

# Energy & Materials

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2.60 Guest Lecture

# Question: How many elements exist in an iPhone???

- An iPhone requires 75 elements!
- Human life requires 30 elements!
- Transistors: Si
- CPU: Si, As, P, Ga, Sb, O
- Reinforced glass: Al, Si, K, O
- Battery: Li, Co, Mn, C
- Electronics wiring: Au, Sn, Ag, Cu
- Color display: Y, Gd, Eu, Tb, Pr
- Touch screen: In, Sn, O
- Capacitors: Ta
- Case: Al

75 / 118

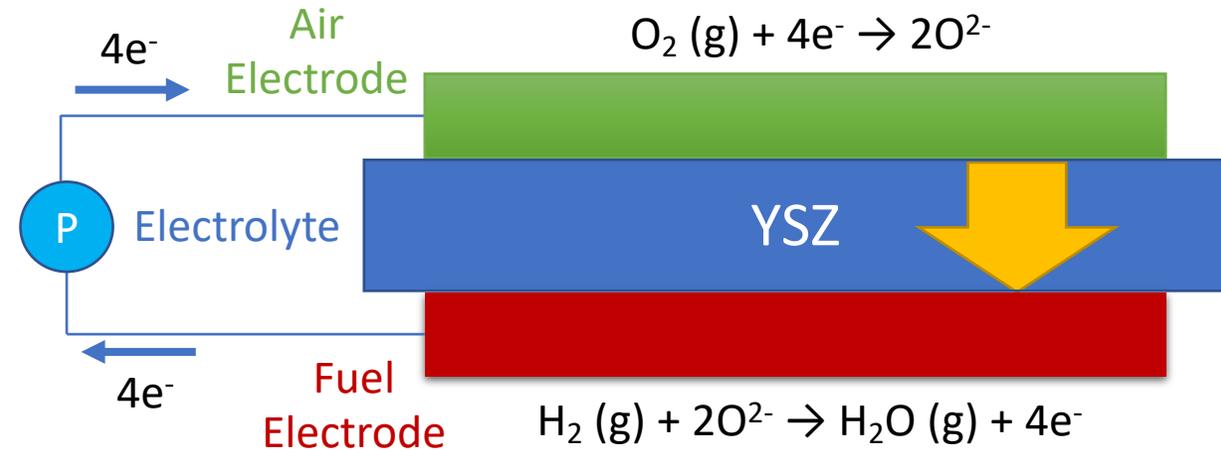
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Uuq Ununquadium	115 Uup Ununpentium	116 Uuh Ununhexium	117 Uus Ununseptium	118 Uuo Ununoctium
58 Ce Cerium		59 Pr Praseodymium	60 Nd Neodymium											68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
90 Th Thorium		91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium			

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# Why are materials needed in energy applications?

- Materials are used in almost every energy conversion device.
- **Reason:** materials have **properties** that allow an engineer to design a system according to the expected operating requirements
- Take a typical Solid Oxide Fuel Cell (SOFC), for example:
  1. Electronic conductivity (electrodes)
  2. Ionic conductivity (electrolyte + electrodes)
  3. Mechanical strength (electrolyte + electrodes)
  4. Catalytic activity (electrodes)
  5. Chemical compatibility under operating conditions of interest (i.e. temperature, gas environment etc.)
  6. Porosity/densification
    - a) Electrodes should be porous
    - b) Electrolyte should be 100% dense
  7. Material compatibility (electrodes do not react with electrolyte or with impurities from the gases)
  8. Others properties

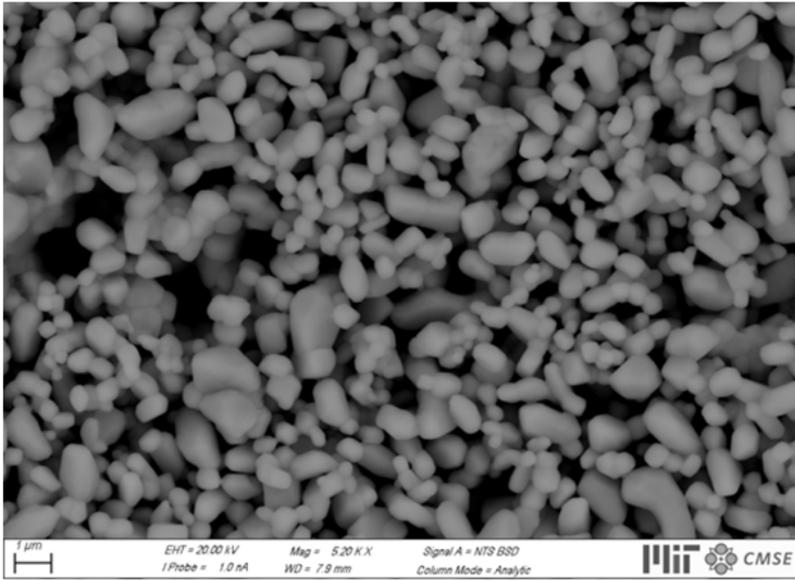
## Typical Solid Oxide Fuel Cell



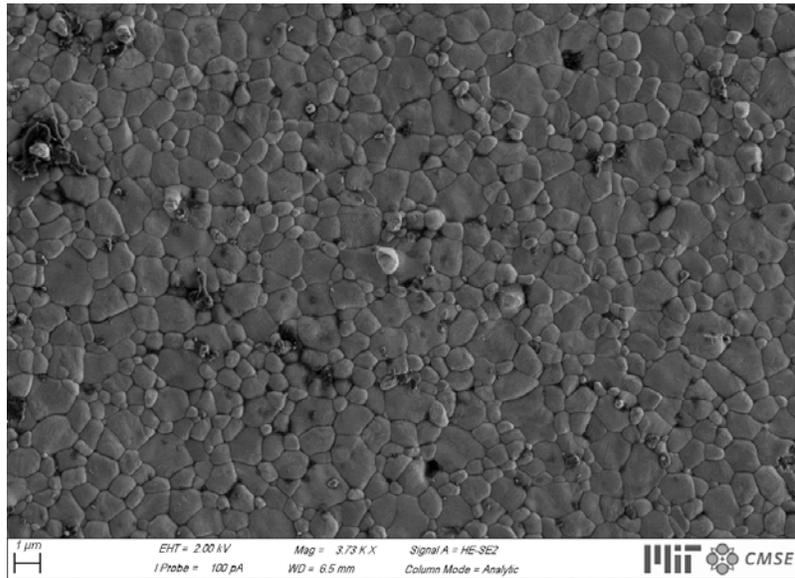
Real Lab Scale Cell

- White: YSZ electrolyte ( $\sim 10\text{-}100\mu\text{m}$ )
- Black: electrode ( $\sim 2\text{-}10\mu\text{m}$ )

# Solid Oxide Fuel Cells (cont'd)

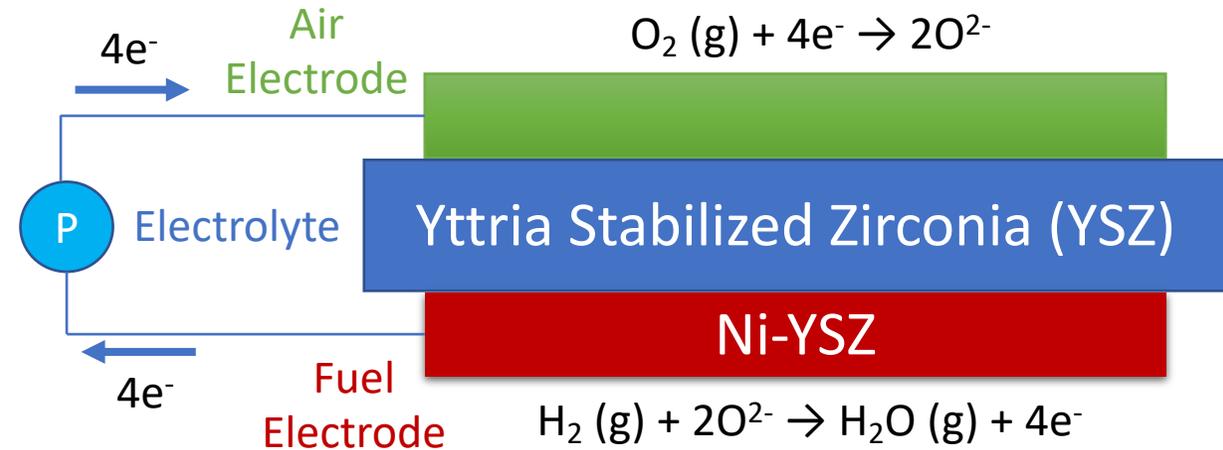


Electrodes should be porous to increase the available surface area for reactions



Electrolytes should be fully dense (i.e. no gaps) to ensure increasing ionic conductivity, mechanical strength and to minimize gas leakage

## Typical Solid Oxide Fuel Cell



But what determines the properties of materials???

# Elements, composition and bonding (Materials' Science)

Periodic table of the elements

Legend:

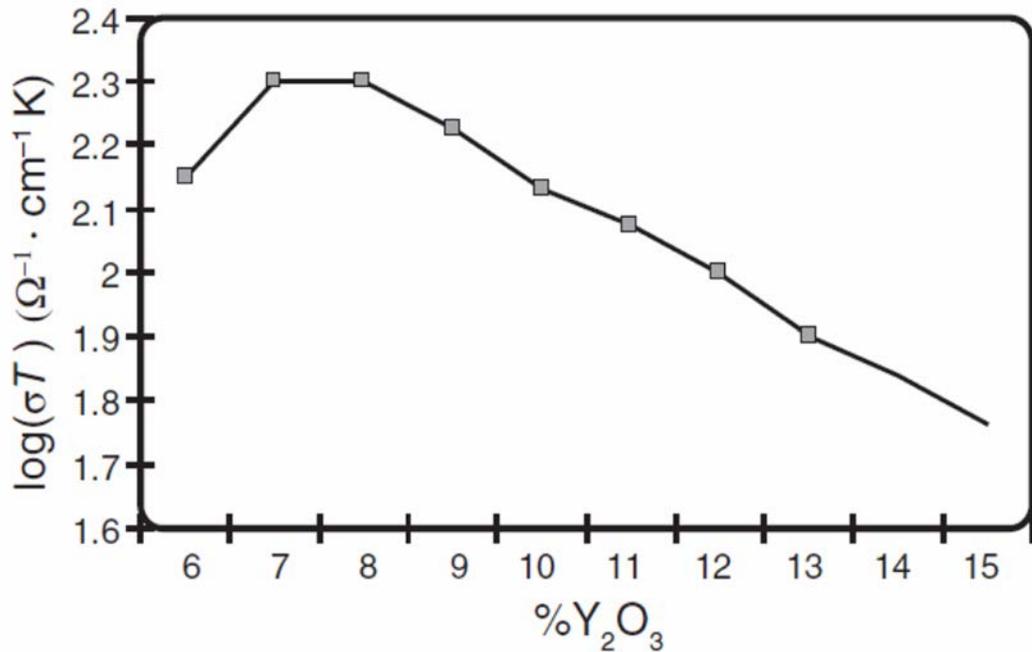
- Alkali metals (orange)
- Alkaline-earth metals (yellow)
- Transition metals (purple)
- Other metals (pink)
- Other nonmetals (red)
- Halogens (green)
- Noble gases (light blue)
- Rare-earth elements (21, 39, 57-71) and lanthanoid elements (57-71) only (light green)
- Actinoid elements (light blue)

group 1*	2	13	14	15	16	17	18										
1 H							2 He										
3 Li	4 Be																
11 Na	12 Mg																
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			

- In general, the properties of materials are dictated by the following characteristics:
  - The elements in the structure of the material
  - The amount of elements in the structure (stoichiometry)
  - The bonding of elements with each other (strong bonds vs. weak bonds)
  - The defects introduced in the material (vacancies, electron, electron holes etc.)
- What makes things difficult (as well as interesting and challenging!):
  - Designing a material has several constraints (i.e. you cannot make every material you want)
  - Properties change according to the operating conditions (temperature, gaseous environment, applied potential etc.)
  - Designing materials requires the use of characterization techniques (*ex-situ* vs. *in-situ*)

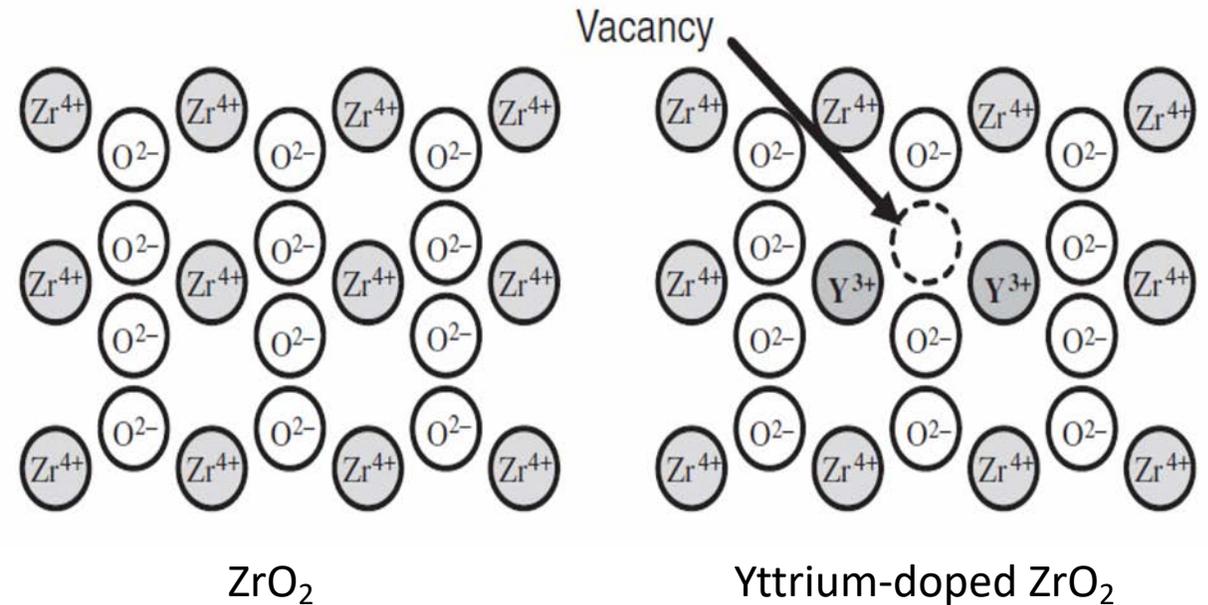
\*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC). © Encyclopædia Britannica, Inc.

# Example 1: Yttrium-doped Zirconium Oxide (YSZ)



Effect of Y<sub>2</sub>O<sub>3</sub> doping in ZrO<sub>2</sub> on the ionic conductivity

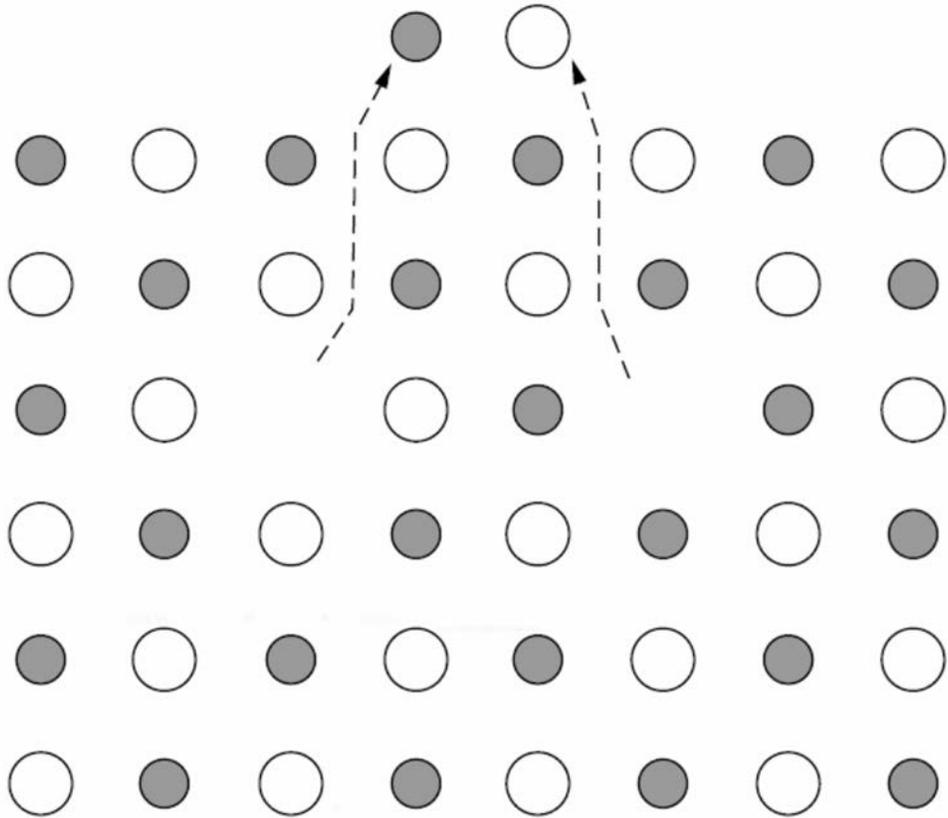
Typical electrolyte has 8% Y<sub>2</sub>O<sub>3</sub> doping



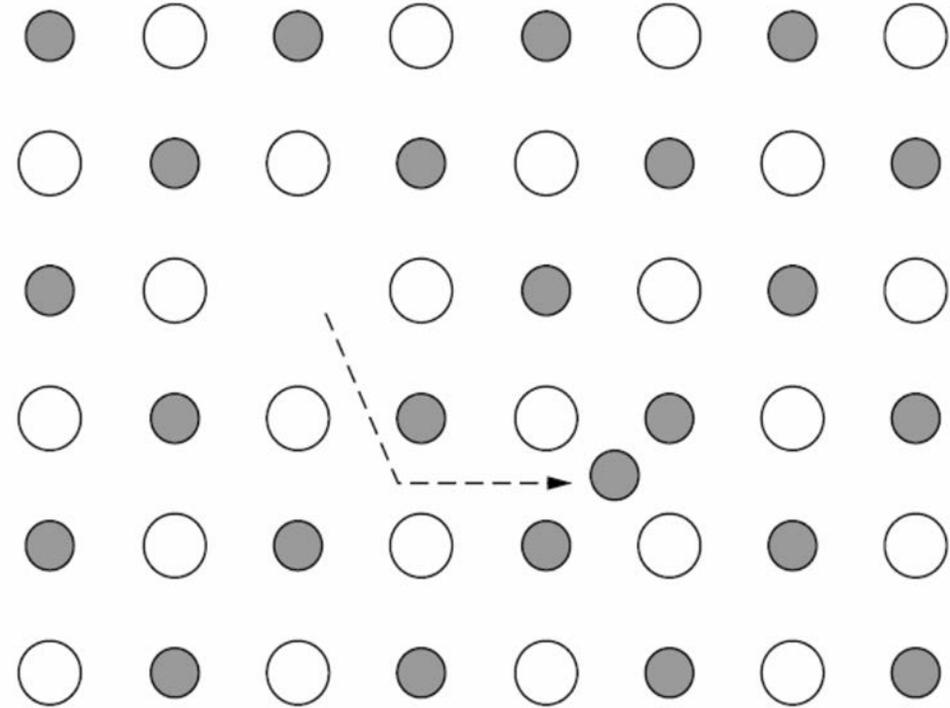
- Charge of Zr: +4
- Charge of Y: +3
- Doping Y for Zr creates a charge imbalance that is compensated by oxygen vacancies (defect species)
- Increasing oxygen vacancies increases the ionic conductivity
- Adding more than 8% Y<sub>2</sub>O<sub>3</sub> makes vacancies interact with each other, hence reducing the ionic conductivity

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# Schottky vs. Frenkel defects (Intrinsic point defects)



Schottky defect: elements leave the crystal leaving behind vacancies



Frenkel defect: an ion leaves its regular lattice site and occupies an interstitial site, leaving behind a vacant site

