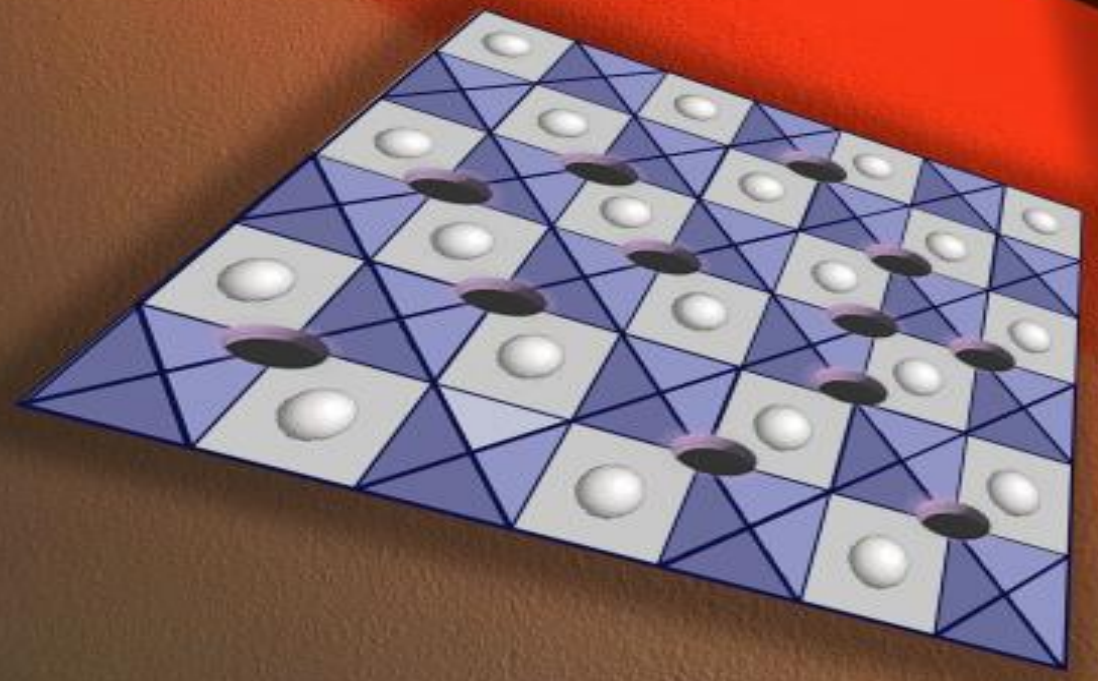
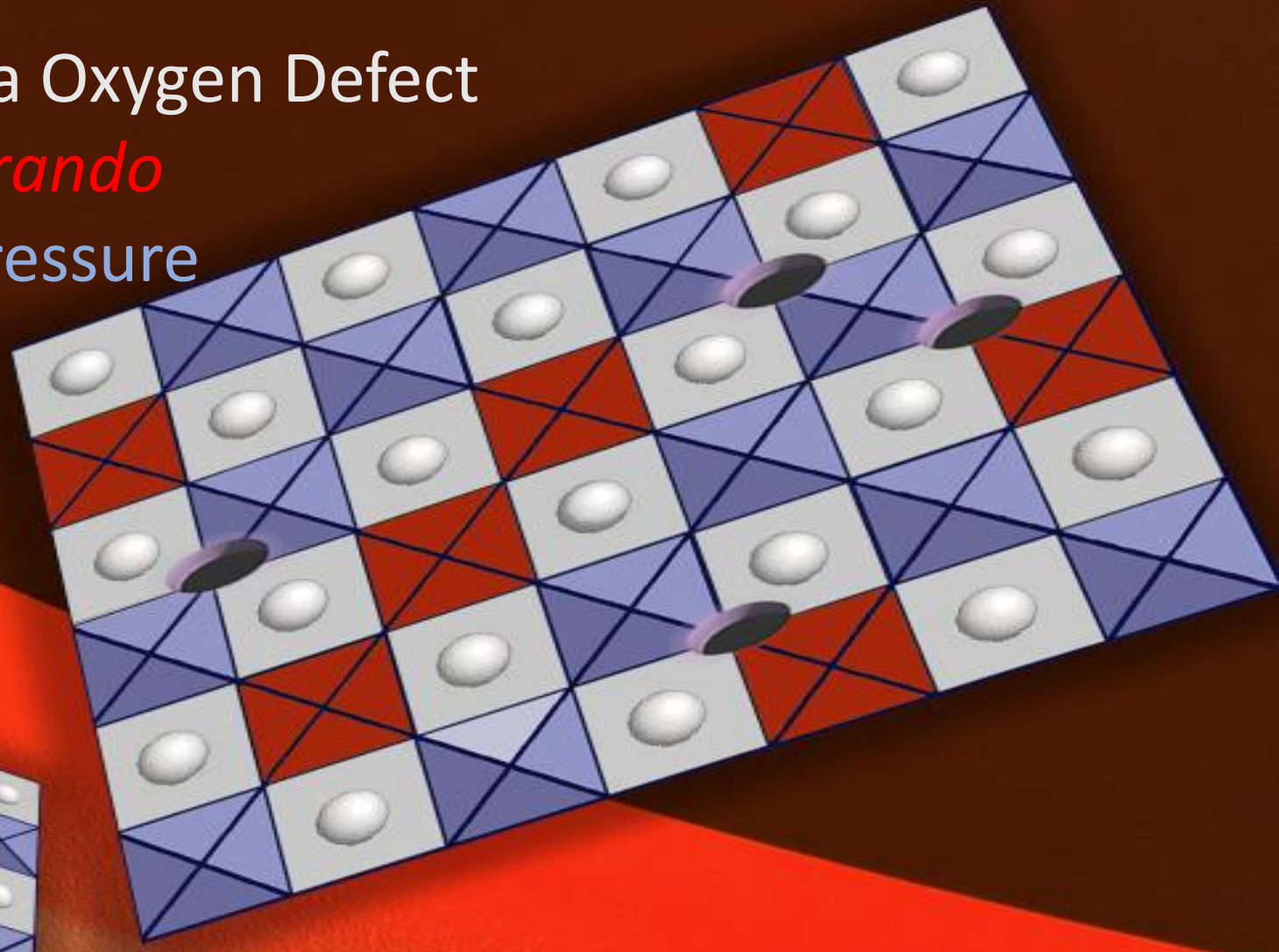
Designing Perovskite Oxides via Oxygen Defect Engineering: *in situ* and *in operando* Studies Enabled by Ambient Pressure X-ray Spectroscopic Tools



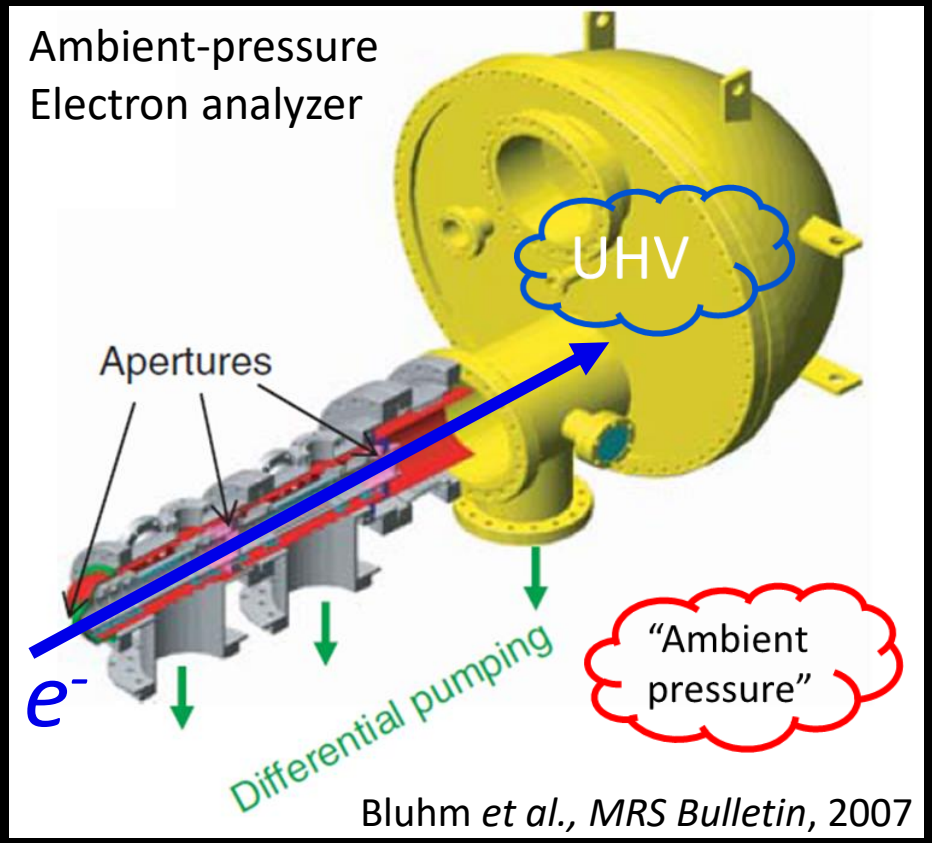


BNL-MIT Meeting

Qiyang Lu, Prof. Bilge Yildiz
DMSE, MIT

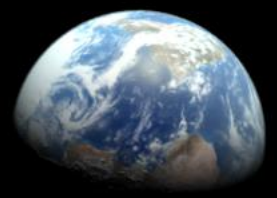
July 25th, 2017

Picture source: NASA



Bluhm *et al.*, *MRS Bulletin*, 2007

"Ambient pressure" ~1 Torr

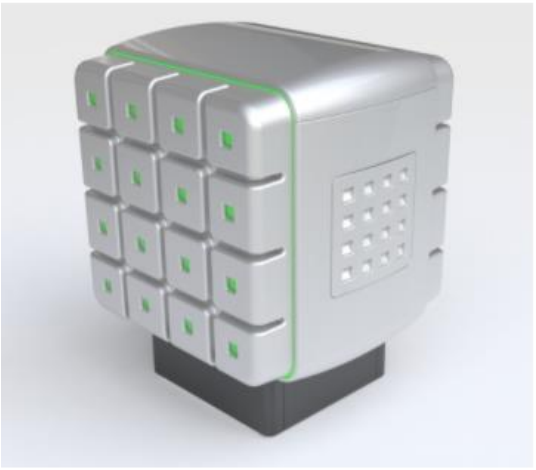


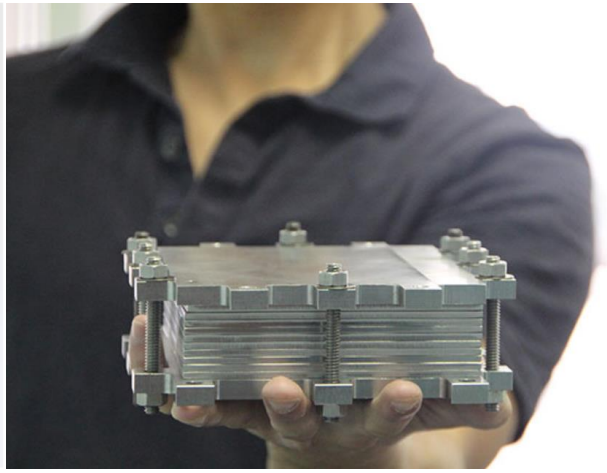
A pressure gap of
~9 order of magnitude
$k_B T ln(p/p_0) \geq 0.3$ eV

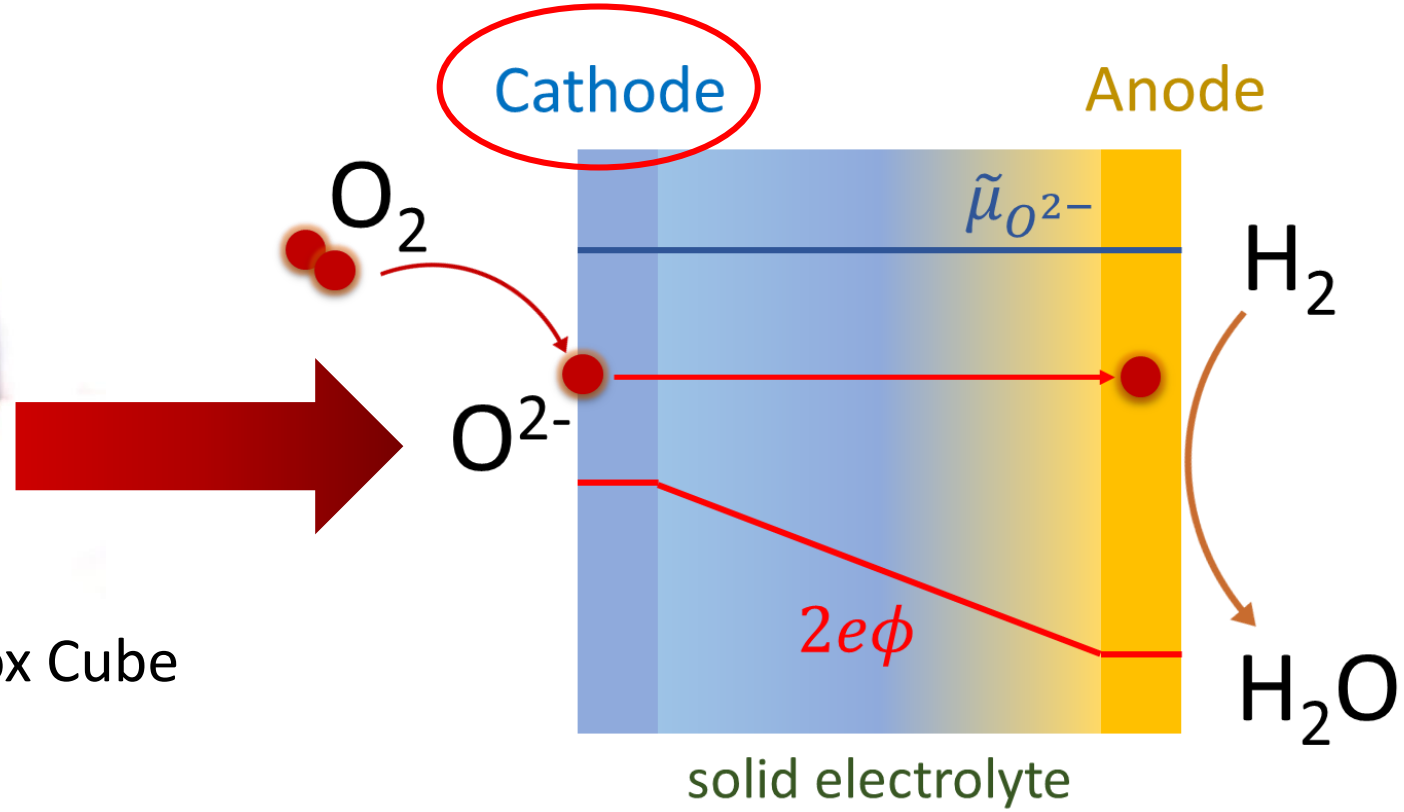
What is going on over there?

