Lecture 1:
Course overview and introduction
Ionic defect formation

Solid State Ionics

Fall 2022

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School of Engineering
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:

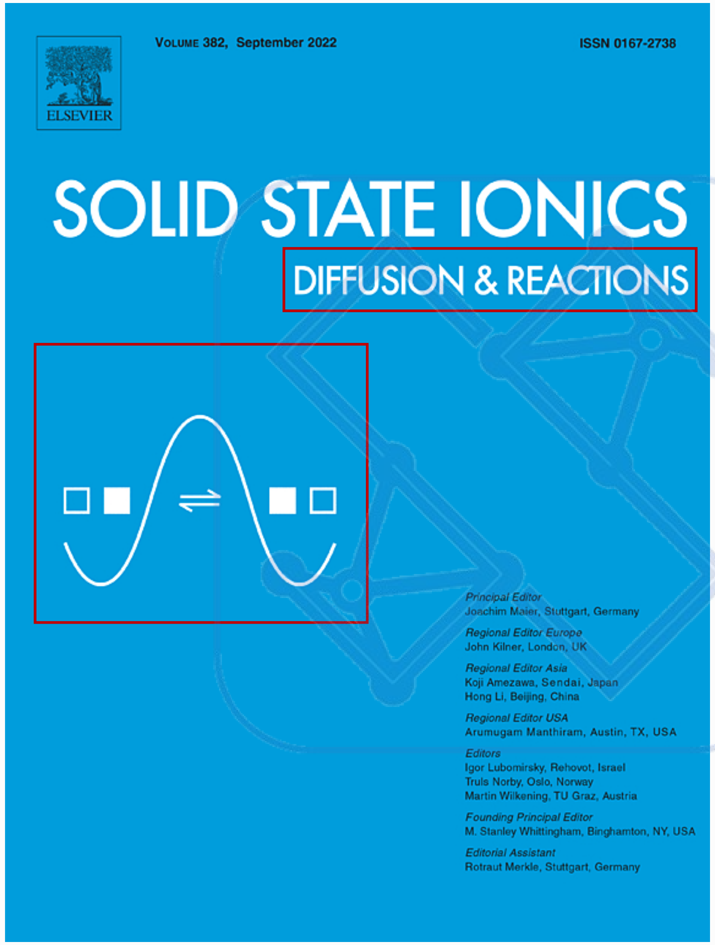
- What will you learn and what do you need to accomplish in this semester?
- *Why do graduate students take graduate-level courses?*

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: 3.785 (2022) ***JCR Q3*** (☹)

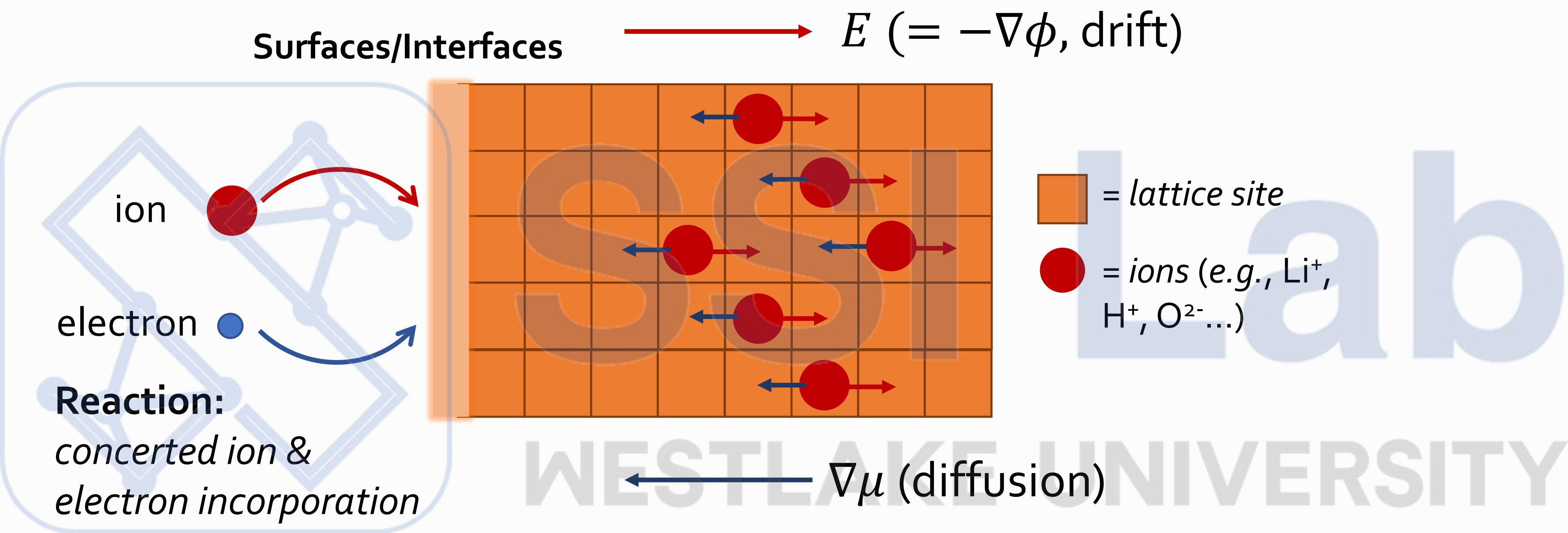
Principle Editor:

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



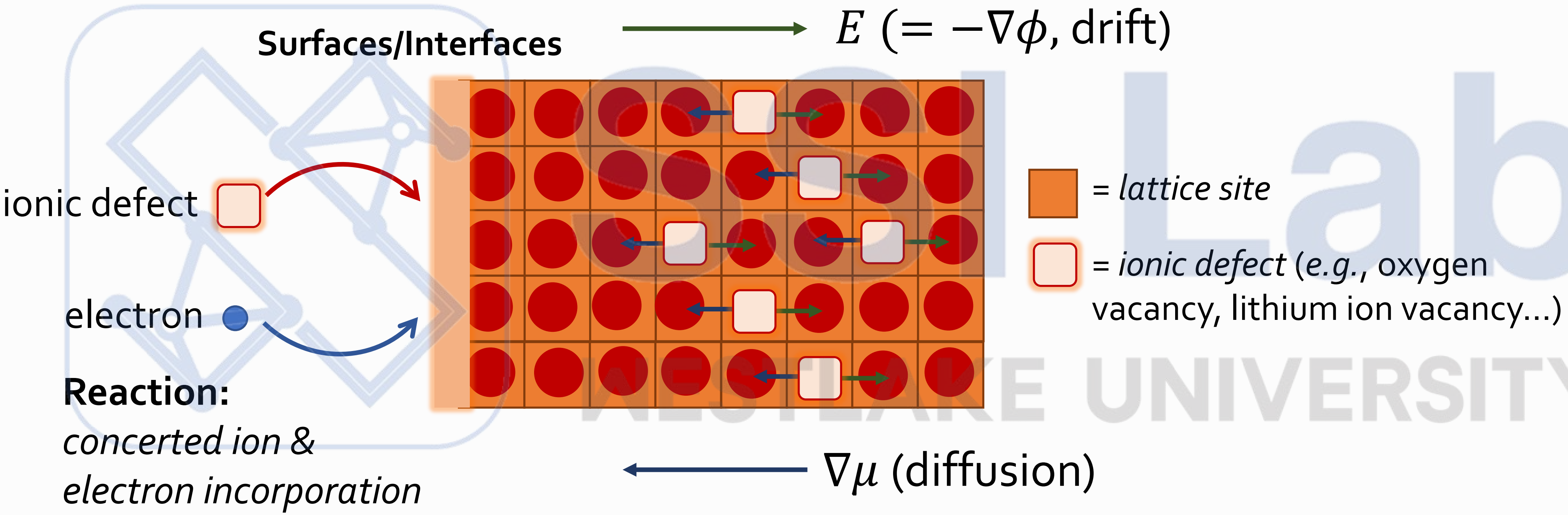
Ion motion: *drift + diffusion*

- 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*.