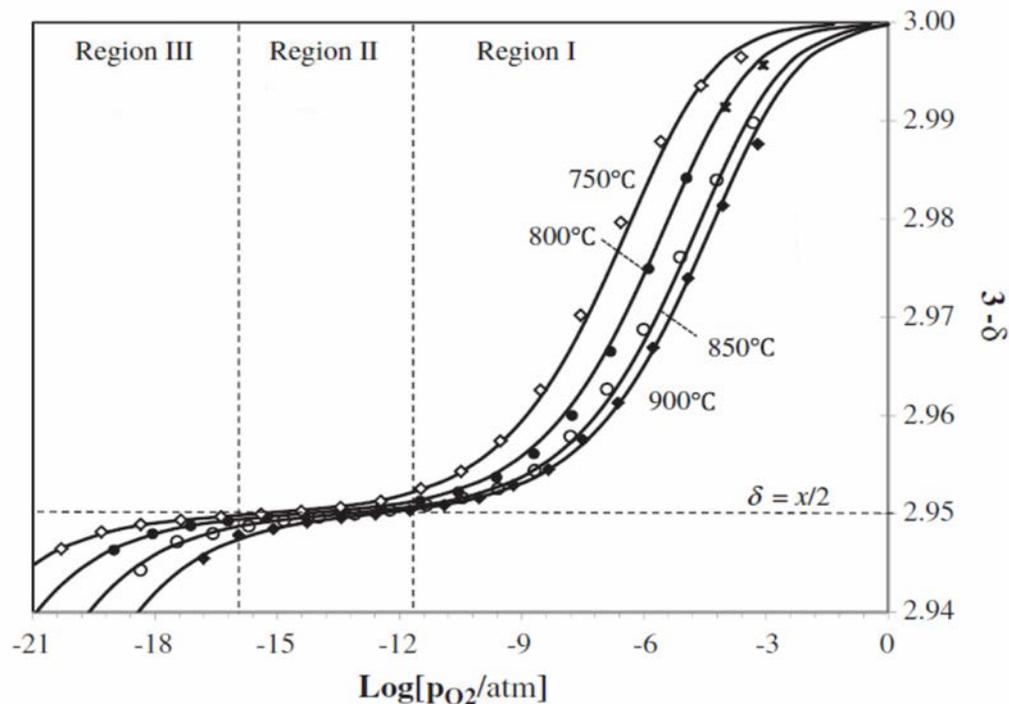
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## Example 2: Extrinsic point defects within $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$

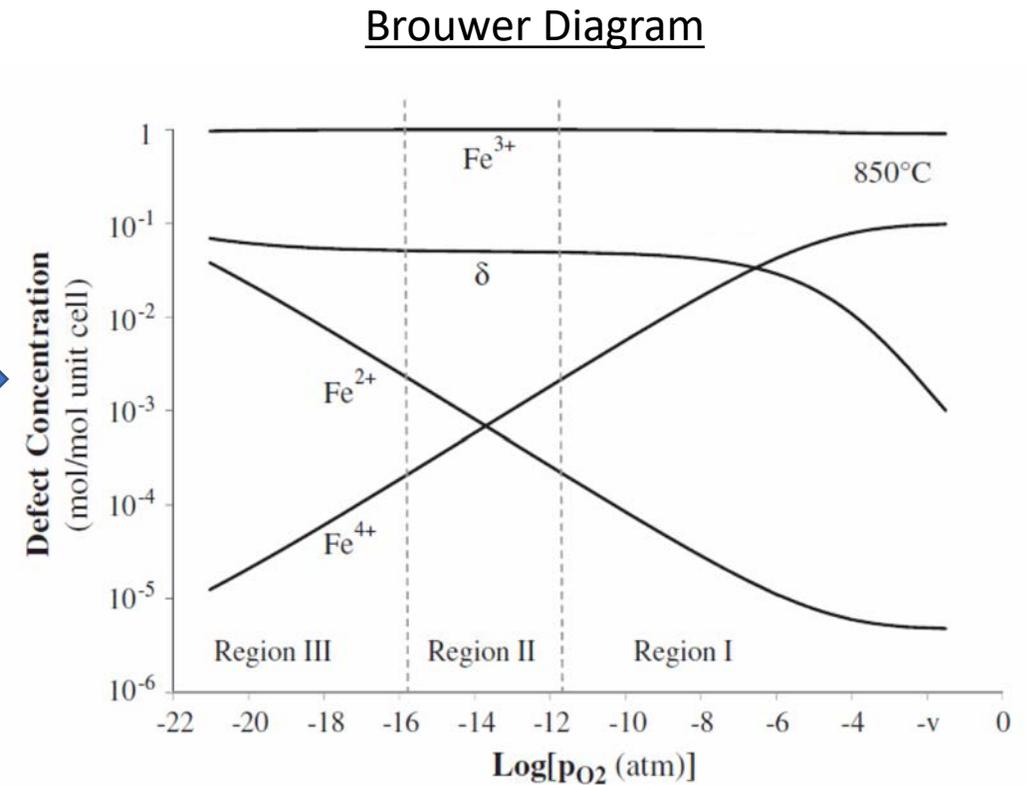
- Extrinsic defects are caused by external influences, such as changes in the gaseous atmosphere, temperature, dopant etc.
- $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$  is used as a ceramic membrane or as a SOFC/SOEC electrode.

Ceramics loose oxygen from their crystal structure due to favorable thermodynamics:

- as the temperature increases
- as the  $\text{O}_2$  partial pressure decreases



Defect Chemistry Models



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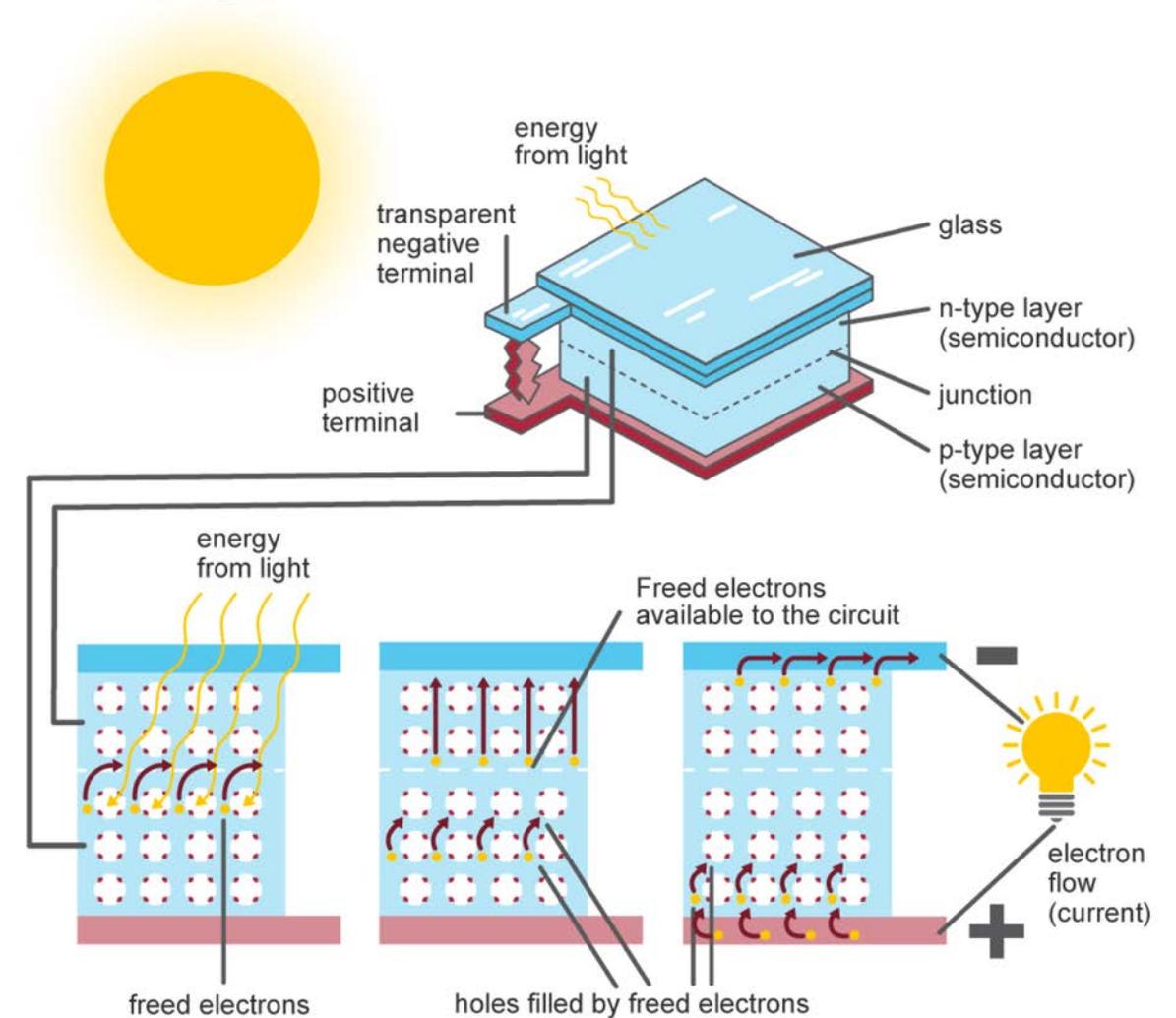
# Example 3: Photovoltaics



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Maximum theoretical efficiency = **86.8%**

## Inside a photovoltaic cell



Source: U.S. Energy Information Administration

Image courtesy of U.S. Energy Information Administration.

# Example 3: Photovoltaics (cont'd)

## Best Research-Cell Efficiencies

Maximum theoretical efficiency = 86.8%

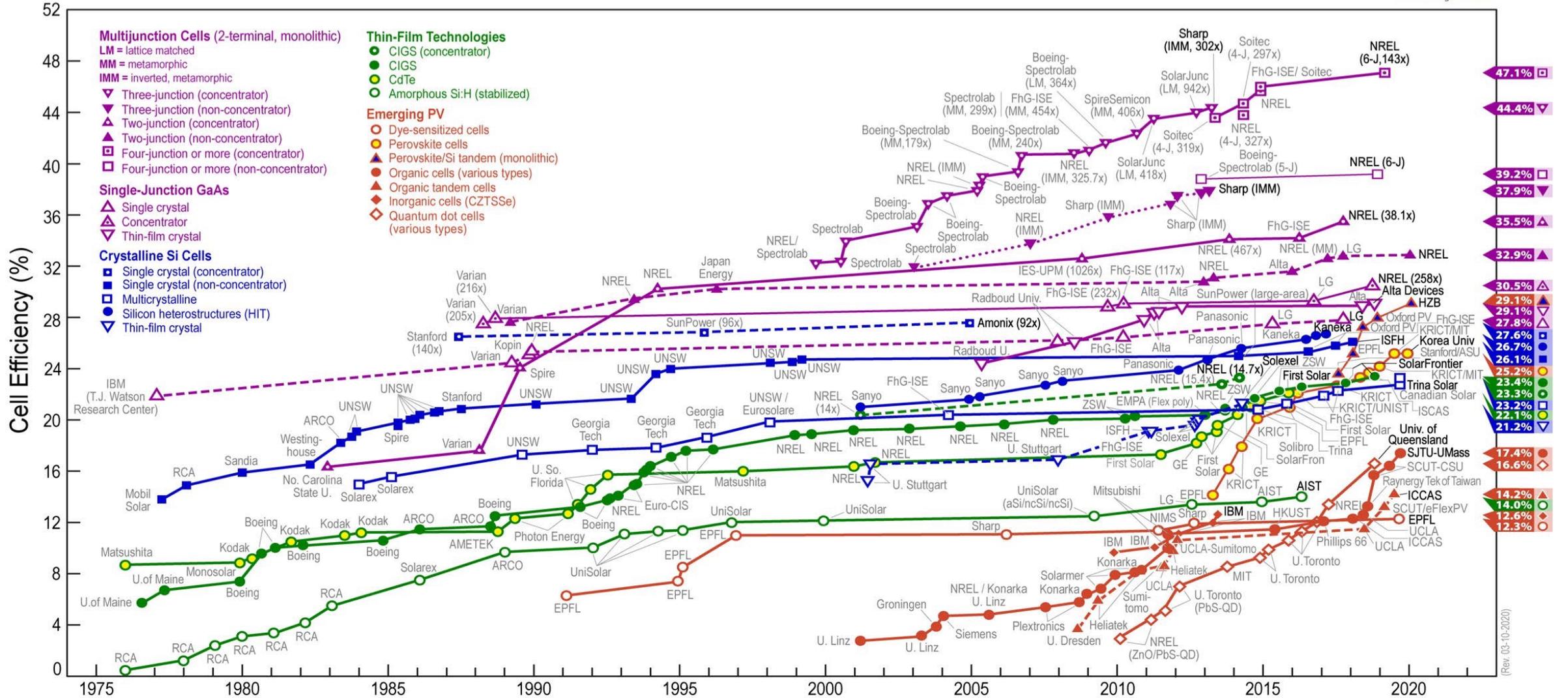


Image courtesy of NREL, DOE.

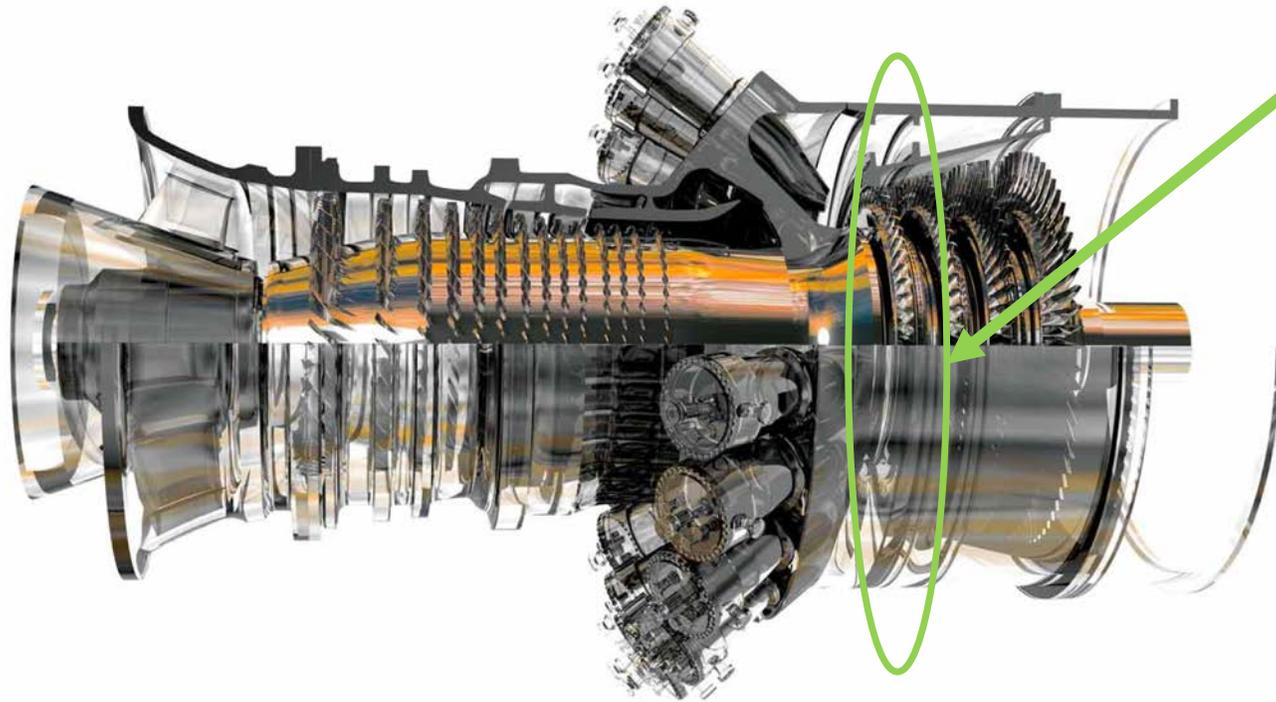
# Materials' and Systems' Engineering



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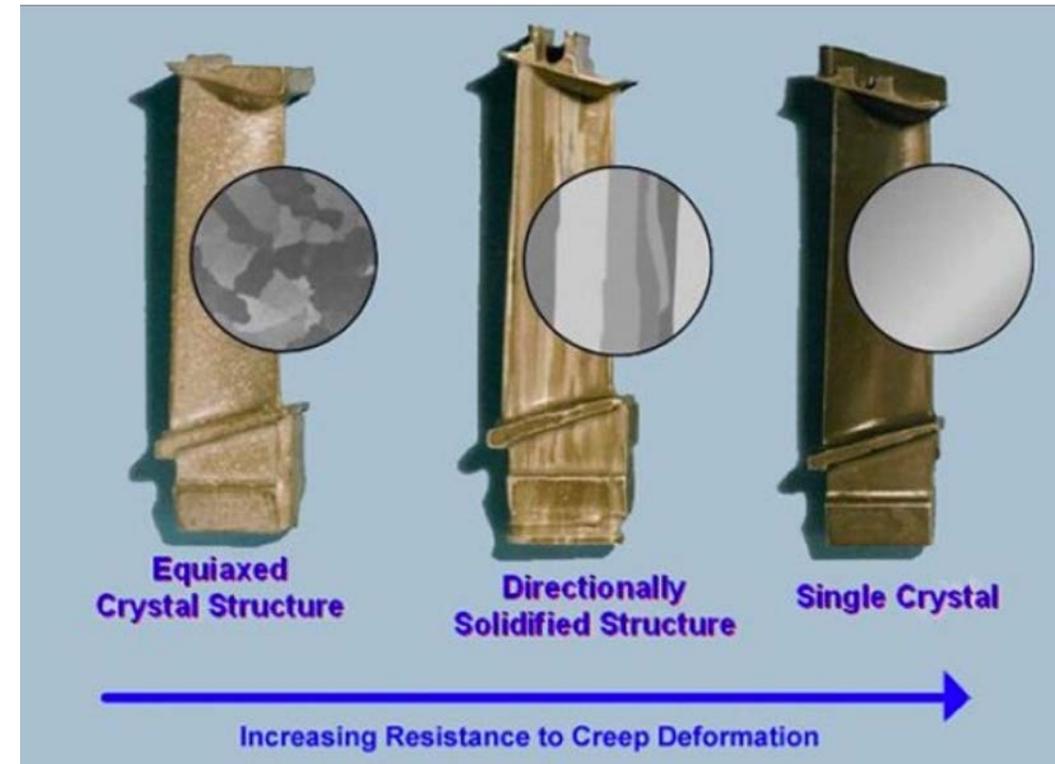
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# Example 1: Increasing efficiency while avoiding creep in a gas turbine



GE 9HA Gas Turbine

High-Pressure Stage made of Single Crystals



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A 605 MW General Electric 9HA can achieve a **Combined Cycle Efficiency of 62.22%** with temperatures as high as **1540°C**.