Conventional surface science techniques
→ Surface chemical information
Ultra-high vacuum (UHV), <10^{-9} Torr

Surface chemistry of SOFC cathodes studied by using ambient pressure (AP) spectroscopic tools



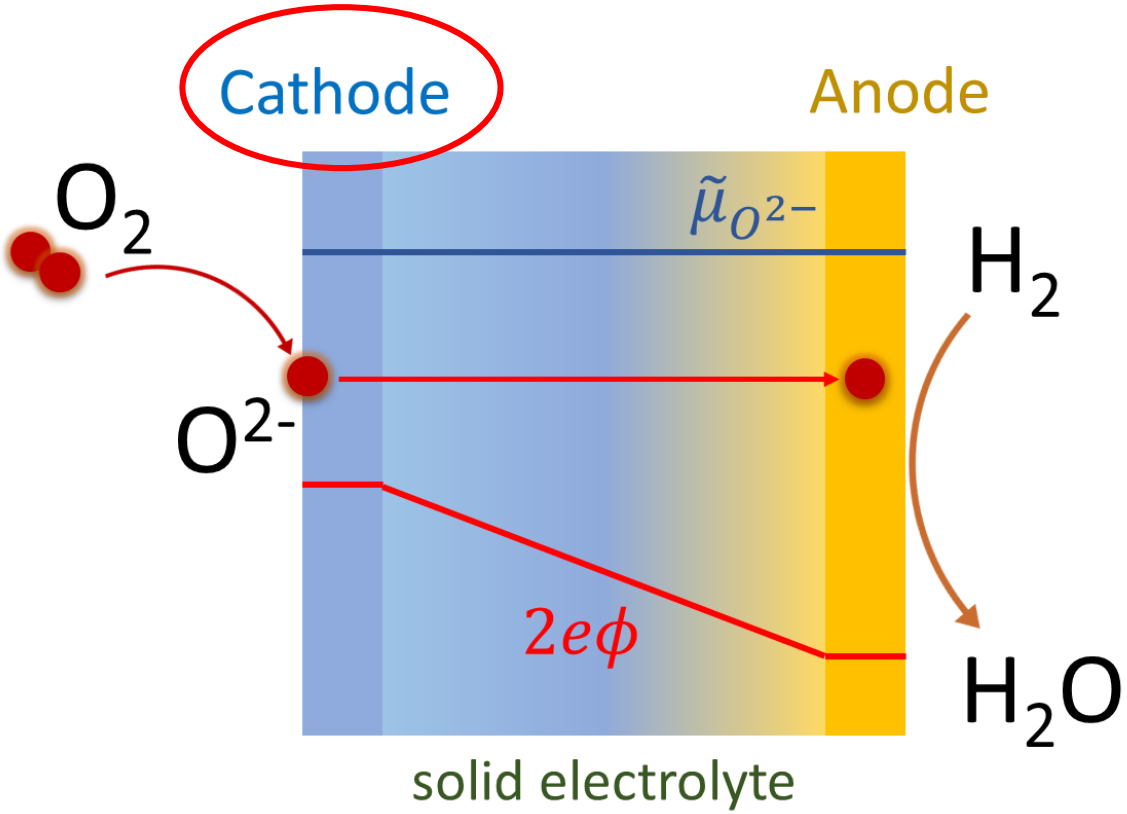


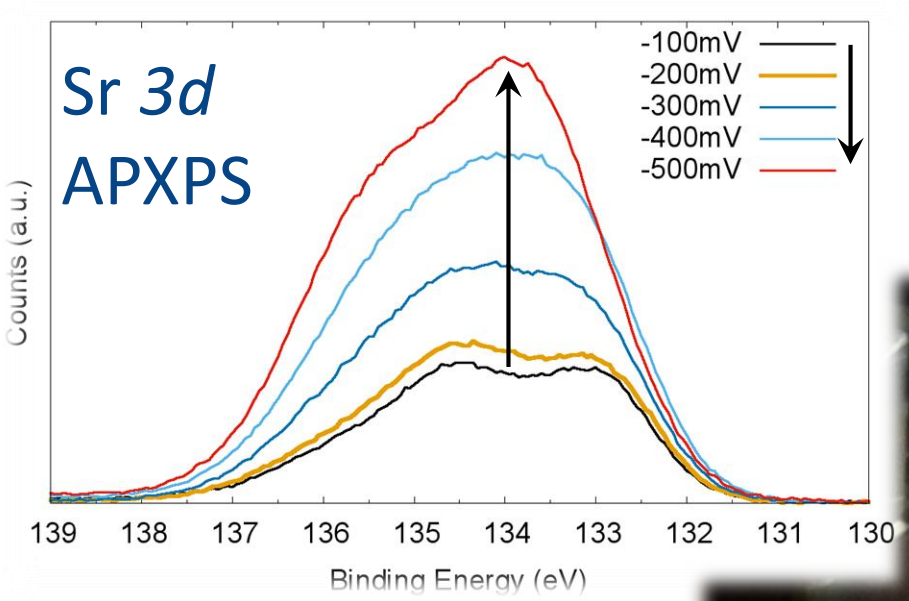


25 kW Solid Oxide Fuel Cell (SOFC) Redox Cube System (Redox Power System, MD)

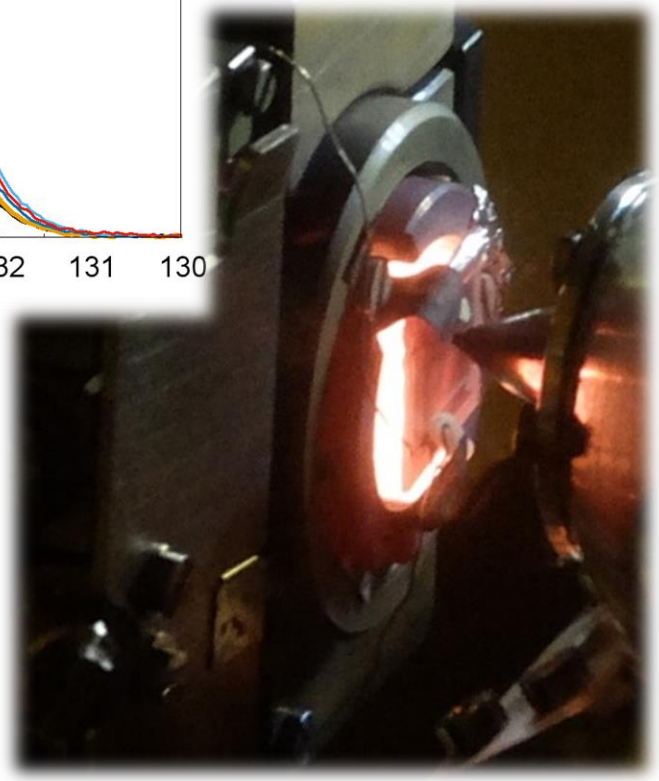
- ✓ High efficiency
- ✓ Fuel flexibility
- ✗ High temperature (>500 °C) & gas environment

Fundamental understanding on surface chemistry of functional oxides at elevated temperature in O_2 atmosphere





650 °C
100 mTorr O_2

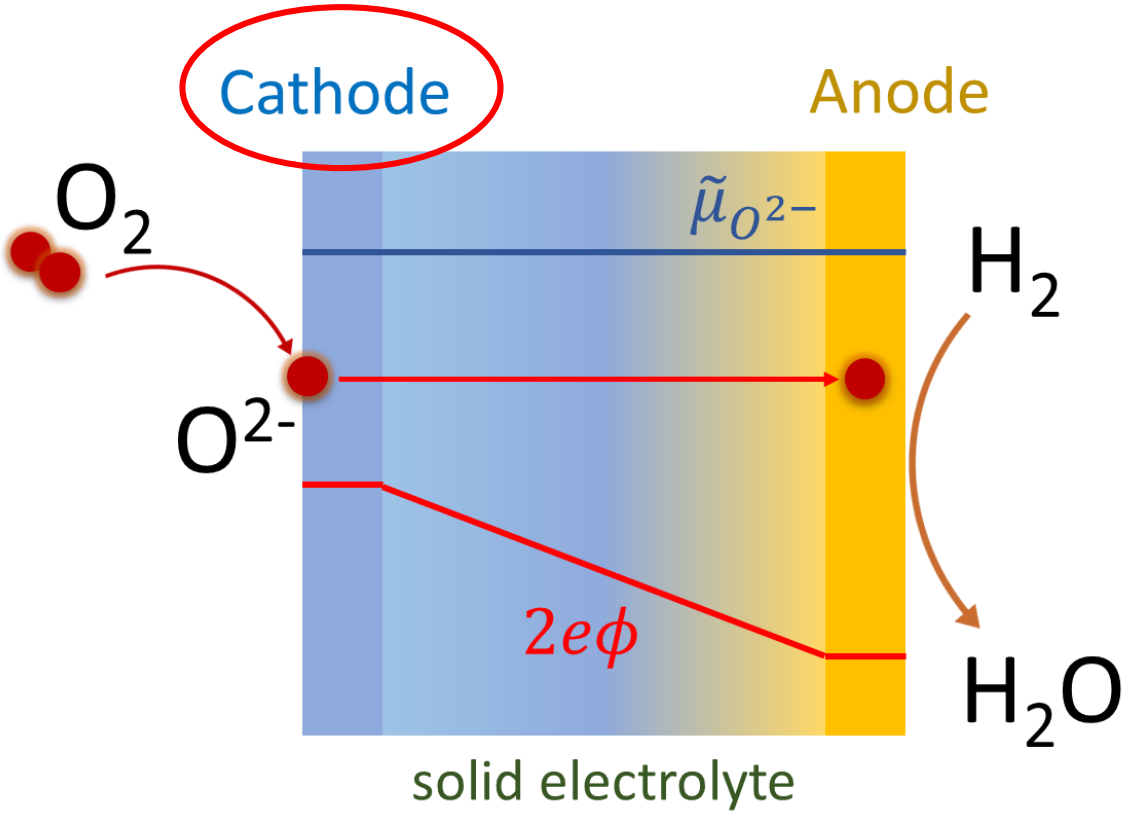


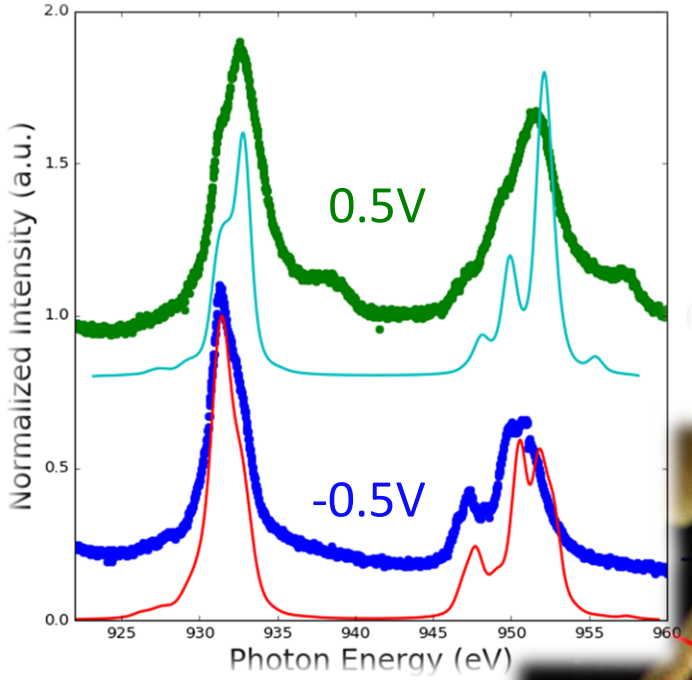
Surface chemistry of $(La,Sr)MnO_3$ Cathodes

11.0.2, ALS

TEMPO, SOLEIL

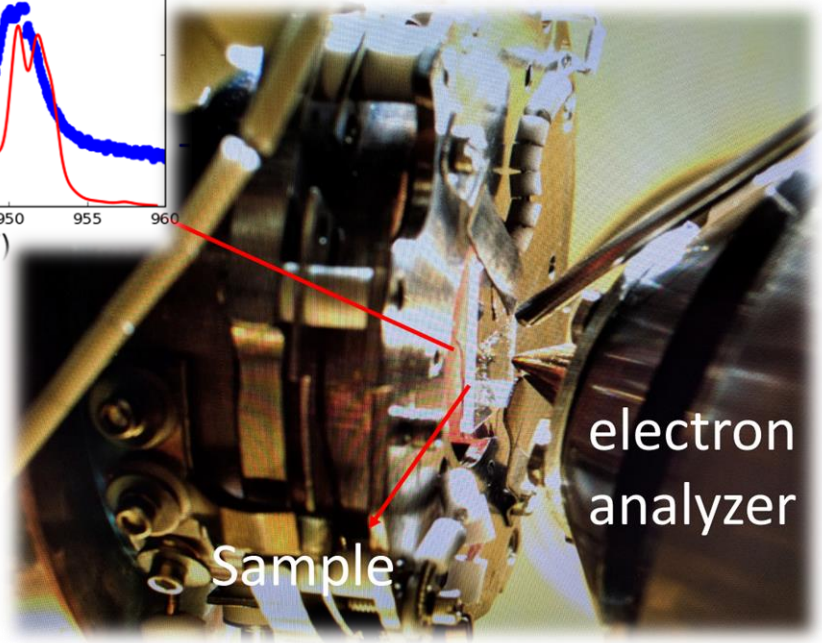
Fundamental understanding on surface chemistry of functional oxides at elevated temperature in O_2 atmosphere





450 °C
200 mTorr O_2
-0.5 V ~ 0.5 V

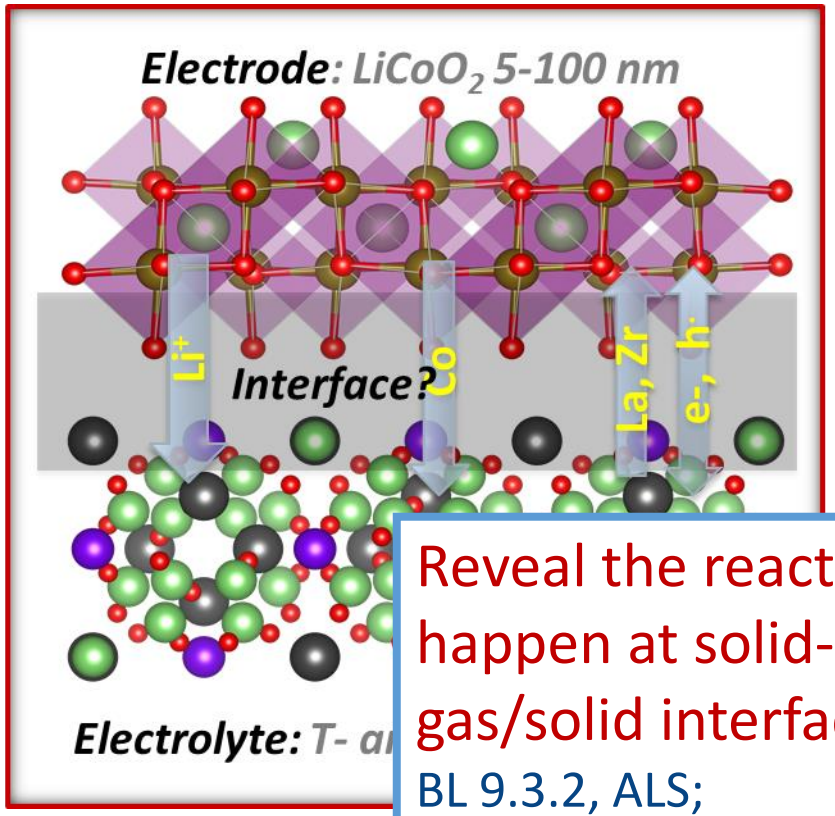
Surface defect chemistry of $(Pr,Ce)O_{2-\delta}$



CSX-2, NSLS-II

Improve efficiency and performance of energy conversion and storage devices by obtaining insights from AP-XPS/XAS

All-solid Li-ion batteries



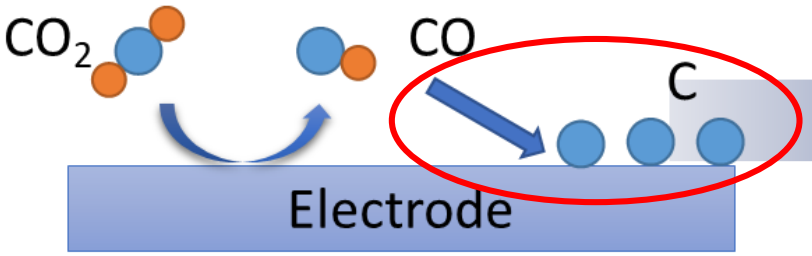
Reveal the reactions happen at solid-gas/solid interfaces

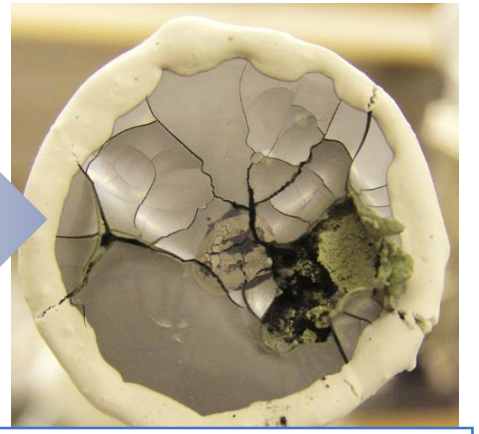
BL 9.3.2, ALS;
CSX-2, NSLS-II (IO-XAS);
Hard X-ray PES: APS