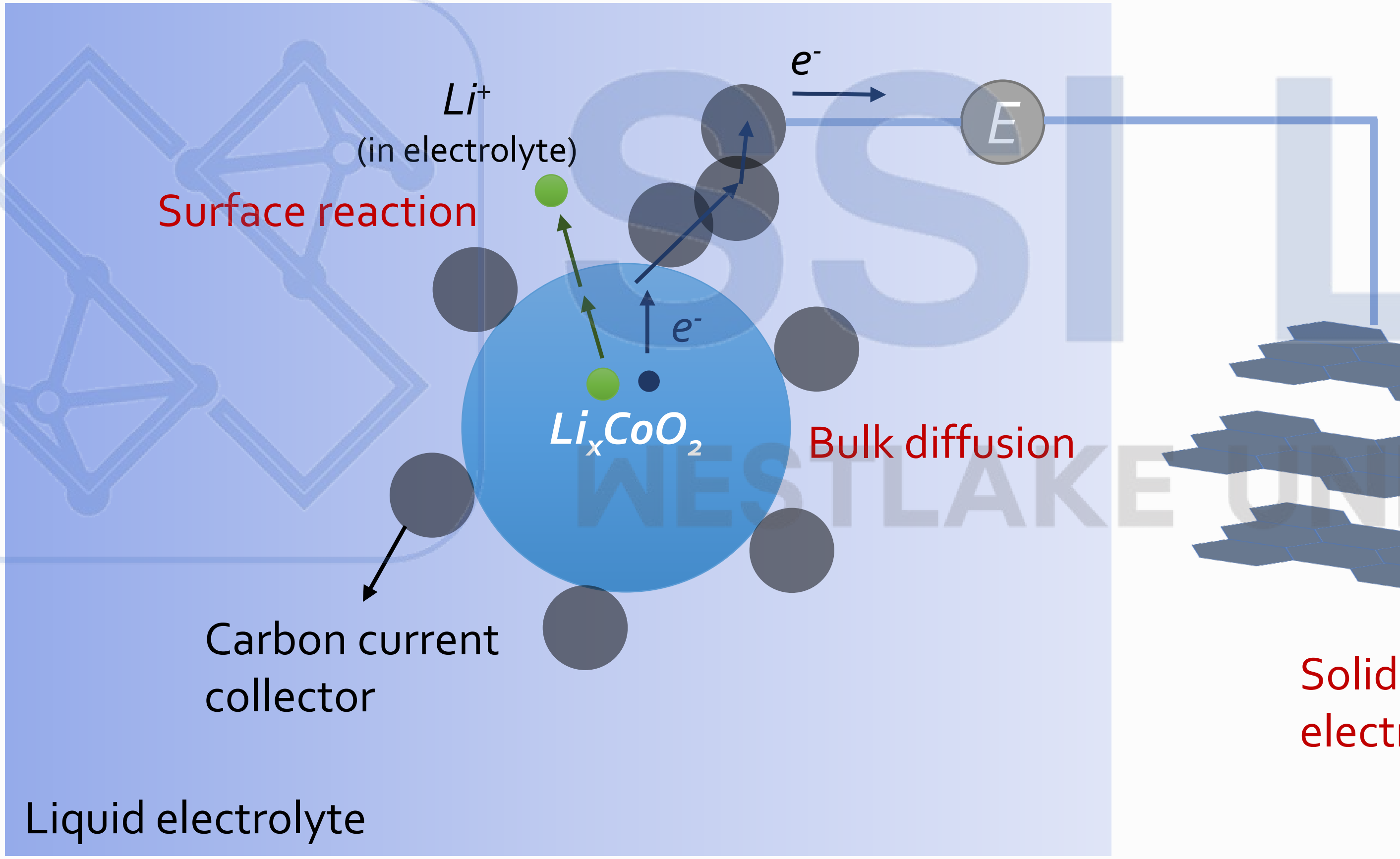
Let's look at this picture from another angle

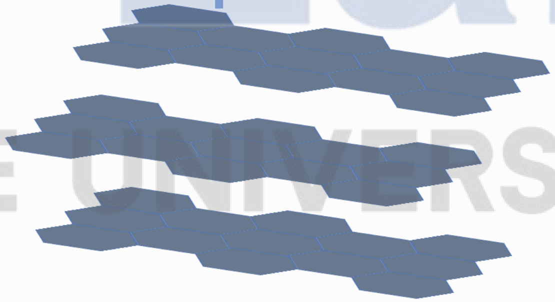


Ion motion: *drift + diffusion*
(similar to electrons/holes in semiconductor physics)

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

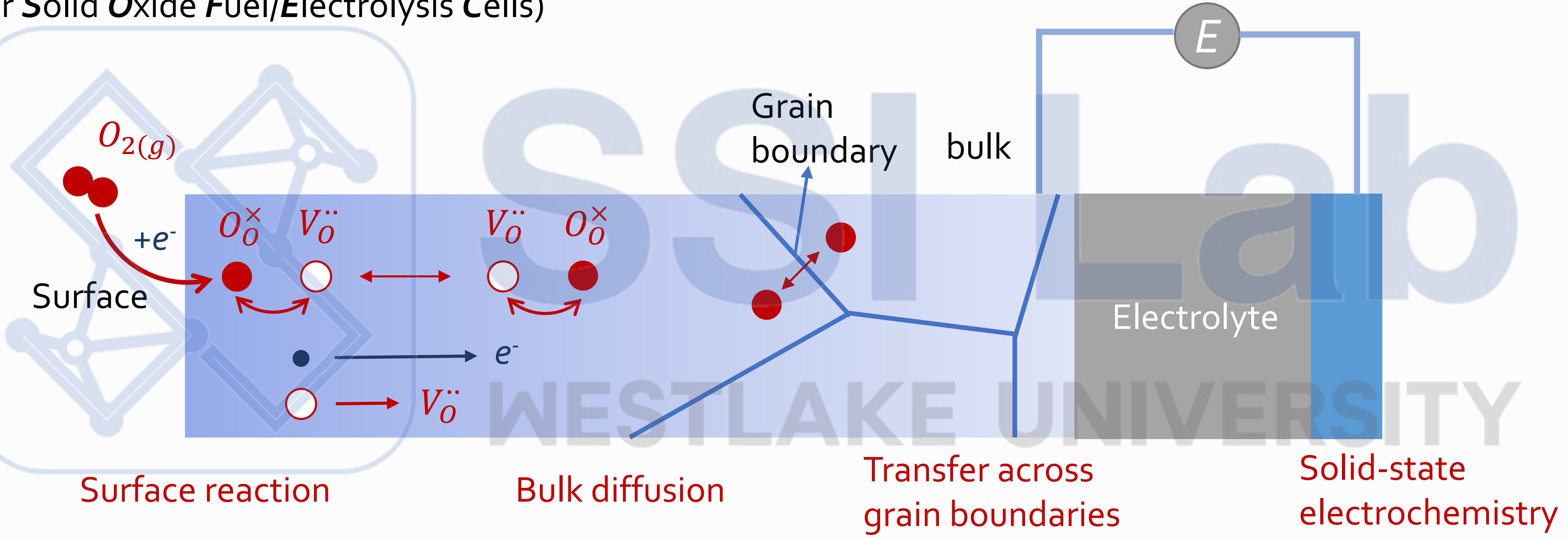
2019 Nobel Laureate
2009-2011 President of International Society for Solid State Ionics (ISSI)

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)



