Lecture 1:
Course overview and introduction
Ionic defect formation

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西湖大學
WESTLAKE UNIVERSITY

Fall 2023 MSE 5007
Solid State Ionics

SSI Lab
WESTLAKE UNIVERSITY

Things we will discuss in this lecture

Course introduction:

- What is **S**olid **S**tate **I**onics (**SSI**)?
- What are the ***key problems*** in this field?
- What does the conventional ***language and research philosophy*** of SSI look like?

Course policy and content:

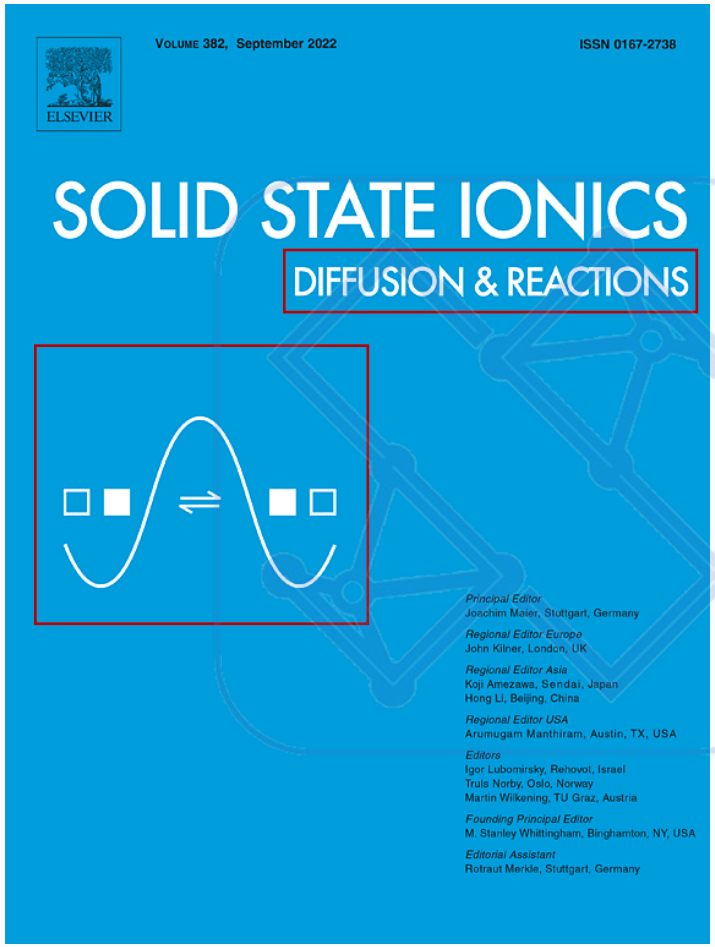
- What will you learn and what do you need to accomplish in this semester?
- *Why do graduate students take graduate-level courses?*

Defect formation in solids:

- Why are *ionic defects* important in solids?
- Why do ionic defects form simultaneously in solids? How to *predict the concentration* of defects in equilibrium?

Goal of this lecture: you should be able to answer the questions above by the end of this lecture :)

What is Solid State Ionics (SSI)?



Solid State Ionics (*Elsevier Journal*)
IF: 3.2 (2023) ***JCR Q3*** (☹)

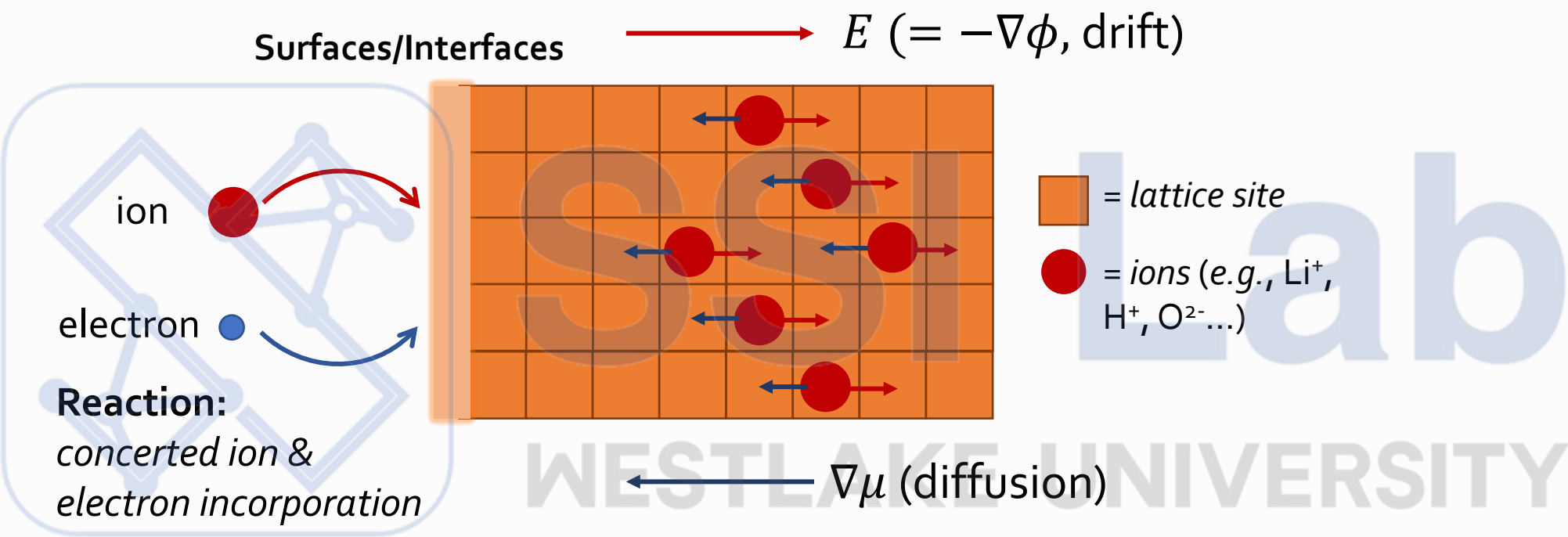
Principle Editor:

Prof. Joachim Maier
Max Planck Institute for Solid State Research
Stuttgart, Germany

This interdisciplinary journal is devoted to the ***physics, chemistry*** *and* ***materials science*** *of* ***diffusion, mass transport****, and* ***reactivity of solids***. The major part of each issue is devoted to articles on:

- physics and chemistry of **defects** in solids;
- **reactions** in and on solids, *e.g.* intercalation, corrosion, oxidation, sintering;
- **ion transport** measurements, mechanisms and theory;
- solid state **electrochemistry**;
- ionically-electronically mixed **conducting solids**.

Diffusion & Reactions of ions/ionic defects in solids



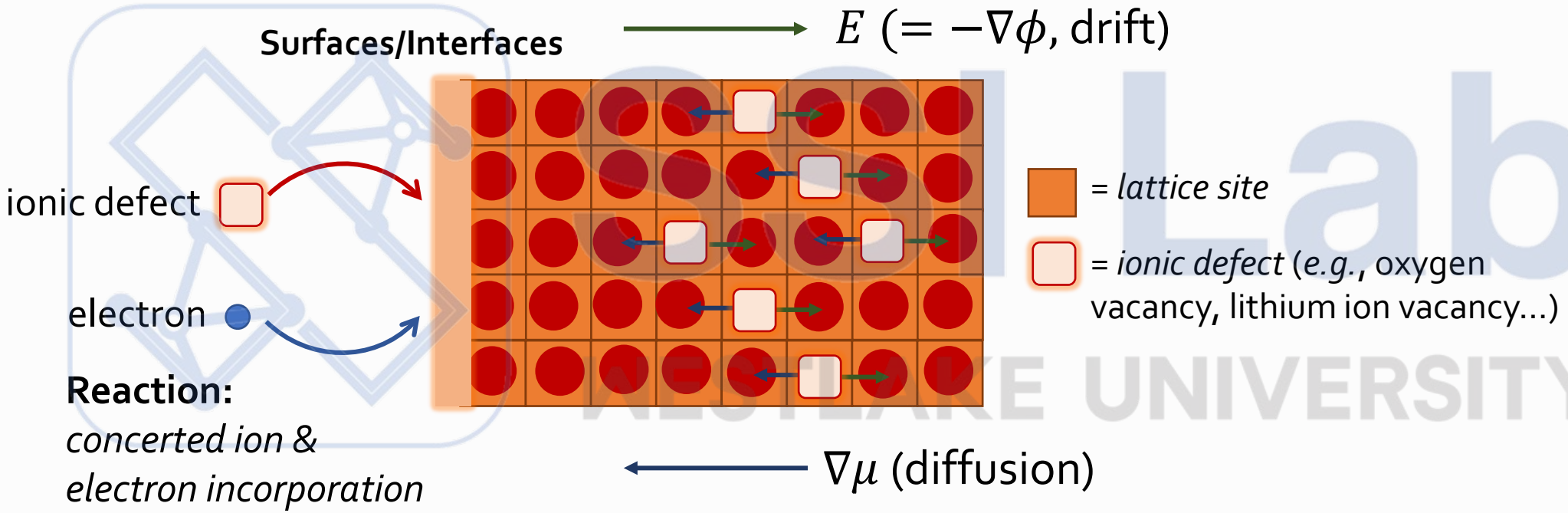
Ion motion: *drift + diffusion*

- Similar to electrons/holes in semiconductor physics;
- Ion mobility is much slower → totally different *temp. and time scales*.

Goal:

By the end of the semester, you will have a clear physical picture on the ***diffusion & reactions*** related with ***ions in solid state*** and have the tools to analyze the *fundamental physical chemistry process*.

Let's look at this picture from another angle

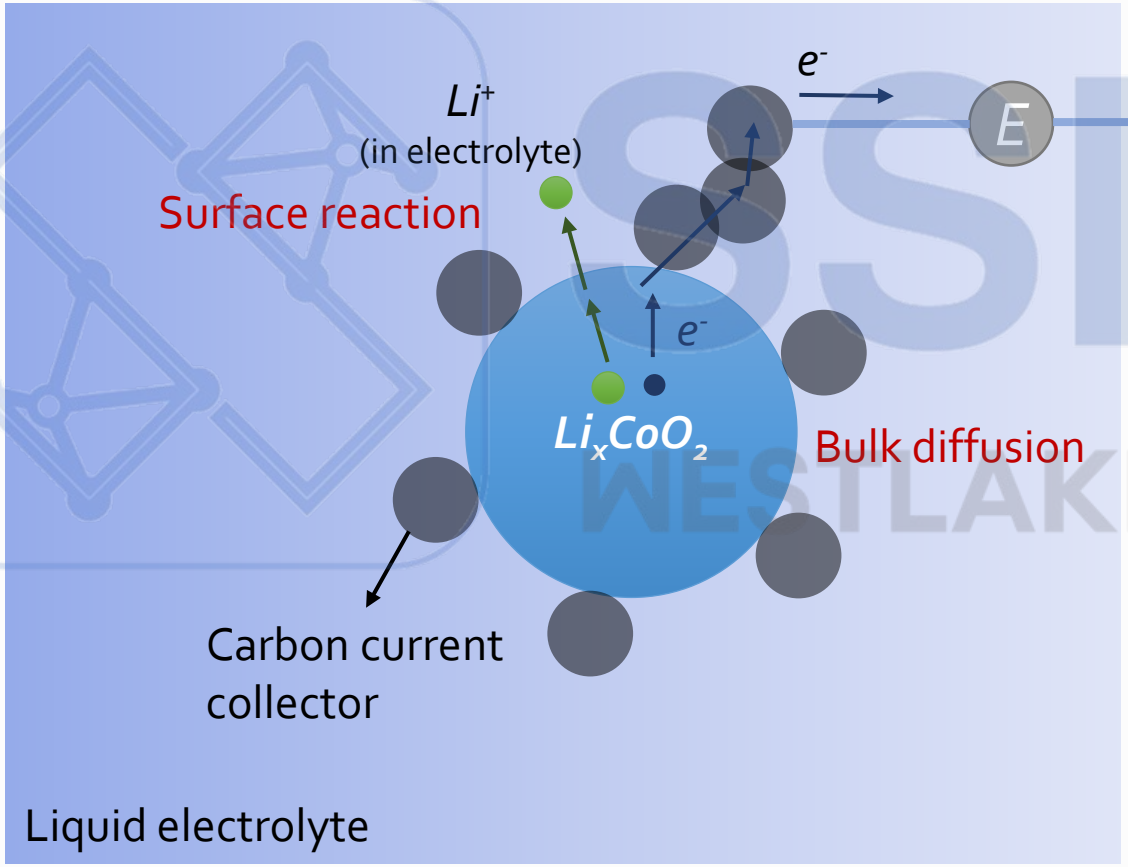


Ion motion: *drift* + *diffusion*
(similar to electrons/holes in semiconductor physics)

Diffusion & Reactions in Li-ion batteries

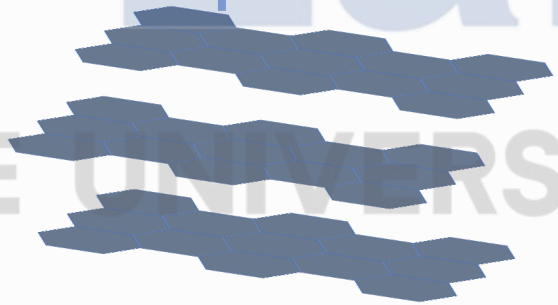
Example 1:

Mixed Li^+ ionic and *electronic* conducting oxides (*e.g.*, Li_xFePO_4)
(Electrodes for ***L***ithium-***I***on ***B***atteries)



Prof. Stan Whittingham

2019 Nobel Laureate
2009-2011 President of International Society for Solid State Ionics (ISSI)

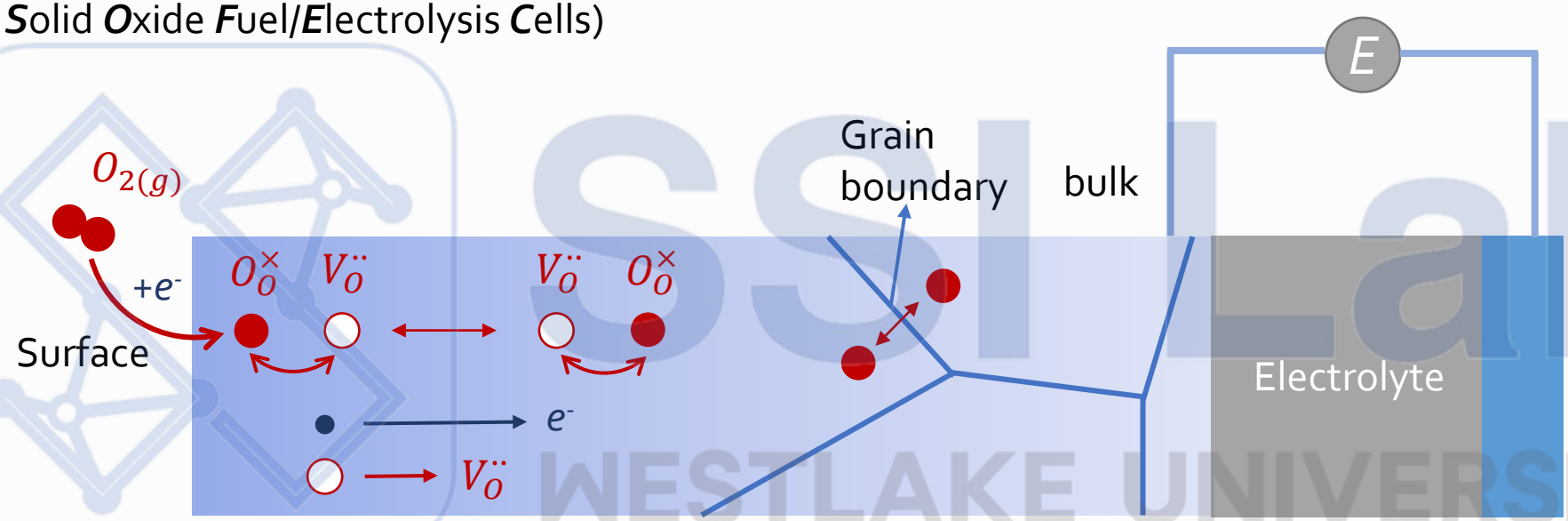


Solid-state electrochemistry

Diffusion & Reactions in Solid Oxide Cells (SOCs)

Example 2:

Mixed ionic and *electronic* conducting oxides at high temperature
(Electrodes for ***S***olid ***O***xide ***F***uel/***E***lectrolysis ***C***ells)



Surface reaction

$$j_O = -k_{surf} c_{surf}$$

Bulk diffusion

$$j_O = -D\nabla c$$

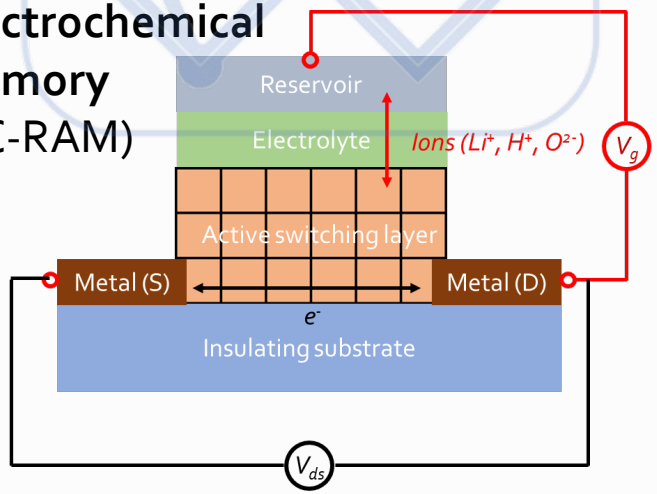
Transfer across grain boundaries

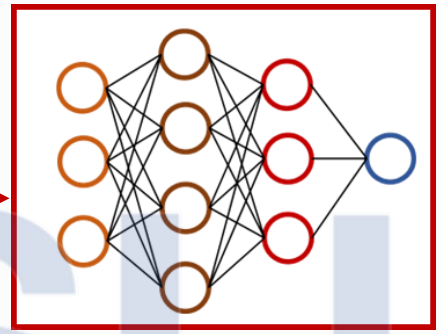
Solid-state electrochemistry

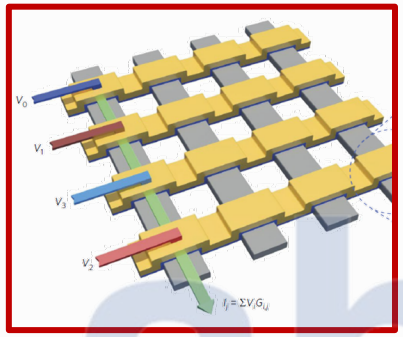
Neuromorphic computing devices for AI and IoT

Example 3: Brain-mimicking ***neuromorphic computing devices***

Electrochemical Memory (EC-RAM)



