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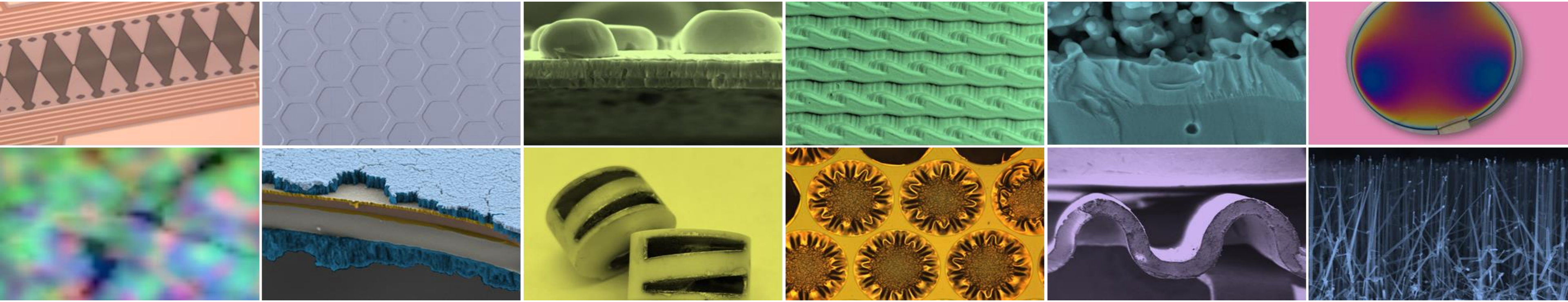
Shaping Energy for a Sustainable Future



Ionotronics

Francesco Chiabrera

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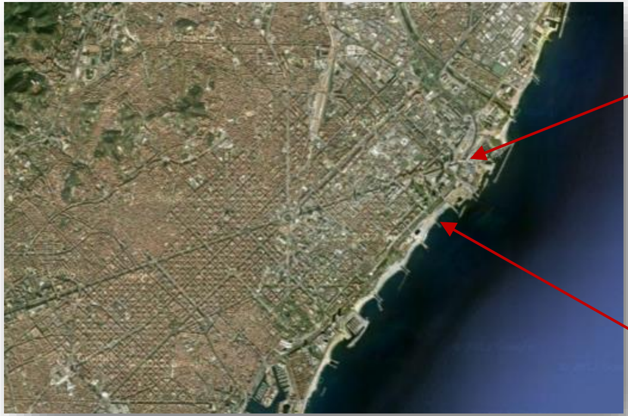
fchiabrera@irec.cat

Solid State Ionics 2024

SSI 2024, Tutorials

Catalonia Institute for Energy Research (IREC)



We are here

This is the beach

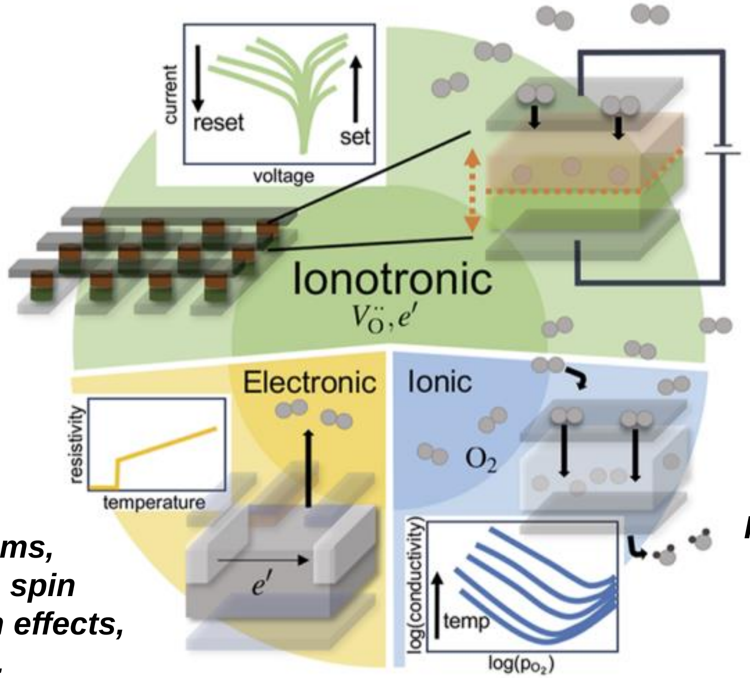
Nanoionics and Fuel Cell group

https://www.atlab.es/

What is ionotronic?

Memristors, Electrochemical ion synapsis, electrochromic windows, magnetoionics, optoionics

Control of device functionalities through the accumulation/ insertion/ variation of ion concentration



Ionotronic phenomena in transition metal oxides

Correlated systems, Superconductors, spin modulation, quantum effects, transistors,…

Ionic conductors, Fuel cells, Sensors,

Wenderott et al., APL Mater. 12, 050901 (2024)

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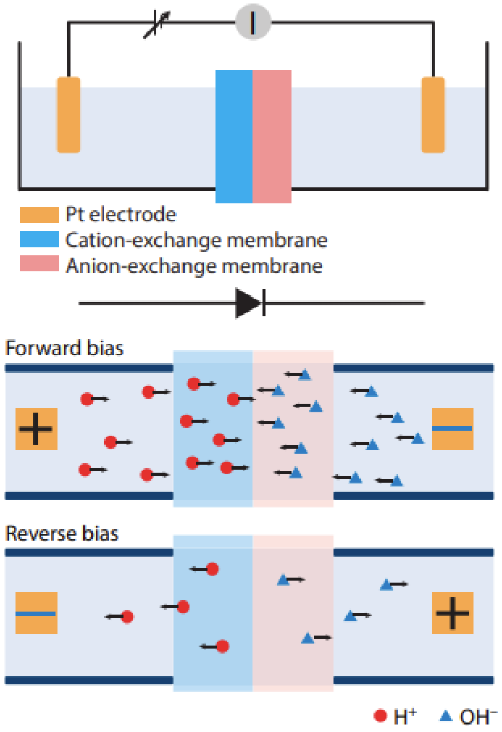
However, Iontronics is also

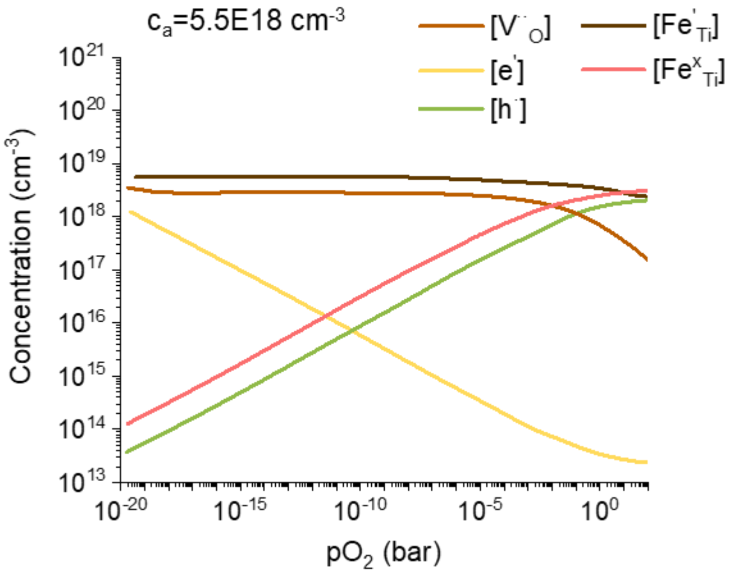
Ions as signal carriers



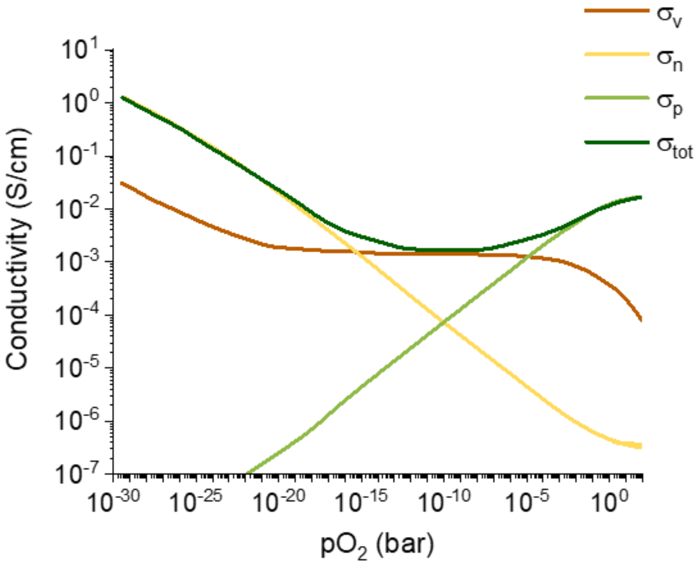
Chun et al., Annu. Rev. Anal. Chem. 2015. 8:441–62

Metal transition oxides: defect concentration and conductivity

Brouwer diagram: $SrTiO_3$ at 900ºC



Conductivity variation



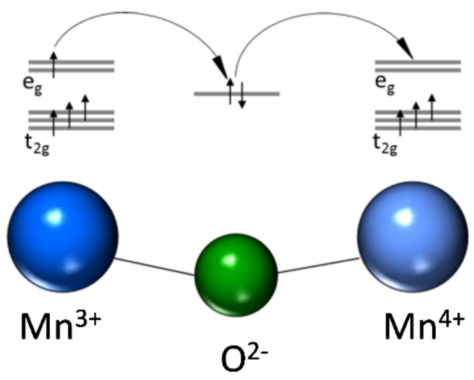
And also magnetic, optical, dielectric,…

I. Denk, et al., J. Am. Ceram. Soc. 78 (12) (1995) 3265e3272

Complex oxides: a very rich playground! Examples: $La_{1-x}Sr_xMnO_3$

Electronic transport

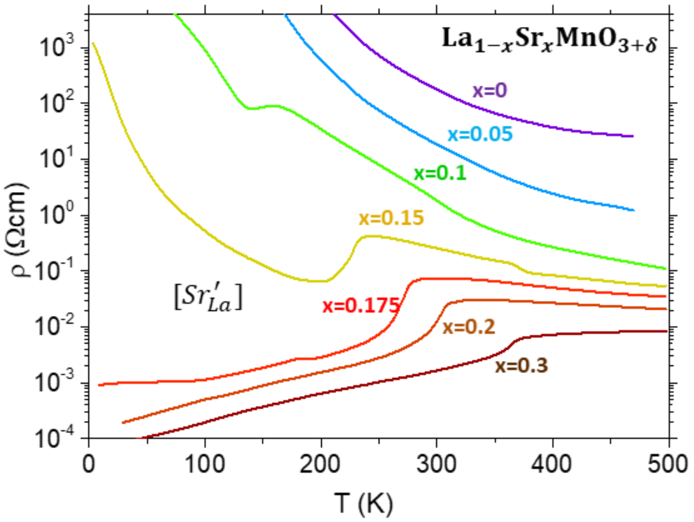
$$[Sr'_{La}] = [h^{\bullet}]$$

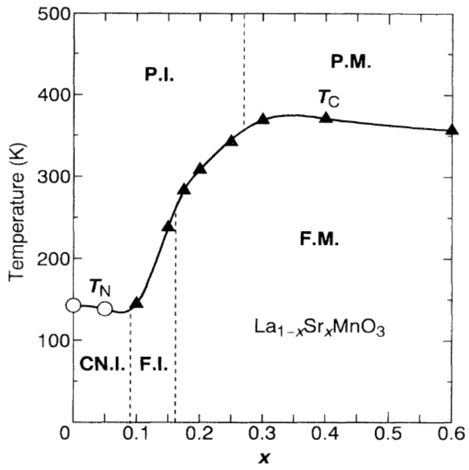


Above Tc: holes localized by electron-phonon coupling phenomena

Below Tc: alignment spins permits double exchange and metallic behavior

Electronic and magnetic properties



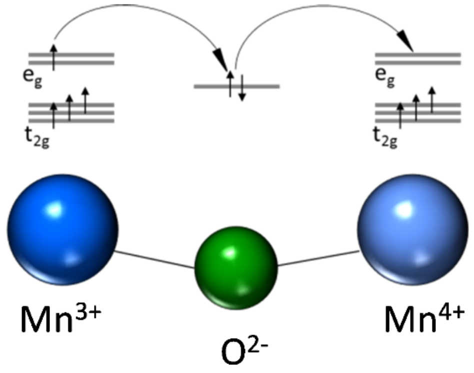


Urushibara, A. *et al.*, *Phys. Rev. B* **51,** 103–109 (1995).

Complex oxides: a very rich playground! Examples: $La_{1-x}Sr_xMnO_3$

Electronic transport

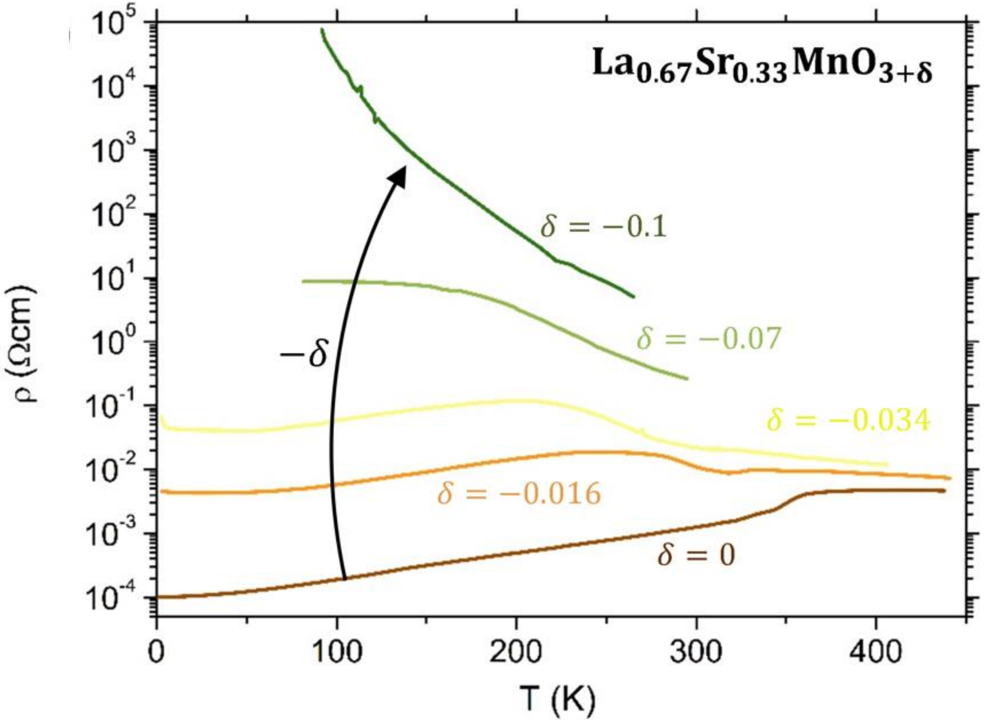
$$[Sr'_{La}] = [h^{\bullet}] + 2[v_O^{\bullet\bullet}]$$



Above Tc: holes localized by electron-phonon coupling phenomena

Below Tc: alignment spins permits double exchange and metallic behavior

Effect of oxygen vacancies on MI transition



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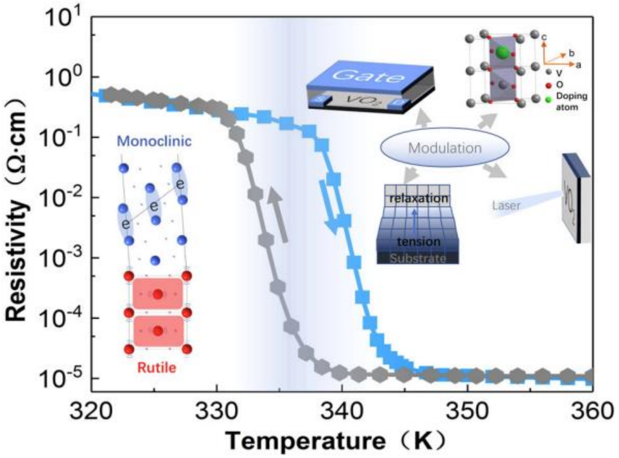
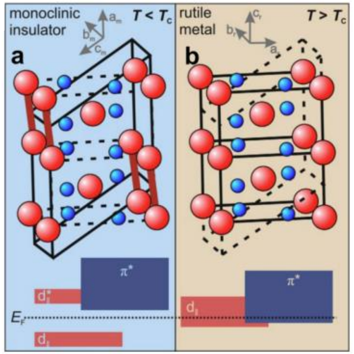
Complex oxides: a very rich playground! Examples: VO_2