$CO_2 \rightarrow CO + O_2$: oxygen production on Mars

Investigate coking mechanism on CeO_2 based catalysts

BL 9.3.2, ALS;
CSX-2, NSLS-II





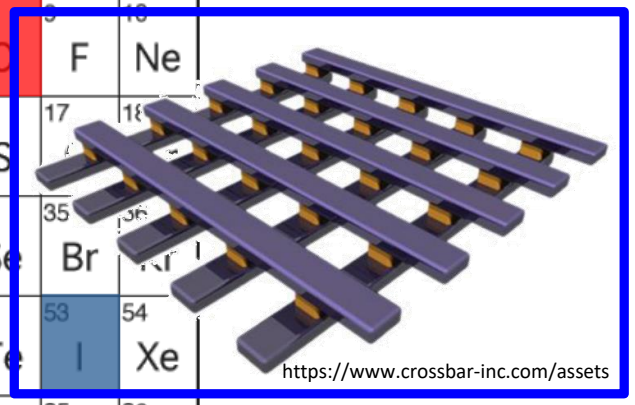
Coking induced fracture

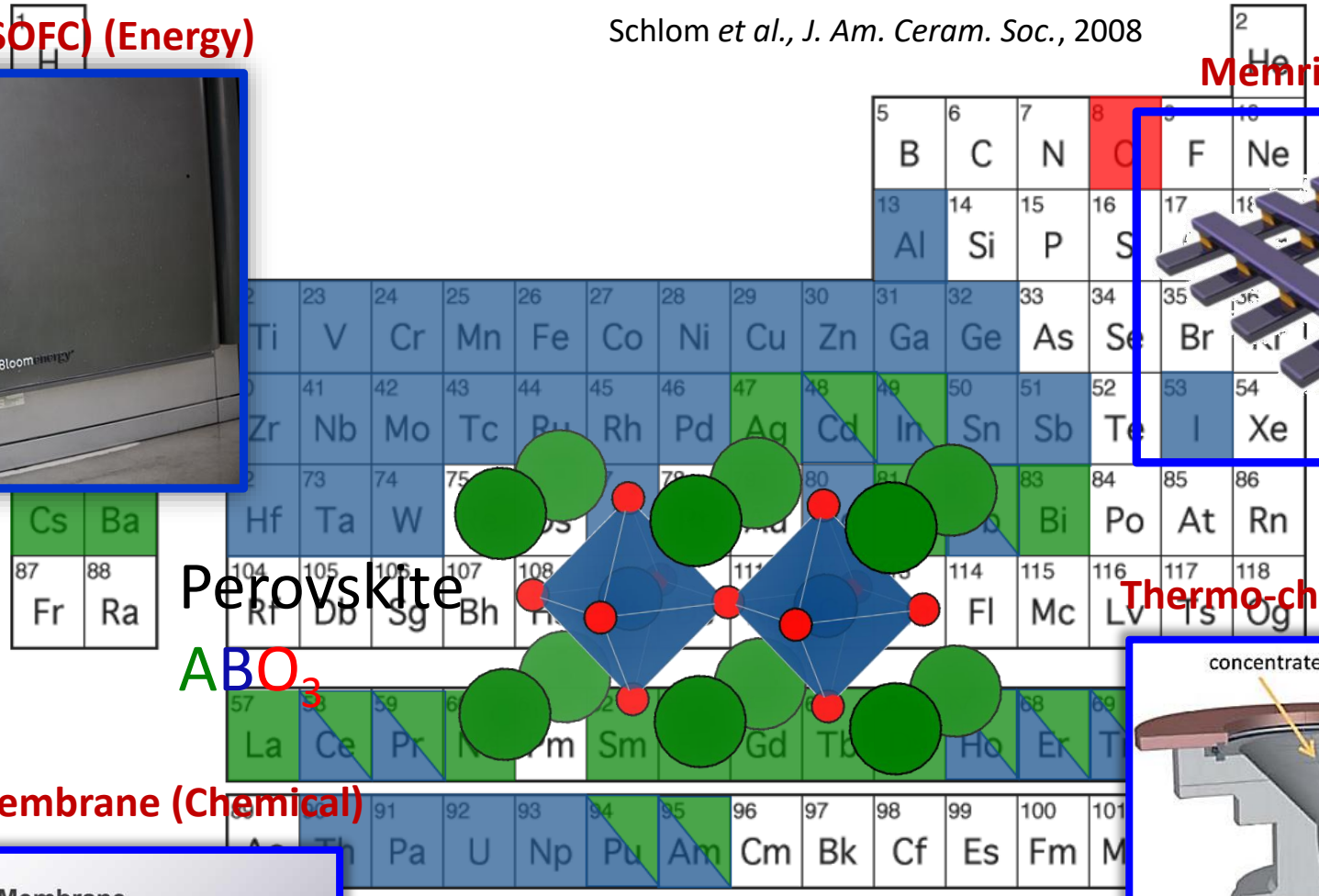
BOSCH
Invented for life

Schlom *et al., J. Am. Ceram. Soc.*, 2008

Solid oxide fuel cell (SOFC) (Energy)

Memristors (Computing)

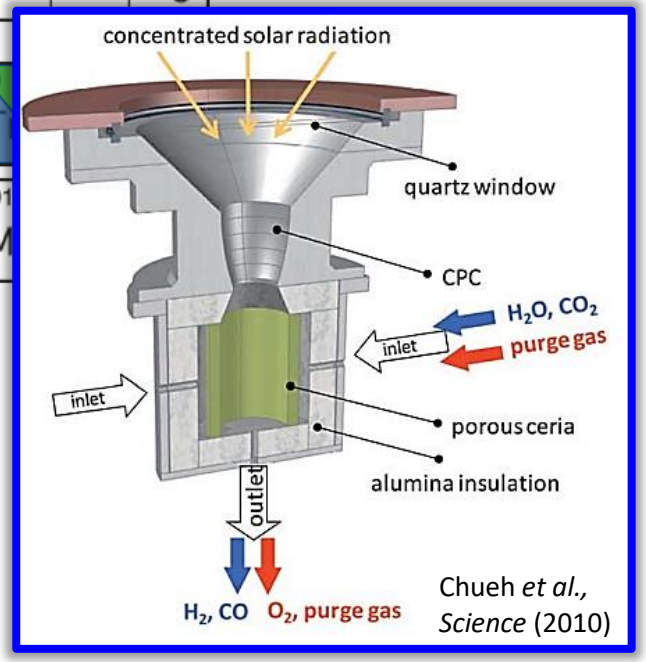




Perovskite

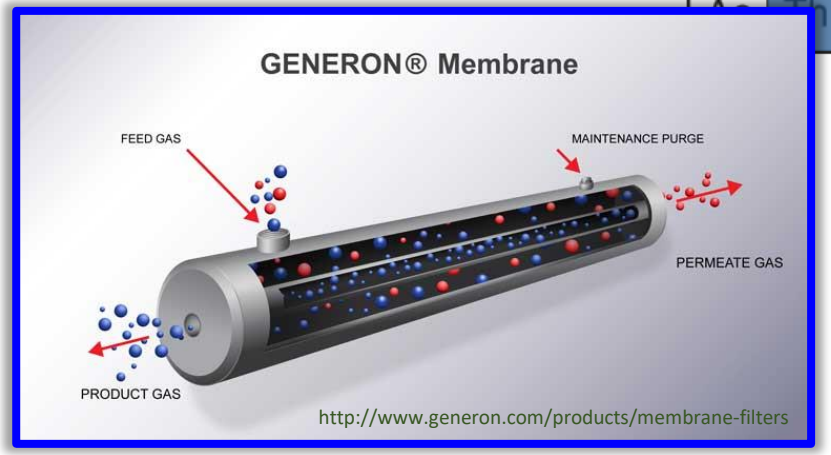
ABO_3

Thermo-chemical splitting (Fuel)

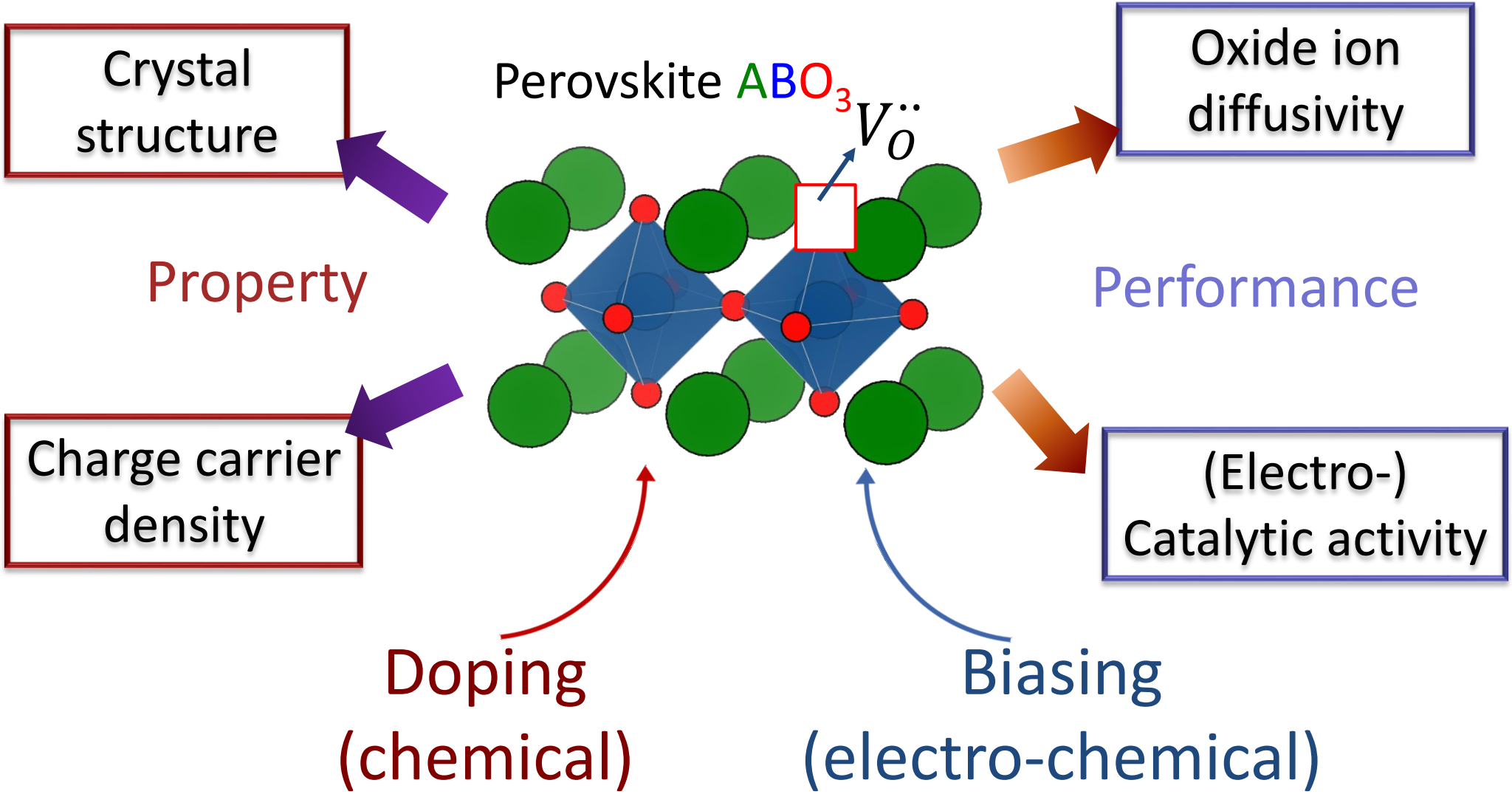


Chueh *et al.*, *Science* (2010)

Oxygen separation membrane (Chemical)



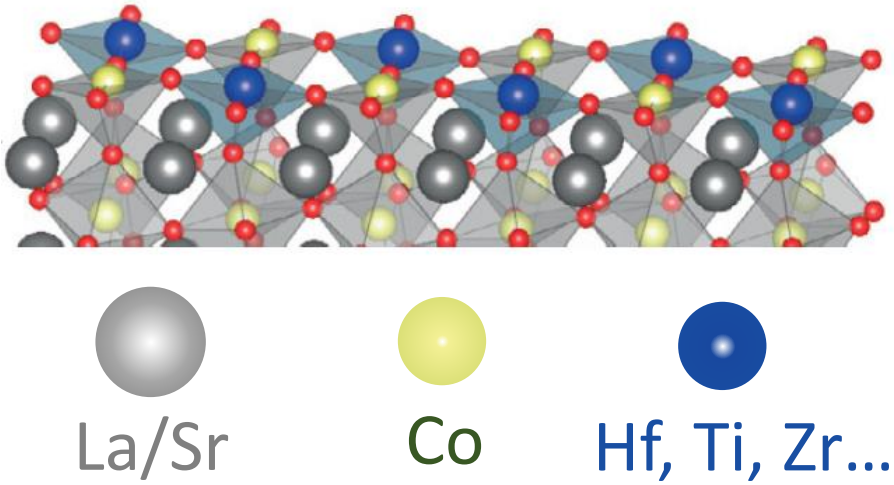
"Crystals are like people: it is the defects that make them interesting."



Different methods for tuning oxygen defect chemistry

Doping (chemical)

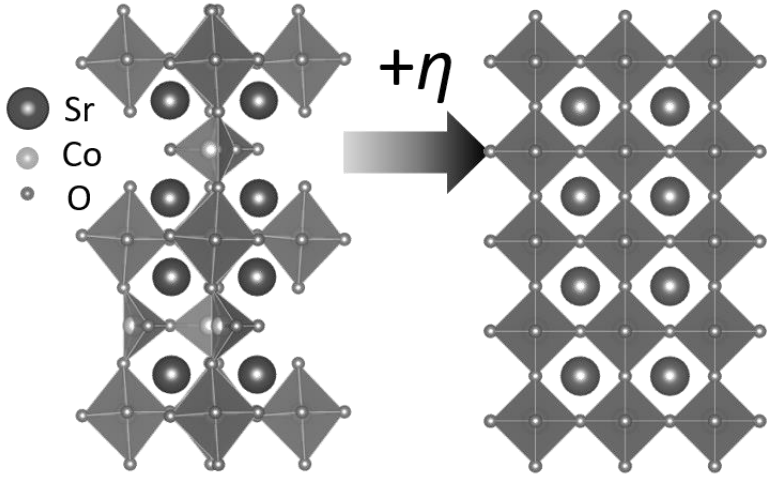
Surface-decorated $La_{0.8}Sr_{0.2}CoO_{3-\delta}$



N. Tsvetkov*, Q. Lu*, B. Yildiz *et al.*, *Nature Materials*, 2016

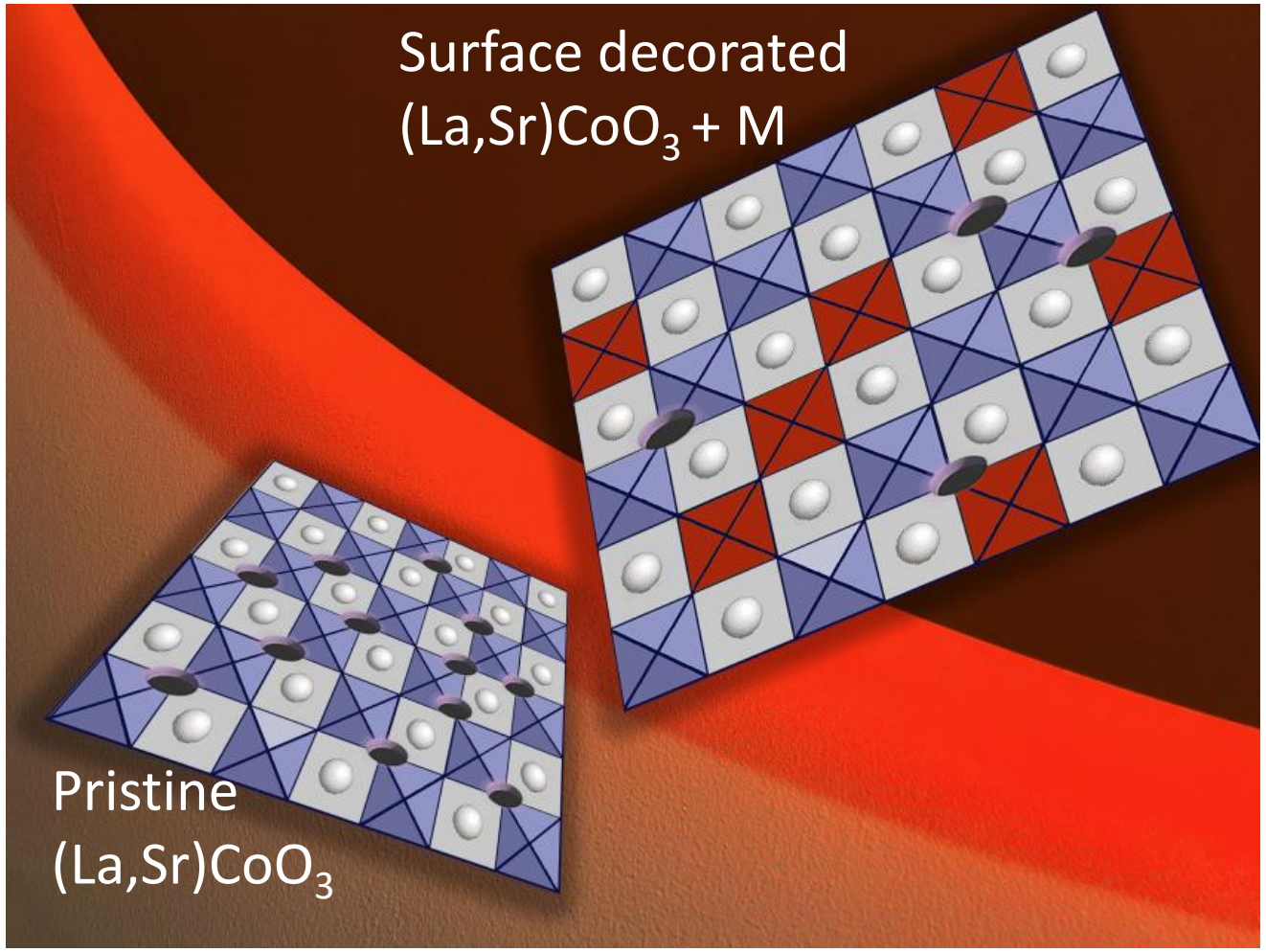
Biasing (electro-chemical)