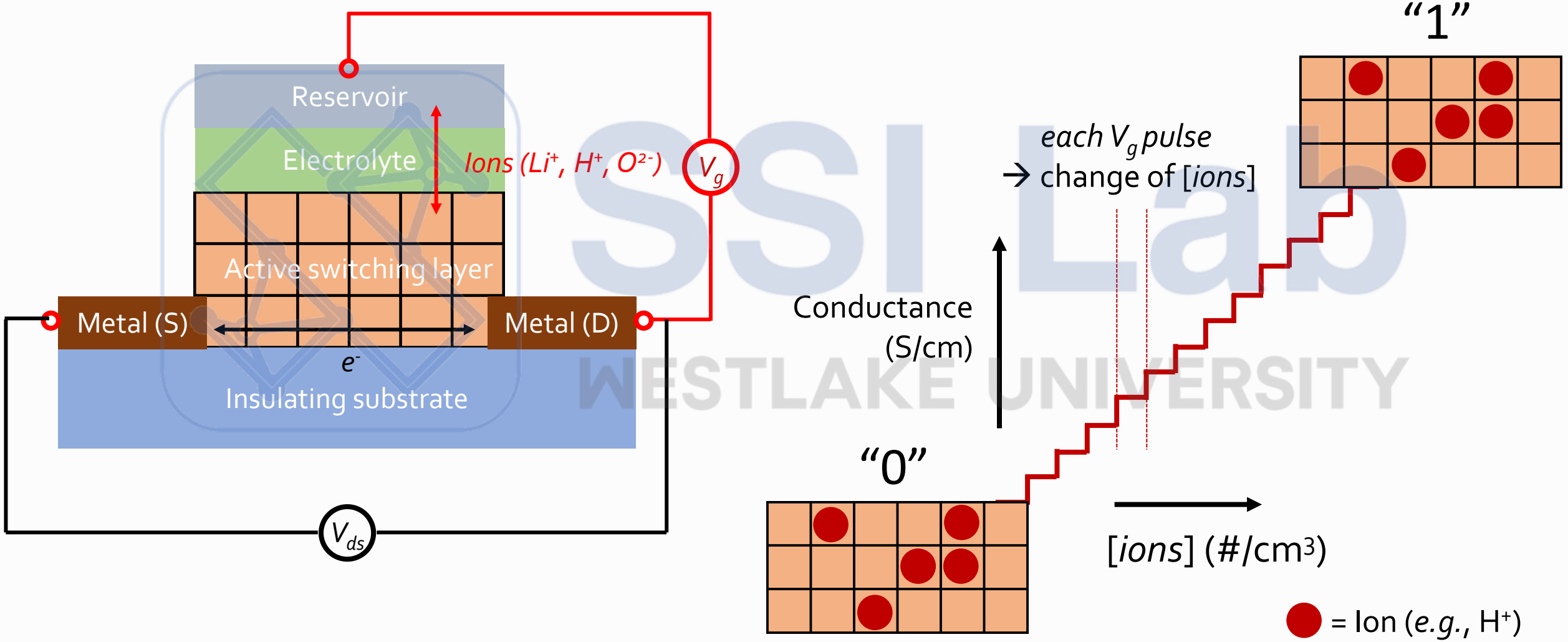




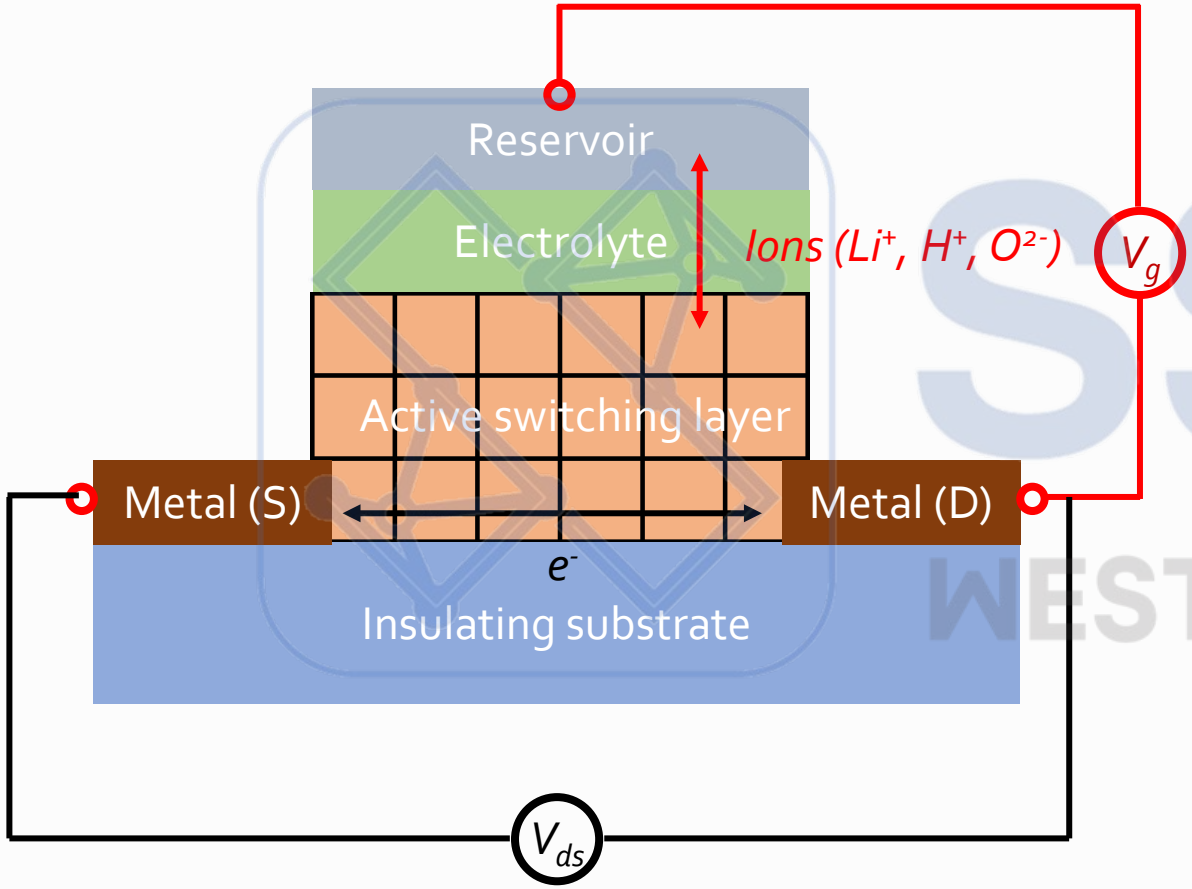
Artificial **I**ntelligence **(AI)**/**N**eural **N**etworks **(ANN)**
Requirements: Multi-state weight updating, computing in memory

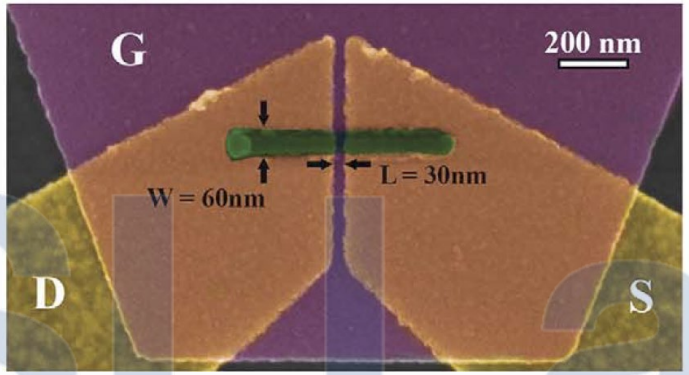
Internet **o**f **T**hings (**IoT**)/Edge Computing
Requirement: Ultra-low power consumption

Electrochemical random access memory (EC-RAM)



Electrochemical random access memory (EC-RAM)

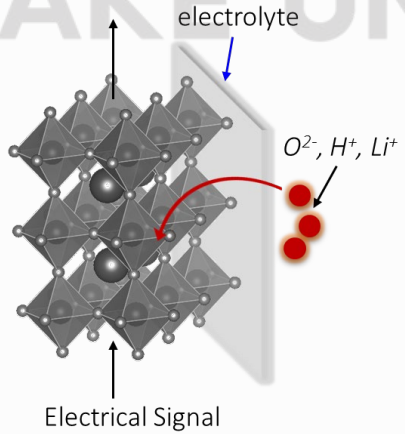




Onen, Li, Yildiz, del Alamo et al., ***Science***, 2022

EC-RAM with nano-sized layers (based on "***nanoionics***")

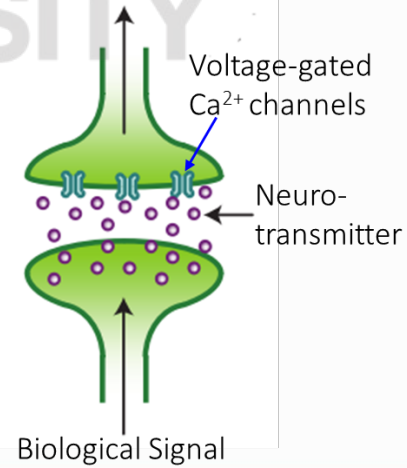
Artificial synapse



10^3 smaller

10^4 faster

Biologic synapse



Integration of ionic and electronic "organs"

"Autonomous system of functional materials"

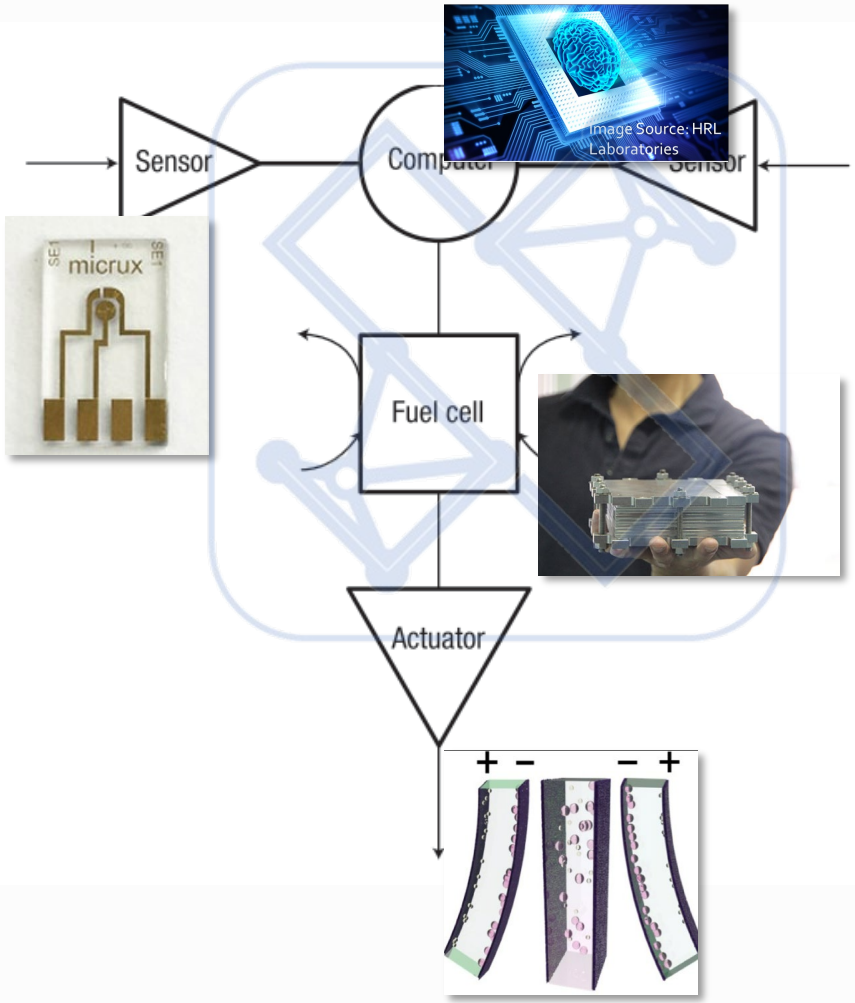


Figure 7 The nano-integration of ionic and electronic 'organs' such as sensors, actuators, computers and fuel cells or batteries results in tiny artificial autonomous systems. Reprinted from ref. 2. Copyright (2004) with permission from John Wiley & Sons Ltd.

Solid state ionics govern all these processes!

Sensors:

chemical —**Electrochemistry**→ *electrical*

Computer:

electrical —**Electrochemistry(?)**→ *electrical*

Fuel Cells:

electrical —**Electrochemistry**→ *chemical*

Actuators:

electrical —**Electrochemistry(?)**→ *mechanical*

Maier, *Nature Materials* **4**, 805–815 (2005)

What will you learn in this course on Solid State Ionics?

Goal:
By the end of the semester, you will have a clear physical picture on the ***diffusion & reactions*** related with ***ions in solid state*** and have the tools to analyze the *fundamental physical chemistry process*.

Chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = h_i - Ts_i$$

Electrochemical potential

$$\tilde{\mu}_i = \mu_i^0 + RT\ln a_i + z_i F\phi$$

→ *Electrostatic potential*

- We will learn the definition of different *potentials;*
- More importantly, we will learn how these potentials determine the behaviors of *ions* and *electrons*.

Boettcher et al., ACS Energy Lett. 2021, 6, 261−266

Course content organized around the concept of potentials

Defect chemical equilibrium

Brouwer diagram:

[def] ~ lna_i

i = charge neutral species (*e.g.*, O2, Li)

Space charge layers (SCLs)

$$\phi\,(x_1) \neq \phi\,(x_2)$$

$$a_i\,(x_1) \neq a_i\,(x_2)$$

- Gouy-Chapman case
- Mott-Schottky case

"frozen" defects

$$\frac{\partial \tilde{\mu}_i}{\partial x} = 0$$

Solid State Ionics:

Transport and *Reaction* of *Ionic defects*

$$\frac{\partial \tilde{\mu}_i}{\partial x} \neq 0$$

$$\tilde{\mu}_i = \mu_i^0 + RTlna_i + z_iF\phi$$

Ionic defect transport

- Diffusion: $\nabla\mu \neq 0$ ($\nabla c \neq 0$)
- Drift: $\nabla\phi \neq 0$
- Coupled drift-diffusion:

$$J_i = -\frac{\sigma_i}{z^2F^2}\nabla\tilde{\mu}_i$$

Concerted ion-electron transport

Chemical diffusivity:

$$D_O^\delta = \frac{RT}{4F^2}\frac{\sigma_O^\delta}{c_O^\delta}$$

Solid-state electrochemistry

- OCP: $E = (\tilde{\mu}_{e',a} - \tilde{\mu}_{e',c})/\mathrm{F}$
- Kinetics: Butler-Volmer *eqn.* Marcus(-Hush-Chidsey)

What will you learn in this course on Solid State Ionics?

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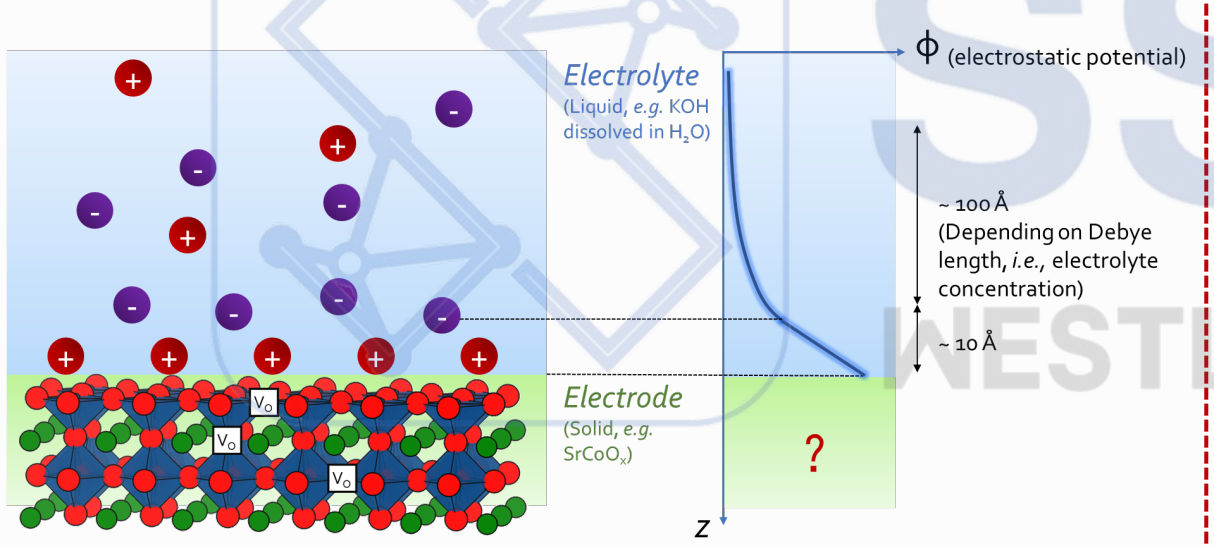
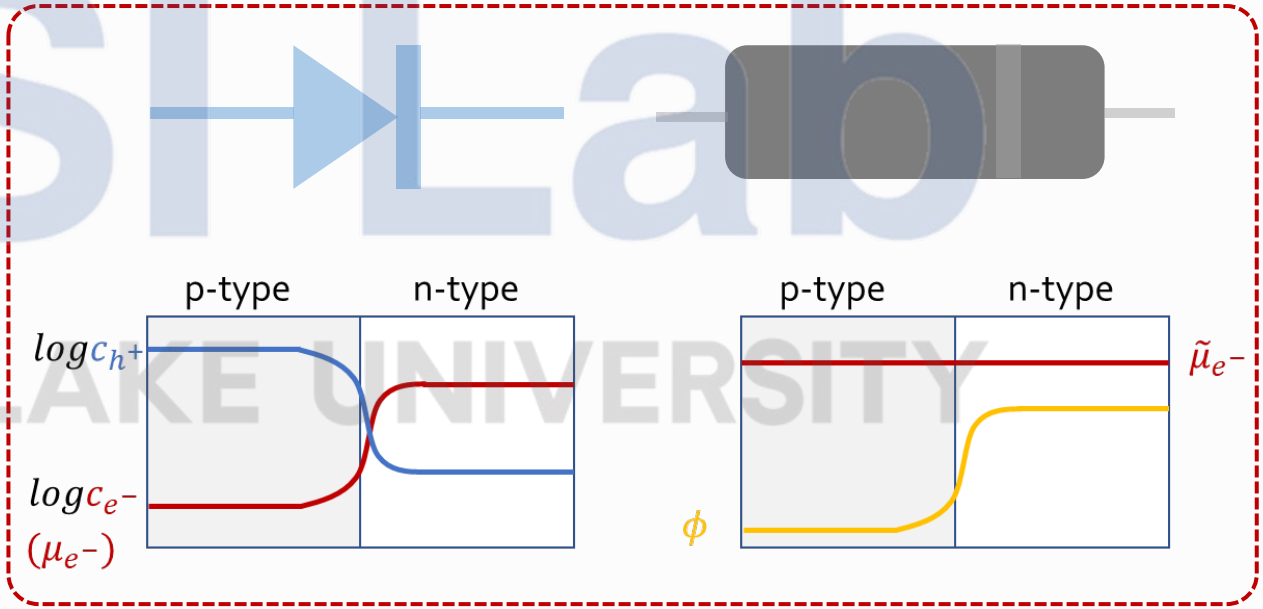


Electric double layers (EDLs)



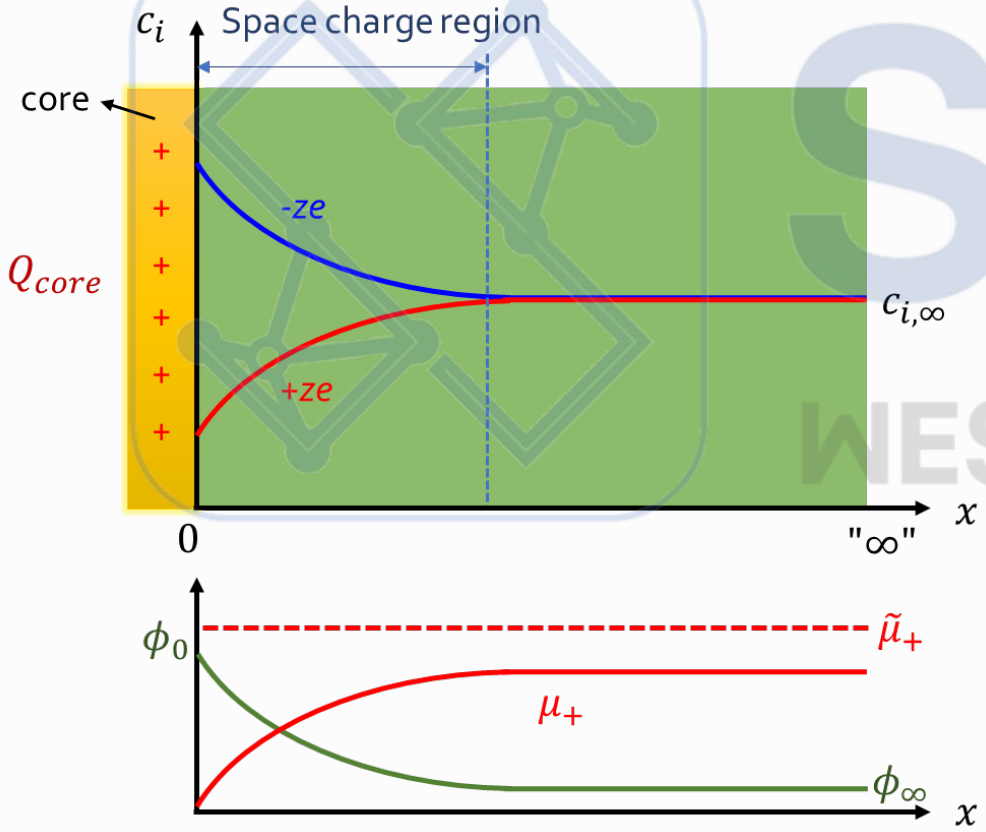
p-n junctions (diodes)

Is there any similarities between EDLs and p-n junctions?

