Electric field driven metal-to-insulator transition at a Al/$LaNiO_3$ interface

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Motivation

What ?
Manipulation of the **electronic structure** in heterostructures of **ultra-thin** films of oxides

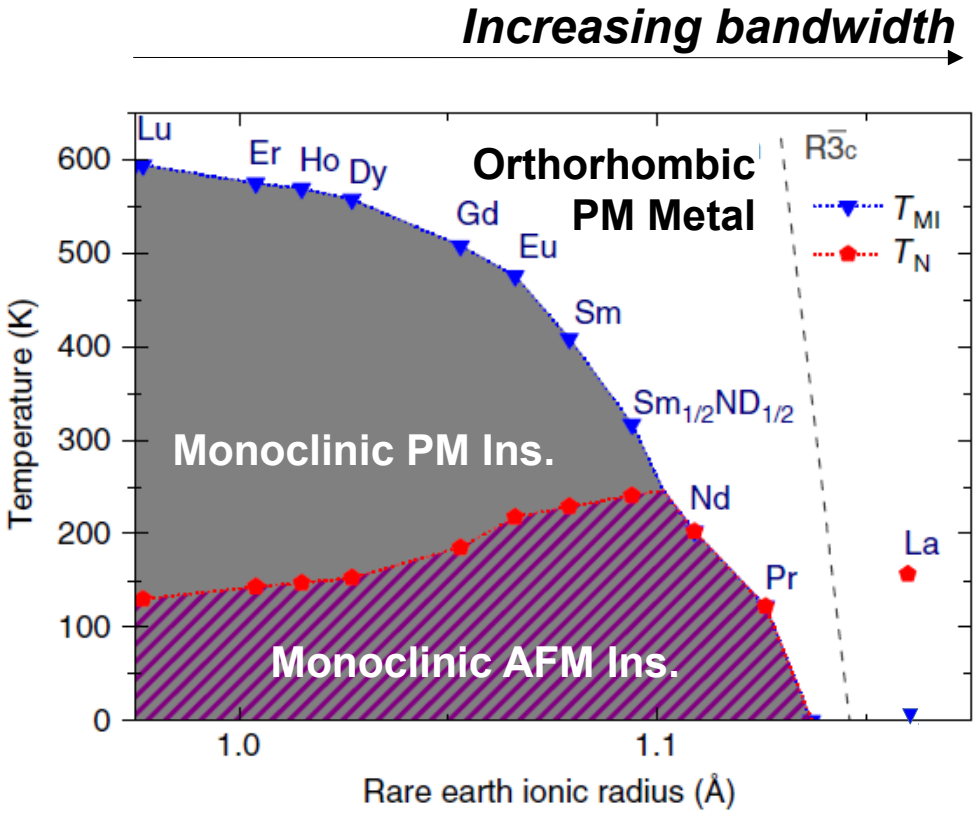
What for?
Inducing **functional properties** (metal-to-insulator transition, magnetism, ...)

Target materials: Rare earth nickelates

- strong **electronic correlations**
- ground state close to a **metal-to-insulator** transition
- Ni sites are **magnetic** and AFM order occurs at low temperature
- possible Ni-O orbital **hybridization**

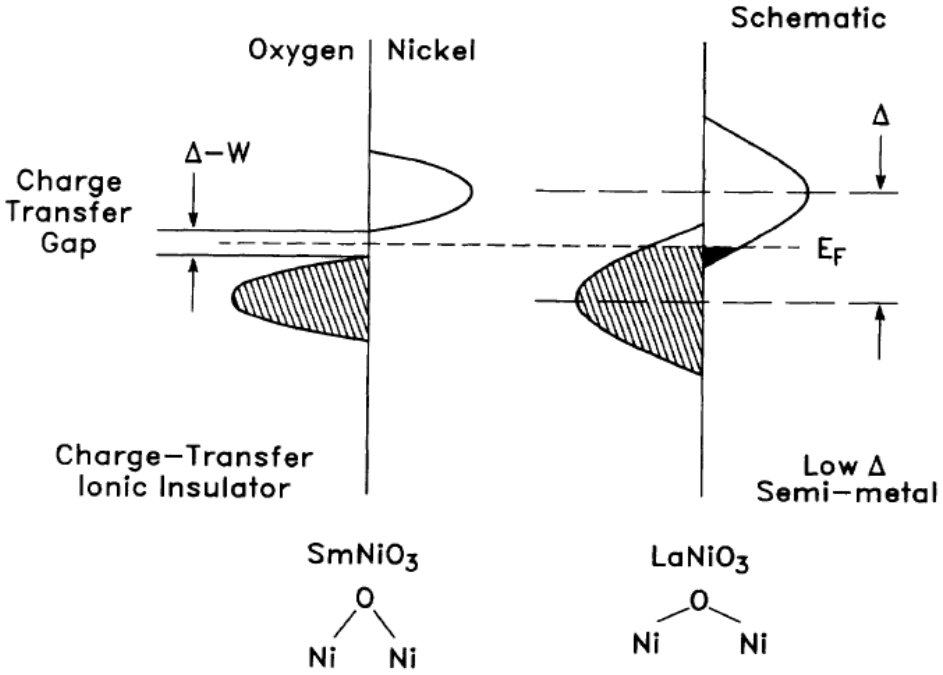
  ➡ sensitive to oxygen vacancies via distortions and band filling

Nickelates phase diagram



H. Guo, Nat. Comm. 9:43 (2018)

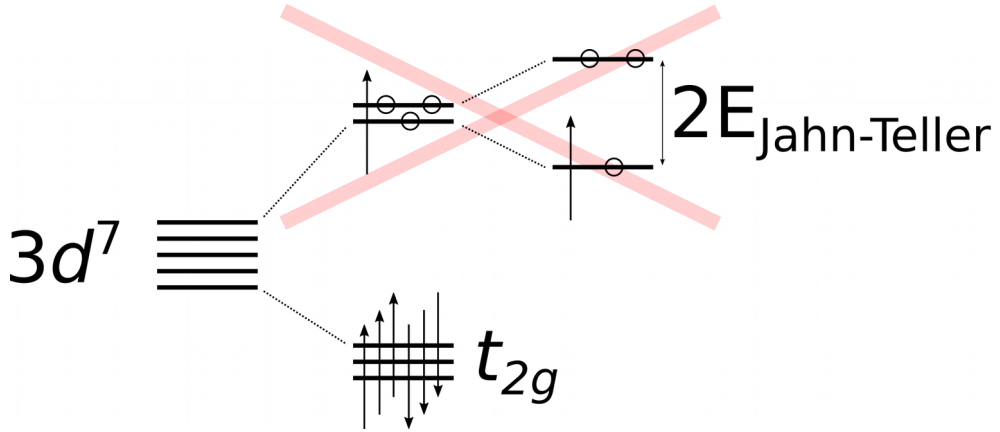
Charge transfer insulator
(Zaanen, Sawatzky & Allen 1985)



Torrance PRB 45 (1992)

How to turn $LaNiO_3$ into an insulator ?