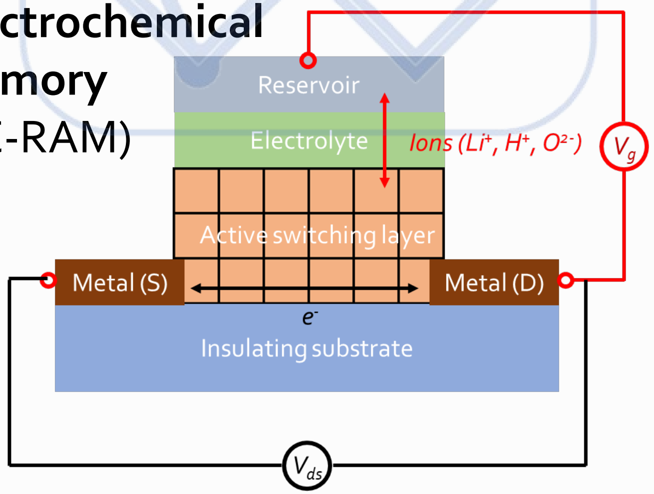
$$j_O = -k_{surf} c_{surf}$$

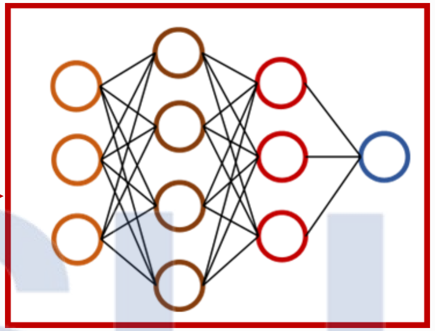
$$j_O = -D\nabla c$$

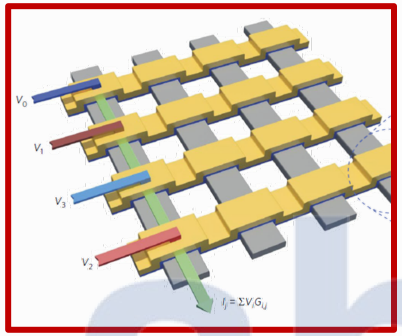
Neuromorphic computing devices for AI and IoT

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

Electrochemical Memory (EC-RAM)