Topotactic phase transition of $SrCoO_x$



Q. Lu and B. Yildiz, Nano Letters, 2016

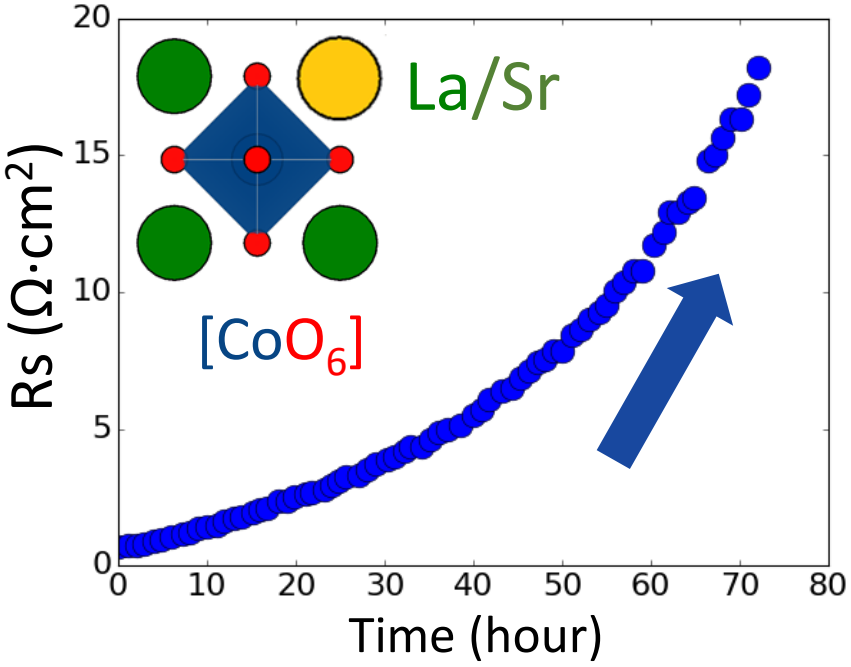
Case study I: surface doping of $(La,Sr)CoO_3$



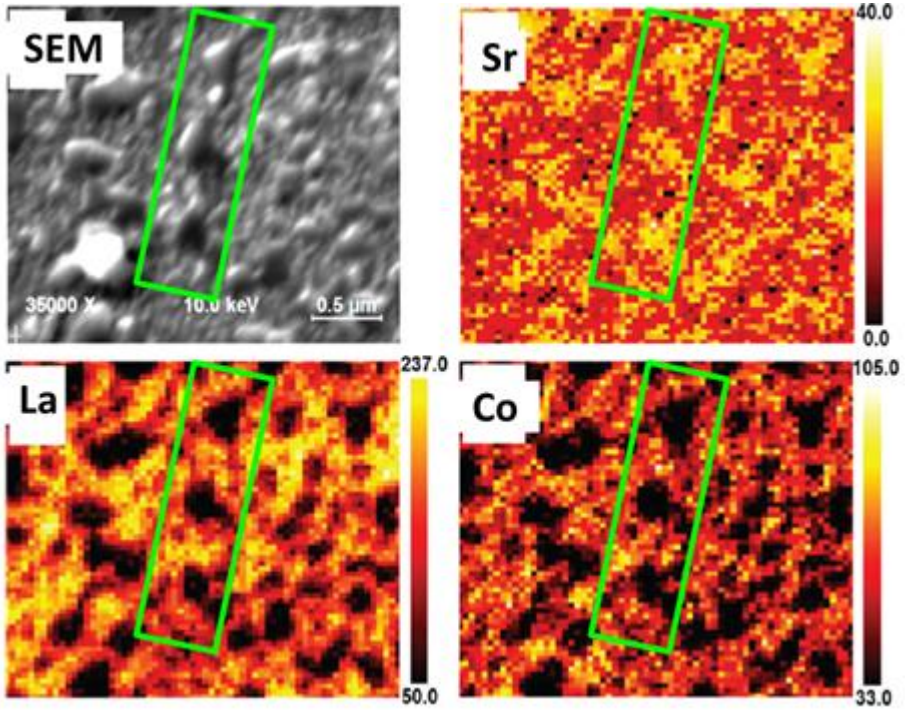
N. Tsvetkov*, Q. Lu*, L. Sun, E. Crumlin, B. Yildiz, *Nature Materials*, 2016

Degradation of electrochemical performance of (La,Sr)CoO_3 (LSC) as cathode of solid oxide fuel cells

650 °C, air



Rs = area-specific resistance (indicator of energy loss)

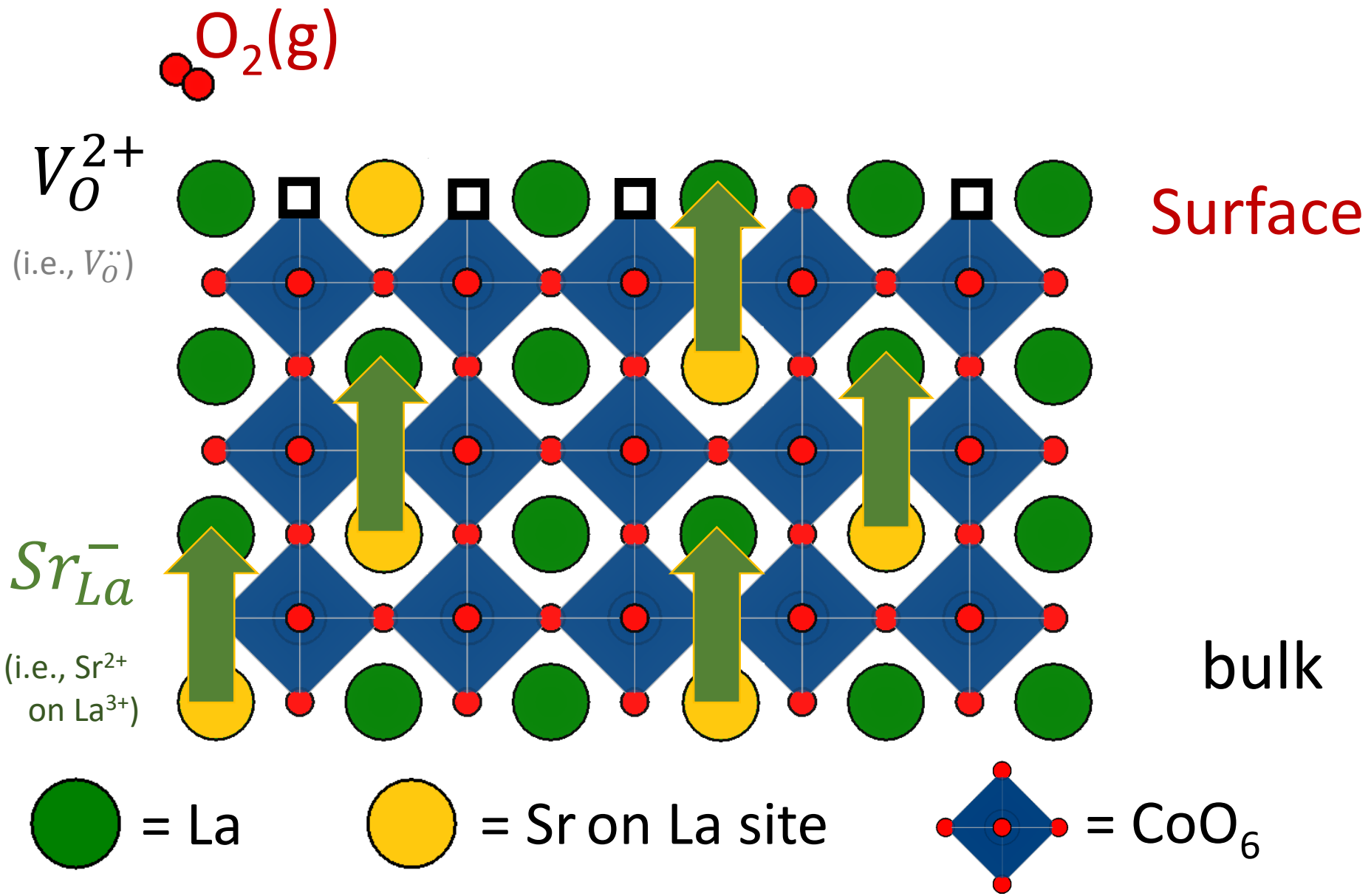


Auger electron microscopy images

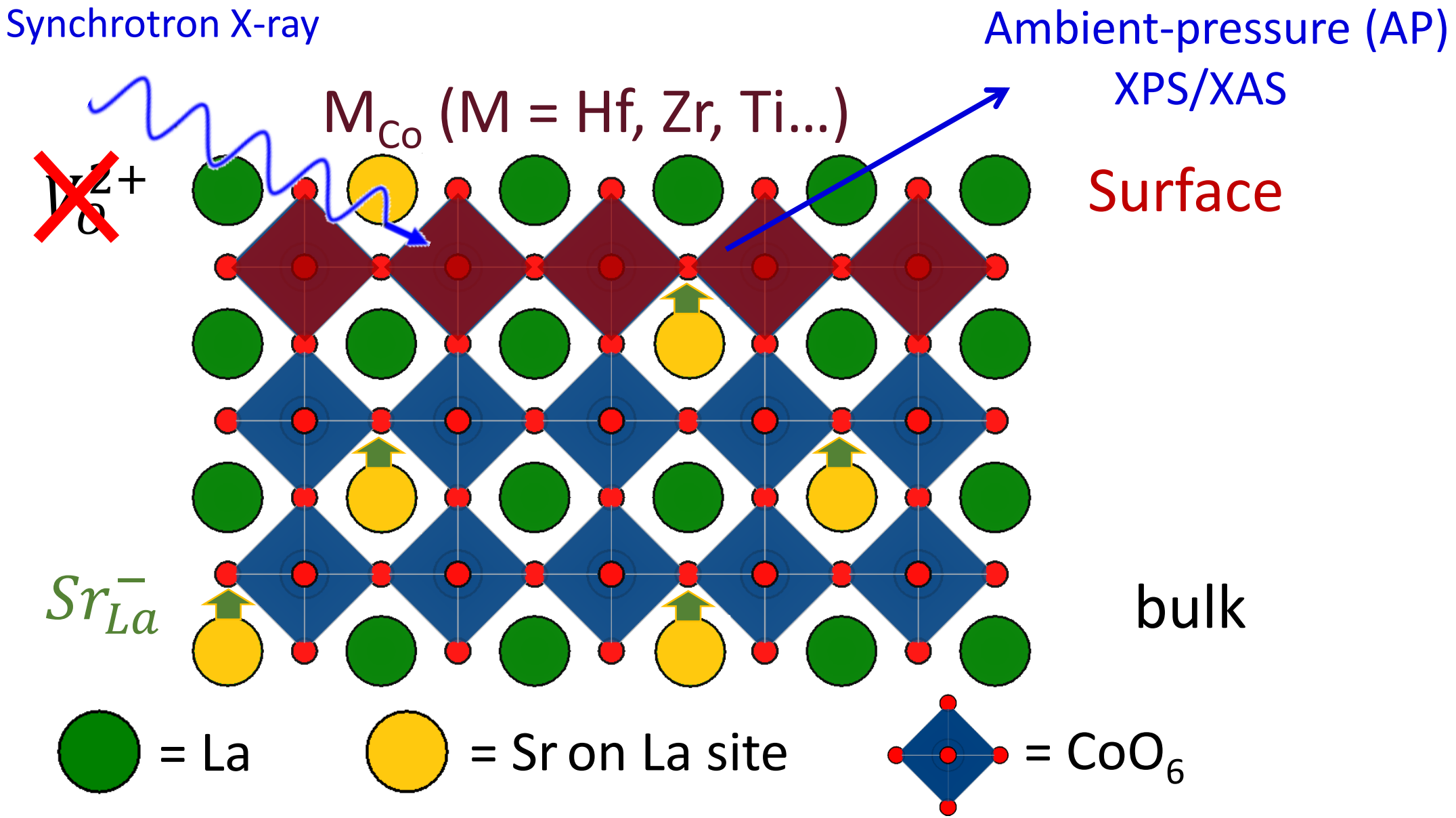
Formation of Sr-enriched species

Z. Cai *et al., Chem. Mater.*, 2012
M. Kubicek *et al., J. Electrochem. Soc.*, 2011

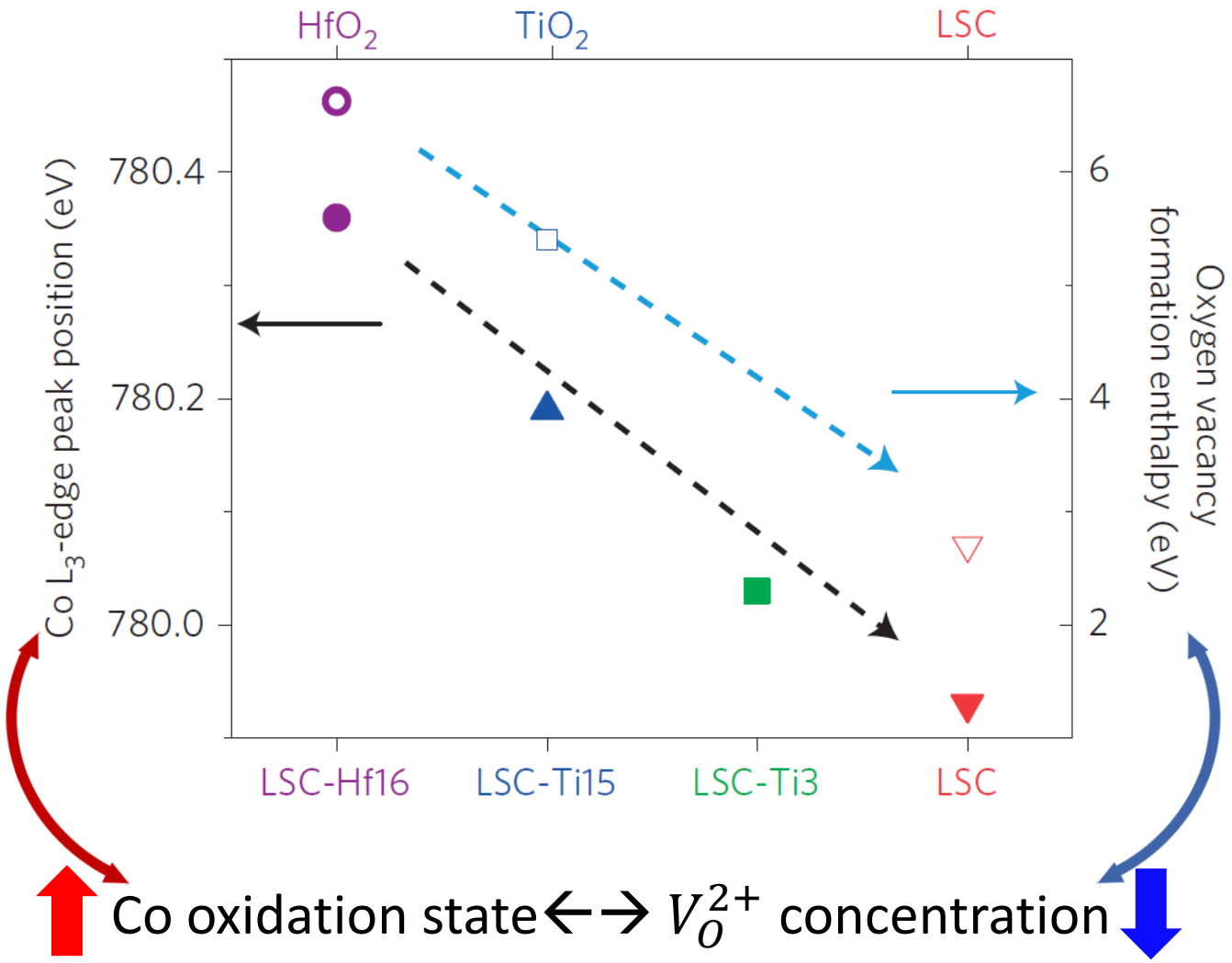
Electrostatic driving force of Sr surface segregation



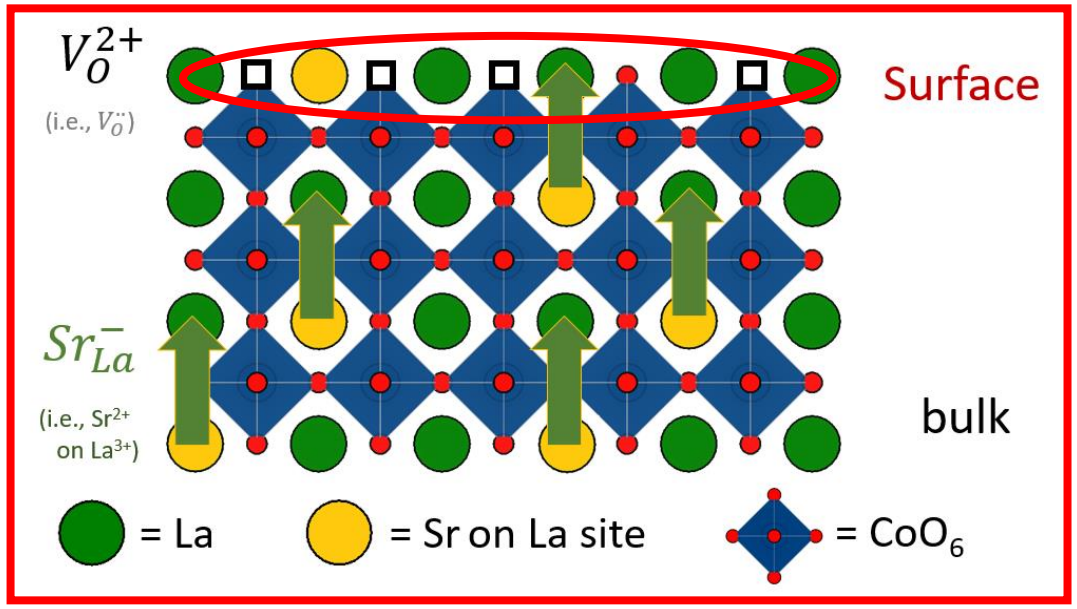
Suppression of Sr surface segregation by doping