Space charge layers

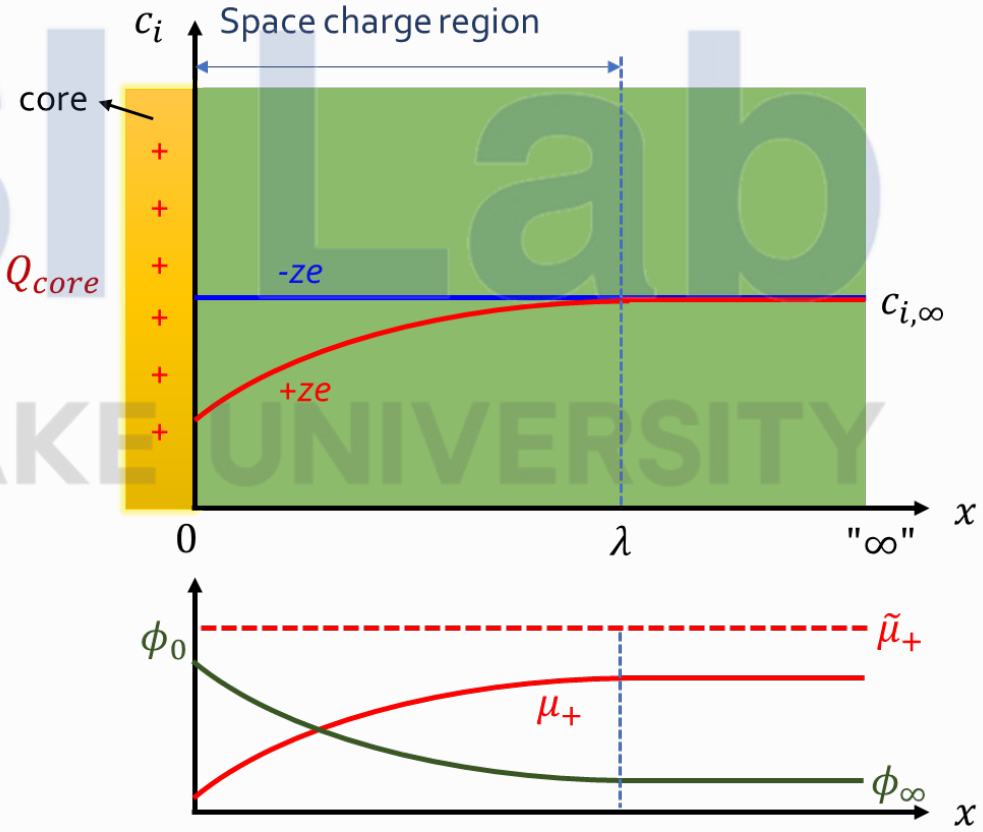
Electric double layers (EDLs)

Gouy-Chapman case



p-n junctions (diodes)

Mott-Schottky case



What we will **NOT** discuss in the course

This is a *Materials Science* course, but not a *materials-specific* course.

Which means that we will NOT discuss any specific materials problems, for example:

- We will discuss how to ***predict*** the open-circuit voltages of batteries, and what happens if the electrode goes through phase transitions.
- We will **NOT** discuss the pros and cons of *each cathode materials* (NMC, LFP, *etc.*).

- We will discuss how to ***understand*** the Butler-Volmer equations, the principles of EIS, *etc.*
- We will **NOT** discuss the *experimental details* for evaluating the performance of electrocatalysts.

Goal:
By the end of the semester, you will have a clear physical picture on the ***diffusion & reactions*** related with ***ions in solid state*** and have the tools to analyze the *fundamental physical chemistry process*.

Course content: week 1-8

Week	Topic
1	Introduction to Solid State Ionics; Review of fundamental thermodynamics;
2	Electronic and ionic point defects; Thermodynamics of point defect formation;
3	Defect reactions; Doping and surface exchange reactions;
4	Brouwer diagram; Simultaneous defect reactions;
5	Migration of point defects;
6	Drift and diffusion of point defects;
7	Chemical (ambipolar) diffusion;
8	Mid-term Exam

Key research directions of Solid State Ionics

- physics and chemistry of **defects** in solids;
- **reactions** in and on solids, *e.g.* intercalation, corrosion, oxidation, sintering;
- **ion transport** measurements, mechanisms and theory;
- solid state **electrochemistry**;
- ionically-electronically mixed **conducting solids**.

Course content: week 9-16

Week	Topic
9	Blocking electrodes and Concentration Polarization;
10	Higher-dimensional defects; Space charge layers; Size effects;
11	Introduction to solid-state electrochemistry; Electrochemical potential;
12	Open-circuit potential; Cell under current loading;
13	Electrocatalysis I: Butler-Volmer equation;
14	Electrocatalysis II: Charge transfer; Marcus Theory; Quantum effects;
15	Chemo-mechanical coupling in crystalline solids;
16	Review and closing remarks;

Key research directions of Solid State Ionics

- physics and chemistry of **defects** in solids;
- **reactions** in and on solids, *e.g.* intercalation, corrosion, oxidation, sintering;
- **ion transport** measurements, mechanisms and theory;
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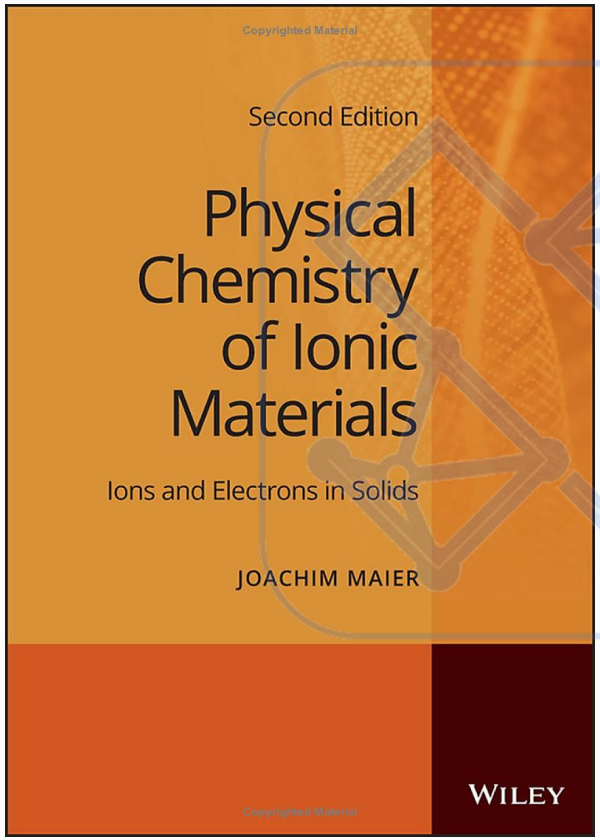
Reference books for Solid State Ionics

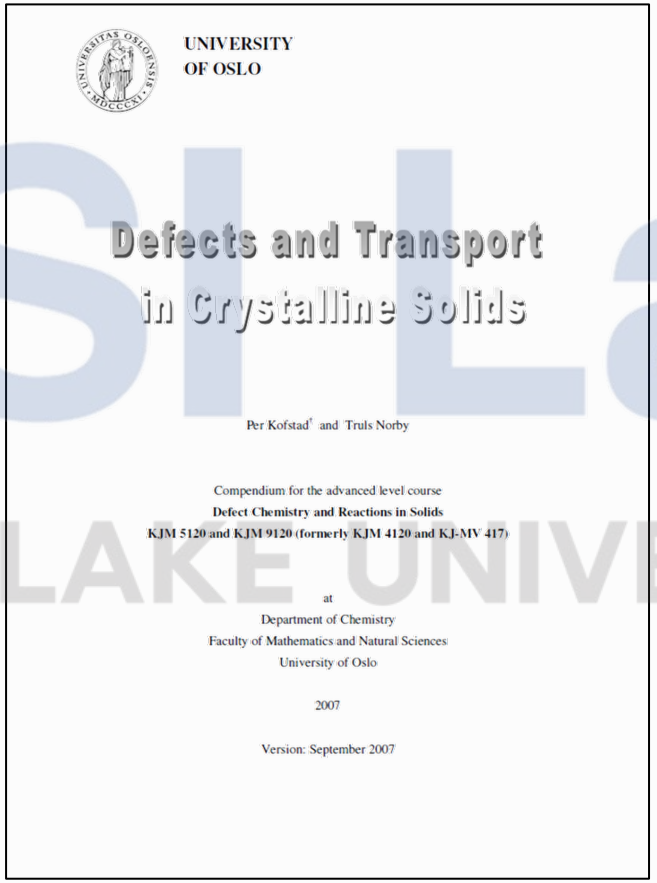


Phys. Chem. of Ionic Materials by J. Maier (MPI)

Pros: The ***bible*** in Solid State Ionics; exceptionally deep and thorough

Cons: Difficult to read (translated from German); takes one a lot of time to understand the mess of notations

2nd edition (2022)



Defects and Transport in Crystalline Solids by Per Kofstad and Truls Norby (U of Oslo)

Pros: Easy to follow; Concise but contains almost all the important topics

Cons: It is written as lecture notes (not a published book).

Learning resources (some in Chinese, yeah:)!)

https://ssi-westlake.com/teaching/

Teaching

Tutorial Articles (in Chinese, **微信公众号文章**)

固态离子学教程系列文章（*WESTON OpenCourse* of Solid State Ionics）

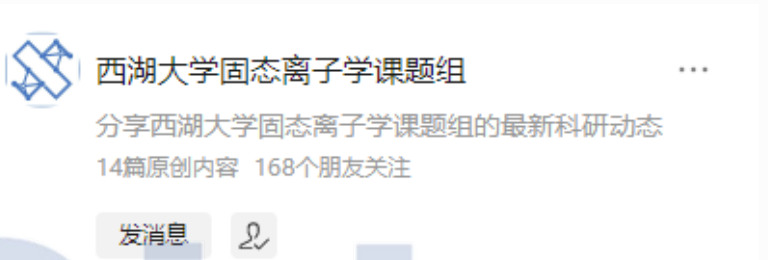
第一章：**固态离子学导论**
第二章：**点缺陷和Brouwer图**
第三章：**离子输运的宏观图像与电化学势**
第四章：**离子输运的微观图像**
第五章：**扩散系数的类型及化学扩散**

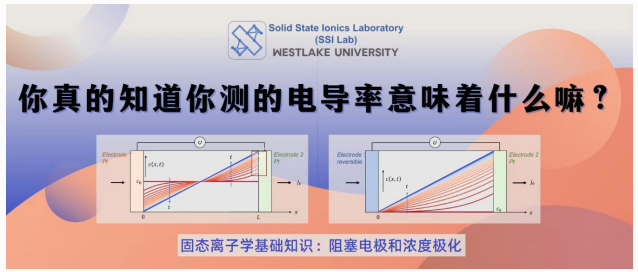
其他文章：

1. **为什么部分3d过渡金属2p XPS分析结果可能是错的？**—论3d过渡金属氧化物的X射线光电子能谱谱图
2. **你真的知道你测到的电导率意味着什么吗？**—固态离子学基础知识：阻塞电极和浓度极化

***Fall 2022* Solid State Ionics** (MSE 5007, Westlake University)

Course description: This course serves as a comprehensive introduction to the fundamental knowledge and methodology in the field of solid state ionics. Solid state ionic materials have wide applications in energy conversion and storage, catalysis, sensing, as well as neuromorphic





Slides from the same course last year
(updated slides this year will be posted on Canvas)

Grading and course policies

Grading Policies:

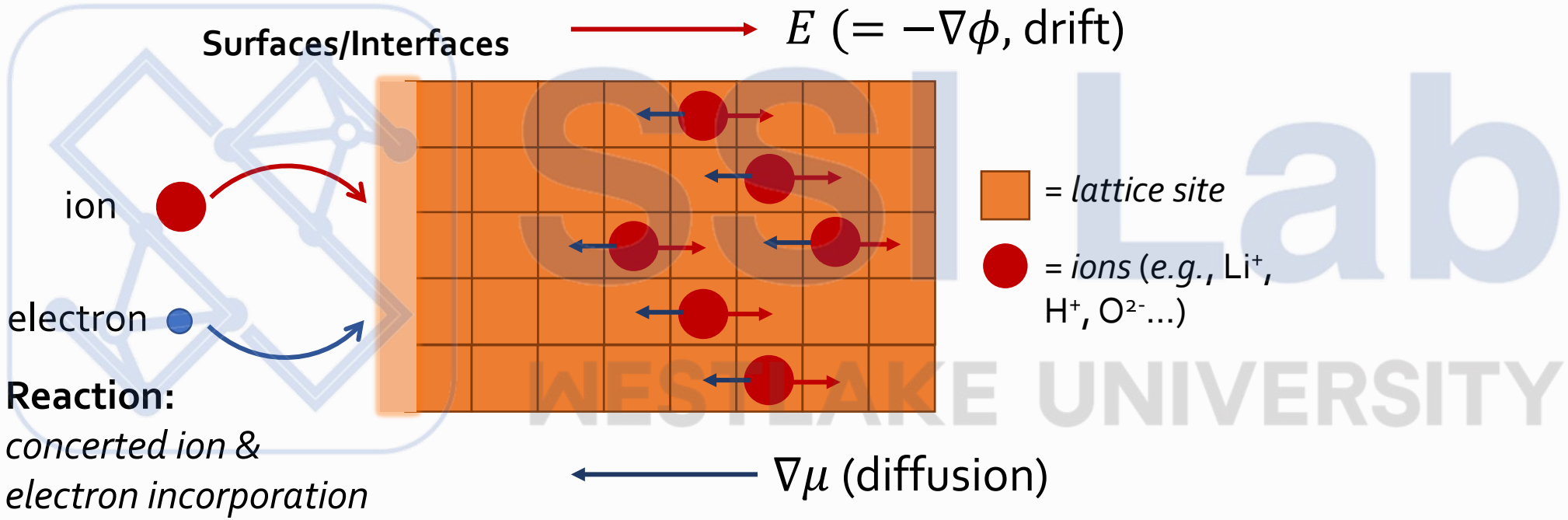
- *Attendance and participation: 15%.* Please attend each lecture **ON TIME**.
- *Homework: 30%.* There will be 3-4 problem sets during this Fall semester. Each problem sets will contain 2-4 problems. Deadline for each problem set will be announced with the homework.
- *Exams: 25% (mid-term exam) + 30% (final exam).* Students will be allowed to ***carry an A4-sized paper as a "cheat sheet"*** during the exams.

Course Policies:

- *Scholarly Honesty Statement*: any plagiarizing or cheating on assignments and/or examinations will be reported to the university.
- *Late homework/Make-up exam policy*: Late homework and make-up exams will only be allowed under very special circumstances. Please contact me and ask for my permission.

Why do graduate students take graduate-level courses?

Let's come back to this picture… but with a twist



Ion motion: *drift* + *diffusion*
(similar to electrons/holes in semiconductor physics)

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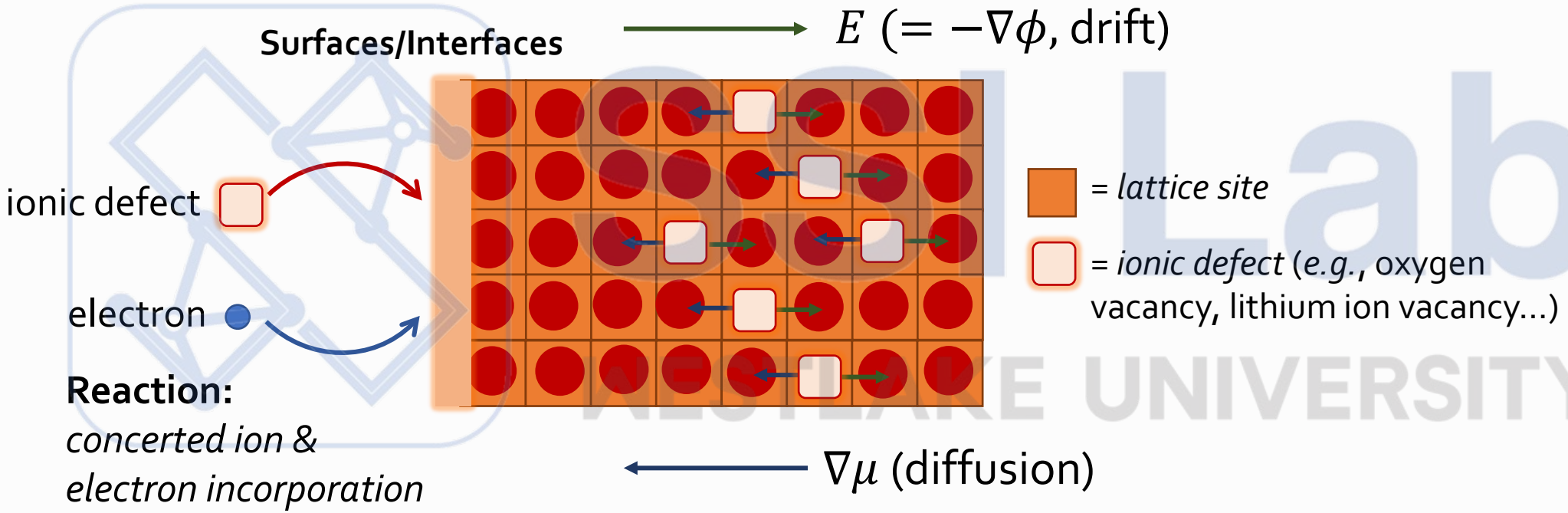
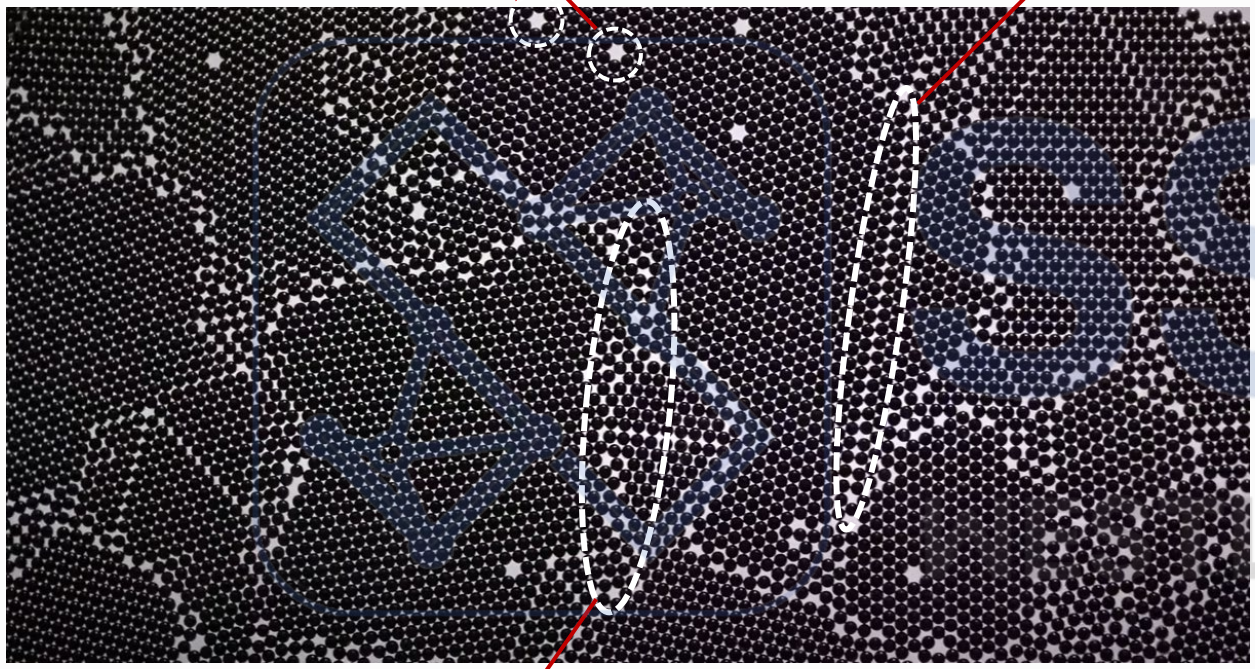
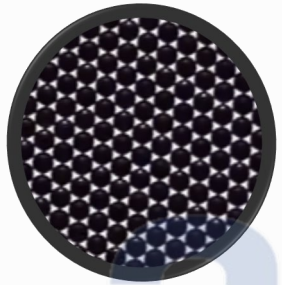


Ion motion: *drift* + *diffusion*
(similar to electrons/holes in semiconductor physics)