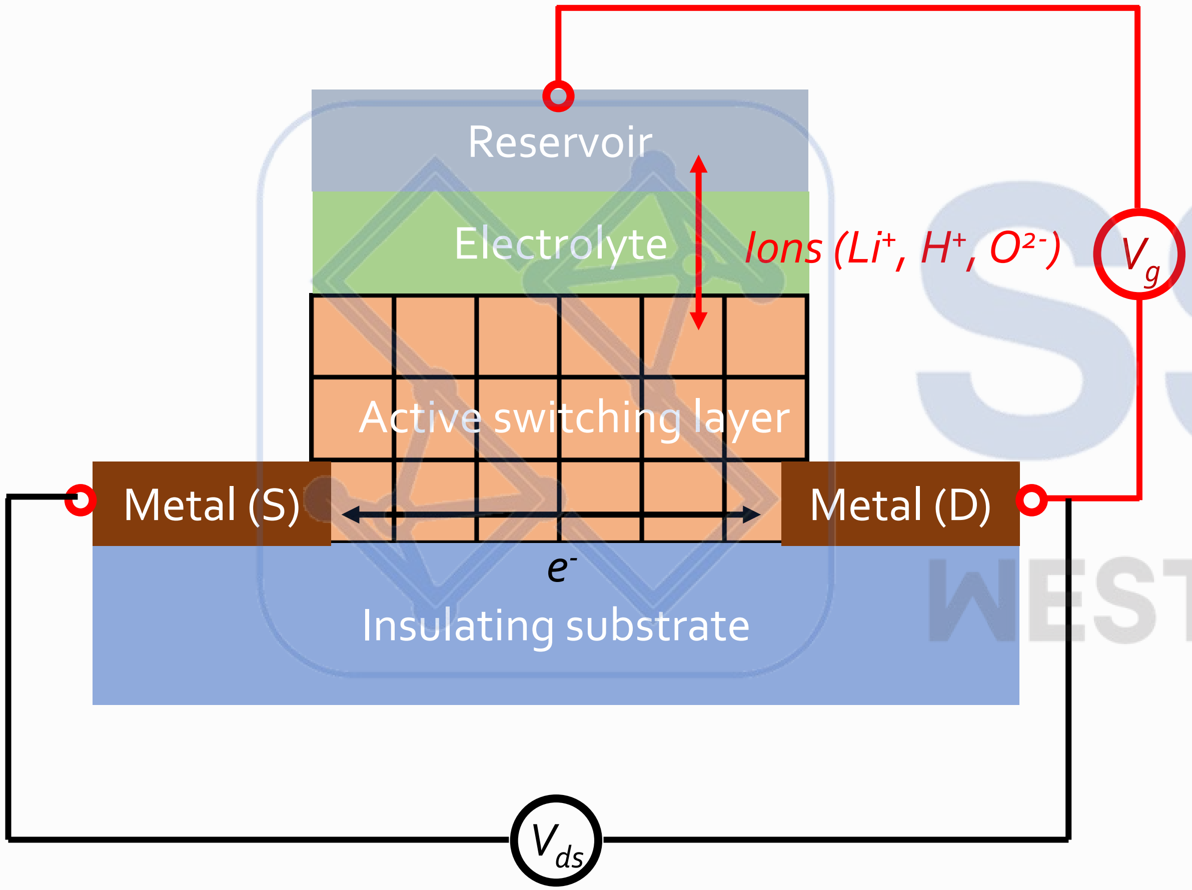


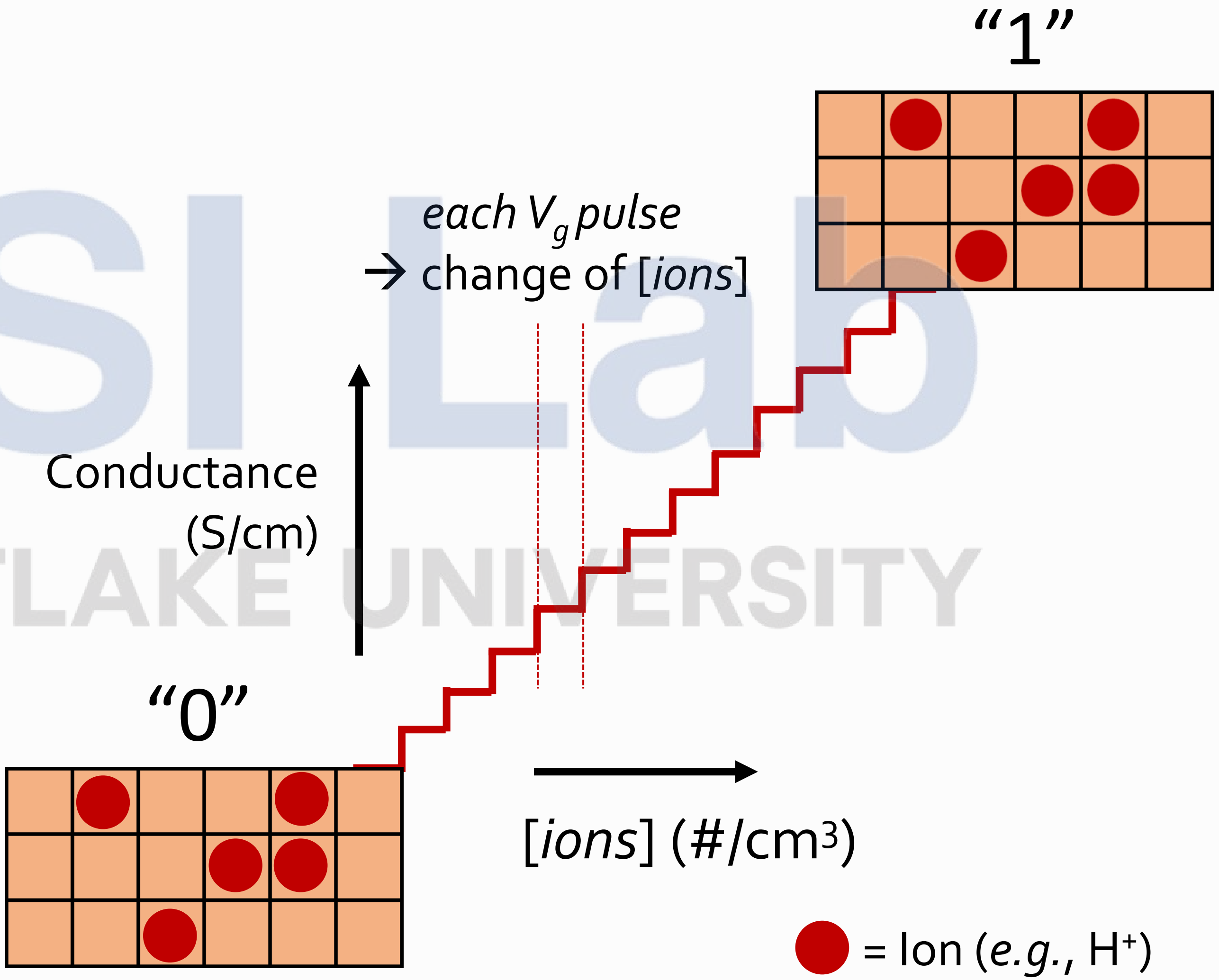


Artificial Intelligence **(AI)/N**eural **N**etworks **(ANN)**
Requirements: Multi-state weight updating, computing in memory

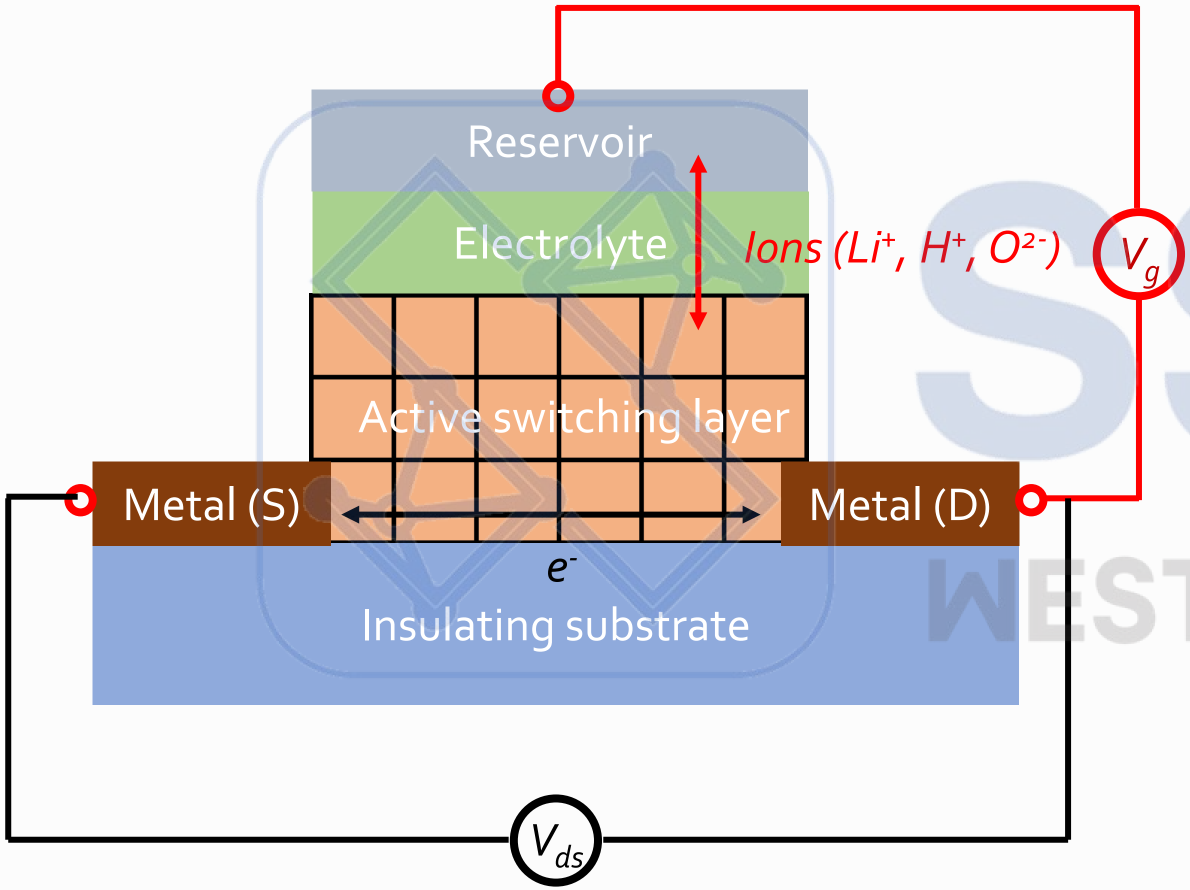
Internet **of T**hings (**IoT**)/Edge Computing
Requirement: Ultra-low power consumption

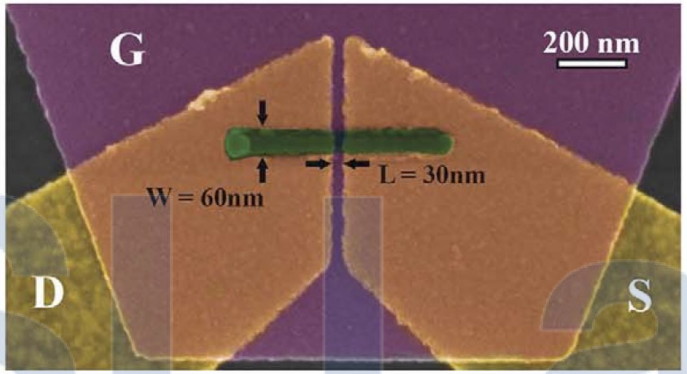
Electrochemical random access memory (EC-RAM)





Electrochemical random access memory (EC-RAM)



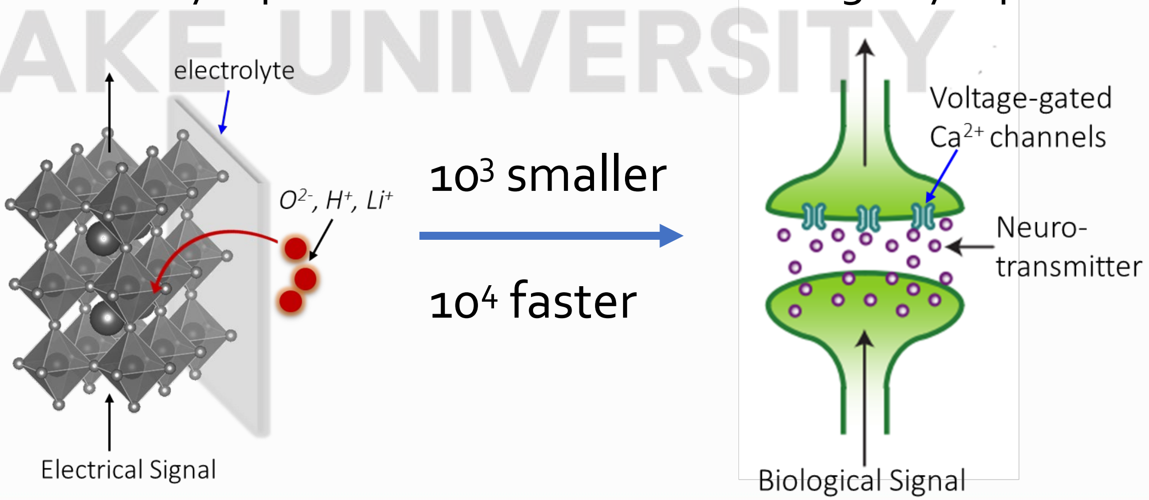


Onen, Li, Yildiz, del Alamo et al., ***Science***, 2022

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

Artificial synapse

Biologic synapse



Integration of ionic and electronic "organs"

"Autonomous system of functional materials"

