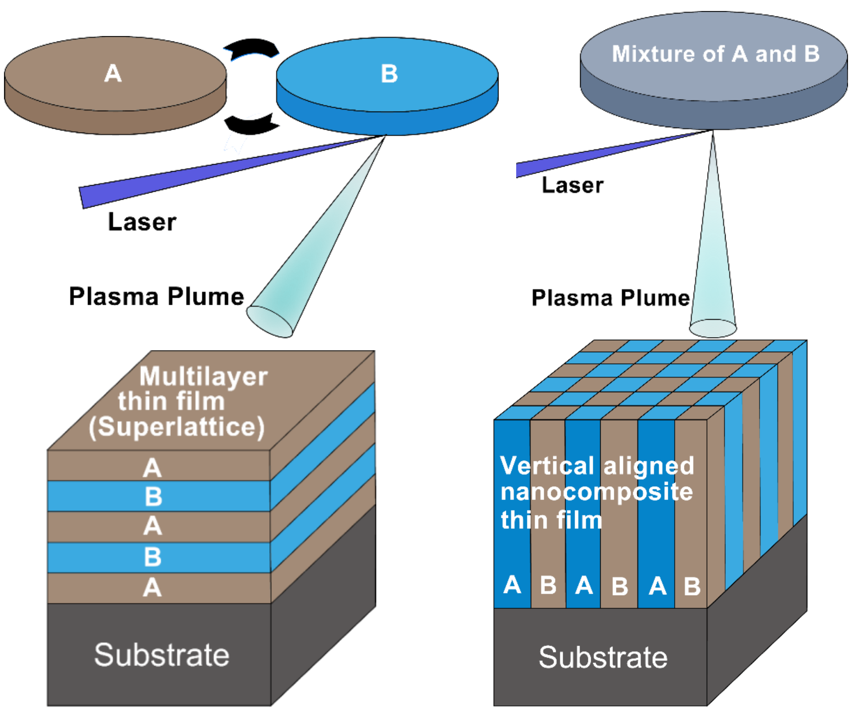
Fabricate and probe single crystal thin films by PLD

Mainly oxides (O^{2-} electrolytes first, then Li^{+} , beyond Li^{+}).

Epitaxial thin films: Perfect, high density, interfaces

The physical and chemical properties of interfaces deviate significantly from those of the bulk.



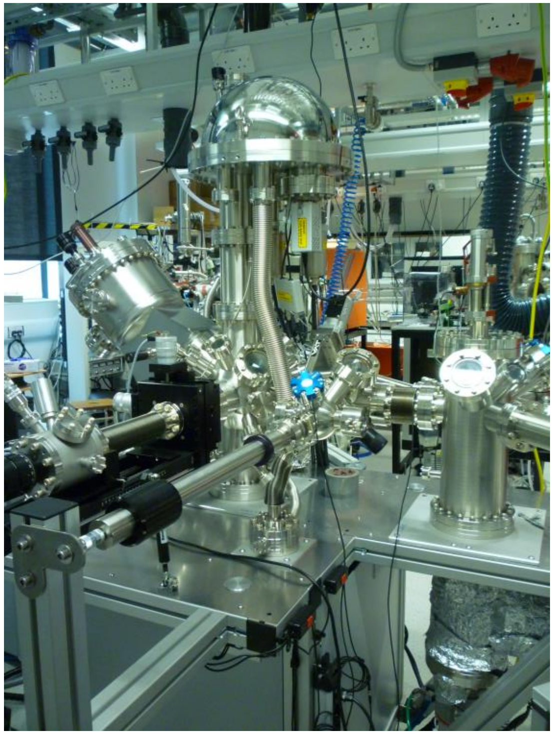


- What is the local structure of the interface?
- How does the interface affect the properties?

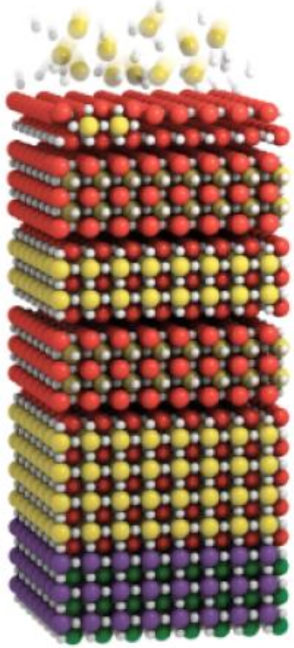
Special features of epitaxial nanocomposite films
High crystallinity and orientation
Size-tunable (few nm to ~ 50 nm)
New strain states possible
Surfaces stabilized
Tunable interfaces
New interfacial phenomena
Spatial ordering possible