The study of defects: core of materials science



What physicists care  *Perfect crystal*

What chemists care  *Single "molecule"*

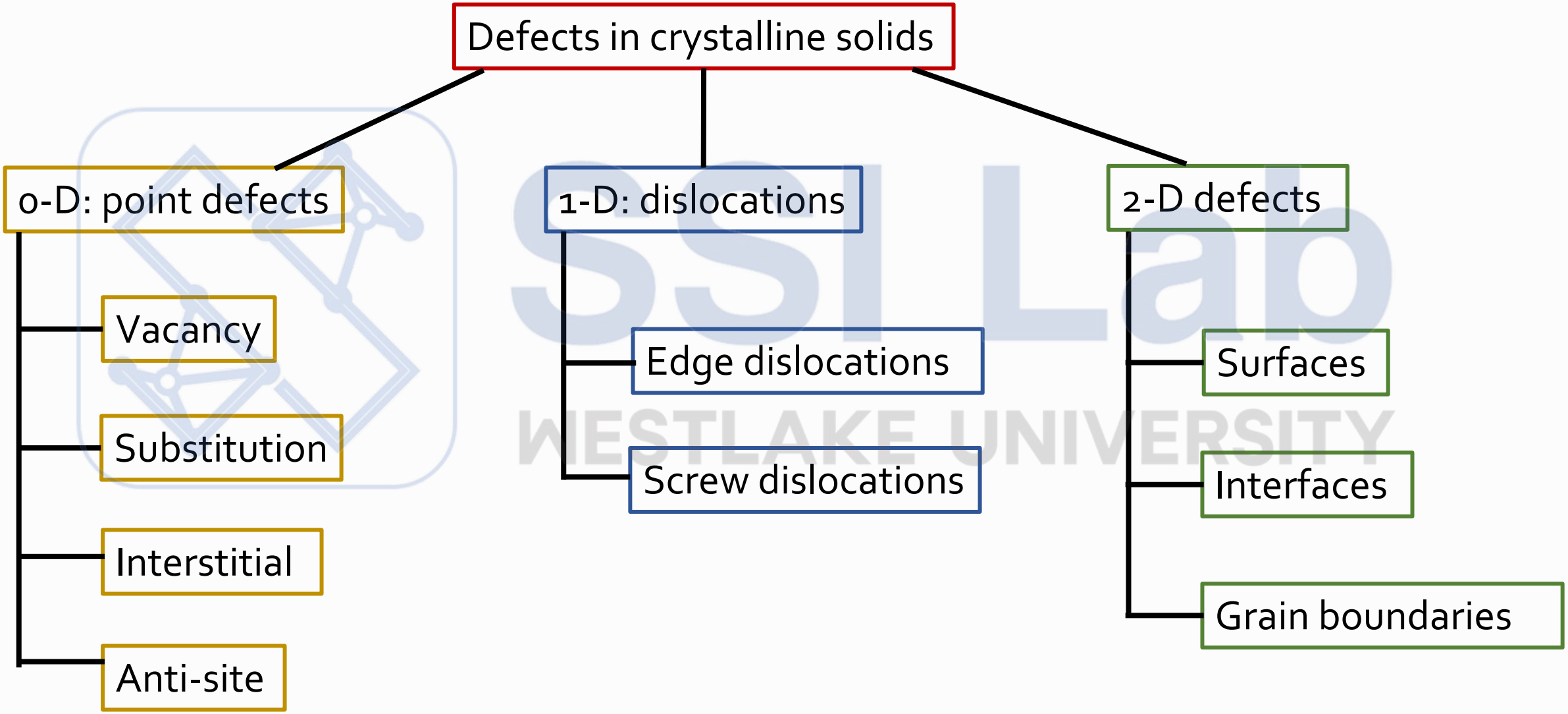
Only the materials scientists dare to tackle the questions related to ***imperfect crystals with defects***!

"Crystals are like people: it is the defects that make them interesting!"

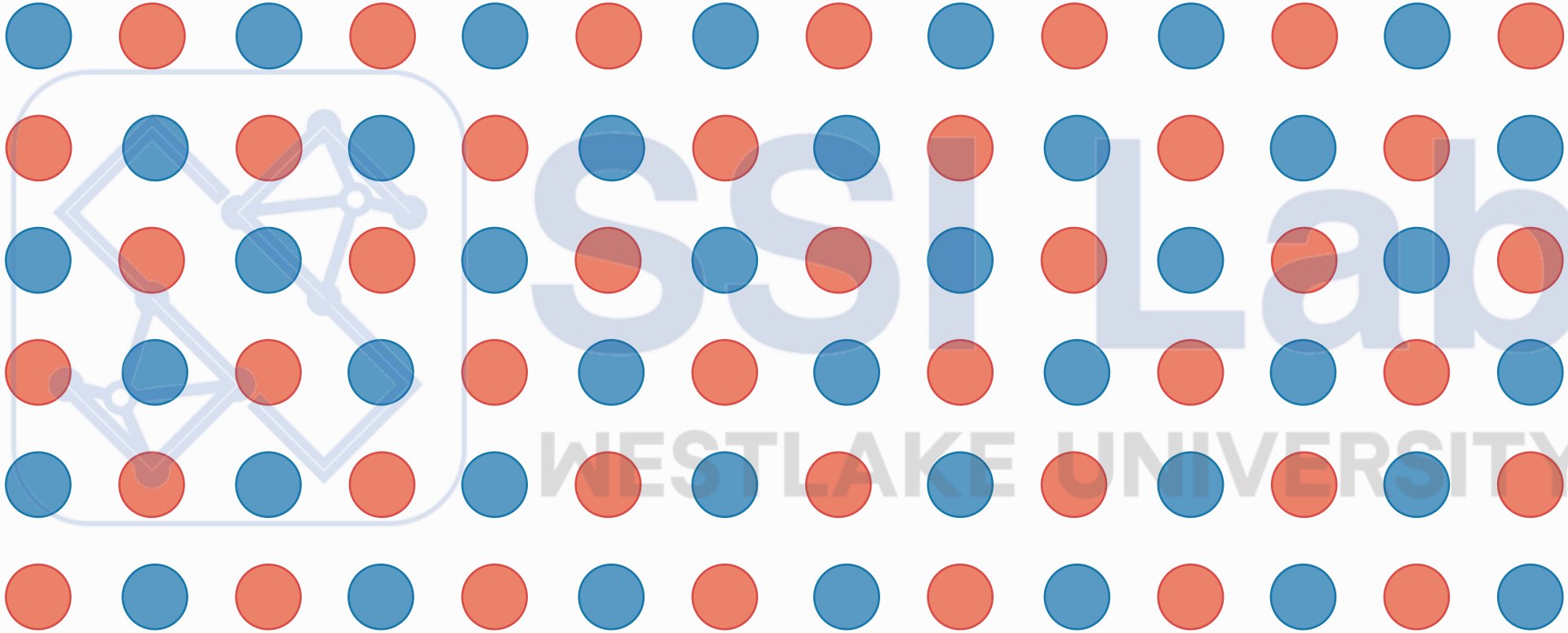
-Sir Colin Humphreys

(Goldsmiths' Professor of Materials Science, University of Cambridge)

Categories of defects with different dimensions



The Perfect (Ionic) Crystalline Solid

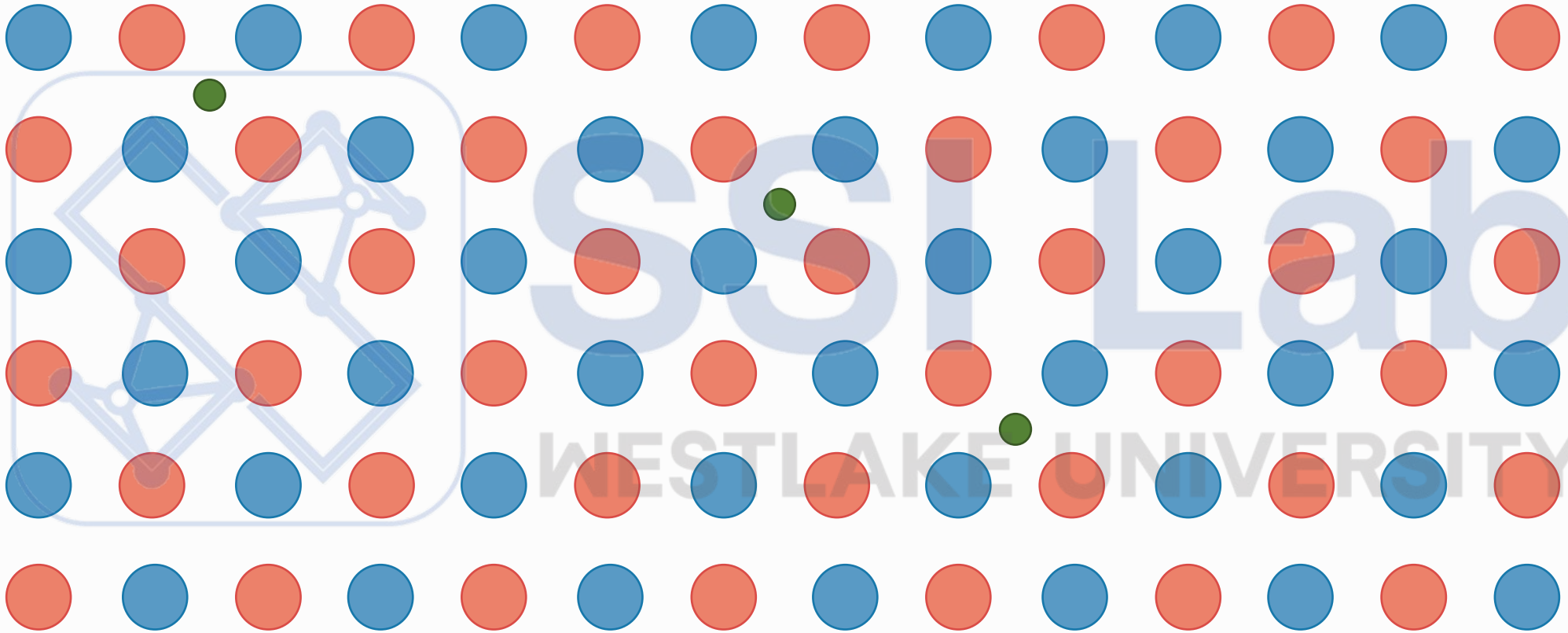


Cation (*e.g.* Na^+)

Anion (*e.g.* Cl^-)

Note: we limit our discussions to ionic compound and in most cases semiconductors/insulators

The Real (Ionic) Crystalline Solid

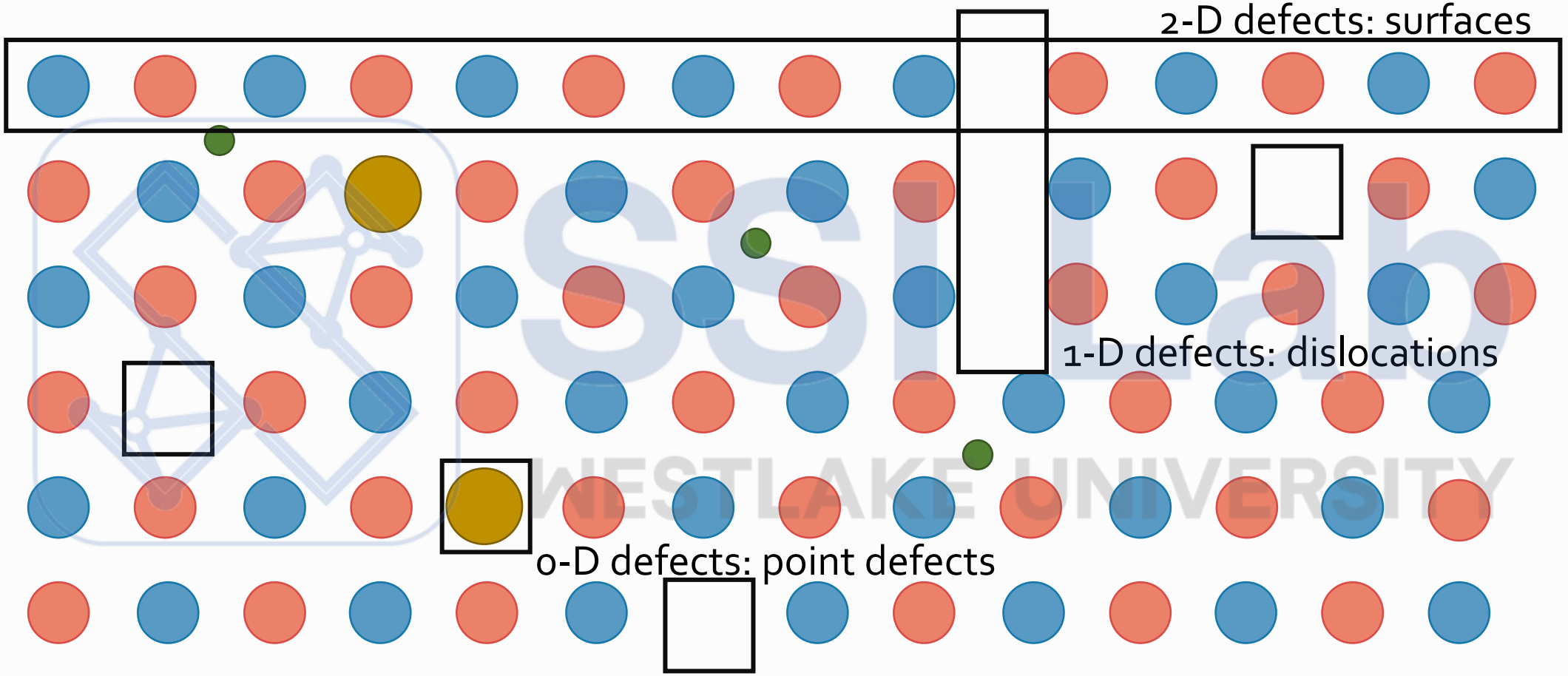


Cation (*e.g.* Na^+)

Anion (*e.g.* Cl^-)

Point (oD) defect

The Real (Ionic) Crystalline Solid

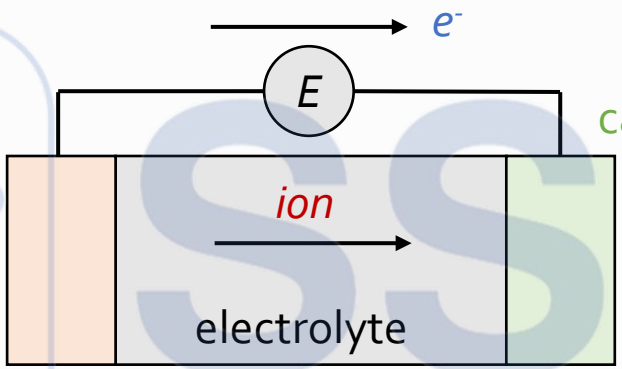


Cation (*e.g.* Na^+)

Anion (*e.g.* Cl^-)

Fundamentals of Electrochemical Energy Systems

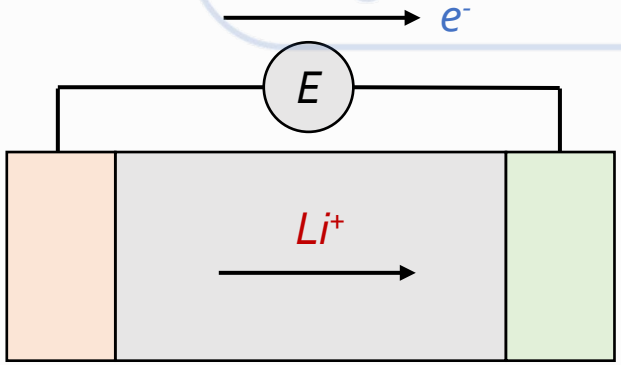
Electrochemical energy systems are based on **concerted motion (transport) of ions + electrons**



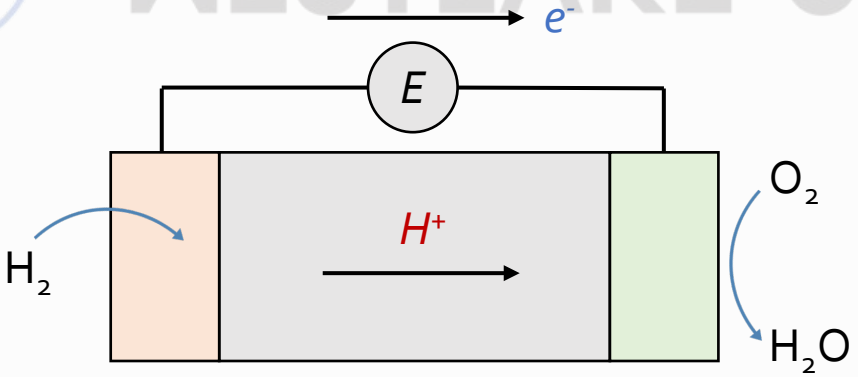
cathode: where ***conventional*** current leaves *reduction* reaction

anode: where ***conventional*** current enters *oxidation* reaction

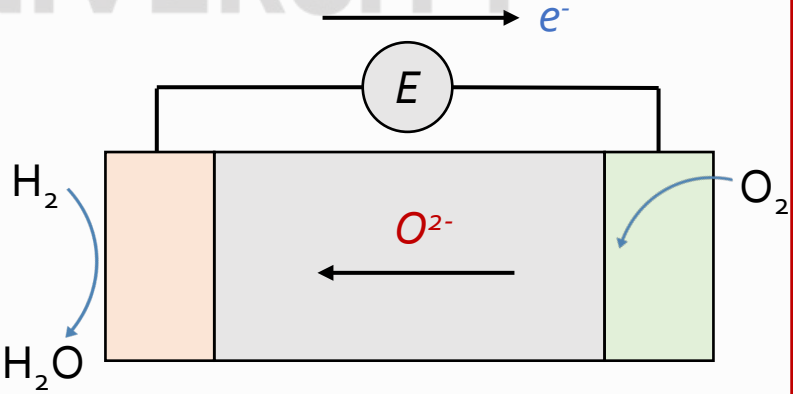
Lithium-ion battery



Proton-**E**xchange **M**embrane **F**uel **C**ell (**PEMFC**)

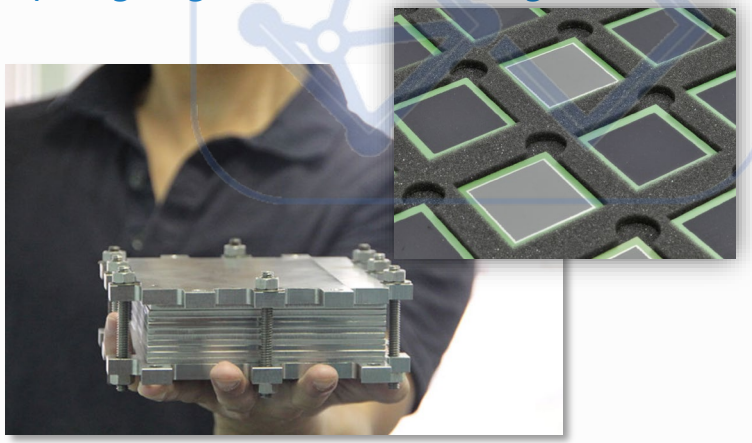


Solid **O**xide **F**uel **C**ell(**SOFC**)

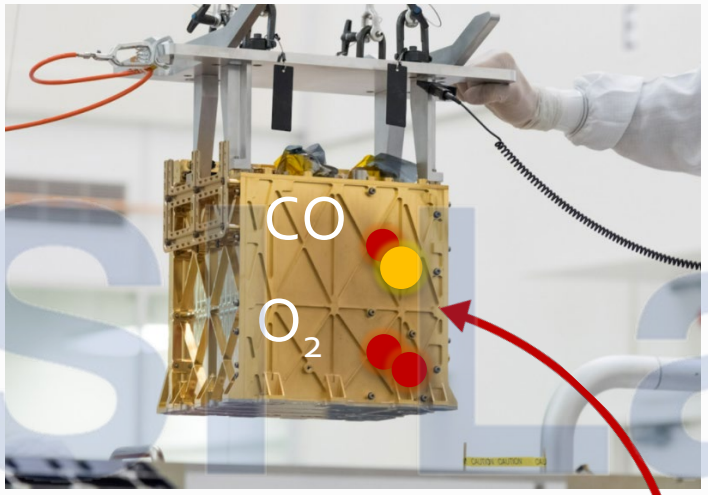


Solid Oxide Fuel/Electrolysis Cells (SOFC/SOECs)

Grand Challenge
Carbon neutrality by 2060 calls for close-loop hydrogen generation and usage