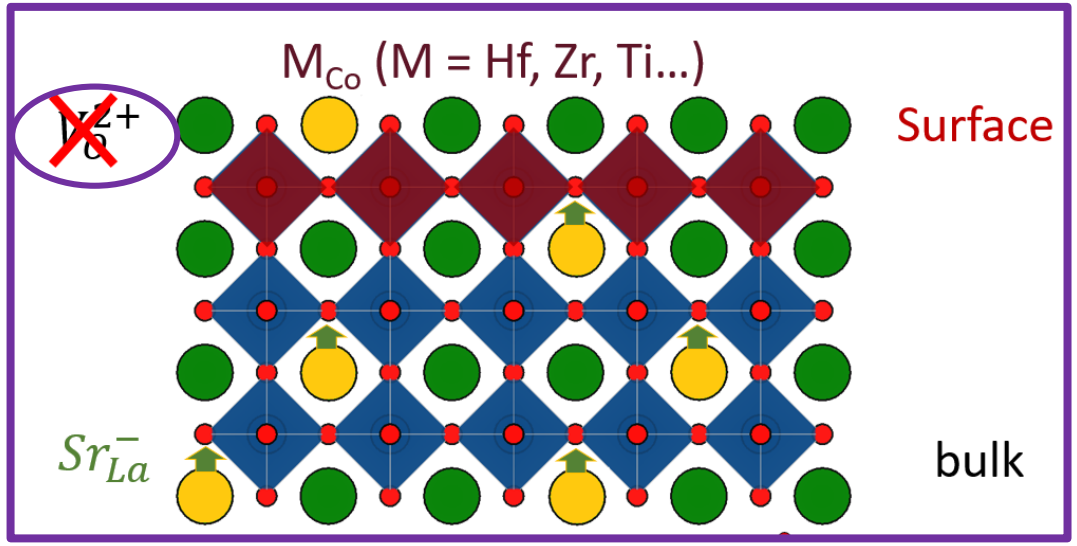


Reduced surface oxygen vacancy concentration achieved by doping

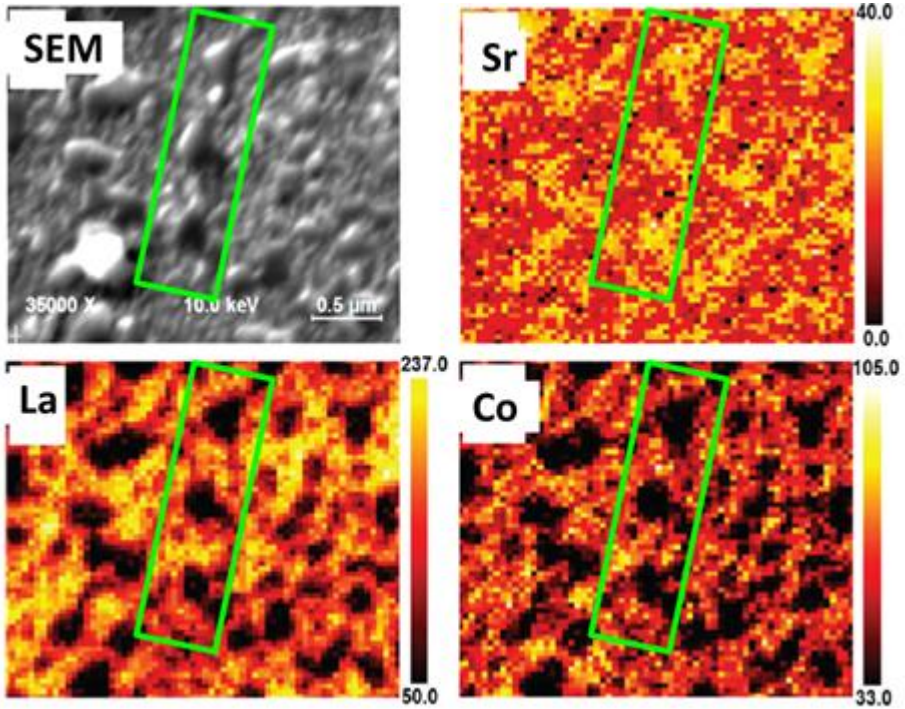


Co oxidation state ←→ V_O^{2+} concentration



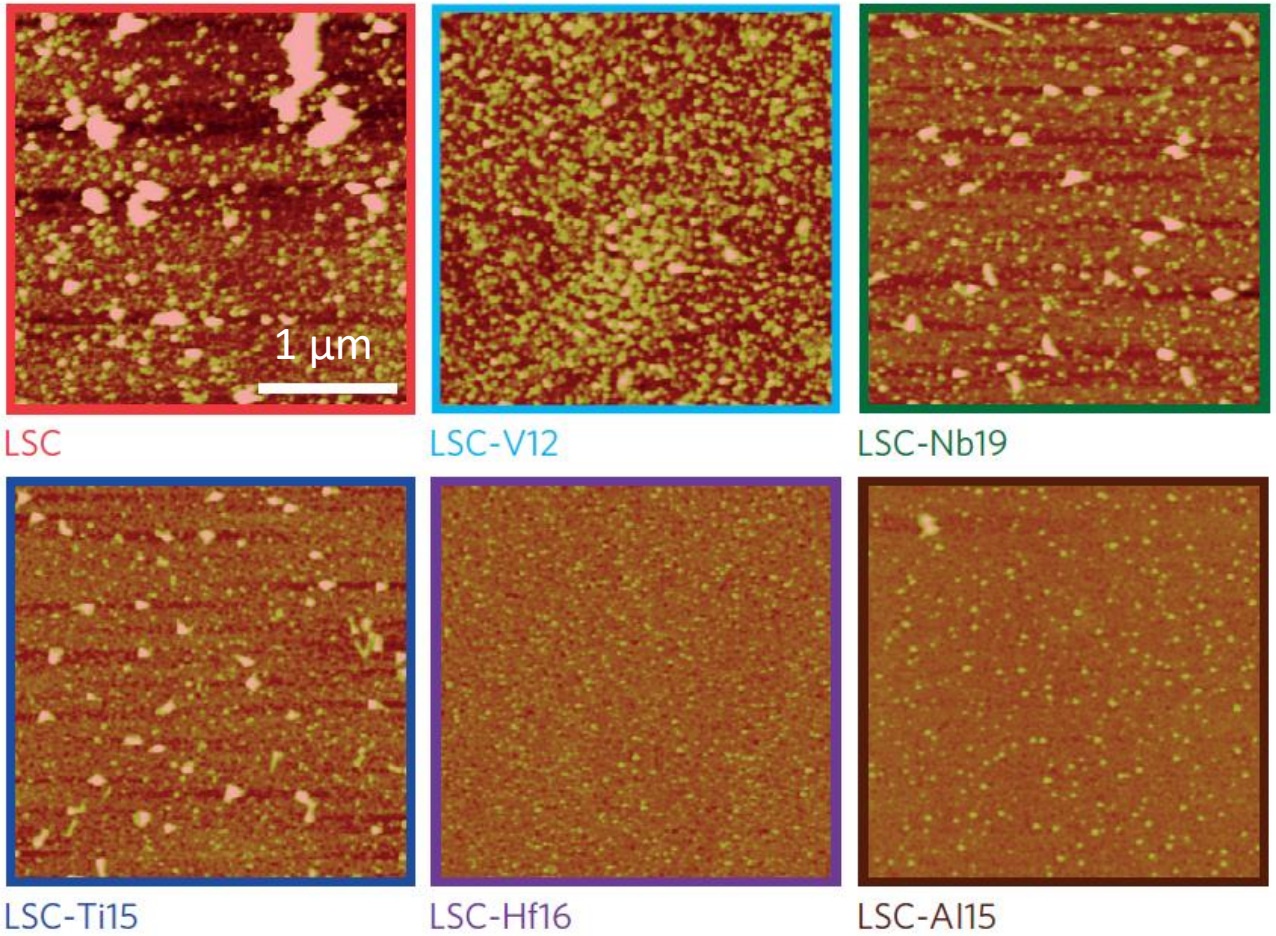


Less surface segregation leads to more stable surface morphology of LSC



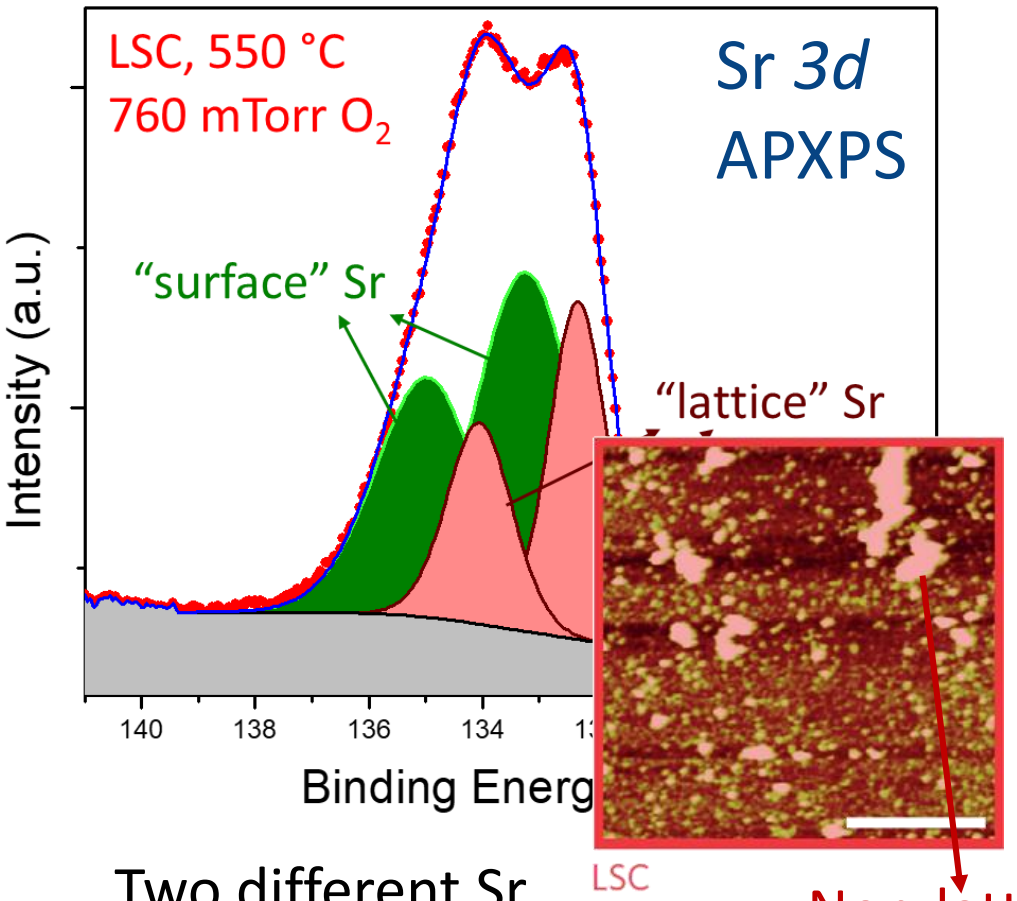
Auger electron microscopy images

Formation of Sr-enriched species



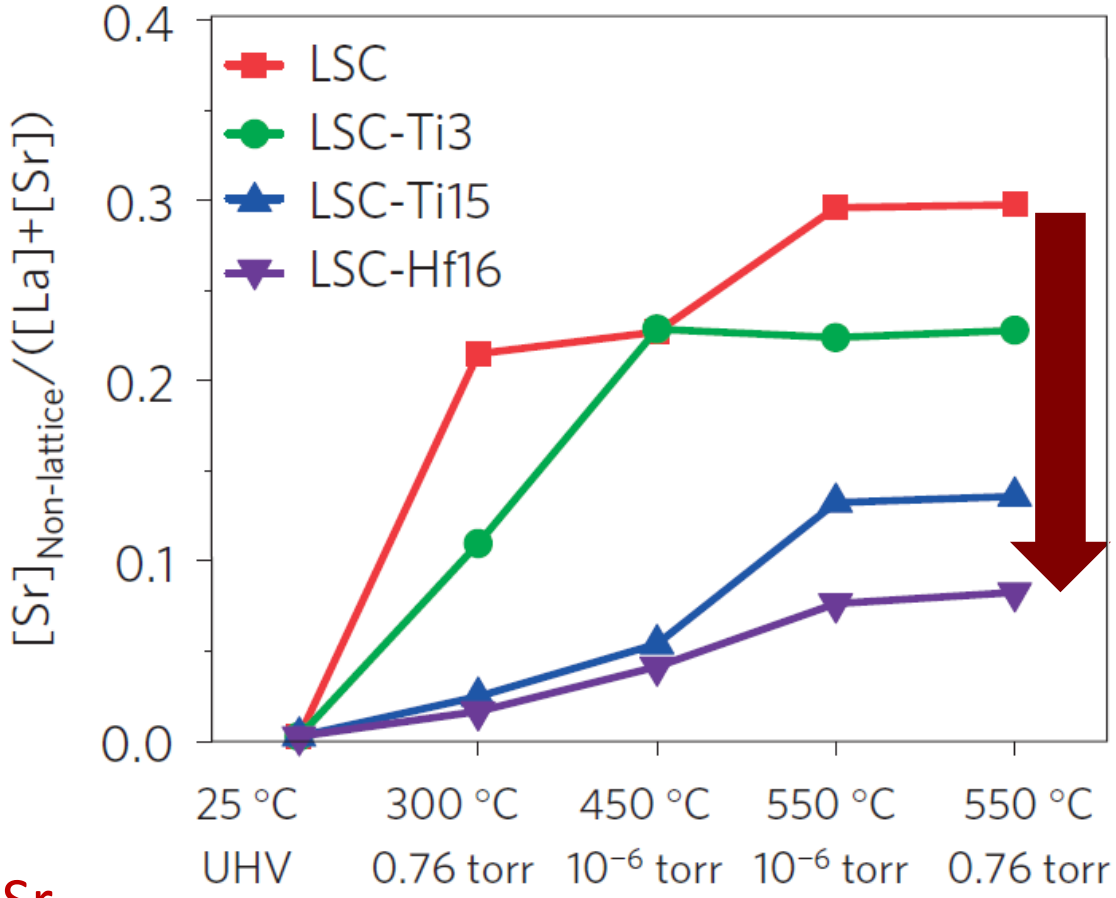
Atomic force microscope (AFM) images
After annealed at 530 °C in air