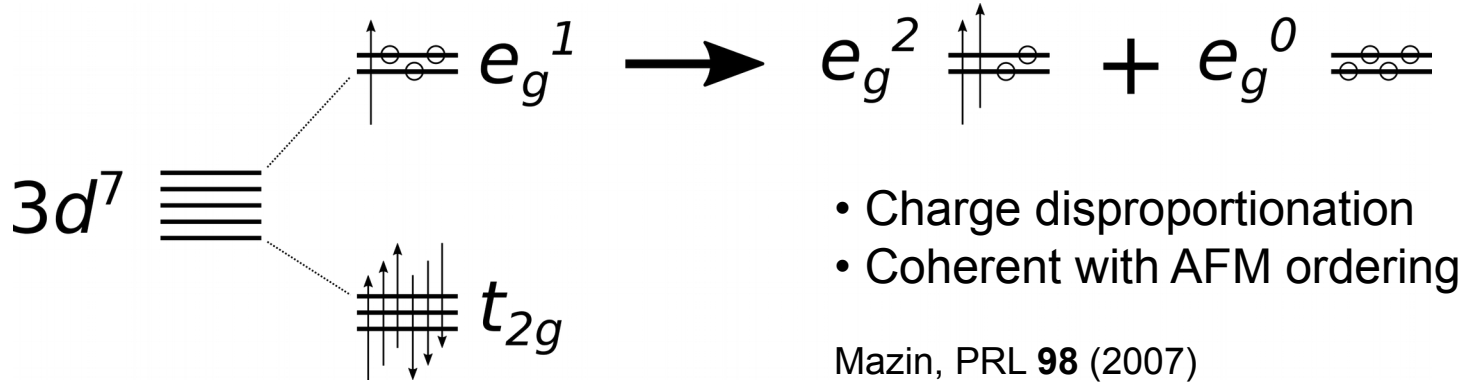
Nickelates ground state



$$-2E_{J\text{-}T} < U - J_{Hund} - 2E_{breath}$$

- Hund coupling competes with U
- O-octahedra breathing distortion

Charge ordered insulator



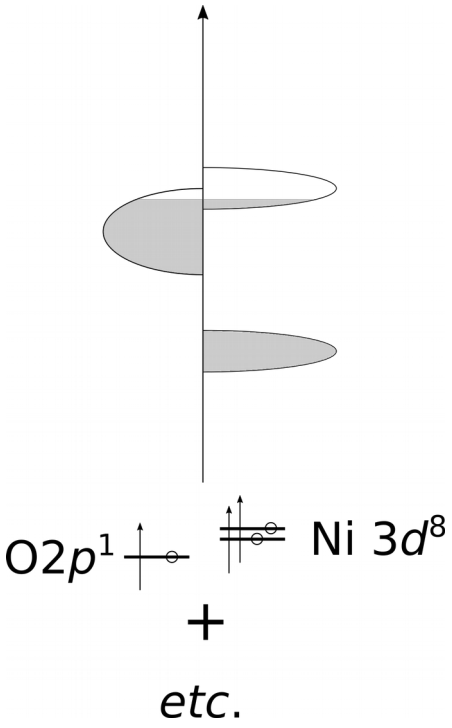
- Charge disproportionation
- Coherent with AFM ordering

Mazin, PRL **98** (2007)

Turning $LaNiO_3$ into an insulator

No charge ordering in $LaNiO_3$

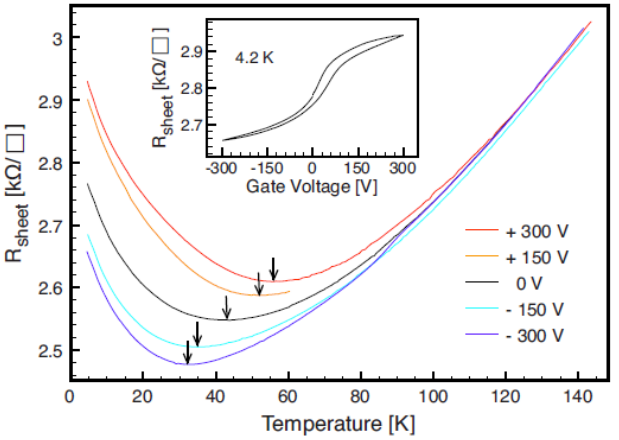
Rhombohedral p-type metal



M. Abbate PRB **65** (2002)

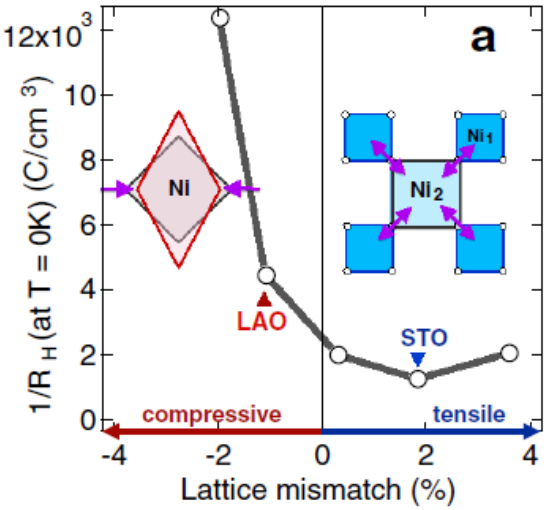
Route #1 :
charge injection
by gate voltage

R. Scherwitzl,
APL **95** (2009)

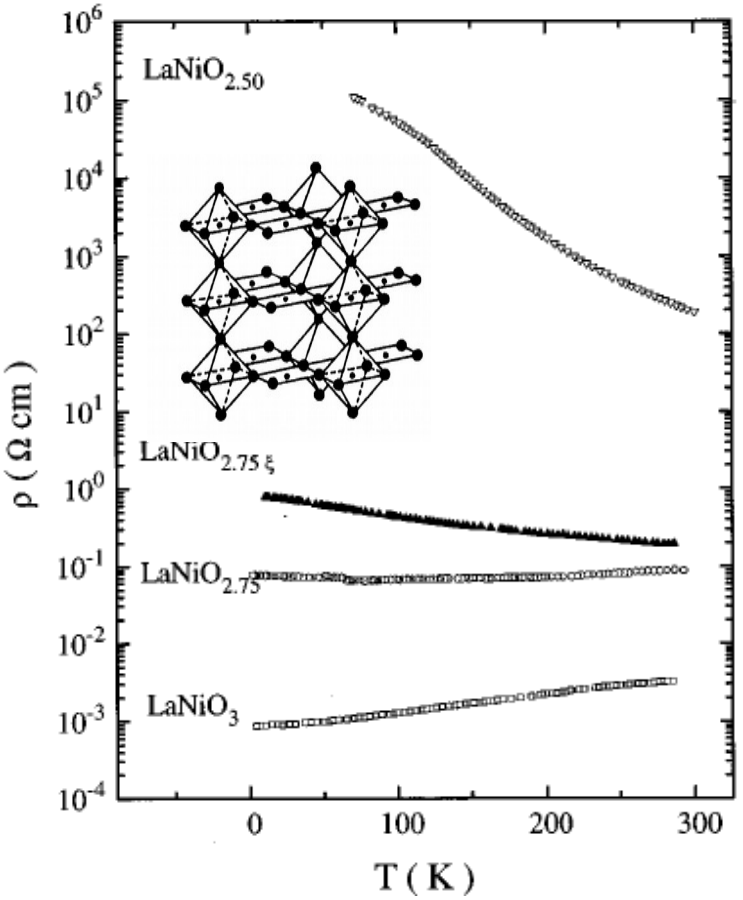


Route #2 :
substrate biaxial strain

J. Chakhalian
PRL **107** (2011)



Turning $LaNiO_3$ into an insulator



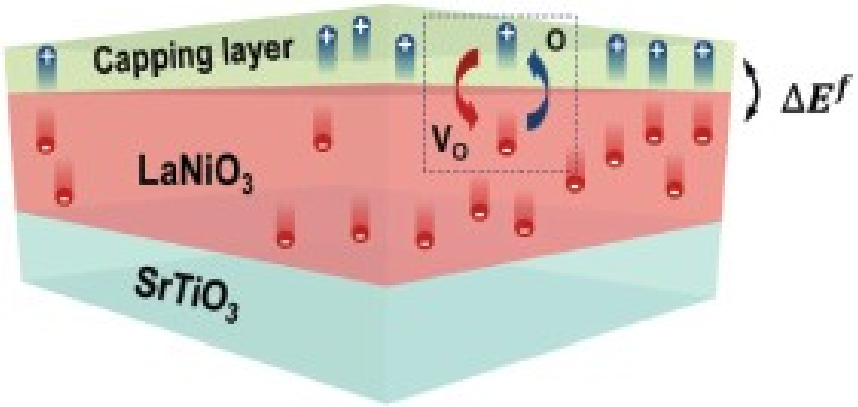
Sanchez, PRB **54** (1996)

Route #3 : oxygen stoichiometry

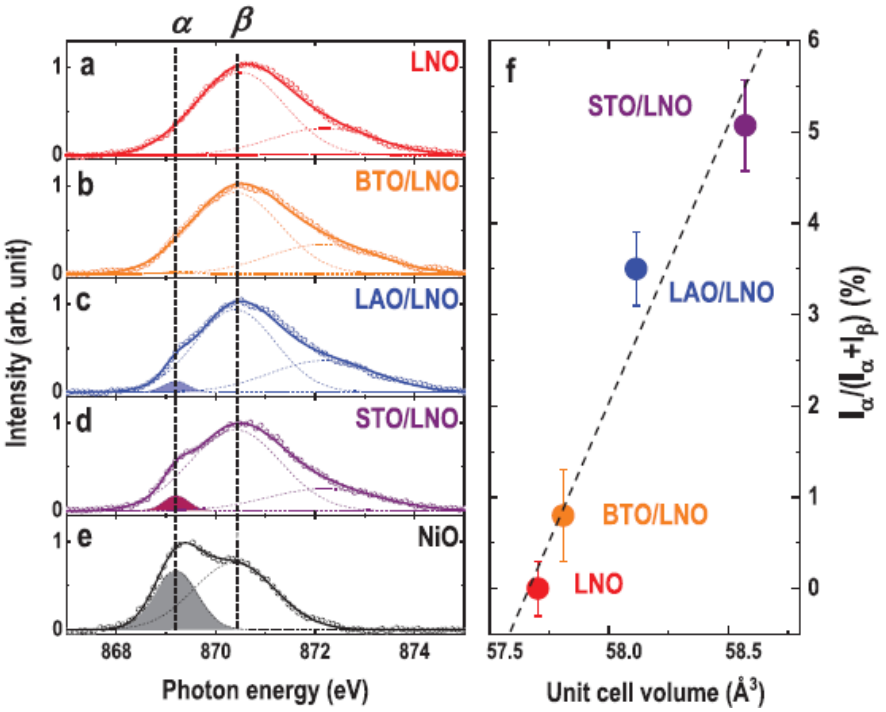
Introducing O vacancies by **vacuum annealing**