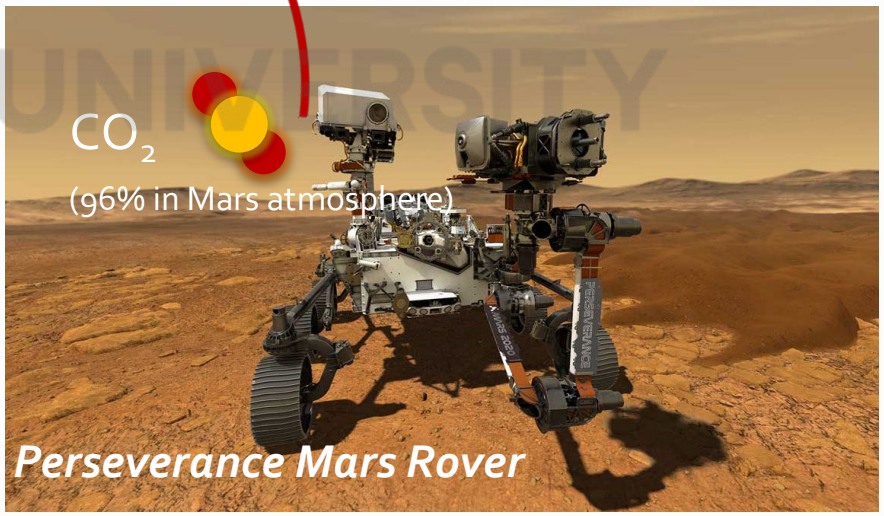
Solution
High-performance ***reversible***
solid oxide fuel/electrolysis cells (SOFC/SOECs)



MOXIE unit on
Perseverance
Mars rover

CO_2 + Renewable Energy

Chemical fuels
(*e.g.*, methane CH_4, methanol CH_3OH)



Solid Oxide Fuel/Electrolysis Cells (SOFC/SOECs)

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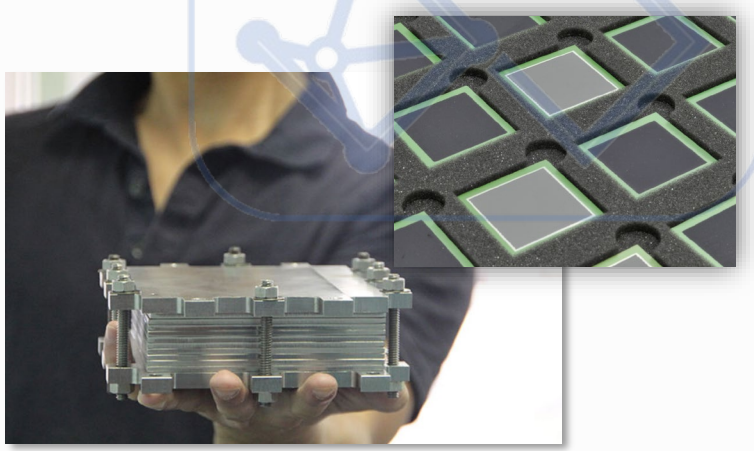

Solution
High-performance ***reversible***
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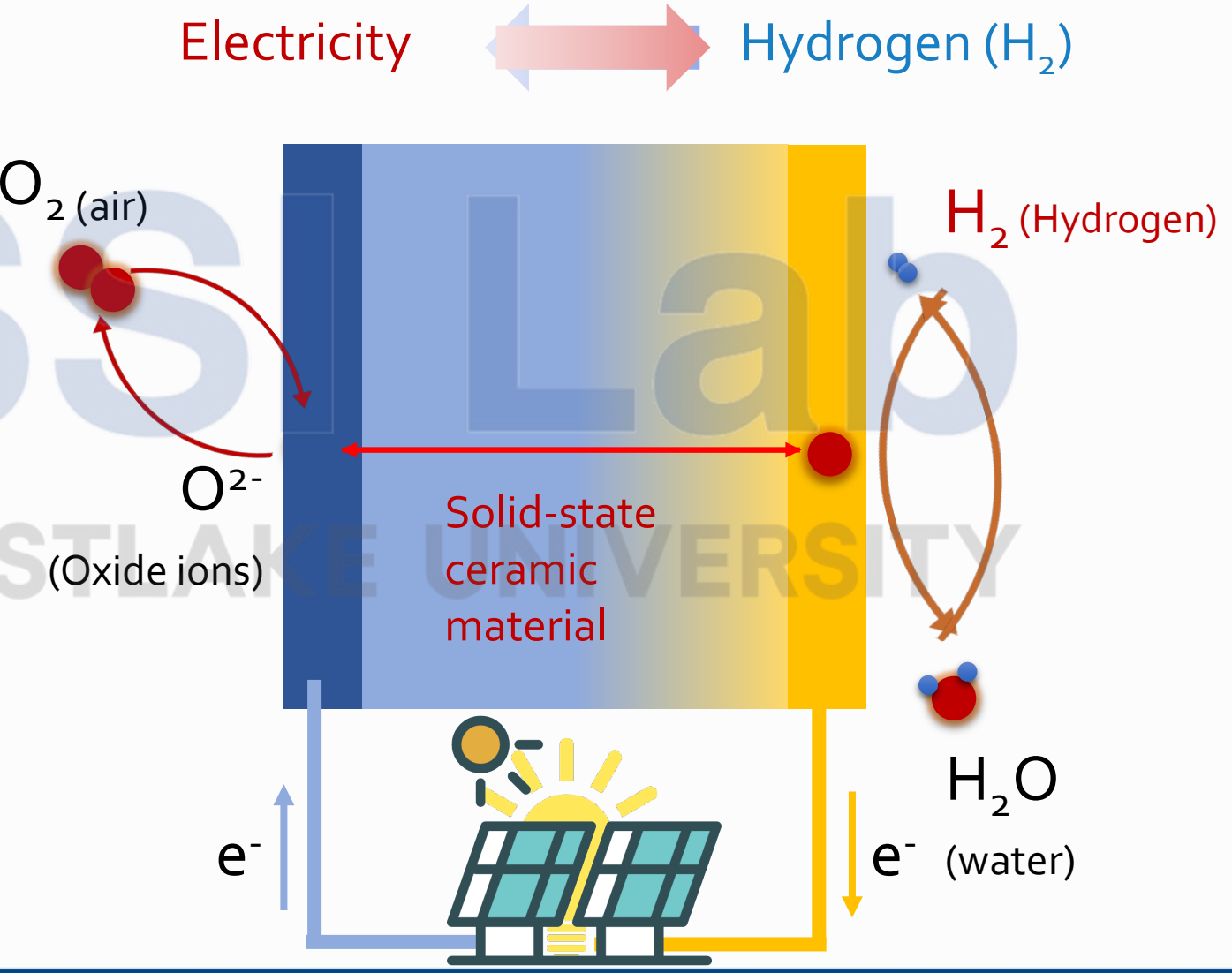
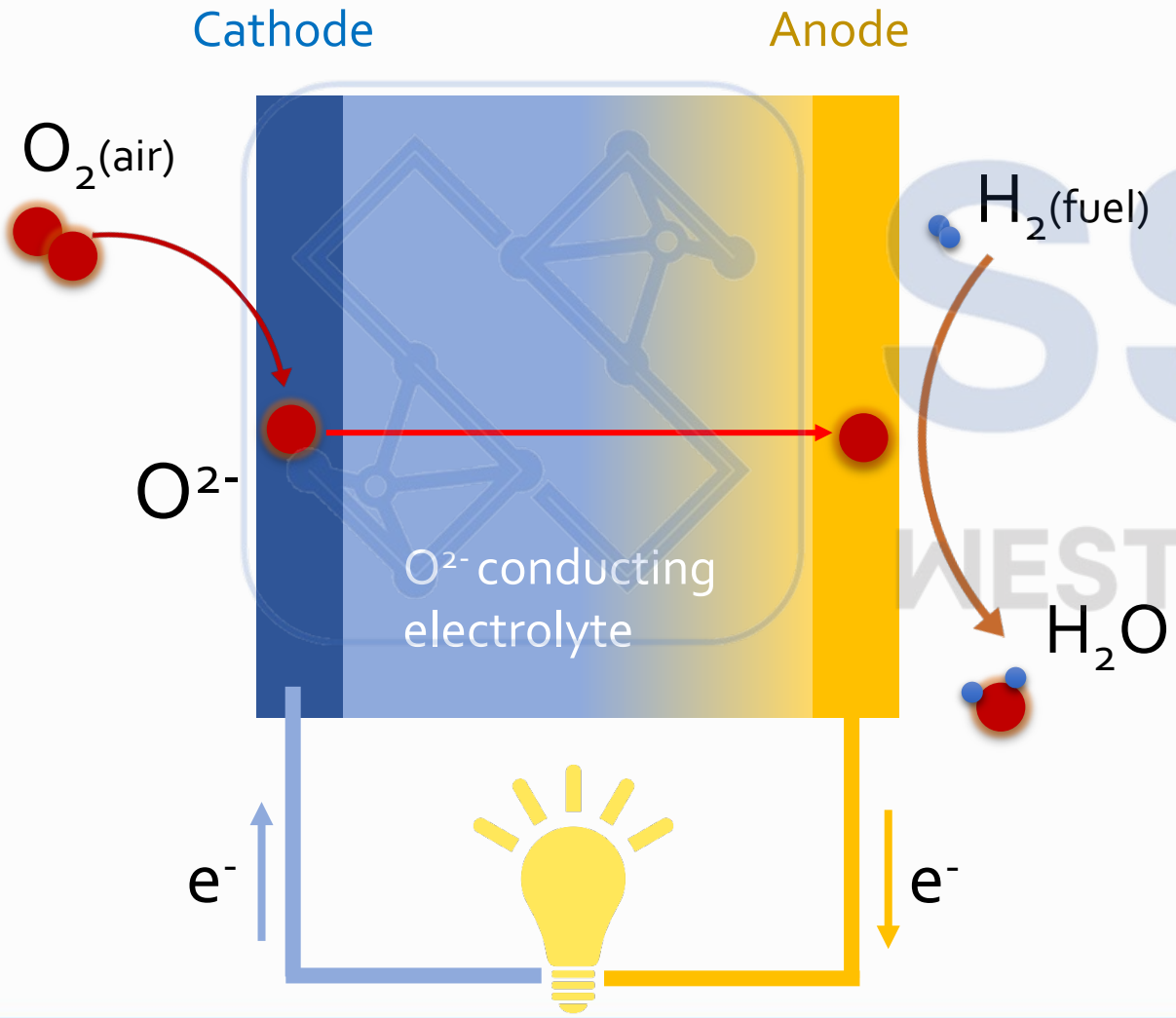
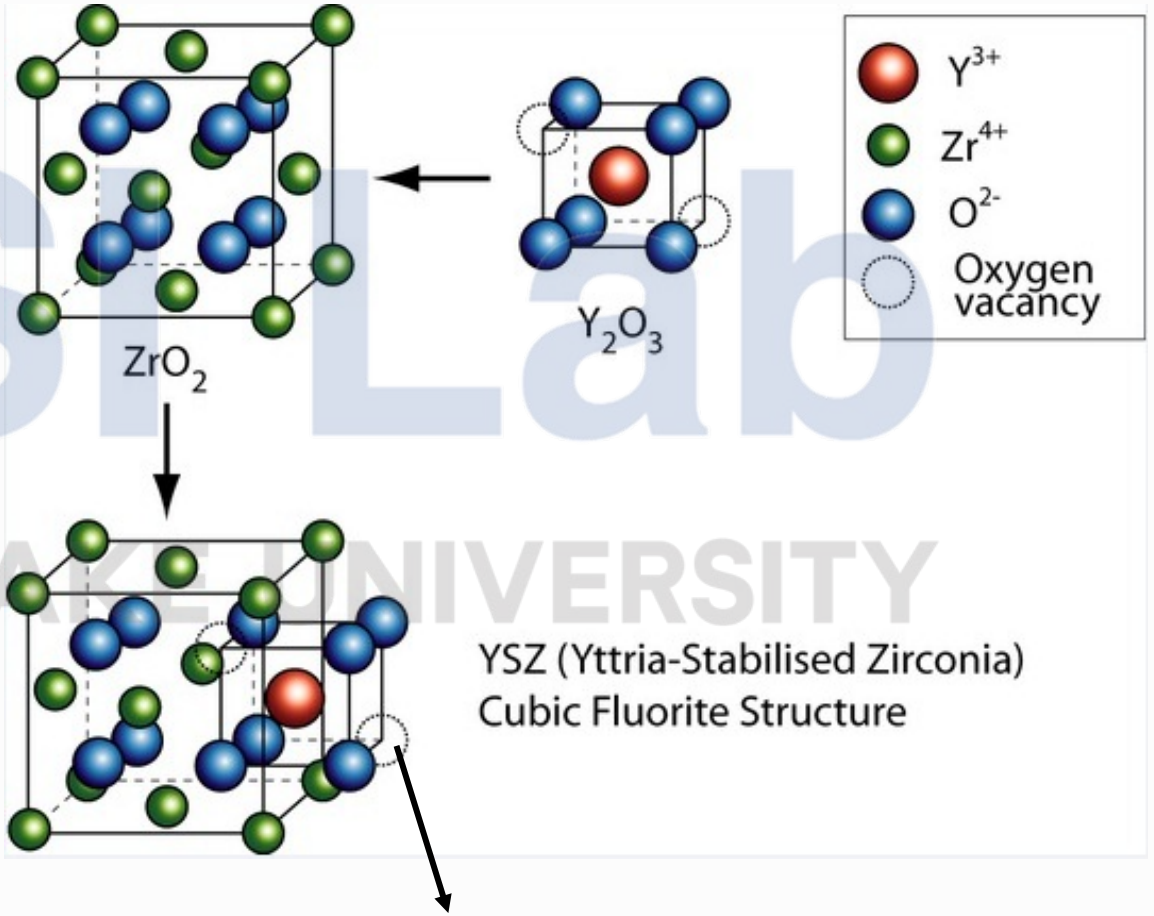


The operation of SOCs relies on ionic point defects

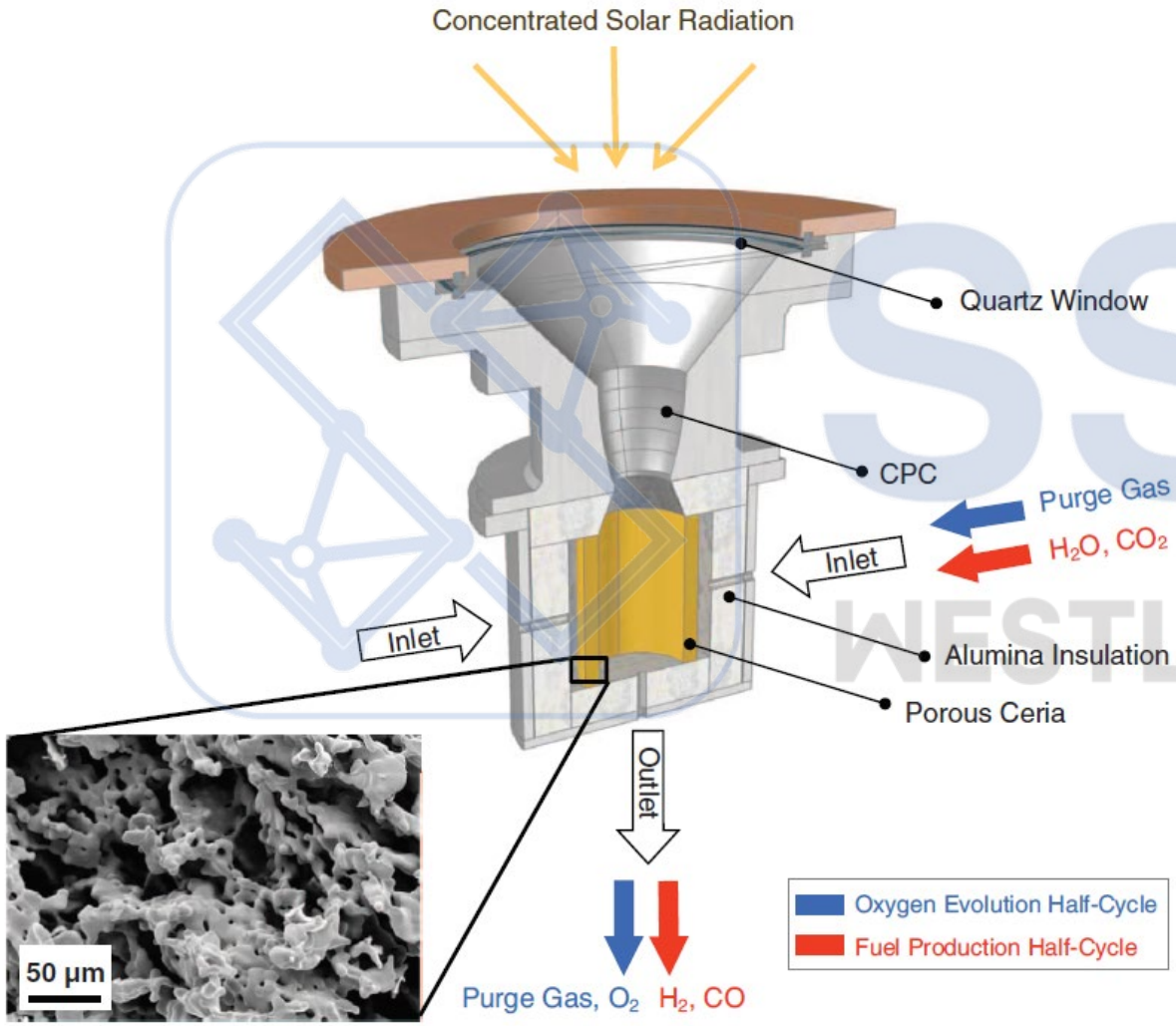


Y_2O_3-stablized ZrO_2 (YSZ) as electrolyte

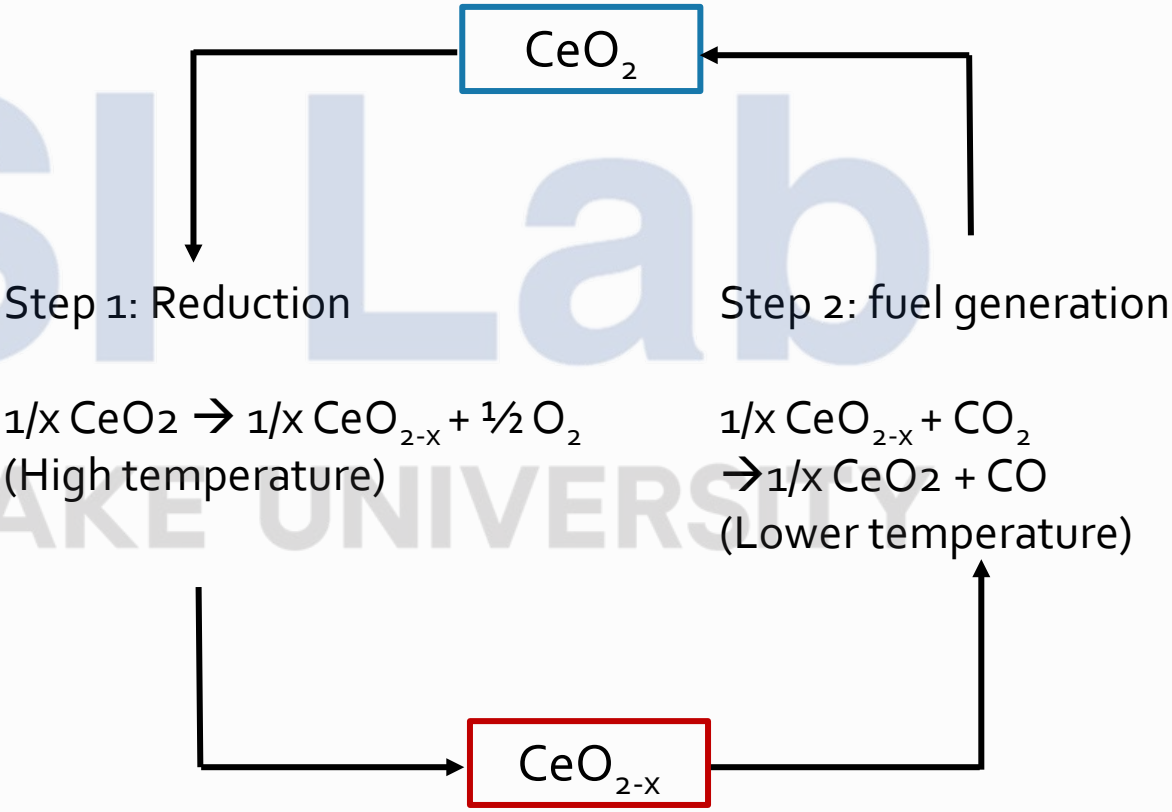


Oxygen vacancies: allow oxygen to migrate through the electrolyte

Another example: thermo-chemical cycle for fuel production (water splitting and/or CO_2 decomposition)

