WP2: Gas-solid reactions

Ian S. Metcalfe
Professor of Chemical Engineering
Newcastle University

i.metcalfe@ncl.ac.uk

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WP2: Gas-solid interfaces: Membranes for gas separation and solid oxide fuel cells

Metcalfe (NCU-Chem. Eng.); Partners: Driscoll, Pickard (CAM-Materials), Dutton, Morris (CAM-Physics), Grey (CAM-Chem), Hofmann (CAM-Eng), Abrahams (QMU)

High temperature, high selectivity carbon dioxide permeable membranes

Micro-SOFCs – Surface and interface modification using ALD/CVD

Model systems, new techniques for looking at oxygen exchange in particular

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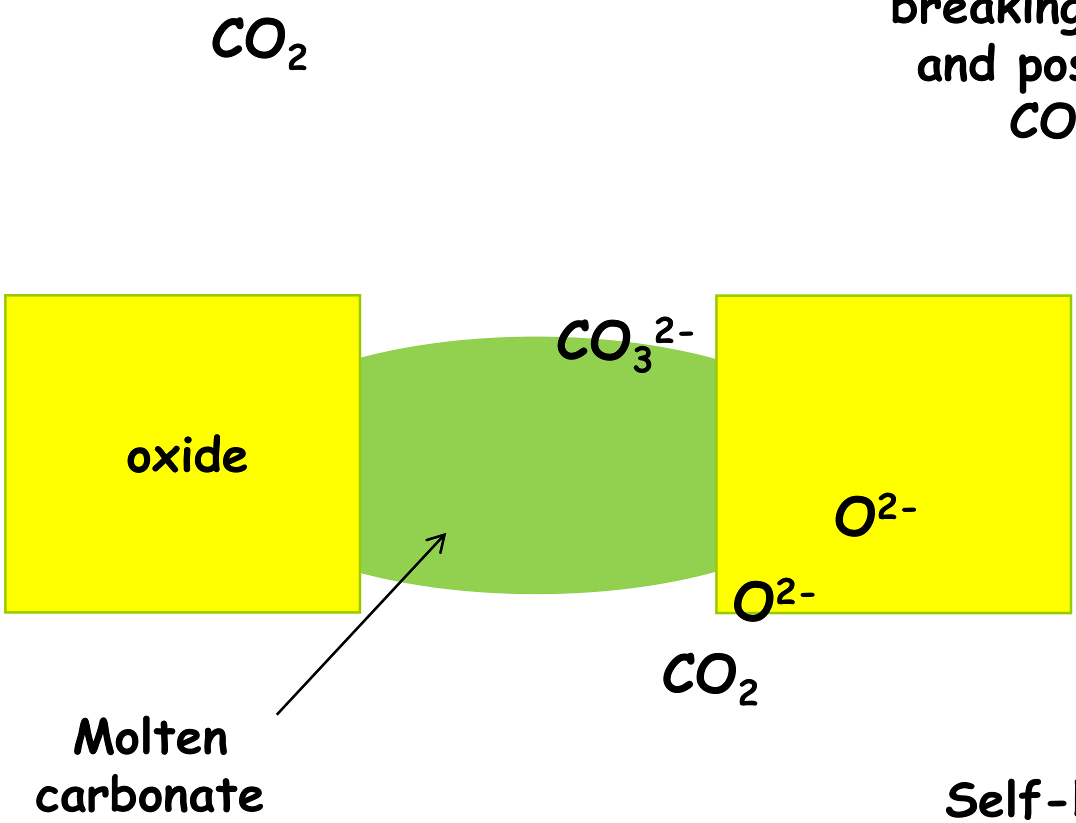
Dual ion conduction - carbon dioxide permeation

Applications: WGS breaking of equilibrium and post-combustion CO2 capture



Self-healing?

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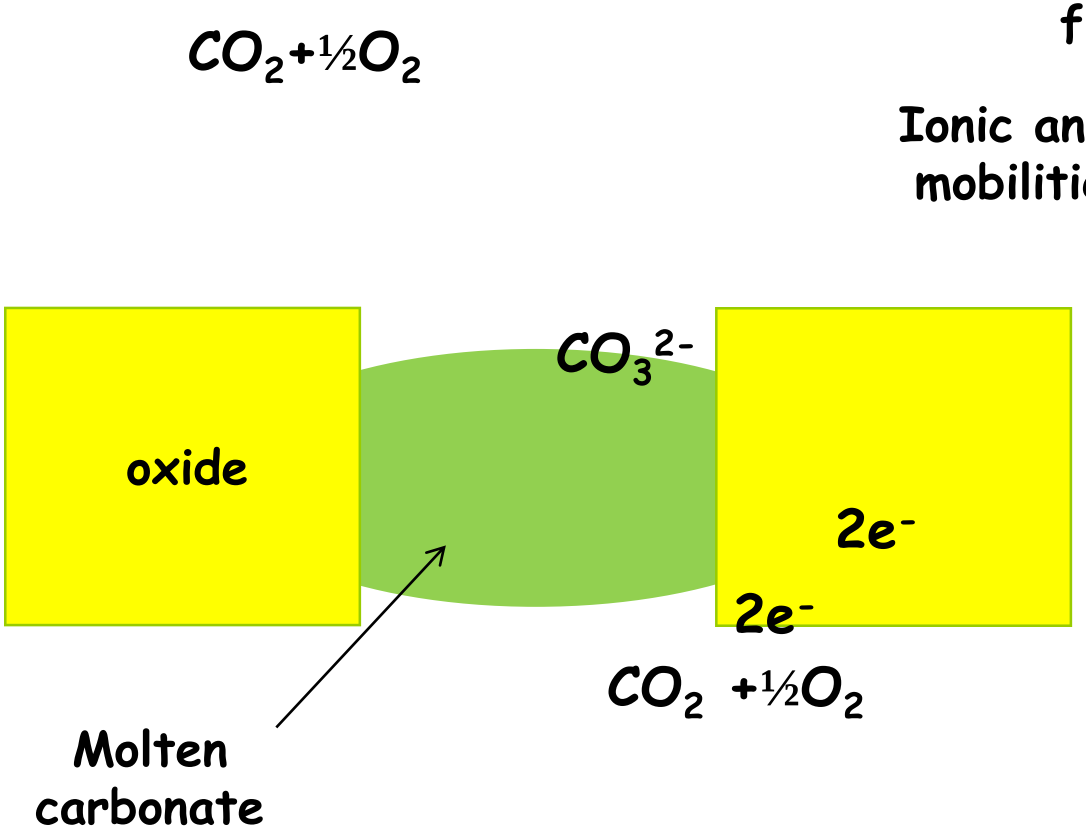
Carbon dioxide permeation – electronically conducting host