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## Example 2: Engineering of the Ni-YSZ anode

- In a Ni-YSZ anode:
  - YSZ provides ionic conductivity
  - Ni provides catalytic activity and electronic conductivity
- However, to create the Ni-YSZ anode, we have to start by mixing Nickel Oxide (NiO) with YSZ
- NiO is a bad electronic conductor and electro-catalyst
- To increase the performance, the NiO-YSZ electrode is heat treated in H<sub>2</sub> so that:
  - NiO transforms to Ni, hence increasing the catalytic activity and electronic conductivity
  - The porosity of the electrode increases (the formation of Ni from NiO leaves behind porosity due to the O removal)

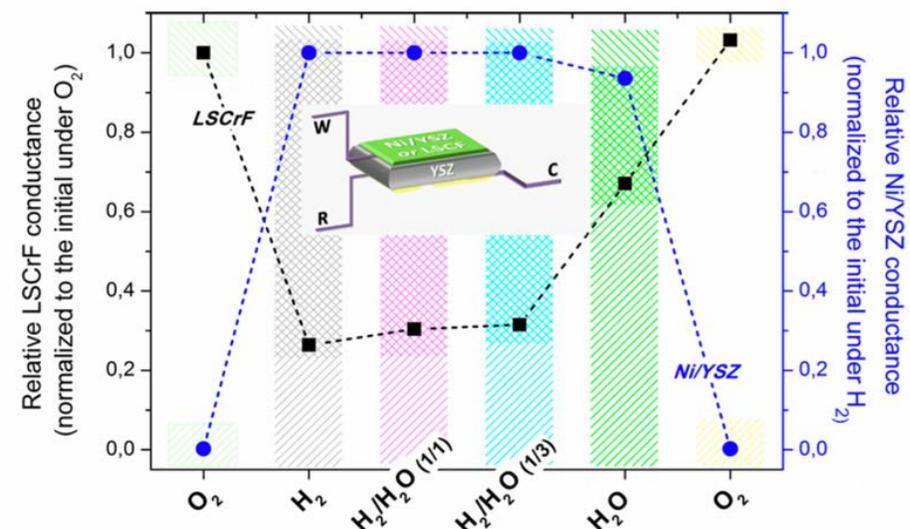
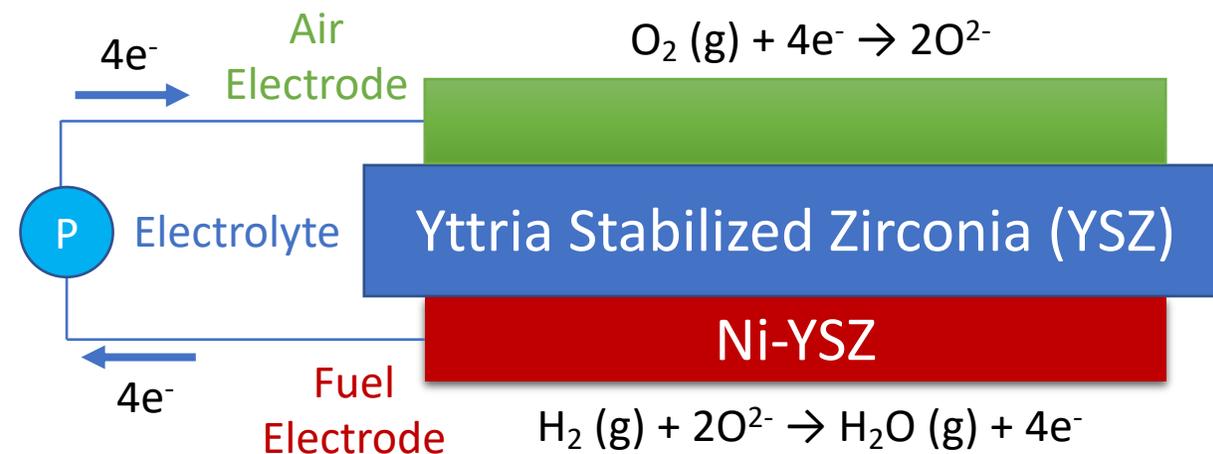


Figure 8. Plot of the reciprocal of the ohmic resistance (electrical conductance) of LSCrF and Ni/YSZ electrodes measured at 500 °C and at open circuit conditions under the indicated gas atmospheres.

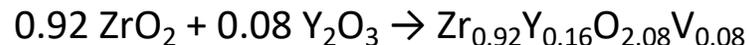
# Materials Science & Engineering for Energy Applications

- To design materials and the corresponding energy conversion systems, we need:
  1. To synthesize the material
  2. To characterize the material:
    - a) Crystal structure
    - b) Microstructure
    - c) Properties (electronic conductivity etc.)
  3. To shape materials
  4. To integrate materials with other components of the system
  5. To test the system
  6. **To iterate (at the end and during each step)!!**
    - a) Identify **problems**
    - b) Improve the material and its integration to the system



# Material synthesis in powder form (the most important step!!!)

- The synthesis of the material in powder form is the first and most important part of the material design
- This is because the powder characteristics (particle size, morphology and surface area) affect the properties of the material
- To synthesize a material, we need:
  1. The precursors: the raw materials
  2. Mixing of the precursors **remembering that you are inducing a reaction!**
  3. Heat treatment to enable cation diffusion (**Calcination**)  
(Cation diffusion is like gas or liquid mixing!!)
- Example: synthesis of 8-YSZ using the solid-state method
  1. Precursors:  $Y_2O_3$  and  $ZrO_2$
  2. Mixing in the appropriate ratio (8%  $Y_2O_3$  and 92%  $ZrO_2$  on molar basis, V stands for oxygen vacancies due to charge imbalance)



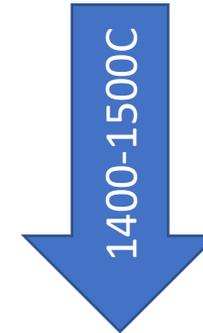
3. Increase the temperature to 1400-1500C



$Y_2O_3$



$ZrO_2$

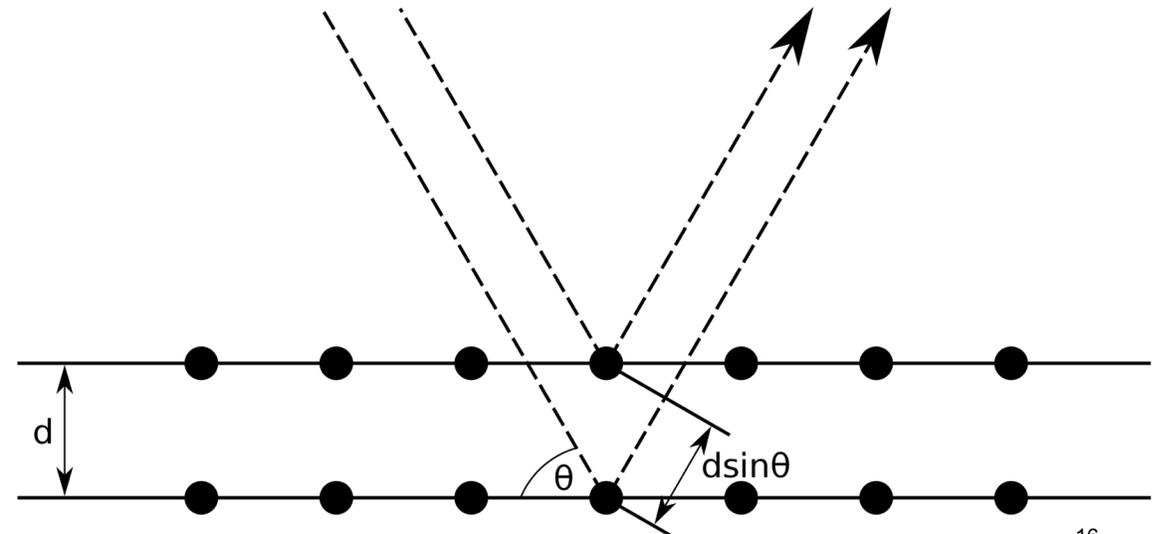
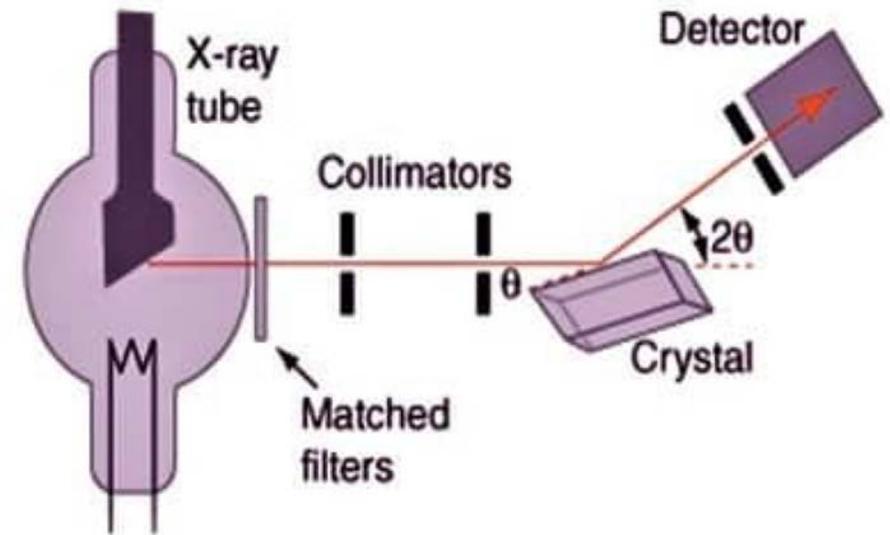


$Zr_{0.92}Y_{0.16}O_{2.08}V_{0.08}$

# How do we know if a material is synthesized as expected?

- X-Ray Diffraction (XRD)
- XRD allows identification of the phases that exist in the bulk of the material
- Similarly to humans, XRD provides a pattern that is the “DNA” of the material
- Operating Principle:
  1. X-ray's bombard a sample under a specific angle
  2. Electron are scattered
  3. A detector measures the number of electrons scattered as the angle changes

- Bragg's law:  $2d \sin\theta = n\lambda$ 
  - d: distance between 2 planes
  - $\theta$ : incident angle
  - $\lambda$ : wavelength of the incident wave
  - n: positive integer



# Examples of XRD patterns of materials synthesized using the solid-state method

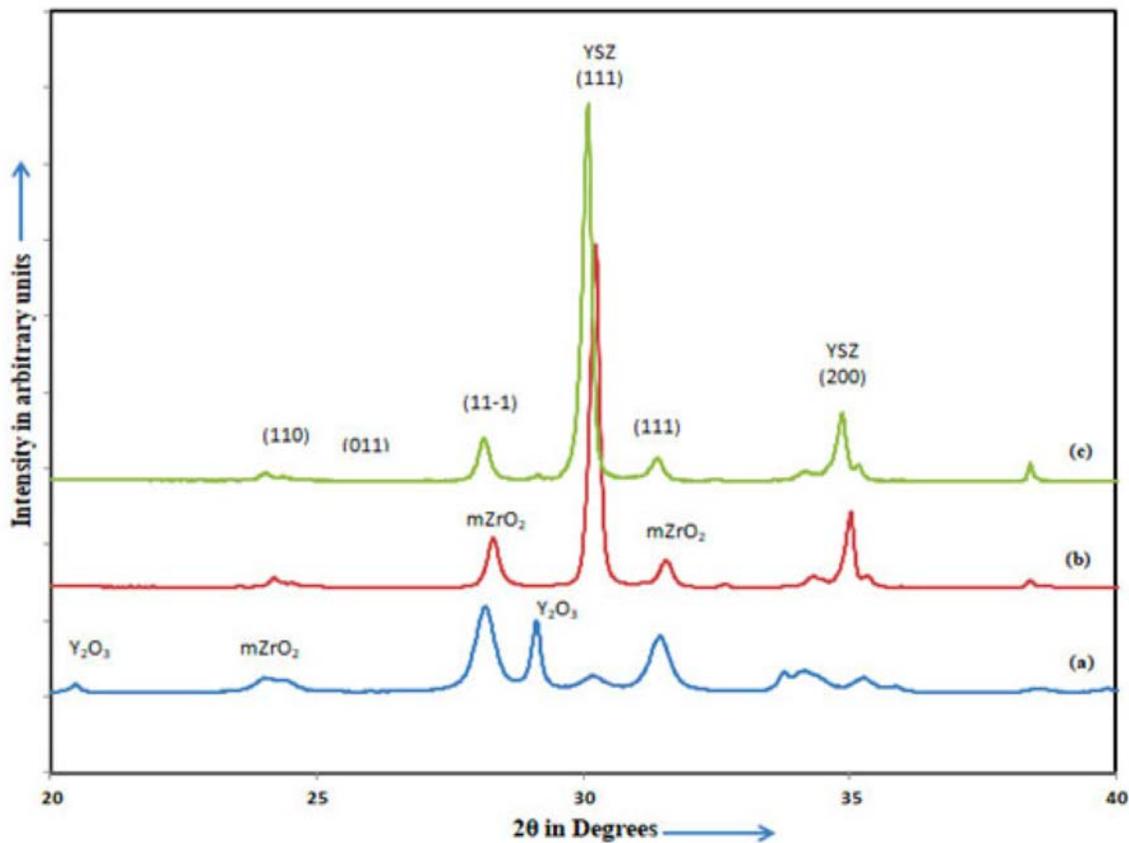
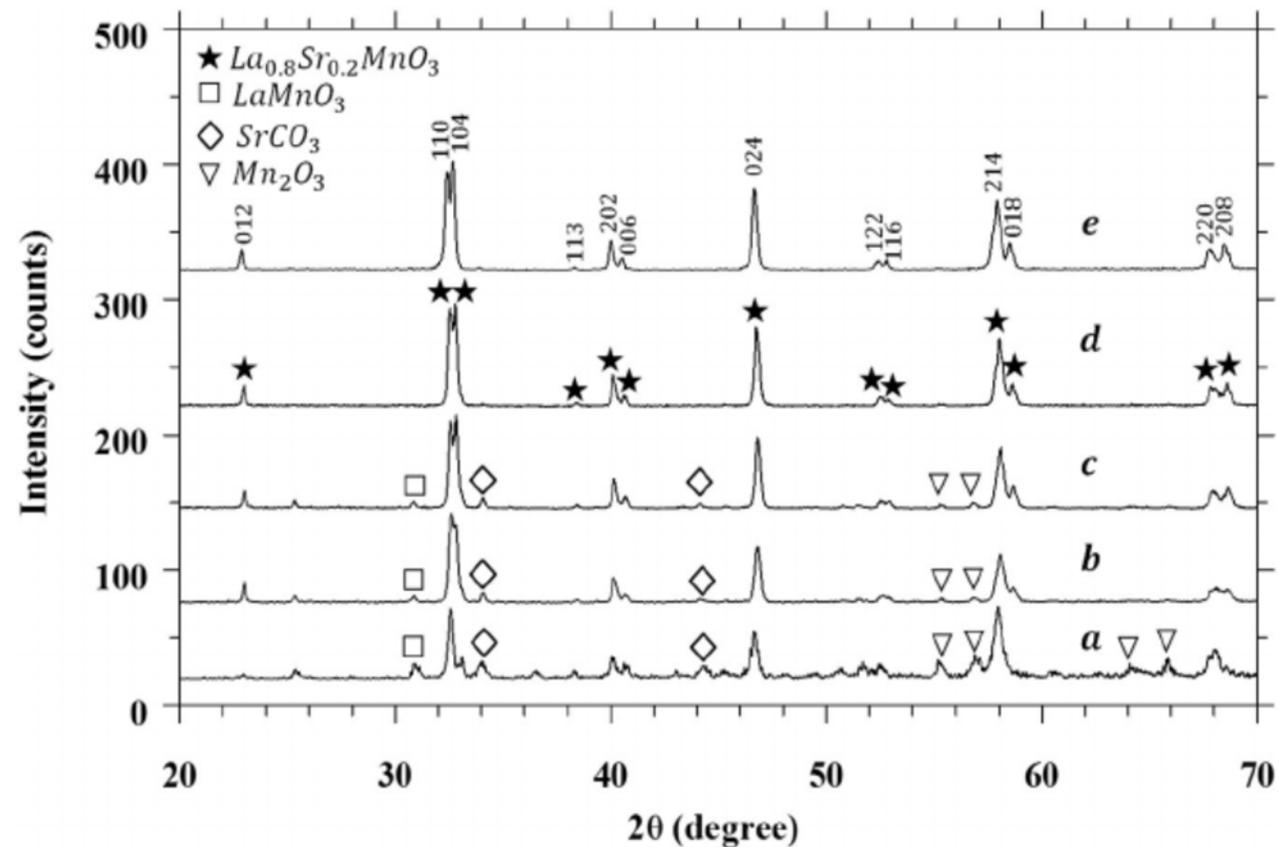


Figure 1: XRD of  $(Zr_{0.92}Y_{0.08})_{1.00}Ti_{0.00}O_2$  (a) precursor (uncalcined product) (b) conventionally sintered at 1400°C for 10 hr (c) microwave sintered at 1400°C for 40 min



X-ray diffraction (XRD) patterns of 20-hour milled powder, followed by heat treatment at (a) 700 °C for 1 hour, (b) 700 °C for 5 h, (c) 700 °C for 10 h, (d) 800 °C for 1 h, (e) 800 °C for 5 h.

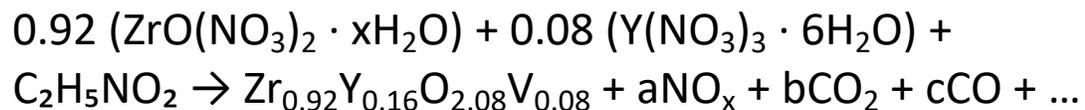
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# Dry vs. wet synthesis methods

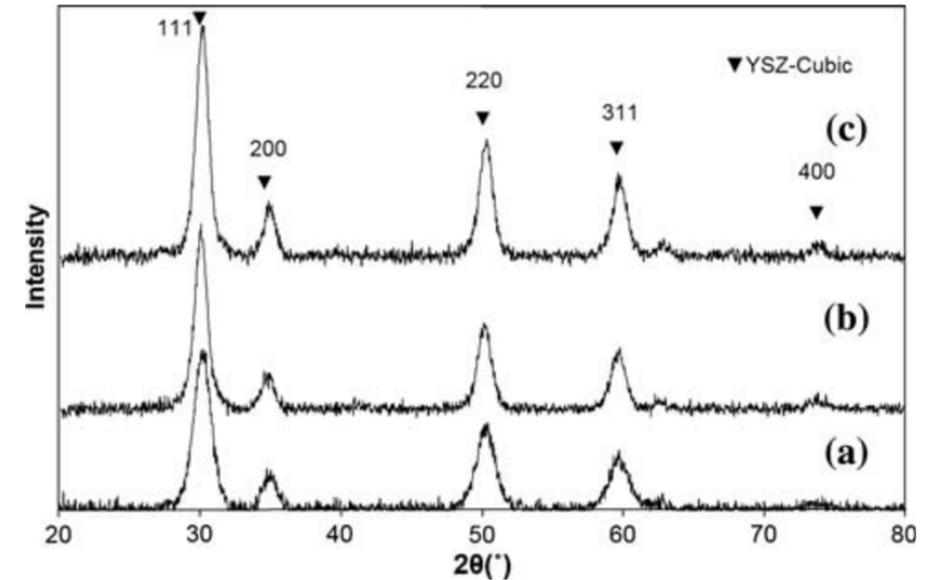
- Dry methods: manual mixing of powder precursors
- Wet methods: use precursors diluted in H<sub>2</sub>O plus a chelating agent to bring cations closer
- Advantages of wet methods
  1. Better control of stoichiometry
  2. Better mixing
  3. Lower calcination temperature
  4. Less contaminations

Example: synthesis of 8-YSZ using a wet method

1. Precursors: Y(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub> · xH<sub>2</sub>O
2. Use citric acid, EDTA, glycine as a chelating agent



3. Dilute these in purified H<sub>2</sub>O and then dehydrate the solution
4. Calcination of the ash at high temperature



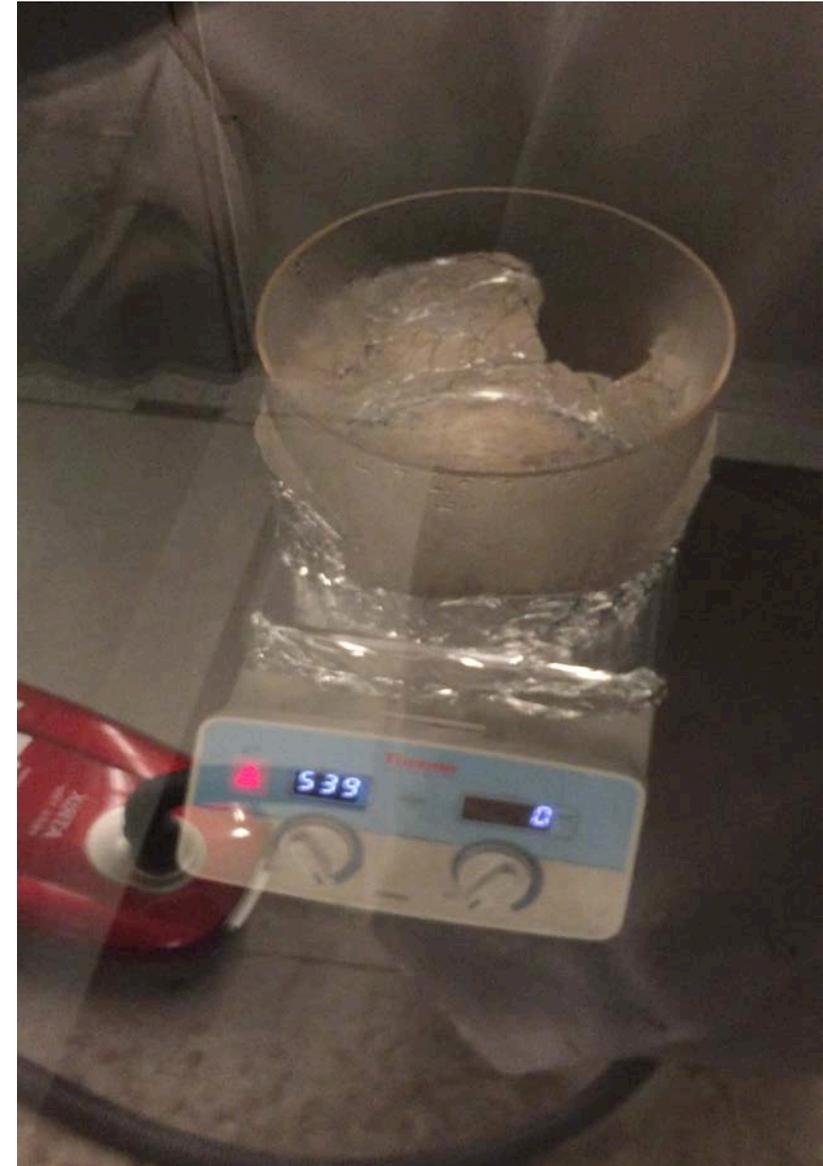
**Fig. 6** X-ray diffraction patterns of the YSZ powders prepared from dried gel calcined at **a** 650 °C/2 h, **b** 730 °C/2 h and **c** 800 °C/2 h

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- Wet synthesis using Citric Acid and Ethylene Glycol
- YSZ synthesized at 650C!!
- Compare that to the solid state method, which requires calcination temperatures ~1400C!

