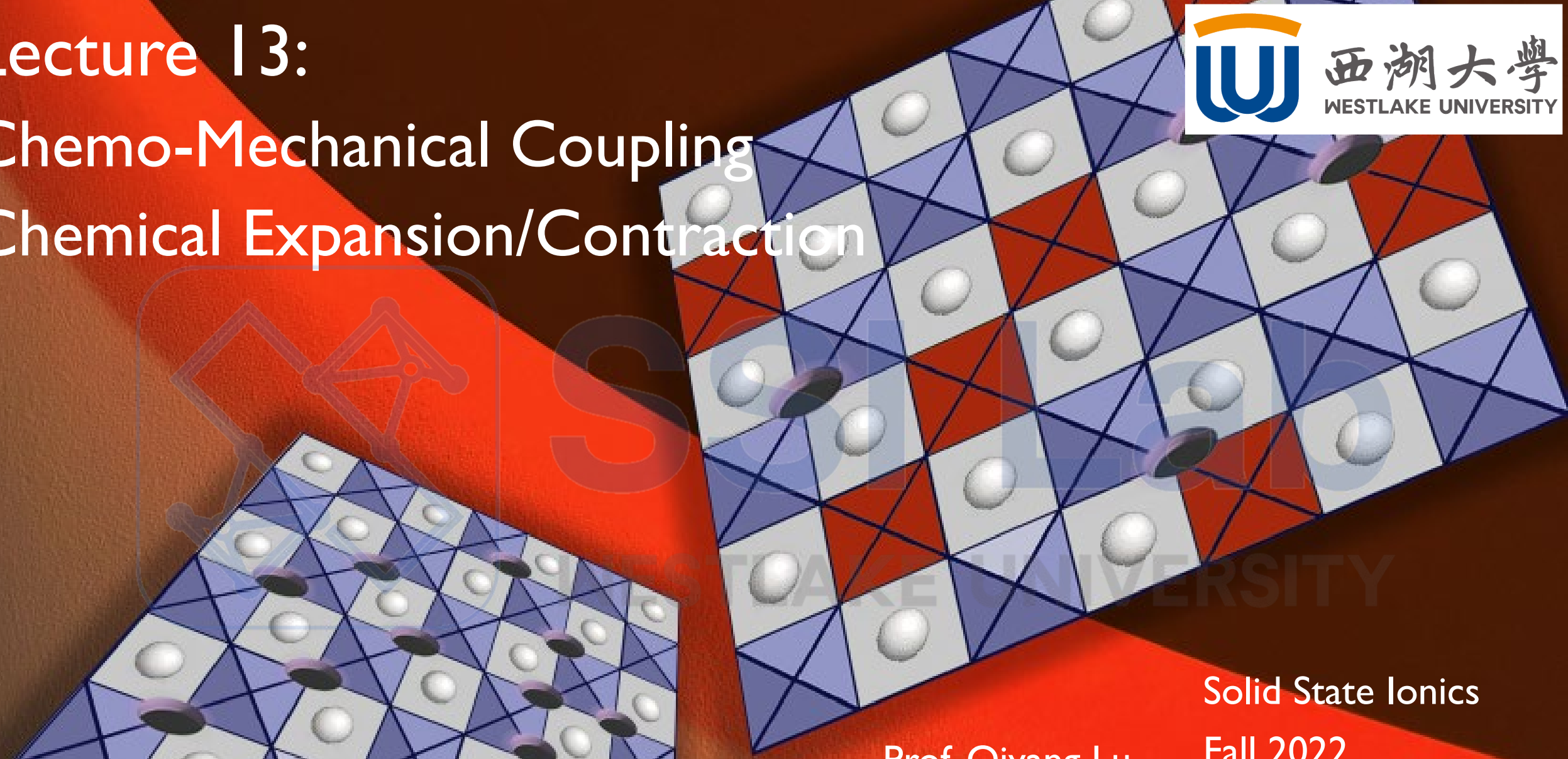
Lecture 13:
Chemo-Mechanical Coupling
Chemical Expansion/Contraction



Prof. Qiyang Lu
School of Engineering
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Solid State Ionics
Fall 2022

西湖大學
WESTLAKE UNIVERSITY

SSI Lab
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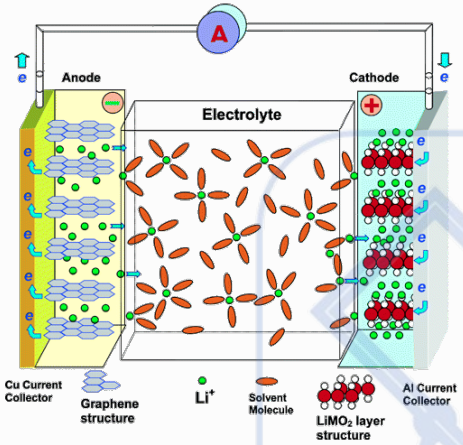
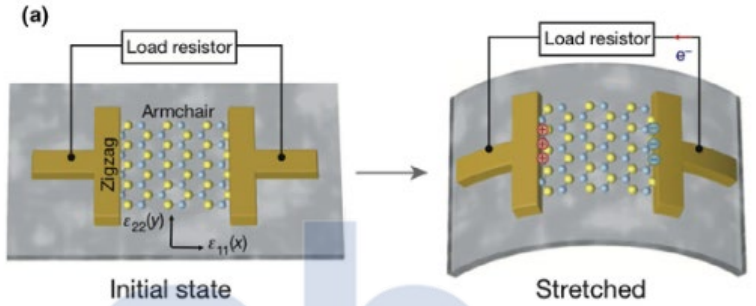
Electro-chemo-mechanical coupling



Xu, ***Chem. Rev.***, 2004



Wu et al., ***Nature***, 2014

Electrical

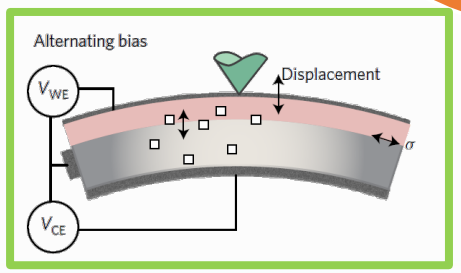
Electrochemistry
(*e.g.*, Batteries)

Electro-mechanics
(*e.g.*, Piezoelectric)

Chemical

Mechanical

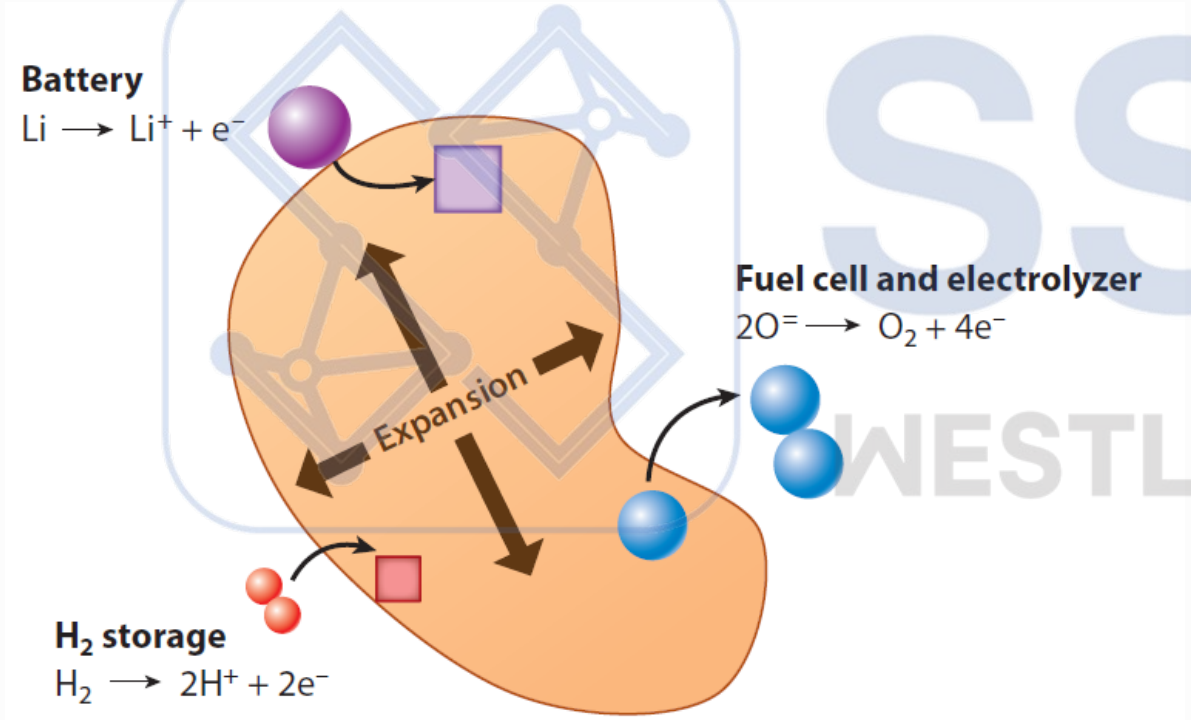
Chemo-mechanics
(*e.g.*, Actuators)



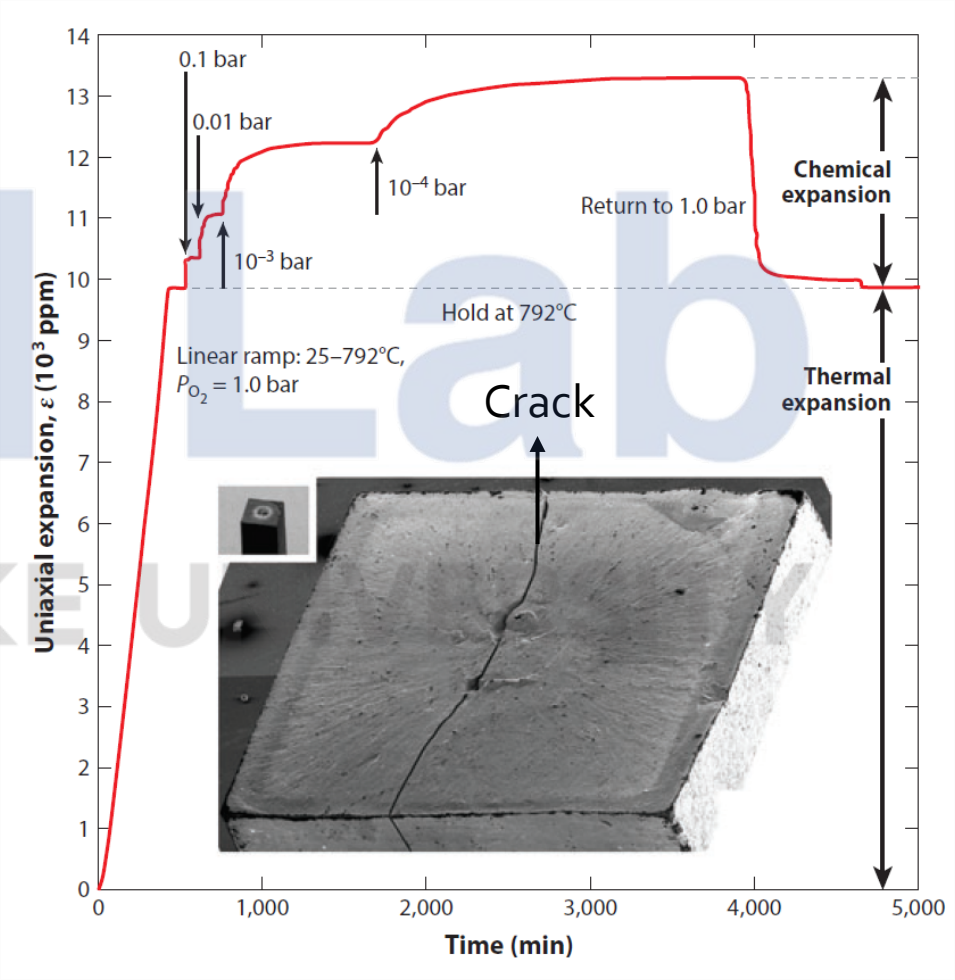
Swallow, Tuller, Van Vliet et al., ***Nat. Mater.*** 2017

Chemical expansion: definition and consequence

Chemical (*i.e.*, point defects) ⟷ Mechanical (*i.e.*, strain, lattice constant)