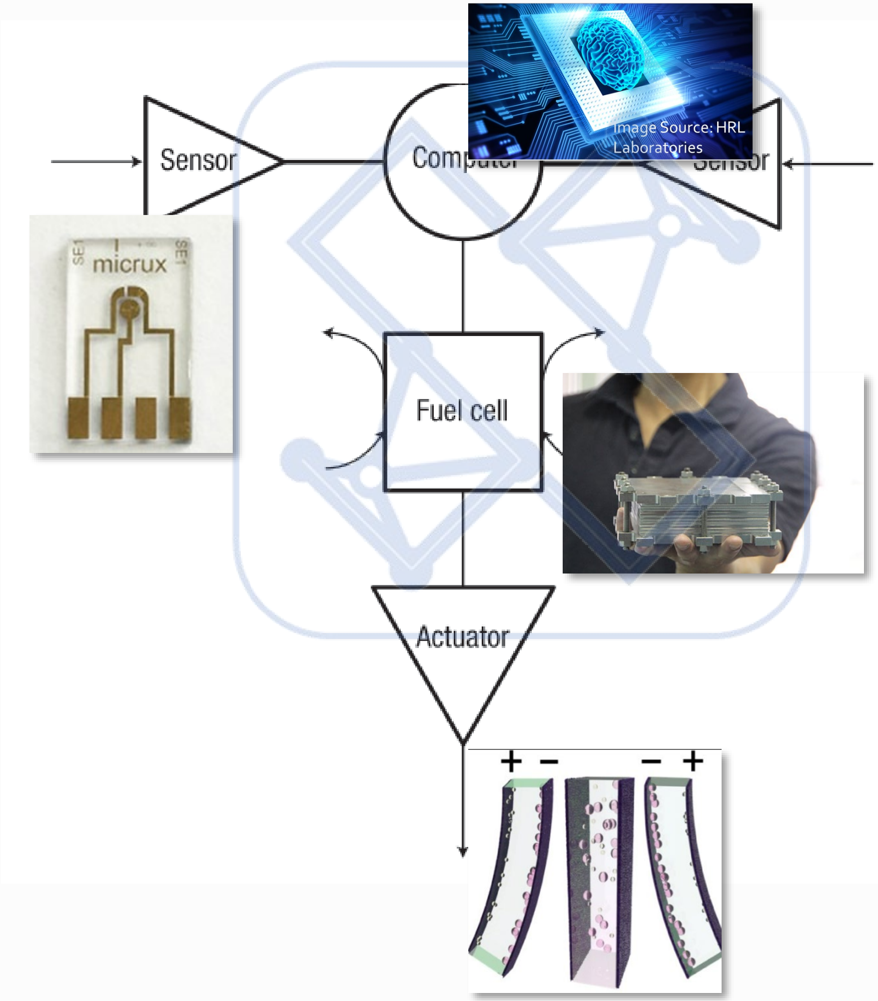


Figure 7 The nano-integration of ionic and electronic 'organs' such as sensors, actuators, computers and fuel cells or batteries results in tiny artificial autonomous systems. Reprinted from ref. 2. Copyright (2004) with permission from John Wiley & Sons Ltd.

Solid state ionics govern all these processes!

Sensors:
chemical —**Electrochemistry**→ *electrical*

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

Fuel Cells:
electrical —**Electrochemistry**→ *chemical*

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

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**.

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Course content: week 9-16

Week	Topic
9	Higher-dimensional defects; Space charge layers; Size effects;
10	Chemo-mechanical coupling in crystalline solids;
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	Frontiers and advanced topics: Photo-ionic effects; Solid state ionics of halide Perovskite, *etc.*
16	Review and closing remarks;

Key research directions of Solid State Ionics

- physics and chemistry of **defects** in solids;
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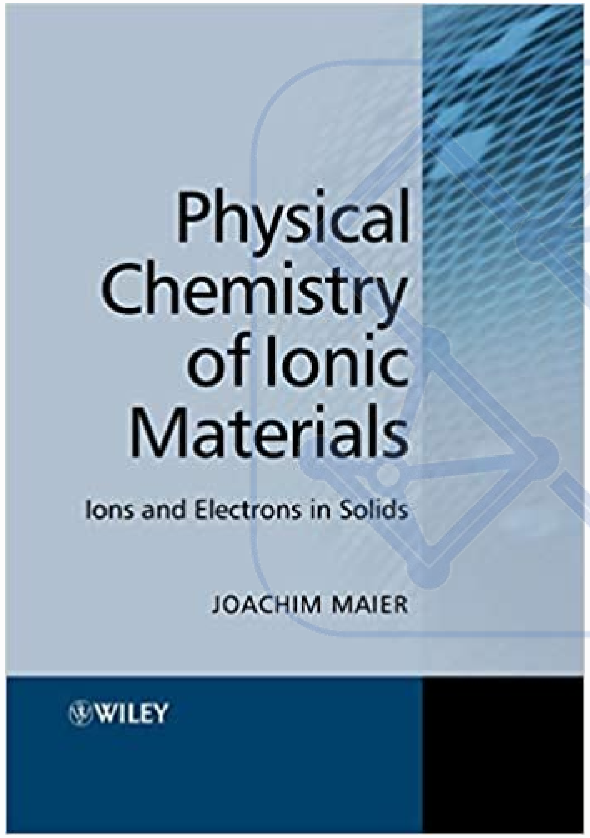
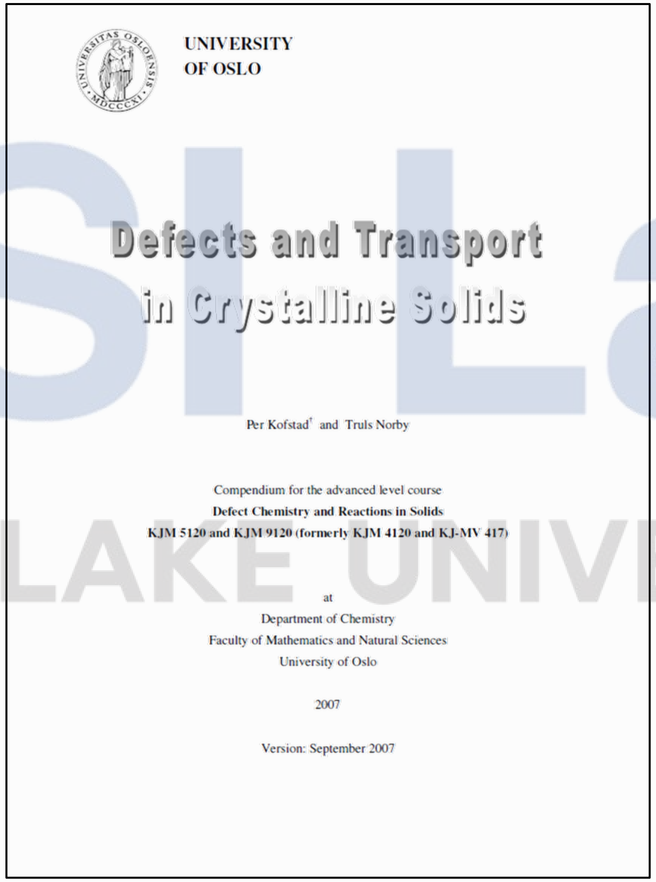
Reference books for Solid State Ionics



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



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 quite a book).