# An example of a wet synthesis method in Prof. Ghoniem's lab

- **Important: do not try this at home!!**
- Materials are synthesized in this way using proper equipment and safety measures
- Synthesis of LSM using glycine as the chelating agent
- First, precursors are mixed to create an aqueous solution
- Then, the mixture is placed on a hot plate (540C) to evaporate the H<sub>2</sub>O and combust the mixture
- When most of H<sub>2</sub>O has evaporated, autoignition of the solid mixture happens instantaneously (note the flame front)
- Also note:
  - Aqueous solution is white
  - LSM powder (raw ash) is black
- To obtain LSM, the raw ash is collected and calcined at high T (800C, 1h)



# Example: synthesis of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ (LSCr)

- LSCr is used in SOFCs as an interconnect material or as an electrode
- Adjusting the pH of the aqueous precursor solution and the amount of Glycine changes the powder morphology and size
- If a dense material is required, options (a) and (c) are the best
- If a porous material is required, the rest of the options are viable
- To choose the best one, one has to measure the surface area of the material
- Surface area: Brunauer–Emmett–Teller (BET) method

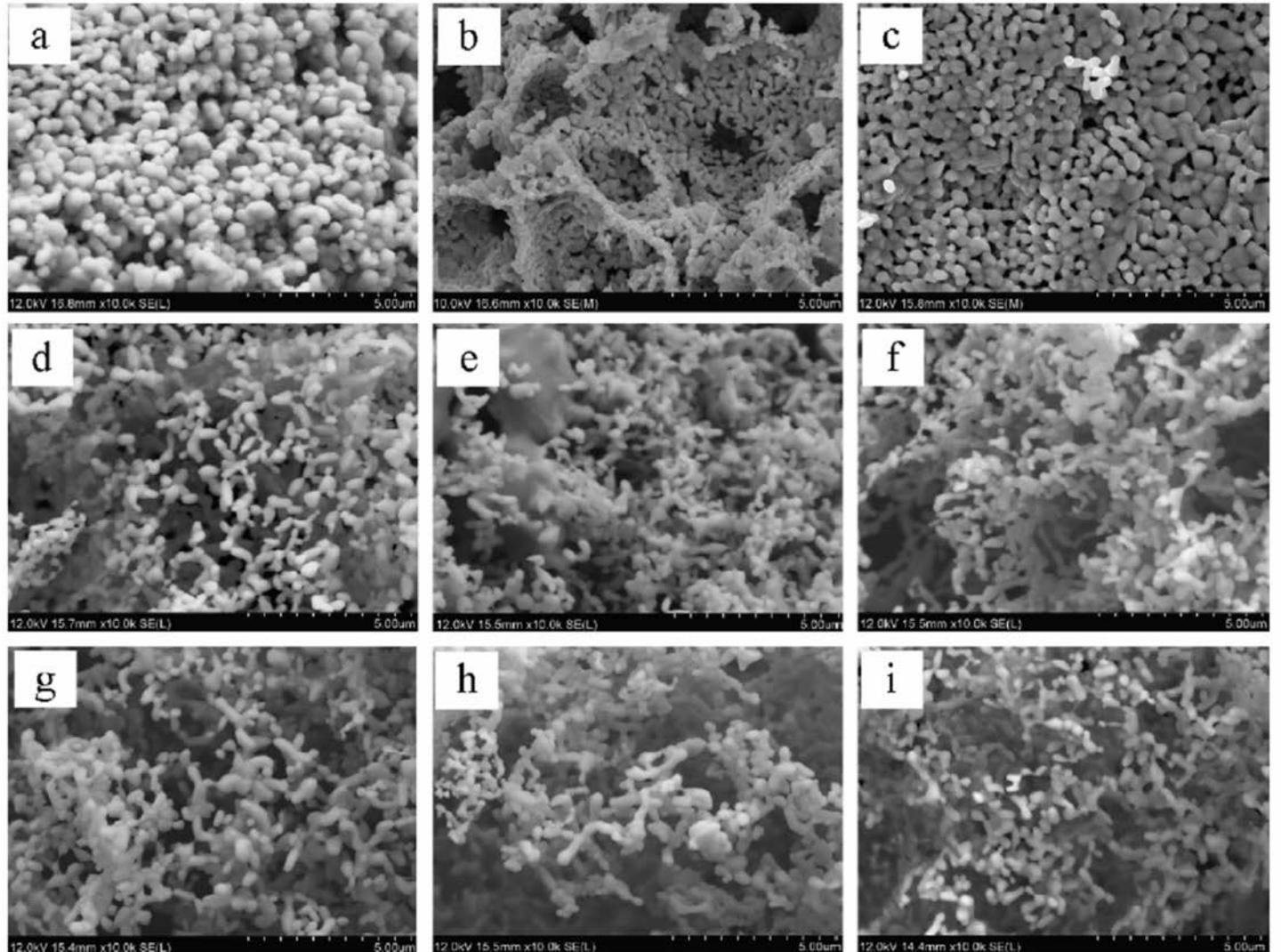


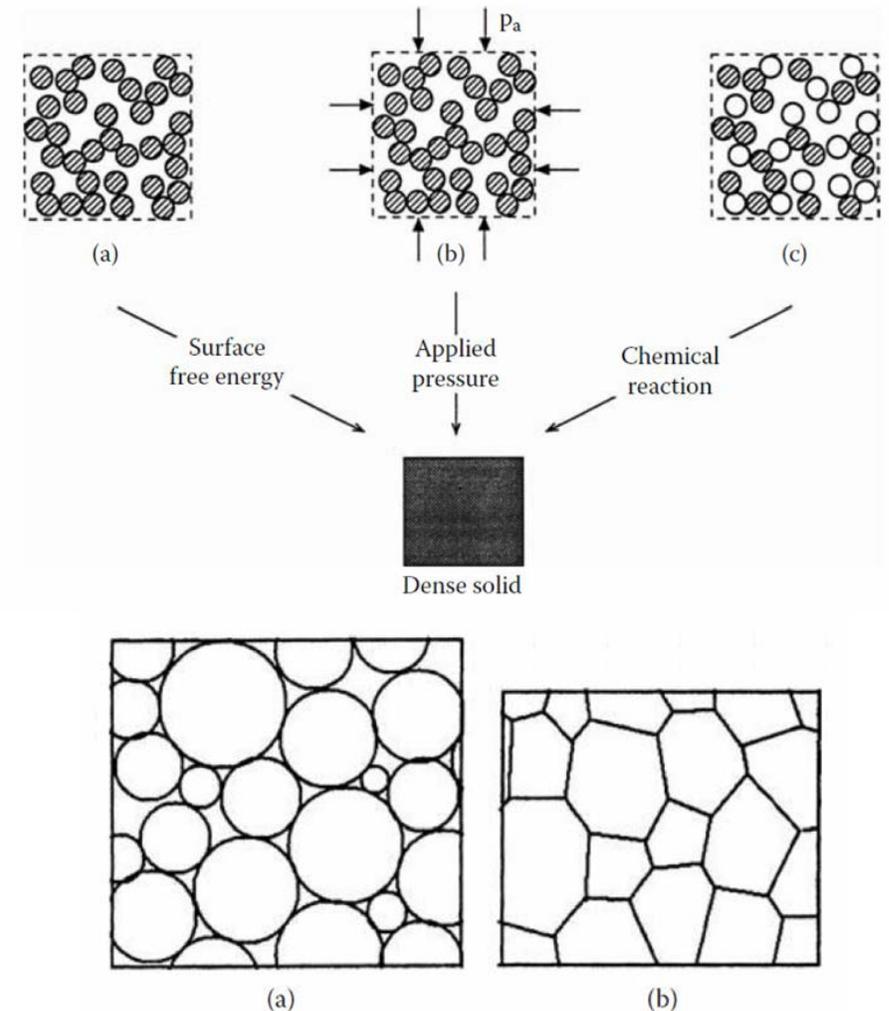
Fig. 5. SEM photographs of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  powders calcined at  $1000\text{ }^\circ\text{C}$  with various pH values and glycine-to-nitrate ratios. (a) pH = 3, 1:1 (b) pH = 2, 1:1 (c) pH = 1, 1:1 (d) pH = 3, 1.5:1 (e) pH = 2, 1.5:1 (f) pH = 1, 1.5:1 (g) pH = 3, 2:1 (h) pH = 2, 2:1 (i) pH = 1, 2:1.

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# Sintering of ceramics

- To create a useful part, the powder has to be shaped using an appropriate method.
- To achieve high densification of a ceramic part, sintering at high temperatures is required (1200C-1600C depending on the material)
- **Sintering of the part is a major challenge because:**
  1. **The material shrinks during the sintering process**
  2. **Properties of the material depend highly on the microstructure and gran/grain boundary distribution!**
- Parameters that affect the sintering of ceramics:
  1. Surface free energy: curvature of particles provides a driving force for densification in order to decrease the surface free energy
  2. Applied pressure: bring particles together while minimizing gaps (can be done before or during the sintering process)
  3. Chemical reaction: change the gaseous environment to make it react with the solid (not frequently employed because the material's microstructure cannot be easily controlled)

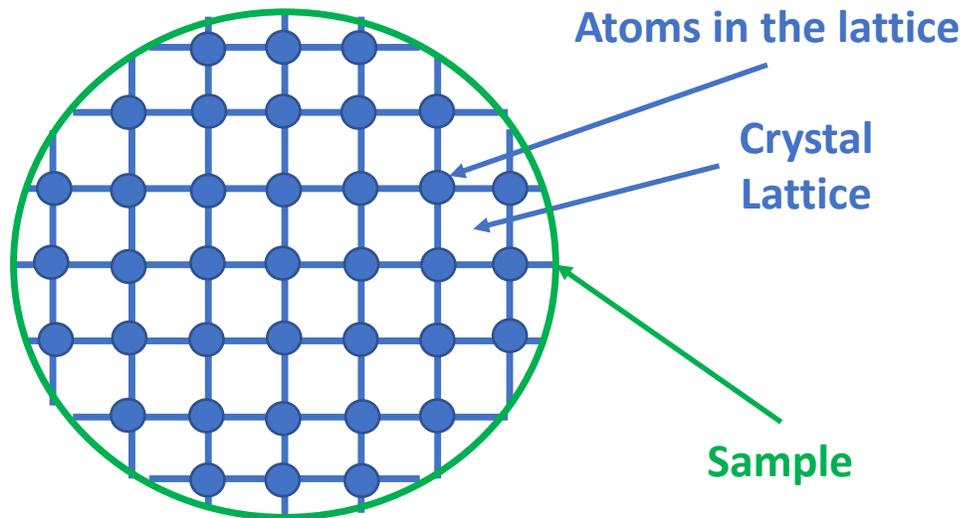
## Driving forces leading to sintering of ceramics



Replacement of free surfaces (a) by grain boundaries (b) during the densification of polycrystalline systems.

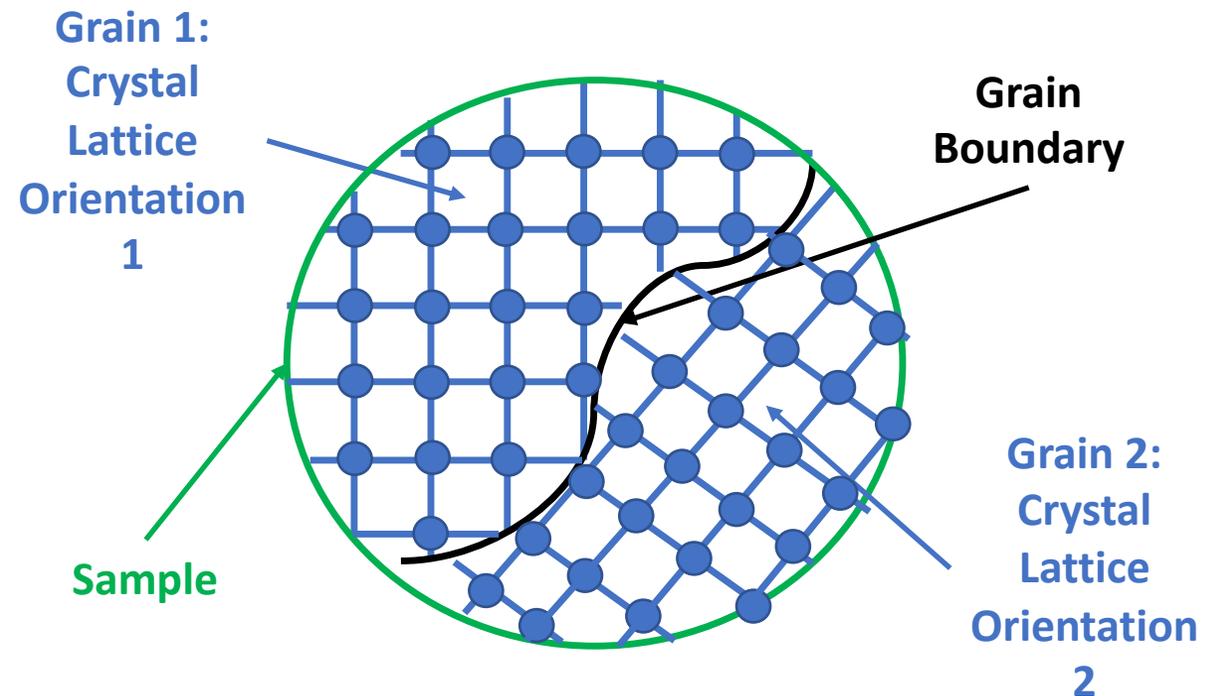
# What is a grain boundary???

- Grain boundaries are 2D defects
- They are internal boundaries inside a crystal
- Lattice orientation changes on the grain boundary



Single crystal: **lattice orientation** is the **same** throughout the material

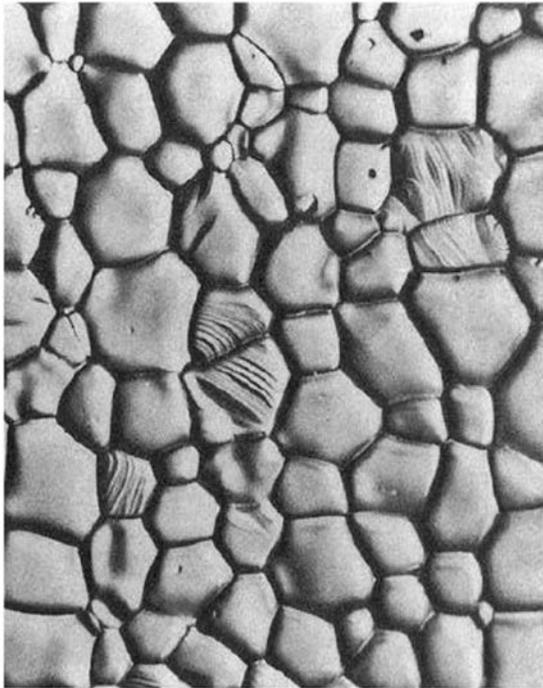
**Same lattice – different orientation!!**



Polycrystalline material: **lattice orientation** is **different** throughout the material

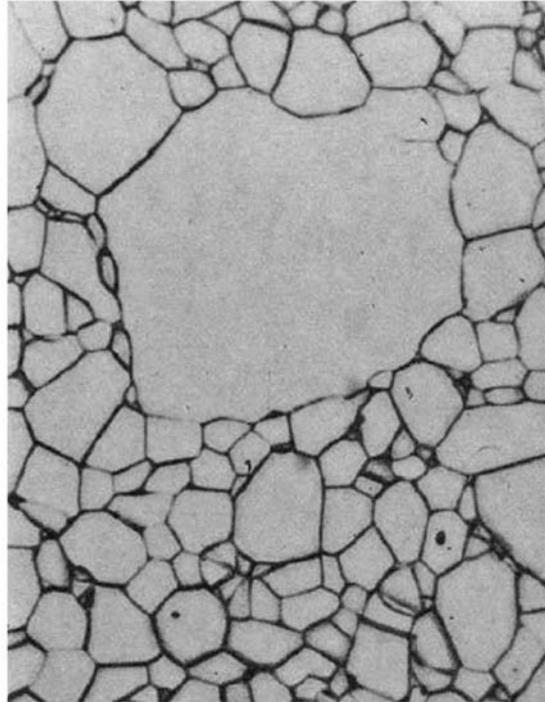
# Example 1: Normal vs. Abnormal Grain Growth

Normal



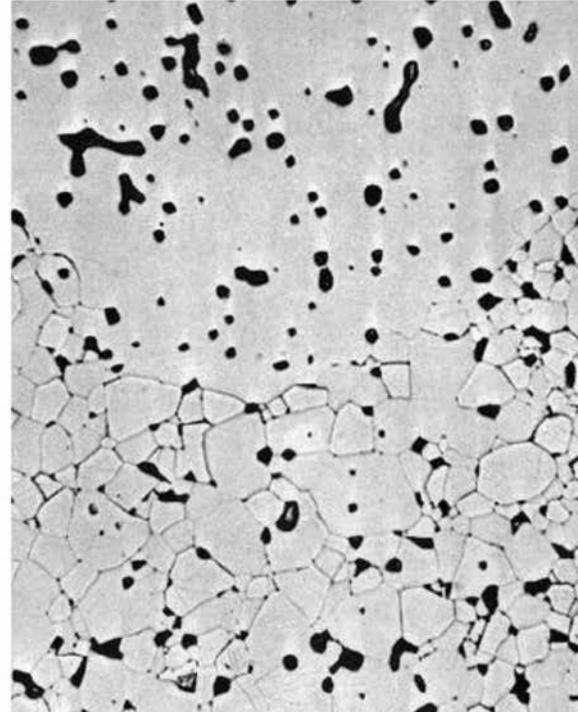
(a)