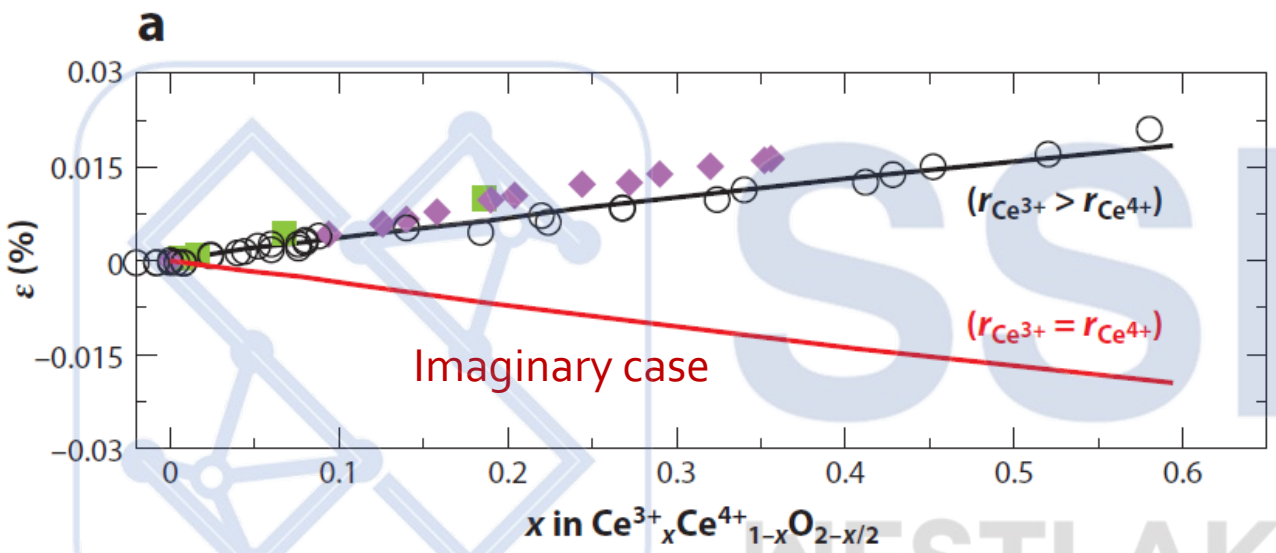


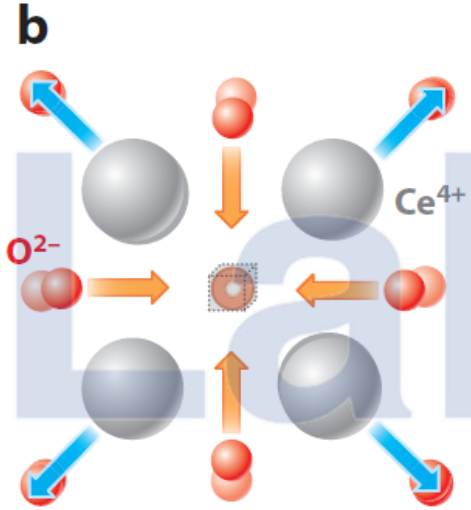
Bishop *et al.*, ***Annu. Rev. Mater. Res.***, 2014



Adler, ***J. Am. Ceram. Soc.***, 2001

$CeO_{2-\delta}$ as a model system to study chemical expansion





Defect chemical reaction in CeO_{2-x}

$$O_O^{\times} \rightarrow \frac{1}{2}O_2 + 2Ce'_{Ce} + V_O^{\cdot\cdot}$$

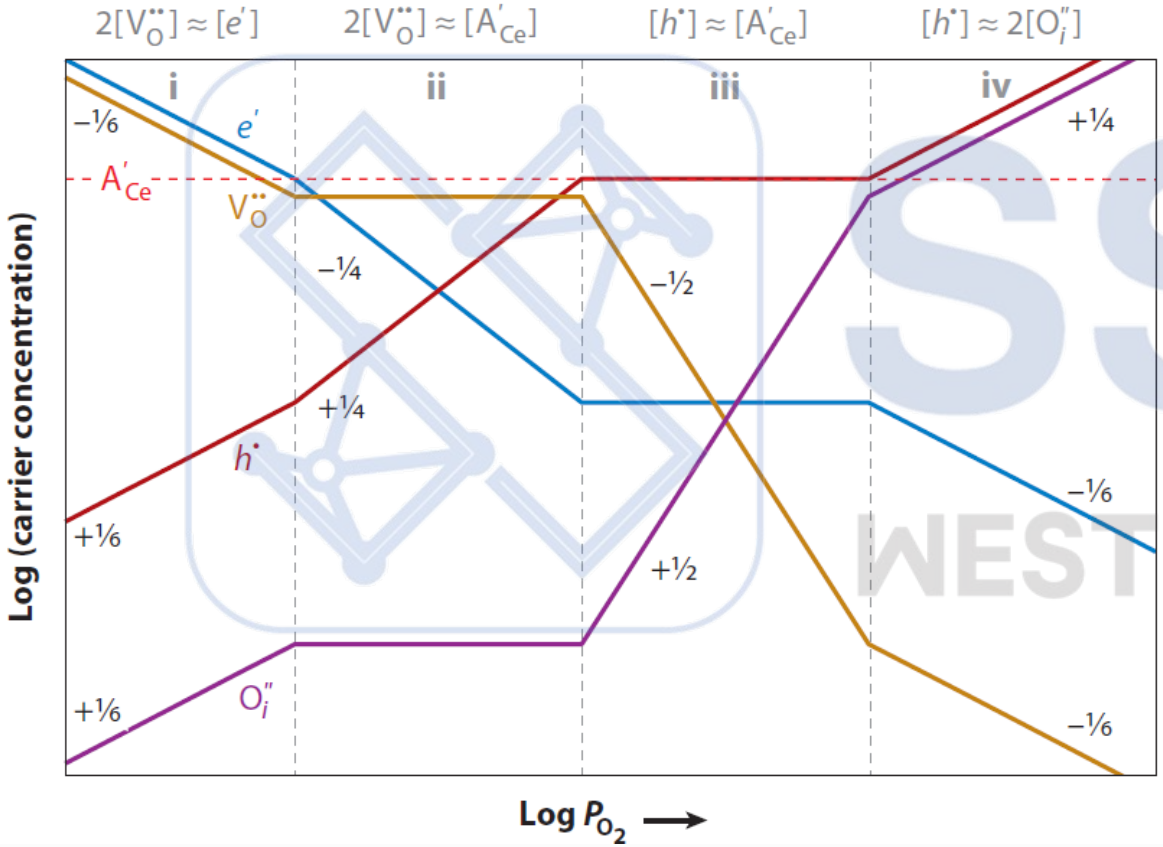
Different effect on lattice constant:

Ce'_{Ce} expansion (ionic radius $Ce^{3+} > Ce^{4+}$)
$V_O^{\cdot\cdot}$ contraction (vacancies = voids)

Overall, increase of x in CeO_{2-x} *increases* lattice constant

Bishop *et al.*, ***Annu. Rev. Mater. Res.***, 2014

How to give a quantitative description on chemical expansion?



$$O_O^{\times} \rightarrow \frac{1}{2}O_2 + 2Ce'_{Ce} + V_O^{\cdot\cdot} \qquad CeO_{2-\delta}$$

$$\varepsilon = \alpha_C [i]$$

Strain def: $\Delta L/L$

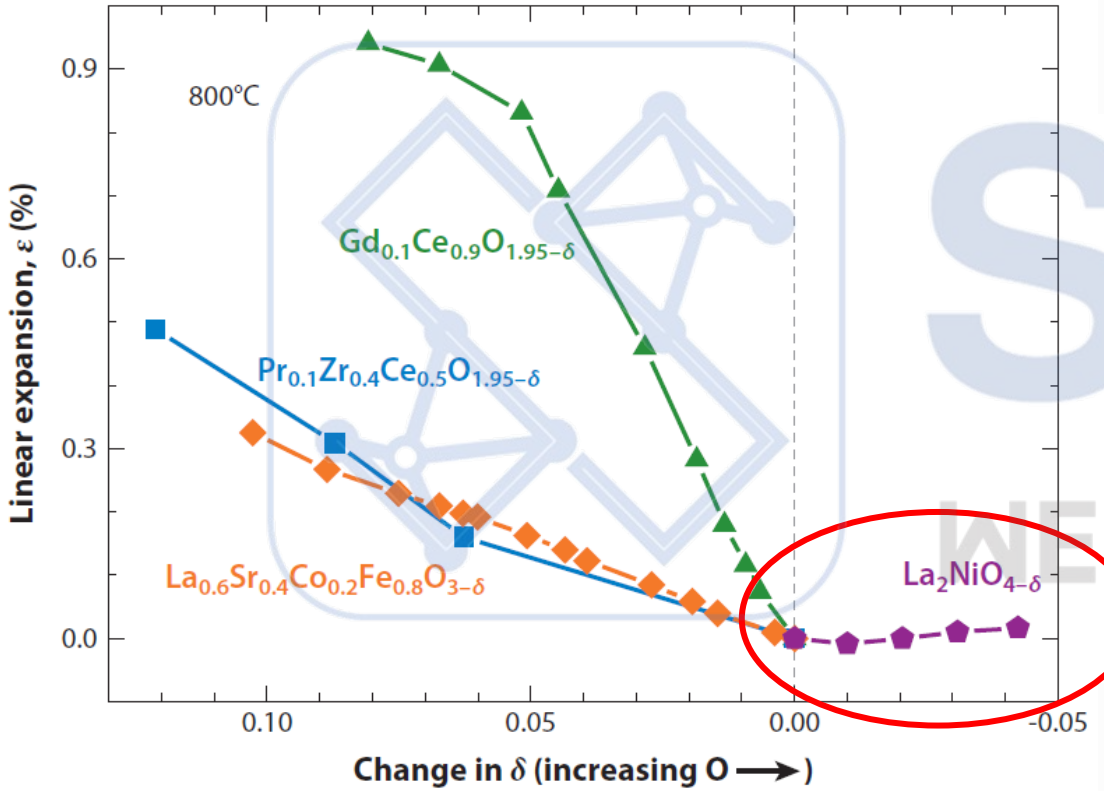
Chemical expansion coefficient

Concentration of defects Unit: #/cm³

Note: concentration of defects expressed by using #/cm³ is different from δ

Tuller and Bishop, ***Annu. Rev. Mater. Res.***, 2011

Chemical expansion in other oxide systems



Note: concentration of defects expressed by using #/cm³ is different from δ

Table 1 Experimentally determined stoichiometric expansion coefficients and corresponding oxygen vacancy radii for different materials together with the DFT values obtained in this work. The chemical expansion coefficients and r_V for A-site and B-site doped $LaGaO_3$ were obtained from averaging several experimental values (which we report in the ESI) taken from ref. 11 and 50

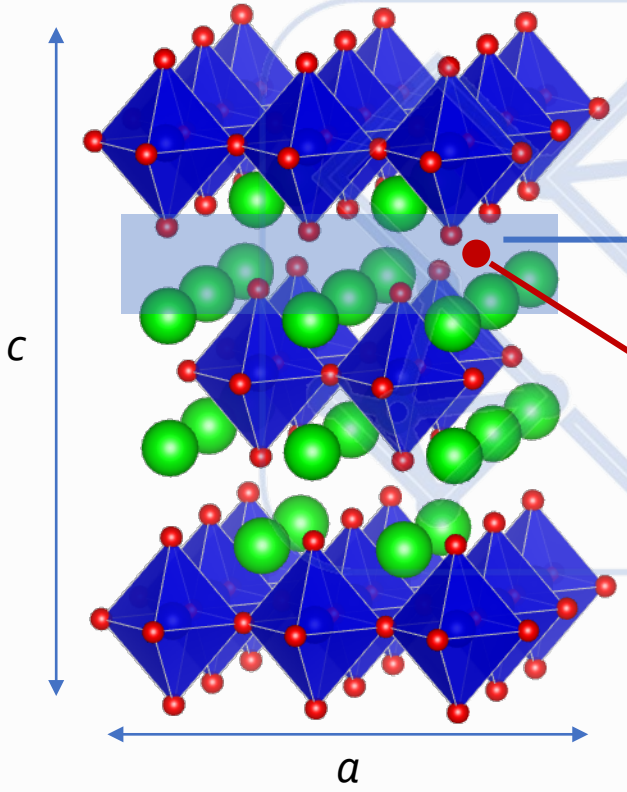
Material	α_S	$\alpha_S^{[]}$ [cm³ × 10²⁴]	r_V [Å]	Ref.
Fixed valence substitution				
La(Ga, Mg)O_3 (Sr A-site substitution)	0.008	0.48	1.30	11 and 50
$La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_{3-x/2}$ (DFT)	0.026 ± 0.004	1.6	1.41	This work
(La, Sr)GaO_3 (Mg B-site substitution)	0.056	3.3	1.29	11 and 50
$La_{0.8}Ga_{1-x}Mg_xO_{3-x/2}$ (DFT)	0.057 ± 0.008	3.4	1.30	This work
$La_{1-x}Sr_xAlO_3$	0.017	0.93	1.36	53
$La_{1-x}Sr_xAlO_3$ (DFT)	0.018 ± 0.014	0.98	1.38	This work
$SrTi_{1-x}Ga_xO_3$ (DFT)	0.040 ± 0.021	2.4	1.57	This work
Multivalent cation				
$CeO_{2-\delta}$ [a]	0.10	4.0	1.169	20
$Pr_{0.1}Zr_{0.4}Ce_{0.5}O_{1.95-\delta}$ [a]	0.046	1.7	0.966	19
$La_{0.9}Sr_{0.1}Ga_{0.95}Ni_{0.05}O_{3-\delta}$ (800–900 °C, oxidizing conditions)	0.040–0.049	2.4–2.9	1.24–1.30	32
$SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ (700–1000 °C, oxidizing conditions)	0.040–0.049	2.38–2.92	1.38–1.43	54

[a] These compounds have the fluorite structure.