Applications: Carbon dioxide removal from flue gas

Ionic and electronic mobilities are high



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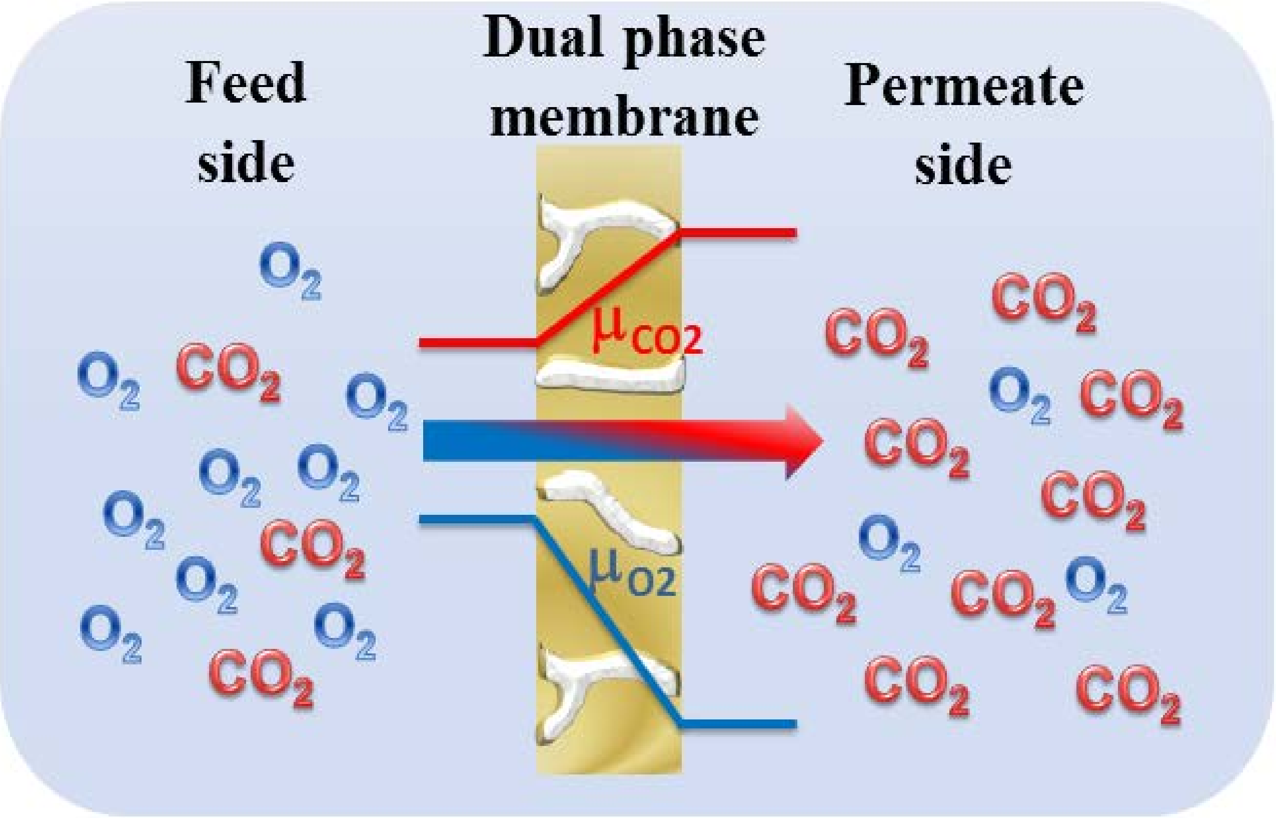
So why don't we just look inside the membrane?