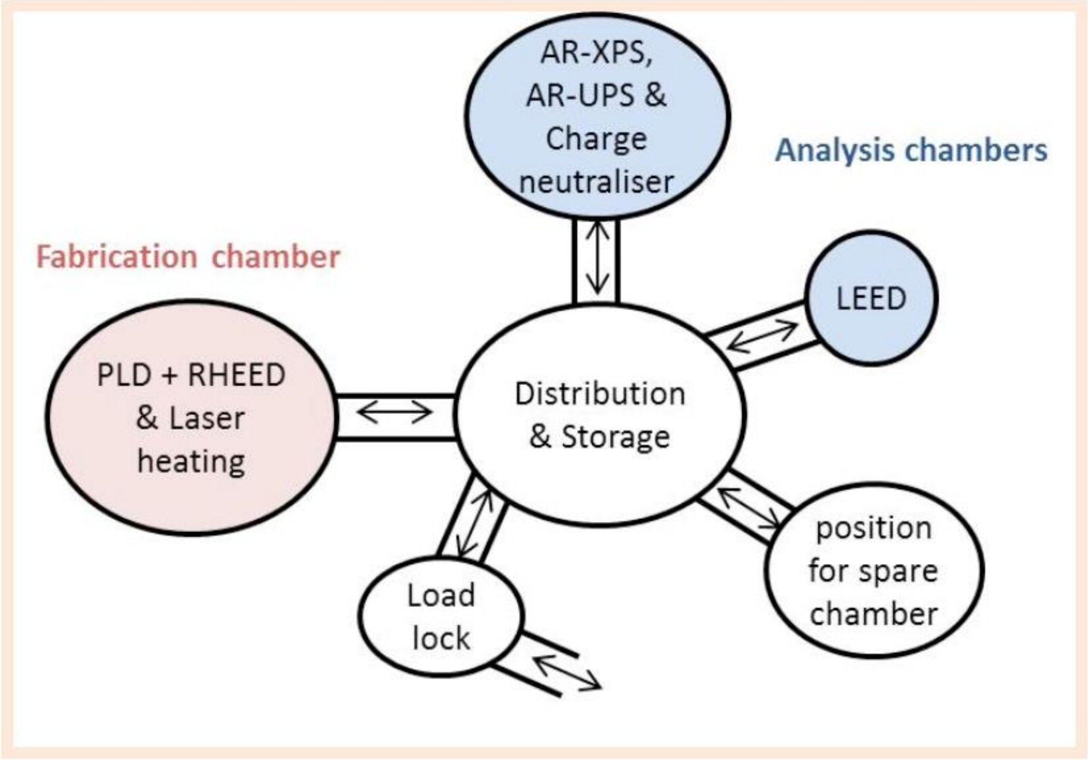
MacManus-Driscoll, J. L., A. Suwardi, and H. Wang. "Composite epitaxial thin films: A new platform for tuning, probing, and exploiting mesoscale oxides." *MRS Bulletin* 40.11 (2015): 933-942
Cho, Seungho, et al. "Self-assembled oxide films with tailored nanoscale ionic and electronic channels for controlled resistive switching." *Nature communications* 7 (2016).