Abnormal



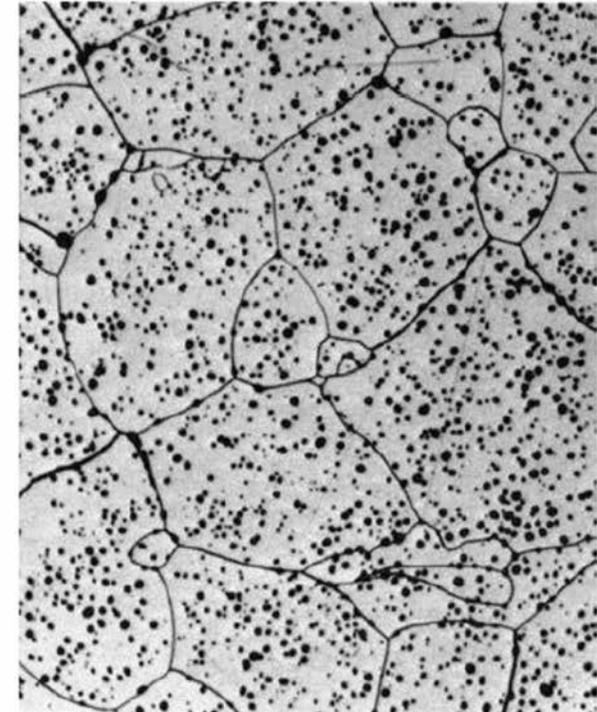
(b)

Abnormal



(c)

Abnormal

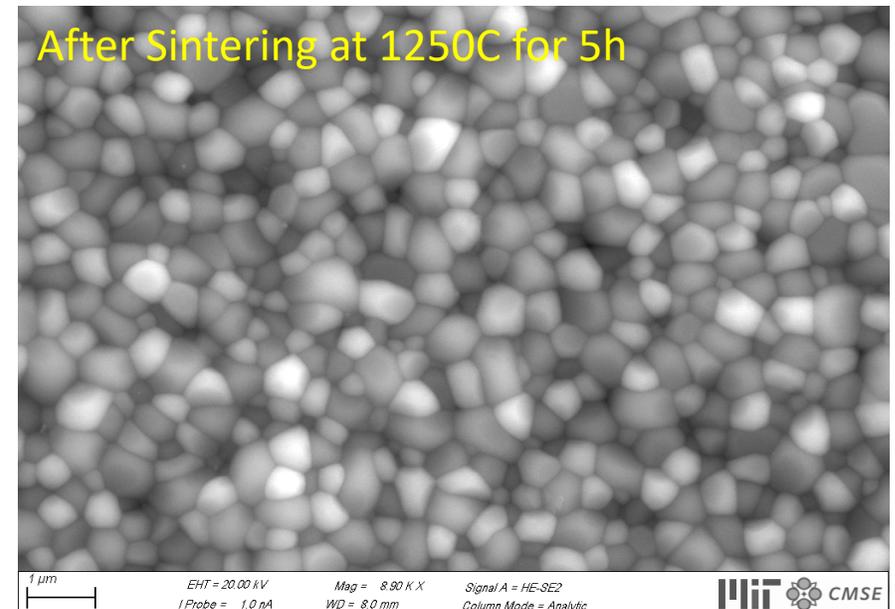
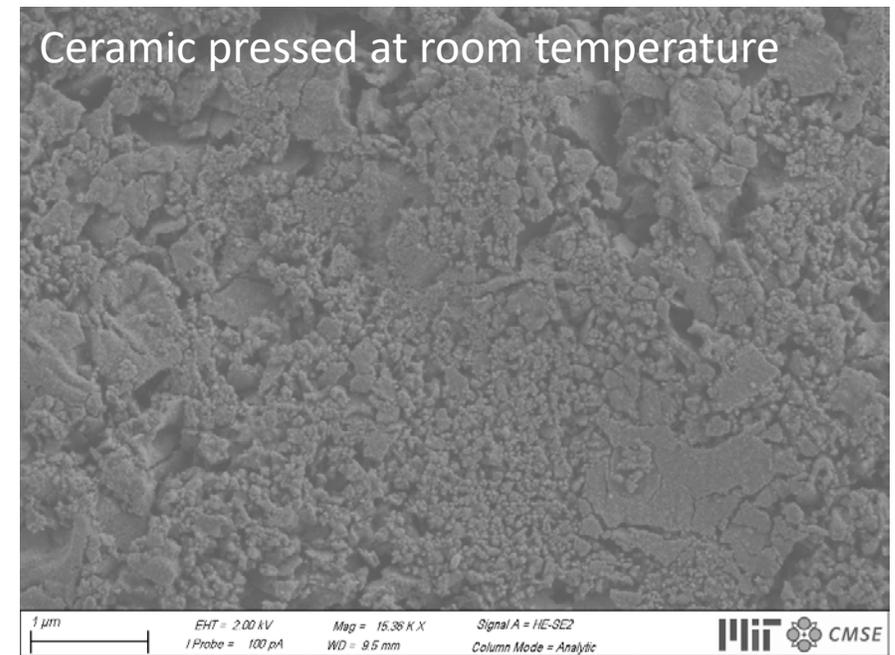


(d)

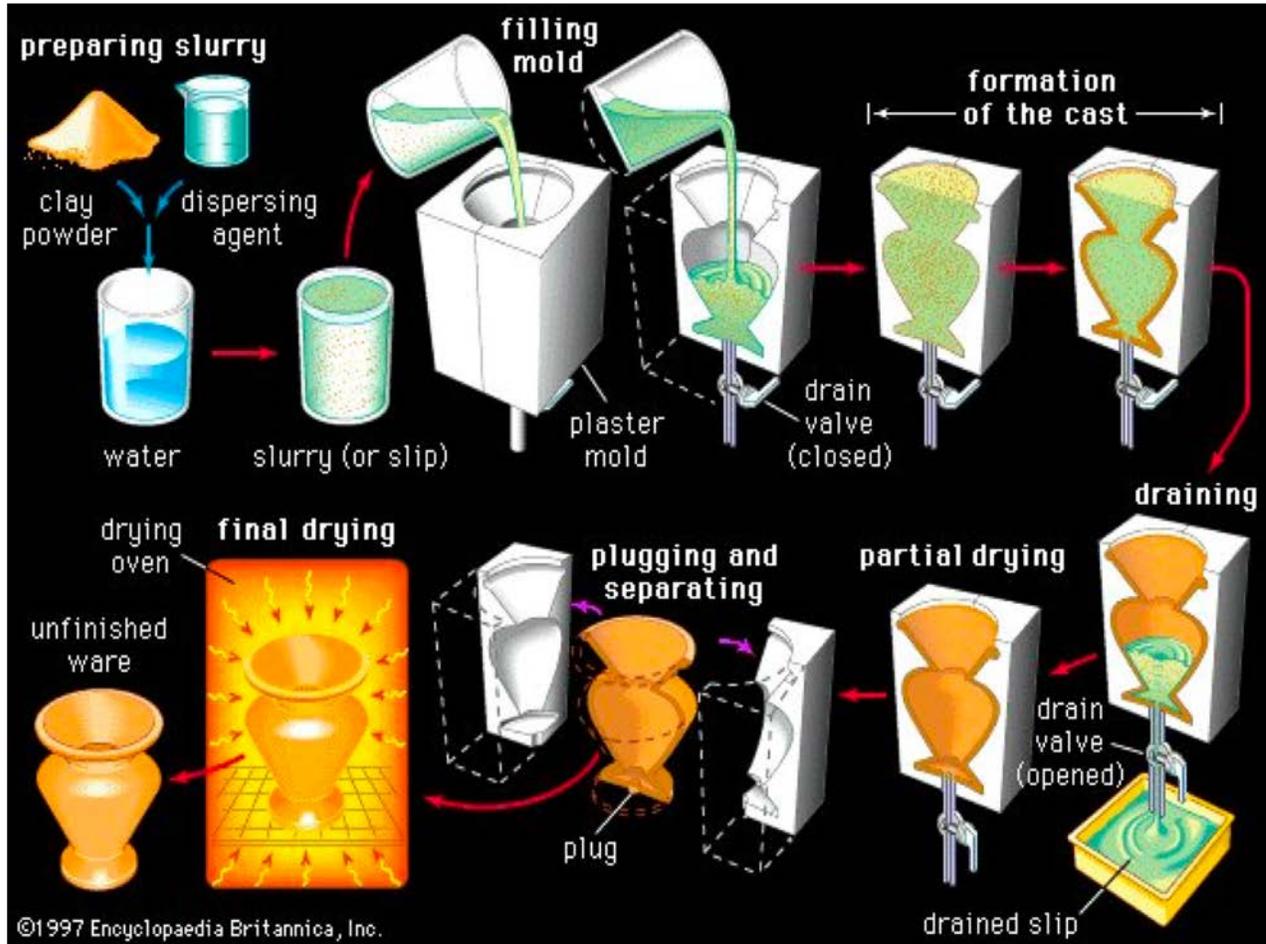
- Abnormal grain growth should be avoided
- It affects the density and the properties of the materials

# Shaping of the powder into a useful part

- For dense ceramic oxides, several shaping methods exist:
  1. Casting (industrial scale)
  2. Uniaxial/Isostatic cold/warm pressing (lab scale)
  3. Tape casting (industrial scale – thin flat plates)
  4. Phase inversion method (industrial scale)
  5. Laser sintering (still in lab scale)
  6. Additive manufacturing (early stages, few materials)
- There are 2 methods frequently employed:
  1. Shaping of the powder at room temperature followed by sintering at high temperature
  2. Simultaneous shaping and sintering at high temperatures
- Machining of ceramic oxides using conventional techniques is usually avoided because ceramic oxides are very brittle.



# Casting (industrial scale)



Casting of Ceramics

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Aluminum Oxide ( $\text{Al}_2\text{O}_3$ ) Tubes

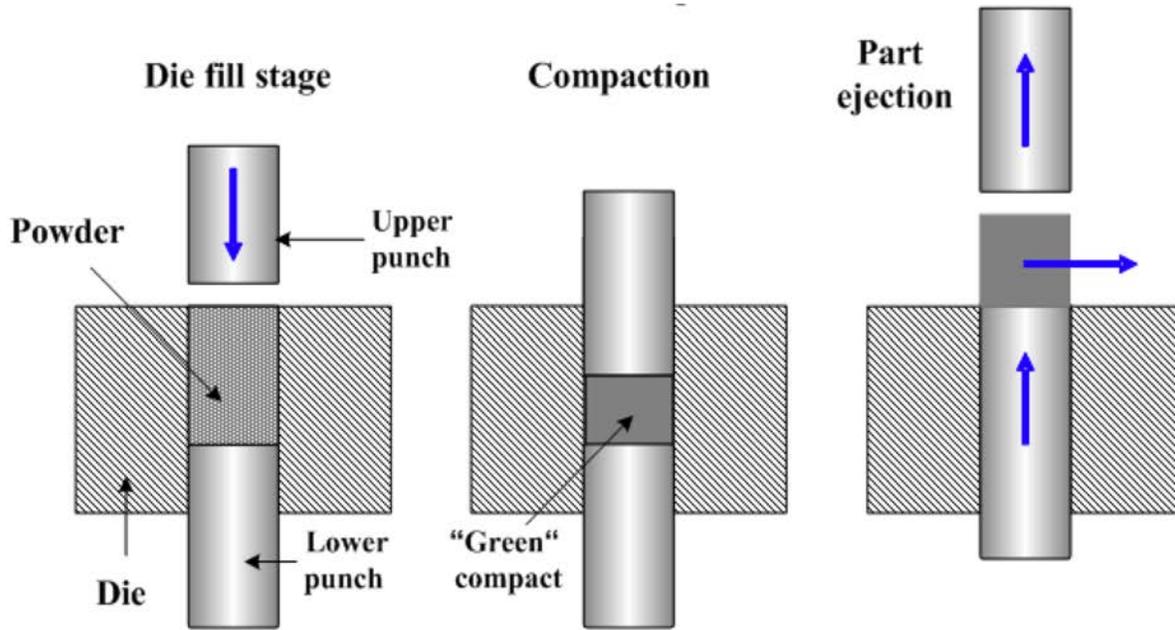
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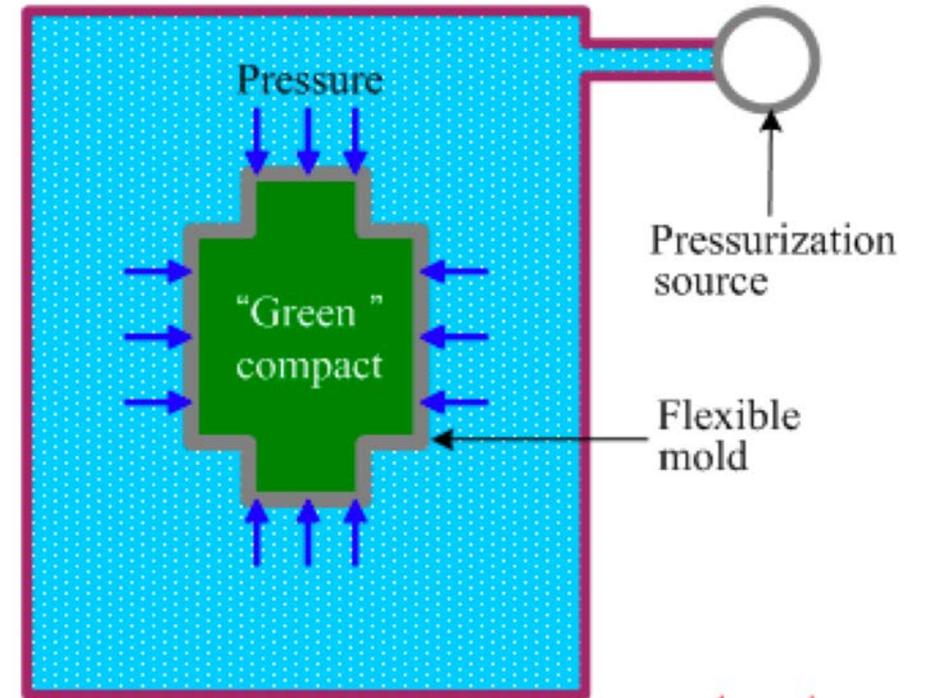
Gas Turbine Blade

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# Uniaxial/isostatic, cold/warm pressing



Cold uniaxial pressing

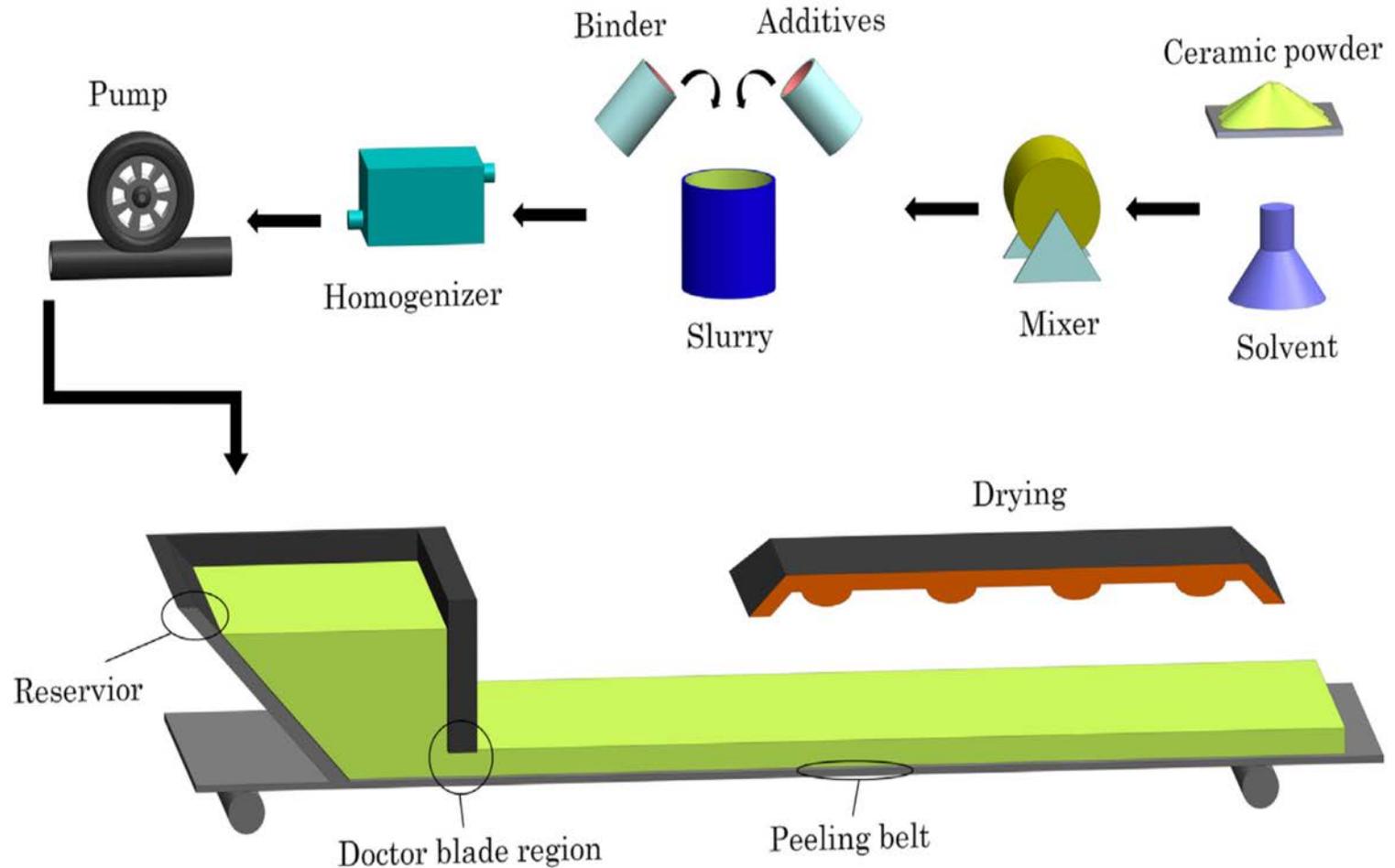


Cold isostatic pressing

- Cold pressing: compaction of powder at room temperature followed by sintering at high temperatures
- Warm pressing: compaction of powder and sintering at the same time

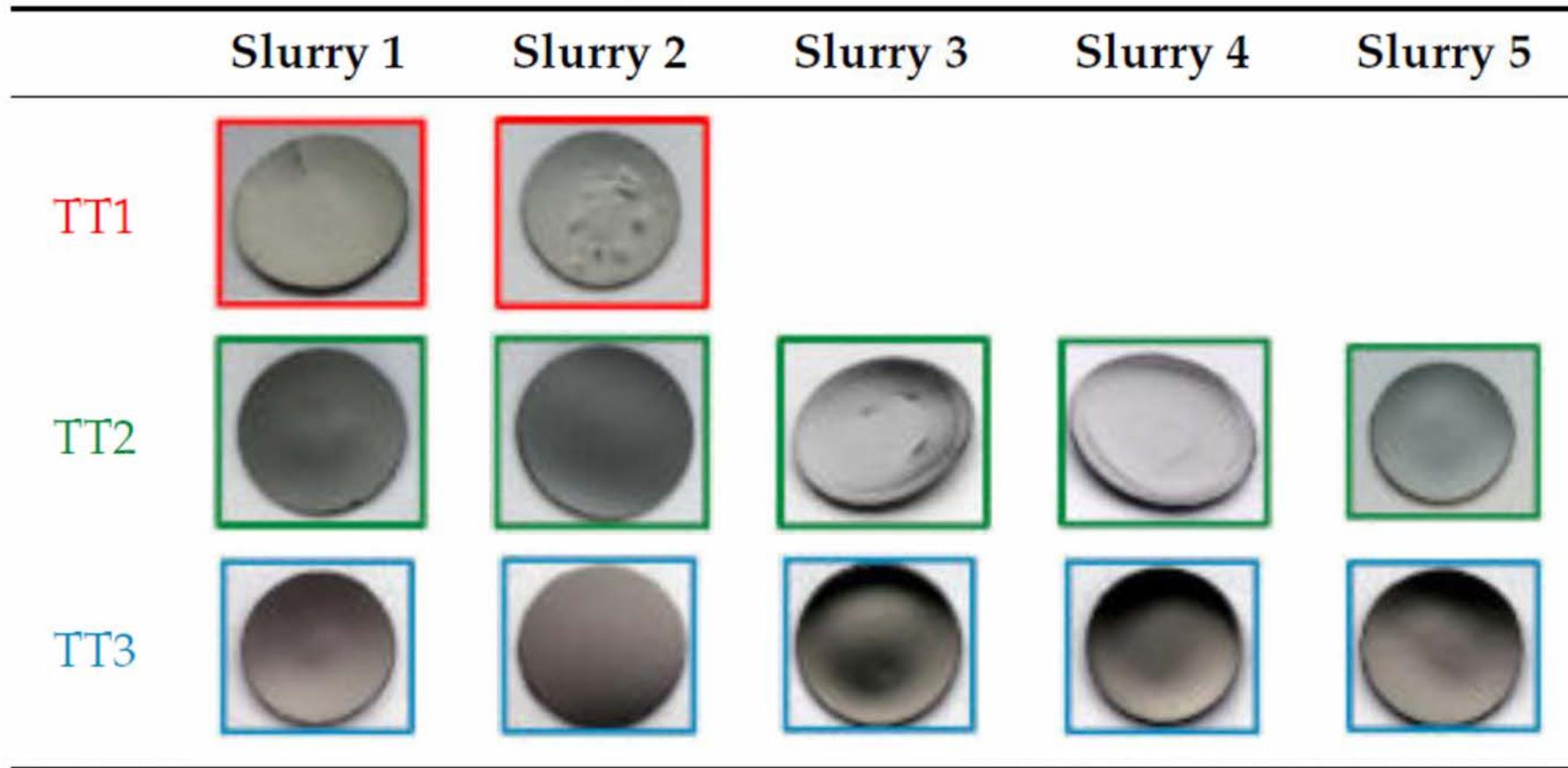
# Tape casting

- Tape casting can only produce ceramics in the form of sheets
- Advantages:
  1. Most popular method of ceramic shaping in industry due to low cost
  2. Thickness of ceramics is low ( $\sim 5\mu\text{m}$ ) and can be controlled by the doctor blade in a repetitive manner
  3. Ceramics with different layers can be made
- Disadvantages:
  1. the slurry includes the powder and additives (binder, plasticizer etc.) and the amount of each has to be optimized for each material based on trial and error and experience
  2. Drying and de-binding also has to be optimized
- Electrolytes are mainly fabricated through tape casting