Metal insulator transition

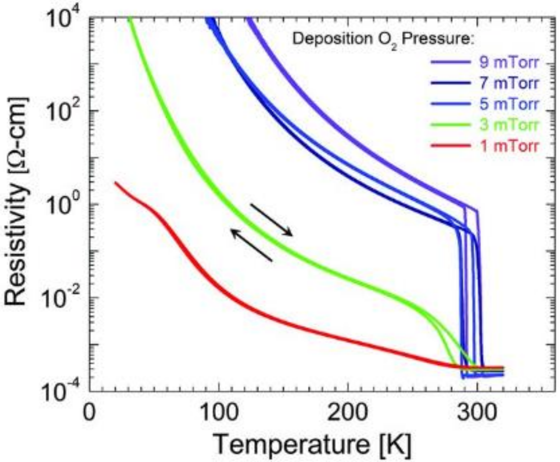


Phase change



Mott insulator Metal

Oxygen vacancy modulation



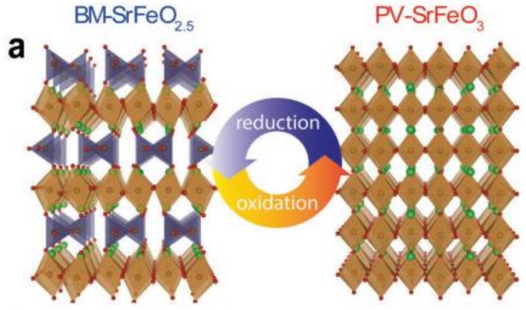
Shao et al. NPG Asia Materials (2018) 10: 581-605

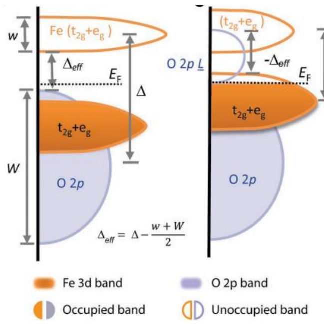
Wegkamp, D. & Stähler, J, Prog. Surf. Sci. (2015) 90, 464–502

Jaewoo Jeong et al., Science,339,1402-1405(2013)

Complex oxides: a very rich playground! Examples: $SrFeO_{3-\delta}$

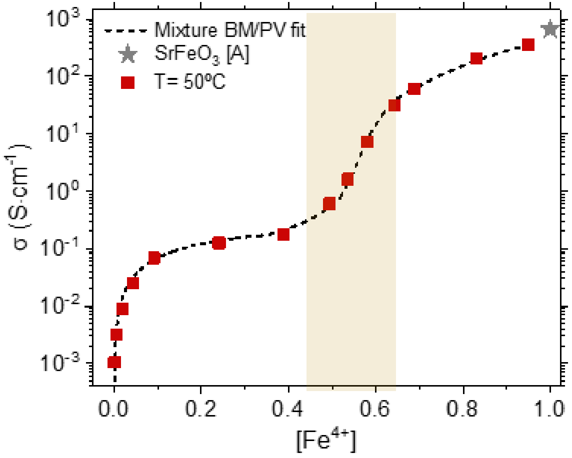
Topotactic transition

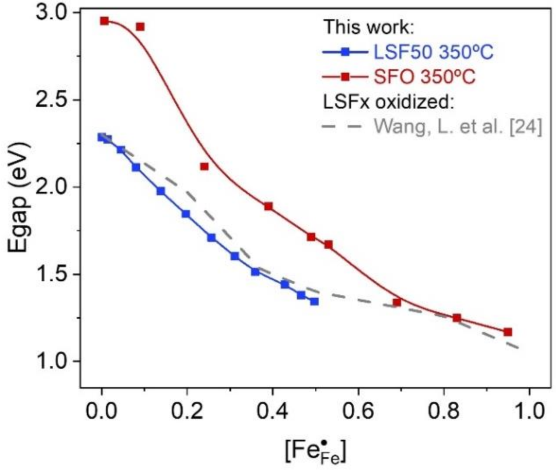




Nallagatla et al., Adv. Mater. 2019, 31, 1903391

Large conductivity and optical modulation



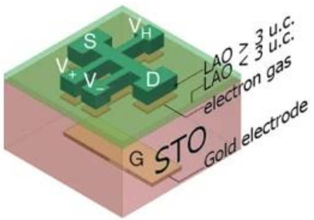


Nizet et al., submitted

How to modulate the ionic concentration of complex oxides?

Field effect

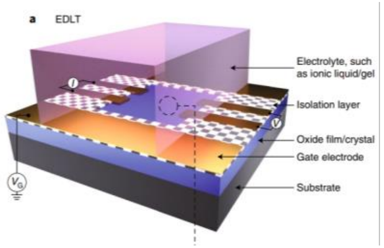
Application of E in the linear range through a dielectric



Caviglia et al, Nature (2008) 456, 624–627

Electrolyte double layer

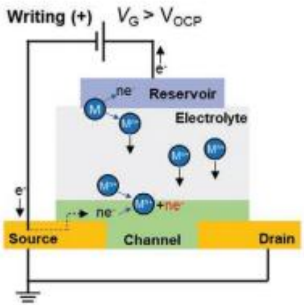
Application of E in the linear range through an ionic conductor



Leighton et al., Nat. Mat., (2019), 18, 13-18

Redox ionic insertion

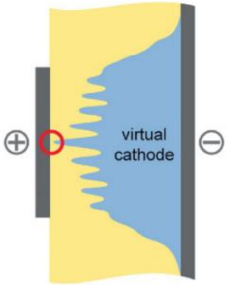
Application of E in the linear range through an ionic conductor



Huang et al., Adv. Mater. 2023, 35, 2205169

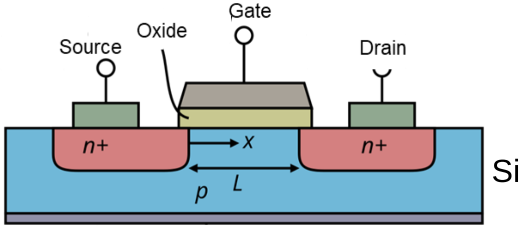
Resistive switching

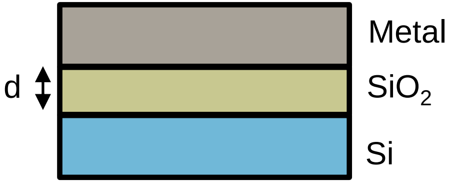
Application of large E directly to the material



Waser el al., Adv. Mater. 2009, 21, 2632–2663

Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET)





$C = \varepsilon_0 \varepsilon_R / d$ (F/cm^2)

$10\ nm, C \sim 0.3\ \mu F/cm^2$

$Q_c = C \cdot V \sim 0.3\ \mu C/cm^2$

Poisson equation

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon_0 \varepsilon_R}$$

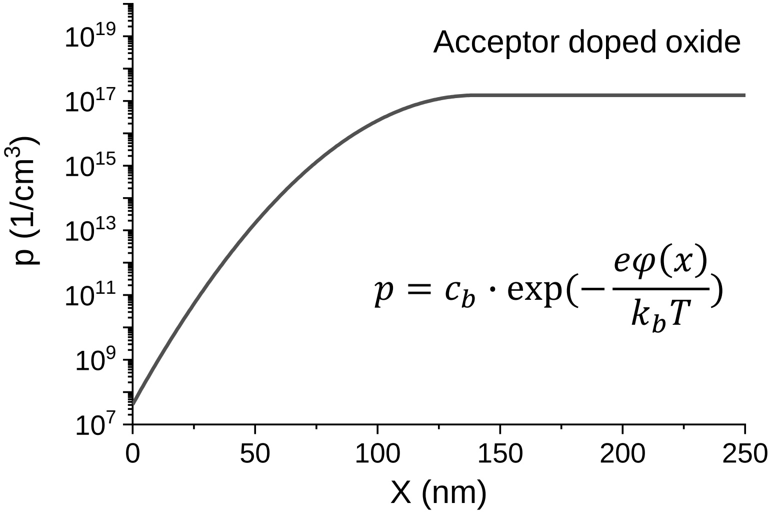
Space charge (sum of all charge and mobile defects)

Depletion approx. 1D

$$\rho = c_b$$

$\varphi(x) = \varphi_0 \left(\frac{x}{\lambda} - 1\right)^2$ for $x < \lambda, \lambda = \left(\frac{2\varepsilon_0 \varepsilon_R \varphi_0}{e c_b}\right)^{\frac{1}{2}}$

$$Q_c = (2\varepsilon_0 \varepsilon_R e \varphi_0)^{\frac{1}{2}}$$



$p = c_b \cdot \exp(-\frac{e\varphi(x)}{k_b T})$

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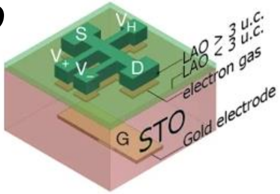
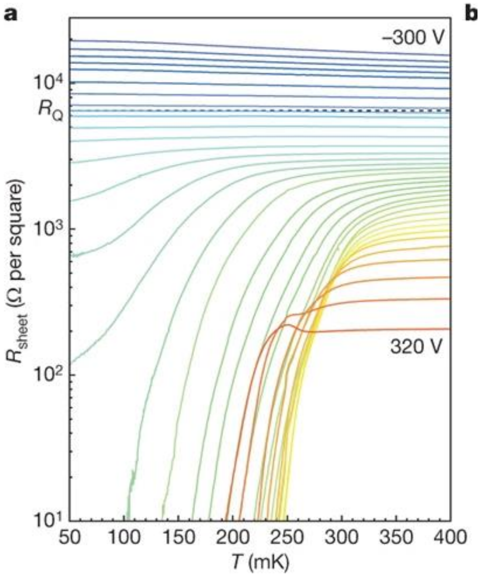
Electric field effect modulation of superconductivity in LAO/STO

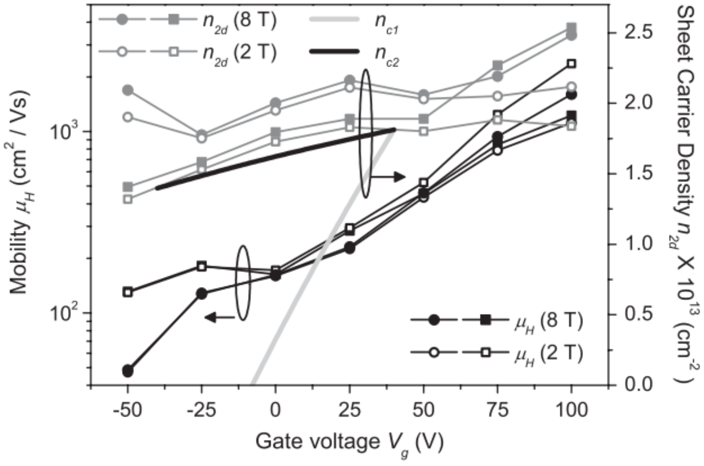
LAO/STO





Caviglia et al, Nature (2008) 456, pages624–627

Mobility modulation rather than carrier



Bell et al., PRL 103, 226802 (2009)

- STO thick and large potentials
- Large dielectric constant at low T
- Very low defect concentration necessary

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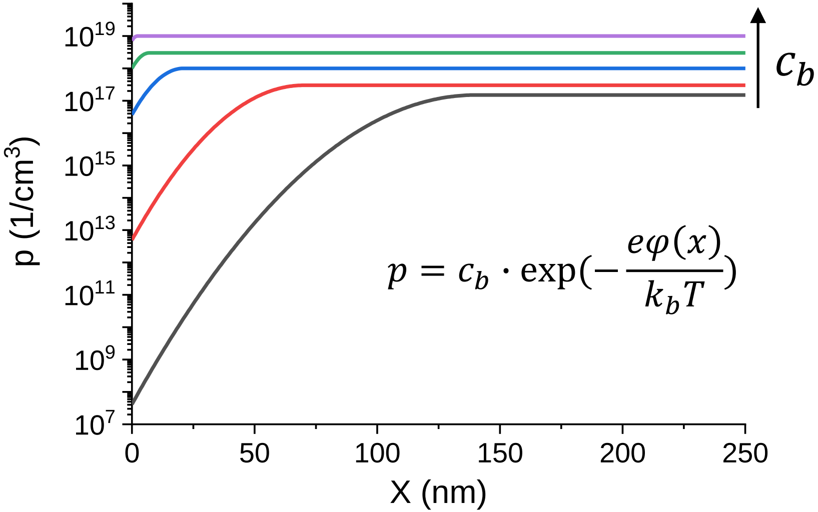
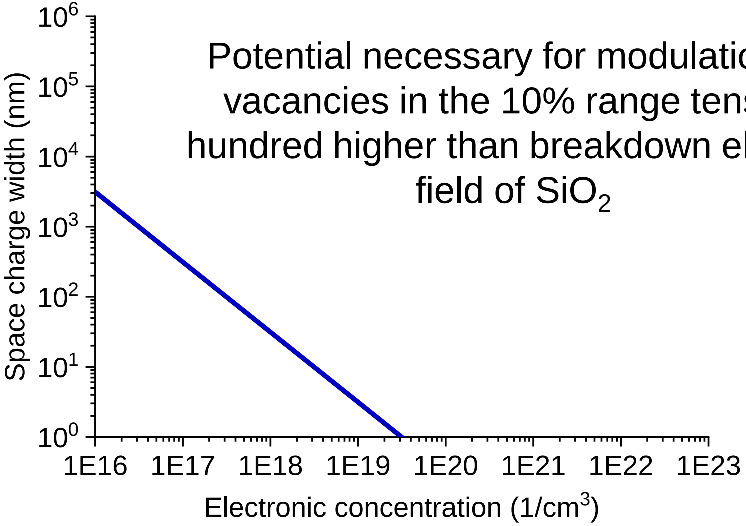
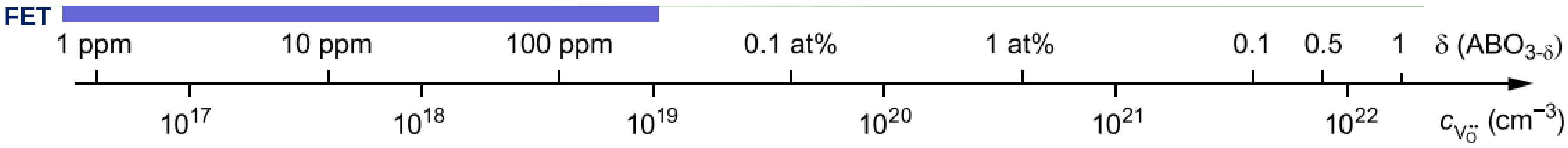
Problem! FET effect non large for high dopant concentration



$$p = c_b \cdot \exp(-\frac{e\varphi(x)}{k_b T})$$



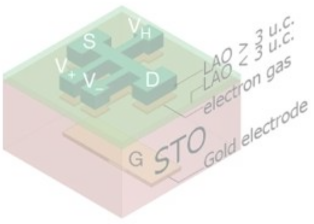
Potential necessary for modulation of vacancies in the 10% range tens to hundred higher than breakdown electric field of SiO_2



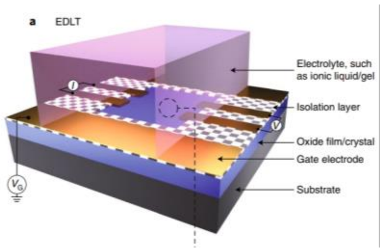
F. Gunkel et al., Appl. Phys. Lett. 116, 120505 (2020)

How to modulate the ionic concentration of complex oxides?