In situ surface chemistry characterization on LSC by using AP-XPS



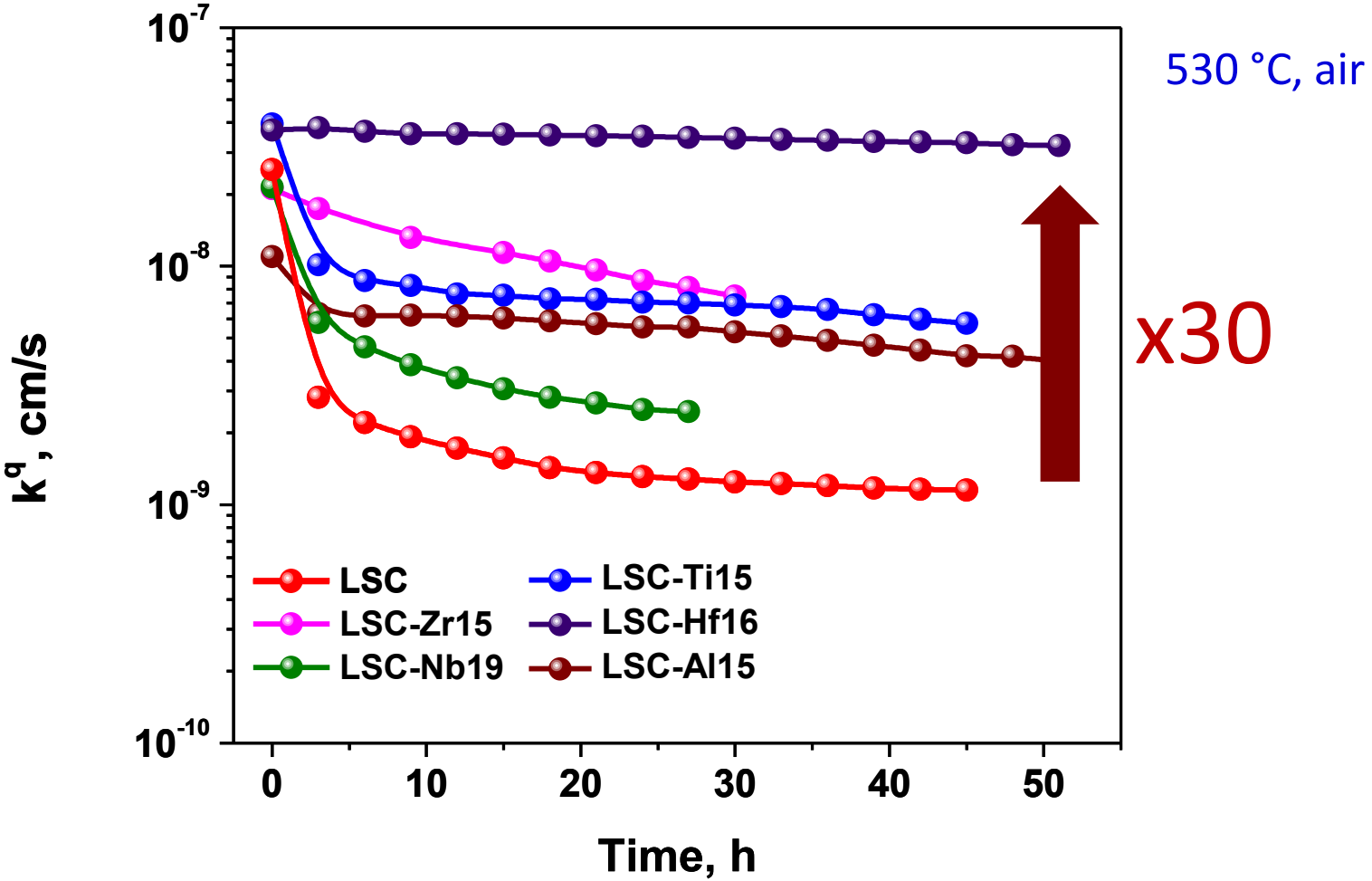
Two different Sr chemical environments

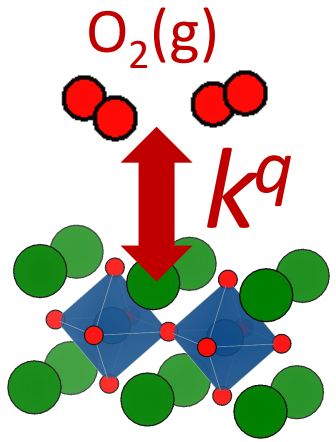
Non-lattice Sr



N. Tsvetkov*, Q. Lu*, L. Sun, E. Crumlin, B. Yildiz, *Nature Materials*, 2016

Enhancement in electrochemical stability gained from surface modifications



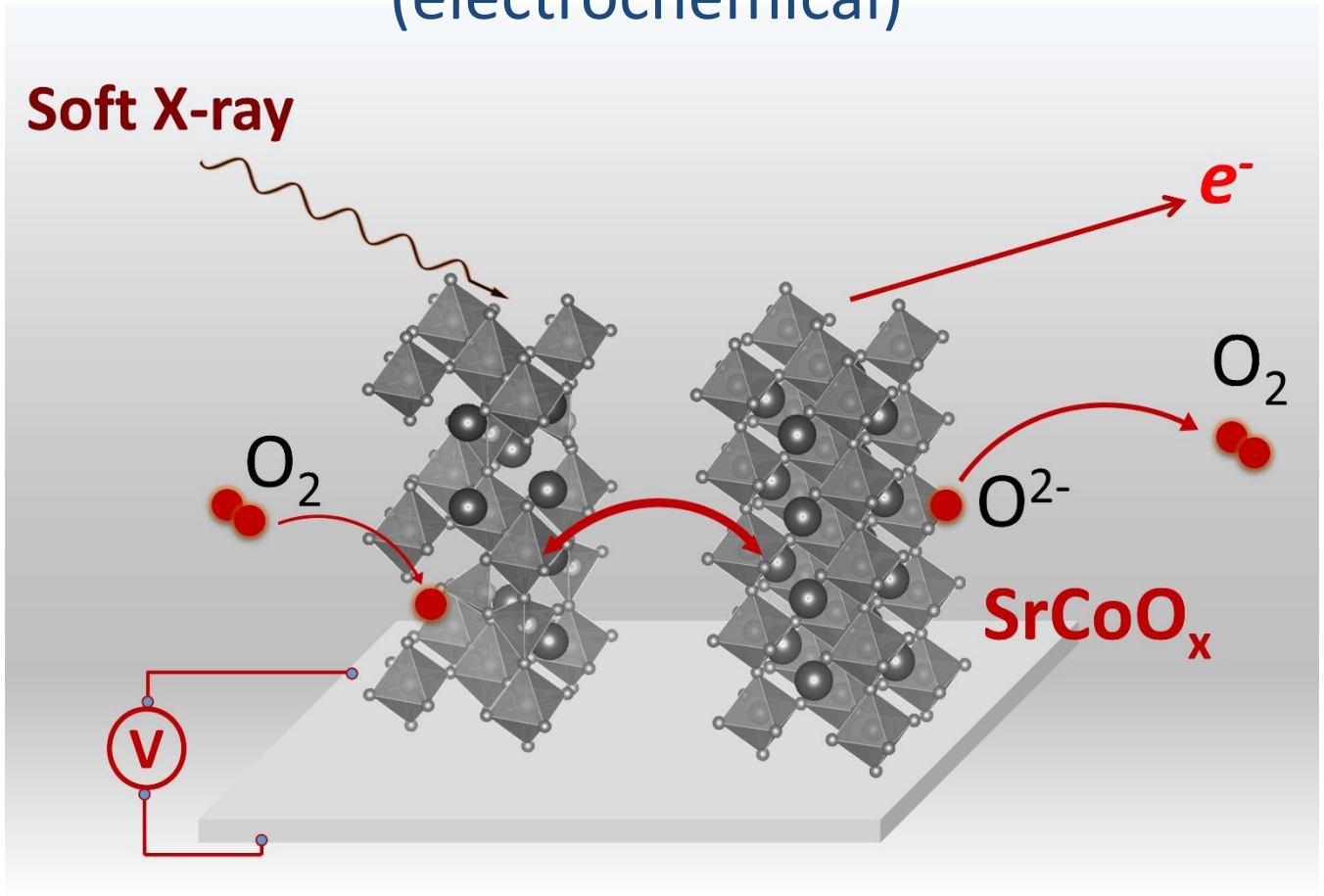


k^q: oxygen surface exchange rate

represents the electrochemical performance

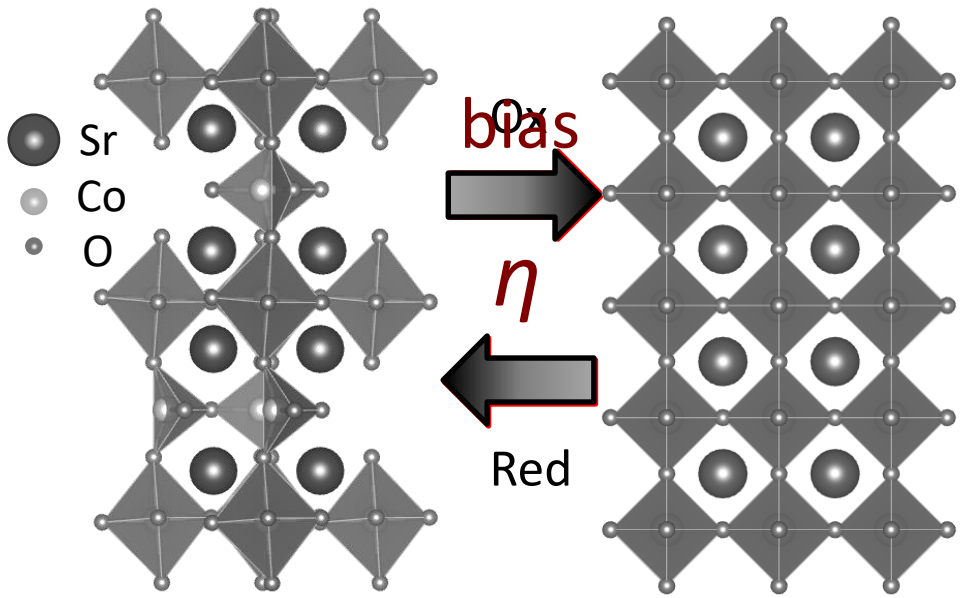
Case study II: phase transition in $SrCoO_x$

Applying electrical biases (electrochemical)



Q. Lu and B. Yildiz, *Nano Letters*, 2016
Q. Lu, H. Blum, B. Yildiz *et al.*, *J. Phys. Chem. C*, 2016

Distinct properties in BM and P phase $SrCoO_x$



Oxygen-deficient
$SrCoO_{2.5}$
Brownmillerite (BM)

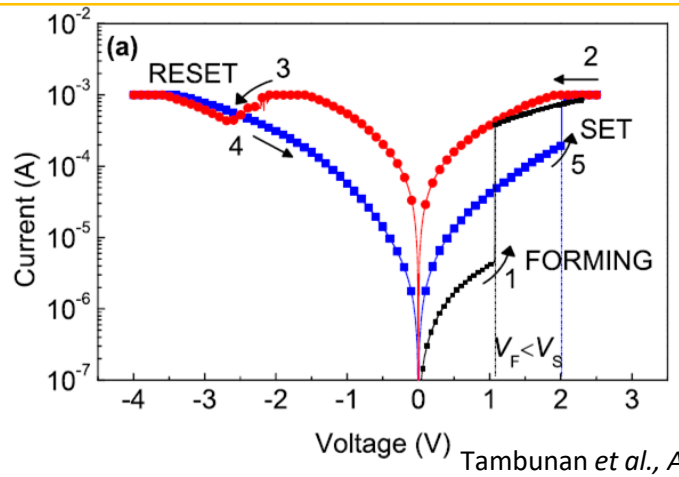
Semiconducting;
Antiferromagnetic;

Oxygen-rich
$SrCoO_{3-\delta}$ (δ<0.5)
Perovskite (P)

Metallic;
Ferromagnetic;

Ezbiri *et al.*, *ChemSusChem*, 2015

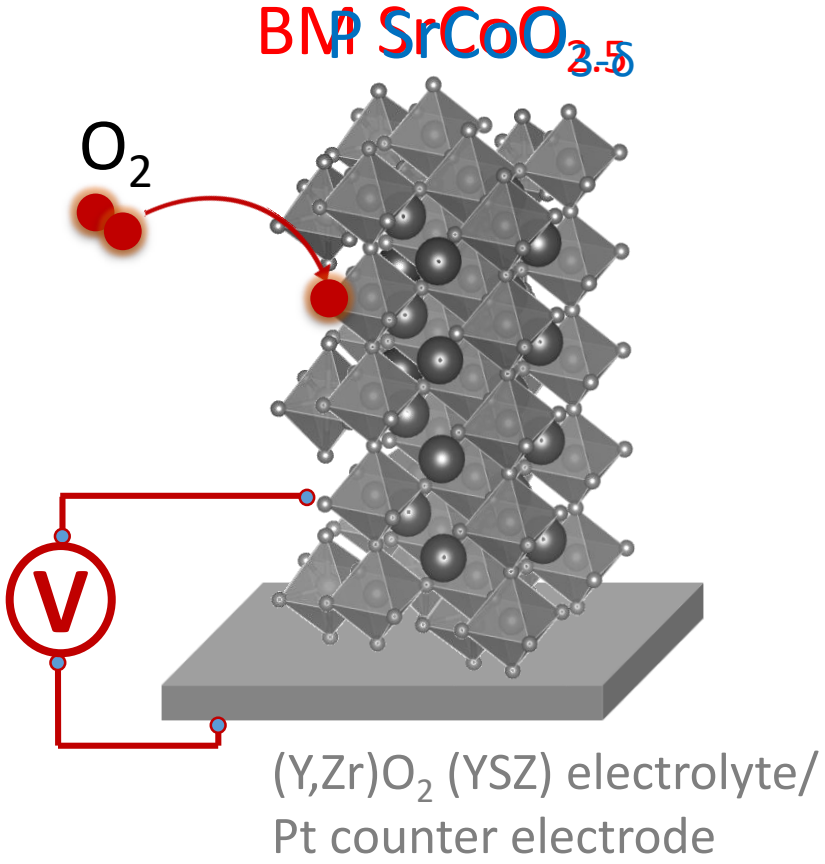
Solar-driven O_2 separation and concentration

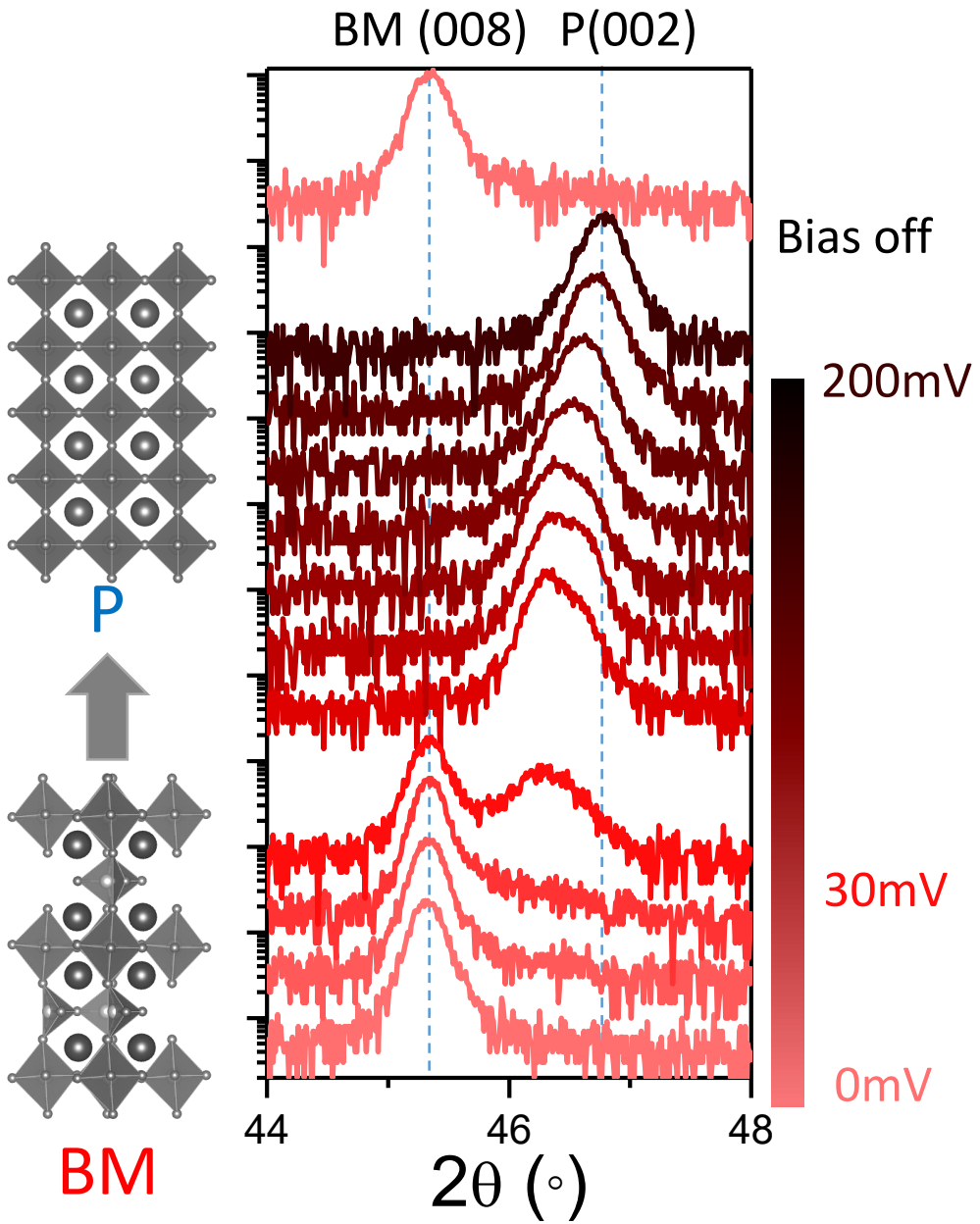


Tambunan *et al.*, *APL*, 2014

Memristors (resistive switching)