Marrocchelli *et al.*, ***PCCP***, 2015

Bishop *et al.*, ***Annu. Rev. Mater. Res.***, 2014

Anisotropic chemical expansion

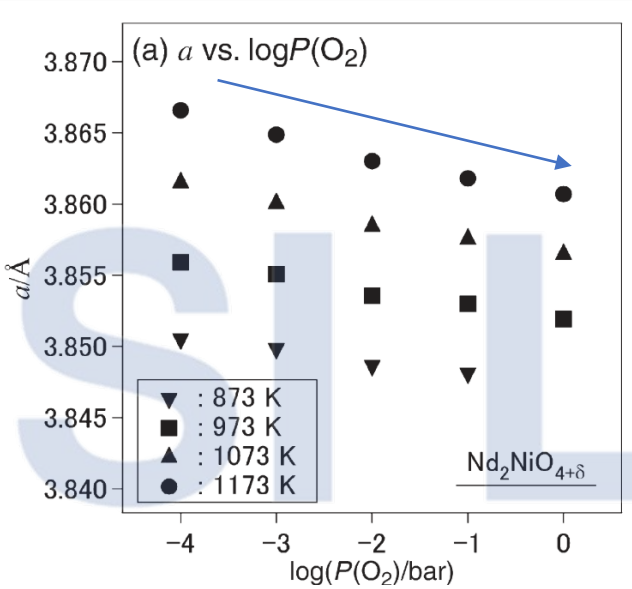


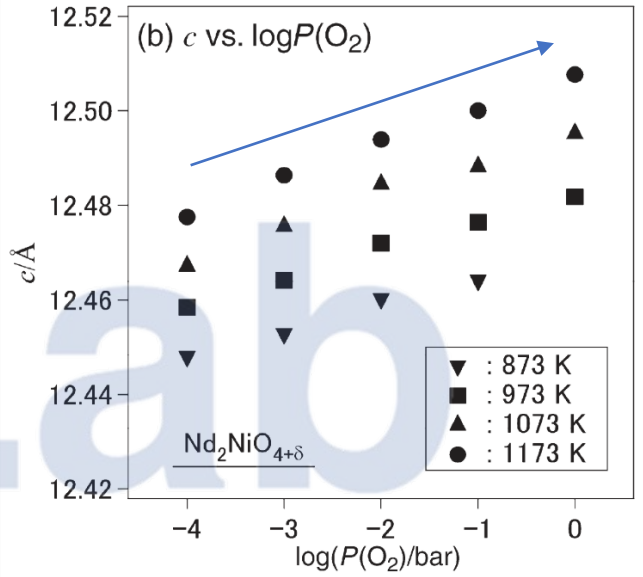
Perovskite layer

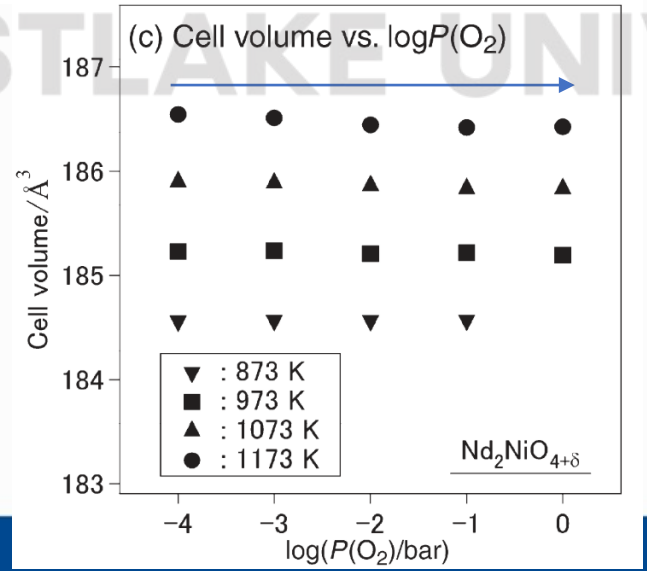
Rock salt (AO) layer

Majority ionic defect
Oxygen interstitials
O_i''
Negatively charged
Charge balanced by
holes ($h^{\cdot}$)

Ruddlesden-Popper phase
A_2BO_4 *e.g.*, Nd_2NiO_4



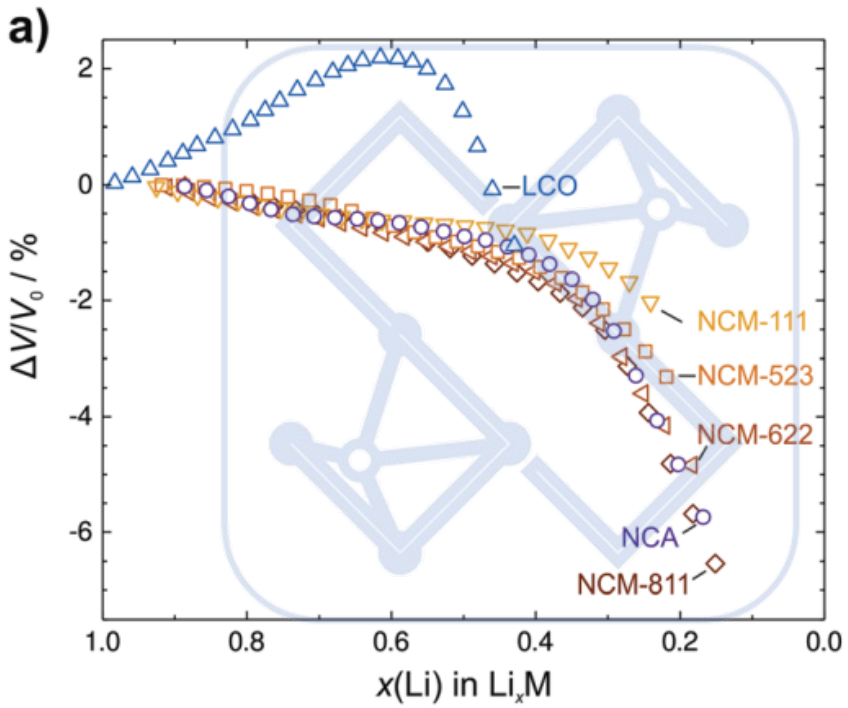


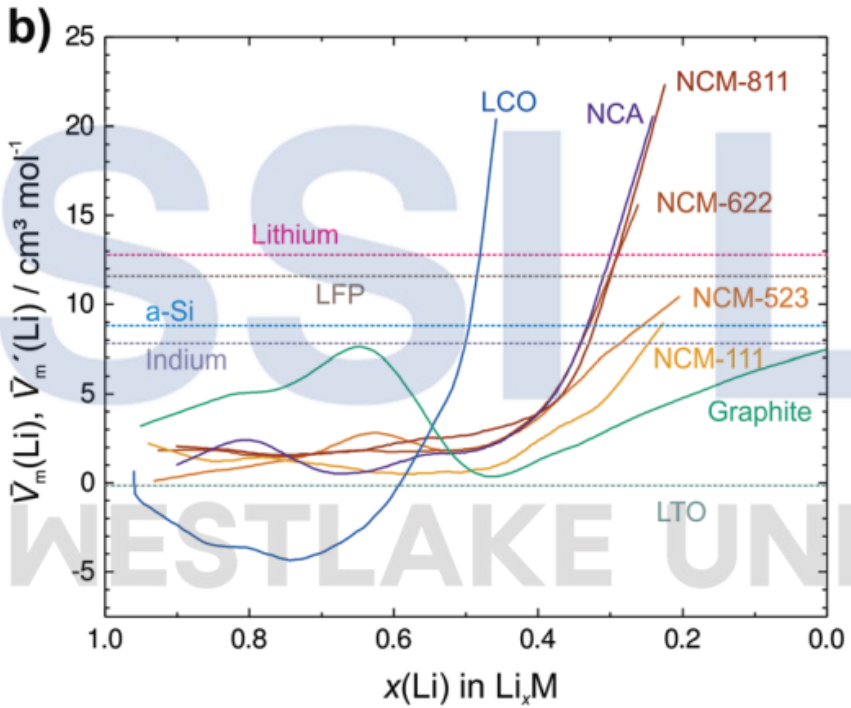


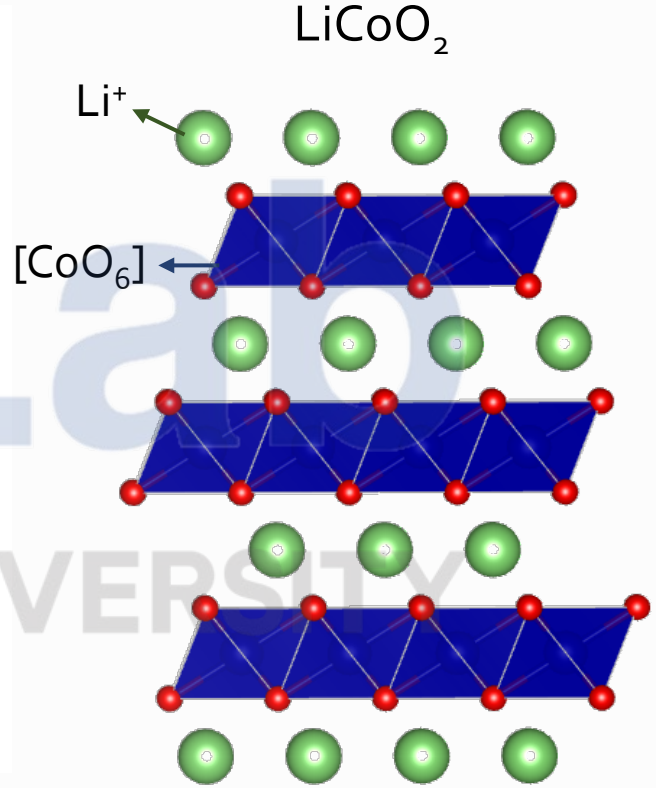
Oxygen interstitials affect *a* and *c* differently.

$pO_2 \rightarrow \delta \rightarrow a, c \rightarrow V$

Anisotropic chemical expansion: battery materials







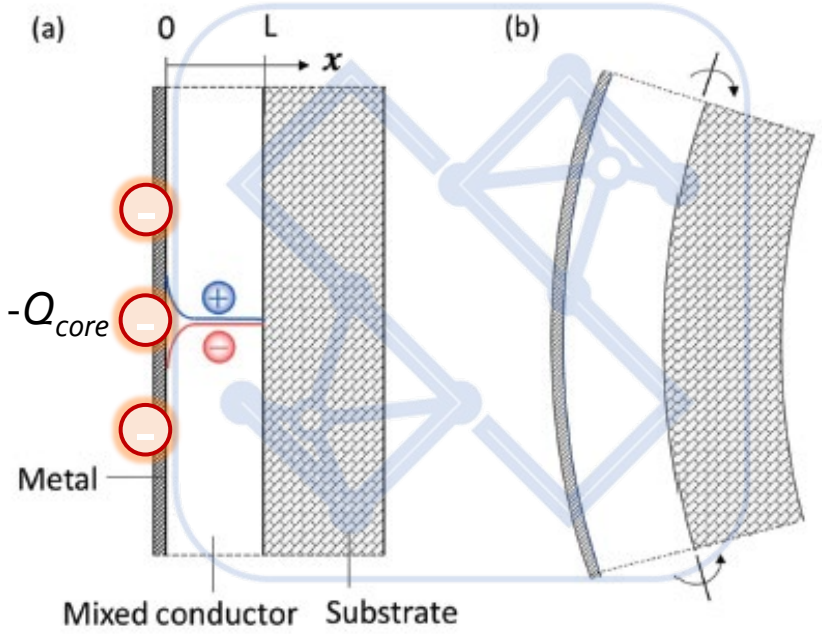
LCO = Li_xCoO_2
NCMxyz = $Li_\delta(Ni_xCo_yMn_z)O_2$
NCA = $Li_\delta(Ni_xCo_yAl_z)O_2$

$$\bar{V}_m(Li) = \left(\frac{\partial V}{\partial n_{Li}}\right)_{T,p,n_i \neq n_{Li}}$$

Partial molar volume of Li

How to model the equilibrium of charged ionic defects under strain/stress?

Space charge layer + stress field



Equilibrium condition: $\tilde{\mu}_i$ is uniform $\quad \tilde{\mu}_i = \mu_i + z_i F\phi$

$$\tilde{\mu}_i = \mu_i + z_i F\phi = \mu_i^0 + PV_{m,i} + RTlna_i + z_i F\phi$$

hydrostatic pressure *partial molar volume*

In dilute limit:

$$\frac{c_i(x)}{c_{i,\mathrm{ref}}} = \exp\left[-\frac{1}{RT}\left[z_i F(\phi(x) - \phi_{\mathrm{ref}}) + V_{m,i}(P(x) - P_{\mathrm{ref}})\right]\right]$$

Electro-chemical coupling

Chemo-mechanical coupling

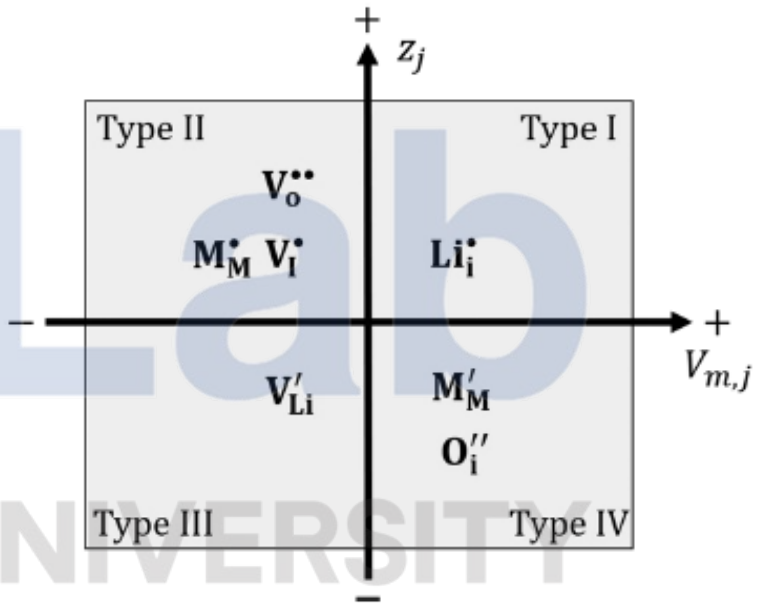
How to model the equilibrium of charged ionic defects under strain/stress?

In dilute limit:

$$\frac{c_i(x)}{c_{i,\mathrm{ref}}} = \exp\left[-\frac{1}{RT}\left[z_i F(\phi(x) - \phi_{\mathrm{ref}}) + V_{m,i}(P(x) - P_{\mathrm{ref}})\right]\right]$$

Electro-chemical coupling

Chemo-mechanical coupling



Note:

- In this picture, electrons and holes are treated as localized charge (polarons) → reduced cations (electrons) lead to expansion while oxidized cations (holes) lead to contraction;
- At equilibrium, the concentration of ionic defects are determined collectively by both electrochemical and chemomechanical coupling.