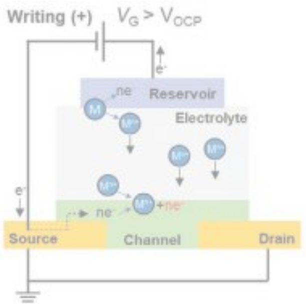
Field effect	***Electrolyte double layer***	*Redox ionic insertion*	*Resistive switching*
Application of E in the linear range through a dielectric	*Application of E in the linear range through an ionic conductor*	*Application of E in the linear range through an ionic conductor*	*Application of large E directly to the material*



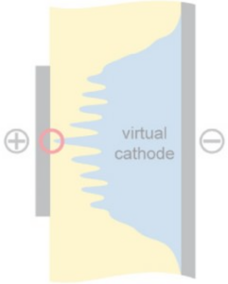
Caviglia et al, Nature (2008) 456, 624–627



Leighton et al., Nat. Mat., (2019), 18, 13-18

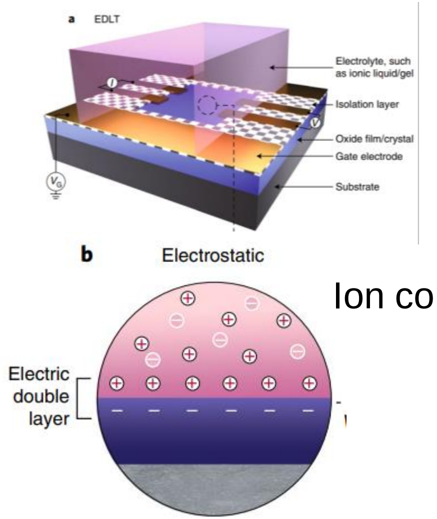


Huang et al., Adv. Mater. 2023, 35, 2205169



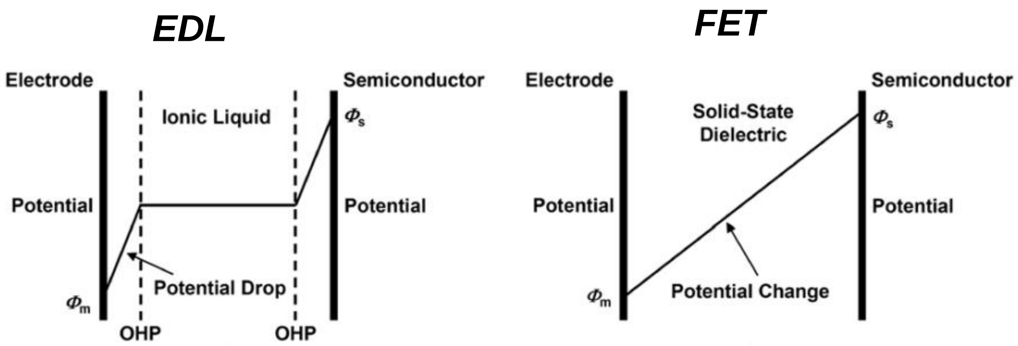
Waser el al., Adv. Mater. 2009, 21, 2632–2663

Electrolyte double layer (EDL) in ionic conductors

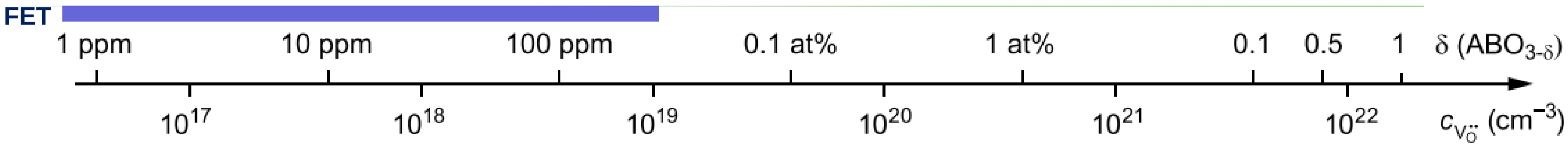


Ion conductor

Leighton et al., Nat. Mat., (2019), 18, 13-18



Fujimoto et al., Phys. Chem. Chem. Phys., 2013, 15, 8983--9006



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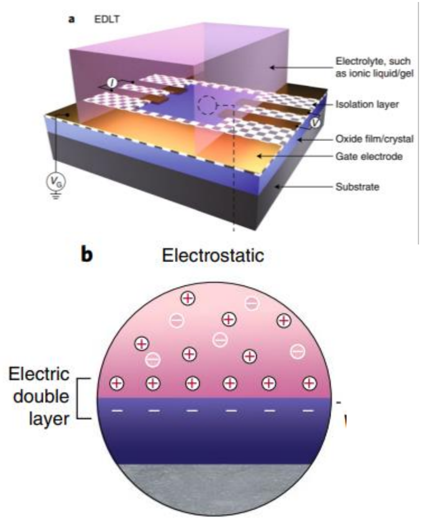
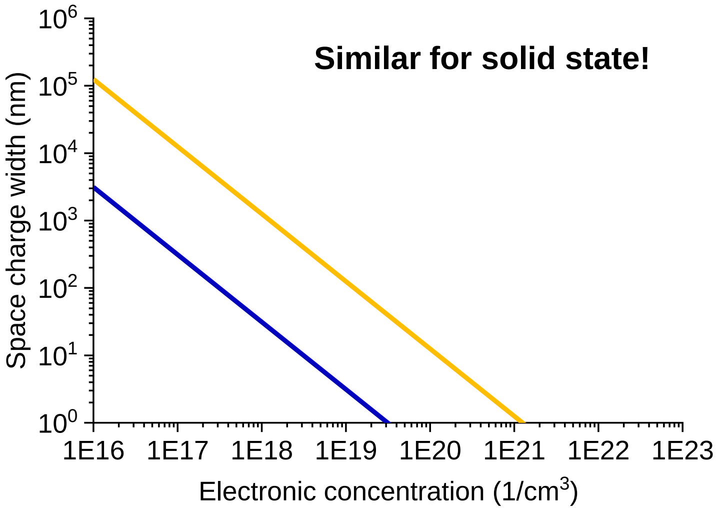


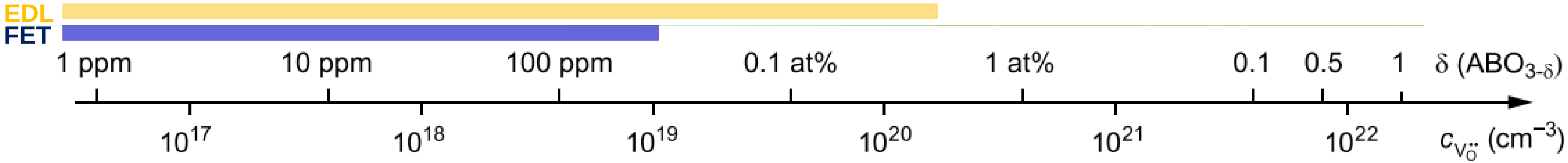
Leighton et al., Nat. Mat., (2019), 18, 13-18

$$C = \frac{\varepsilon_0 \varepsilon_R}{d} \sim \frac{10\varepsilon_0}{10^{-7}} \sim 10\ \mu F/cm^2$$

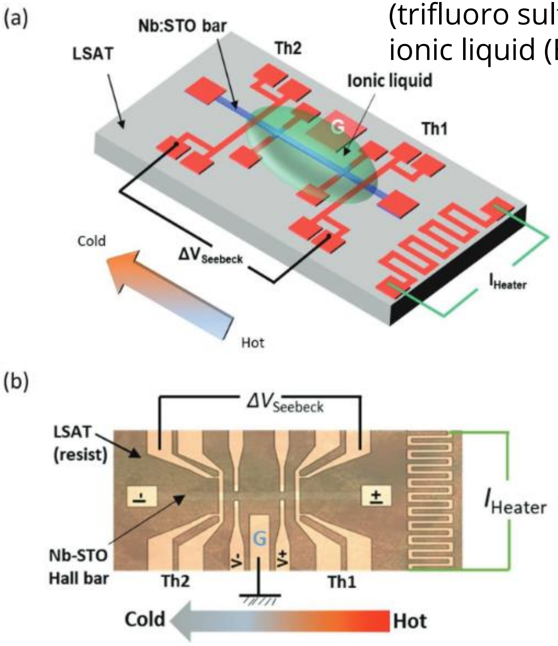
$$Q_c = C \cdot V \sim 10\ \mu C/cm^2$$

Switch time: $\tau = RC$

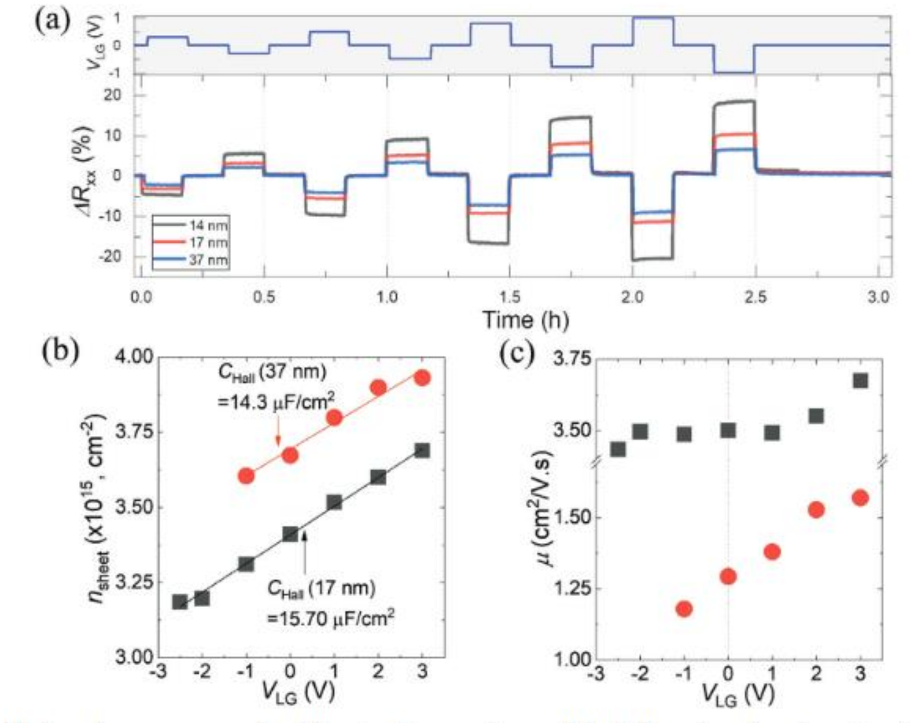




EDL modulation of charge carriers in Nb:SrTiO3 thin films



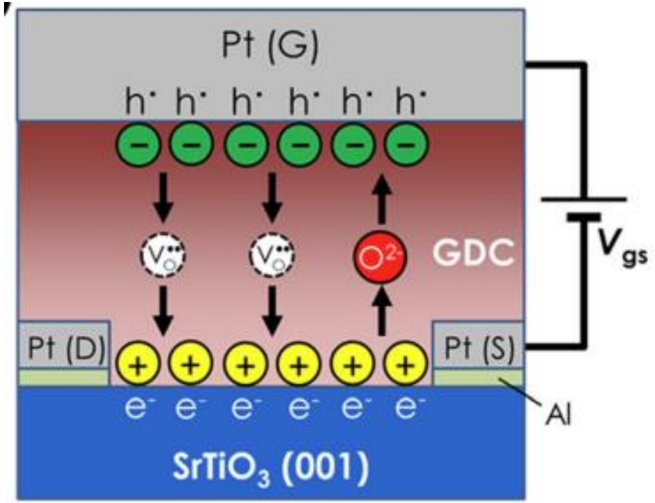
1-ethyl-3-methylimidazolium-bis (trifluoro sulfonyl) amide ionic liquid (EMIM-TFSI)

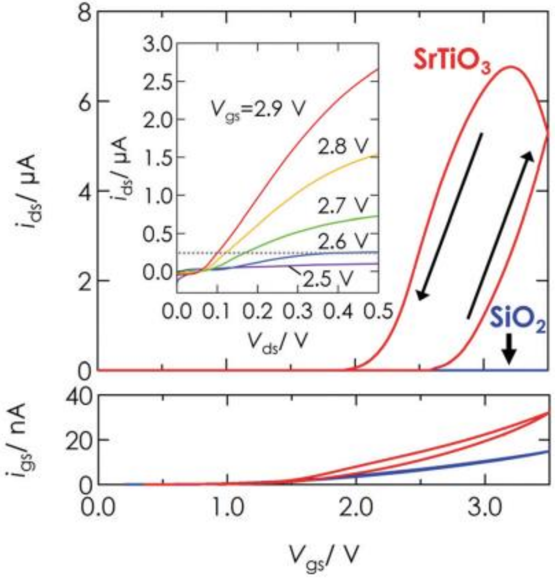


A. Chatterjee et al., Adv. Electron. Mater. 2024, 10, 2300683

EDL modulation in solid-state ionic conductors

T=200 ºC





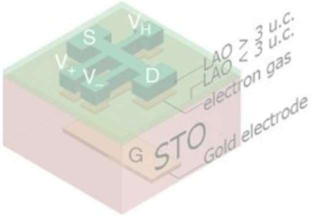
$$C \sim 14\ \mu F/cm^2$$

Takashi Tsuchiya et al., APPLIED PHYSICS LETTERS 103, 073110 (2013)

How to modulate the ionic concentration of complex oxides?

Field effect

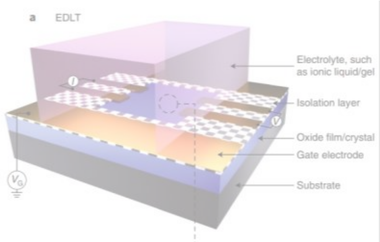
Application of E in the linear range through a dielectric



Caviglia et al, Nature (2008) 456, 624–627

Electrolyte double layer

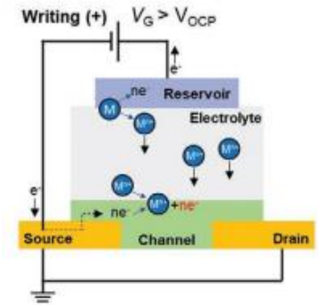
Application of E in the linear range through an ionic conductor



Leighton et al., Nat. Mat., (2019), 18, 13-18

Redox ionic insertion

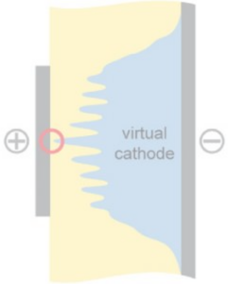
Application of E in the linear range through an ionic conductor



Huang et al., Adv. Mater. 2023, 35, 2205169

Resistive switching

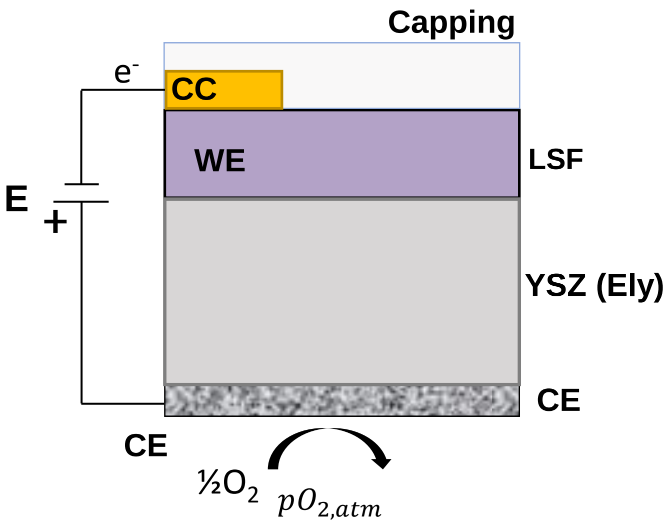
Application of large E directly to the material



Waser el al., Adv. Mater. 2009, 21, 2632–2663

Electrolyte redox-ion insertion: a useful case study

Oxygen modulation in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ (LSF)



1st Ideal case:

- Surface capped
- No diffusion losses
- No insertion losses at LSF/YSZ
- Resistive electrolyte

$$\frac{1}{2}O_2 + 2e' \leftrightharpoons O^{2-}$$

Electrochemical potential

$$\mu_O + 2\tilde{\mu}_{e'} = \tilde{\mu}_{O^{2-}}$$

Same for gradients

$$\nabla\mu_O + 2\nabla\tilde{\mu}_{e'} = \nabla\tilde{\mu}_{O^{2-}}$$

At equilibrium (capping) $\nabla\tilde{\mu}_{O^{2-}} = 0$ *No flux*

Difference → $\Delta\mu_O = -2\Delta\tilde{\mu}_{e'} = 2e\Delta E$

$$\mu_o^{WE} = 2e\Delta E + \mu_o^{ATM} = 2e\Delta E + \frac{kT}{2}\ln\left(\frac{pO_{2,atm}}{1bar}\right)$$

$$\mu_O^{ATM} = 1/2\mu_{O_2}^{ATM}$$

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Oxygen modulation in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ (LSF)

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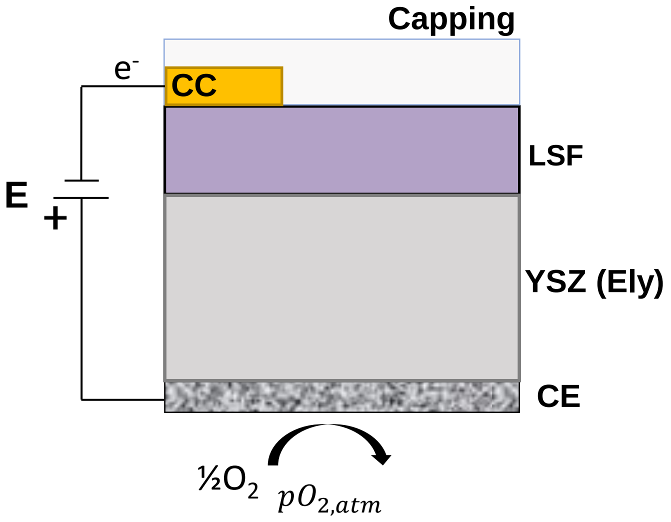


$$\mu_o^{WE} = 2e\Delta E + \frac{kT}{2}\ln(\frac{pO_{2,atm}}{1bar})$$

Using the definition of chem. Pot

Equivalent pO2 of the electrode:

$$\mu_o^{WE} = \frac{kT}{2}\ln\left(\frac{pO_{2,eq}}{1bar}\right)$$

$$\longrightarrow \quad pO_{2,eq} = pO_{2,atm} \cdot \exp(\frac{4e\Delta E}{k_b T})$$

Material's defect chemistry

$$\frac{1}{2}O_2 + v_O^{\bullet\bullet} \leftrightarrow O_O^x + 2h^\bullet$$

$$K_{ox} = \frac{pO_{2.eq}^{1/2}[v_O^{\bullet\bullet}]}{[O_O^x][h^\bullet]^2}$$

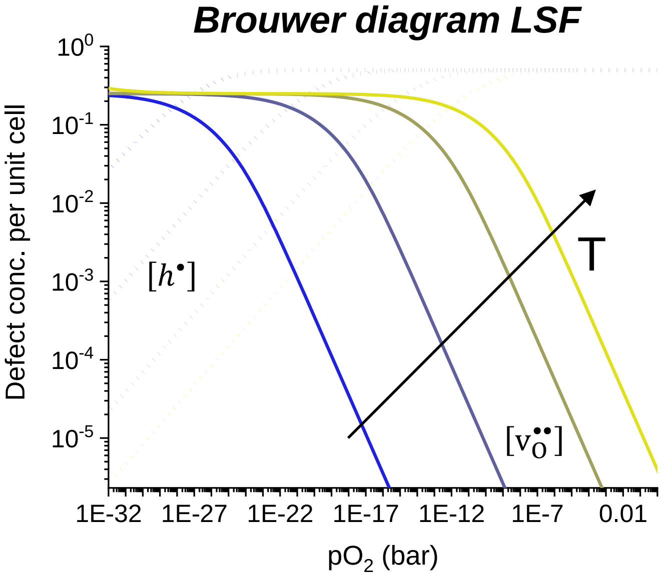
Schmid et al., Phys. Chem. Chem. Phys., 2018, 20, 12016