Dual phase membranes for up-hill CO2 permeation



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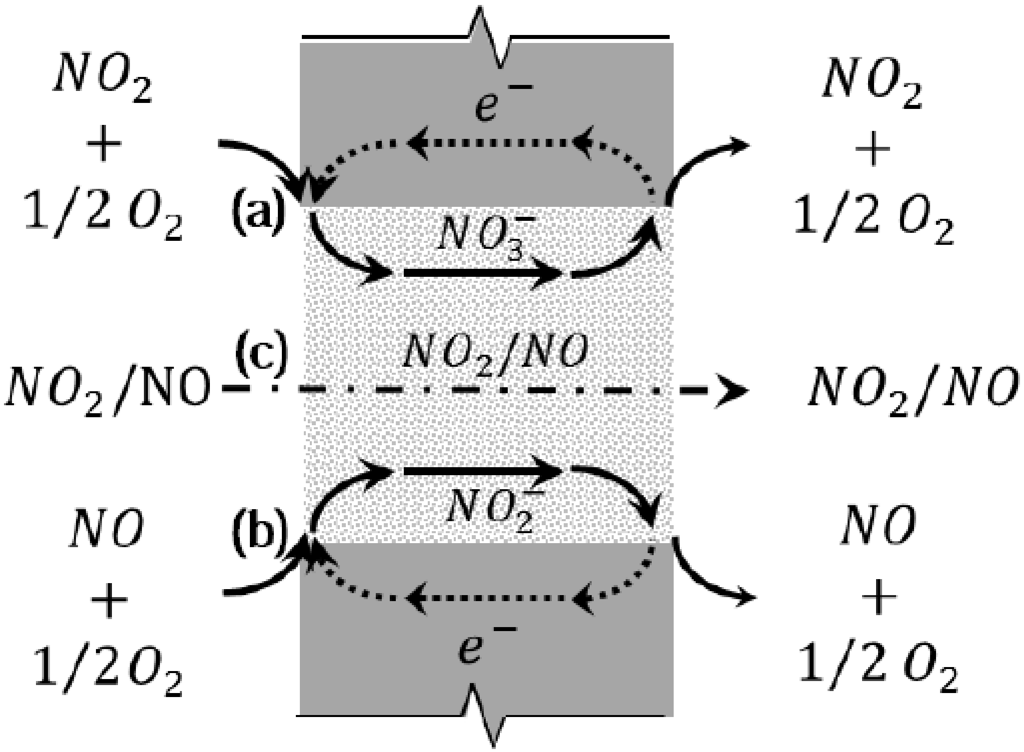
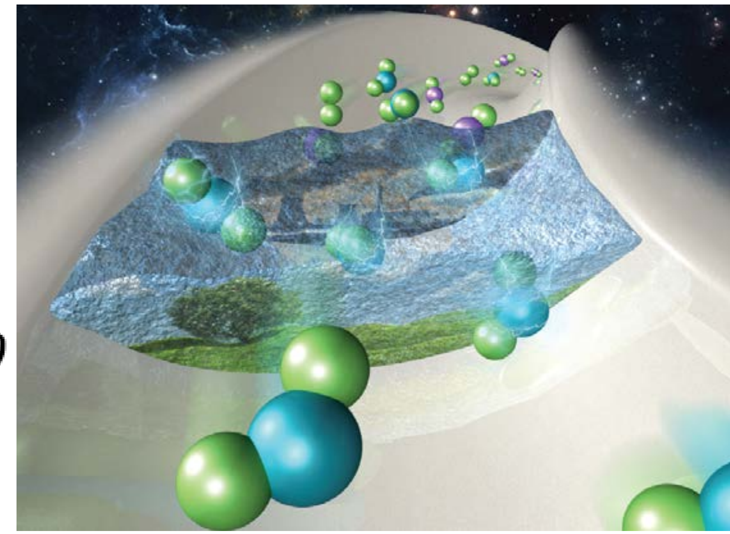
NOx permeation





Ceramic Support

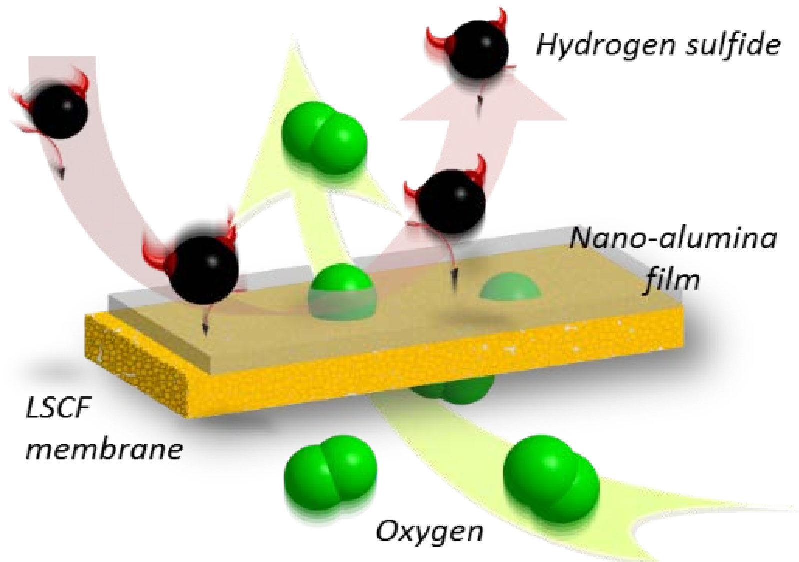
G. Zhang, E. I. Papaioannou, I. S. Metcalfe,
Energy Environ. Sci. 8 (2015) 1220–1223.