- O-vacancies **order** → brown-millerite
- change of the Ni **coordination**
- reduction of the Ni **valence** below 3+
- destruction of the electrical **conduction**

Tailoring the O vacancy density



O vacancy formation energy difference rules the ionic spontaneous transport



Perovskite capping layer
→ creates O vacancies

E.-J. Guo, Adv. Mat. (2018)

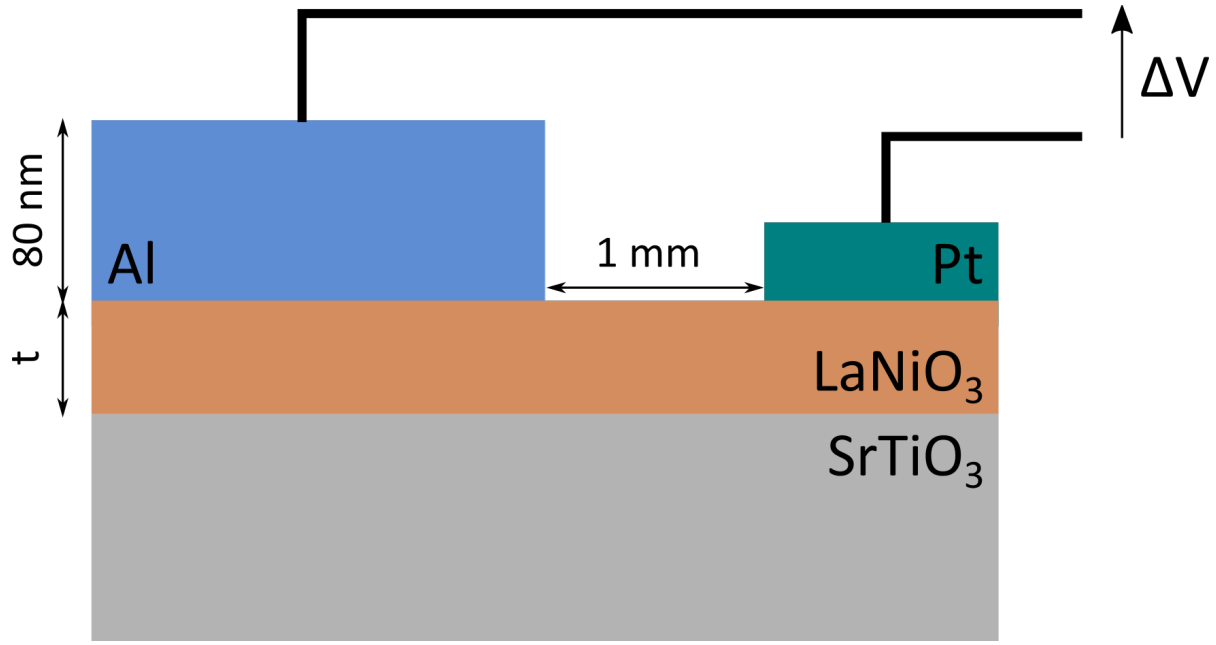
How to tune O vacancy density with an external stimulus?

Vacancy creation by Al capping

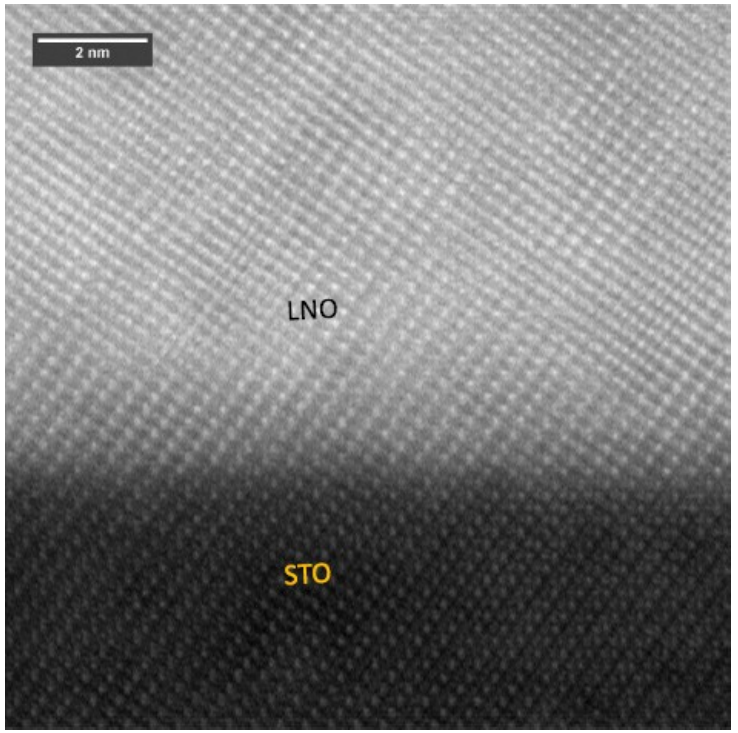
Pulse laser deposition of $LaNiO_3$
rf-sputtering of Al capping layer

A **redox reaction** is expected
→ reduction of $LaNiO_3$
→ oxidization of Al

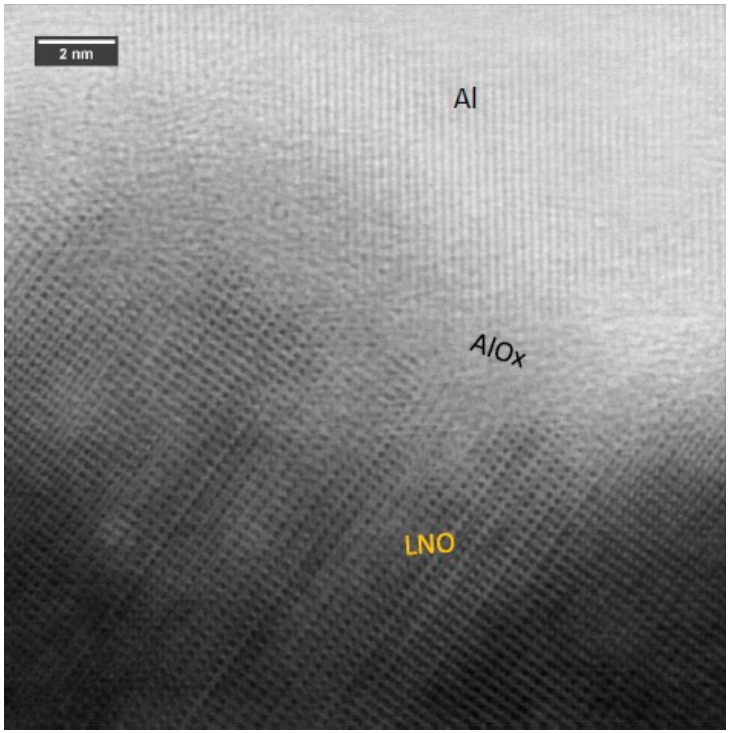
Q. Fu *et al.*, Surf. Sc. Rep. **62** (2007)
T.C. Rödel *et al.*, Acta Mat. **28** (2016)