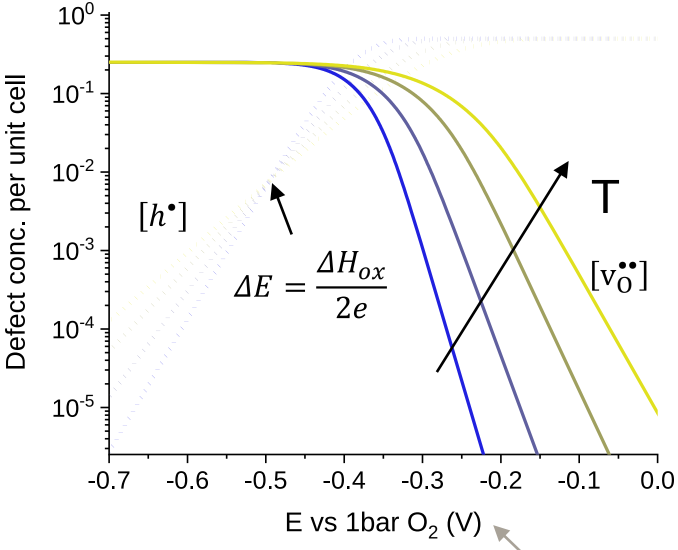
Defect modulation by electrolyte ionic insertion

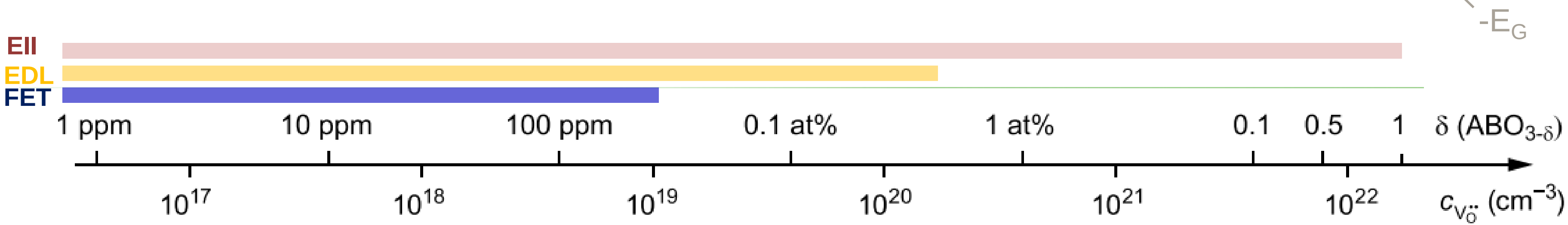
$$\begin{cases} K_{ox} = \dfrac{pO_{2,eq}^{1/2}[v_O^{\bullet\bullet}]}{[O_O^x][h^\bullet]^2} \\ [Sr'_{La}] = [h^\bullet] + 2[v_O^{\bullet\bullet}] \\ [O_O^x] = 3 - [v_O^{\bullet\bullet}] \end{cases}$$

$$K_{ox} = \exp\left(\frac{\Delta S_{ox}}{k_b} - \frac{\Delta H_{ox}}{k_b T}\right)$$

$$pO_{2,eq} = pO_{2,atm} \cdot \exp\left(\frac{4e\Delta E}{k_b T}\right)$$





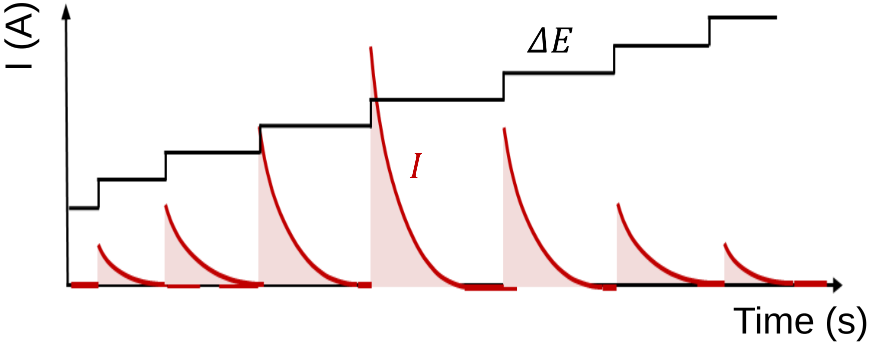


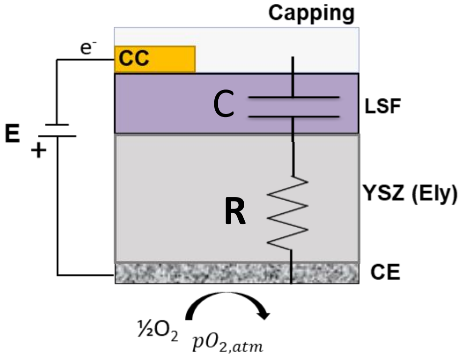
IREC Shaping Energy for a Sustainable Future

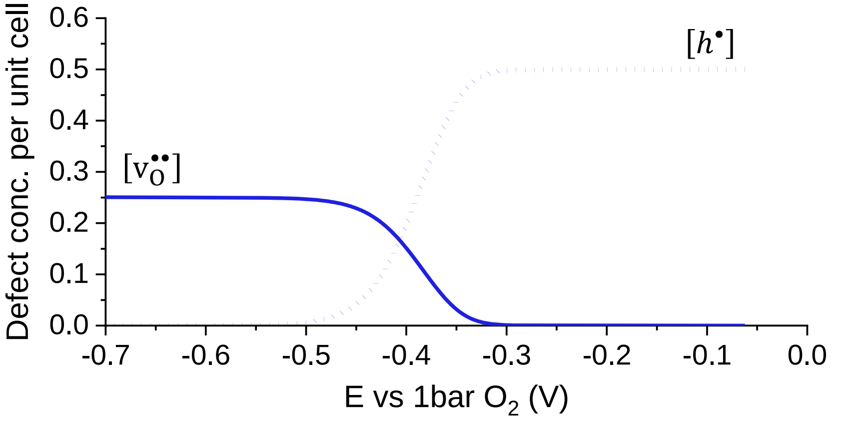
Current-Voltage relation and insertion characteristics

1st Ideal case:

- Surface capped
- No diffusion losses
- No insertion losses at LSF/YSZ
- Resistive electrolyte
- Fast electronic conduction







Relation vac-current

$$\Delta[v_O^{\bullet\bullet}] = -\frac{c_{LSF}^3}{2eV_{film}} \int_0^t I_G(t)dt$$

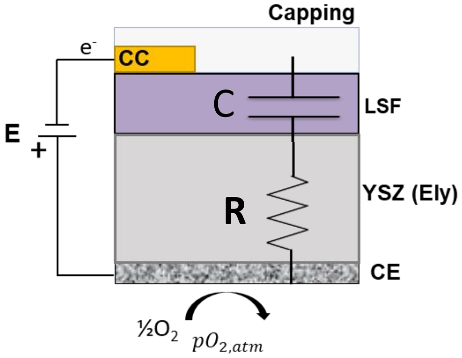
Time constant

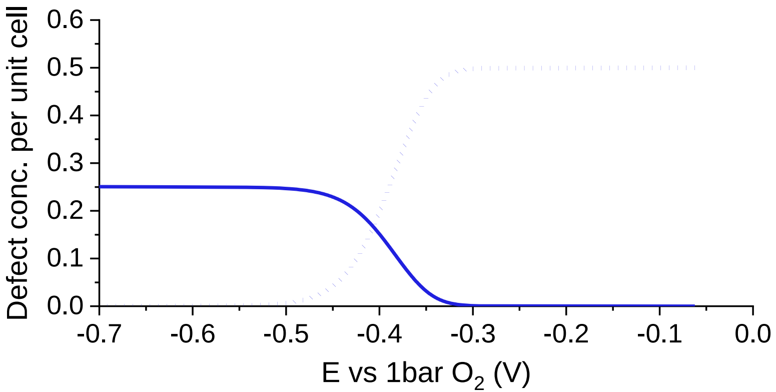
$$\tau = RC_{chem}$$

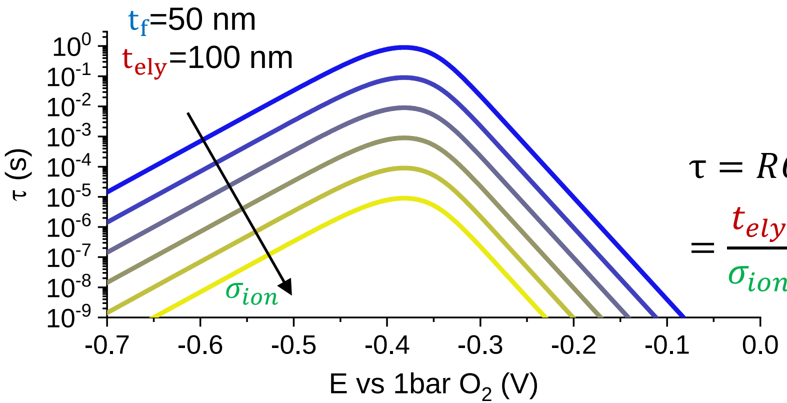
Switching time

1st Ideal case:

- Surface capped
- No diffusion losses
- No insertion losses at LSF/YSZ
- Resistive electrolyte
- Fast electronic conduction







$$\boldsymbol{\tau = RC_{chem}}$$

$$R = \frac{1}{\sigma_{ion}} \cdot \frac{t_{ely}}{A}$$

$$C_{chem} = -\frac{V_f}{c_{uc}^3} 4e^2 \cdot \frac{dc_O}{d\mu_O} = \frac{t_f \cdot A}{c_{uc}^3} \frac{e^2}{k_b T} \cdot \left(\frac{1}{4[v_O^{\bullet\bullet}]} + \frac{1}{[h^\bullet]} \right)^{-1}$$

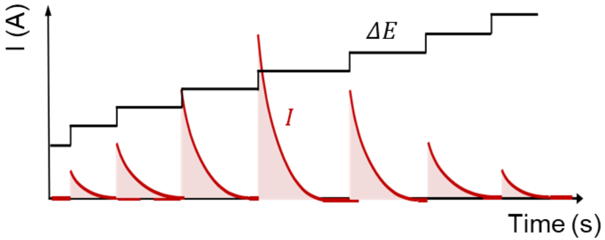
$$\tau = RC_{chem} = \frac{t_{ely}}{\sigma_{ion}} \cdot t_f \cdot \frac{e^2}{c_{uc}^3 k_b T} \cdot \left(\frac{1}{4[v_O^{\bullet\bullet}]} + \frac{1}{[h^\bullet]} \right)^{-1}$$

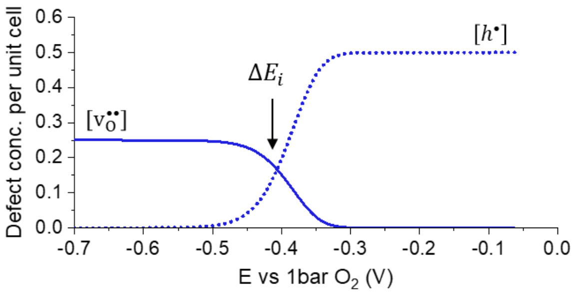
Schmid et al., Phys. Chem. Chem. Phys., 2018, 20, 12016

Insertion E:

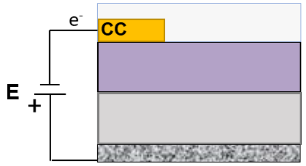
$$\frac{1}{2}O_2 + v_O^{\bullet\bullet} \leftrightarrow O_O^x + 2h^\bullet$$

$$\Delta E_i = -\frac{k_b T}{2e} \ln K_{ox}$$



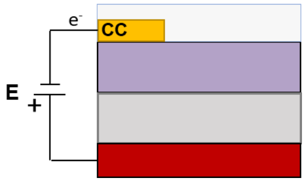


Asymmetric semi-open



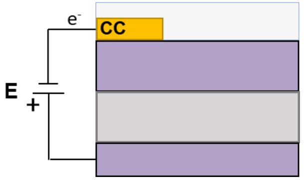
$\Delta V = \Delta E_i$ only depends on the material's equilibrium

Asymmetric battery-like



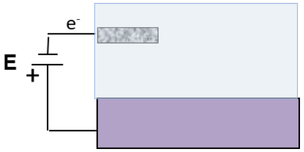
$\Delta V = \Delta E_G - \Delta E_C$

Symmetric battery-like



$\Delta V \sim 0$

Asymmetric with ely redox



ΔE_i depends on the material's equilibrium and the redox reaction

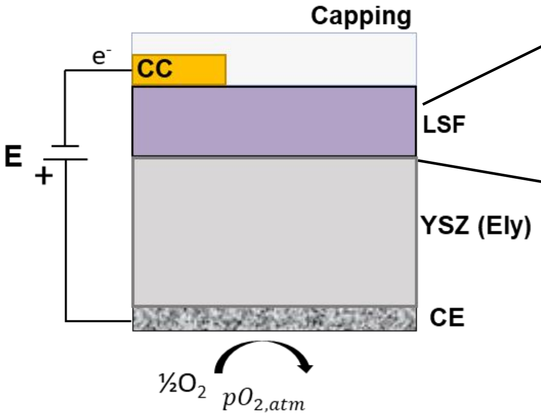
$\Delta V = \Delta E_{red} - \Delta E_C$

Shaping Energy for a Sustainable Future

Ion insertion in pseudo-real systems

2st Ideal case:

- Surface capped
- Diffusion losses
- Insertion losses
- Resistive electrolyte
- Fast electronic conduction



Ion transport:

$$\frac{\partial[\mathrm{v}_{\mathrm{O}}^{\bullet\bullet}]}{\partial t} = -\nabla\cdot(-\boldsymbol{D}_{\boldsymbol{chem}}\nabla[\mathrm{v}_{\mathrm{O}}^{\bullet\bullet}])$$

$$\tau \sim \frac{x^2}{2\boldsymbol{D}_{\boldsymbol{chem}}}$$

Diffusion slow down ions and creates conc. gradients

Ion insertion:

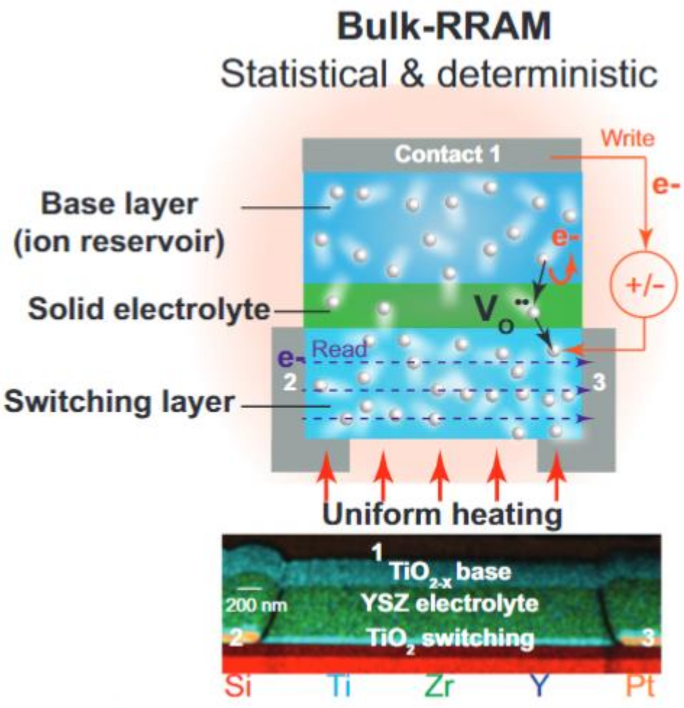
$$i = i_0(\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta}{RT}\right))$$

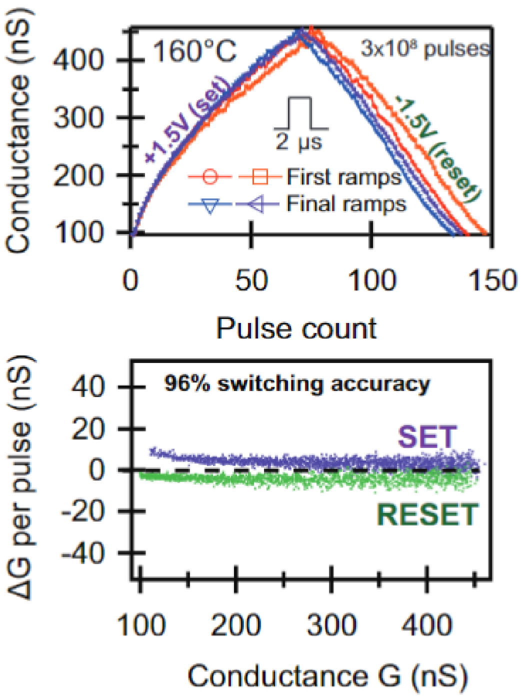
$$\eta = \phi_{ele} - \phi_{ion} - E_{eq}([\mathrm{v}_{\mathrm{O}}^{\bullet\bullet}])$$