Advanced pulsed laser deposition used to grow very high quality epitaxial films



Build up atomic layer by layer

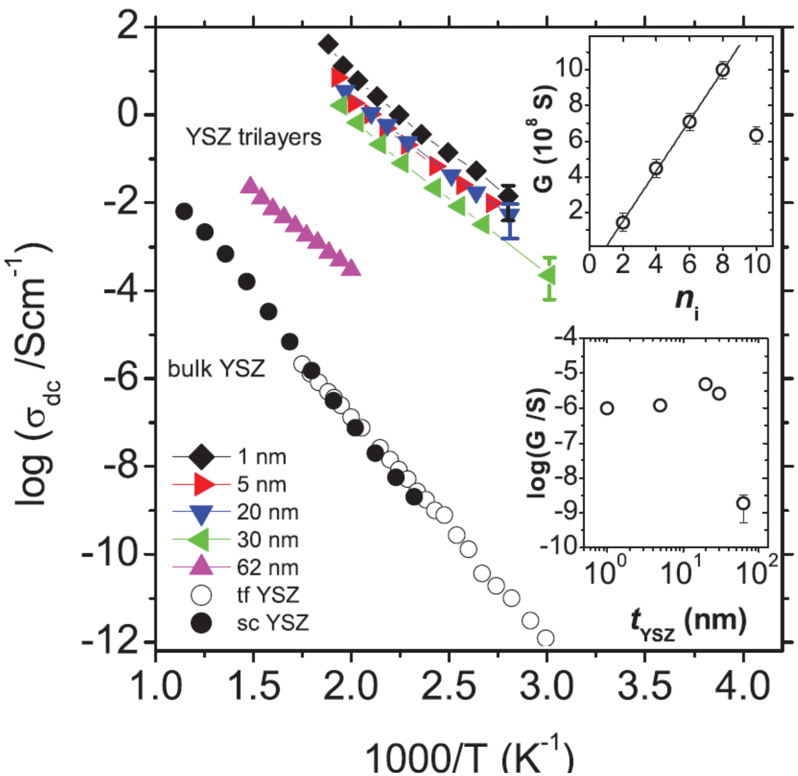


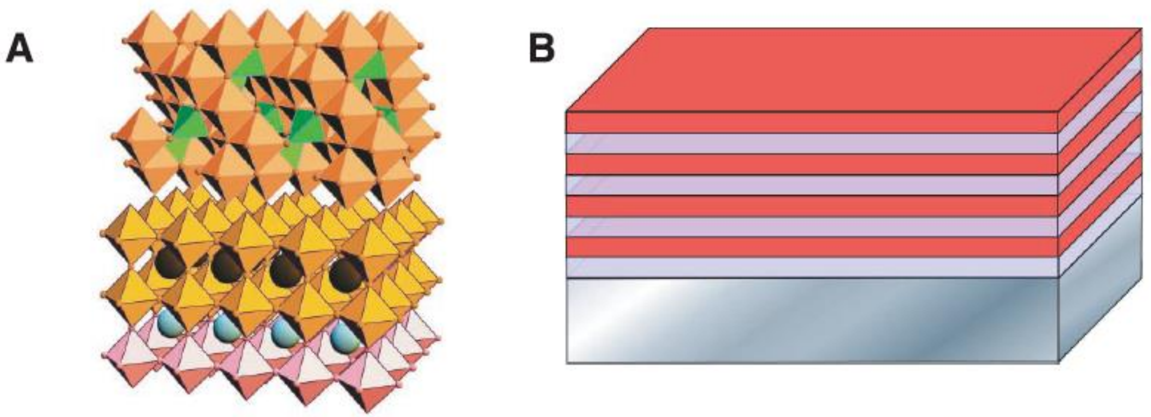


Enhanced oxygen ion conduction in lateral heterostructures

Colossal ionic conductivity at YSZ/$SrTiO_3$ interfaces

– J. Garcia-Barriocanal, J. Santamaria* *et al.*, Science **321**, 676 (2008).