Redox reaction

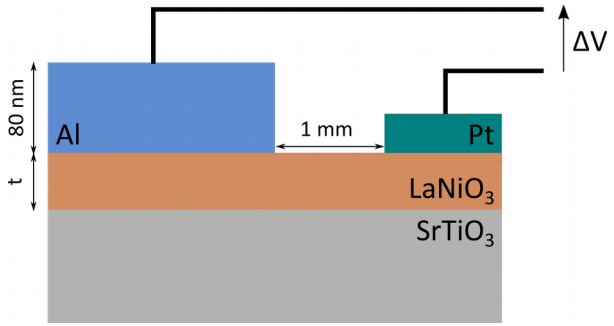


Epitaxial $LaNiO_3$ films

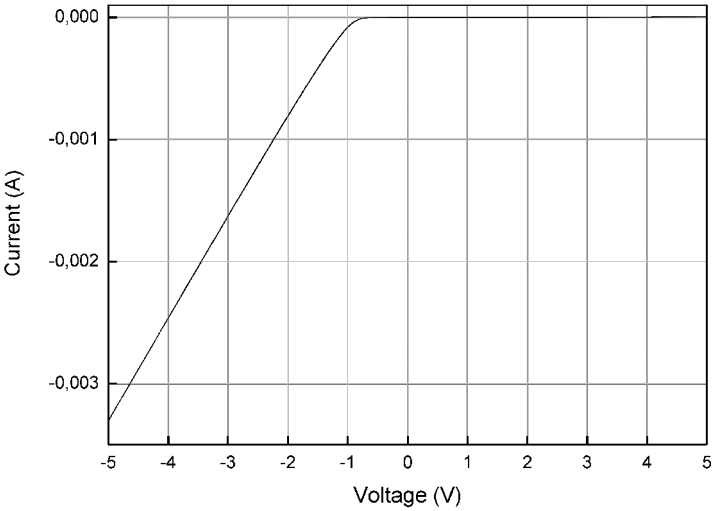


Formation of AlO_x at the interface

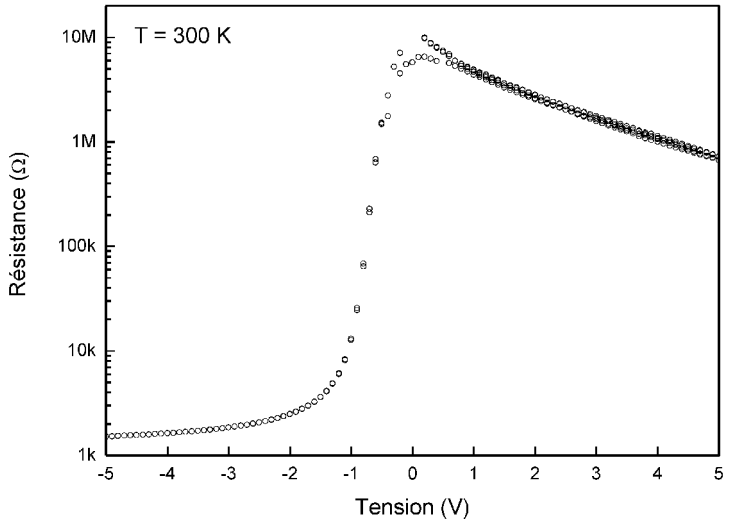
I(V) curve



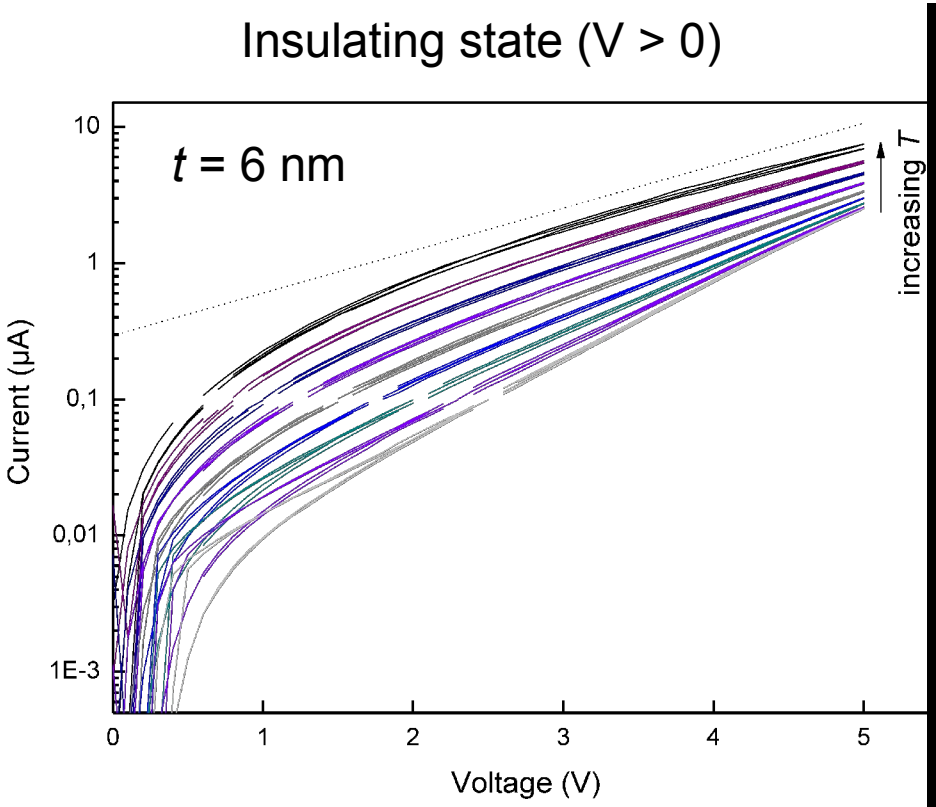
2-probe set-up

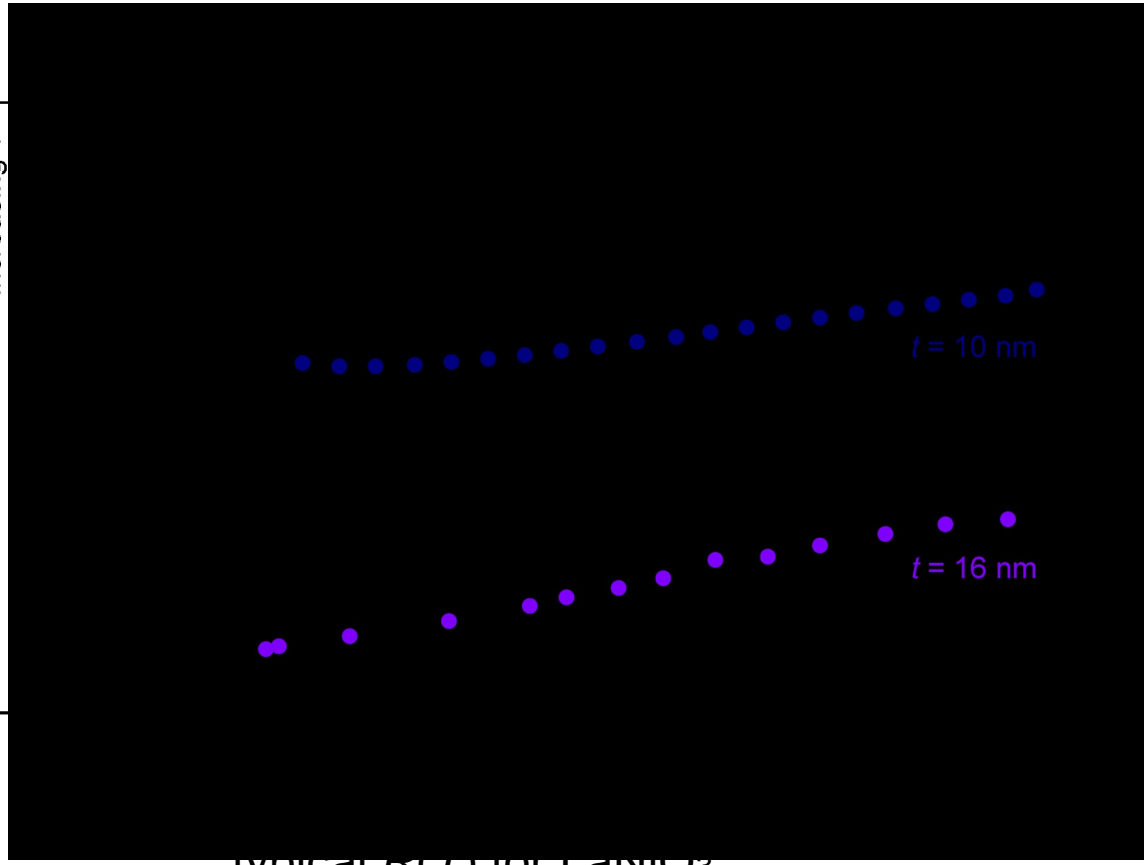


- Diode-like characteristics
- Almost fully reversible
- Robust over tens of cycles
- Electro-resistance up to 10^5 % at room temperature