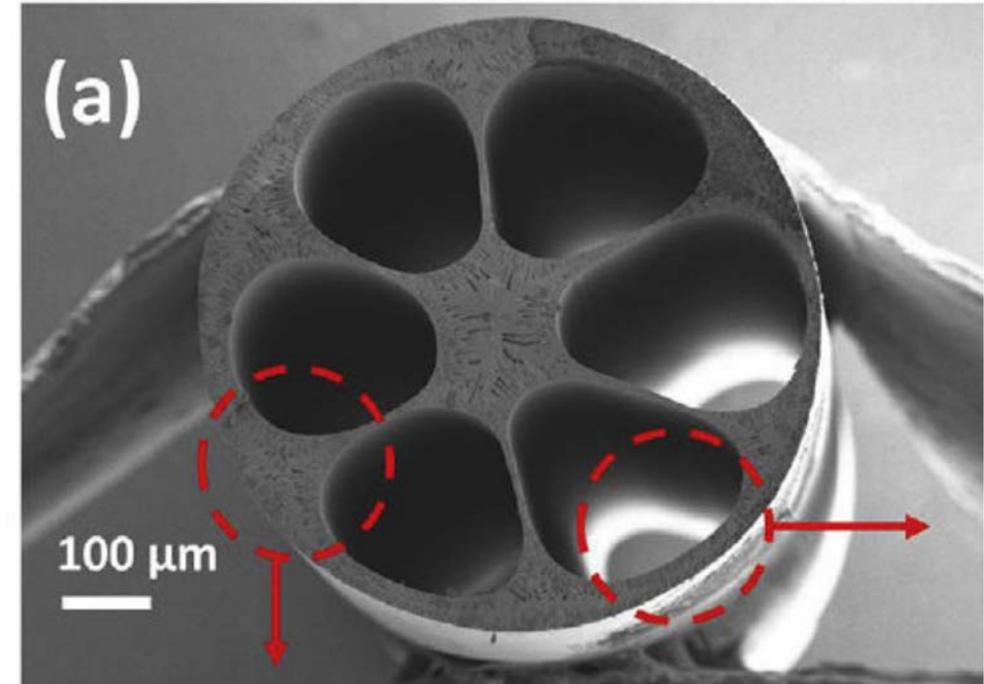
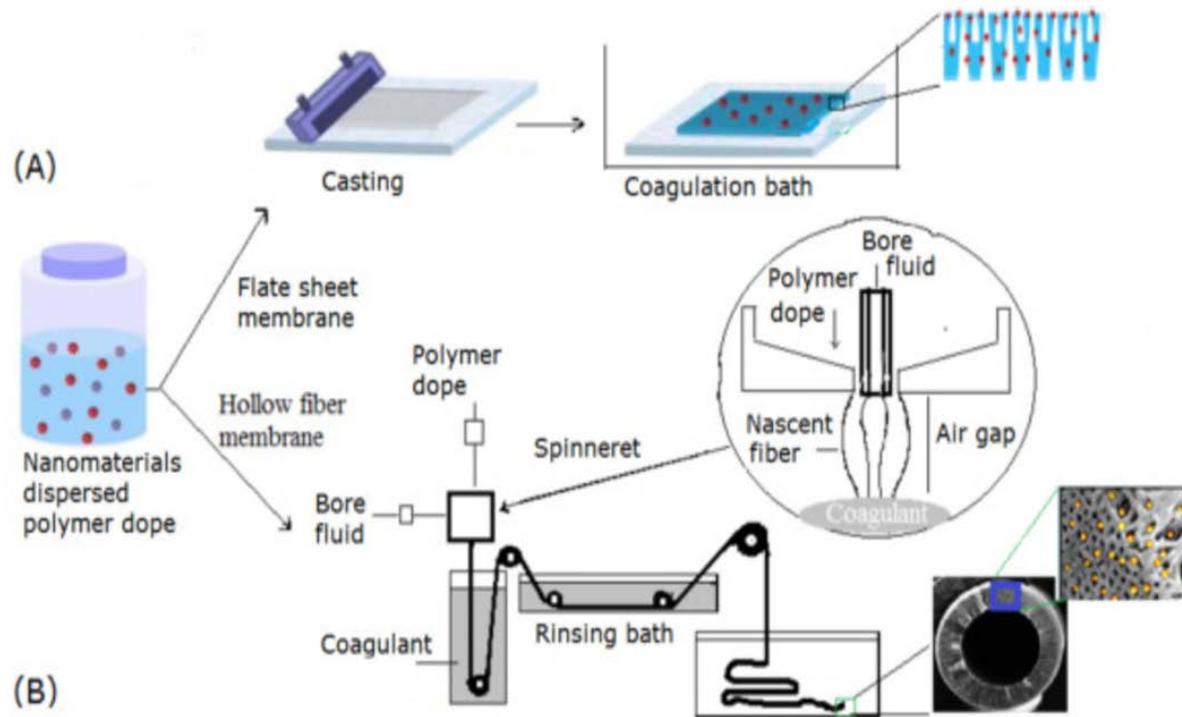
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# Example: effect of slurry composition and thermal treatment on final ceramic



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# Phase inversion



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Phase inversion is suitable for flat or tubular ceramics

Process:

1. Create a suspension of the material including additives
2. Cast the suspension using a blade
3. Immerse into a bath to enable coagulation

A  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  membrane used for  $\text{O}_2$  separation from air made using the phase-inversion technique.

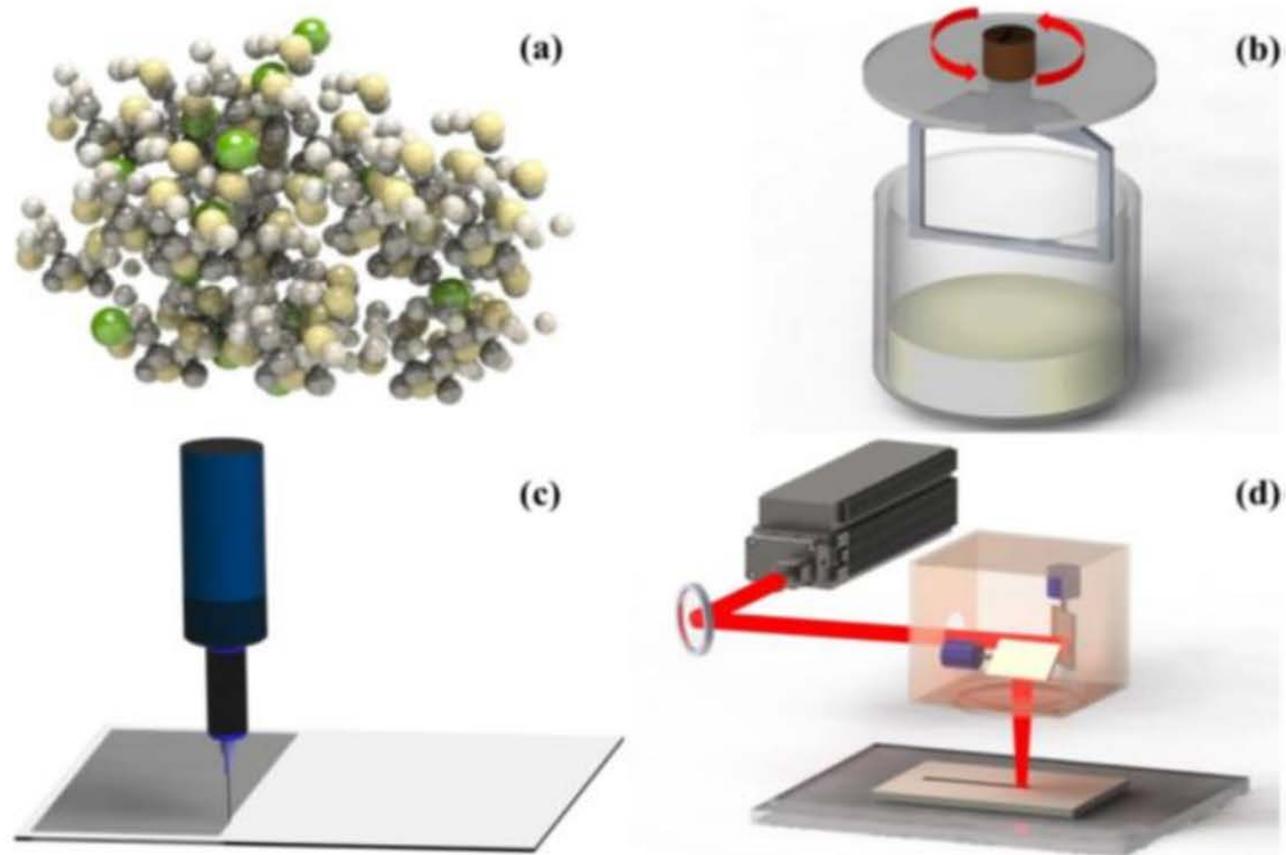
T. Li et. al. J. Membrane Science 578 (2019) 203-208

# Phase inversion

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Please click the link below to see the video.

[https://www.youtube.com/watch?v=WTrjqXbzhjE&feature=emb\\_logo](https://www.youtube.com/watch?v=WTrjqXbzhjE&feature=emb_logo)

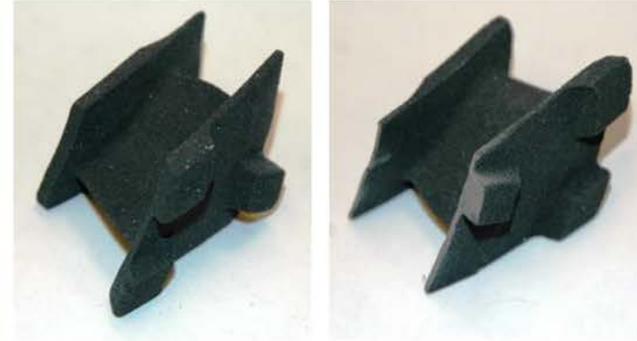
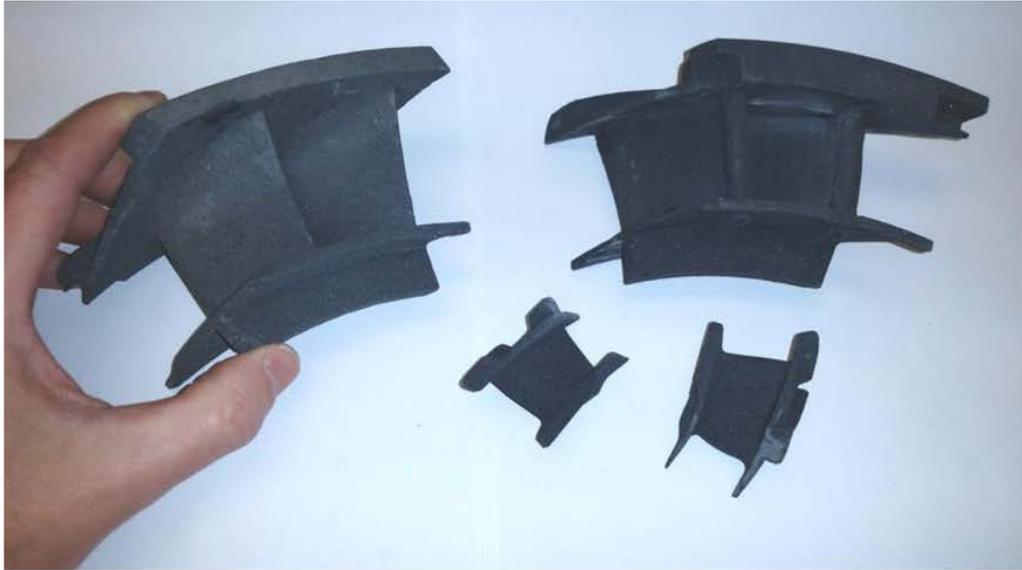
# Rapid Laser Reactive Sintering



Schematic description of rapid laser reactive sintering (RLRS) process. (a) Mix precursor solids, (b) prepare precursor paste, (c) deposit precursor layer, and (d) perform RLRS

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# Additive manufacturing of SiC turbine nozzle (still on its early stages)



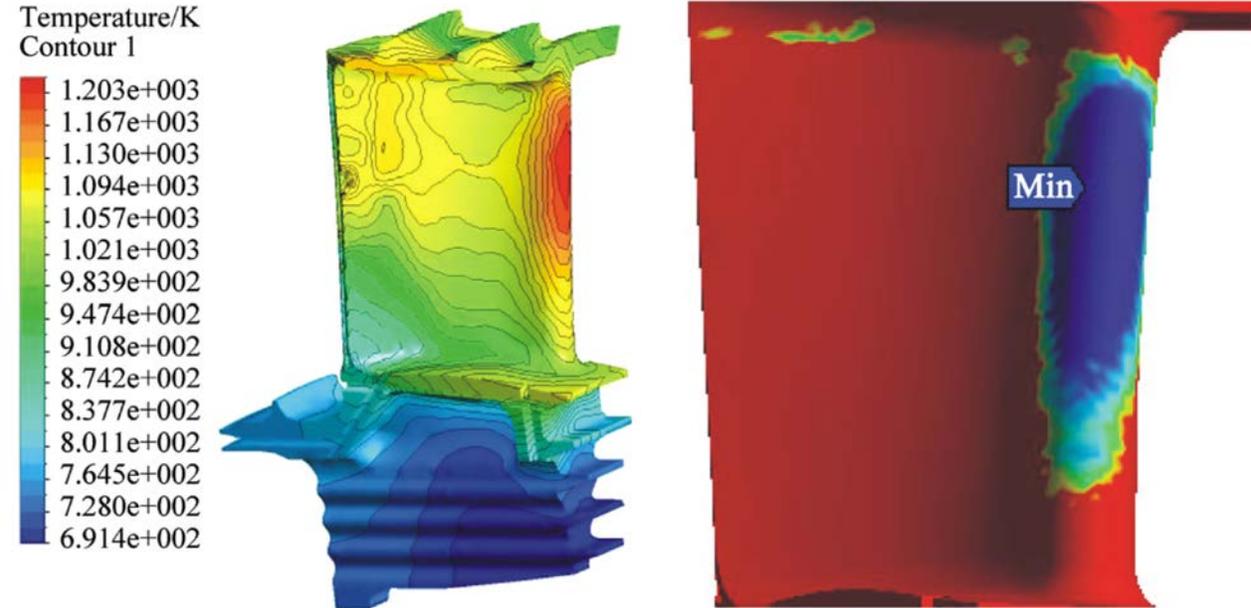
First stage nozzle segments.



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# Computational methods in Material Science

- Given the availability of computational resources, the use of computational models for the prediction of material properties has increased during the last decades.
- Modeling is important because it allows to obtain information that we cannot extract directly through measurements.
- Models exist in all scales depending on the scientific/engineering question that needs to be answered.
- All models are based on assumptions!
- Each model has its own limitations depending on the scale it is formulated for!
- What is important is to know:
  1. The question you want to answer
  2. Which model will give an answer
  3. How fast and/or how accurate will the answer be



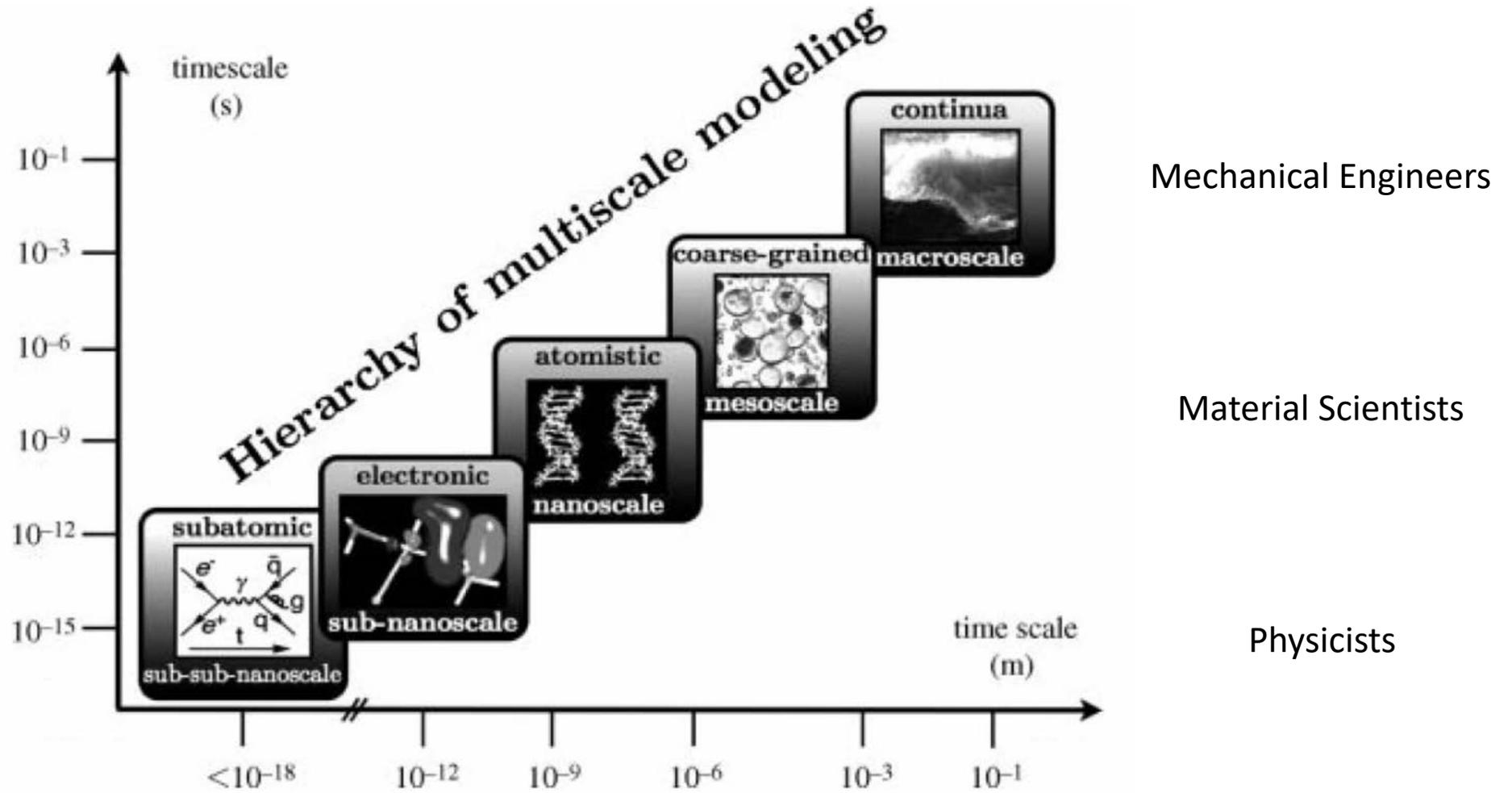
Temperature (left) and creep (right) profiles for a gas turbine blade