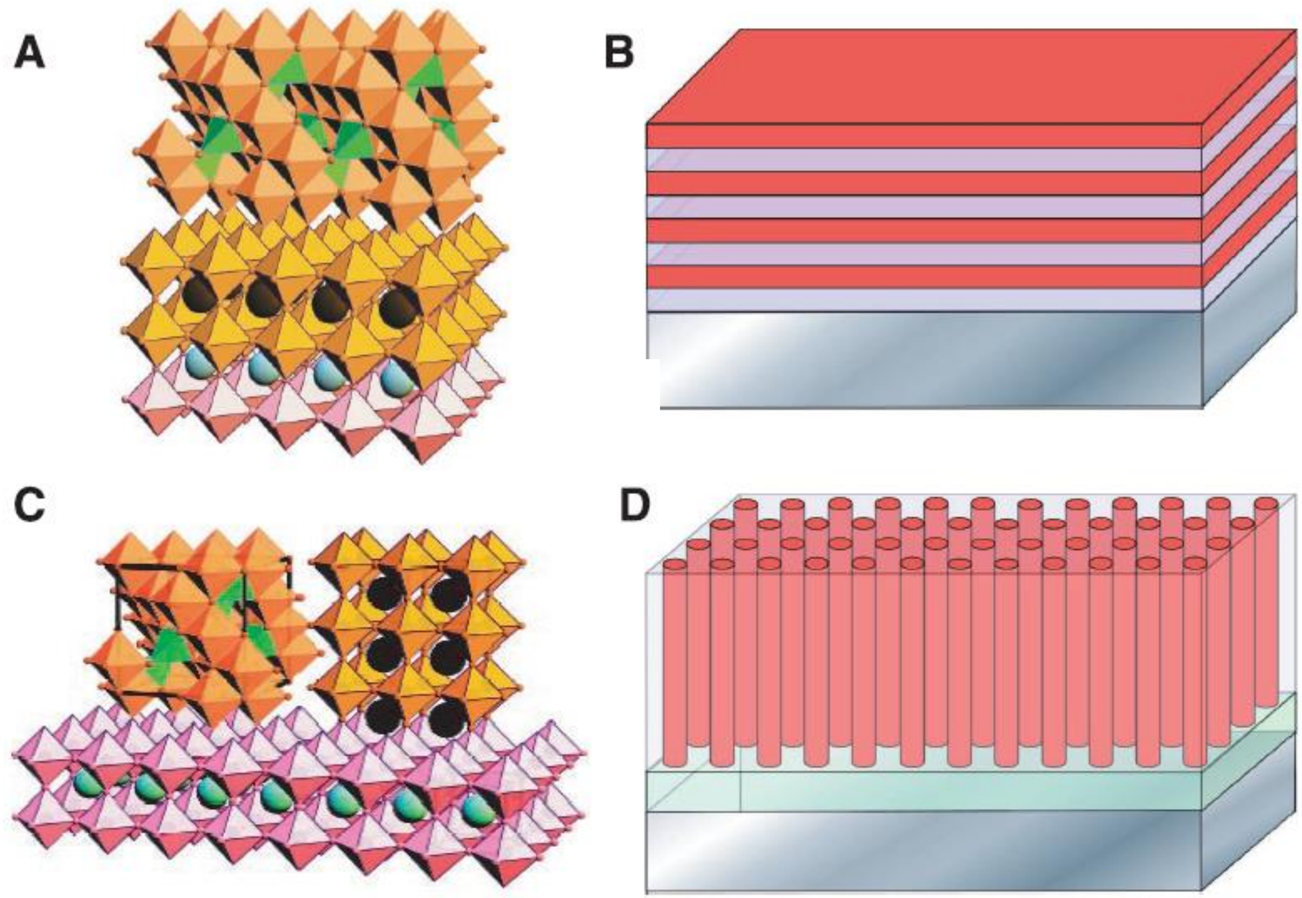




Lateral versus vertical interfaced thin films

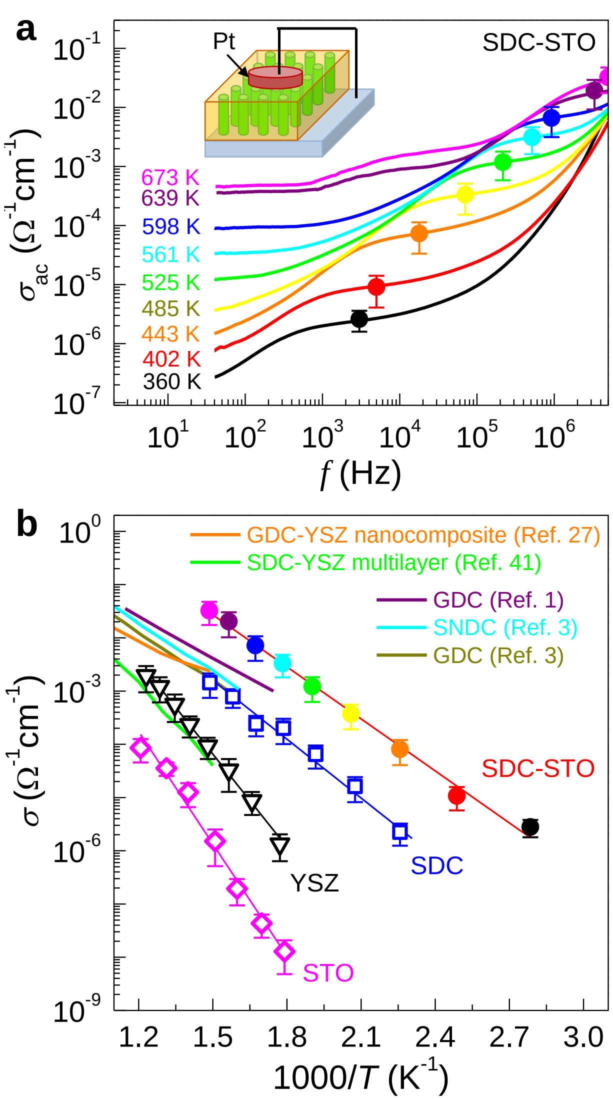
Lateral heterostructures

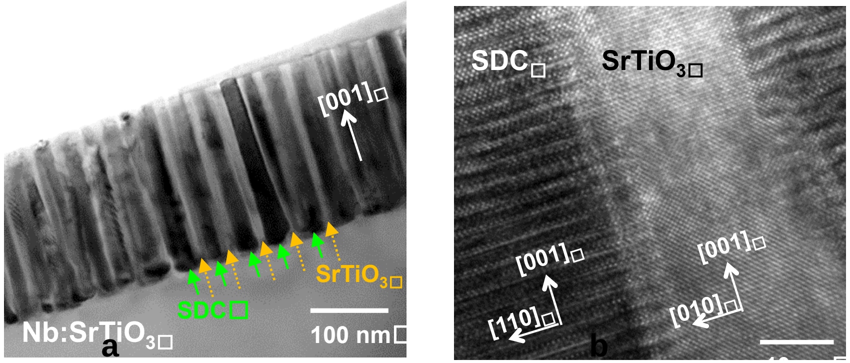
Vertical heterostructures

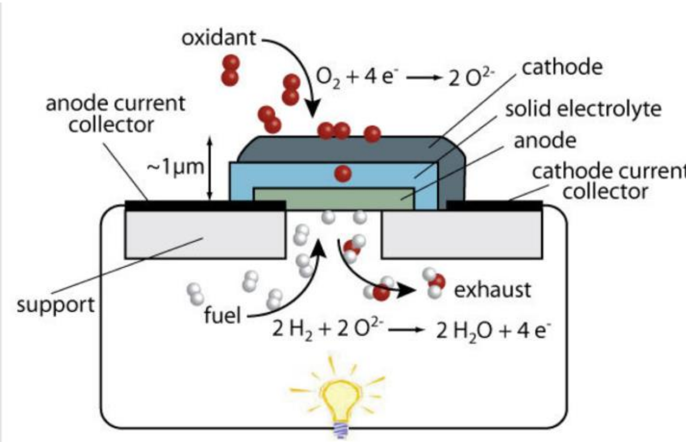


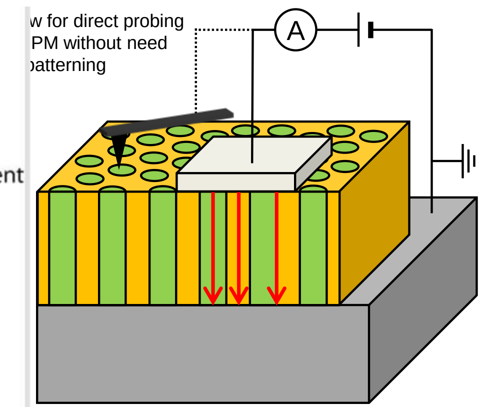
Very high ionic conductivity in Sm-doped CeO_2 (SDC)