$$NO_3^- \leftrightarrow NO_2^- + 1/2\, O_2$$

$$NO_2 \leftrightarrow NO + 1/2\, O_2$$

Atomic layer deposition

☐ Proposed structure

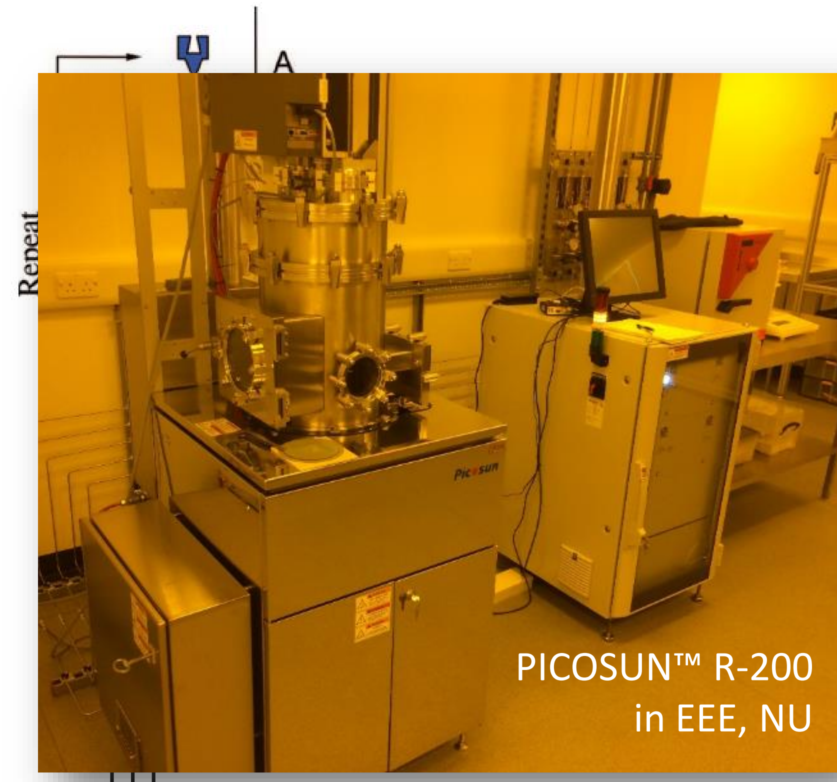


Expected feature:

- Isolating LSCF from H_2S or other sulfur
- Dense Alumina (AlO_x) nanofilm
- Conformal to the bulk LSCF membrane

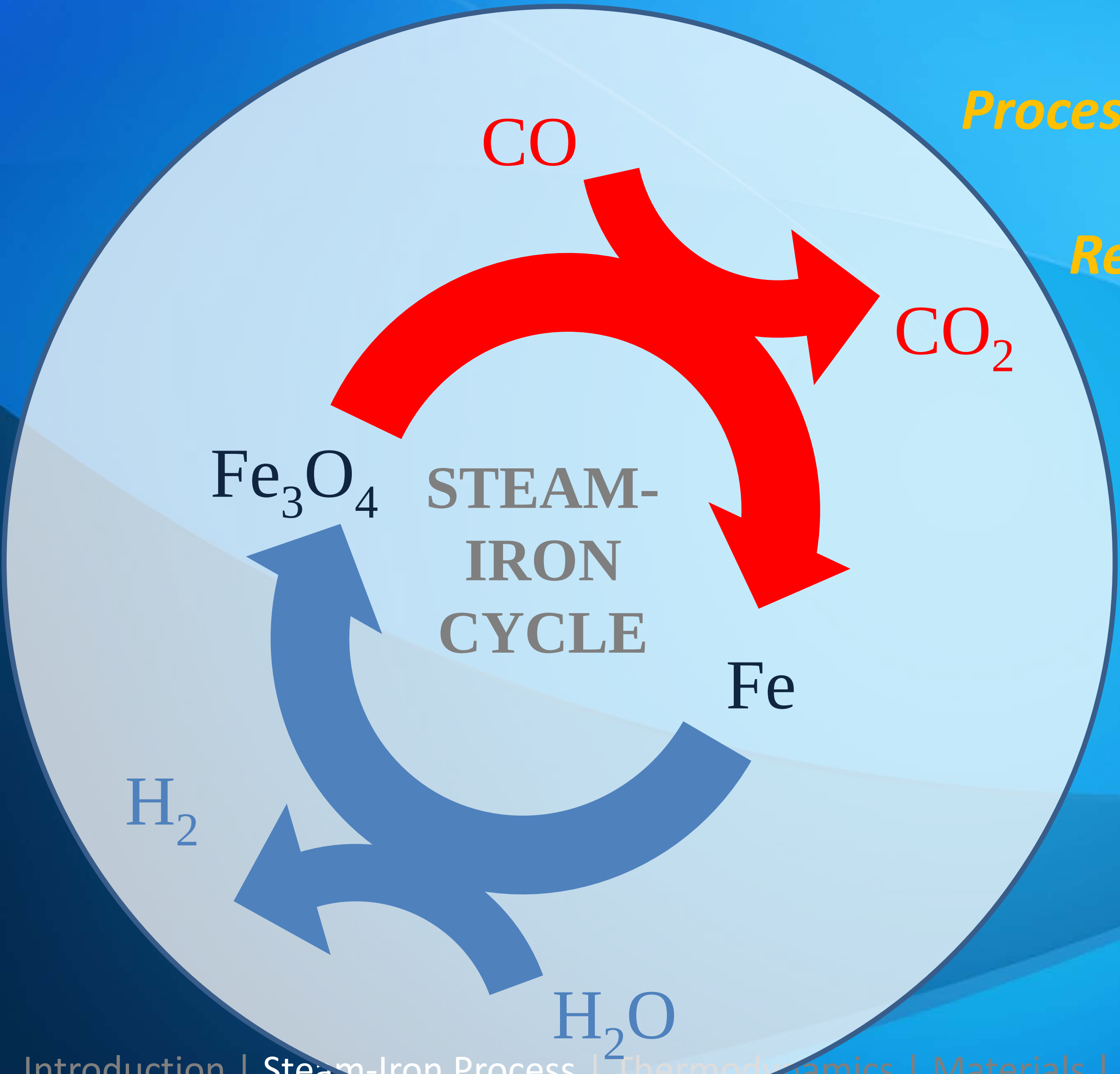
☐ Ultra thin film fabrication

- ❑ Sputtering
- ❑ Pulsed-laser deposition (PLD)
- ❑ Atomic layer deposition(ALD)



Steam-Iron Process

(using natural gas reducing feed)