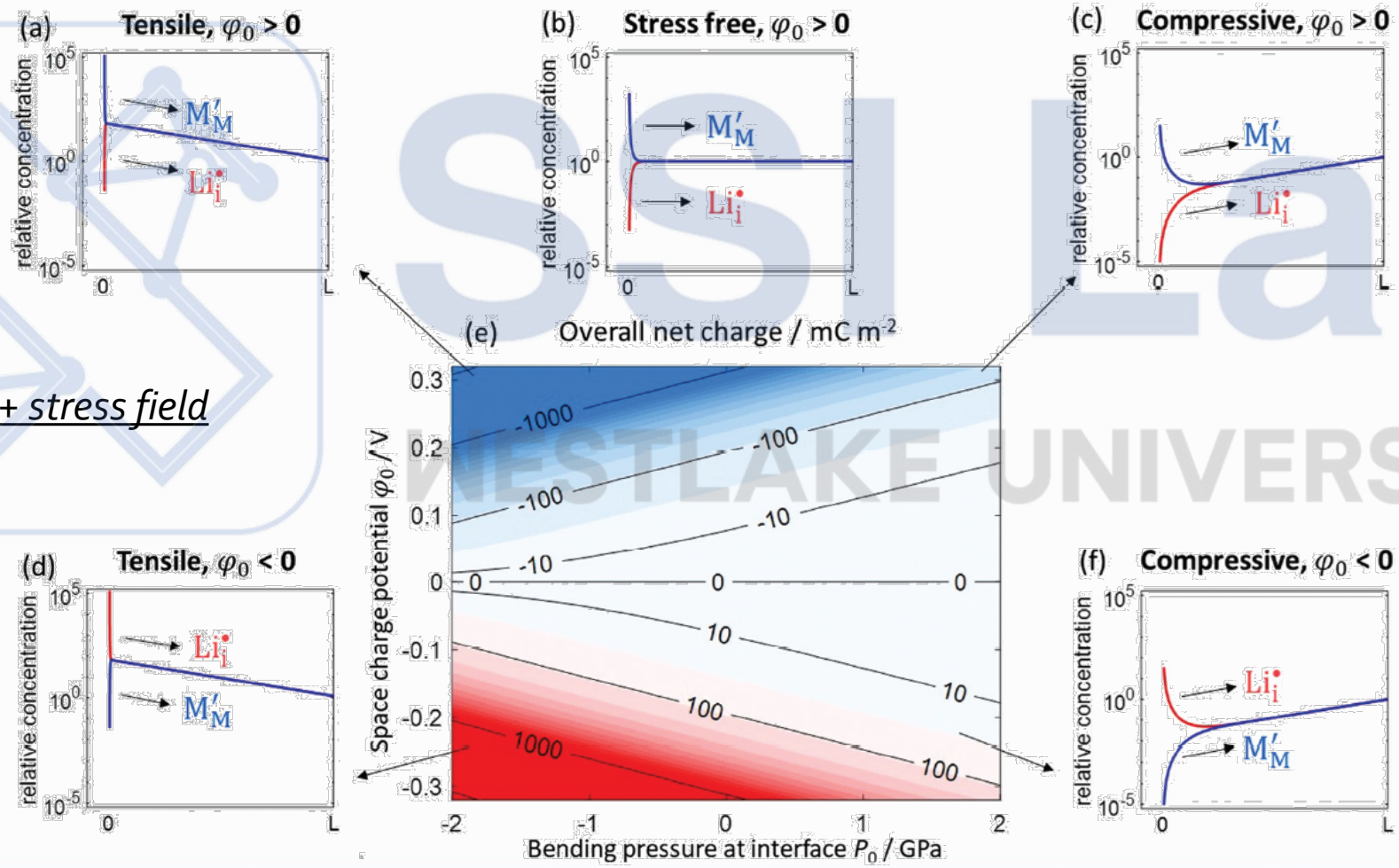
Vacancy: $V_{m,i} < 0$

Interstitial: $V_{m,i} > 0$

How to model the equilibrium of charged ionic defects under strain/stress?

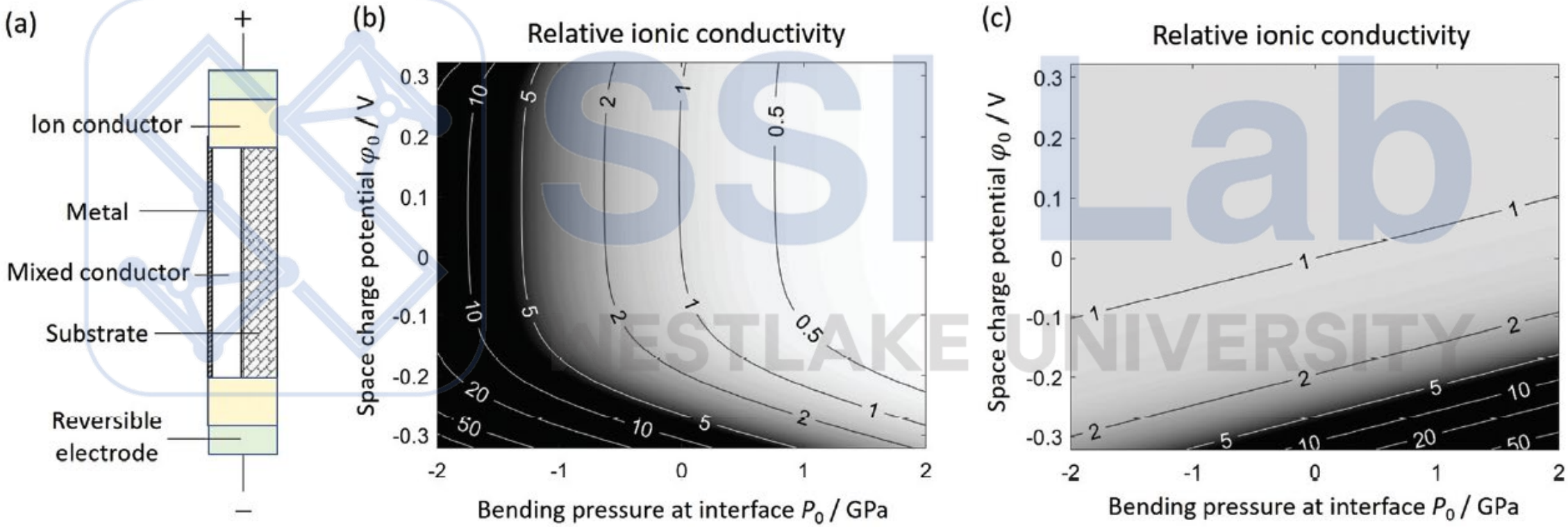
$$\frac{c_i(x)}{c_{i,\mathrm{ref}}} = \exp\left[-\frac{1}{RT}\left[z_i F(\phi(x) - \phi_{\mathrm{ref}}) + V_{m,i}(P(x) - P_{\mathrm{ref}})\right]\right]$$

Space charge layer + stress field

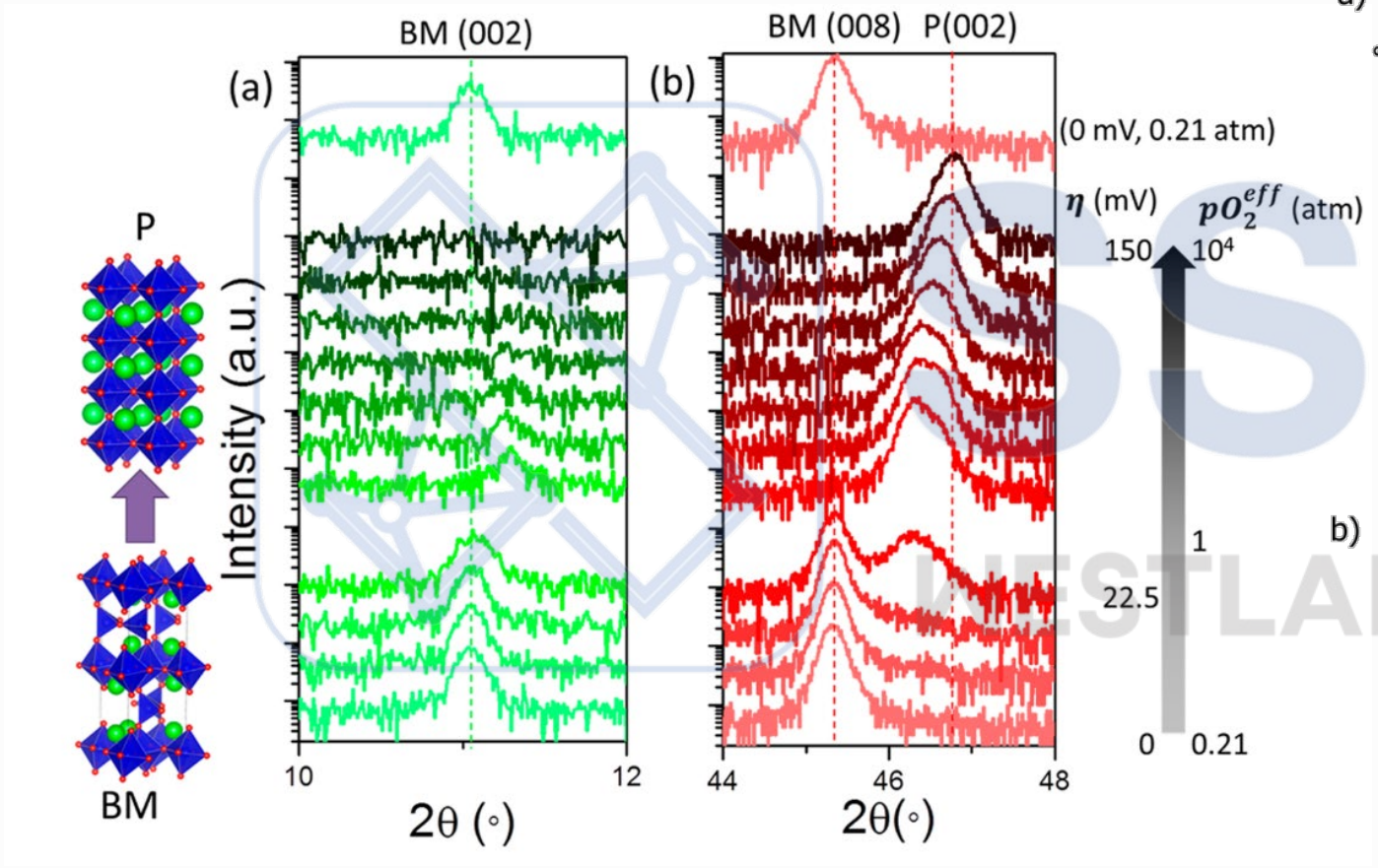


How to model the equilibrium of charged ionic defects under strain/stress?

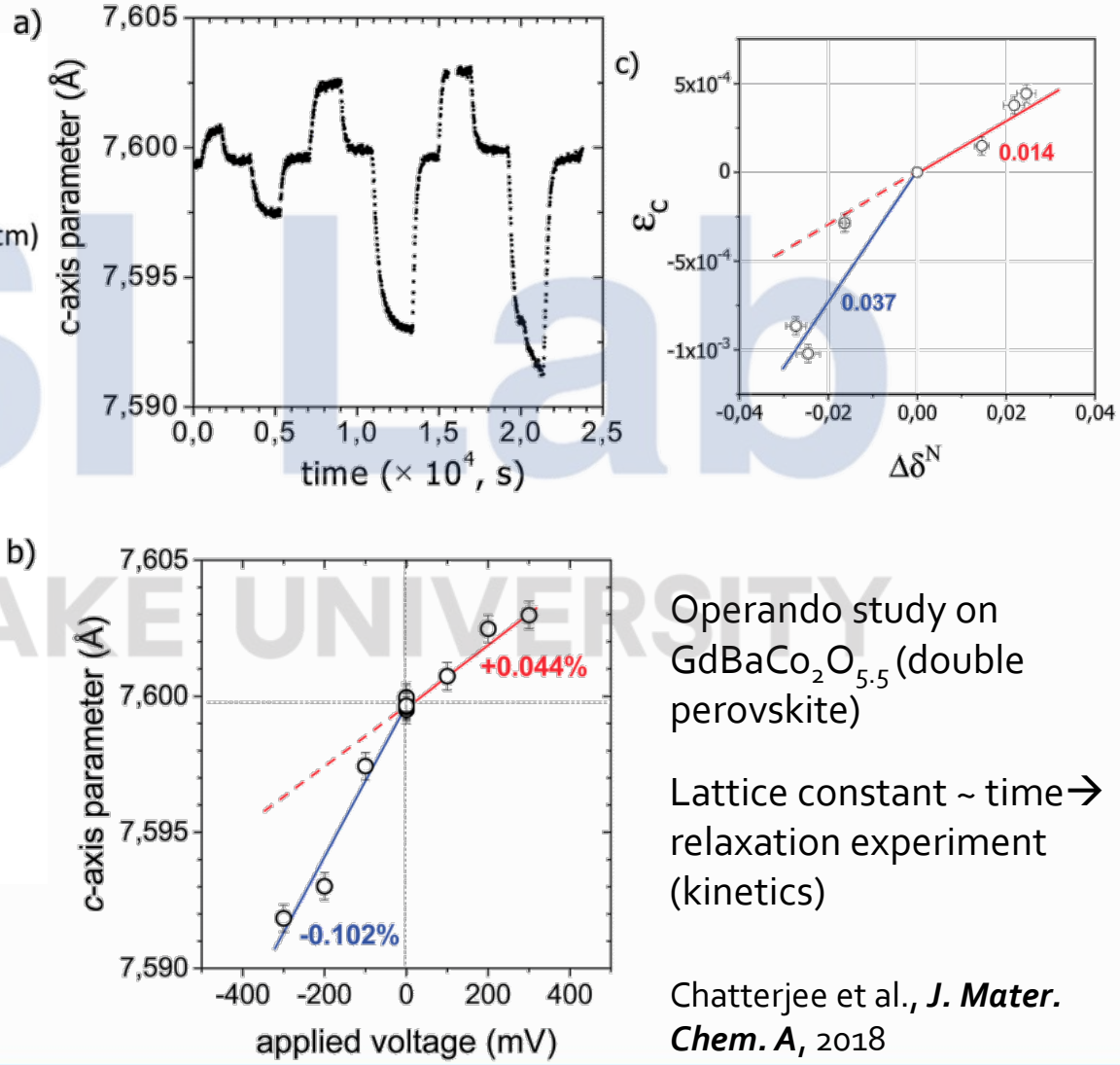
$$\frac{c_i(x)}{c_{i,\mathrm{ref}}} = \exp\left[-\frac{1}{RT}\left[z_i F(\phi(x) - \phi_{\mathrm{ref}}) + V_{m,i}(P(x) - P_{\mathrm{ref}})\right]\right]$$