σ~0.1 $\Omega^{-1}cm^{-1}$ at 350°C









Micro-SOFC

Thin film battery

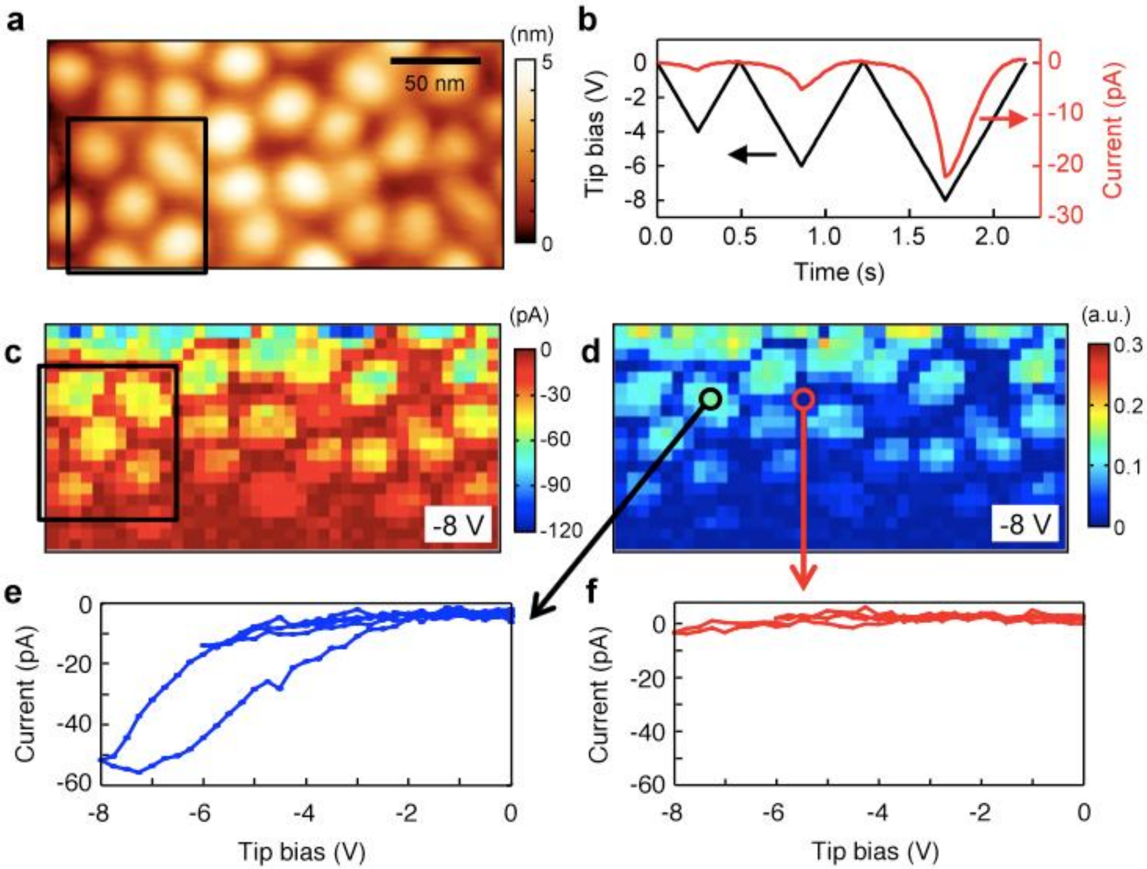
Nat. Comm. 2015; 6:8588.

Adv. Fun. Mat. 2015;25:4328.

Nano Letters 2015;15;7362.

Electrochemical strain microscopy (ESM) and (FORC-IV) curves show very high ionic conduction in the nanopillars

110° C



FORC-IV loop area allows estimation of the electrochemical activity.

SDC columns show high electrochemical activity
(Large loop area).

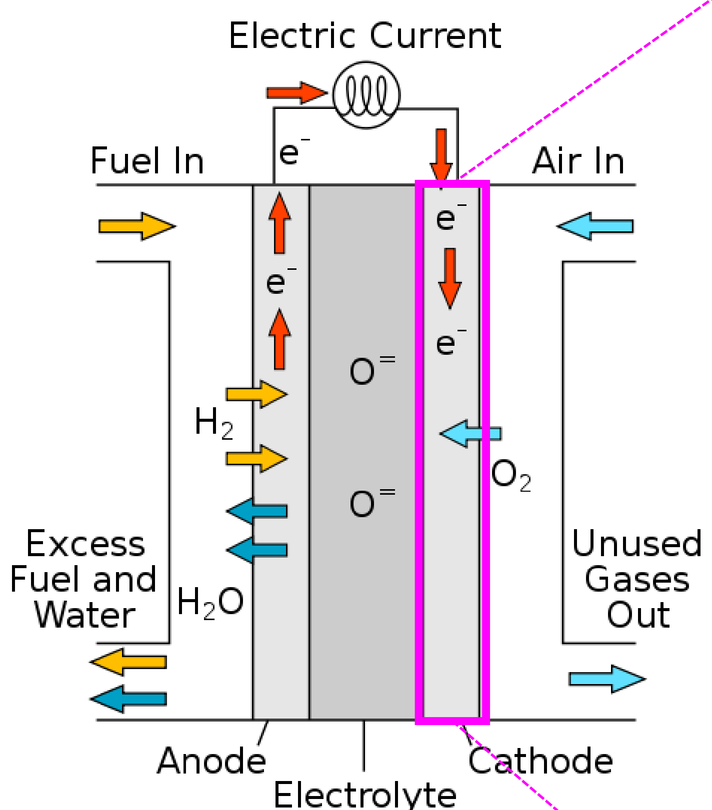
Cores of SDC columns has a larger relative loop area compared with the outskirts of column.