M.R. Reyhani et. al. Propulsion and Power Research 2013;2(2):148-161

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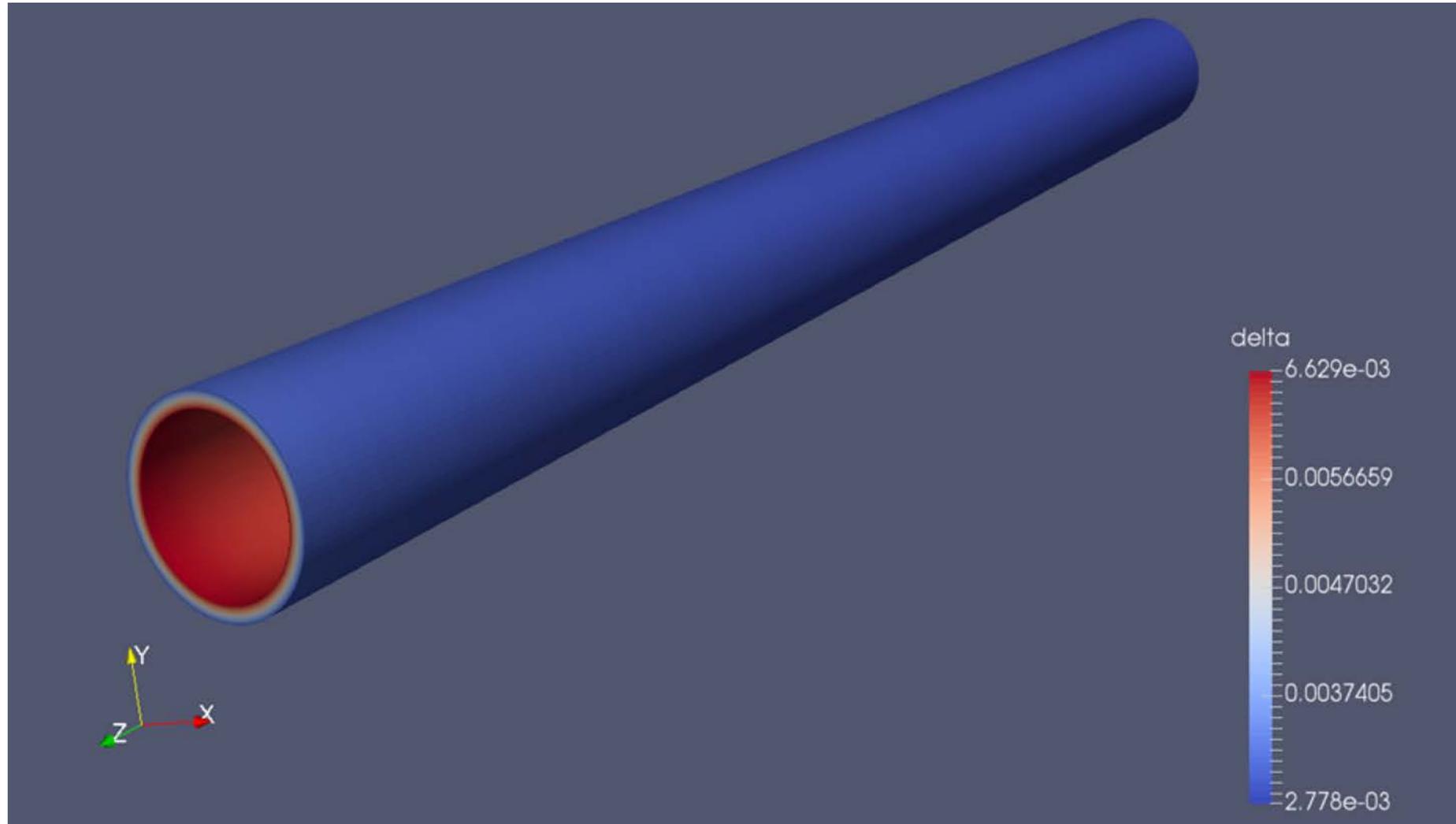
If the question is to understand the creep behavior, we will use a continuous model, i.e. we are not going to calculate creep induced by elements in the atomic scale, which will take forever!!

# Computational methods depending on the scale of interest



More detailed models take longer to run!!!

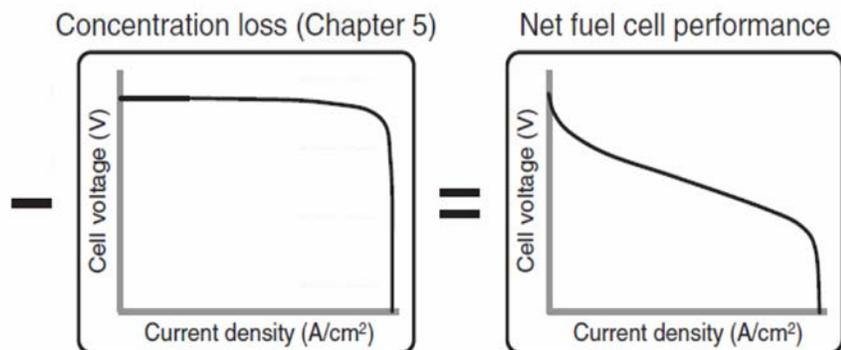
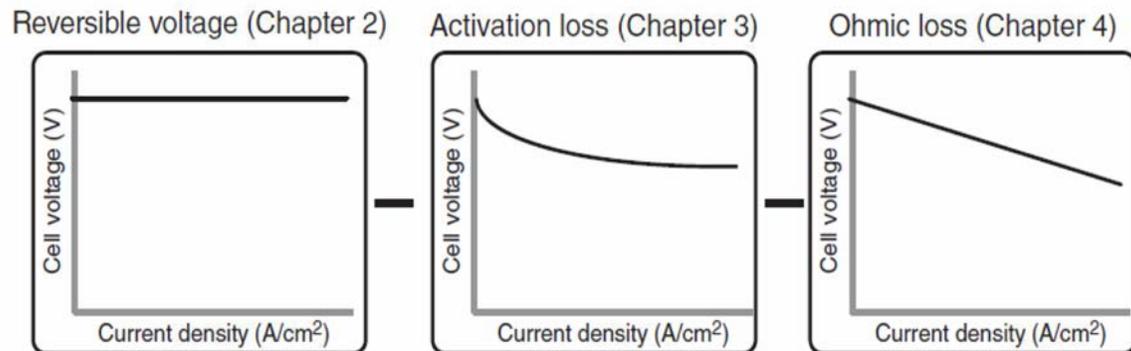
# CFD models for design of reactors based on ceramic materials



Design of tubular ceramic membranes using state-of-the-art defect chemistry models

# Micro-kinetic models for fuel cells

## Simplified modeling of an I-V curve



$$V = E_{thermo} - \eta_{act} - \eta_{ohmic} - \eta_{conc}$$

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## Heterogeneous reaction mechanism on Ni-based catalysts

	Reaction	A <sup>a</sup>	n	E <sup>a</sup>
1	H <sub>2</sub> + (Ni) + (Ni) → H(Ni) + H(Ni)	1.000 · 10 <sup>-02b</sup>	0.0	0.00
2	H(Ni) + H(Ni) → (Ni) + (Ni) + H <sub>2</sub>	5.593 · 10 <sup>+19</sup>	0.0	88.12
3	O <sub>2</sub> + (Ni) + (Ni) → O(Ni) + O(Ni)	1.000 · 10 <sup>-02b</sup>	0.0	0.00
4	O(Ni) + O(Ni) → (Ni) + (Ni) + O <sub>2</sub>	2.508 · 10 <sup>+23</sup>	0.0	470.39
5	CH <sub>4</sub> + (Ni) → CH <sub>4</sub> (Ni)	8.000 · 10 <sup>-03b</sup>	0.0	0.00
6	CH <sub>4</sub> (Ni) → (Ni) + CH <sub>4</sub>	5.302 · 10 <sup>+15</sup>	0.0	33.15
7	H <sub>2</sub> O + (Ni) → H <sub>2</sub> O(Ni)	1.000 · 10 <sup>-01b</sup>	0.0	0.00
8	H <sub>2</sub> O(Ni) → (Ni) + H <sub>2</sub> O	4.579 · 10 <sup>+12</sup>	0.0	62.68
9	CO <sub>2</sub> + (Ni) → CO <sub>2</sub> (Ni)	1.000 · 10 <sup>-05b</sup>	0.0	0.00
10	CO <sub>2</sub> (Ni) → (Ni) + CO <sub>2</sub>	9.334 · 10 <sup>+07</sup>	0.0	28.80
11	CO + (Ni) → CO(Ni)	5.000 · 10 <sup>-01b</sup>	0.0	0.00
12	CO(Ni) → (Ni) + CO	4.041 · 10 <sup>+11</sup>	0.0	112.85
	ε <sub>CO(s)</sub>			-50.0 <sup>c</sup>
13	O(Ni) + H(Ni) → OH(Ni) + (Ni)	5.000 · 10 <sup>+22</sup>	0.0	97.90
14	OH(Ni) + (Ni) → O(Ni) + H(Ni)	2.005 · 10 <sup>+21</sup>	0.0	37.19
15	OH(Ni) + H(Ni) → H <sub>2</sub> O(Ni) + (Ni)	3.000 · 10 <sup>+20</sup>	0.0	42.70
16	H <sub>2</sub> O(Ni) + (Ni) → OH(Ni) + H(Ni)	2.175 · 10 <sup>+21</sup>	0.0	91.36
17	OH(Ni) + OH(Ni) → O(Ni) + H <sub>2</sub> O(Ni)	3.000 · 10 <sup>+21</sup>	0.0	100.00
18	O(Ni) + H <sub>2</sub> O(Ni) → OH(Ni) + OH(Ni)	5.423 · 10 <sup>+23</sup>	0.0	209.37
19	O(Ni) + C(Ni) → CO(Ni) + (Ni)	5.200 · 10 <sup>+23</sup>	0.0	148.10
20	CO(Ni) + (Ni) → O(Ni) + C(Ni)	1.418 · 10 <sup>+22</sup>	-3.0	115.97
	ε <sub>CO(s)</sub>			-50.0 <sup>c</sup>
21	O(Ni) + CO(Ni) → CO <sub>2</sub> (Ni) + (Ni)	2.000 · 10 <sup>+19</sup>	0.0	123.60
	ε <sub>CO(s)</sub>			-50.0 <sup>c</sup>
22	CO <sub>2</sub> (Ni) + (Ni) → O(Ni) + CO(Ni)	3.214 · 10 <sup>+23</sup>	-1.0	86.50
23	HCO(Ni) + (Ni) → CO(Ni) + H(Ni)	3.700 · 10 <sup>+21</sup>	0.0	0.0
	ε <sub>CO(s)</sub>			50.0 <sup>c</sup>
24	CO(Ni) + H(Ni) → HCO(Ni) + (Ni)	2.338 · 10 <sup>+20</sup>	-1.0	127.98
25	HCO(Ni) + (Ni) → O(Ni) + CH(Ni)	3.700 · 10 <sup>+24</sup>	-3.0	95.80
26	O(Ni) + CH(Ni) → HCO(Ni) + (Ni)	7.914 · 10 <sup>+20</sup>	0.0	114.22
27	CH <sub>4</sub> (Ni) + (Ni) → CH <sub>3</sub> (Ni) + H(Ni)	3.700 · 10 <sup>+21</sup>	0.0	57.70
28	CH <sub>3</sub> (Ni) + H(Ni) → CH <sub>4</sub> (Ni) + (Ni)	4.438 · 10 <sup>+21</sup>	0.0	58.83
29	CH <sub>3</sub> (Ni) + (Ni) → CH <sub>2</sub> (Ni) + H(Ni)	3.700 · 10 <sup>+24</sup>	0.0	100.00
30	CH <sub>2</sub> (Ni) + H(Ni) → CH <sub>3</sub> (Ni) + (Ni)	9.513 · 10 <sup>+22</sup>	0.0	52.58
31	CH <sub>2</sub> (Ni) + (Ni) → CH(Ni) + H(Ni)	3.700 · 10 <sup>+24</sup>	0.0	97.10
32	CH(Ni) + H(Ni) → CH <sub>2</sub> (Ni) + (Ni)	3.008 · 10 <sup>+24</sup>	0.0	76.43
33	CH(Ni) + (Ni) → C(Ni) + H(Ni)	3.700 · 10 <sup>+21</sup>	0.0	18.80
34	C(Ni) + H(Ni) → CH(Ni) + (Ni)	4.400 · 10 <sup>+22</sup>	0.0	160.49
35	O(Ni) + CH <sub>4</sub> (Ni) → CH <sub>3</sub> (Ni) + OH(Ni)	1.700 · 10 <sup>+24</sup>	0.0	88.30
36	CH <sub>3</sub> (Ni) + OH(Ni) → O(Ni) + CH <sub>4</sub> (Ni)	8.178 · 10 <sup>+22</sup>	0.0	28.72
37	O(Ni) + CH <sub>3</sub> (Ni) → CH <sub>2</sub> (Ni) + OH(Ni)	3.700 · 10 <sup>+24</sup>	0.0	130.10
38	CH <sub>2</sub> (Ni) + OH(Ni) → O(Ni) + CH <sub>3</sub> (Ni)	3.815 · 10 <sup>+21</sup>	0.0	21.97
39	O(Ni) + CH <sub>2</sub> (Ni) → CH(Ni) + OH(Ni)	3.700 · 10 <sup>+24</sup>	0.0	126.80
40	CH(Ni) + OH(Ni) → O(Ni) + CH <sub>2</sub> (Ni)	1.206 · 10 <sup>+23</sup>	0.0	45.42
41	O(Ni) + CH(Ni) → C(Ni) + OH(Ni)	3.700 · 10 <sup>+21</sup>	0.0	48.10
42	C(Ni) + OH(Ni) → O(Ni) + CH(Ni)	1.764 · 10 <sup>+21</sup>	0.0	129.08

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# Density Functional Theory (DFT)

- In DFT, one solves for the so-called Kohn-Sham equations (not the Schrödinger equation):

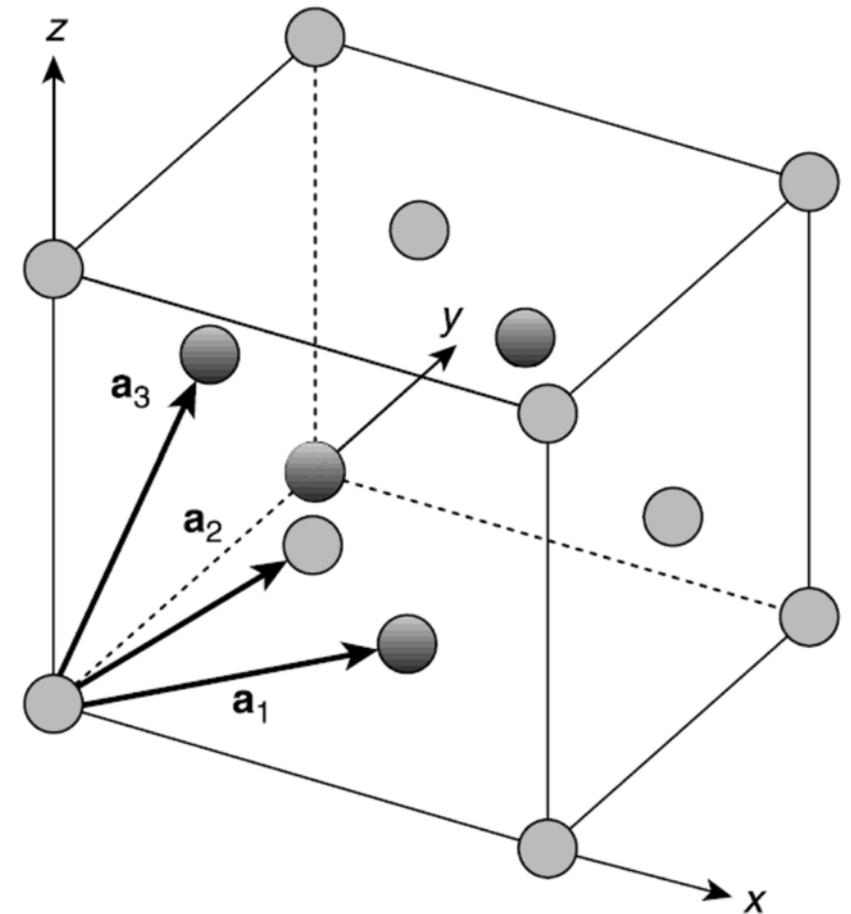
$$\left[ -\frac{\hbar}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (1)$$

Electron Kinetic Energy	Electron- Nuclei Interaction	Electron- Electron Interaction	Exchange- Correlation Functional
-------------------------------	------------------------------------	--------------------------------------	--

- $V_H$  and  $V_{XC}$  are a function of the electron density  $n(\mathbf{r})$ :

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \quad (2)$$

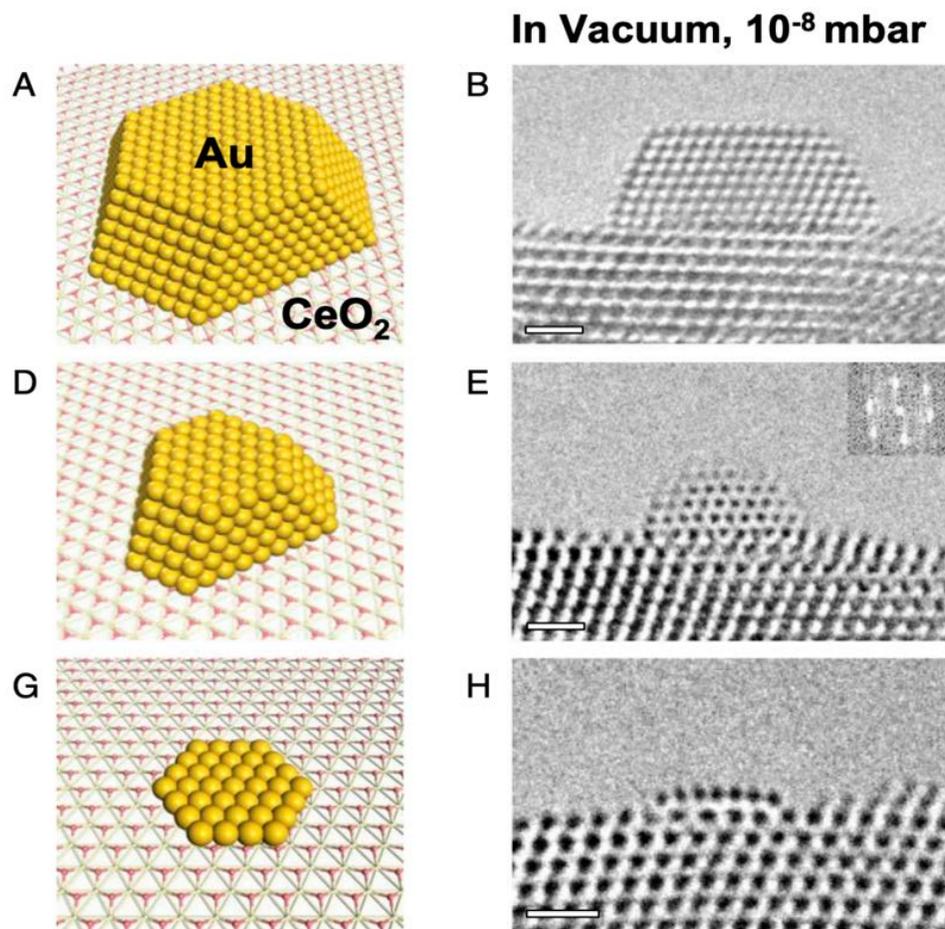
- Iterative algorithm:
  1. Assume an electron density  $n(\mathbf{r})$
  2. Solve the Kohn-Sham equations to compute  $\psi_i(\mathbf{r})$  using equation (1)
  3. Calculate the updated electron density  $n(\mathbf{r})$  using equation (2)
  4. If  $n(\mathbf{r})$  of steps 1 and 3 are the same, the ground energy has been determined. If not,  $n(\mathbf{r})$  has to be updated and the algorithm is repeated.