Process invented in 1907

Requires no separation step

High Purity H_2

Cyclic Process

A. Murugan, A. Thursfield and I. S. Metcalfe, Energy Environ. Sci. 4(11) (2011) 4639-4649.

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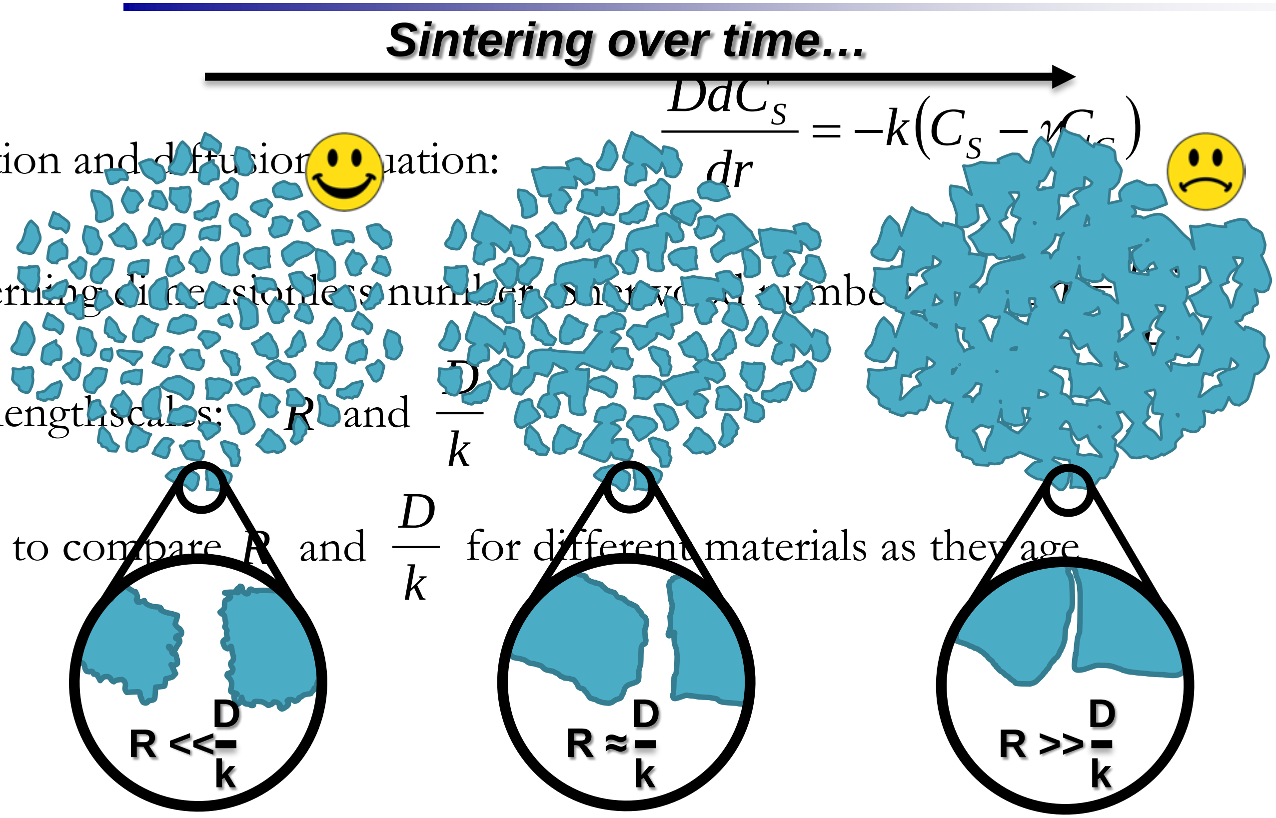

- Reaction and diffusion equation: $\frac{DdC_S}{dr} = -k(C_S - \gamma C_G)$
- Governing dimensionless number … number …
- Two lengthscales: R and $\frac{D}{k}$
- Need to compare R and $\frac{D}{k}$ for different materials as they age.
- Iron oxide kinetics are problematic – sintering and crystallite size becomes greater than chemical length scale.

At start $R << \frac{D}{k}$ but on sintering $R >> \frac{D}{k}$

Rational kinetic design of an OCM

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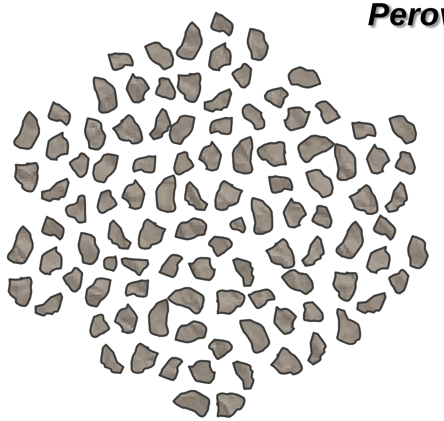
- Need materials that always have $R << \dfrac{D}{k}$, small R or high $\dfrac{D}{k}$

- Perovskite oxides do not sinter easily (already low surface area)
- Phase stable under reducing conditions