Grading and course policies

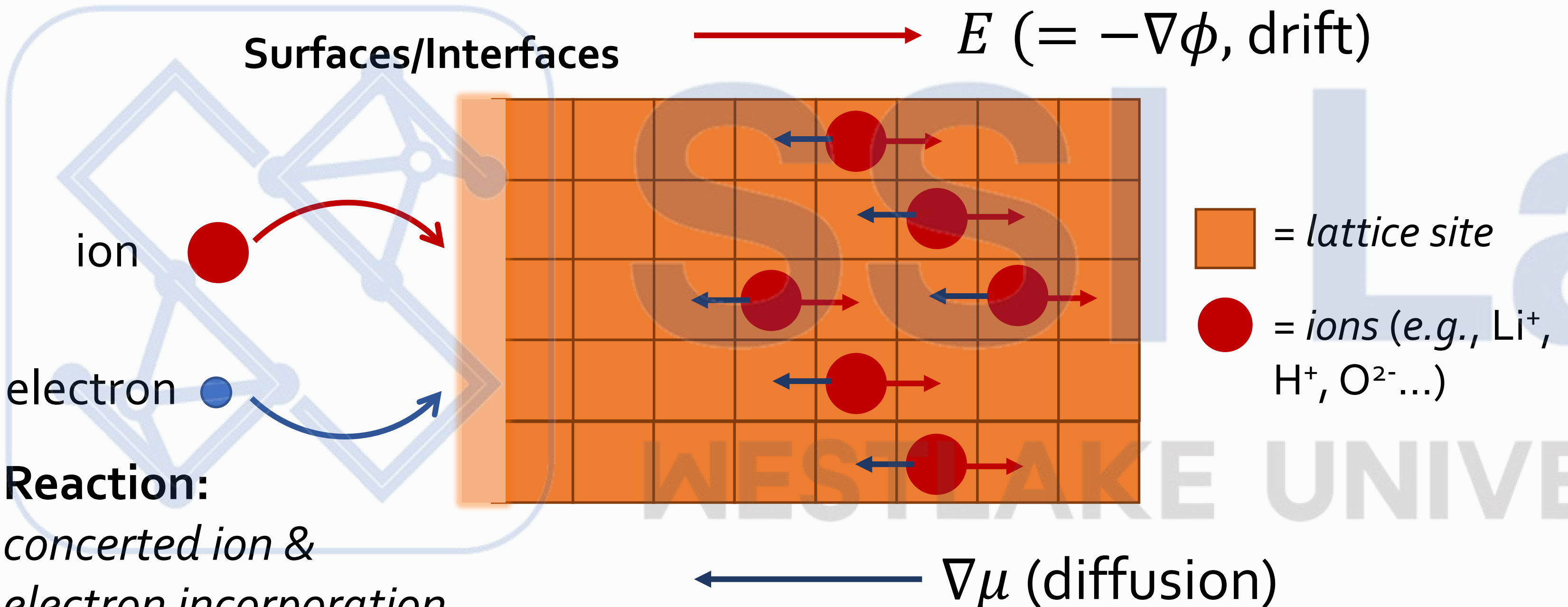
Grading Policies:

- *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.

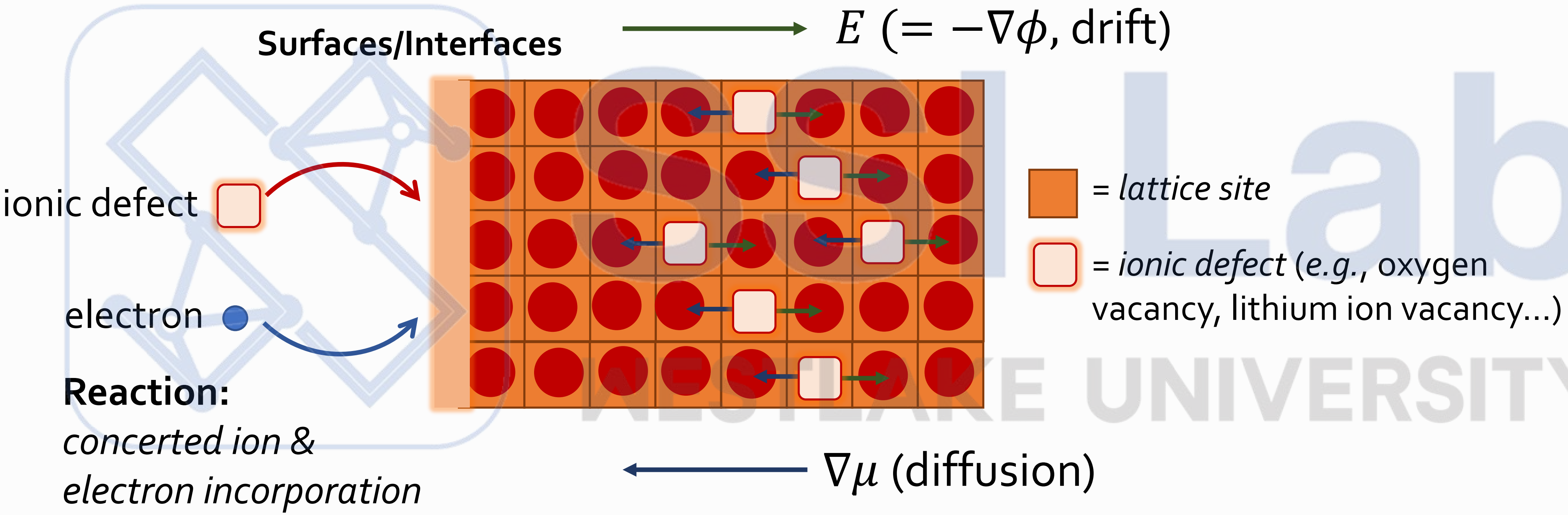
Let's come back to this picture… but with a twist



Reaction:
concerted ion & electron incorporation

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

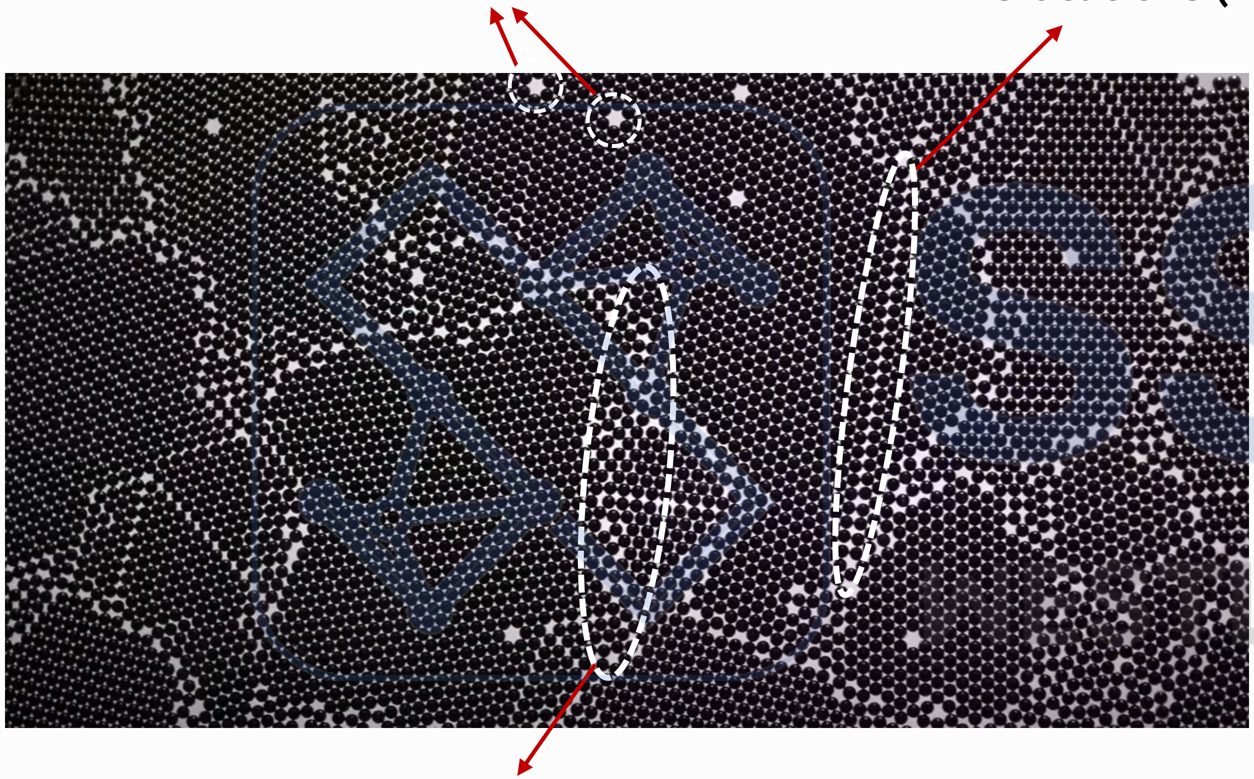
Let's come back to this picture… but with a twist

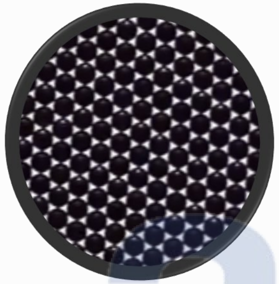


Ion motion: *drift + diffusion*

(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!"