How to probe chemical expansion: X-ray diffraction (XRD)



In situ XRD to monitor chemical expansion in $SrCoO_x$



Operando study on $GdBaCo_2O_{5.5}$ (double perovskite)

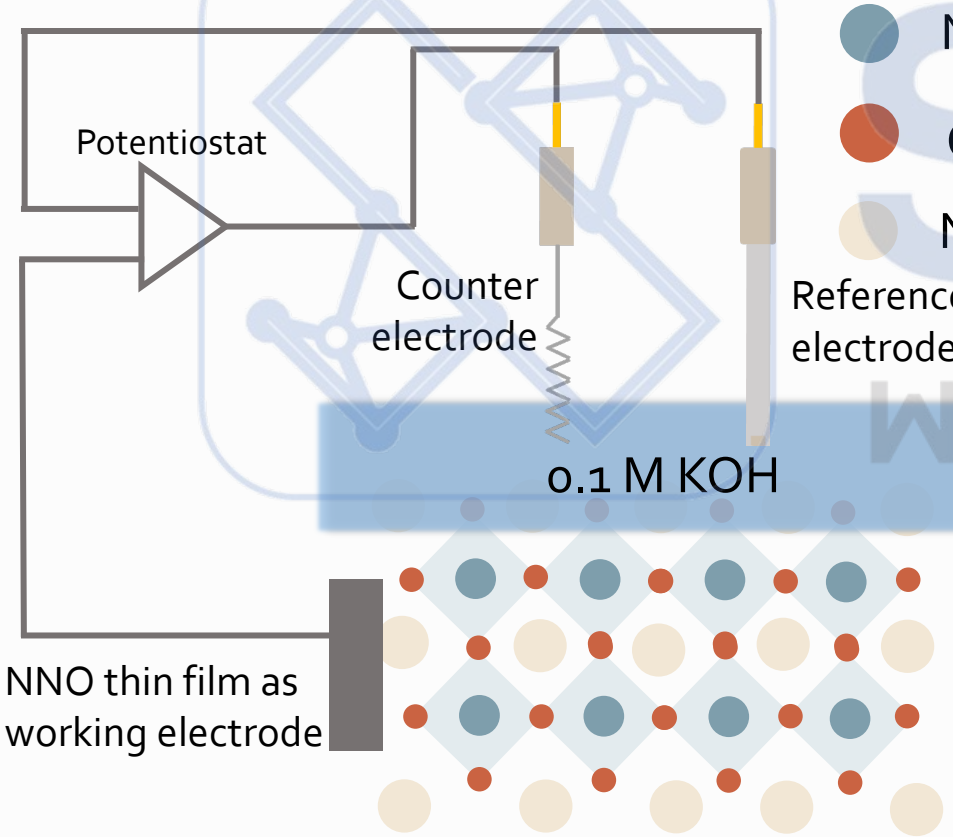
Lattice constant ~ time→ relaxation experiment (kinetics)

Chatterjee et al., ***J. Mater. Chem. A***, 2018

Lu and Yildiz, ***Nano Lett.***, 2016

How to probe chemical expansion: X-ray diffraction (XRD)

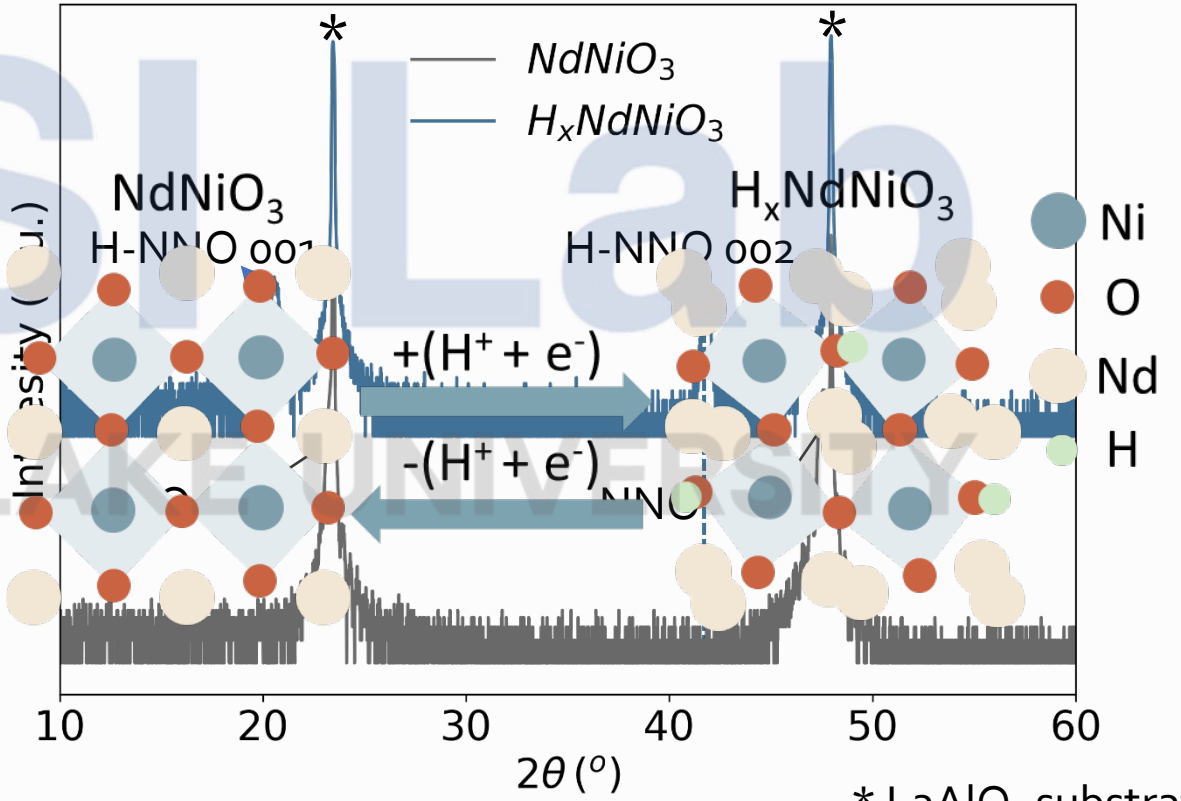
Hydrogenation of $NdNiO_3$ thin films w/ a ***3-electrode*** electrochemical system



Pristine $NdNiO_3$ (NNO) c_{pc} = 3.816 Å

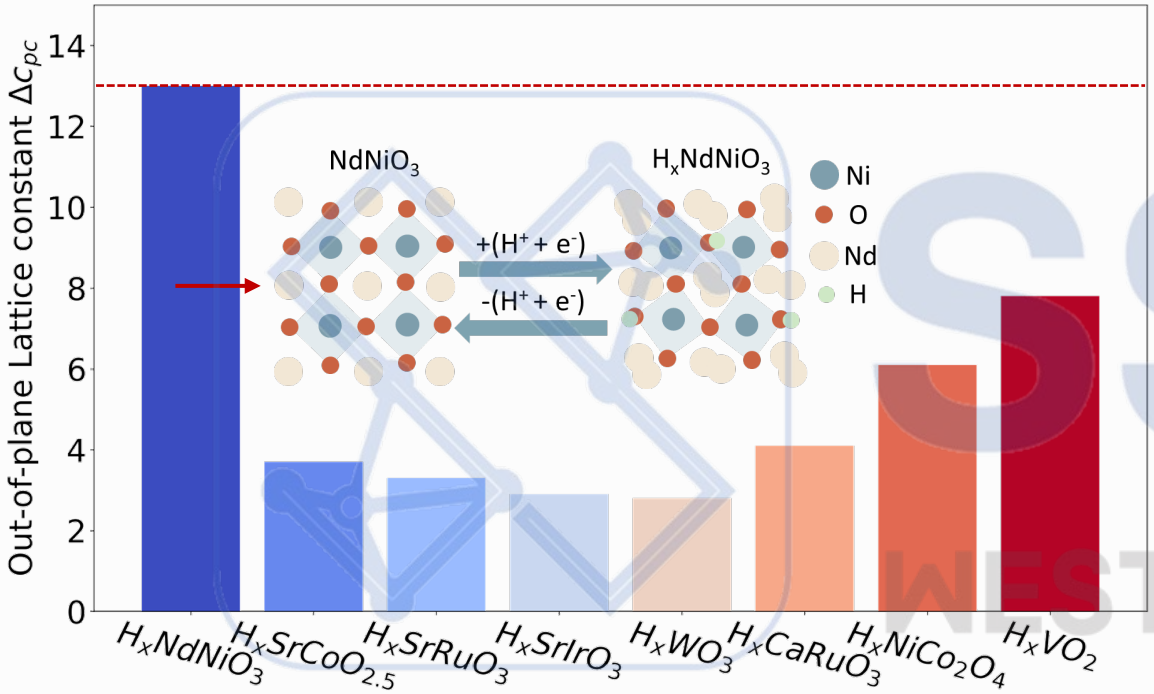
Hydrogenated $NdNiO_3$ (H-NNO) c_{pc} = 4.312 Å

$\Delta c/c$ = 13% (!)



* $LaAlO_3$ substrate

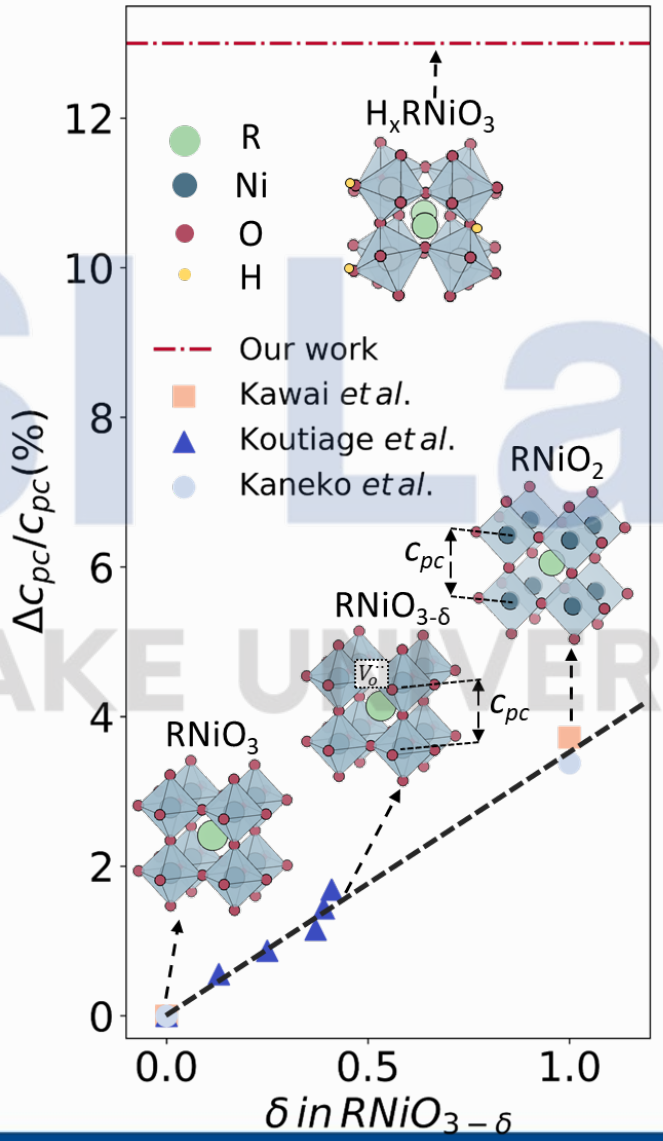
The chemical expansion in H_xNdNiO_3 is by far largest in oxide thin films reported in the literature



$$H_2O + 2Ni_{Ni}^{\times} + O_O^{\times} \rightarrow +2Ni'_{Ni} + 2OH_O^{\cdot}$$

$r(Ni^{3+})$ << $r(Ni^{2+})$

Chemical expansion expected w/ reduced cations (although not as large as 13%)