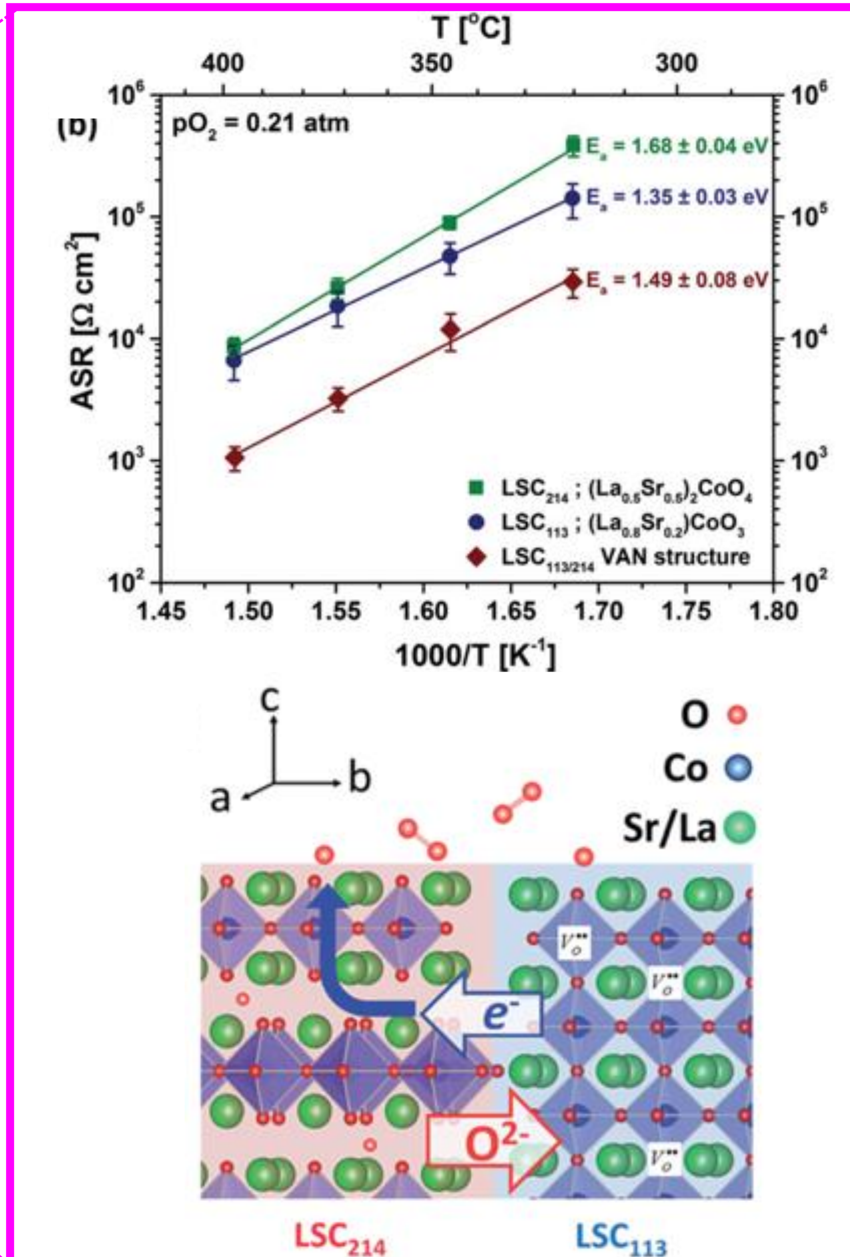
Ionic conduction values match
with macroscopic measurements.