Electrical properties

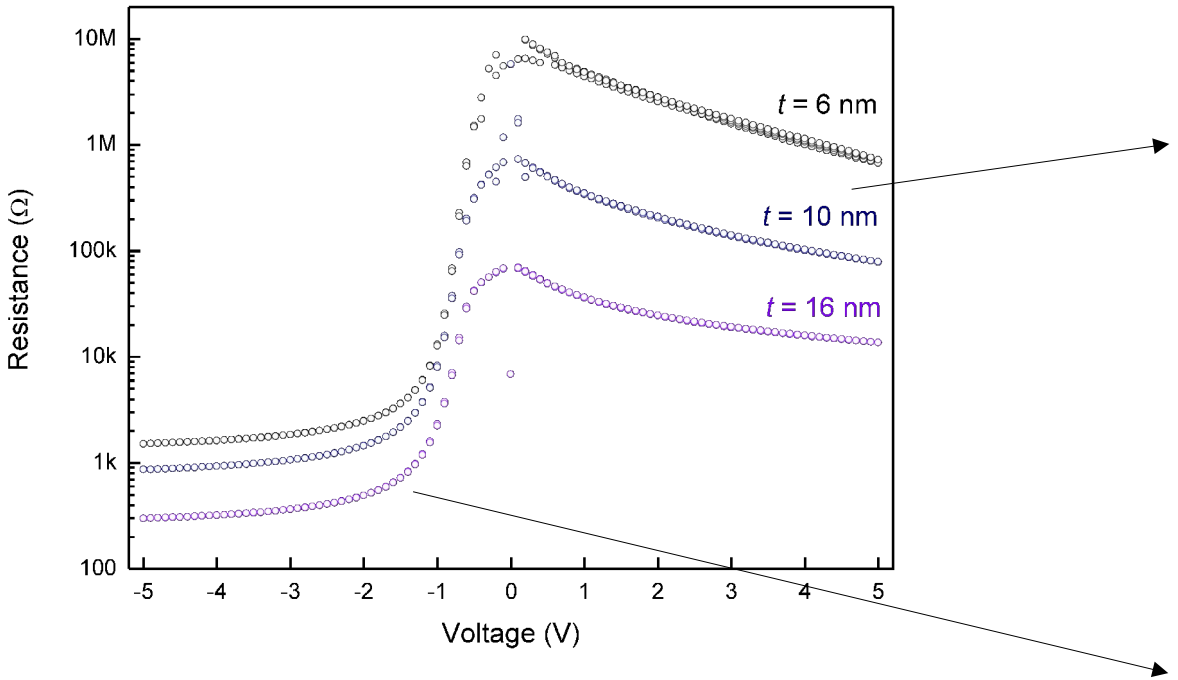


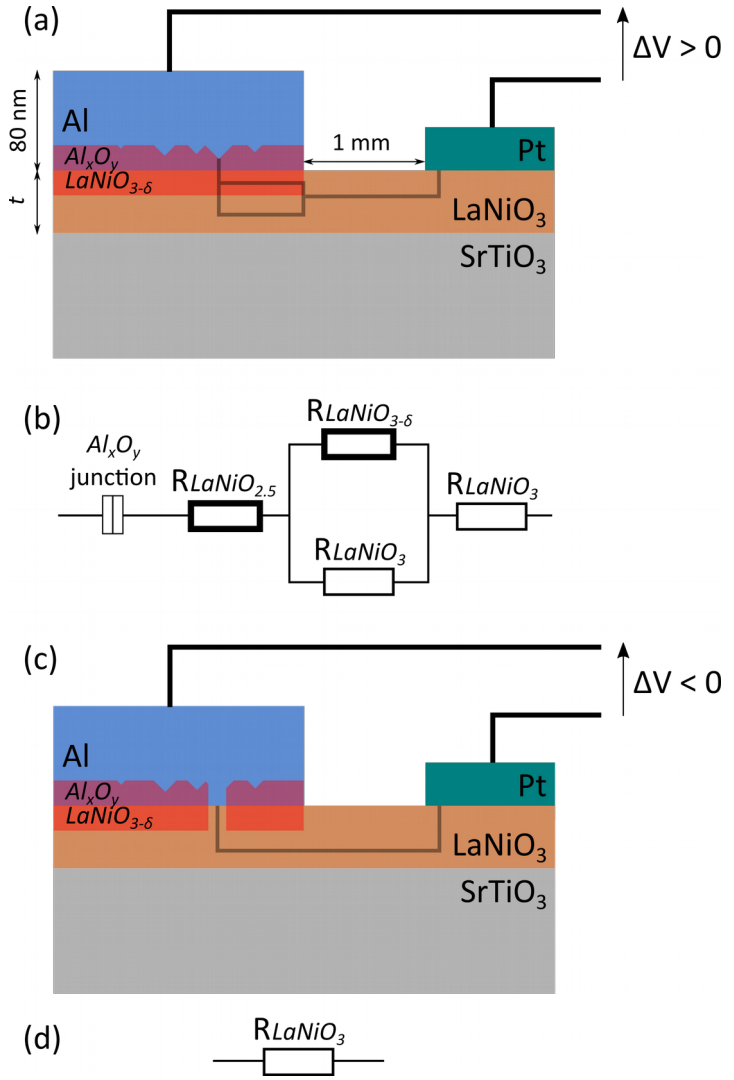


non Schottky behaviour
tunnel-like conductivity
probable multiple tunnelling process
unclear barrier height,active area

typical $R(T)$ for $LaNiO_3$
ρ_0 ~ 2000 µΩ.cm
Direct bias “heals” the native compounds

Conducting paths





Direct bias resistance scales with thickness
Reverse bias resistance is shunted by pristine oxide
$LaNiO_{3-\delta}$ layer is around 6 nm thick
B.Tian *et al.* PCCP **19** (2017)

Sketch of the redox reaction

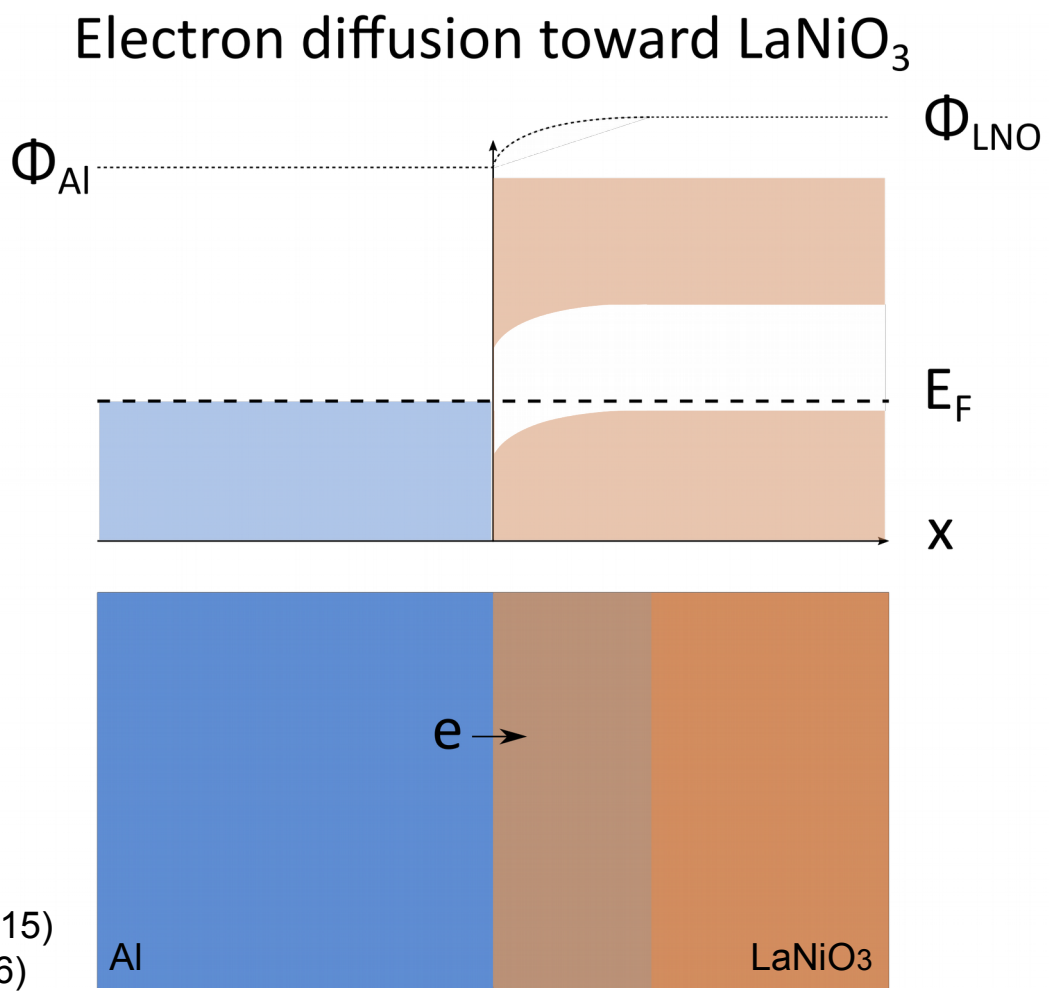
$\Phi LaNiO_3$ = 5.5 eV

$\Phi Al/Al_2O_3$ = 3.9 eV

• recombination of extra electrons with free holes
→ filling of the valence band
→ space charge

• looks like a Schottky contact…

… but there is more.