Ion insertion reduces the effects of an applied potential

Huang et al., Adv. Mater. 2023, 35, 2205169

Examples: Oxygen modulated Electrochemical ionic synapsis

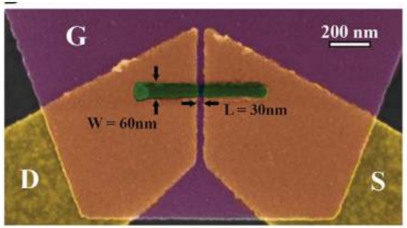


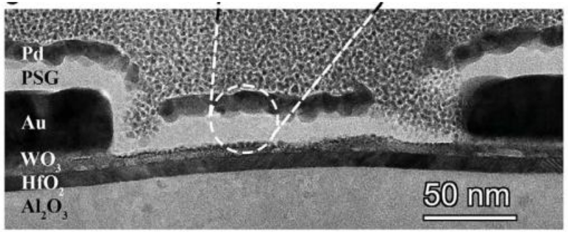


Li et al., Adv. Mater. 2020, 32, 2003984

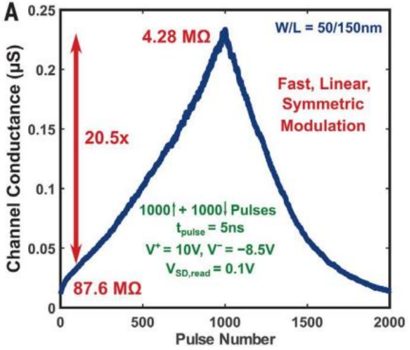
Nanosecond protonic programmable resistors

phosphosilicate glass as electrolyte

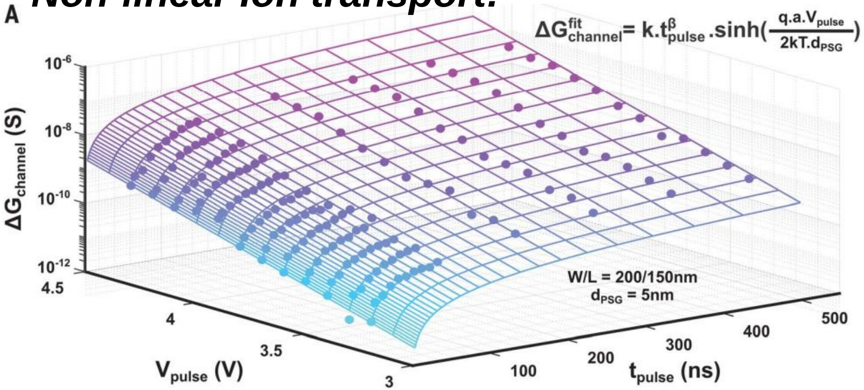




ns pulses modulation



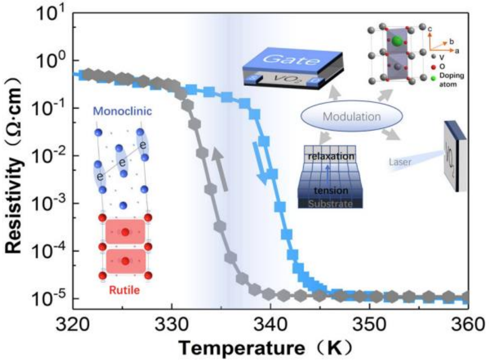
Non-linear Ion transport:



Onen et al., Science 377, 539–543 (2022)

Oxygen vacancy modulation in ionic liquids

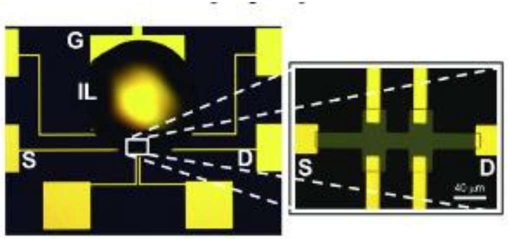
Metal insulator transition in VO_2



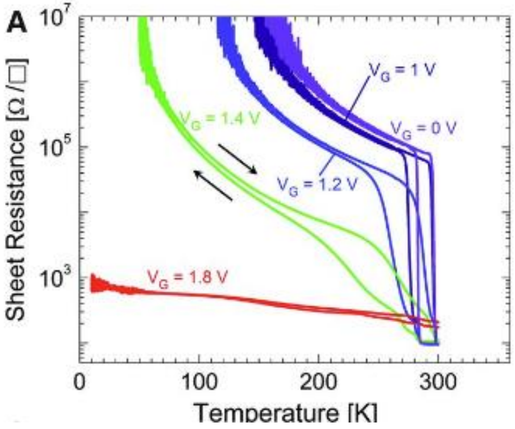
Shao et al. NPG Asia Materials (2018) 10: 581-605

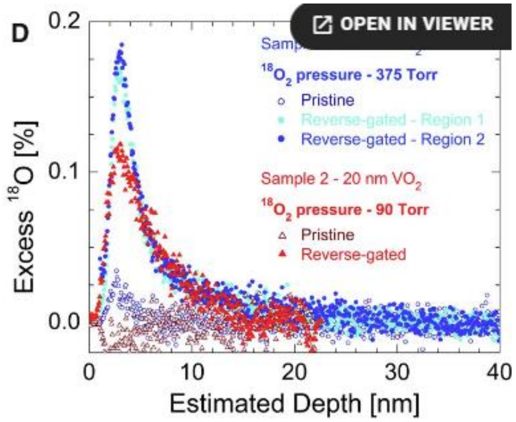
Wegkamp, D. & Stähler, J, Prog. Surf. Sci. (2015) 90, 464–502

Oxygen vacancy creation in gated thin films



1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (HMIM-TFSI)





Jaewoo Jeong et al., Science,339,1402-1405(2013)

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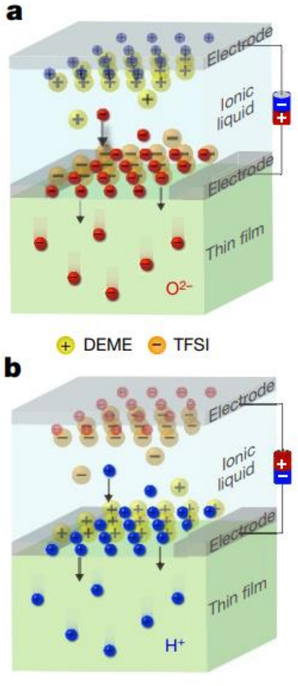
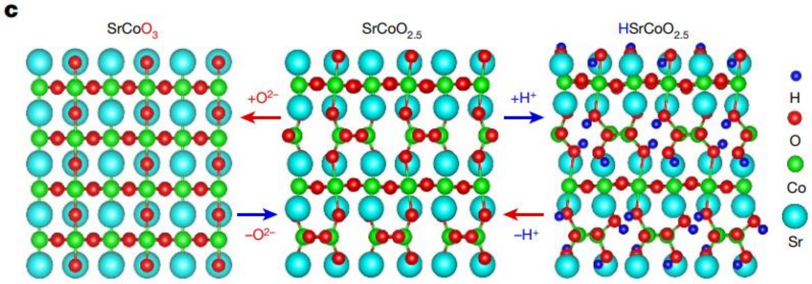
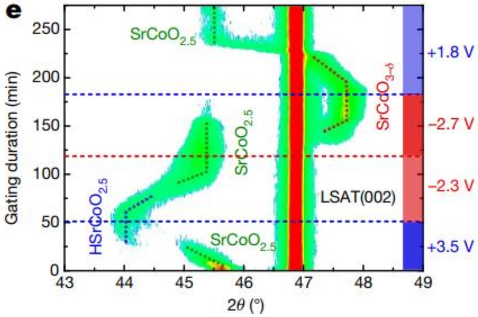
Oxygen vacancy and protonic modulation in ionic liquids



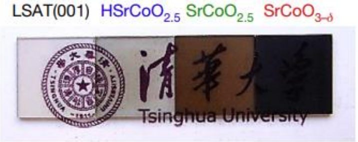
PV **BM** **P-BM**

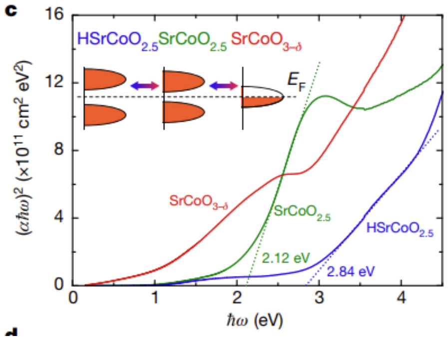


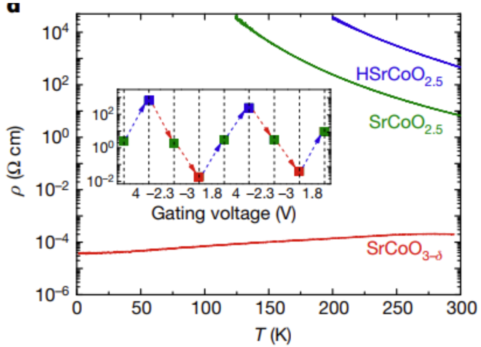
Evolution lattice parameter



Tri-state modulation of functional properties





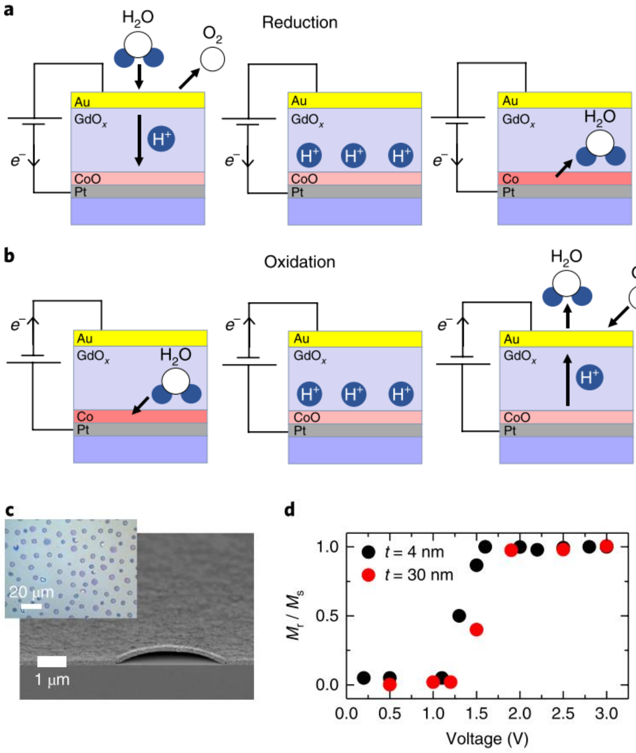


Oxygen and protons from water traces in the ely

Lu, N *et al. Nature* **546**, 124–128 (2017).

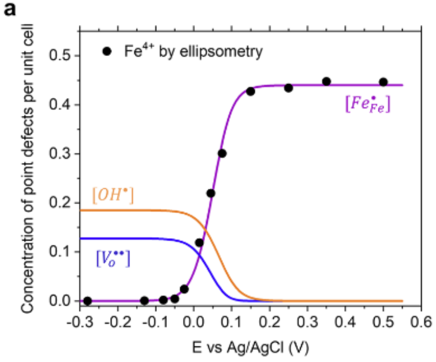
Protons and humidity may be very relevant!

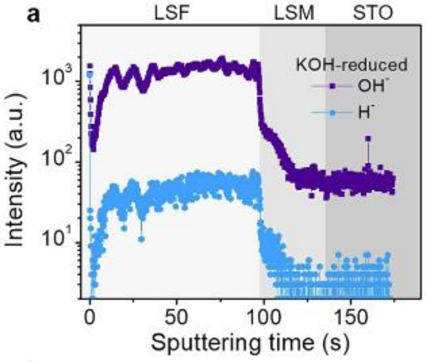
Water splitting mediated oxidation of Co



Tan, A.J., *et al.*, *Nature Mater* **18**, 35–41 (2019)

Protonation at RT of LSF in alkaline electrolytes





Tang et al., ACS Appl. Mater. Interfaces 2022, 14, 18486−18497

- Water splitting (and proton diffusion) can promote oxidation (although it is not oxygen that is moving)
- Materials that do not host protons at high T can be protonated at RT (endothermic reaction): need of low T defect chemistry

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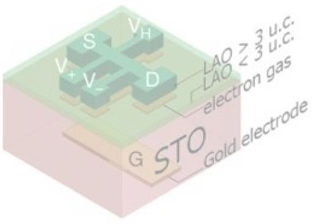
How to modulate the ionic concentration of complex oxides?

Field effect

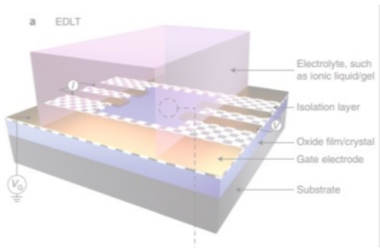
Application of E in the linear range through a dielectric



Caviglia et al, Nature (2008) 456, 624–627

Electrolyte double layer

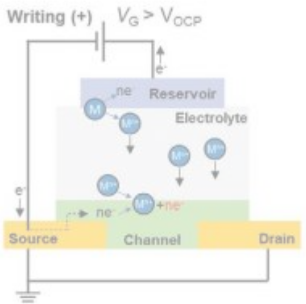
Application of E in the linear range through an ionic conductor



Leighton et al., Nat. Mat., (2019), 18, 13-18

Redox ionic insertion

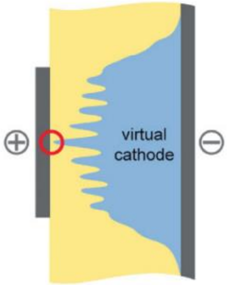
Application of E in the linear range through an ionic conductor



Huang et al., Adv. Mater. 2023, 35, 2205169

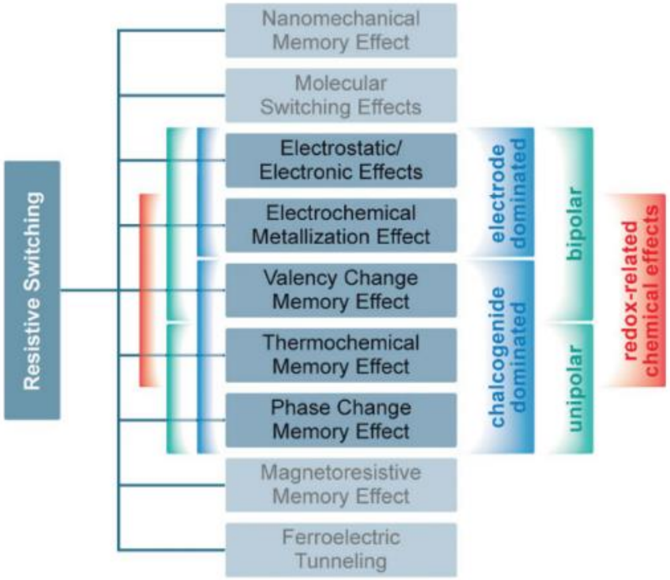
Resistive switching

Application of large E directly to the material



Waser el al., Adv. Mater. 2009, 21, 2632–2663

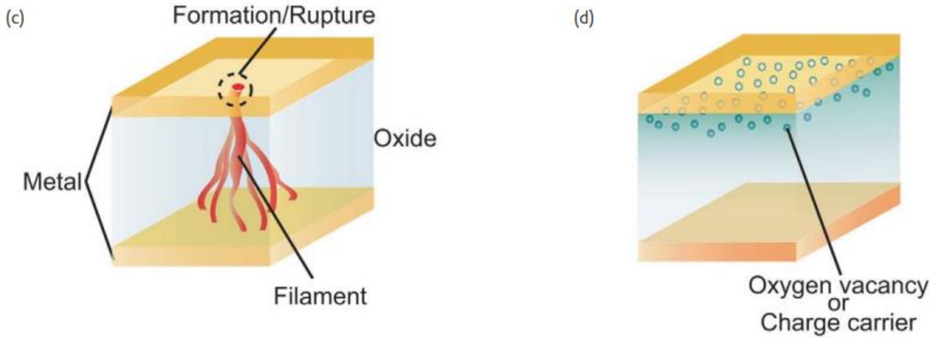
Redox-based resistive switching

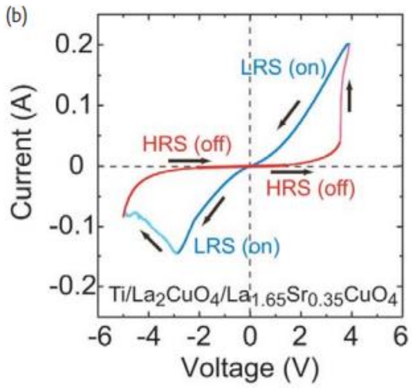


Waser el al., Adv. Mater. 2009, 21, 2632–2663

Filamentary

Interface-type

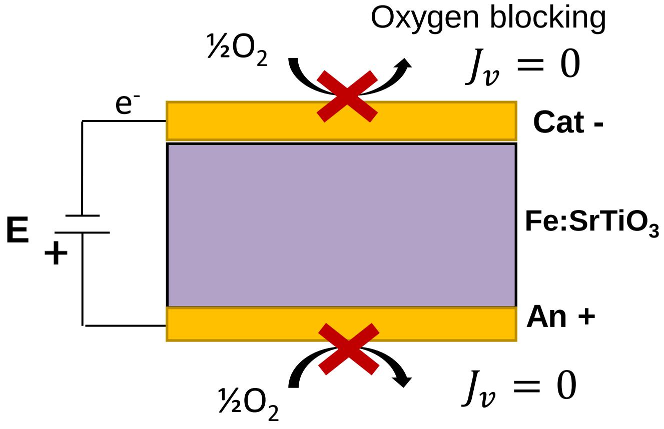




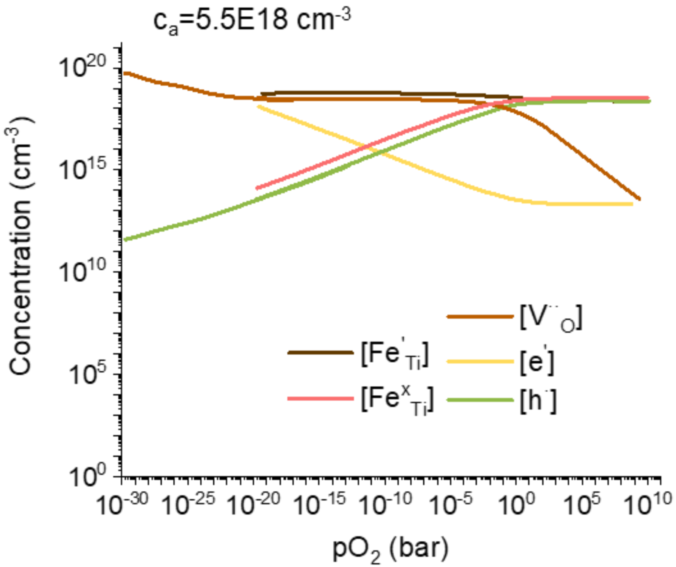
Akihito Sawa, Materials Today, 2008, 1, 6, 28-36