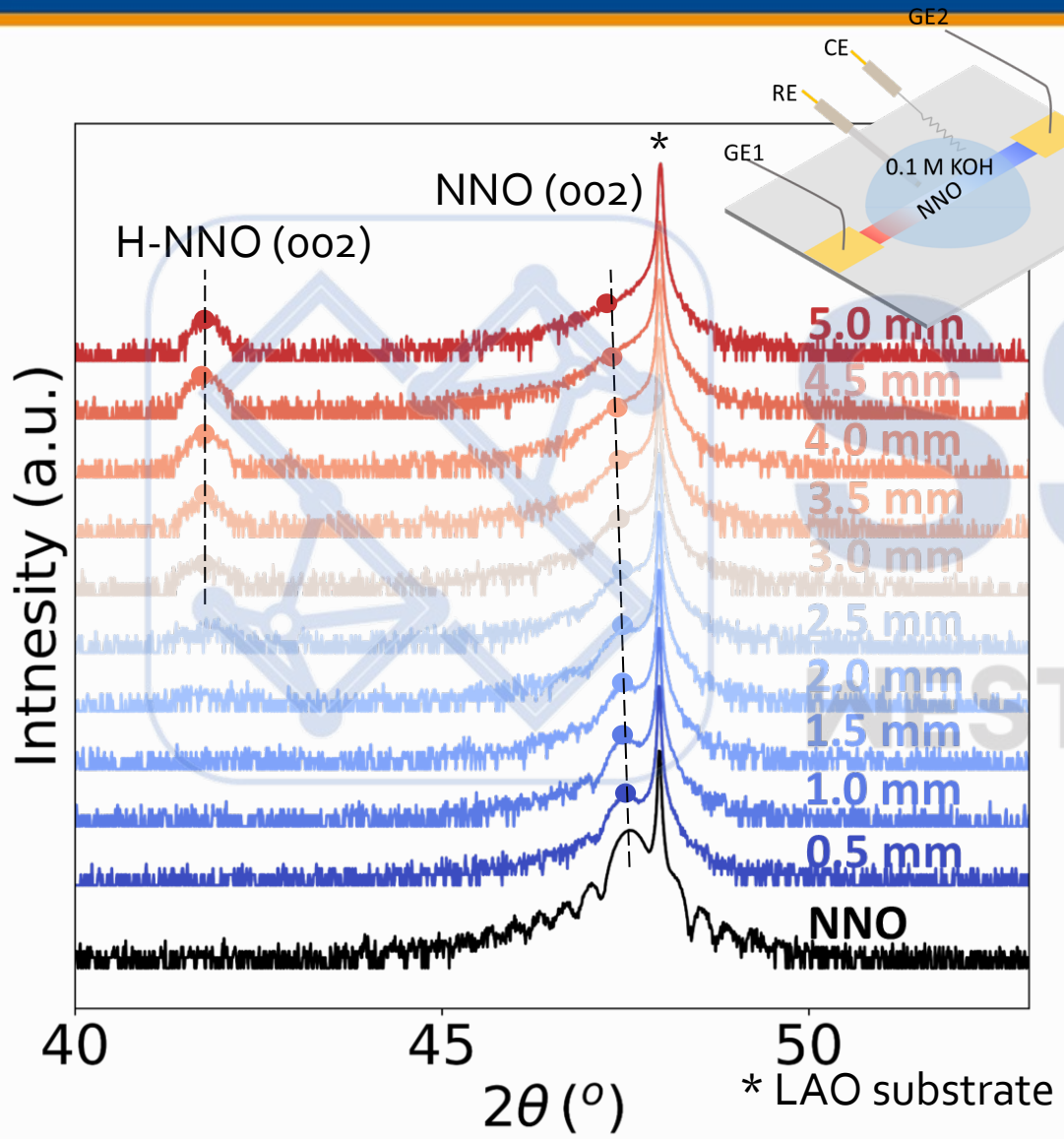
$$H_2O + 2Ni_{Ni}^{\times} + O_O^{\times} \rightarrow +2Ni'_{Ni} + 2\boxed{OH_O^{\cdot}}$$

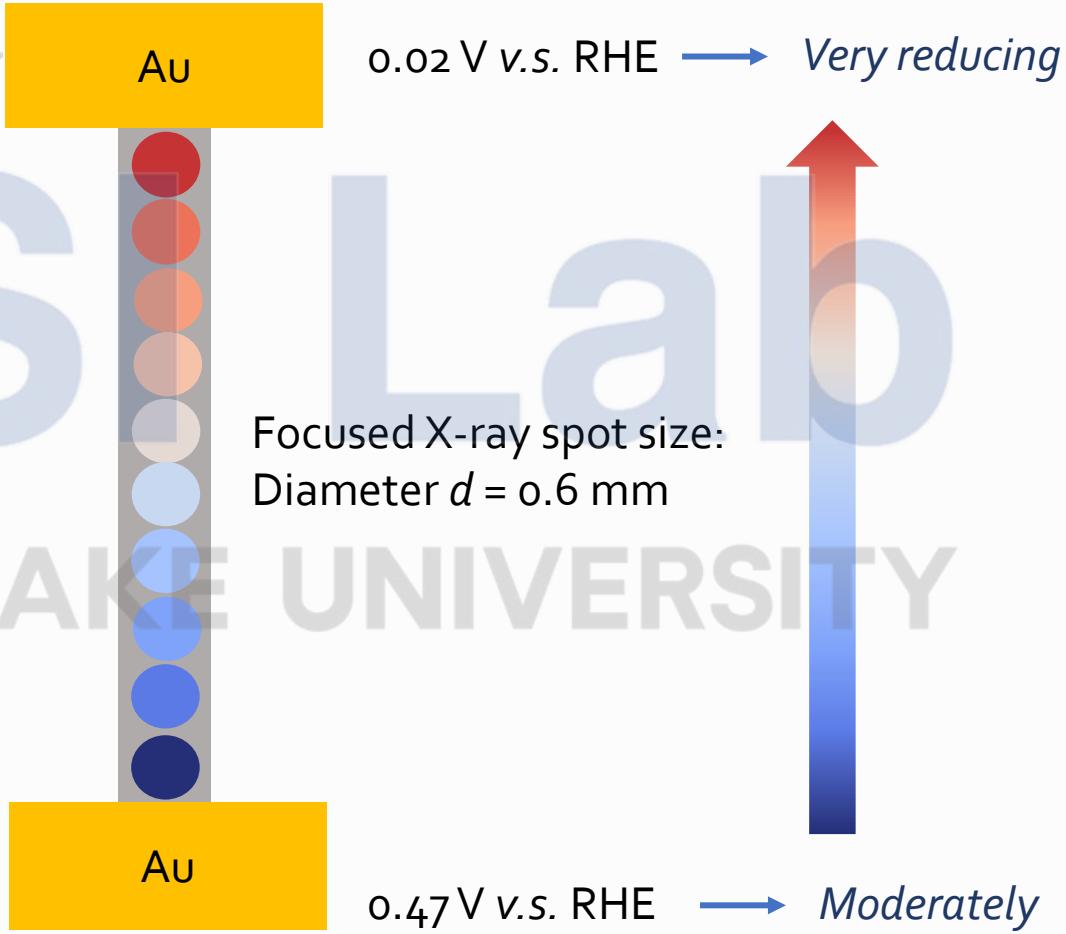
Filled oxygen vacancy
→ ***Increased*** *expansion*

$$2Ni_{Ni}^{\times} + O_O^{\times} \rightarrow \frac{1}{2}O_2 + 2Ni'_{Ni} + \boxed{V_O^{\cdot\cdot}}$$

Oxygen vacancy
→ *Contraction*

Concentration gradient of protons in $NdNiO_3$ thin films enables efficient characterizations





How to probe chemical expansion: optical measurement (MOSS)

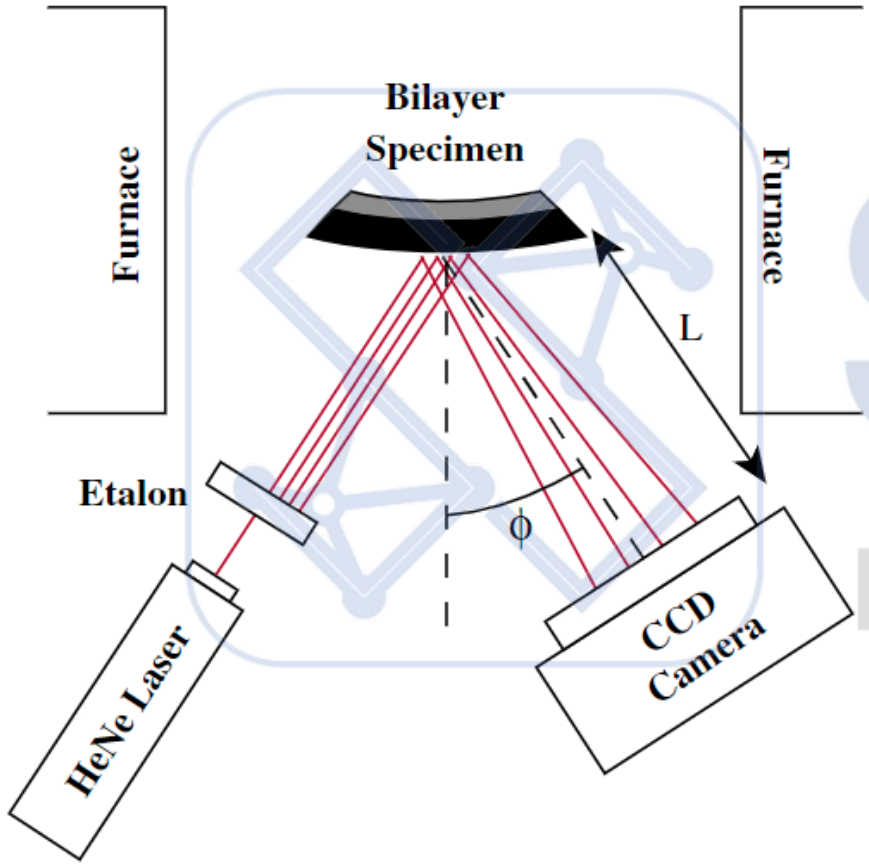
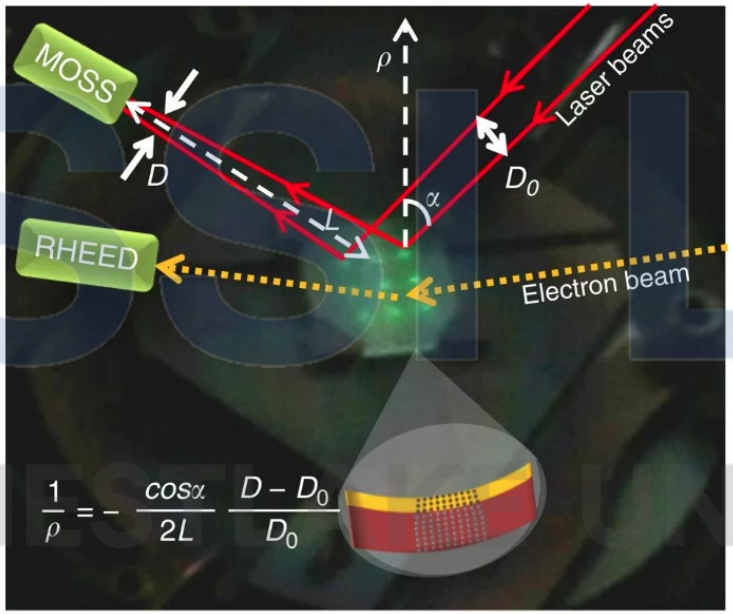
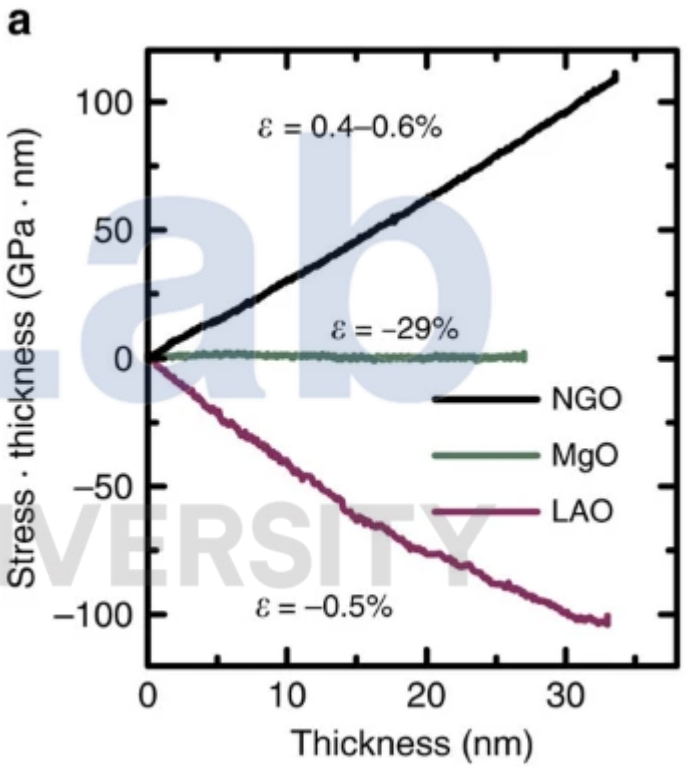


Fig. 1. Multi-beam optical stress sensor (MOSS) curvature measurement schematic.

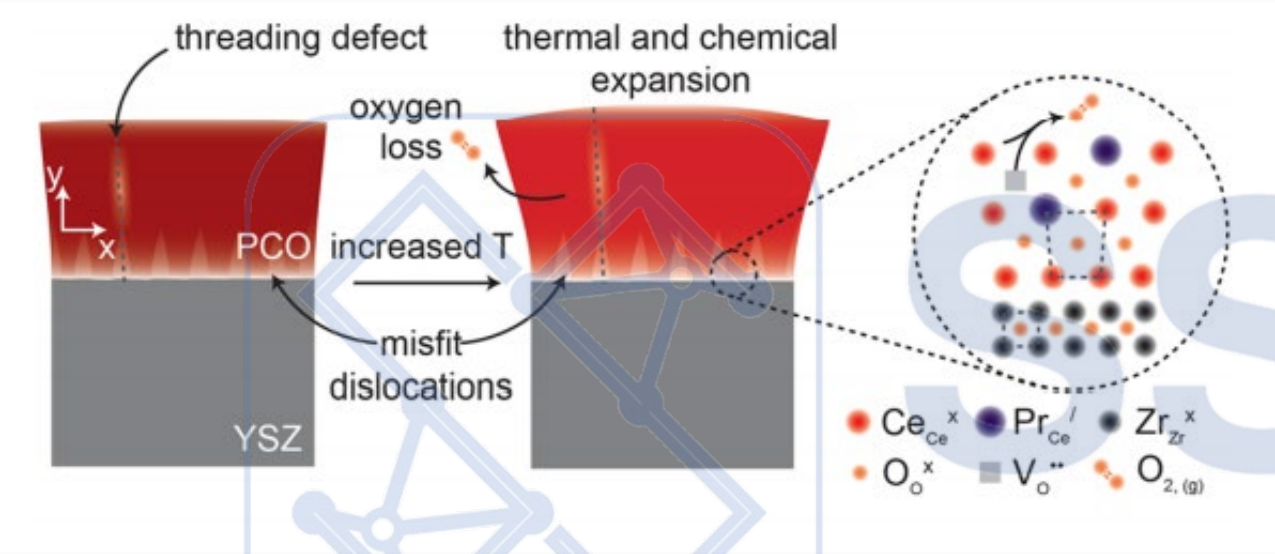
Figure 1: Working principle of the multi-beam optical stress sensor (MOSS).