Y.-C. Yeo *et al.*J. Appl. Phys., **92** (2002)
W. T. Hong *et al.*, J. Phys. Chem. C **119** (2015)
R. Jacobs *et al.*, Adv. Funct. Mater. **26** (2016)

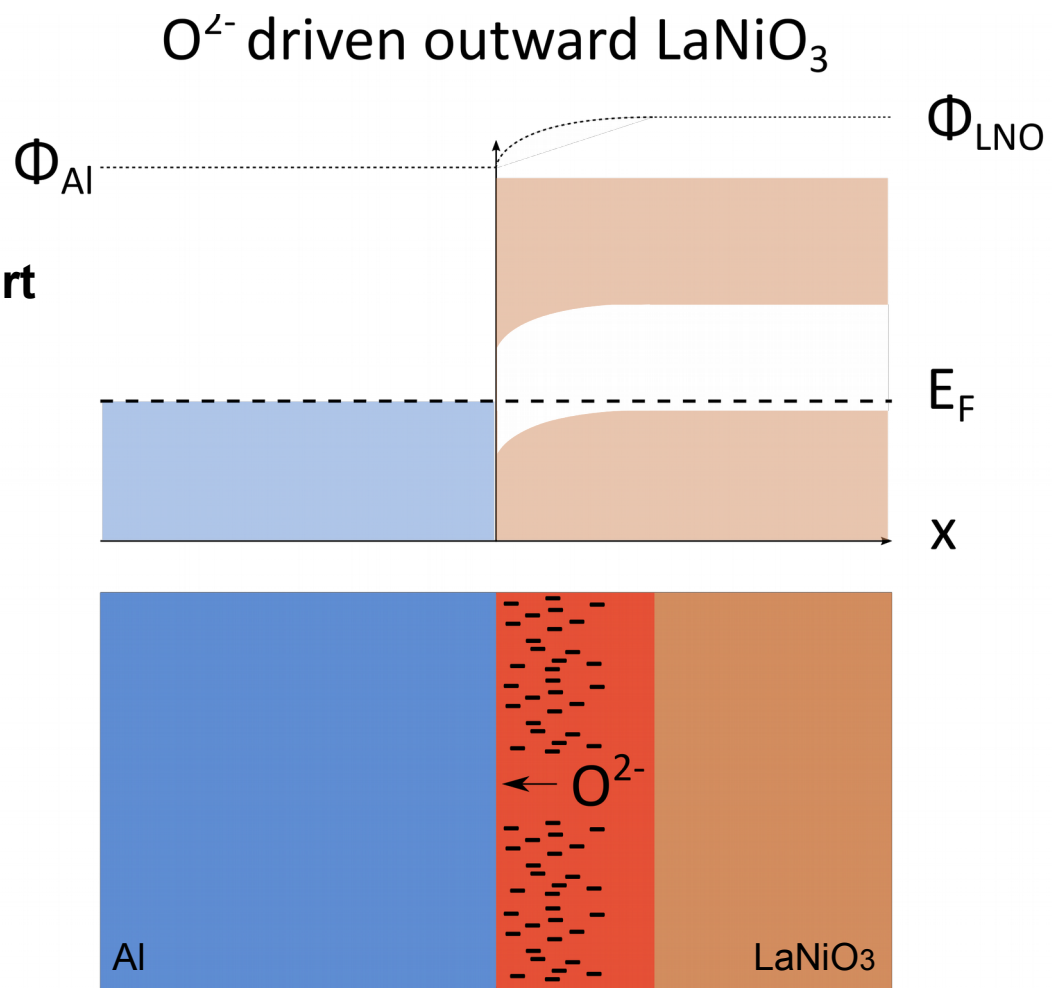
Sketch of the redox reaction

- **charge transfer + mass transport**

- High oxygen mobility in $LaNiO_3$

T. Mayeshiba PCCP **17** (2015)

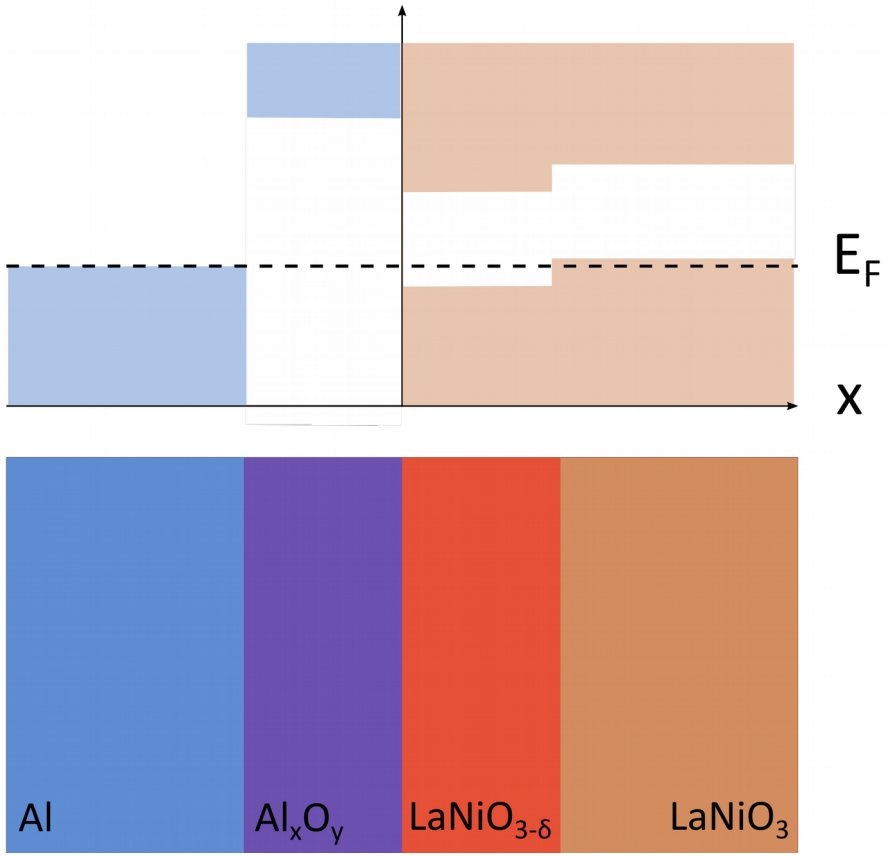
- O-defective planes favor O mobility some more



Sketch of the redox reaction

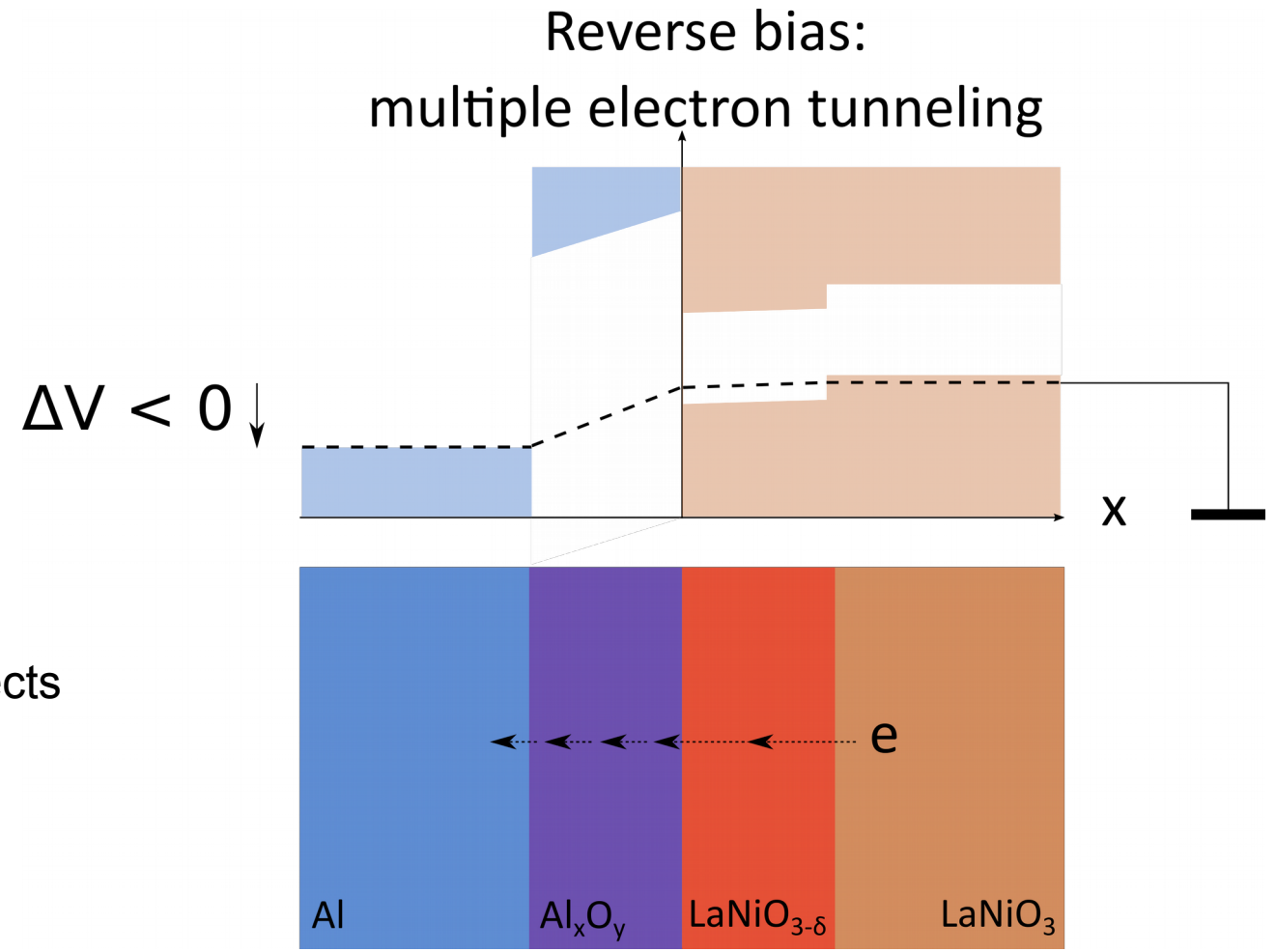
- formation of two extra compounds
- neutral and stable interface