S.M. Yang and S. Kalinin, ORNL

Very high crystalline quality, not space charge effects

Enhanced O_2 reduction reaction on a cathode surface





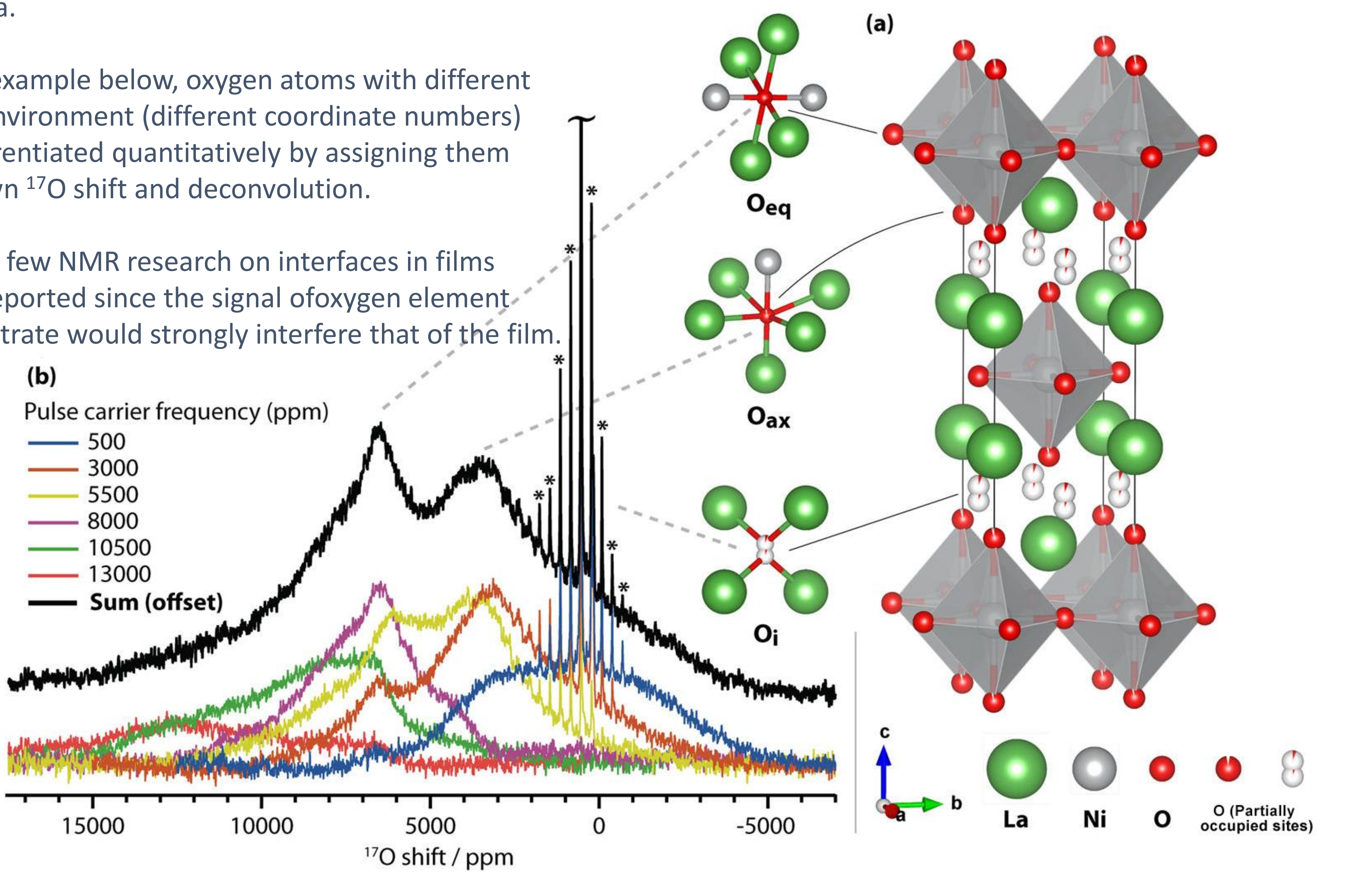
W. Ma, B. Yildiz* *et al.*, J. Mater. Chem. A **3,** 207 (2015).

Solid-state NMR as a probe of interfacial phenomena

- Solid-state NMR spectroscopic techniques help to clarify the local structure and dynamics of interfacial phenomena.

- In the example below, oxygen atoms with different chemical environment (different coordinate numbers) were differentiated quantitatively by assigning them to their own ^{17}O shift and deconvolution.

- To date few NMR research on interfaces in films has been reported since the signal ofoxygen element in the substrate would strongly interfere that of the film.