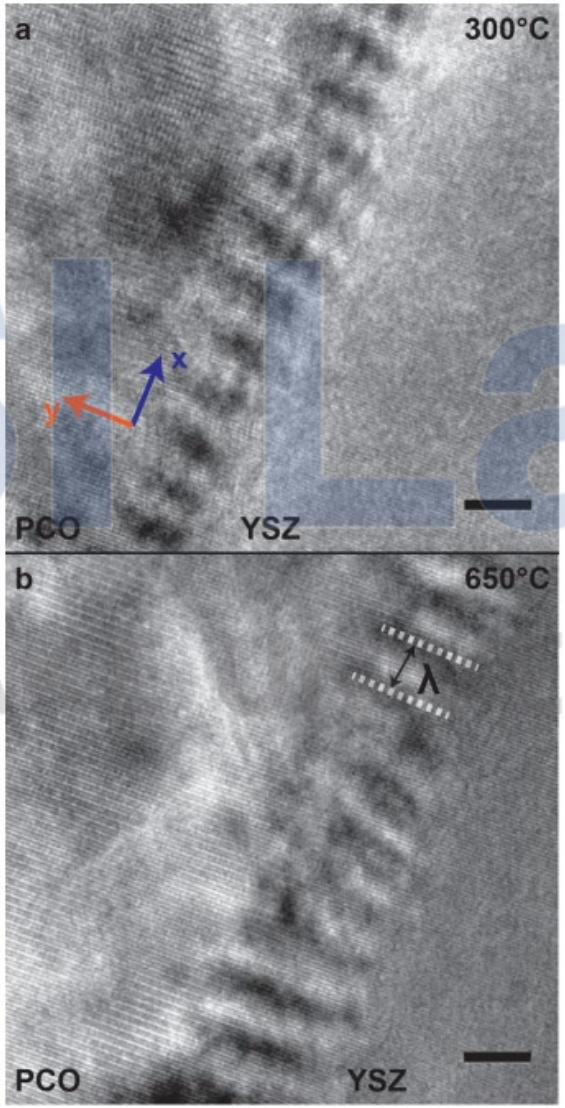


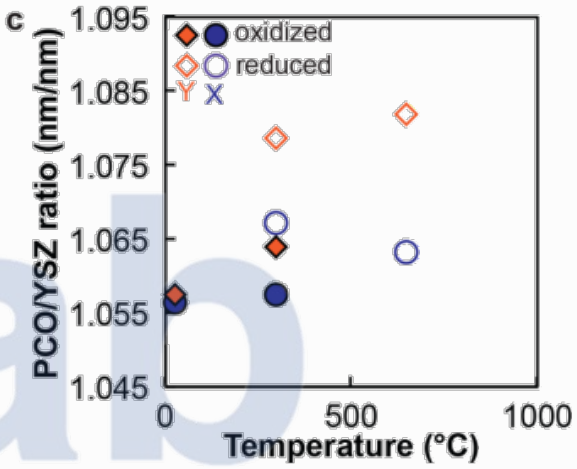


In situ monitoring of stress in oxide thin films during PLD deposition

How to probe chemical expansion: electron microscopy



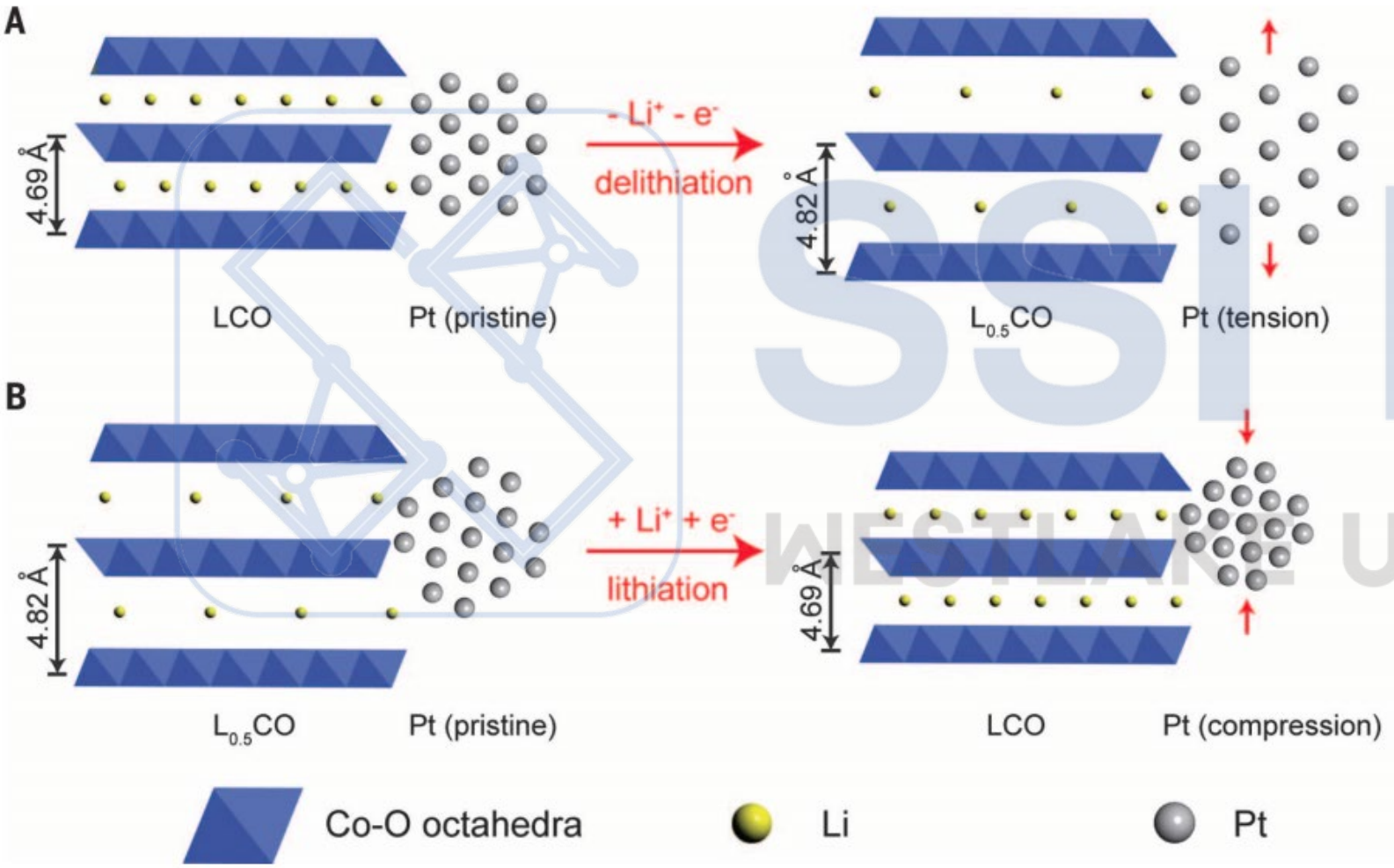


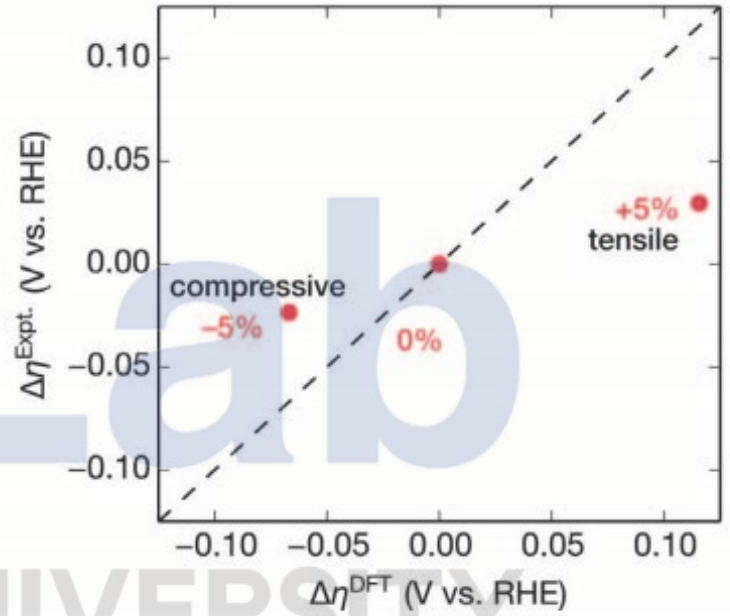


- *In situ* monitoring of strain in $(Pr,Ce)O_{2-x}$ thin films by using *in situ* TEM
- Lattice mismatch between substrate (YSZ) and thin film (PCO) introduces interfacial misfit dislocations
- Chemical expansion can be observed by tracking lattice parameter ratio between PCO and YSZ.

Swallow *et al.*, ***ACS Nano***, 2018

Effect of chemical expansion on electrocatalytic activity

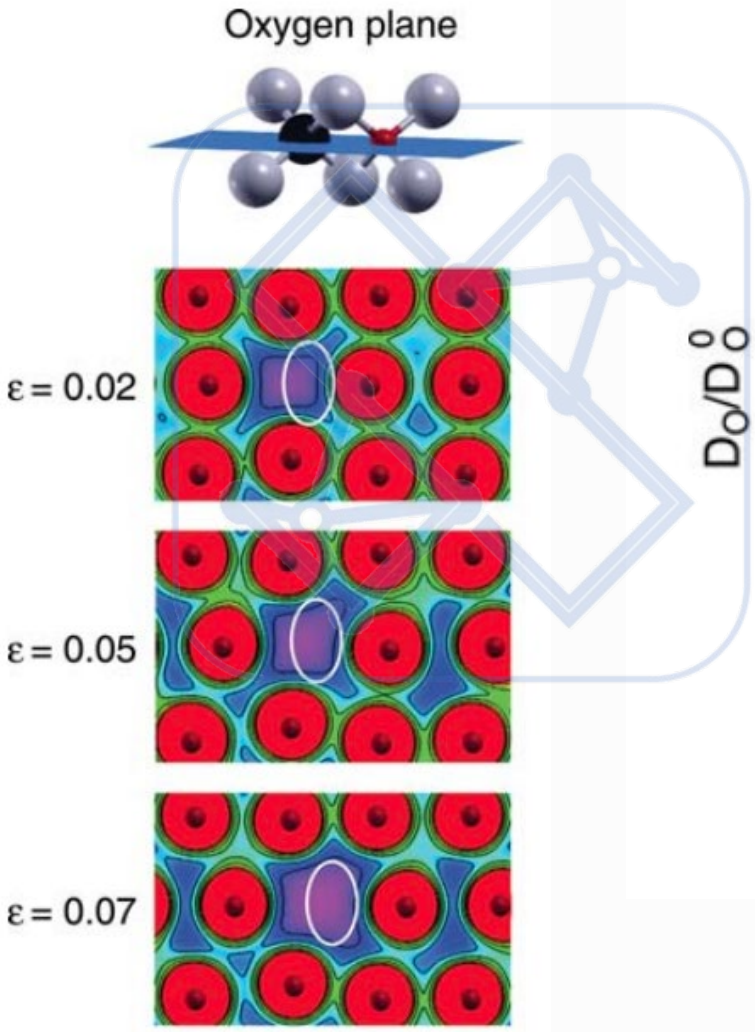


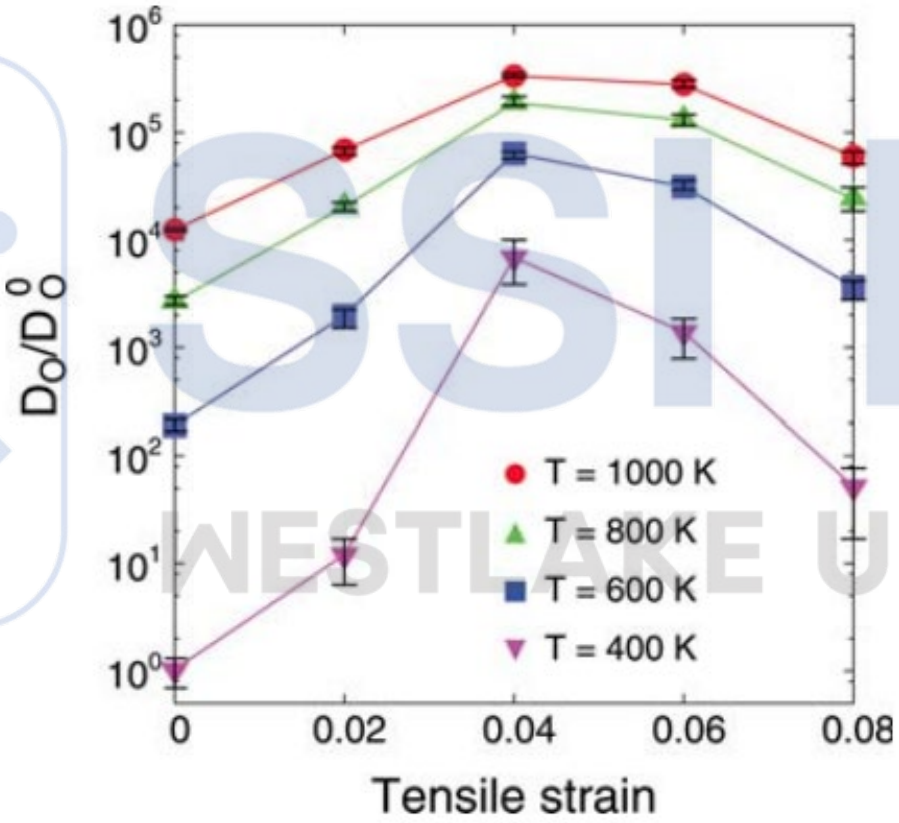


- Strain introduced into Pt by chemically expanding/contracting Li_xCoO_2 lattice;
- Introduced strain affects the ORR activity of Pt.