Perovskite Oxide – MIEC material



Does NOT sintering easily over time…

$R << \frac{D}{k}$

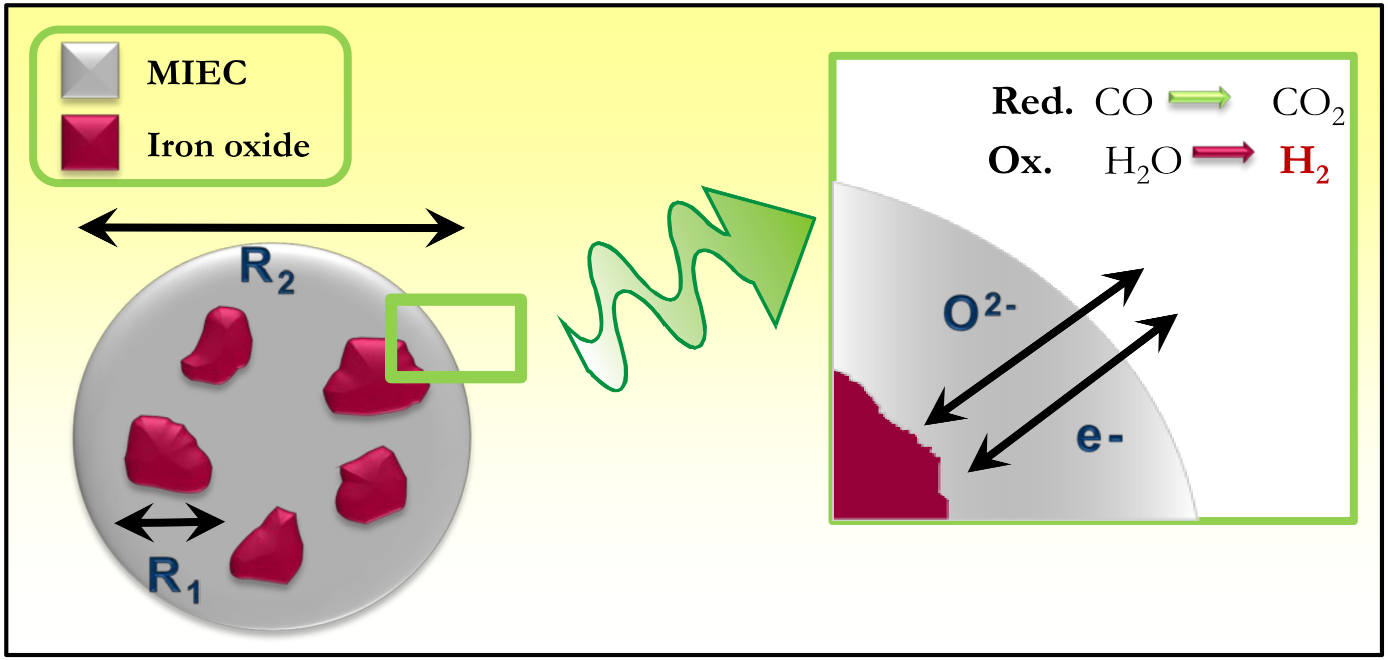
$$5\frac{m^2}{g},\ 5\frac{g}{cc},\ 25\times10^4\ \frac{cm^2}{cm^3}$$

$$R \approx 4\mu m$$

- Perovskites can be designed to have long chemical length scales,

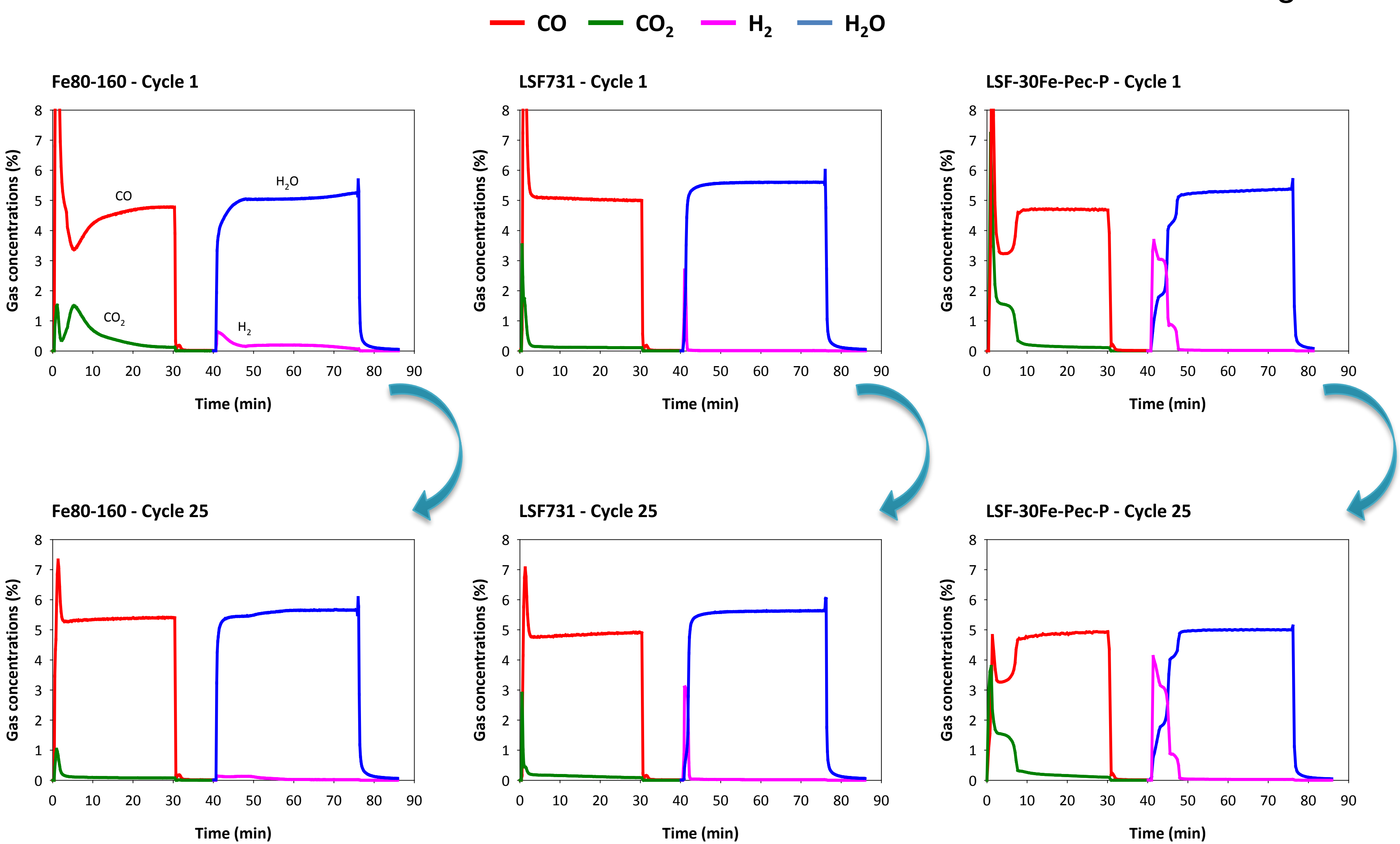
$\dfrac{D}{k}$ always high ≈ 100 - 300 micron (need high D/k but not at expense of low k!)