An example: defect modulation in $SrTiO_3$ under bias

T=200ºC



Brouwer diagram: *$SrTiO_3$* at 900ºC



Defect model

$$K_{R2} = n^2 [V_O^{\cdot\cdot}] \sqrt{p_{O_2}}$$

$$K_{R3} = [Fe'_{Ti}]p \Big/ [Fe^{\times}_{Ti}]$$

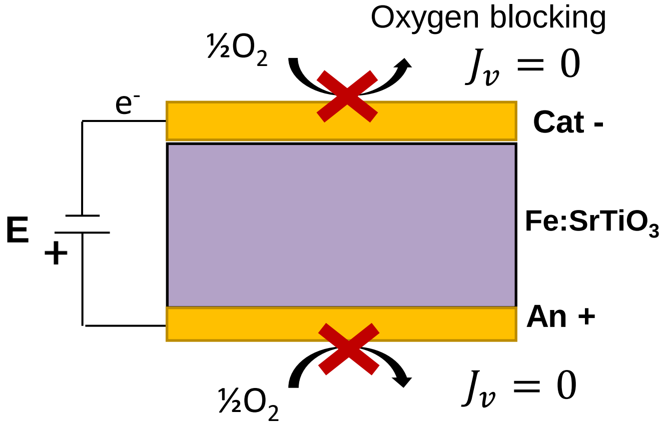
$$K_{R4} = np$$

Baiatu et al., J. Am. Ceram. Soc., 7s 161 M63-73 (1990)

Wang et al., Acta Materialia 108 (2016) 229e240

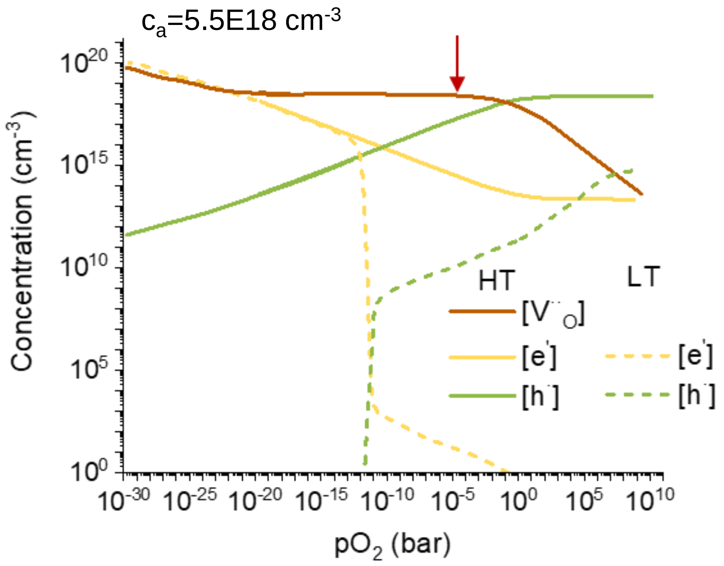
An example: defect modulation in $SrTiO_3$ under bias

T=200ºC



- Frozen oxygen equilibrium
- Hole trapping at LT
- Initial conditions: vacancies main defect

"Quenched" $SrTiO_3$ at 200ºC



Defect model

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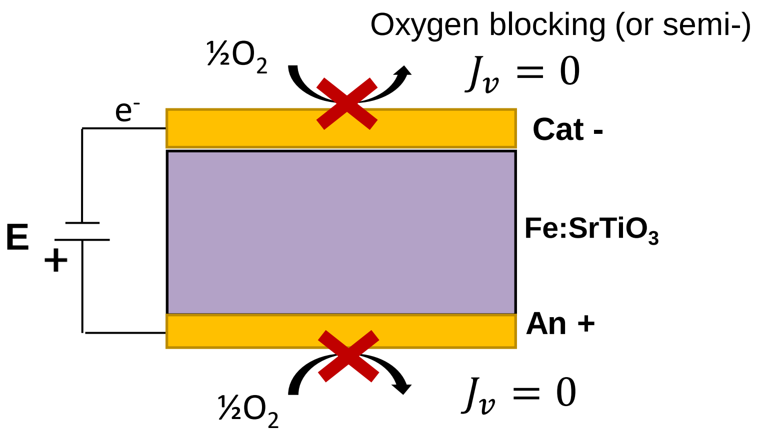
Wang et al., Acta Materialia 108 (2016) 229e240

An example: defect modulation in $SrTiO_3$ under bias



- Frozen oxygen equilibrium
- Hole trapping at LT
- Initial conditions: vacancies main defect

Nernst-Plant transport equation (dilute)

Diffusion Drift

$$J_v = -2eD_v \cdot \frac{\partial[\mathrm{v_O^{\bullet\bullet}}]}{\partial x} + 2e\mu_v[\mathrm{v_O^{\bullet\bullet}}] \cdot E_x$$

$$\frac{\partial[\mathrm{v_O^{\bullet\bullet}}]}{\partial t} = -\frac{\partial J_v}{\partial x}$$

Local equilibria: electrons and holes moves faster than oxygen vacancies and are always in equilibrium (from defect model)

$$\sigma(x,t) = 2e\mu_v[\mathrm{v_O^{\bullet\bullet}}] + e\mu_n n + e\mu_p p$$

Maxwell equation $$E_x(x,t) = \frac{J_{drift}}{\sigma(x,t)}$$

Poisson equation $$\rho(x,t) = \varepsilon_0 \varepsilon_r \frac{\partial E_x}{\partial x}$$

Baiatu et al., J. Am. Ceram. Soc., 7s 161 M63-73 (1990)

Wang et al., Acta Materialia 108 (2016) 229e240

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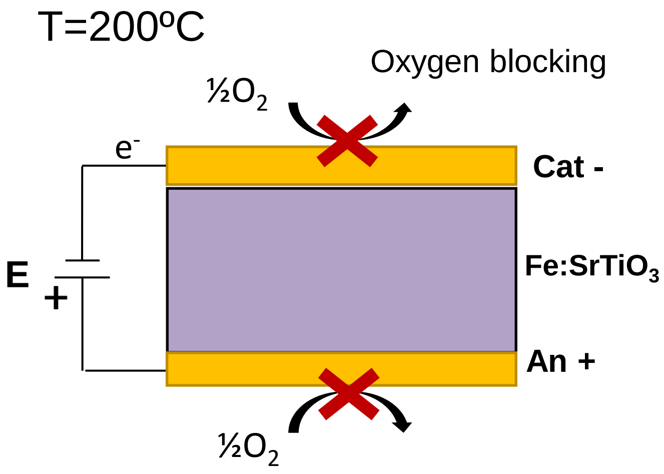
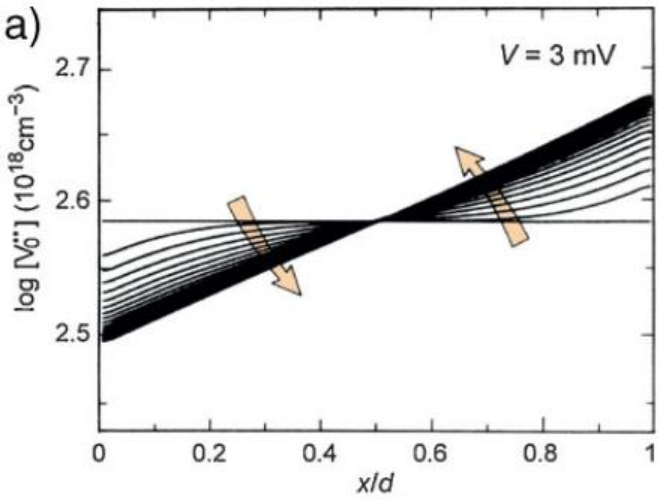
Small potentials: linear variation, no substantial changes

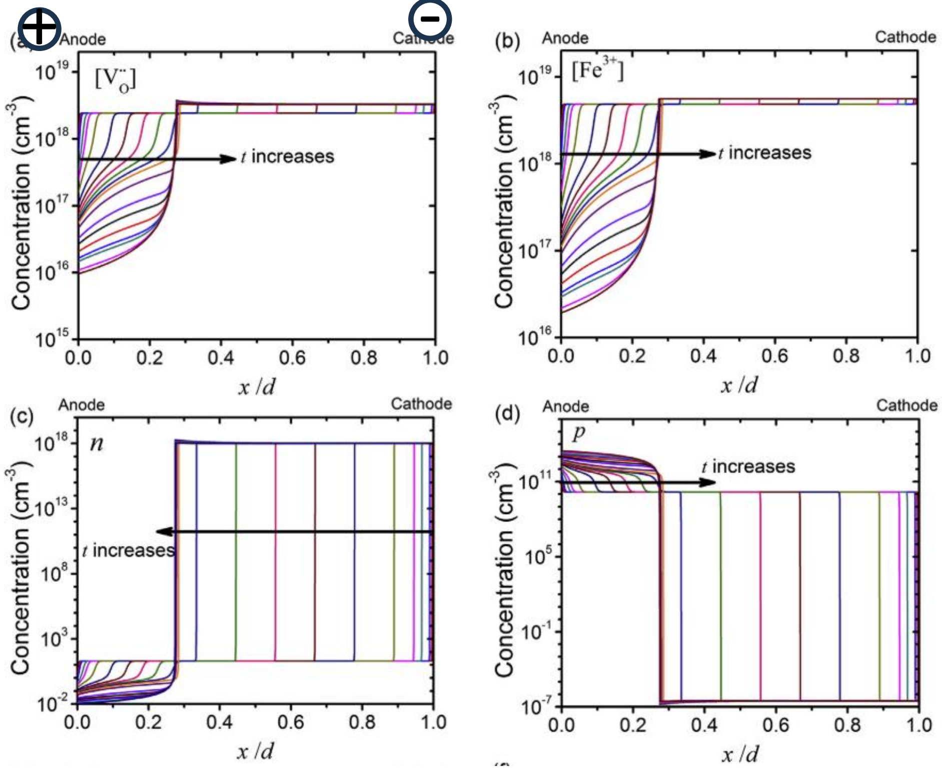


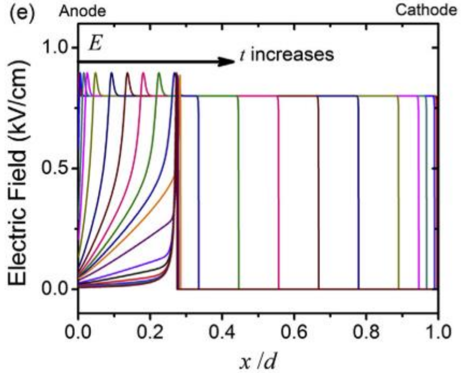


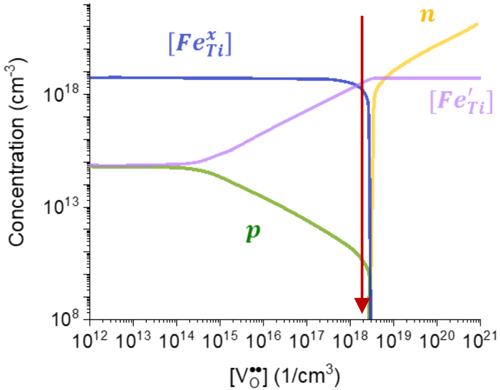
$$\frac{\partial [v_O^{\bullet\bullet}]}{\partial x} = -\frac{\sigma_v E_x}{2eD_v}$$

Evolution of the defect concentration after the application of large E

$E = 240\,V,\ E_x = 800\,\frac{V}{cm},\ t = 0.3\ cm,\ T = 200ºC$



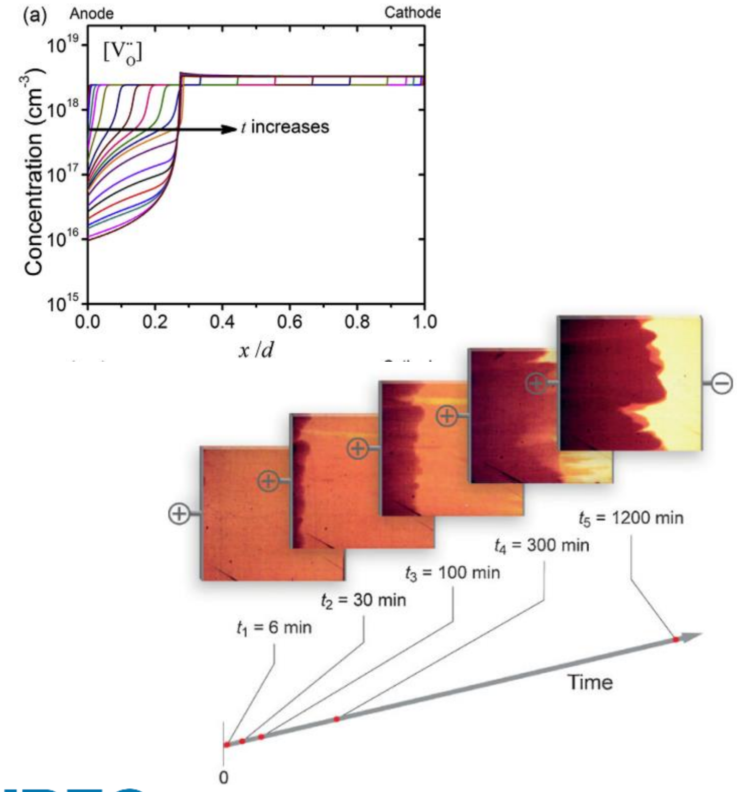




Wang et al., Acta Materialia 108 (2016) 229e240

Consequences of the ion redistribution

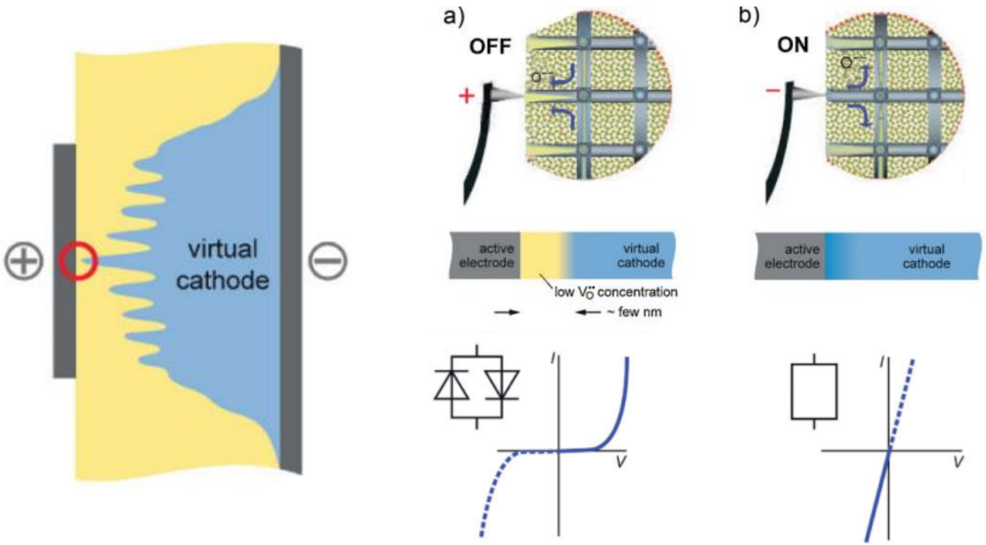
Change of color due to Fe^{4+}



Resistive switching

Anode partially leaking: $O_O^x \rightarrow \frac{1}{2}O_2 + v_O^{\bullet\bullet} + 2e'$

Injection of $v_O^{\bullet\bullet}$ that moves towards the cathode, a n-type region. Extended defects create filaments that grows till creating a contact between cathode and anode (ON).