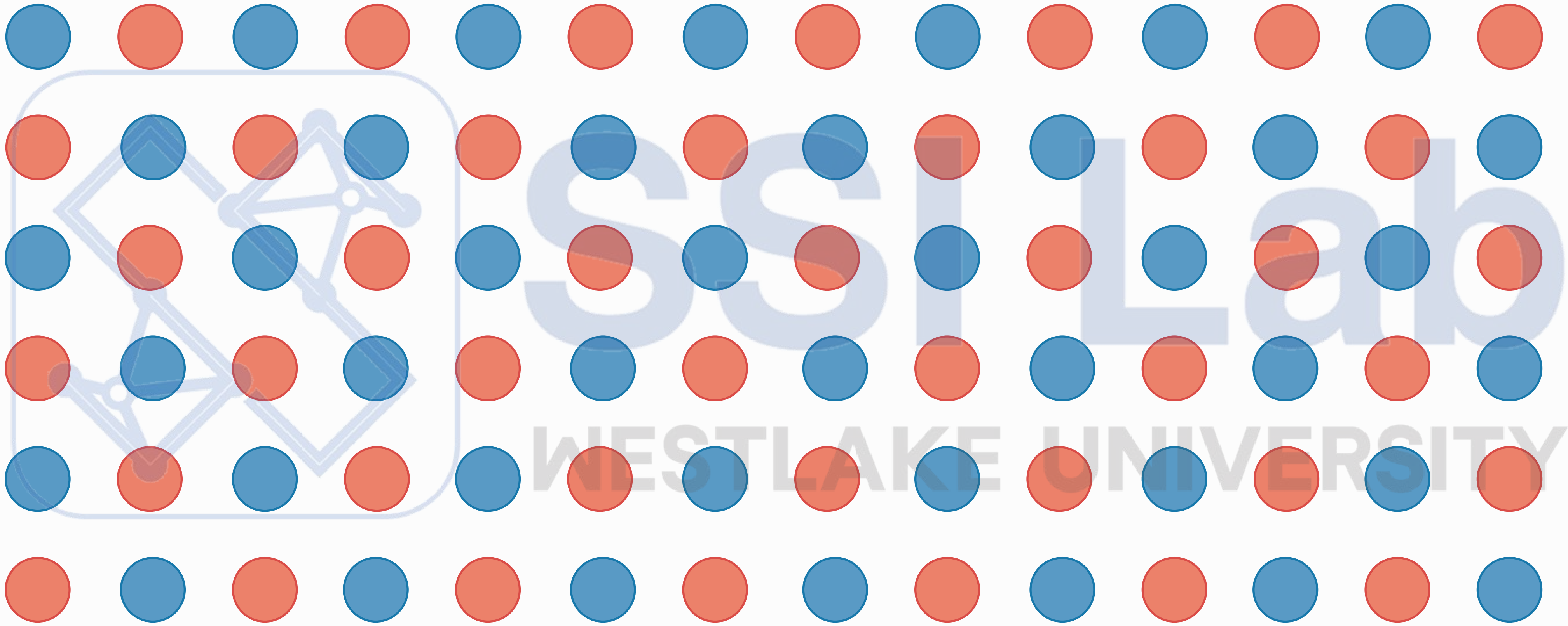
-Sir Colin Humphreys

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

Categories of defects with different dimensions

- Defects in crystalline solids
  - 0-D: point defects
    - Vacancy
    - Substitution
    - Interstitial
    - Anti-site
  - 1-D: dislocations
    - Edge dislocations
    - Screw dislocations
  - 2-D defects
    - Surfaces
    - Interfaces
    - Grain boundaries

The Perfect (Ionic) Crystalline Solid

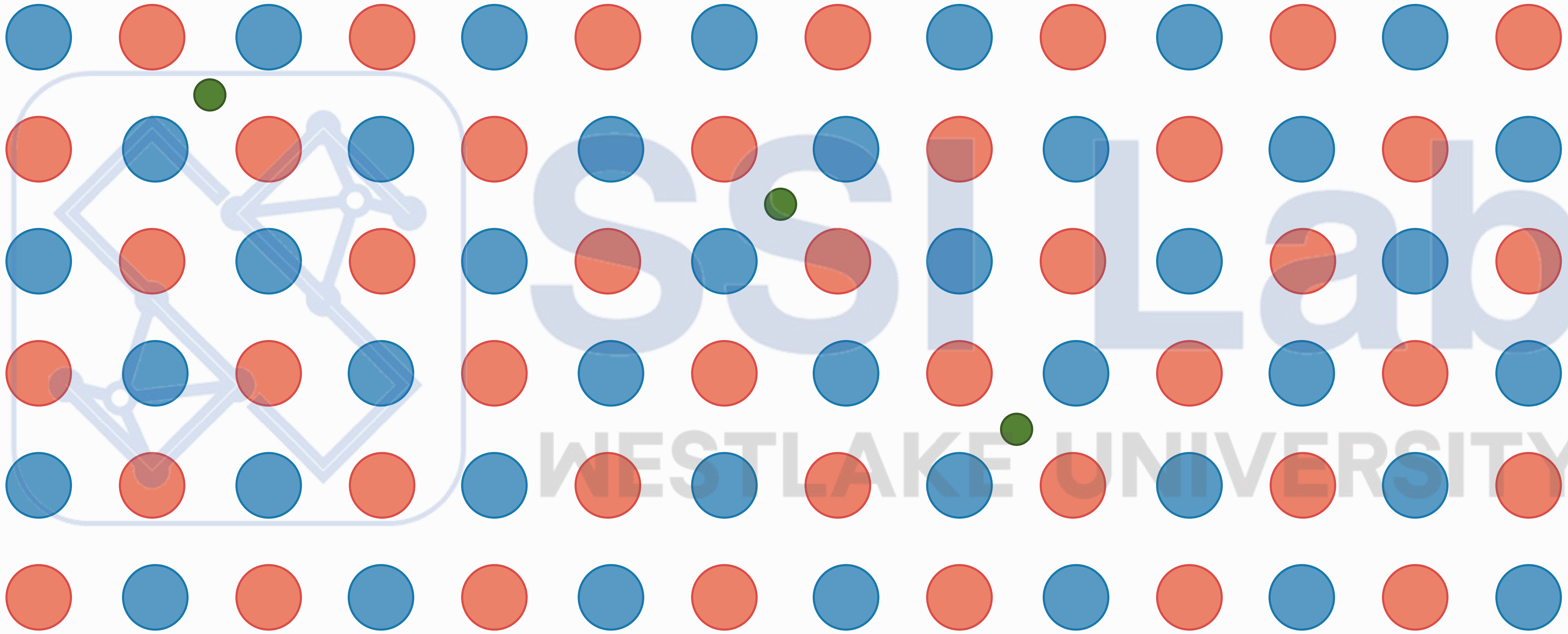


Cation
(*e.g.* Na^+)