Proposal → **COMPOSITE MATERIALS**

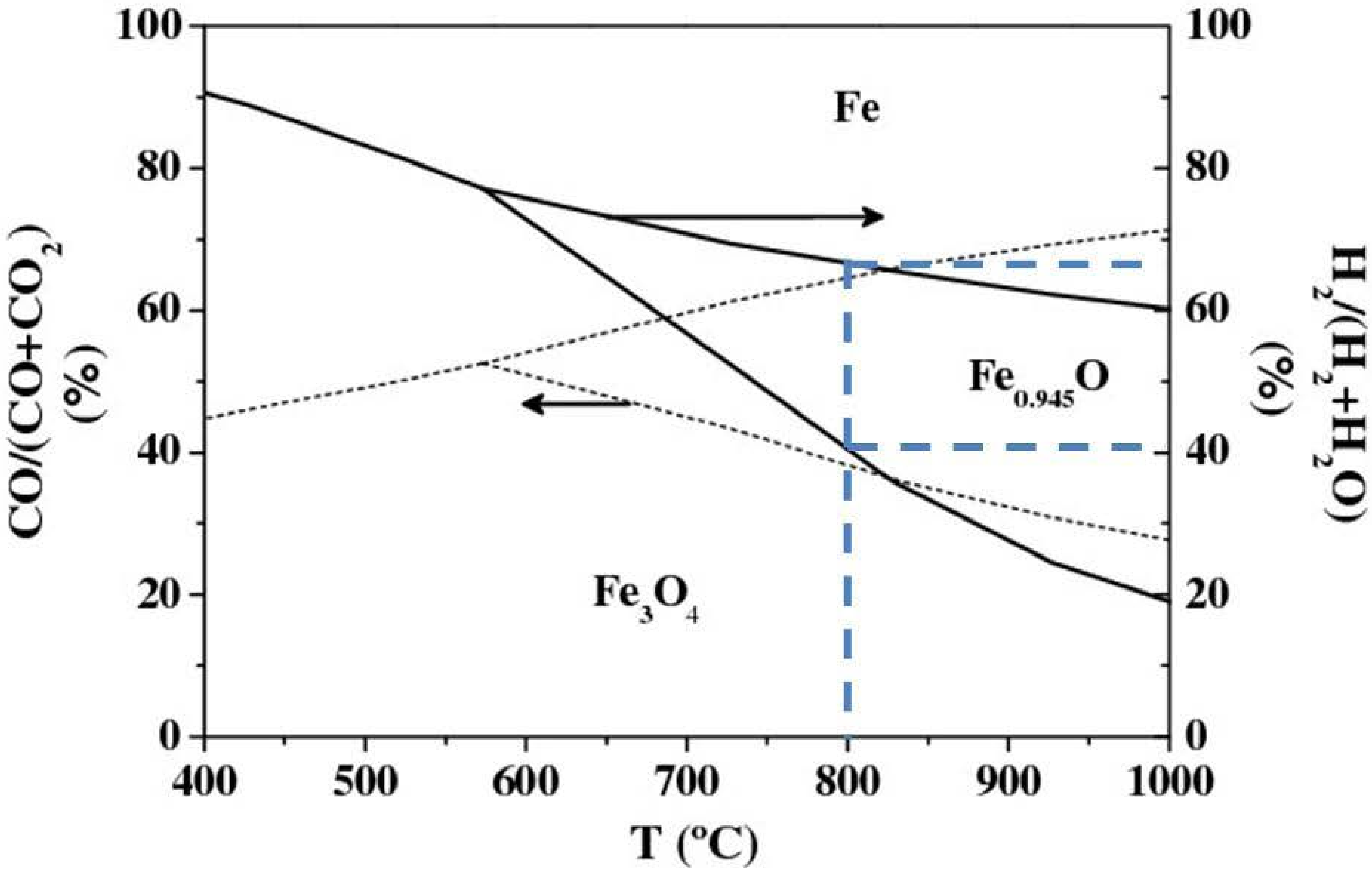


Results – 1st and 25th cycles

850°C 50 mg



Baur-Glaessner phase diagram



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Surface oxygen adsorption and incorporation – Henny Bouwmeester

$$n\frac{\partial f_g^{18}}{\partial t} = -\Re_0 S\left(f_g^{18} - f_o^{18}\right)$$