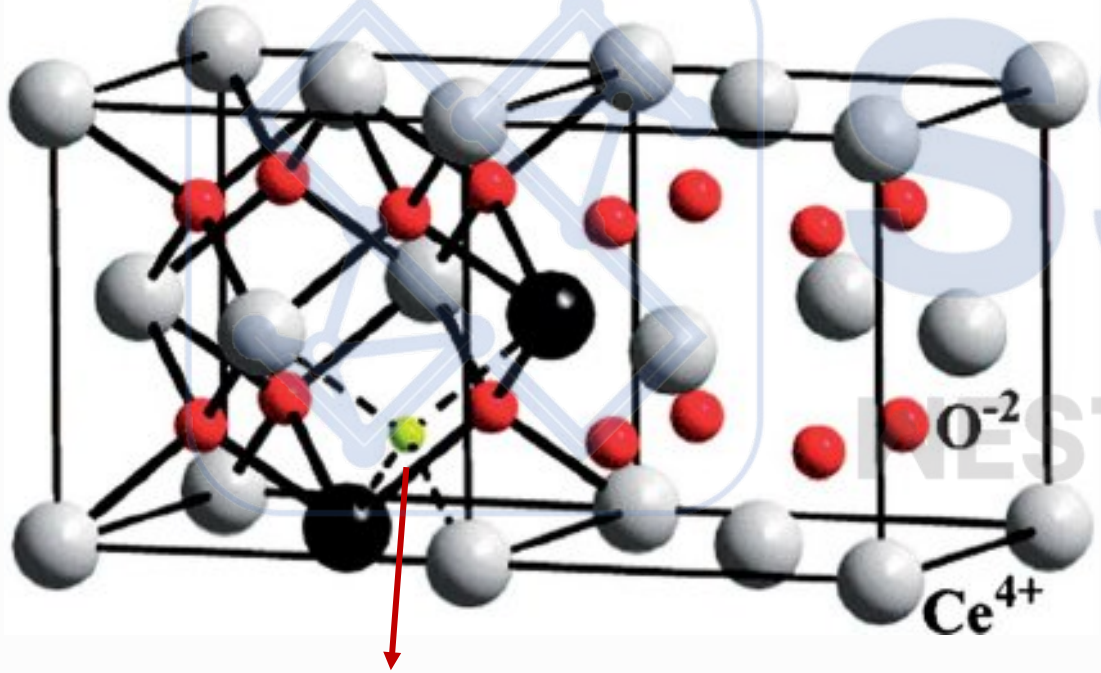


Chueh *et al.*, Science, 2010

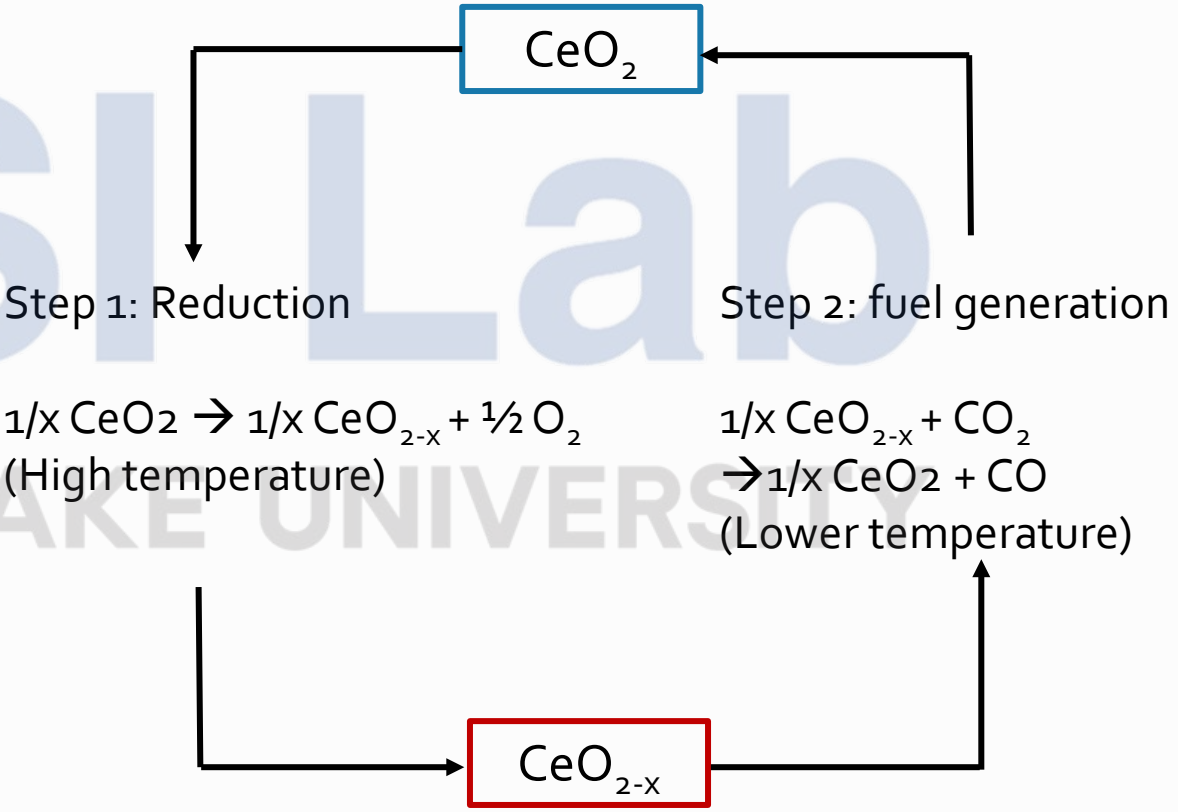


Thermo-chemical cycle for fuel production (water splitting and/or CO_2 decomposition): the role of point defects

Ceria: "breathable" material



Oxygen vacancies: allow exchange of oxygen with surrounding gas environment



Vacancy and Interstitial Defect

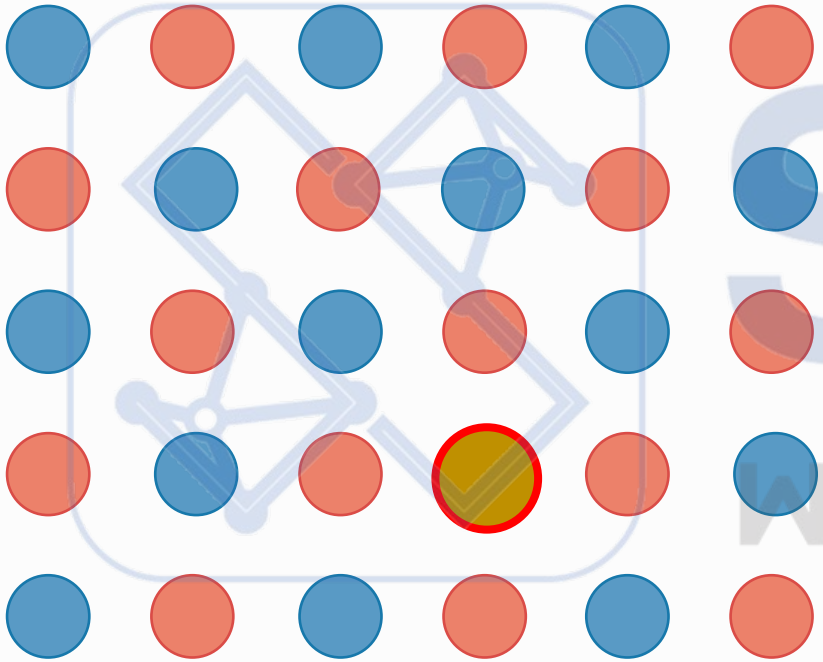
Cation Vacancy
Anion Vacancy

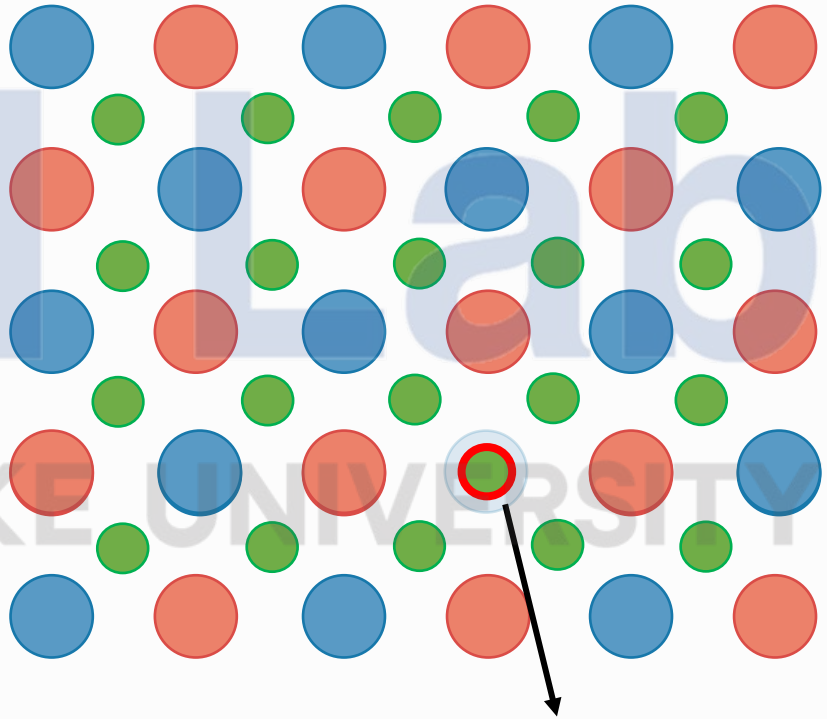
Cation
(e.g. Na^+)

Anion
(e.g. Cl^-)

Cation Interstitial
Anion Interstitial

Substitutional and anti-site defects





Substitutional defect
(*i.e.* impurities)

Cation
(e.g. Na^+)

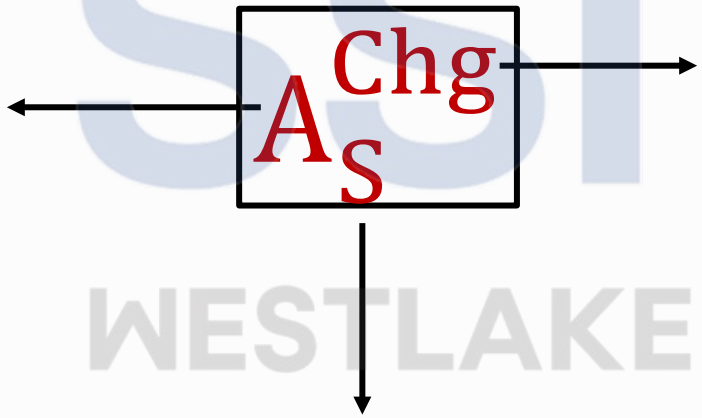
Anion
(e.g. Cl^-)

Anti-site defect

Cation 2

Kröger-Vink Notation

The language of defect chemistry: keeps track of type, lattice site and charge of point defects



Defect type:

"V" for vacancy

Everything else:
notation of the **occupying** atom

Charge:

Difference of charge between the occupying atom and occupied atom

Positive charge: •
Negative charge: ′
Neutral: x

Lattice Site:

"i" for interstitial
Everything else:
Notation of the atom that is **occupied**

Kröger-Vink Notation: Examples

The language of defect chemistry: keeps track of type, lattice site and charge of point defects

E.g. 1:

Y_2O_3 doped ZrO_2 (YSZ)

Doping Y(3+) into Zr(4+) site

Oxygen(O^{2-}) vacancy

E.g. 2:

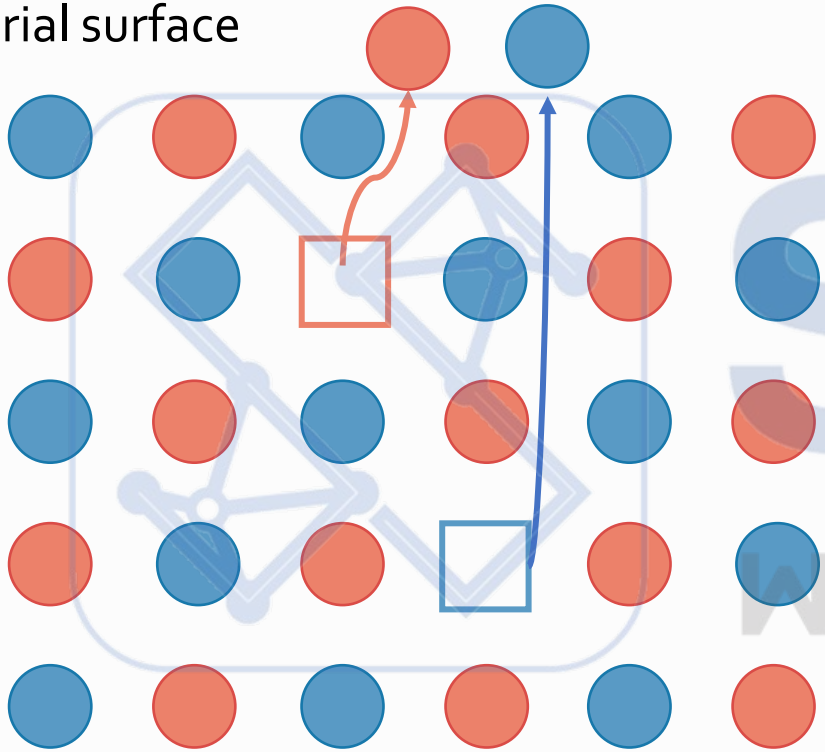
Schottky pair in NaCl

Sodium (Na^+) vacancy

Chlorine(Cl^-) vacancy

Schottky Reaction (or commonly Schottky Pair)

Material surface



Cation (e.g. Na^+)

Anion (e.g. Cl^-)

Cation Vacancy (V'_{Na})

Anion Vacancy ($V^{\cdot}_{Cl}$)

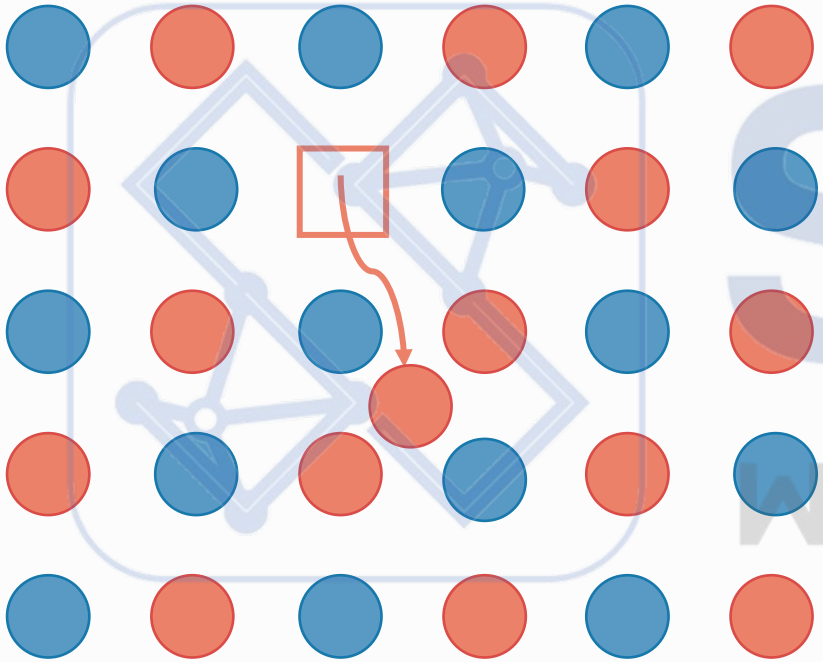
How to write the chemical formula for Schottky reaction?

$$Na^{\times}_{Na} + Cl^{\times}_{Cl} \leftrightharpoons V'_{Na} + V^{\cdot}_{Cl}$$ + Ions at surfaces

Or more commonly:

$$null \leftrightharpoons V'_{Na} + V^{\cdot}_{Cl}$$ (*null* means the perfect lattice)

Frenkel Reaction (or commonly Frenkel Pair)



Cation (e.g. Na^+)

Anion (e.g. Cl^-)

Anion Vacancy ($V_{Cl}^{\cdot}$)

Anion Interstitial (Cl_i')

How to write the chemical formula for Frenkel reaction?

$$Cl_{Cl}^{\times} \leftrightharpoons Cl_i' + V_{Cl}^{\cdot}$$

Or more commonly:

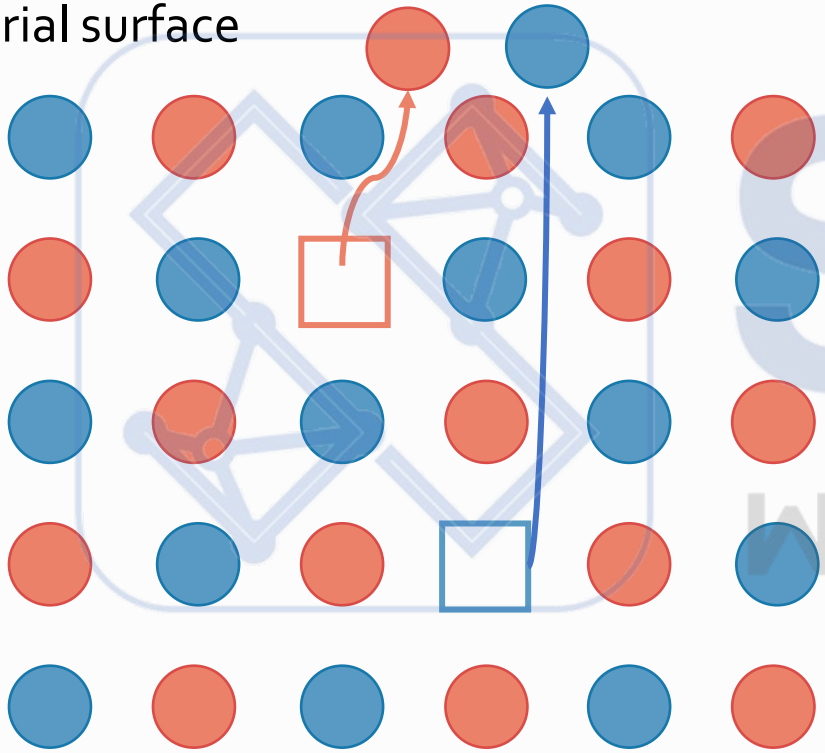
$$null \leftrightharpoons Cl_i' + V_{Cl}^{\cdot}$$

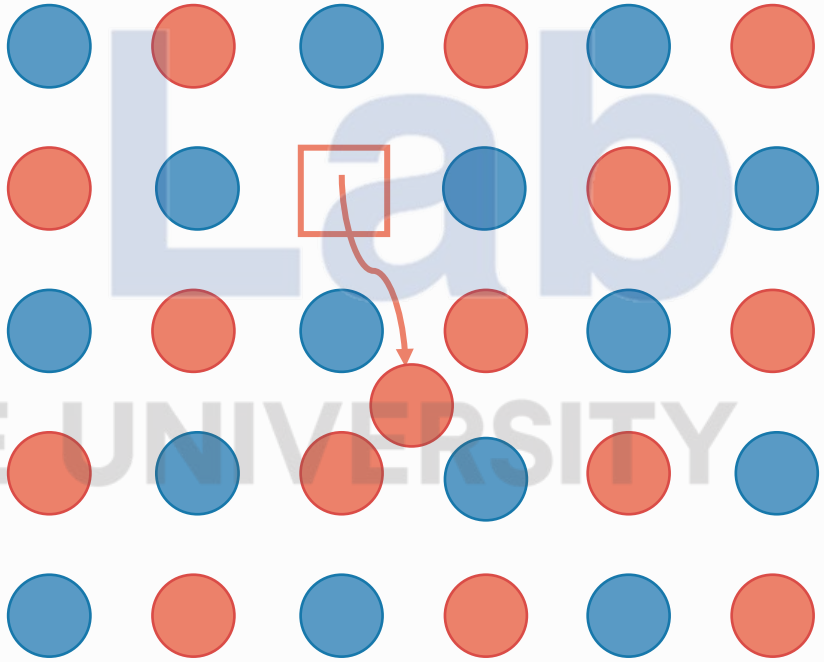
(*null* means the perfect lattice)

Defect chemical equilibrium

Question: How to predict defect concentrations at equilibrium?