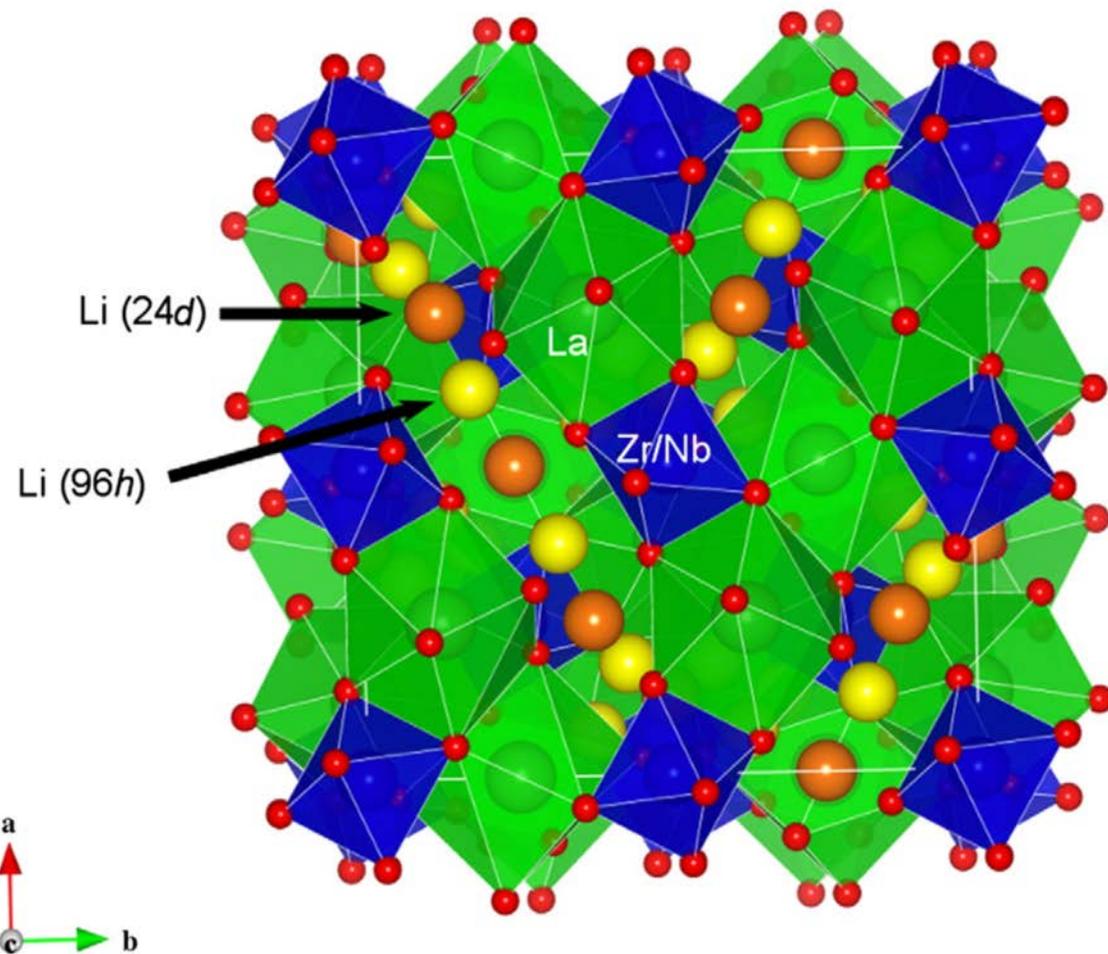
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# Example 1: DFT calculations for catalysis and Li-ion electrolytes

## Gold (Au) clusters on Cerium Oxide ( $\text{CeO}_2$ )



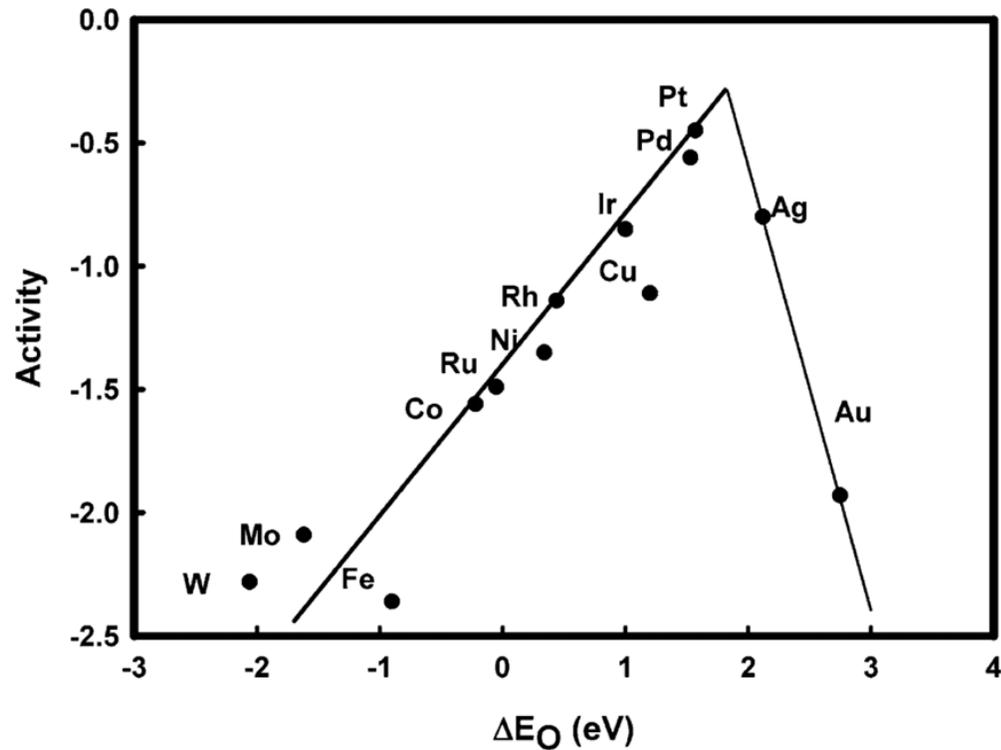
## Lithium garnets (Li-ion battery electrolytes)



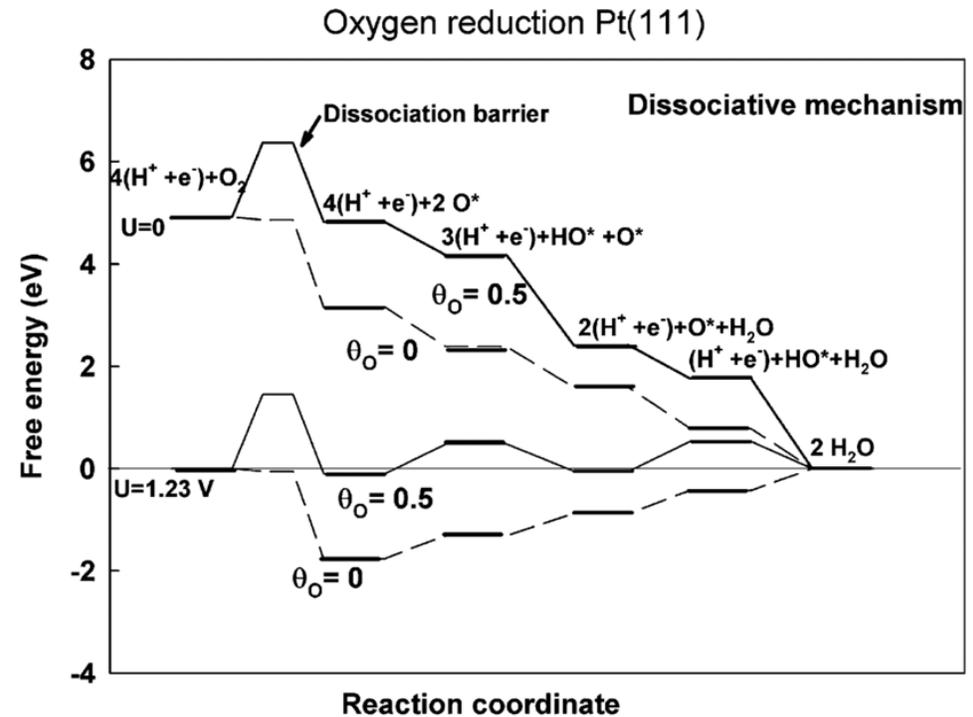
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## Example 2: DFT Calculations of Oxygen Reduction on Pt



Volcano plot of catalytic activity

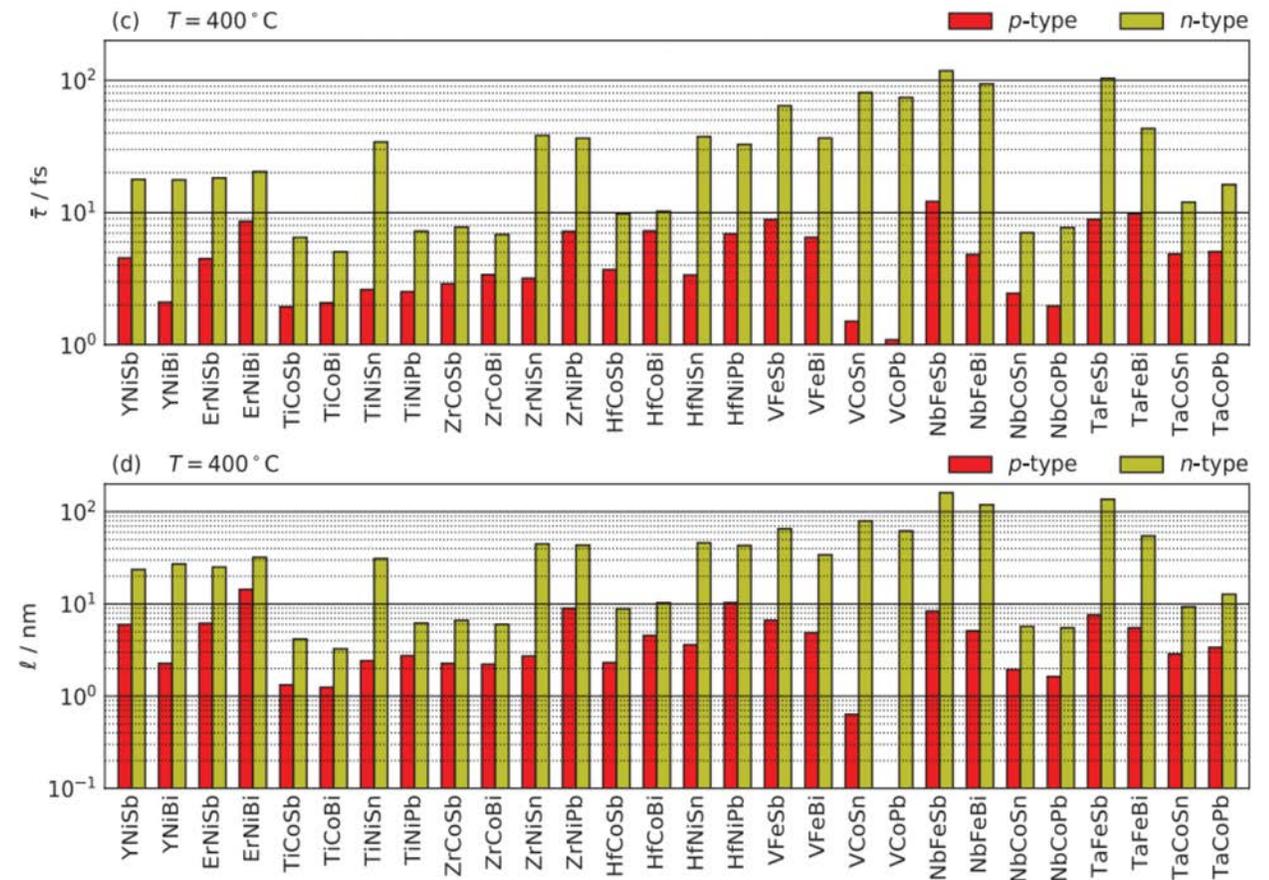
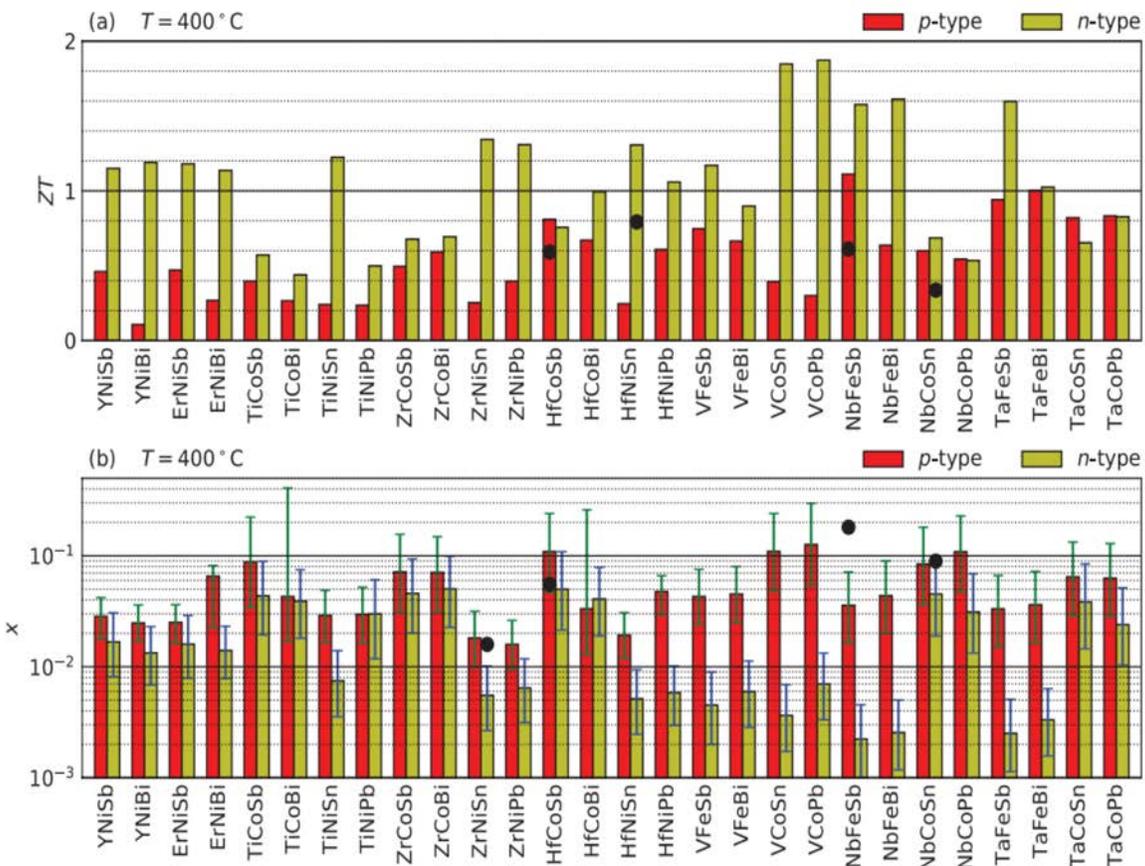


Calculation of intermediate steps of the reaction

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- DFT can be used to predict properties of materials
- But remember that it has its own assumptions and limitations

# High-throughput screening of materials: Thermoelectric materials (1)



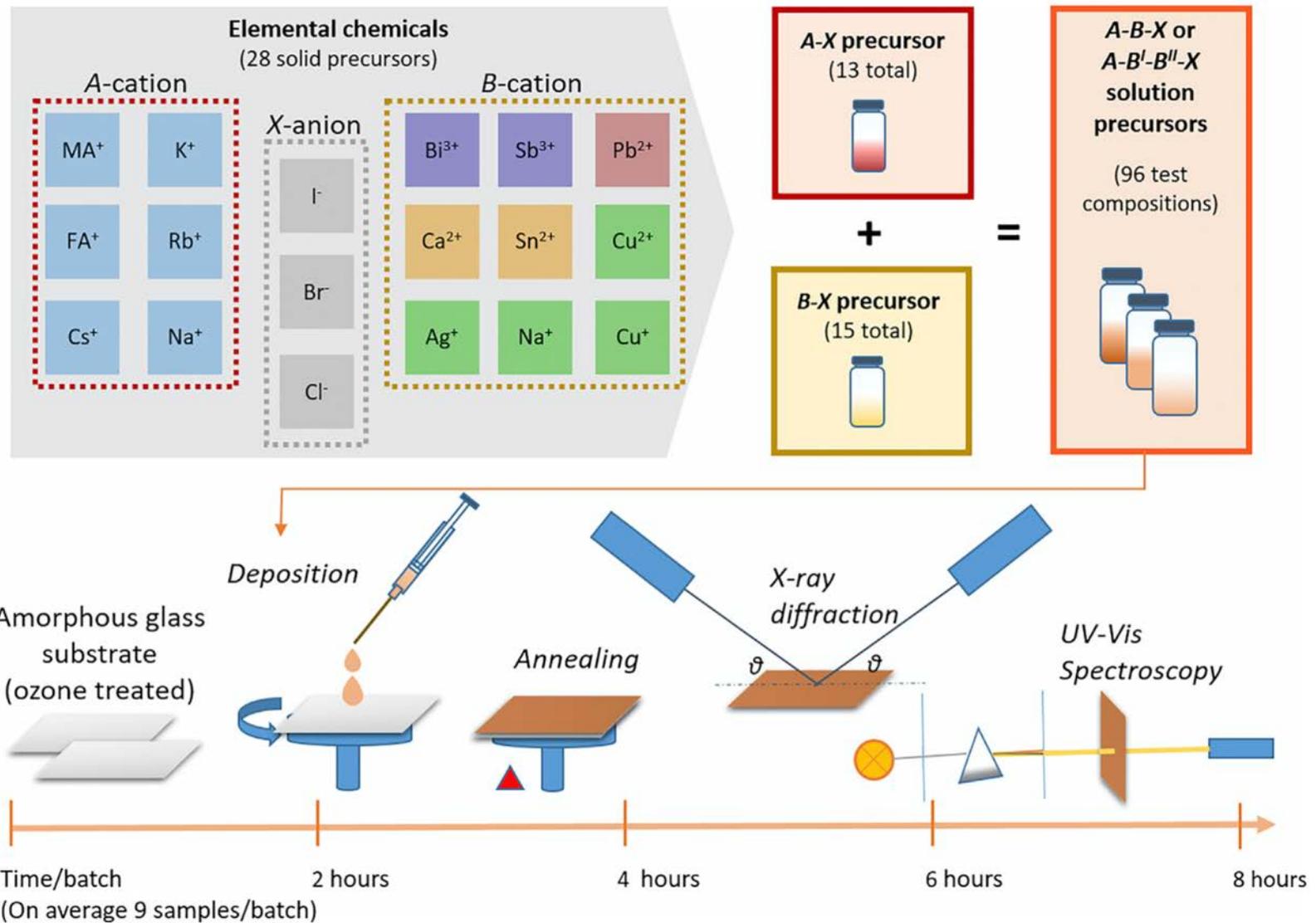
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## Computational Screening

Can the predicted materials be synthesized?

# High-throughput screening of materials: Photovoltaics (2)

## Experimental Screening



# Summary

- Materials are part of every energy conversion technology
- This presentation covered several energy conversion technologies involving the use of materials with focus on ceramic oxides
- Defect chemistry in materials
- Synthesis of materials
- Shaping of materials
- Computational methods
- High-throughput screening



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2.60J Fundamentals of Advanced Energy Conversion  
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