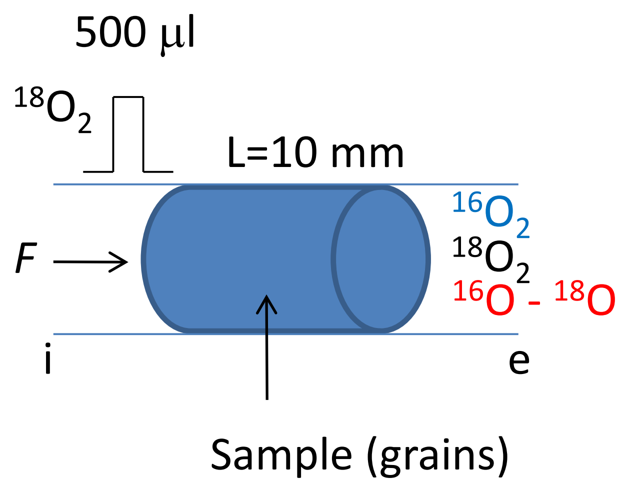
Ideal plug flow

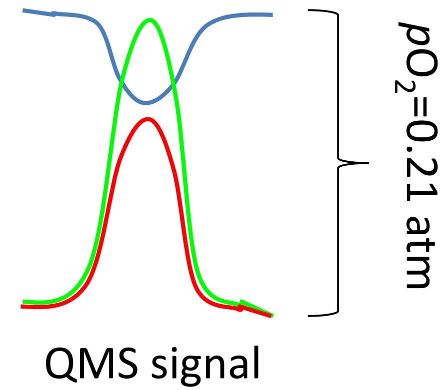
$$\Re_0 = \frac{n}{\tau_r S}\ln\left(\frac{f_{g,i}^{18}}{f_{g,e}^{18}}\right)$$

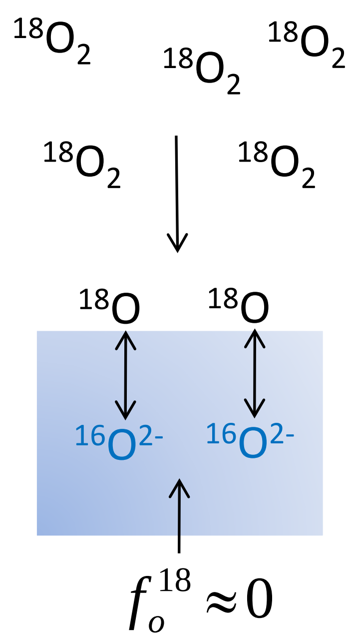
$\tau_r = (V_b \varepsilon / F)$; ~5-40 mS

S BET surface area

n O atoms in gas phase







possible combinations:

^{16}O - ^{16}O m/z = 32

^{16}O - ^{18}O m/z = 34

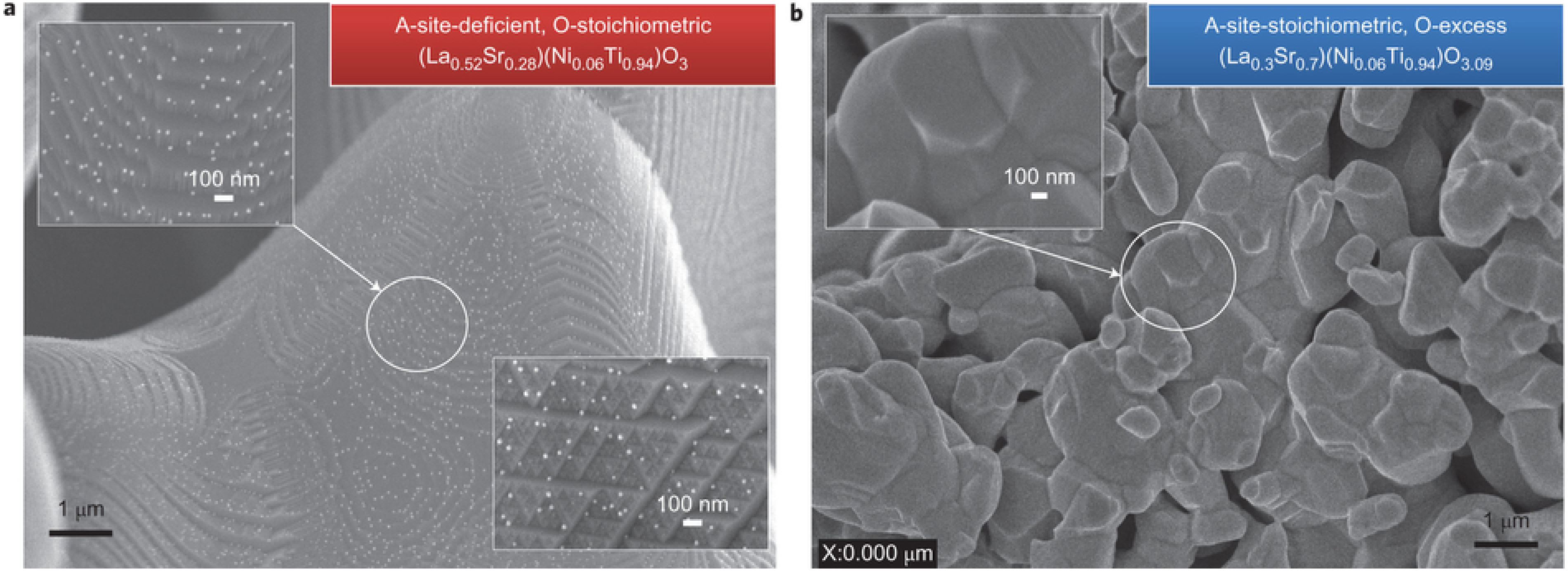
^{18}O - ^{18}O m/z = 36

$p^{16}O_2 = p^{18}O_2$ = 0.21 atm and T is fixed
i.e., at equilibrium

Catalyic modification of interaces

•George Tsekouras, David N. Miller, Hervé Ménard & John T. S. Irvine
Nature Chemistry **5**, 916–923 (2013) doi:10.1038/nchem.1773

a, Exsolutions from the initially A-site-deficient, O-stoichiometric $La_{0.52}Sr_{0.28}Ni_{0.06}Ti_{0.94}O_3$ after reduction at 930 °C (20 hours) in 5%H_2/Ar. **b**, A-site-stoichiometric, O-excess $La_{0.3}Sr_{0.7}Ni_{0.06}Ti_{0.94}O_{3.09}$ sample reduced at 930 °C (20 hours) in 5%H_2/Ar indicates that no exsolution has occurred.



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