Oxydation of Al & formation of $LaNiO_{3-\delta}$



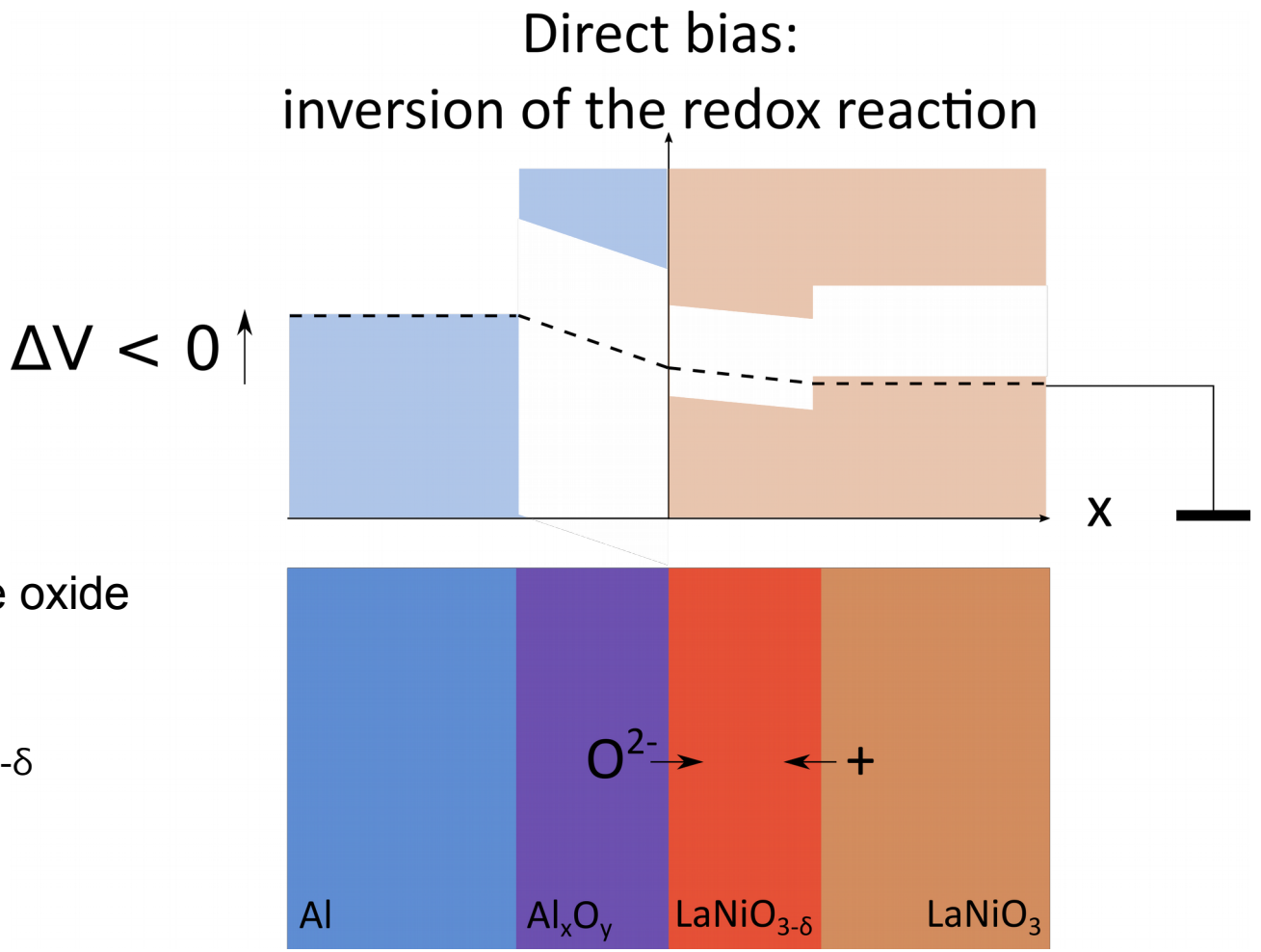
Out of equilibrium

- voltage drops across AlO_x barrier
- no free carriers
  no mobile ions
- tunneling through defects



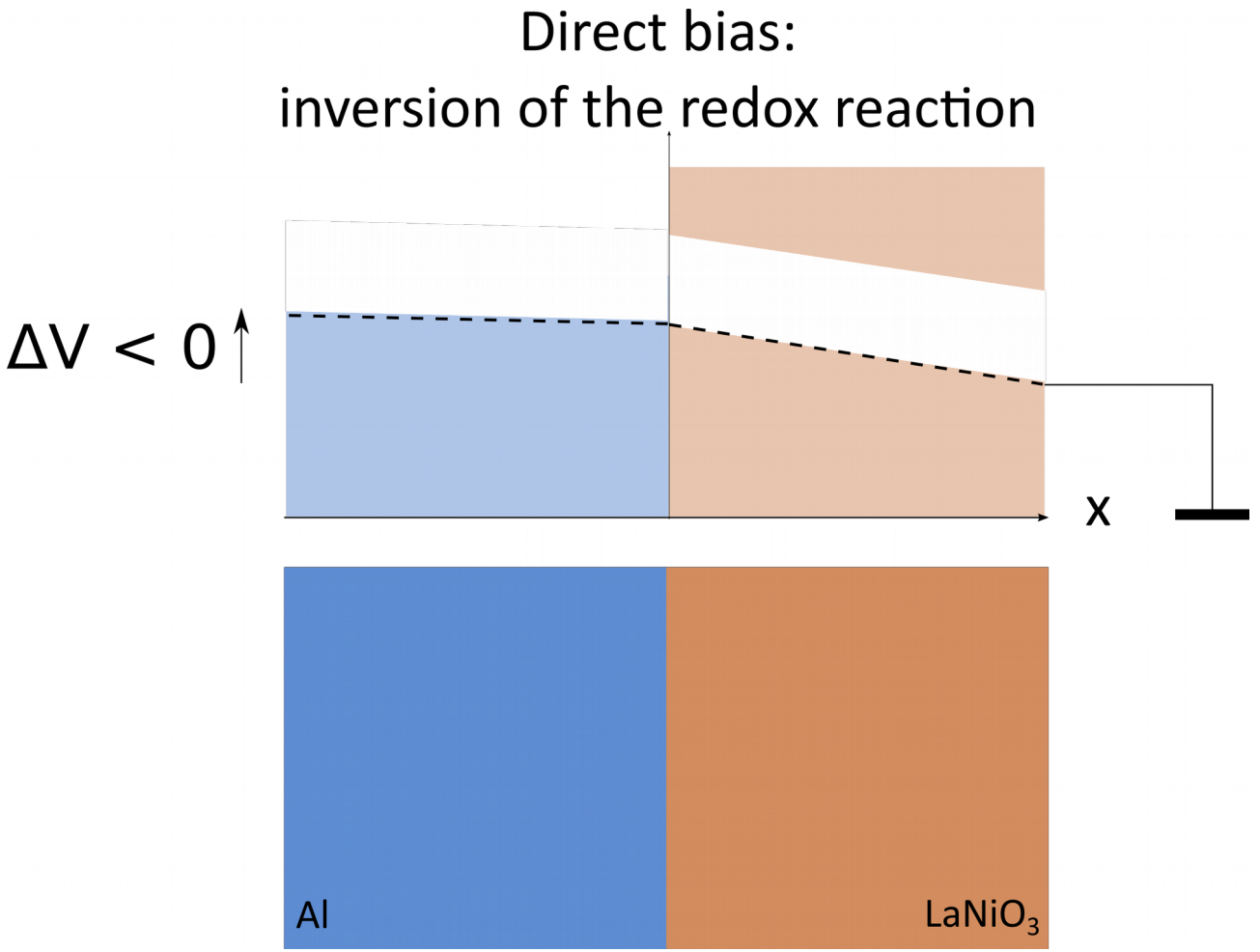
Out of equilibrium

- oxygen ions are driven toward the oxide
- free oxygen sites in the oxide
- free holes are driven from $LaNiO_3$ to $LaNiO_{3-\delta}$