Wang *et al.*, ***Science***, 2013

Effect of strain on ion migration





Diffusivity of oxide ion in (Y,Zr)O_2 (YSZ) increases with tensile strain (up to ~10^3).

$$D = D_0 \exp(-\frac{\Delta H_{mig}}{RT})$$

w/ strain: $\Delta H_{mig} = \Delta H_{mig}^0 + \sigma \cdot \varepsilon$

stress *strain*

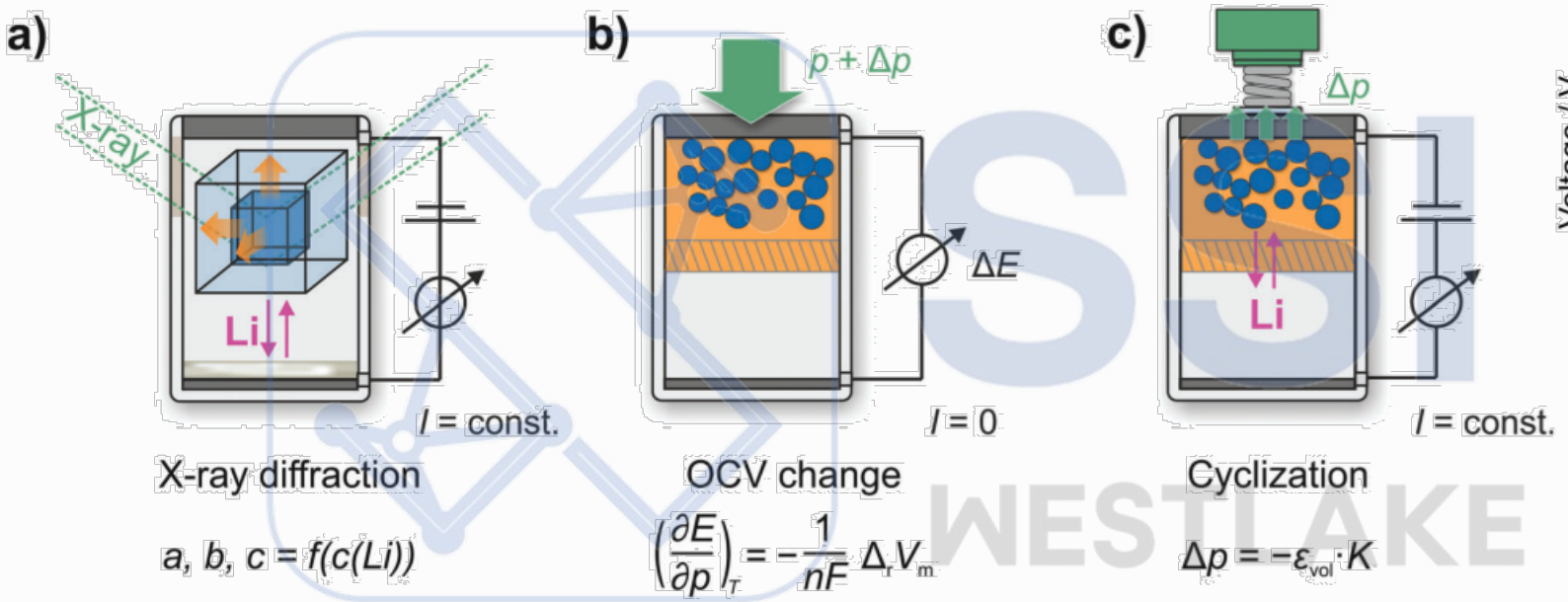
$$\sigma = E\,\varepsilon$$

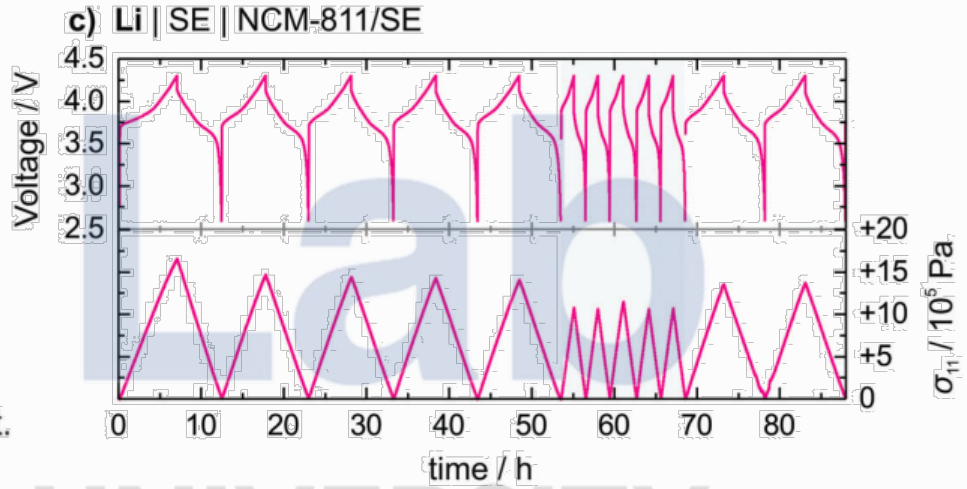
Young's modulus
(1D case)

Kushima and Yildiz, ***J. Mater. Chem.***, 2010

Effect of chemical expansion on energy storage devices

Solid state battery (SSB) → very large volume change due to (de-)intercalation of Li^+





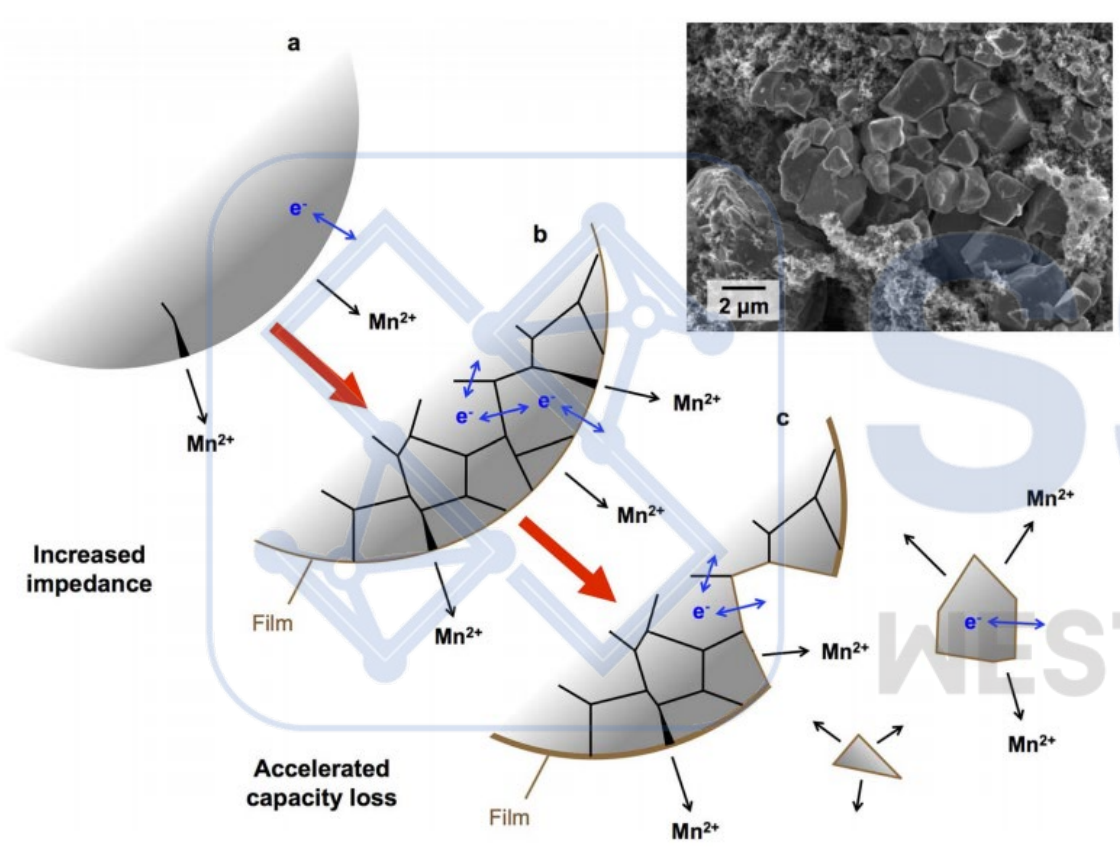
Battery cycling → stress change (constant volume)

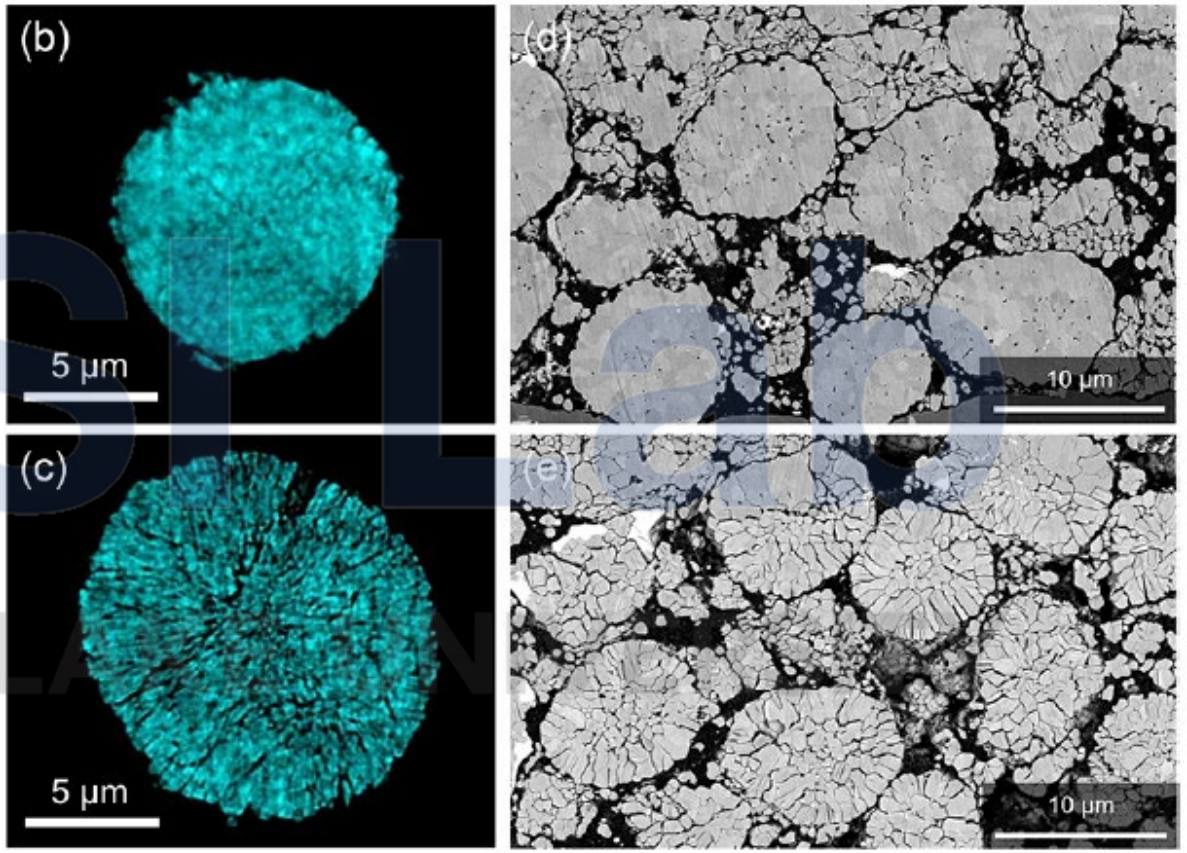
$$\mu_{Li} = \mu_i^0 + PV_{m,i} + RTlna_i \longrightarrow$$ OCV changes as a function of pressure P (!)

hydrostatic pressure *partial molar volume*

Koerver *et al.*, ***EES***, 2018

Effect of chemical expansion on energy storage devices





Fracture of battery cathode materials (*e.g.*, $Li_xMn_2O_4$)

→ Capacity loss due to disconnected primary particles.

McGrogan *et al.*, ***JES***, 2018; Xue, Dong, Shao-Horn, Li *et al.*, ***Nat. Energy***, 2021

Things we have discussed in this lecture

Chemo-mechanical coupling (chemical expansion/contraction):

- What is the microscopic mechanism of lattice expansion/contraction induced by point defects?
- How to describe and quantify the change of lattice constant induced by point defects?
- What are the consequences of chemical expansion/contraction in the context of energy storage and conversion devices?

Goal of this lecture: you should be able to answer the questions above now (hopefully) :)

西湖大學
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End of Lecture 13
Solid State Ionics Fall 2022

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