In situ diffraction showing phase transition in $SrCoO_x$



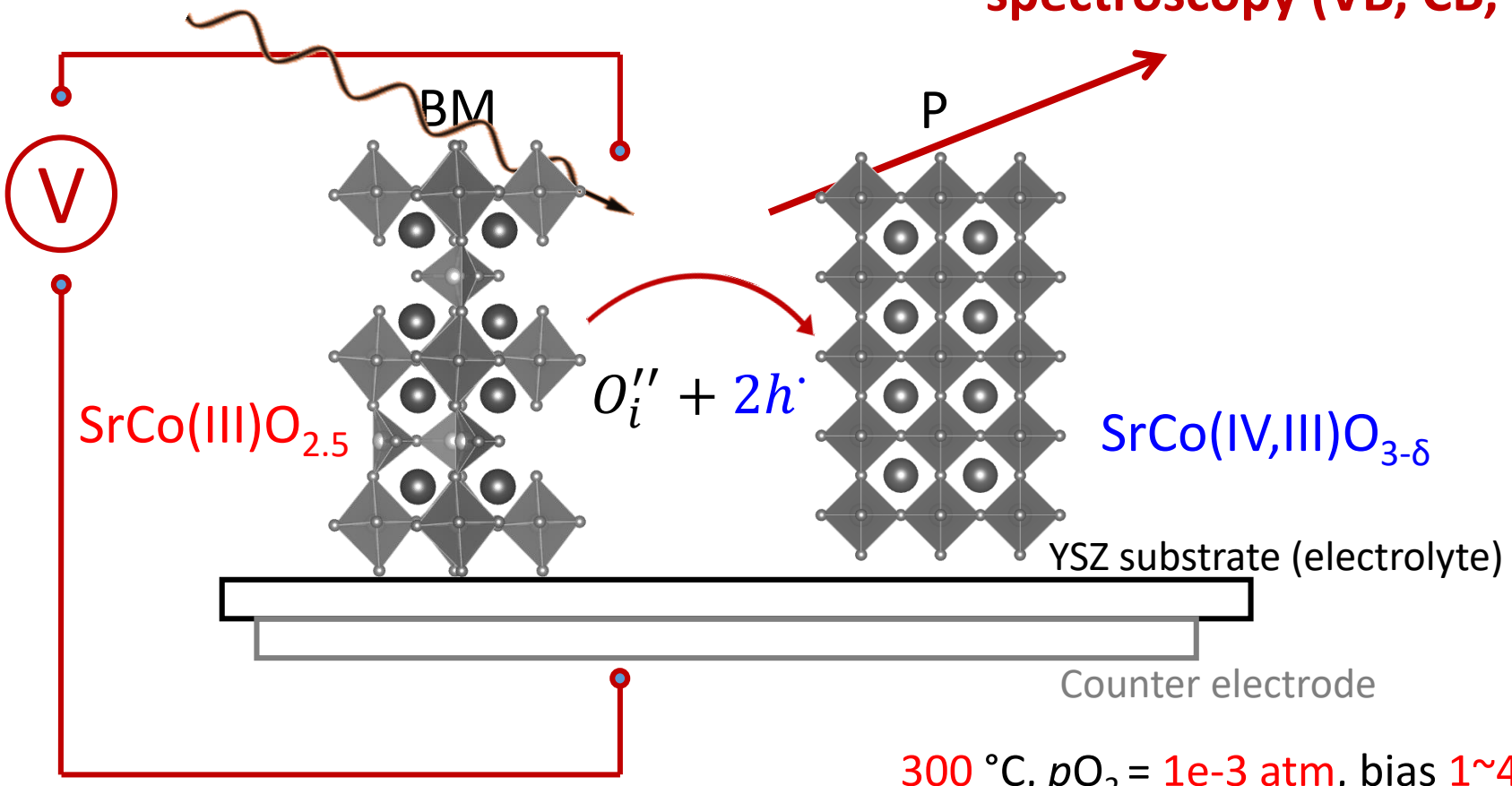


Q. Lu and B. Yildiz, *Nano Letters*, 2016

In situ probing the change in electronic structure of $SrCoO_x$

Soft X-ray (<1 keV, BL 11.0.2, ALS)

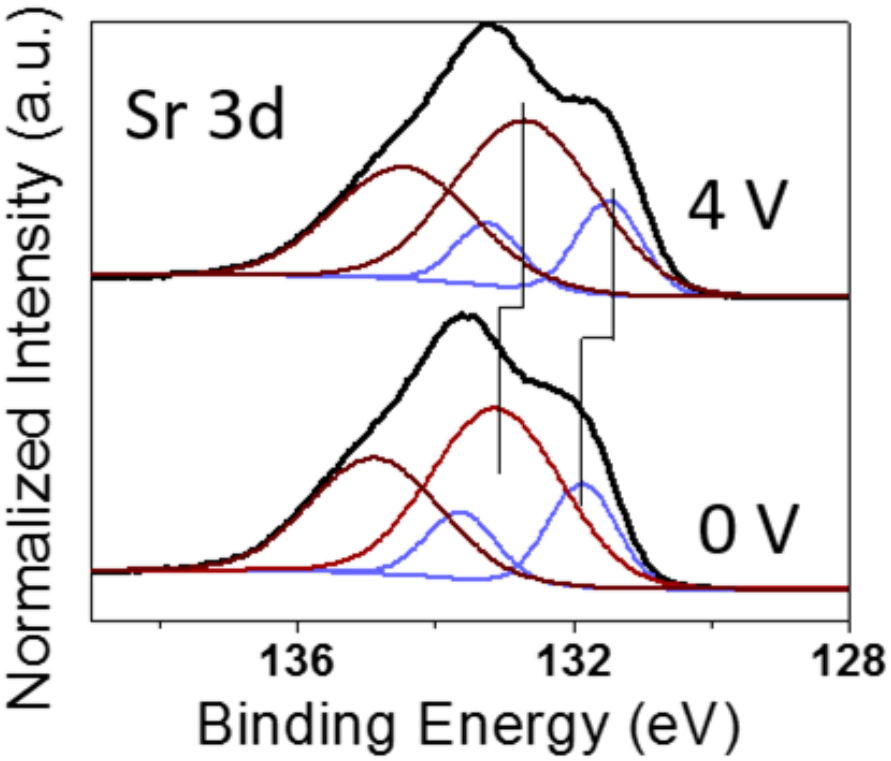
Ambient-pressure X-ray spectroscopy (VB, CB, E_f)

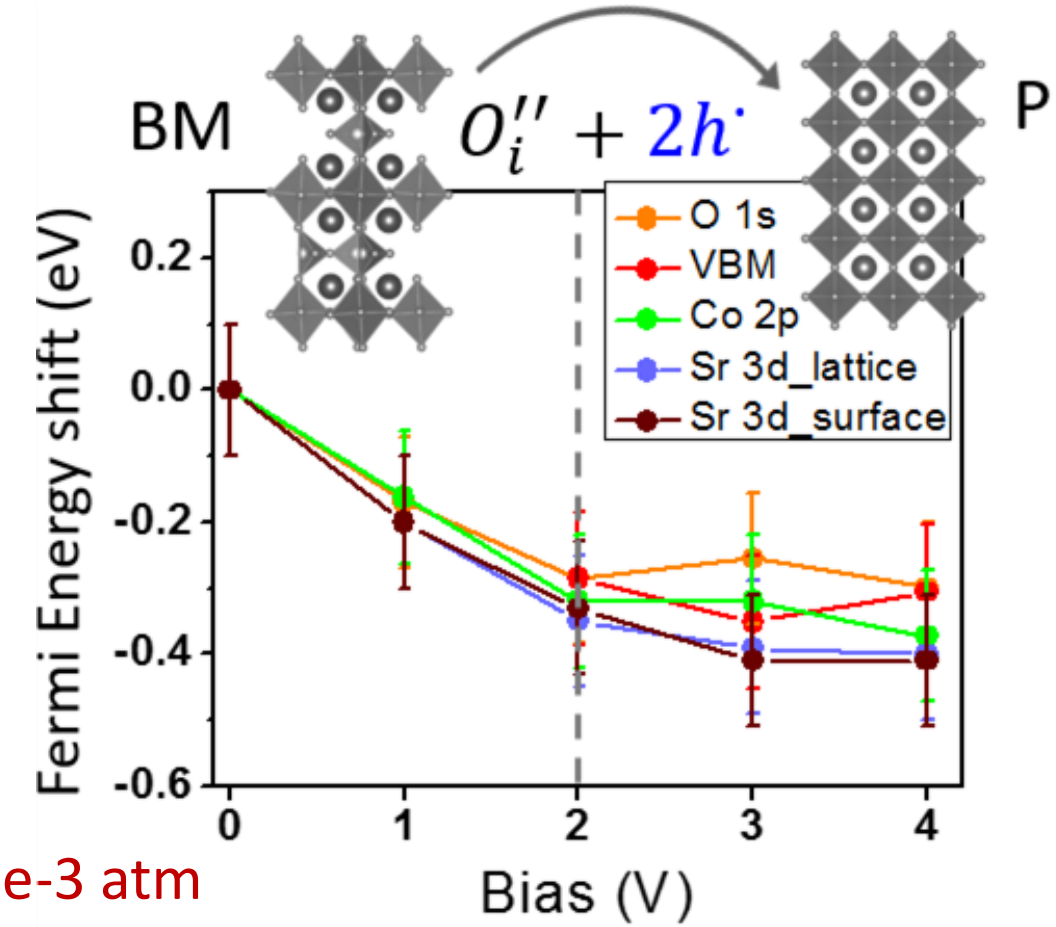


300 °C, pO_2 = 1e-3 atm, bias 1~4 V
(BM→P transition bias = 2V)

Q. Lu, H. Bluhm, B. Yildiz *et al.*, *J. Phys. Chem. C*, 2016

Downwards shift of Fermi level during the BM➔P phase transition

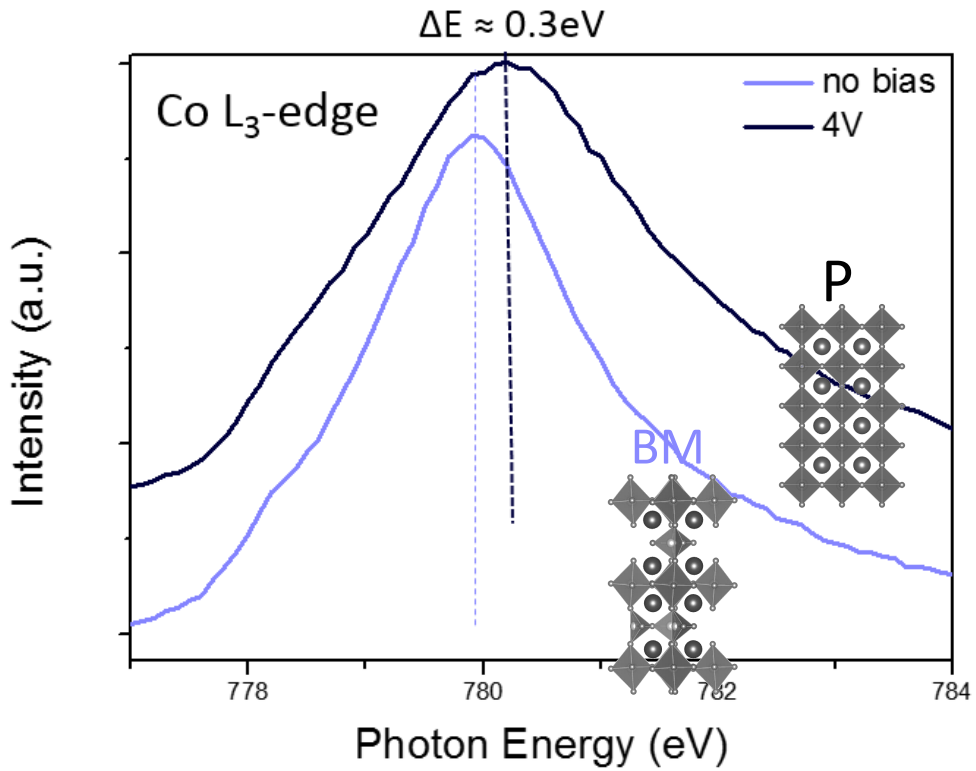


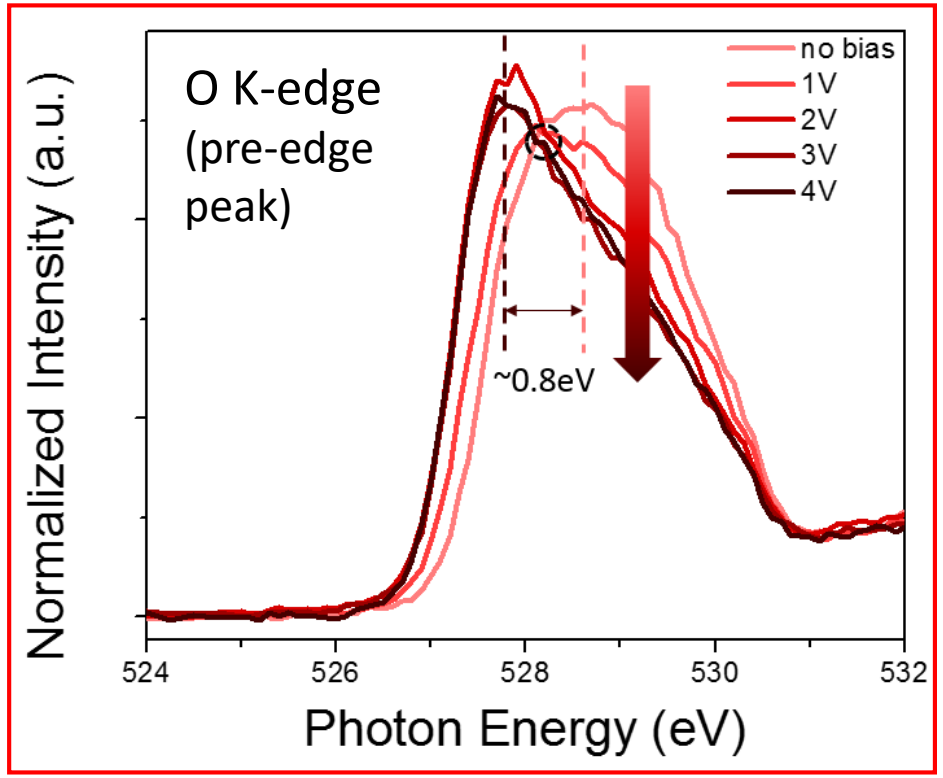


300 °C, pO_2 = 1e-3 atm

Fermi energy down-shift, introduced by extra holes during BM→P transition, detected by AP-XPS

X-ray absorption spectra (XAS) data showed strong hybridization between Co *3d* and O *2p*



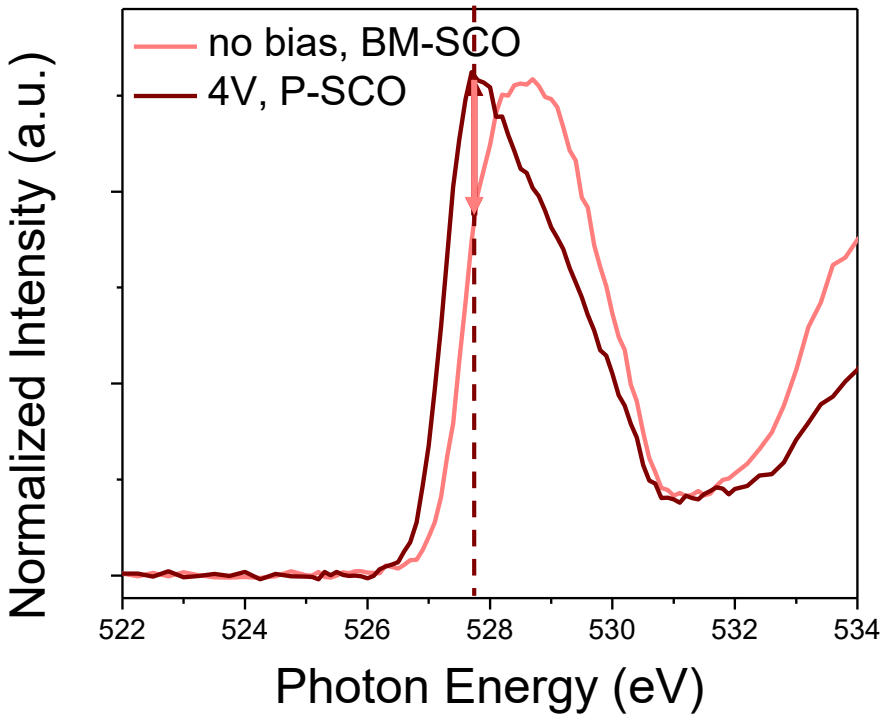


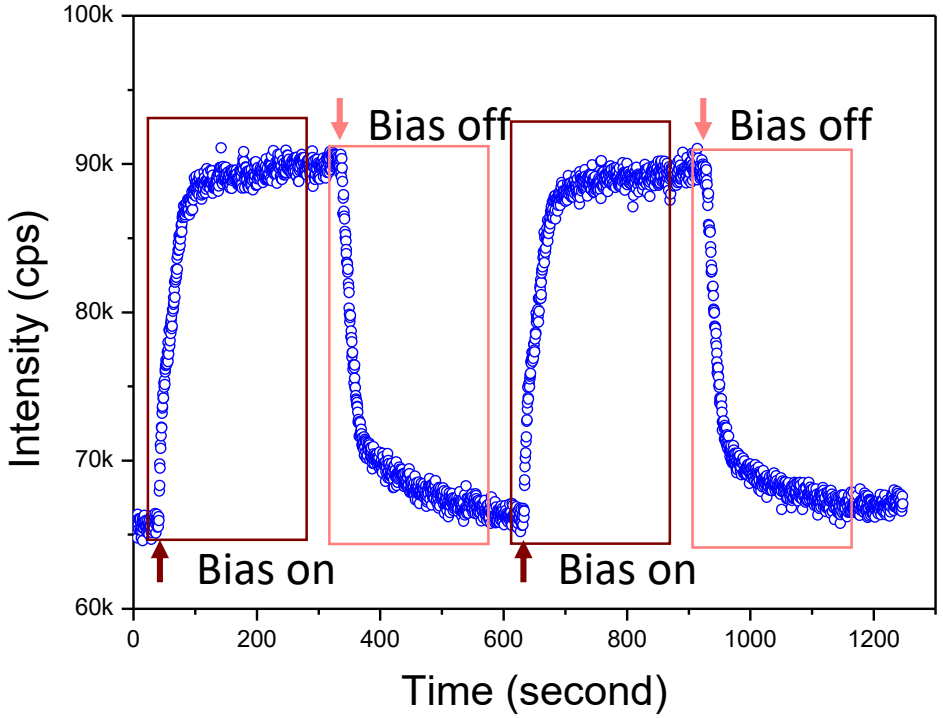
$SrCo(III)O_{2.5} \rightarrow SrCo(IV,III)O_{3-\delta}$

$$1/2\, O_2 \rightarrow O_i'' + 2h^{\cdot}$$

$3d^6\underline{L}$ for Co cations in $SrCoO_{3-\delta}$
($\underline{L}$: O *2p* ligand hole)