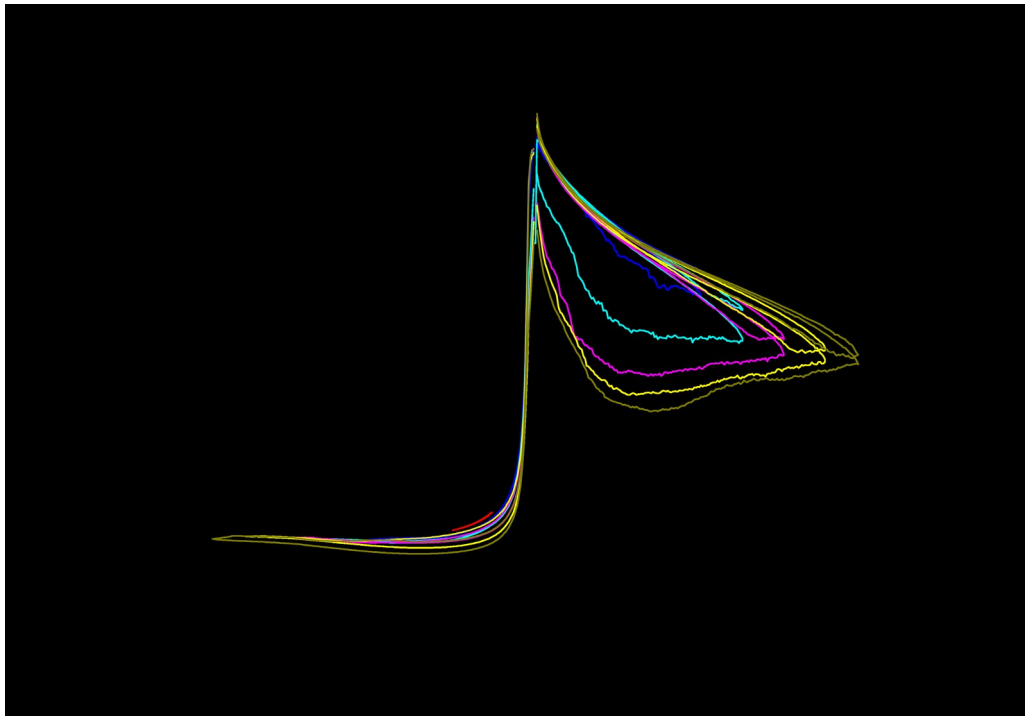


Out of equilibrium

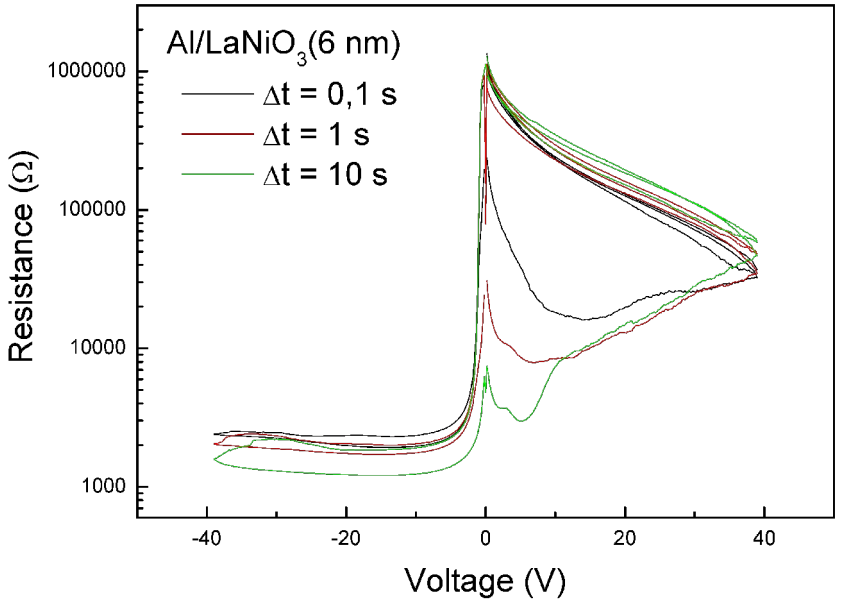
- metallic Al
- metallic $LaNiO_3$



At higher field

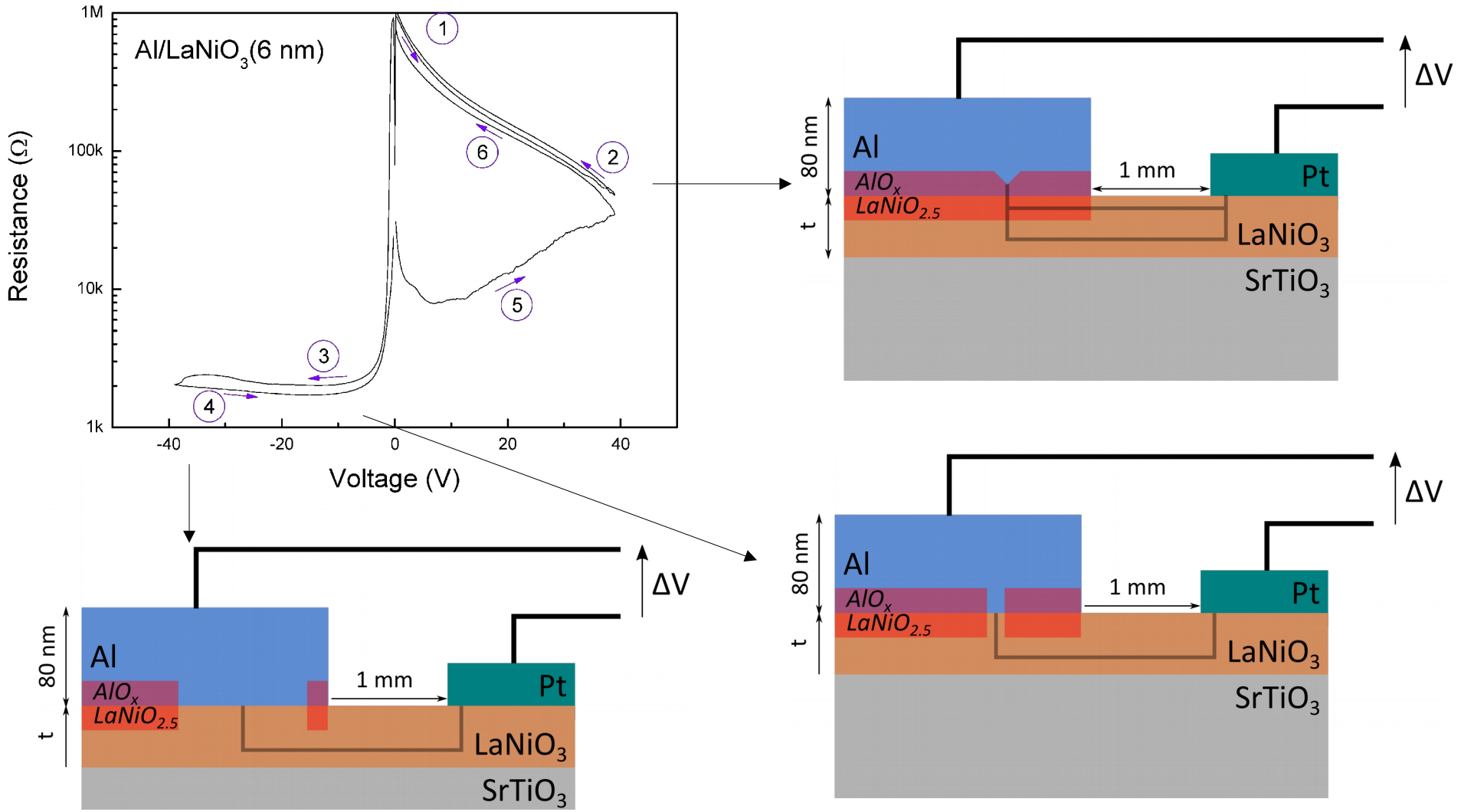


R(V) is irreversible for V > 5 V



Irreversibility ← kinetic process

Evolution of the conducting path



Summary

• LNO combines key parameters (ionic mobility, low vacancy formation energy, p-type conduction, high work function) for manipulation of the oxygen vacancy

• **Resistive switch** is enhanced by the oxidization of aluminum

• **Electro-resistive** effect up to 100 000 % at room temperature

• Functionalisation of a conductive oxide by a straightforward and **inexpensive** process

• **X-ray reflectivity** measured as a function of the applied voltage to probe the heterostructure composition