Material surface





Schottky Reaction

$$null \leftrightharpoons V'_{Na} + V^{\cdot}_{Cl}$$

Frenkel Reaction

$$null \leftrightharpoons Cl'_{i} + V^{\cdot}_{Cl}$$

Review of fundamentals in thermodynamics

Gibbs free energy

$$G = U + PV - TS$$

$$G = H - TS$$

H: enthalpy; S: entropy;

the *maximum reversible work* that may be performed by a thermodynamic system at a ***constant temperature*** **(*T*)** ***and pressure*** **(*P*)**

The differential Gibbs free energy

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

Chemical potential μ_i is the ***partial molar*** Gibbs free energy of species *i* at constant *T* and *P*

At constant T and P, we define chemical potential of species *i* (μ_i)as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = h_i - Ts_i$$

Note: lower case → partial molar quantities

Review of thermodynamics: chemical potential

At constant T and P, we define chemical potential of species *i* (μ_i)as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = h_i - Ts_i$$

How to link chemical potential of species *i* (μ_i) with its concentration c_i?

$$\mu_i = \mu_i^0 + RTlna_i = \mu_i^0 + RTln(\gamma_i c_i)$$

μ_i^0: chemical potential at ***standard*** condition

At dilute limit, $\gamma_i \rightarrow 1$, therefore $\mu_i = \mu_i^0 + RTlnc_i$

Note: lower case → partial molar quantities

Review of thermodynamics: configurational entropy

Gibbs free energy

$$G = U + PV - TS$$

$$G = H - TS$$

H: enthalpy; S: entropy;

Boltzmann's entropy formula

$$S = k_B \ln \Omega$$

k_B: Boltzmann constant; $k_B T = 26\ meV$ at RT

Ω: # of possible configurations

Note: in the equation above, the possibility of each configuration is the same (same weighting).

If one relaxes this assumption, with possibility of state n as P_n, then we have:

$$S = -k_B \sum_{n=1}^{\Omega} P_n \ln P_n$$

so-called "cross entropy" formula

Why do defects form in crystalline solids?

At given *T* and pressure *p*, the criteria for reaching equilibrium is to minimize Gibbs free energy *G*, for each defect formed, we have:

$$\Delta_{\text{def}}G = \Delta_{\text{def}}H - T\Delta_{\text{def}}S$$

In order to have a spontaneous process, there must be: $\Delta_{\text{def}}G < 0$

However, $\Delta_{\text{def}}H = H_{real} - H_{perfect} > 0$, *i.e.*, *creating defects requires external energy*

At *T* = o K, we always have: $\Delta_{\text{defect}}G > 0$, *i.e.*, *perfect crystal exists at absolution zero T.*

Then why do defects form?

$-T\Delta_{\text{def}}S$, *i.e.*, ***Entropic*** Contribution

Entropic Contribution

There are two important sources of entropy related to defect formation:

Vibrational entropy $\Delta_{vib}S$

Related to change in phonon mode (lattice vibration) caused by introducing defects.

Linearly scales up with # of defects
Assumption: dilute defect concentration (*i.e.*, ignore interactions between defects)

Configurational entropy $\Delta_{cfg}S$

Related to *increased ways* to configure the lattice caused by introducing defects. (i.e., more *information*)

More complicated dependence on # of defects
The main source of entropy term

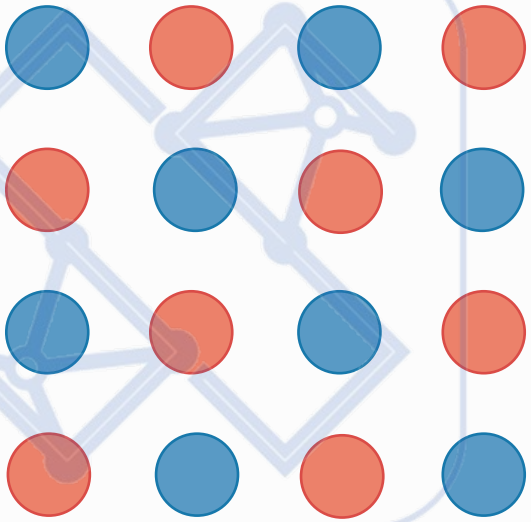
If we introduce n_D defects into the lattice, we have:

$$\Delta_{\mathrm{def}}G = (n_D/N_A)\,(\Delta_{\mathrm{def}}h - T\Delta_{\mathrm{vib}}s) - T\Delta_{\mathrm{cfg}}S(n_D)$$

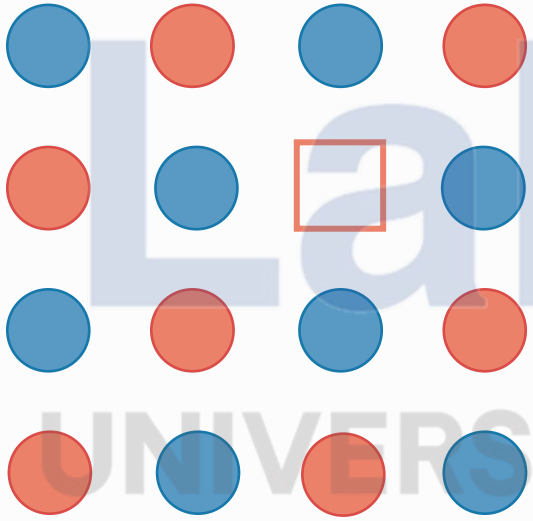
Note: lower case → partial molar quantities

Configurational Entropy

Perfect Crystal



Real Crystal with one vacancy



Only 1 way to configure the lattice

8 different ways to configure the lattice

$$\#\text{ of ways to configure the lattice} = \frac{N!}{(N-n_D)!n_D!}$$

N = # of total lattice sites

n_D = # of defects

Configurational Entropy

$$\#\text{ of ways to configure the lattice} = \frac{N!}{(N-n_D)!n_D!}$$

N = # of total lattice sites
n_D = # of defects

Boltzmann's entropy formula $S_{cfg} = k_B \ln \Omega = k_B(\ln N! - \ln(N-n_D)! - \ln n_D!)$

Stirling's approximation: $\ln N! \approx N \ln N - N$ →

$$S_{cfg} = k_B(N \ln N - N - (N-n_D)\ln(N-n_D) + (N-n_D) - n_D \ln n_D + n_D)$$

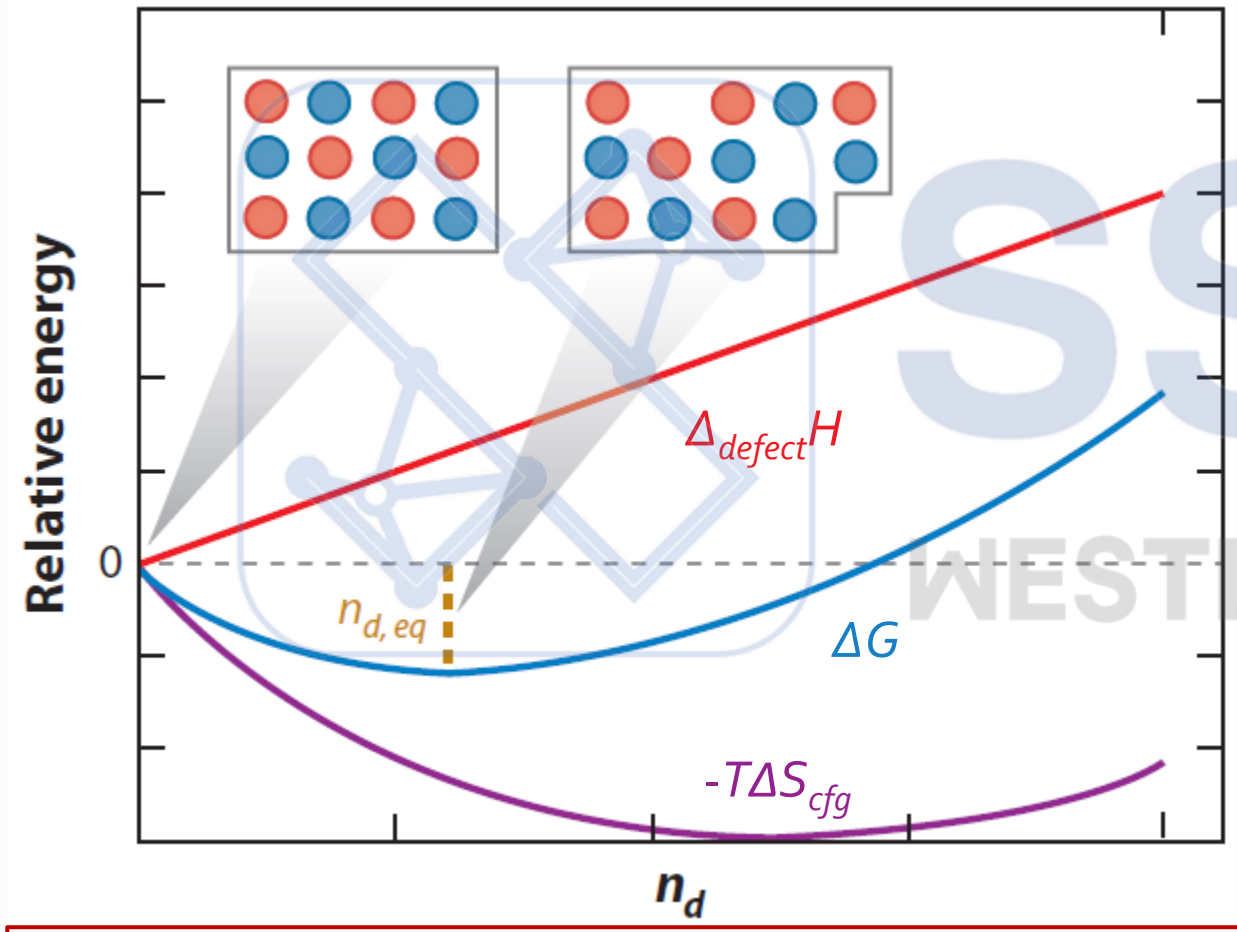
$$S_{cfg,D} = k_B N \ln \frac{N}{N-n_D} + k_B n_D \ln \frac{N-n_D}{n_D}$$

Partial configurational entropy $s_{cfg,D} = \frac{\partial S_{cfg,D}}{\partial(n_D/N_A)} = -k_B N_A \ln \frac{n_D}{N-n_D} = -R \ln \frac{[D]}{1-[D]}$ $[D] = \frac{n_D}{N}$

Note: lower case → partial molar quantities $R = k_B N_A$

Defect concentration at equilibrium

Bishop and Tuller, *Ann. Rev. Mater. Sci.*, 2011



$$s_{cfg,D} = \frac{\partial S_{cfg,D}}{\partial (n_D/N_A)} = -R\ln\frac{n_D}{N-n_D} = -R\ln\frac{[D]}{1-[D]}$$

If $N \gg n_D$ ($[D] \ll 1$), then: $s_{cfg,D} \approx -R\ln[D]$

Equilibrium means $\Delta_{\mathrm{def}}G(n_D)$ reaches minimal, *i.e.*,

$$\frac{\partial \Delta_{\mathrm{def}}G}{\partial (n_D/N_A)} = 0 \longrightarrow \Delta_{\mathrm{def}}h - T\Delta_{\mathrm{vib}}s = -RT\ln\frac{n_D}{N}$$

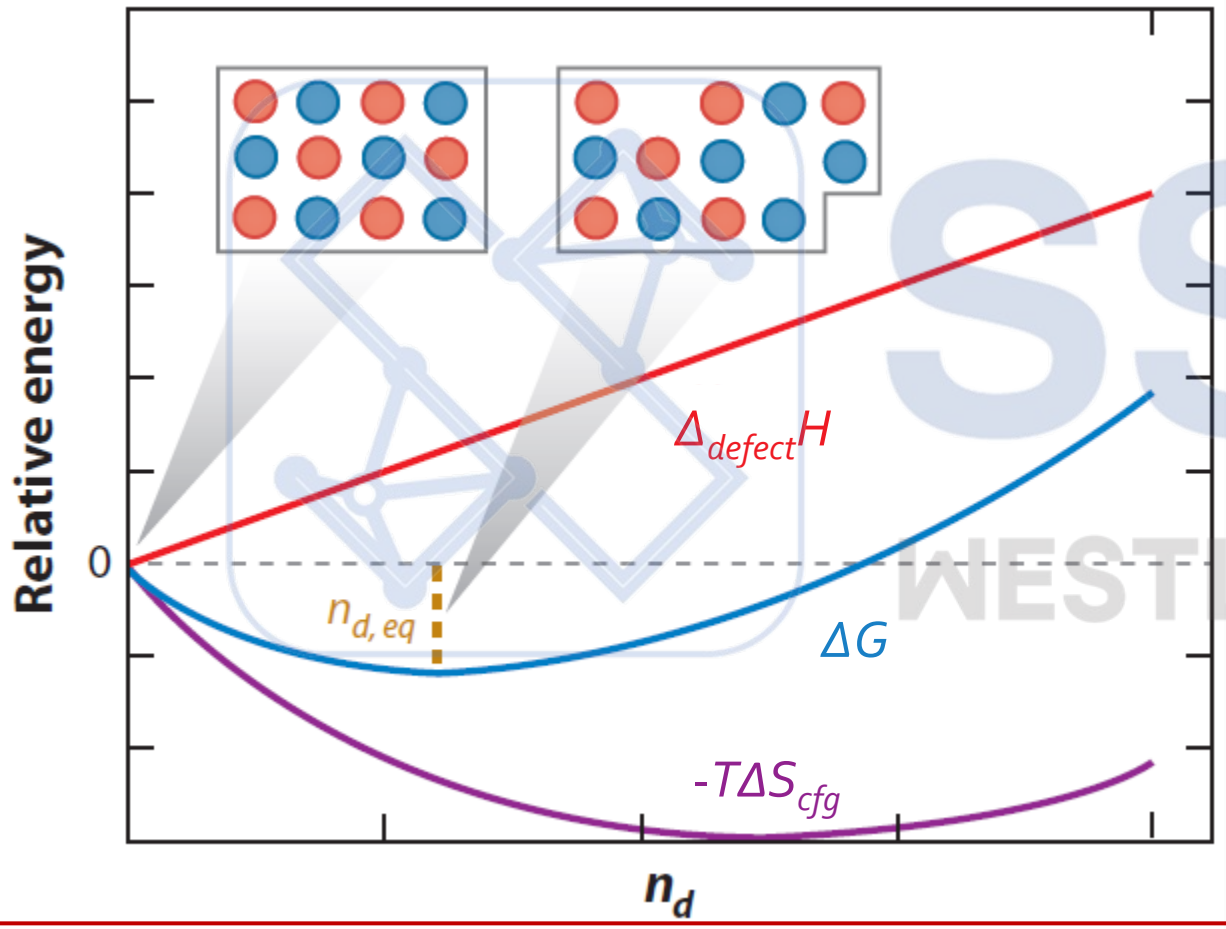
$$[D]_{eq} = \frac{n_{D,eq}}{N} = \exp\left(\frac{\Delta_{\mathrm{vib}}s}{R}\right)\exp\left(-\frac{\Delta_{\mathrm{def}}h}{RT}\right)$$

$$n_{D,eq} = N\exp\left(\frac{\Delta_{\mathrm{vib}}s}{R}\right)\exp\left(-\frac{\Delta_{\mathrm{def}}h}{RT}\right)$$

$$\Delta_{\mathrm{def}}G = (n_D/N_A)\left(\Delta_{\mathrm{def}}h - T\Delta_{\mathrm{vib}}s\right) - T\Delta_{\mathrm{cfg}}S(n_D)$$

Defect concentration at equilibrium

Bishop and Tuller, *Ann. Rev. Mater. Sci.*, 2011



$$\Delta_{\text{def}}G = (n_D/N_A)\,(\Delta_{\text{def}}h - T\Delta_{\text{vib}}s) - T\Delta_{\text{cfg}}S(n_D)$$

If one solves for defect concentration at equilibrium, we have:

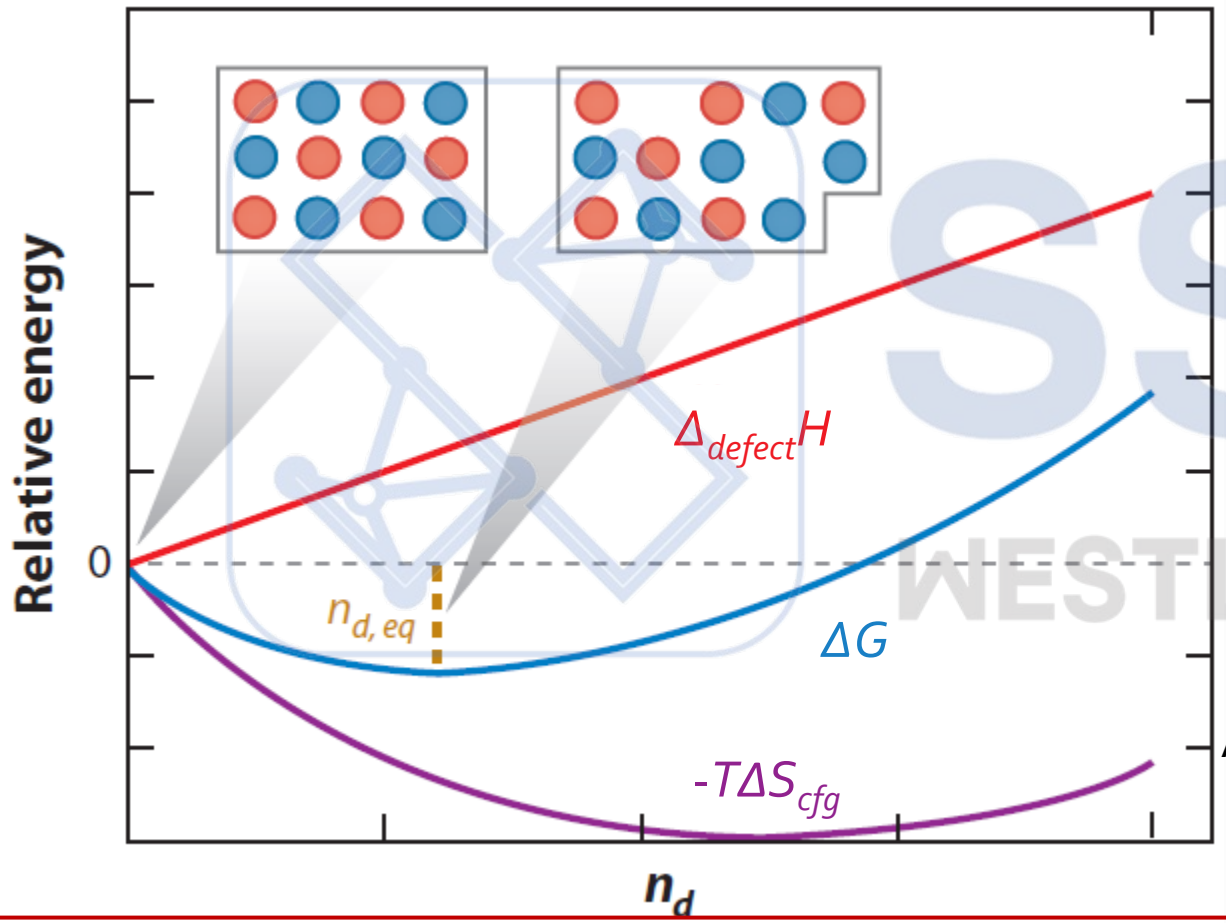
$$n_{D,eq} = N \exp\left(\frac{\Delta_{\text{vib}}s}{R}\right) \exp\left(-\frac{\Delta_{\text{def}}h}{RT}\right)$$

Assumption: dilute defect concentration (*i.e.*, ignore interactions between defects)

Note:
conventionally thermodynamic quantities have unit of **kJ/mol**,
If in eV, then it is more convenient to change R → k_B ($R = k_B N_A$)

Defect concentration at equilibrium

Bishop and Tuller, *Ann. Rev. Mater. Sci.*, 2011



Another way to understand the equilibrium condition:

$$\mu_D = \frac{\partial \Delta_{\mathrm{def}} G}{\partial (n_D/N_A)} = h - Ts_{vib} - Ts_{ctg}$$

μ_D ↓ *Chemical potential*

$$s_{cfg,D} \approx -R\ln[D] \rightarrow \mu_D = \underbrace{h - Ts_{vib}}_{\mu_D^0} + RT\ln[D]$$

At equilibrium, $\mu_D = \frac{\partial \Delta_{\mathrm{def}} G}{\partial (n_D/N_A)} = 0 \rightarrow$

$$[D] = \exp\left(-\frac{\mu_D^0}{RT}\right) = K(T)$$

$$\Delta_{\mathrm{def}} G = (n_D/N_A)\left(\Delta_{\mathrm{def}} h - T\Delta_{\mathrm{vib}} s\right) - T\Delta_{\mathrm{cfg}} S(n_D)$$

Note: lower case → partial molar quantities

Defect chemical equilibrium: more than one defect type

Let's go back to the defect chemical reaction, taking Frenkel reaction as an example.