Kinetics of the phase transition studied using X-ray adsorption



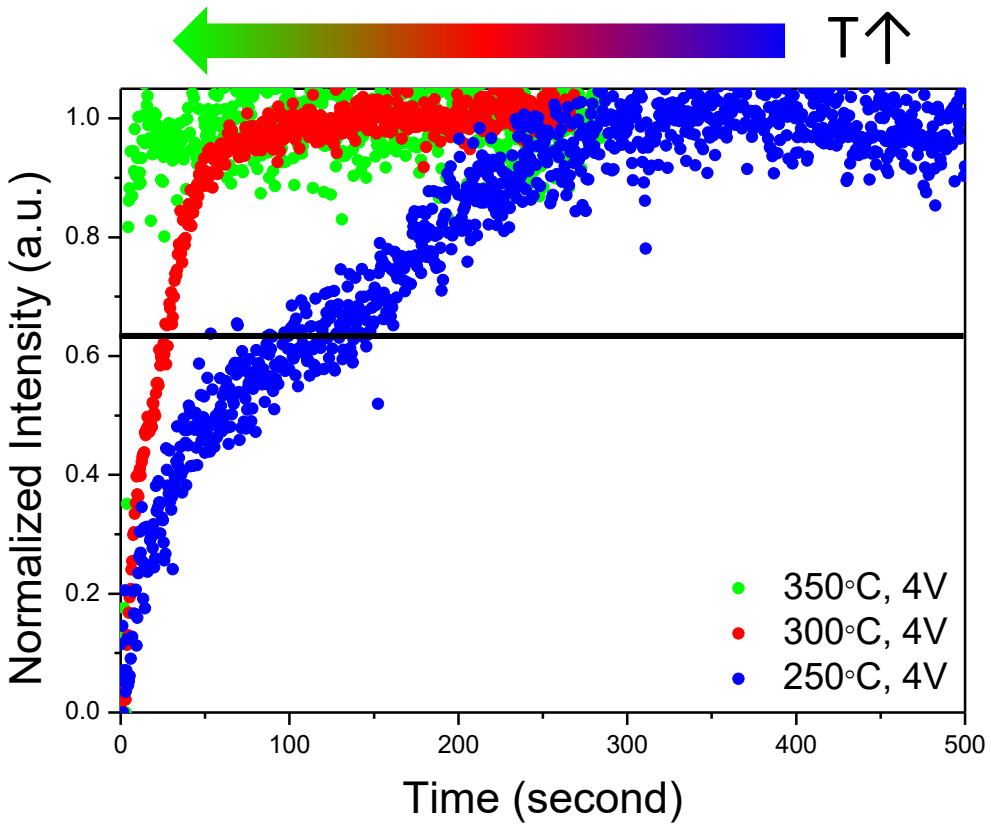


O K-edge pre-edge peak

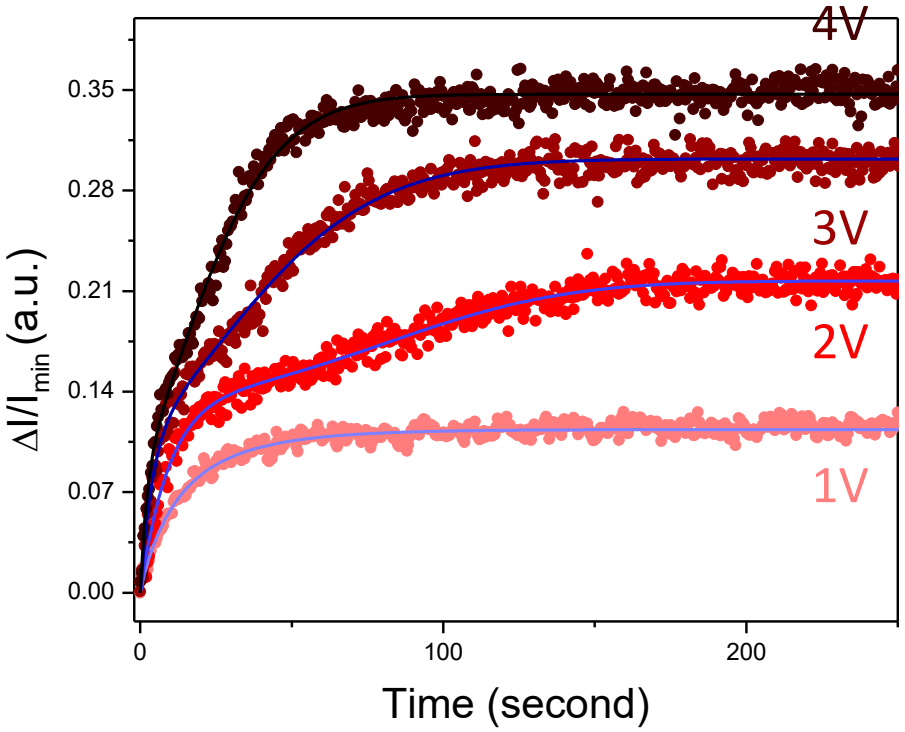
Relaxation (Intensity-time) curves

Kinetics of the phase transition studied using X-ray adsorption

$$\Delta I(t) = \Delta I_0\left(1 - a_1 \exp\left(-\frac{t}{\tau_1}\right) - (1 - a_1)\exp\left(-\left(\frac{t}{\tau_2}\right)^{n_2}\right)\right)$$



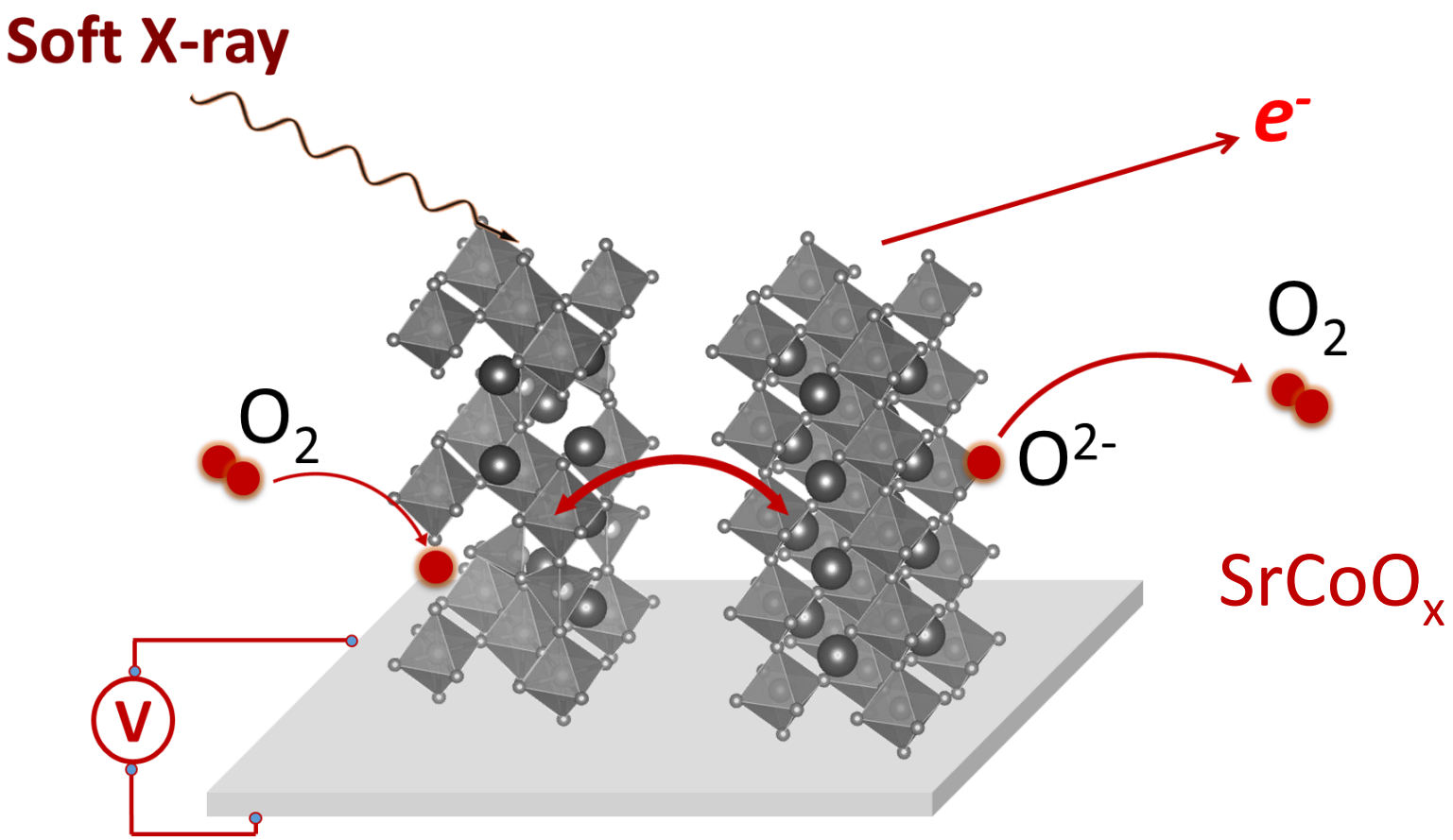
Temperature-dependence



Voltage-dependence

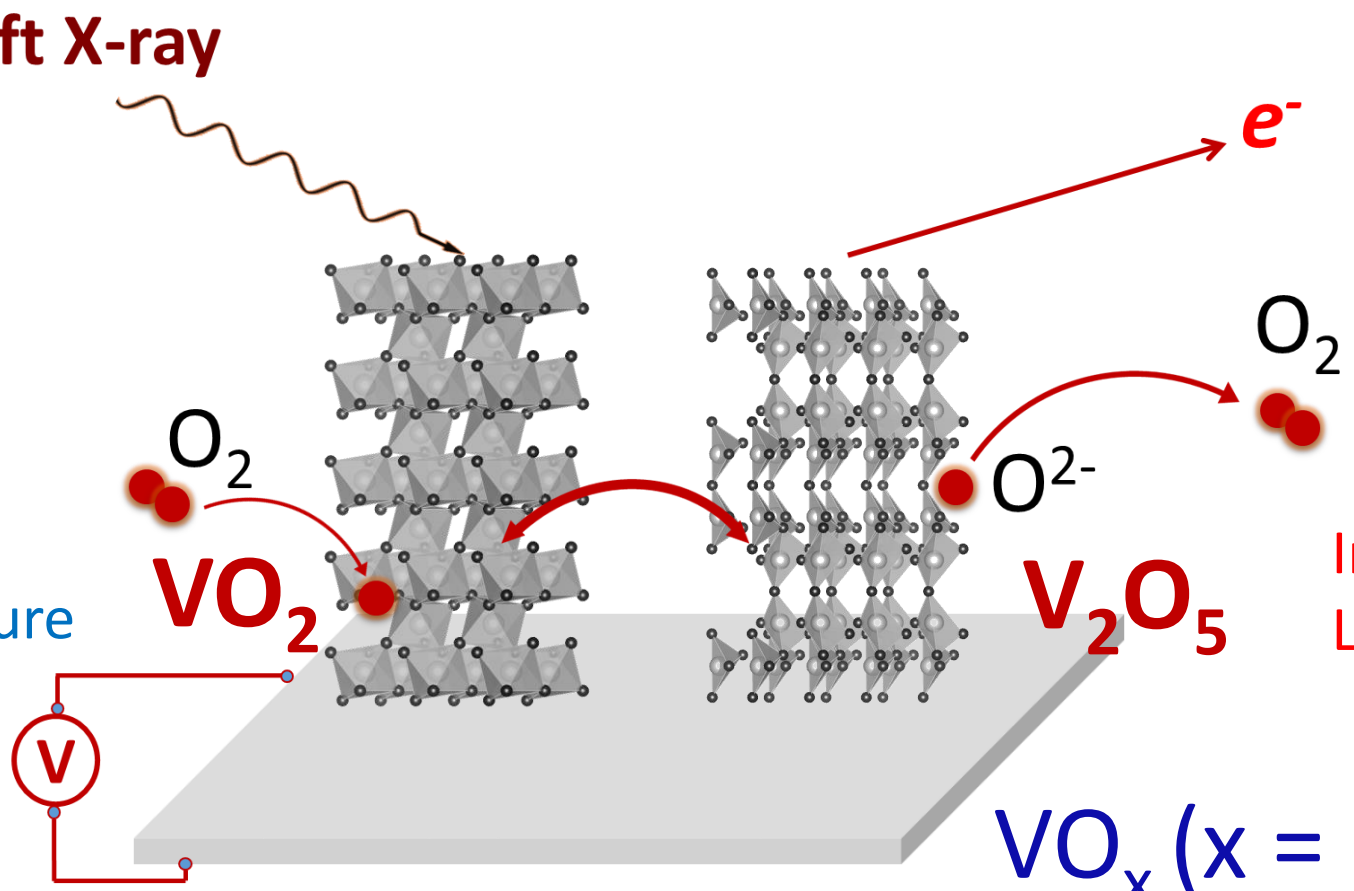
Q. Lu, H. Bluhm, B. Yildiz *et al.*, *J. Phys. Chem. C*, 2016

Applying the same idea to other materials systems



Applying the same idea to other materials systems

Metal-to insulator transition at ~340 K
Close-packed structure



Insulator (E_g = 2.2 eV)
Layered structure

VO_x (x = 2~2.5)

Q. Lu, S. R. Bishop, D. Lee, H. Bluhm, H. L. Tuller, H. Lee, B. Yildiz, *submitted*

Electrochemically driven phase transition in VO_x probed by AP-XAS

Unpublished data

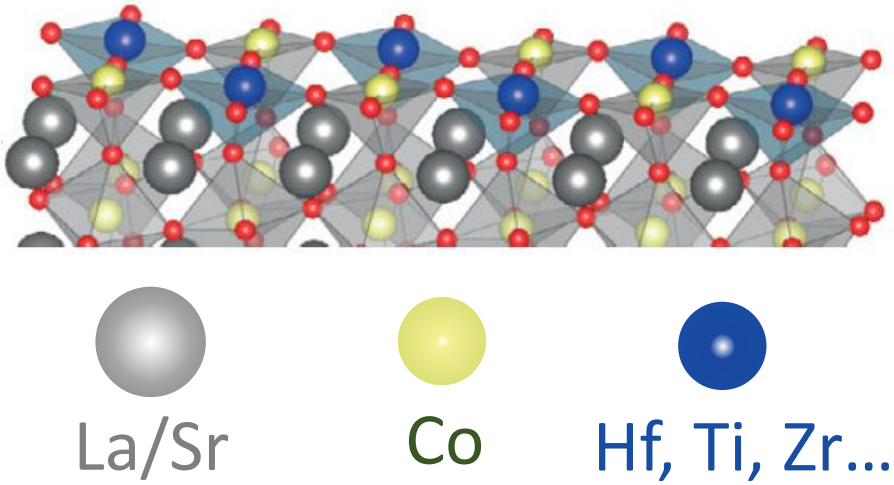
New type of reversible metal-insulator-transition (MIT) triggered electrochemically in VO_x

Unpublished data

Different methods for tuning oxygen defect chemistry

Doping (chemical)

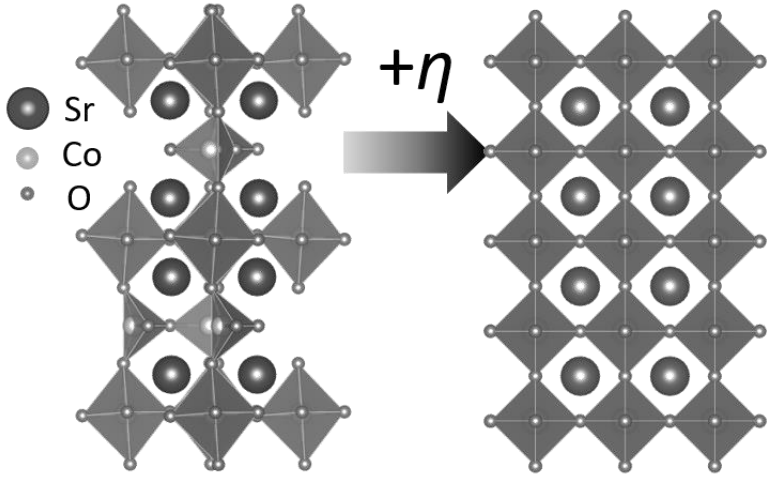
Surface-decorated $La_{0.8}Sr_{0.2}CoO_{3-\delta}$



N. Tsvetkov*, Q. Lu*, B. Yildiz *et al.*, *Nature Materials*, 2016

Biasing (electro-chemical)

Topotactic phase transition of $SrCoO_x$



Q. Lu and B. Yildiz, Nano Letters, 2016

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Thank you for your attention!