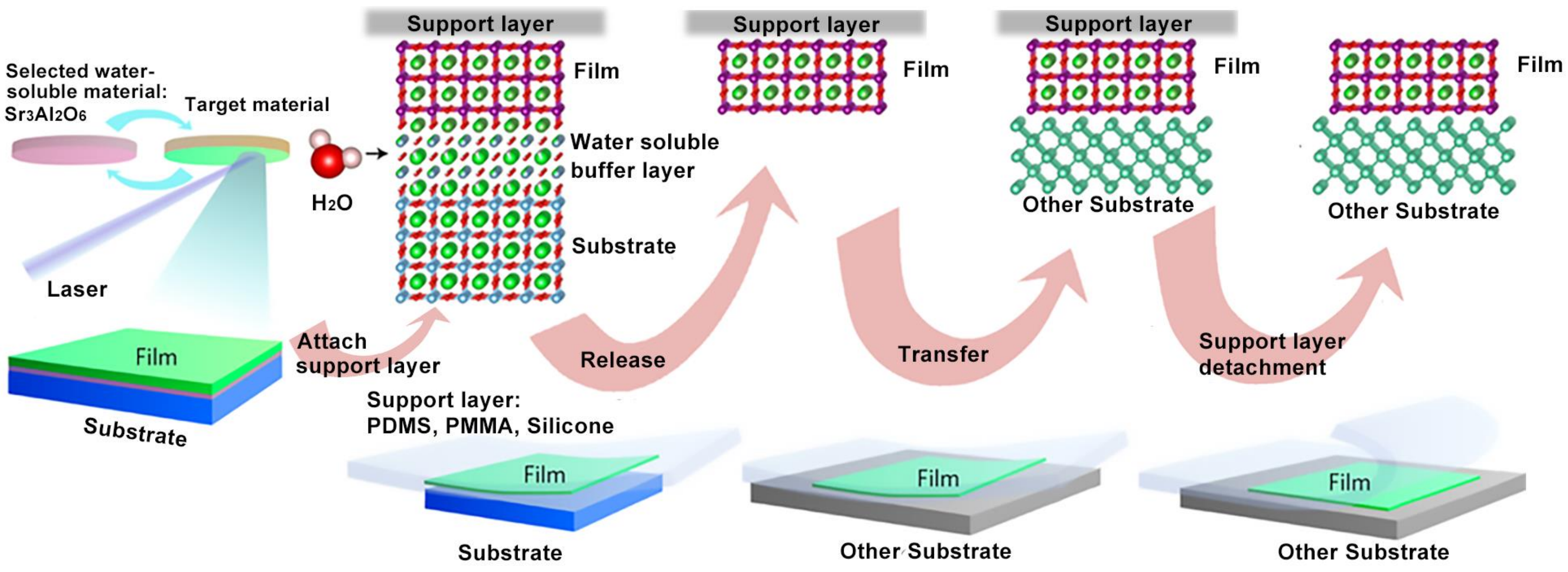


Halat, David M., et al. "Probing Oxide-Ion Mobility in the Mixed Ionic–Electronic Conductor La2NiO4+ δ by Solid-State 17O MAS NMR Spectroscopy." *J. Am. Chem. Soc.* 138.36 (2016): 11958-11969.

The 2D membrane transfer process

- Freestanding perovskite membranes could be obtained by selectively water etching. The key point is the epitaxial growth of water-soluble Sr3Al2O6 on perovskite substrate, followed by *in situ* growth of films and heterostructures.

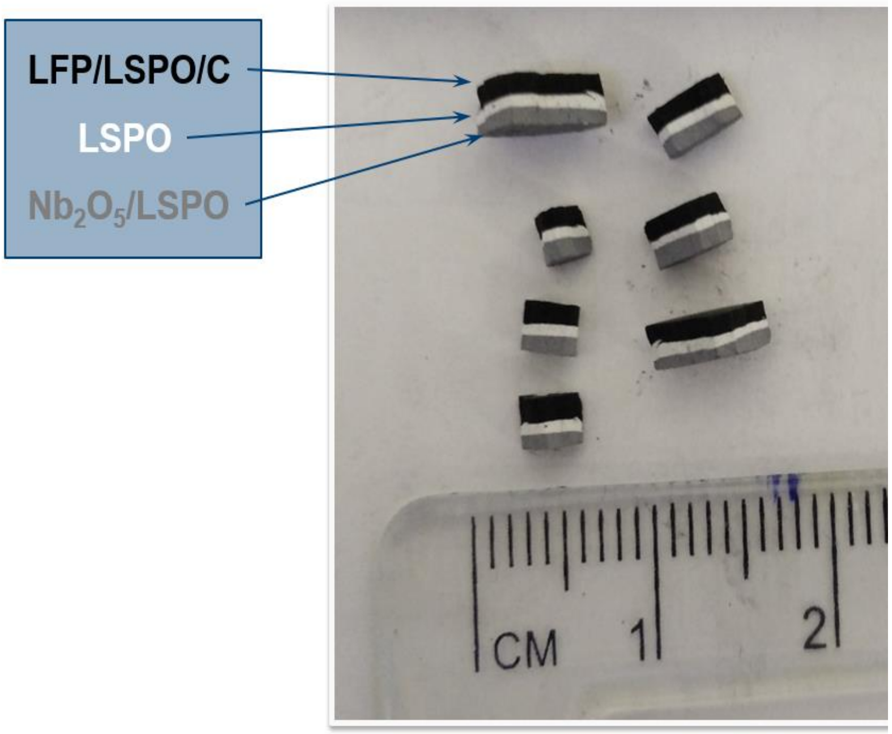
- The freestanding film could be transferred to arbitrary substrates, which allows us to study the film independently. The high resolution solid-state NMR characterization would also be allowable.



Lu, Di, et al. "Synthesis of freestanding single-crystal perovskite films and heterostructures by etching of sacrificial water-soluble layers." *Nature Materials* (2016).

From ideal systems to real systems

Spark Plasma Sintering



- High density composite pellets prepared by Spark Plasma Sinter (SPS) furnace
- Control of particle size, shape, and morphology
    - Graded composites to optimise *electrochemical performance*
    - Uniform composites for ease of *characterisation*

All solid-state battteries prepared by Spark Plasma Synthesis (SPS)

Relevant to WP2: Nanocomposite films readily made into nanoporous membranes

~2 nm stable walls in variable thickness films