From any given chemical reaction aA + bB ⇌ cC + dD

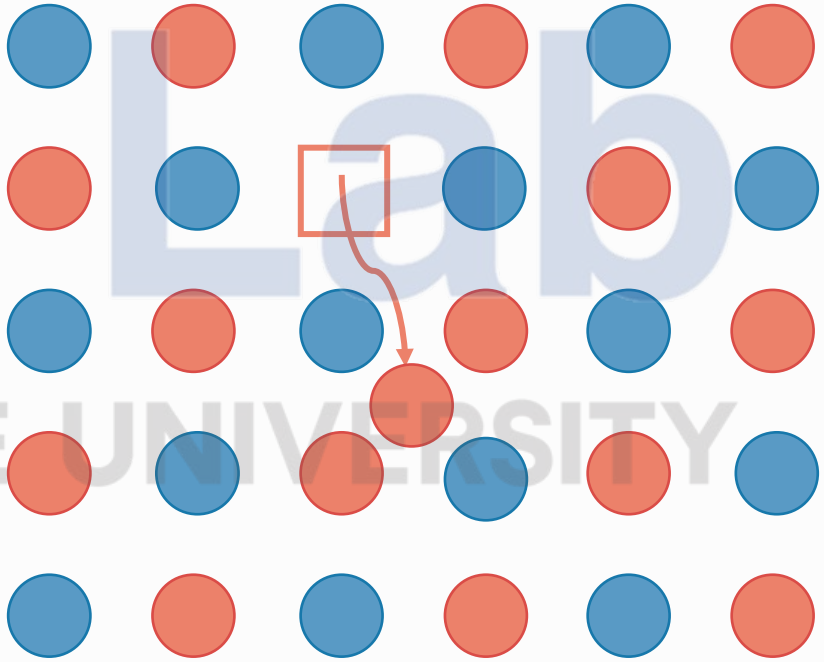
At equilibrium: $a\mu_A + b\mu_B = c\mu_C + d\mu_D$

We know $\mu_i = \mu_i^0 + RTlna_i$

$$\Delta g_{rxn}^0 = \Delta h_{rxn}^0 - T\Delta s_{rxn}^0 = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0$$
$$= -RTln\,K = -RT\ln\frac{a_C^c a_D^d}{a_A^a a_B^b}$$

rxn: reaction

K: equilibrium constant



Frenkel Reaction

$$null \leftrightharpoons Cl_i' + V_{Cl}^{\cdot}$$

If we apply the same treatment to Frenkel reaction:

$$\Delta g_{Frk}^0 = \Delta h_{Frk}^0 - T\Delta s_{Frk}^0 = \mu_{Cl_i'}^0 + \mu_{V_{Cl}^{\cdot}}^0 = -RT\ln([Cl_i'][V_{Cl}^{\cdot}])$$

Defect chemical equilibrium

Recall the conservation principles of chemical reactions

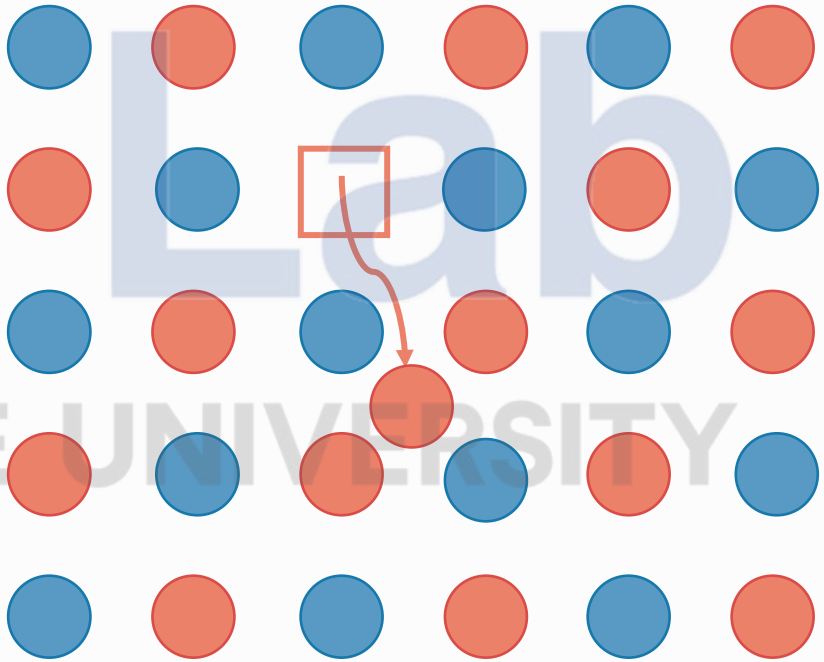
$$\Delta g^0_{Frk} = \Delta h^0_{Frk} - T\Delta s^0_{Frk} = \mu^0_{Cl'_i} + \mu^0_{V^{\cdot}_{Cl}} = -RT\ln([Cl'_i][V^{\cdot}_{Cl}])$$

Conservation rules of chemical reactions:

1. Conservation of mass
2. Conservation of charge
3. Conservation of lattice site ratios (for crystalline solids)

These means: $[Cl'_i] = [V^{\cdot}_{Cl}]$, therefore:

$$[Cl'_i] = [V^{\cdot}_{Cl}] = \exp\left(\frac{\Delta s^0_{Frk}}{2R}\right)\exp\left(-\frac{\Delta h^0_{Frk}}{2RT}\right)$$



Frenkel Reaction

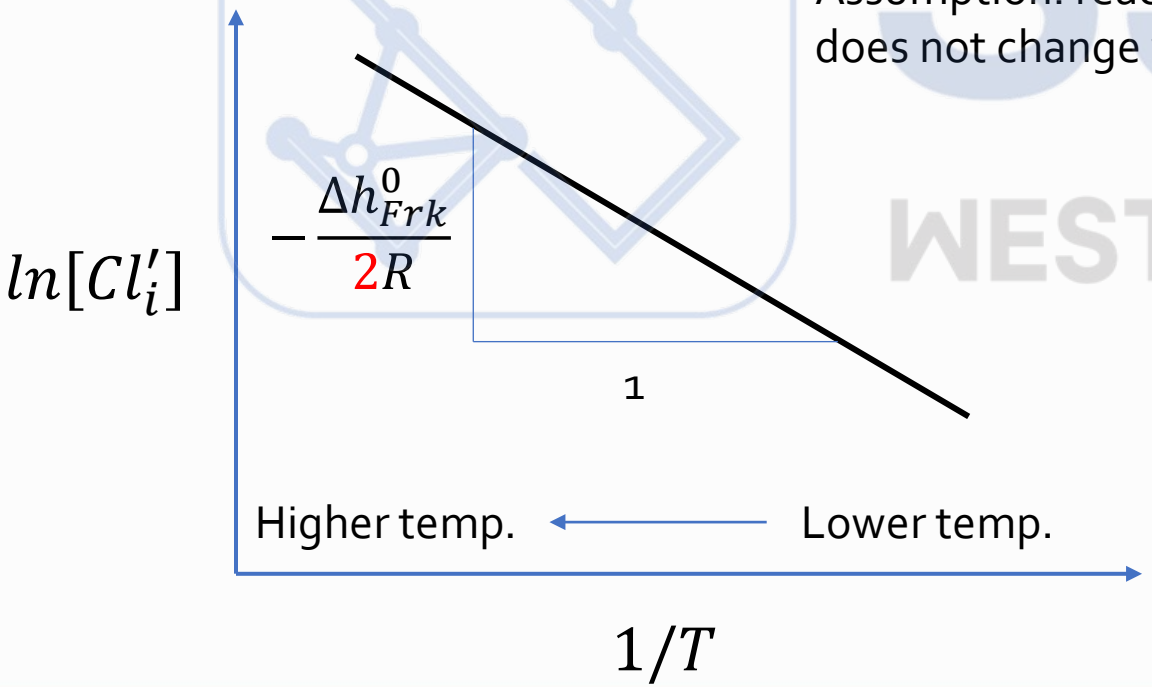
$$null \leftrightharpoons \mathrm{Cl}'_\mathrm{i} + \mathrm{V}^{\cdot}_{\mathrm{Cl}}$$

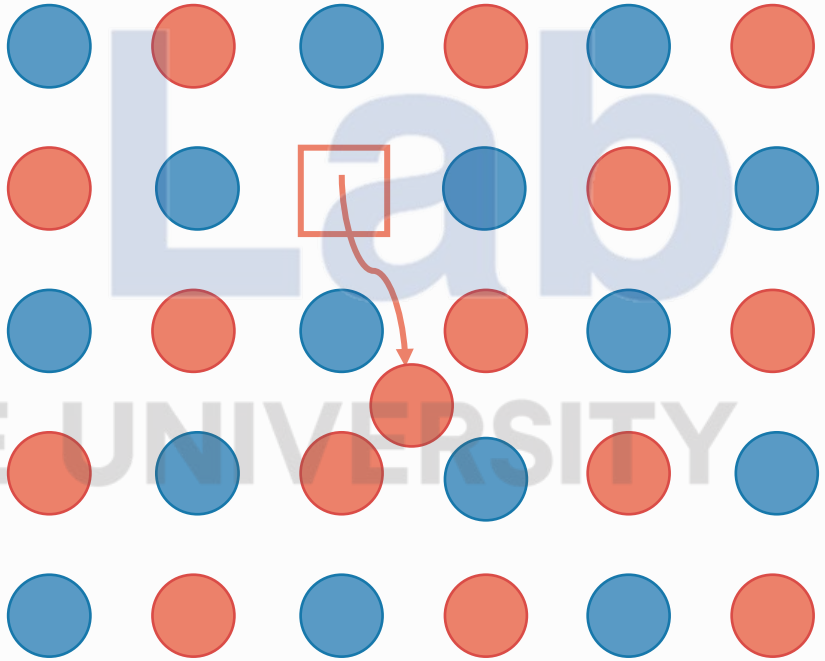
Defect chemical equilibrium

How does defect concentration change with temperature *T*?

$$[Cl_i'] = [V_{Cl}^{\cdot}] = \exp\left(\frac{\Delta s_{Frk}^0}{2R}\right)\exp\left(-\frac{\Delta h_{Frk}^0}{2RT}\right)$$

Assumption: reaction enthalpy does not change with *T*



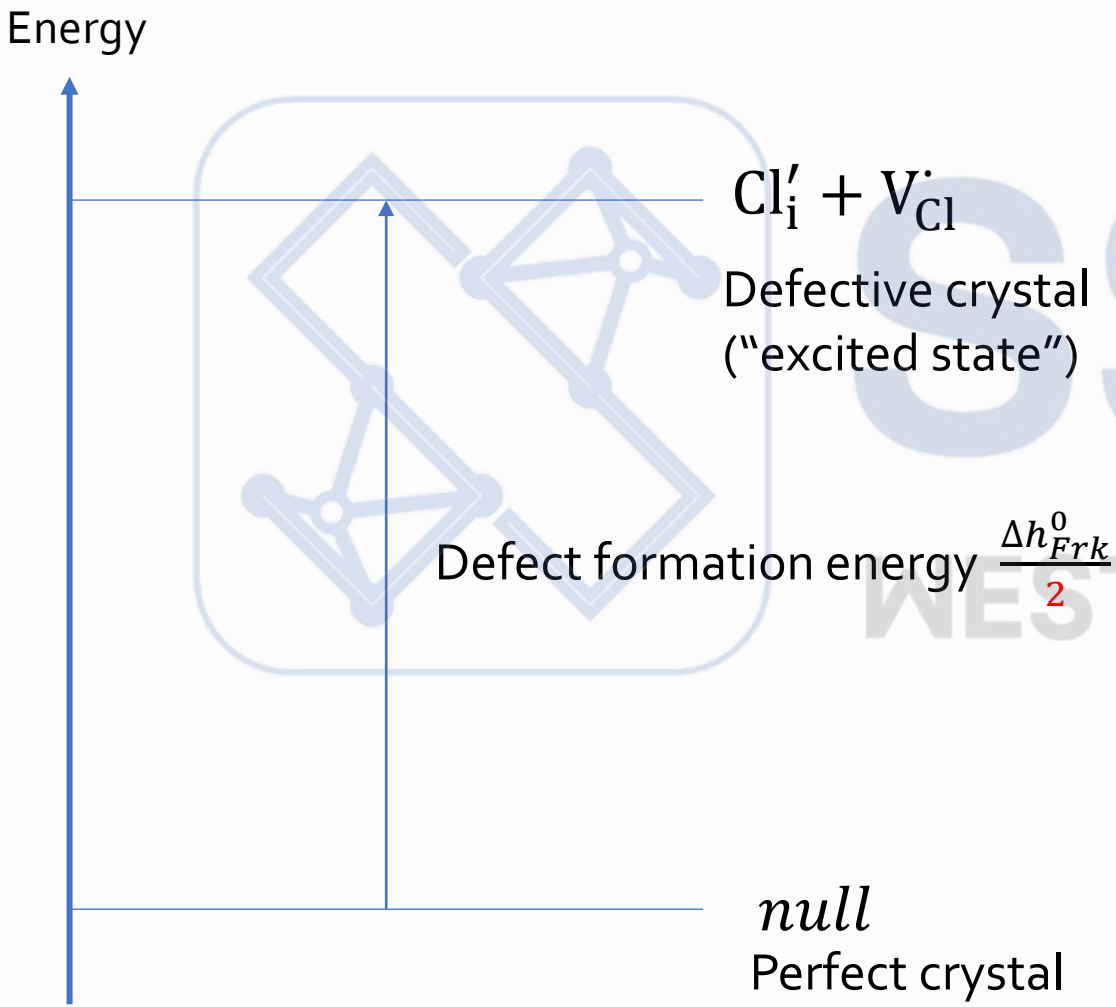


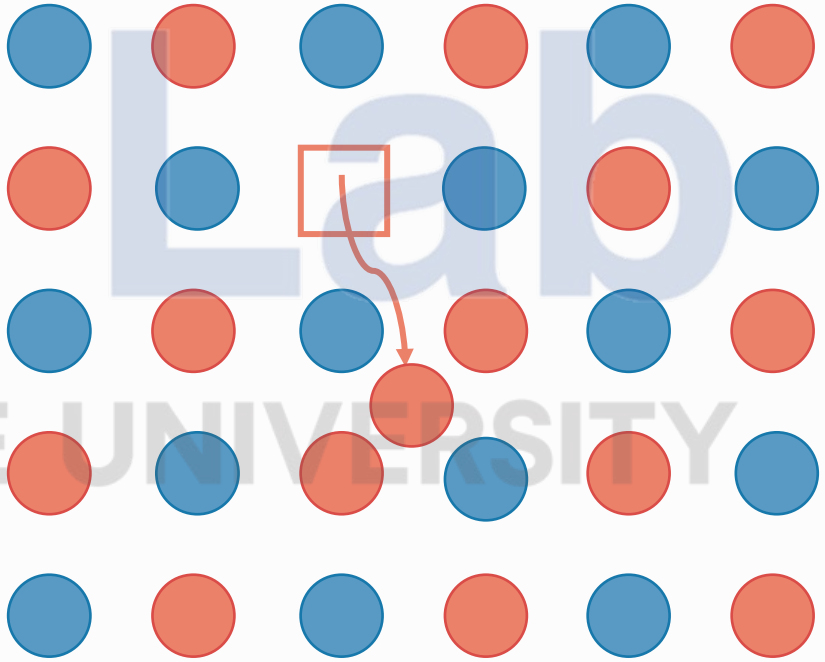
Frenkel Reaction

$$null \leftrightharpoons \mathrm{Cl_i'} + \mathrm{V_{Cl}^{\cdot}}$$

Another way to look at this problem

$$[Cl_i'] = [V_{Cl}^{\cdot}] = \exp\left(\frac{\Delta s_{Frk}^0}{2R}\right)\exp\left(-\frac{\Delta h_{Frk}^0}{2RT}\right)$$

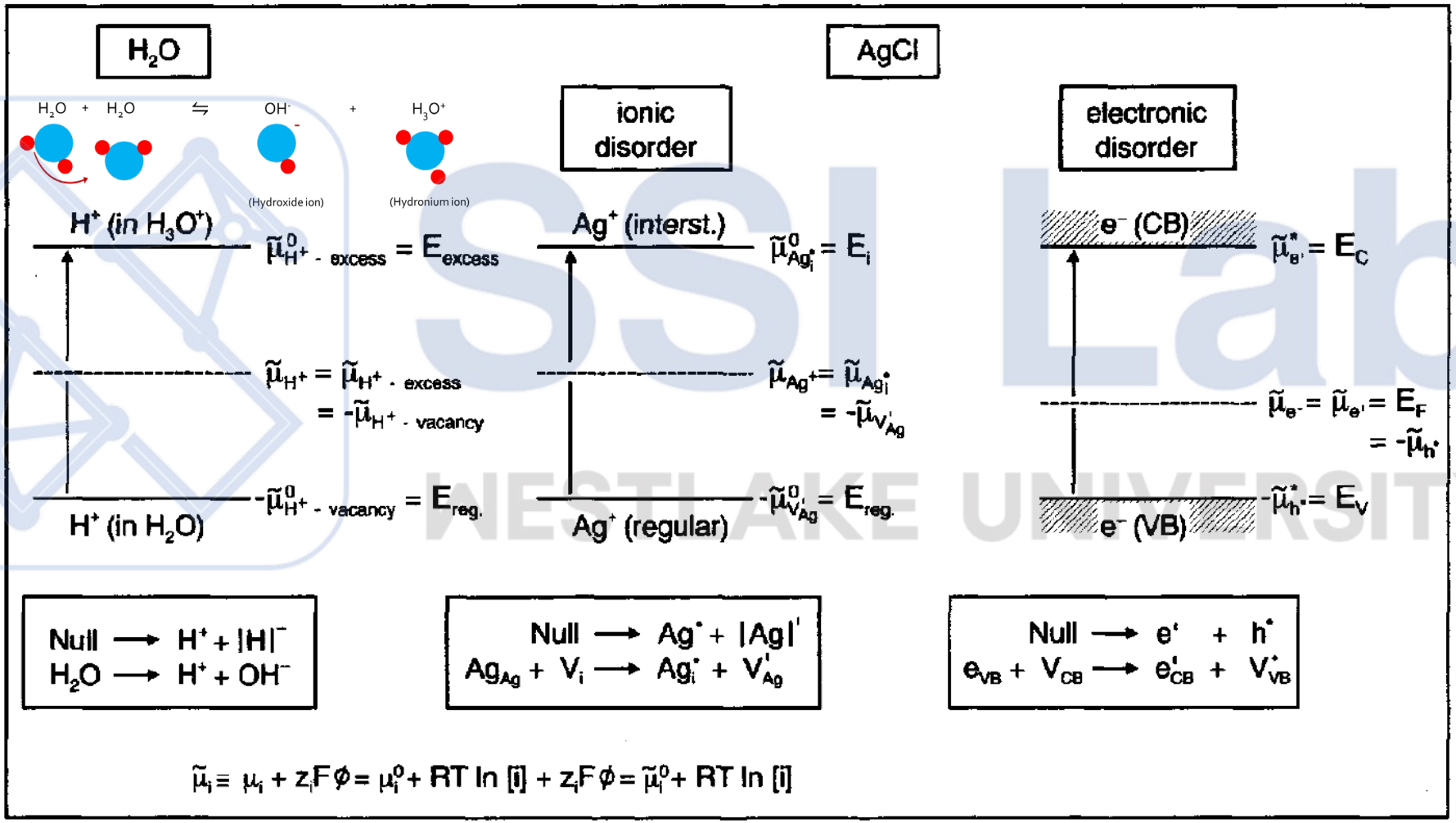




Frenkel Reaction

$$null \leftrightharpoons Cl_i' + V_{Cl}^{\cdot}$$

Link to the case of water and electronic defects in semiconductors



Maier, *Phys. Chem. of Ionic Mater.*

西湖大學
WESTLAKE UNIVERSITY

End of Lecture 1
Solid State Ionics Fall 2023

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