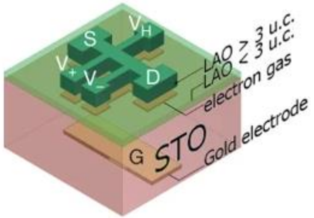
Waser el al., Adv. Mater. 2009, 21, 2632–2663

Recap

Iontronics: control of functional properties (electronic magnetic, optical,..) through the accumulation/ insertion/ variation of ion concentration for advanced devices such as: Memristors, Electrochemical ion synapsis (programmable resistances), electrochromic windows, magnetoionic memories and transistors,…

Field effect

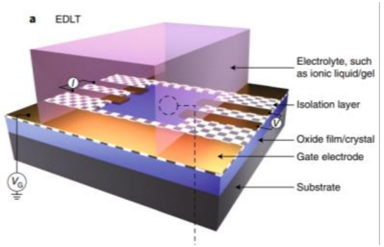
Application of E in the linear range through a dielectric



Caviglia et al, Nature (2008) 456, 624–627

Electrolyte double layer

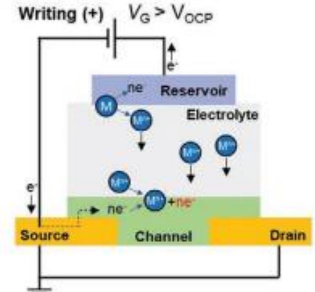
Application of E in the linear range through an ionic conductor



Leighton et al., Nat. Mat., (2019), 18, 13-18

Redox ionic insertion

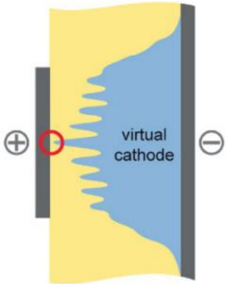
Application of E in the linear range through an ionic conductor



Huang et al., Adv. Mater. 2023, 35, 2205169

Resistive switching

Application of large E directly to the material

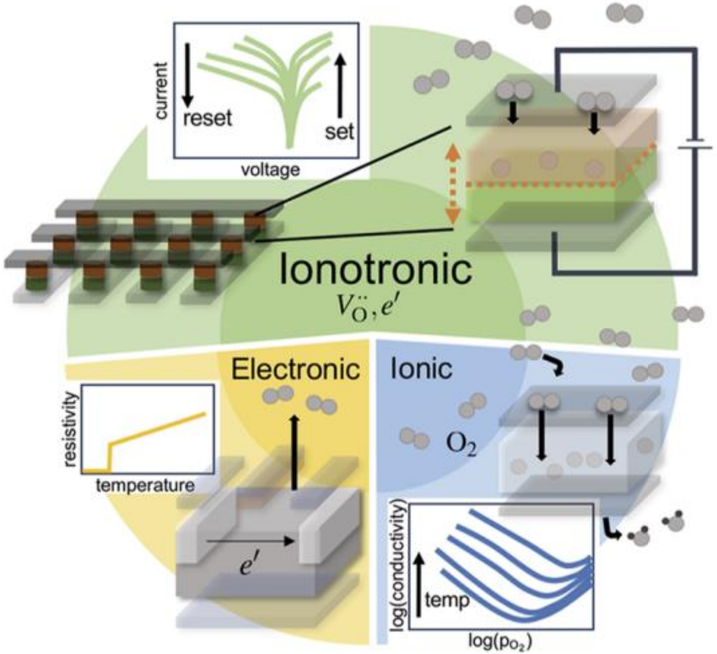


Waser el al., Adv. Mater. 2009, 21, 2632–2663

Shaping Energy for a Sustainable Future

Thank you for your attention!

This project has funding from a Marie Skłodowska Curie Actions Postdoctoral Fellowship grant (101107093).

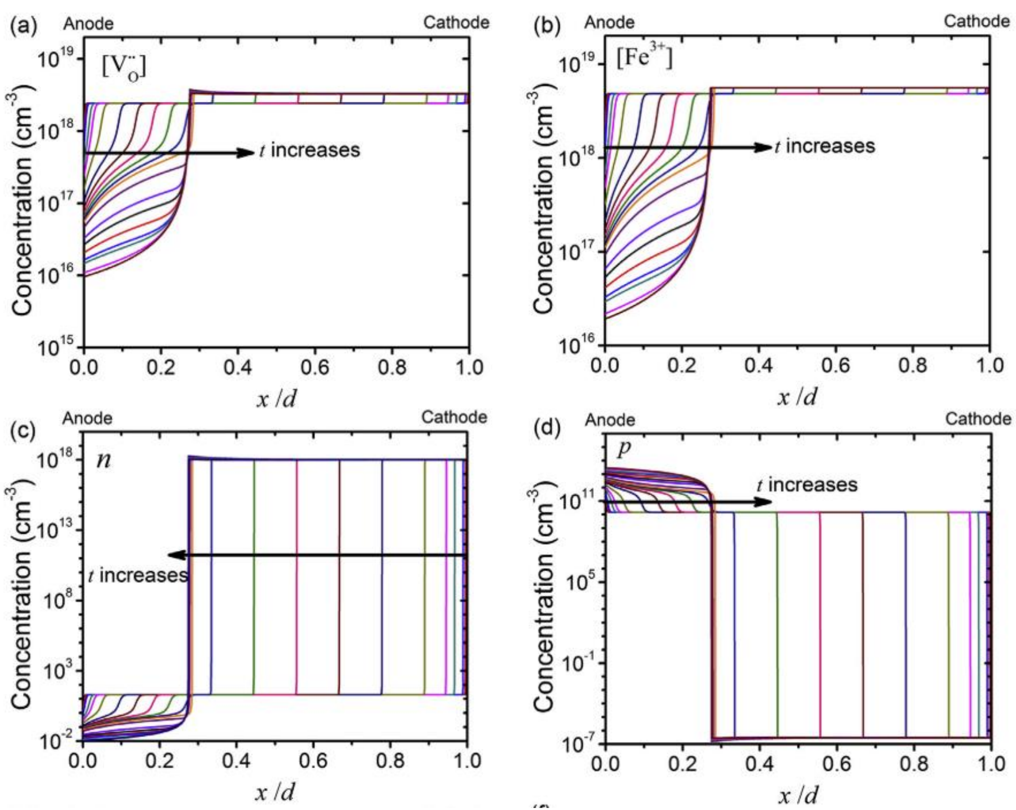


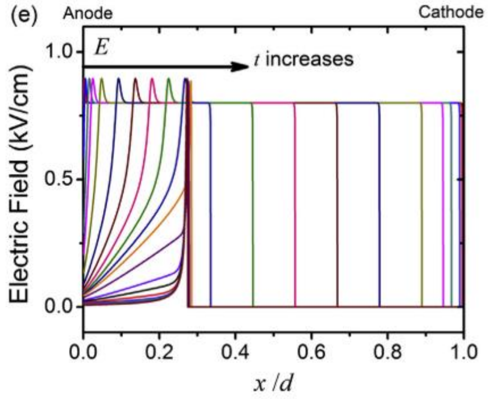
fchiabrera@irec.cat

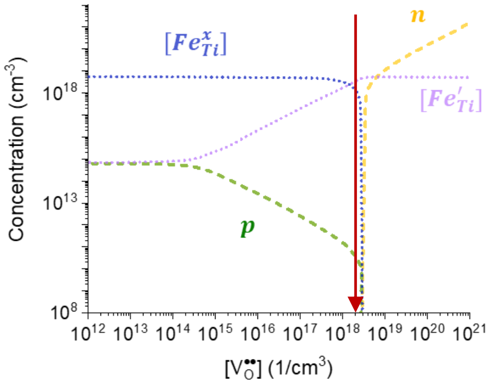
Wenderott et al., APL Mater. 12, 050901 (2024)

Shaping Energy for a Sustainable Future

Evolution of the defect concentration after the application of large E

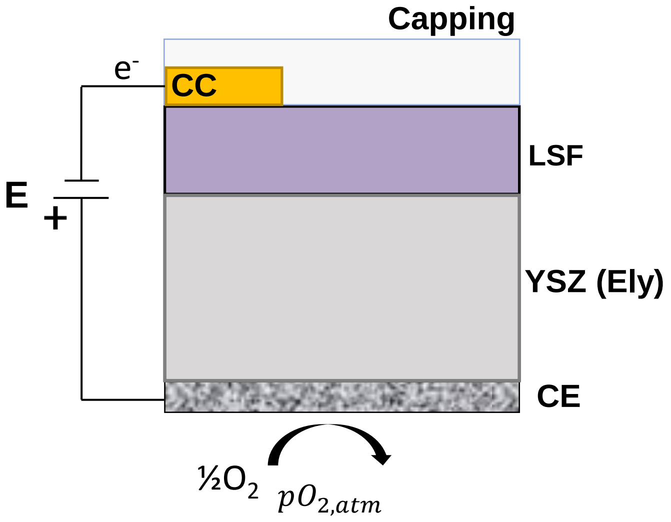






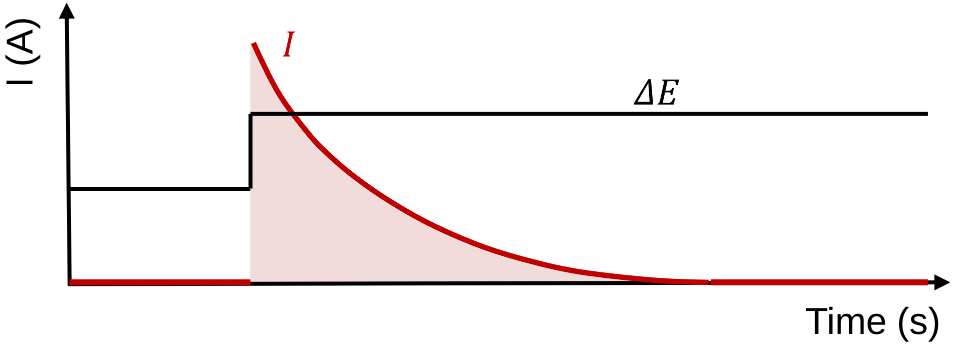
Wang et al., Acta Materialia 108 (2016) 229e240

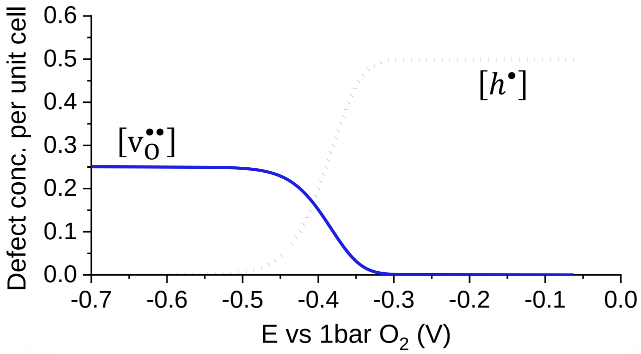
Oxygen modulation in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ (LSF)



1st Ideal case:

- Surface capped
- No diffusion losses
- No insertion losses at LSF/YSZ
- Resistive electrolyte





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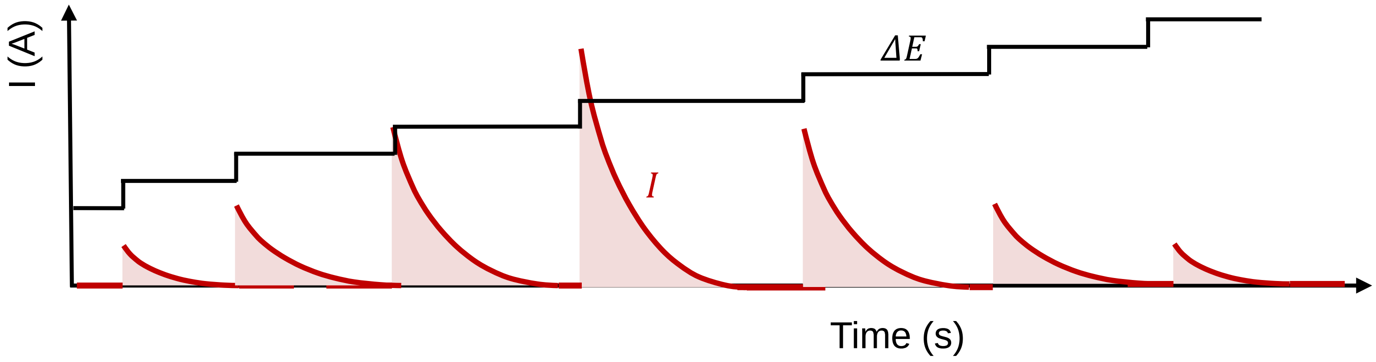
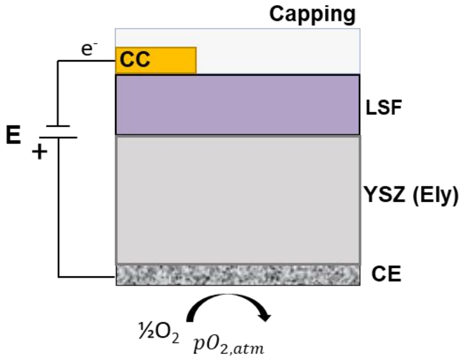
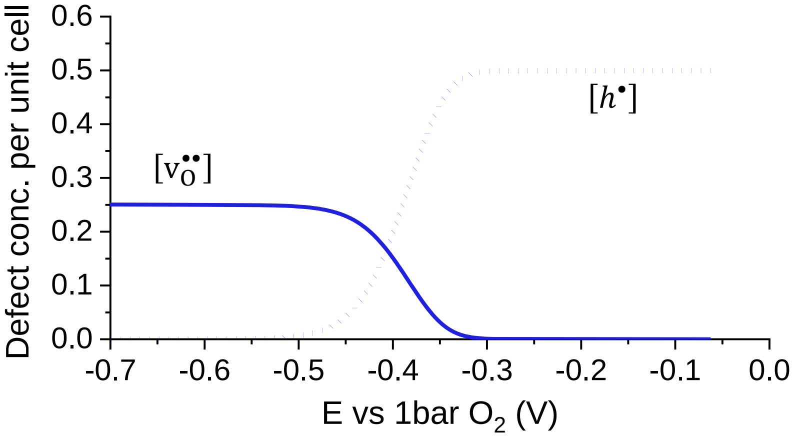


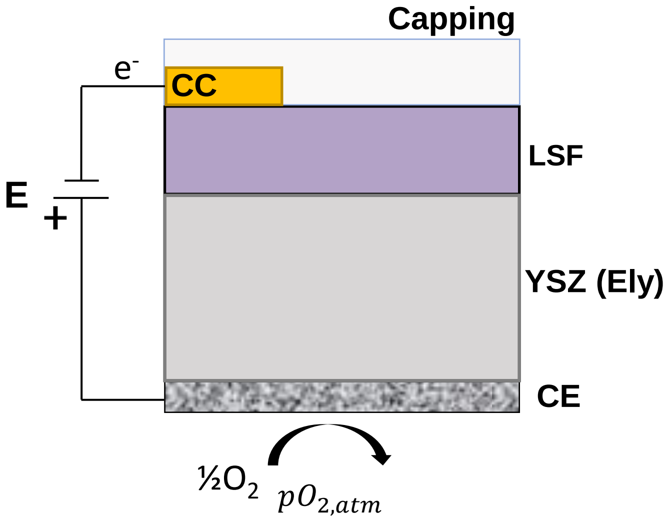




$$\Delta[\mathrm{v}_{\mathrm{O}}^{\bullet\bullet}] = -\frac{c_{LSF}^{3}}{2eV_{film}} \int$$

Electrolyte redox-Ion insertion: a useful case study

Oxygen modulation in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ (LSF)



1st Ideal case:

- No oxygen incorporation on the surface (capped)
- No diffusion losses
- No insertion losses at LSF/YSZ
- CE no resistive

$$\frac{1}{2}O_2 + 2e' \leftrightharpoons O^{2-}$$

Same for differences

$$\mu_O + 2\tilde{\mu}_{e'} = \tilde{\mu}_{O^{2-}} \qquad \Delta\mu_O + 2\Delta\tilde{\mu}_{e'} = \Delta\tilde{\mu}_{O^{2-}}$$

$$\nabla\tilde{\mu}_{O^{2-}} = 0$$ *No flux*

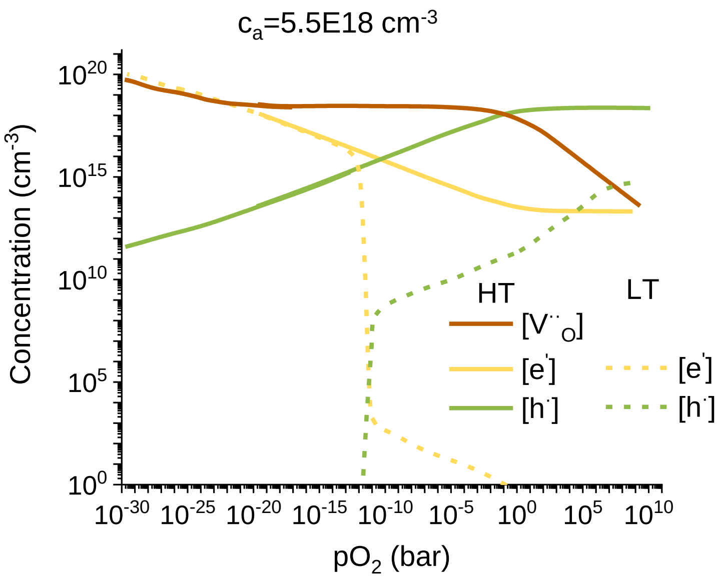
$$\Delta\mu_O = -2\Delta\tilde{\mu}_{e'} = 2e\Delta E$$

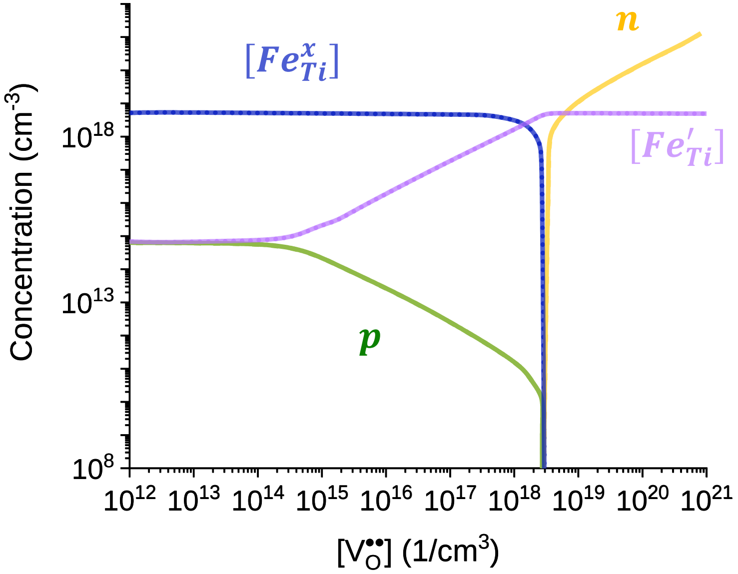
$$\boldsymbol{\mu_o^{LSF} = 2e\Delta E + \mu_o^{ATM} = 2e\Delta E + \frac{kT}{2}\ln\left(\frac{pO_{2,atm}}{1bar}\right)}$$

$$\mu_O^{ATM} = 1/2\mu_{O_2}^{ATM}$$

Defect concentration as a function of the oxygen vacancy concentration

Quenched Brouwer diagram of $SrTiO_3$

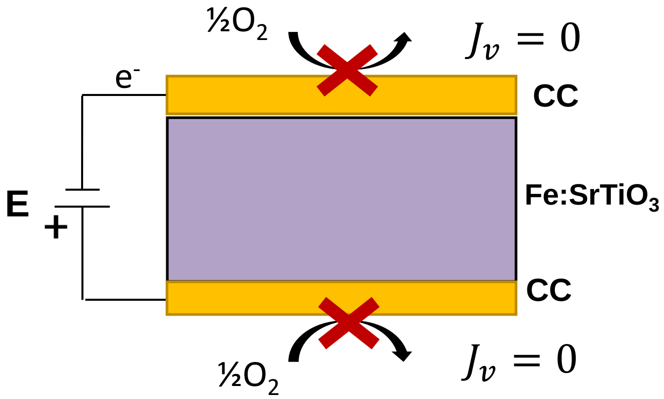




- Frozen $[v_O^{\bullet\bullet}]$
- Hole trapping at LT

Low potentials (small variation from equilibrium)

Oxygen blocking (or semi-)



Nernst-Plant transport equation (dilute)

Diffusion

Drift

$$J_i = -z_i e D_i \cdot \frac{\partial [i]}{\partial x} + z_i e \mu_i [i] \cdot \frac{\partial E}{\partial x}$$

$i = v_O^{\bullet\bullet}, h^{\bullet}, e'$

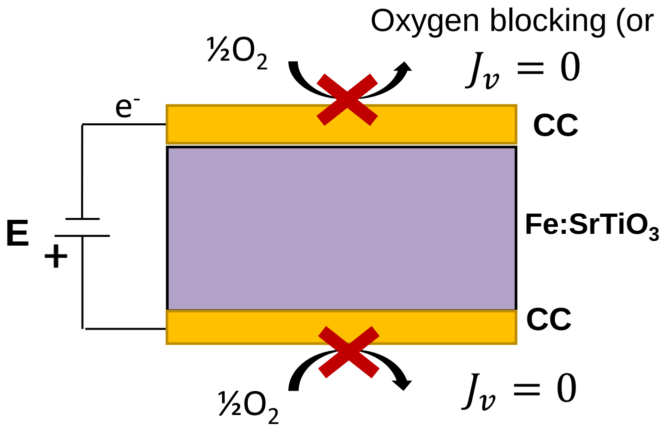
$$\frac{\partial [v_O^{\bullet\bullet}]}{\partial x} = \mu_i [v_O^{\bullet\bullet}] \cdot \frac{\partial E}{\partial x}$$

Assumptic
and are al

Steady state:

Baiatu et al., J. Am. Ceram. Soc., 7s 161 M63-73 (1990)

Wang et al., Acta Materialia 108 (2016) 229e240



Nernst-Plant transport equation (dilute)

Diffusion Drift

$$J_i = -z_i e D_i \cdot \frac{\partial [i]}{\partial x} + z_i e \mu_i [i] \cdot \frac{\partial E}{\partial x}$$

$$i = v_O^{\bullet\bullet}, h^{\bullet}, e'$$

$$\frac{\partial [i]}{\partial t} = -\frac{\partial J_i}{\partial x}$$

Assumption: electrons and holes moves faster than oxygen vacancies and are always in equilibrium

Steady state: ***Low E***

Baiatu et al., J. Am. Ceram. Soc., 7s 161 M63-73 (1990)

Wang et al., Acta Materialia 108 (2016) 229e240

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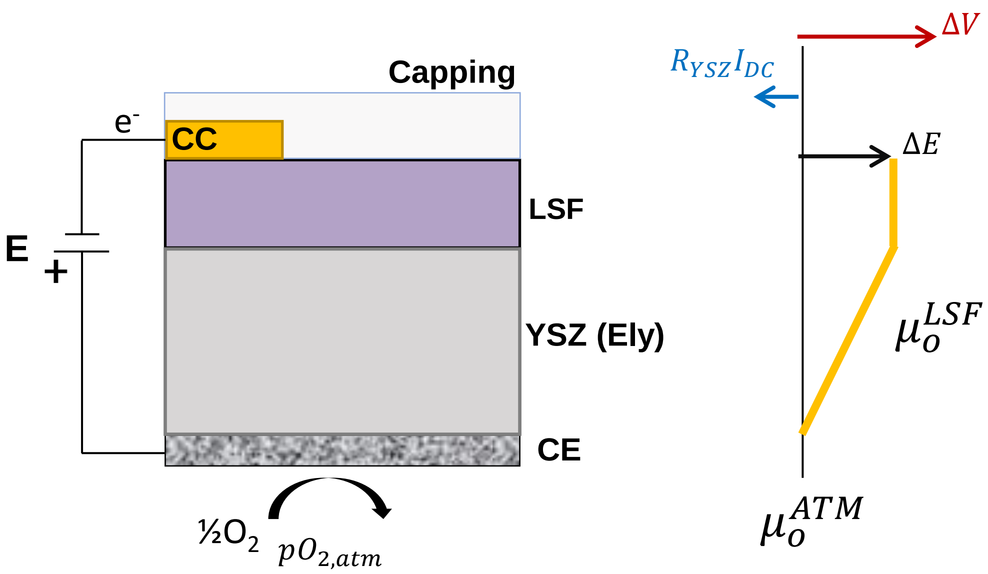
Oxygen modulation in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ (LSF)



1st Ideal case:

- No oxygen incorporation on the surface (capped)
- No diffusion losses
- No insertion losses at LSF/YSZ
- CE no resistive

$$\mu_O^{ATM} = 1/2\mu_{O_2}^{ATM} = \frac{kT}{2}\ln(\frac{pO_{2,atm}}{1bar})$$

$$\mu_O^{LSF} = 2F\Delta E + \frac{RT}{2F}\ln(\frac{pO_{2,atm}}{1bar})$$

$$\Delta E = \Delta V - R_{YSZ}I_{DC}$$

$$\frac{1}{2}O_2 + 2e' + V_{O,YSZ}^{\bullet\bullet} \leftrightharpoons O_{YSZ}^{2-}$$

$$O_{YSZ}^{2-} \leftrightharpoons O_{YSZ}^{2-}$$

$$O_{YSZ}^{2-} + V_{O,LSF}^{\bullet\bullet} \leftrightharpoons O_{LSF}^{2-} + V_{O,YSZ}^{\bullet\bullet} + 2h^{\bullet} + 2e'$$

But first a useful recap:

General chemical reaction:

$$\sum_i^R \nu_i R_i \Leftrightarrow \sum_j^R \nu_j P_j$$

$$\Delta G = \sum_i^P \mu_i \nu_i - \sum_j^R \mu_j \nu_j$$

Inserting def. of chemical potential:

$$\Delta G = G_0 + RTln(\frac{\prod_i^P (\mathrm{c_i})^{\nu_i}}{\prod_j^R (\mathrm{c_j})^{\nu_j}})$$

Equilibrium: $\Delta G = 0$

Electrochemical reaction:

$$\sum_i^R \nu_i R_i^q \Leftrightarrow \sum_j^R \nu_j P_j^q$$

$$\Delta G = \sum_i^P \tilde{\mu}_i \nu_i - \sum_j^R \tilde{\mu}_j \nu_j$$

Inserting def. of electrochemical potential:

$$\eta = \eta_0 + \frac{RT}{z_i F} \ln(\frac{\prod_i^P (\mathrm{c_i})^{\nu_i}}{\prod_j^R (\mathrm{c_j})^{\nu_j}})$$

Equilibrium: $\eta = 0$

$$\mu_i = (\frac{\partial G}{\partial n_i})_{T,p,n_1,n_2,...}$$

$$\mu_i = \mu_i^0 + \mathrm{RTln(a_i)}$$

gas $a_{O_2} = \mathrm{pO_2}$

defect $a_i = \mathrm{c_i}$

Electrochemical potential

$$\tilde{\mu}_i = \mu_i + z_i F \eta$$

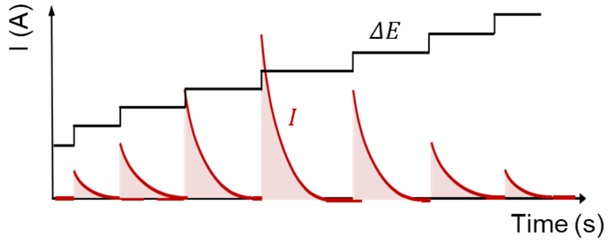
$$\eta = \frac{\Delta G}{\mathrm{z_i F}}$$

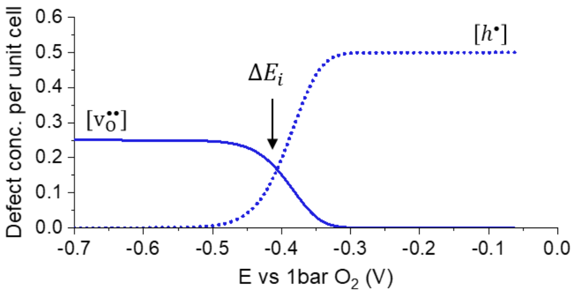
About the insertion potential

Insertion E:

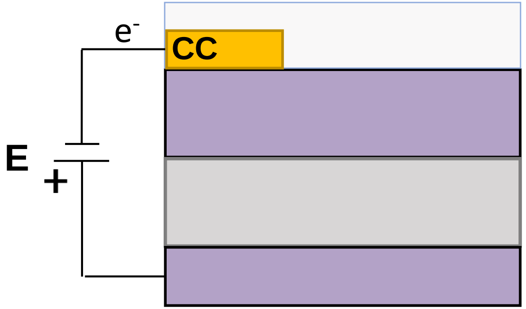
$$\frac{1}{2}O_2 + v_O^{\bullet\bullet} \leftrightarrow O_O^x + 2h^{\bullet}$$

$$\Delta E_i = -\frac{k_b T}{2e} \ln K_{ox}$$

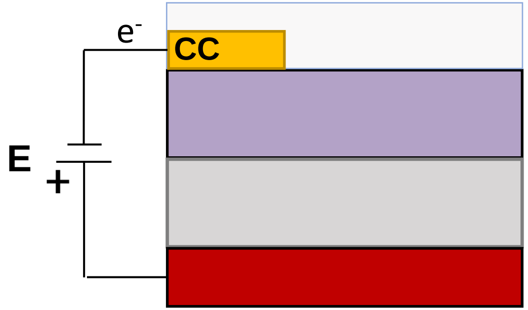




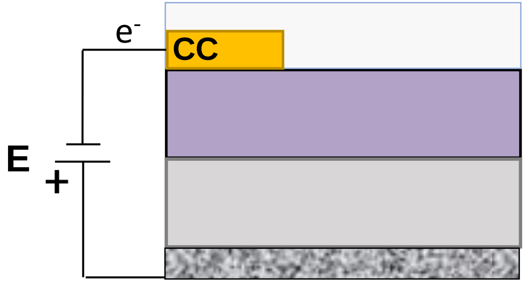
Symmetric battery-like



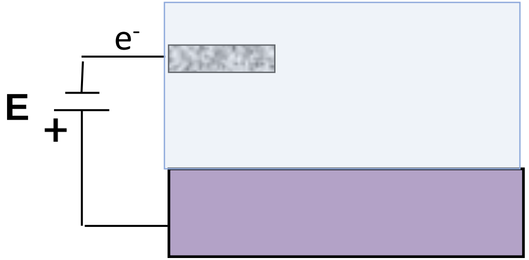
Asymmetric battery-like



Asymmetric semi-open



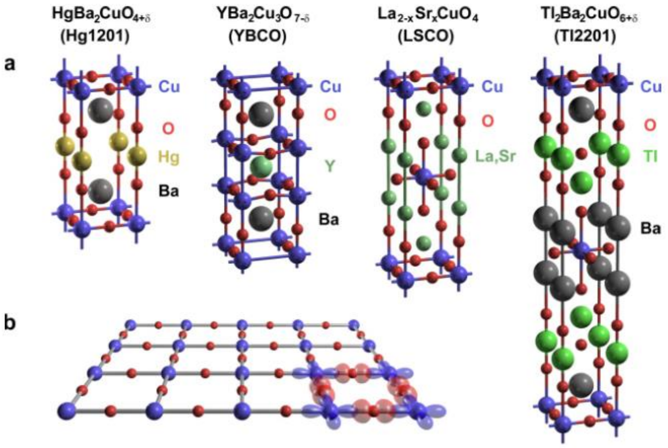
Asymmetric with ely redox



Liquid

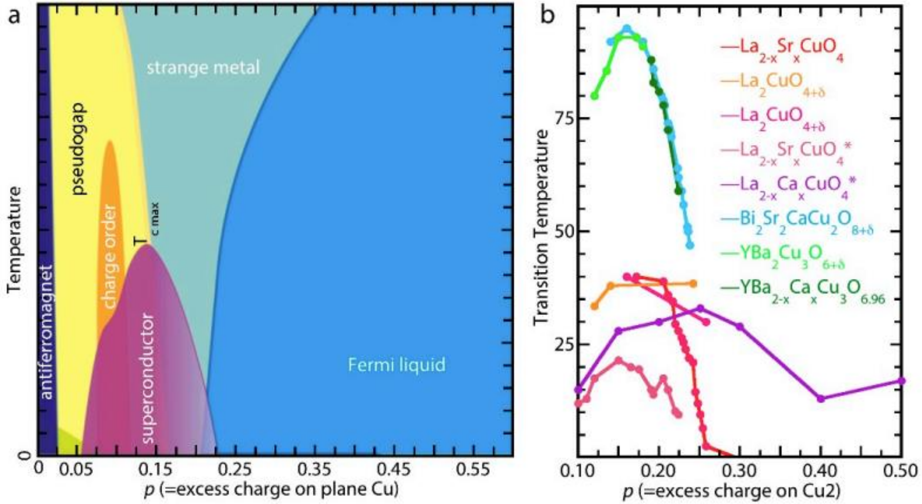
Electronic properties of complex oxides

Layered structures: cuprates



N. Barišić, PNAS 2013 110 (30)

High T superconductors



L. Sederholm, Condens. Matter 2021, 6, 50

$La_{2-x}Sr_xCuO_4$ $\qquad [Sr'_{La}] = [h^{\bullet}]$