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

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

The Real (Ionic) Crystalline Solid

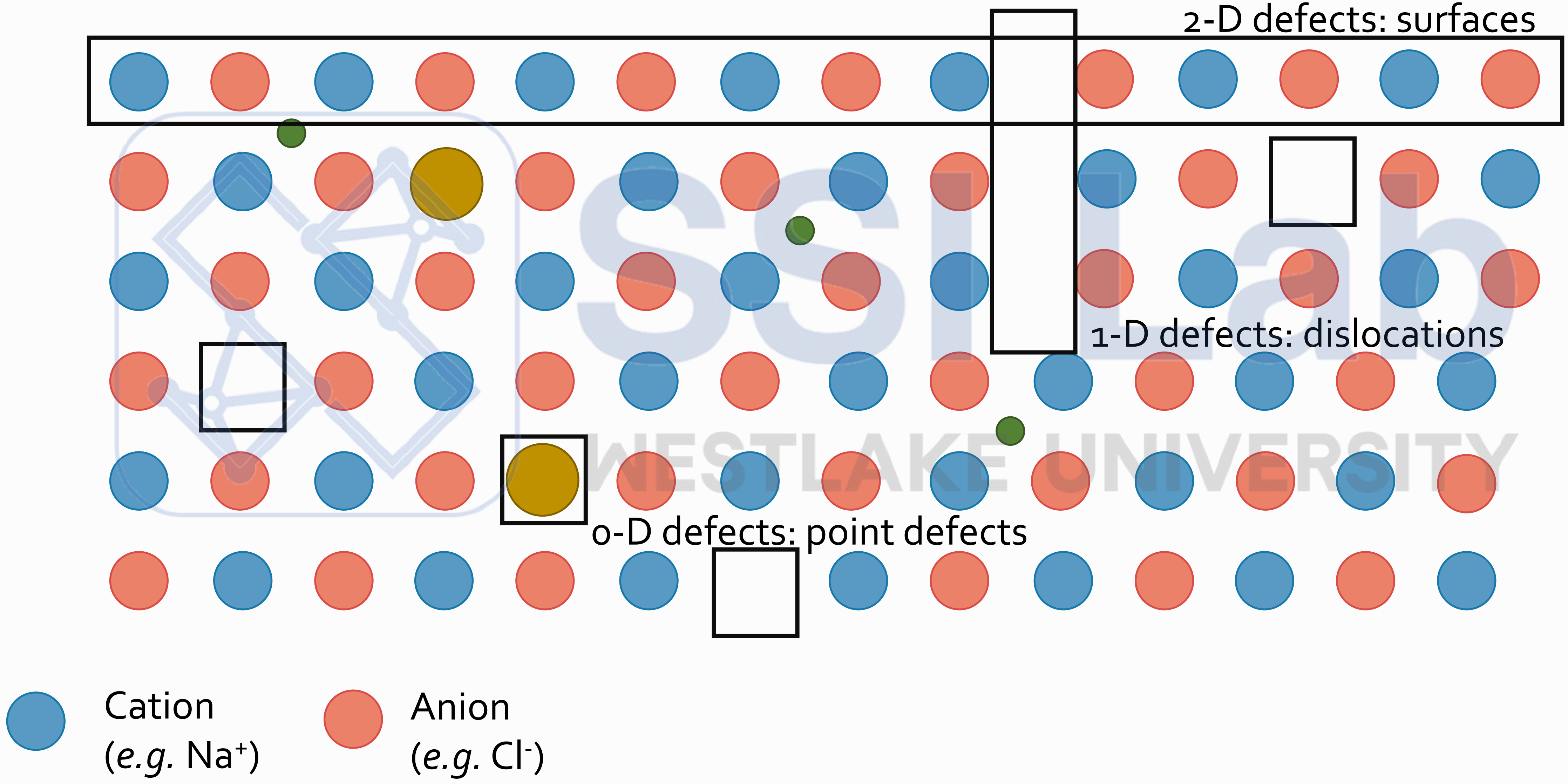


Cation
(*e.g.* Na^+)

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

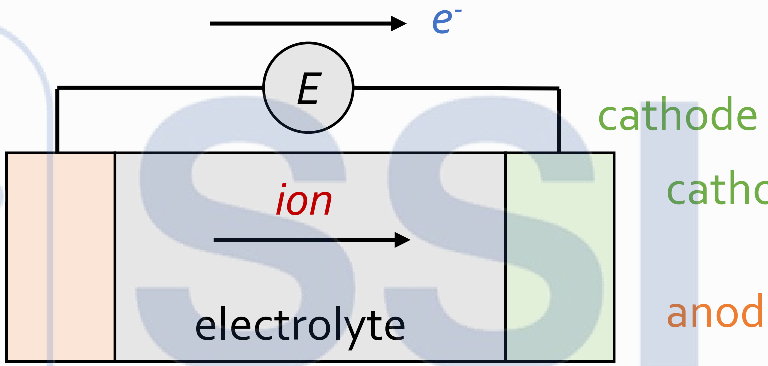
Point (0D) defect

The Real (Ionic) Crystalline Solid



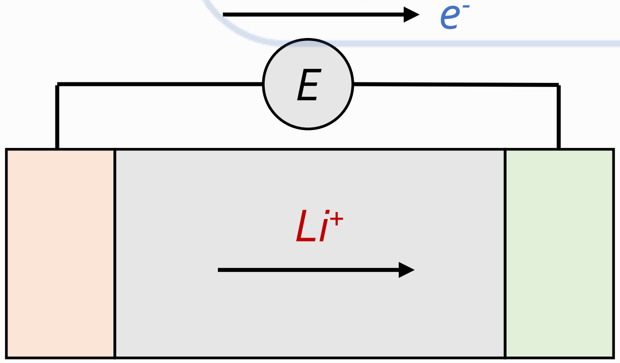
Fundamentals of Electrochemical Energy Systems

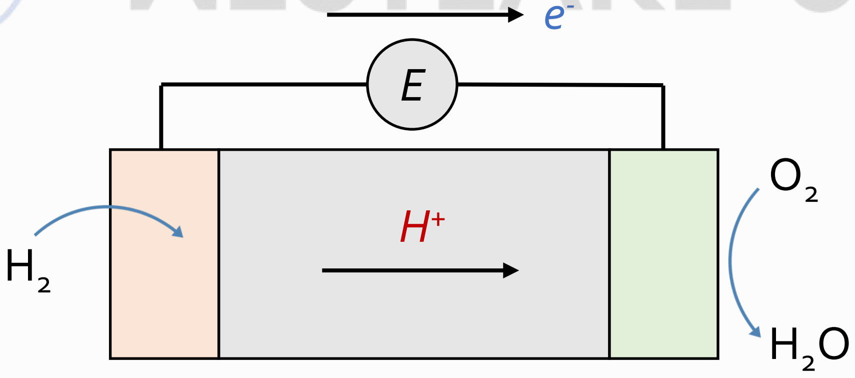
Electrochemical energy systems are based on **concerted motion (transport) of ions + electrons**

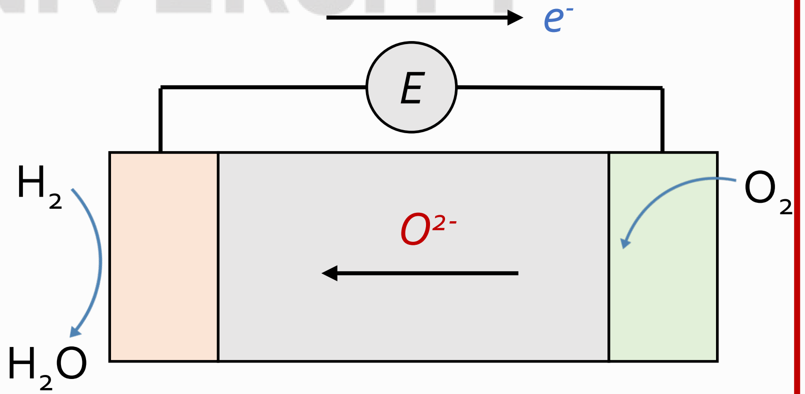


cathode: where ***conventional*** current leaves
reduction reaction

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

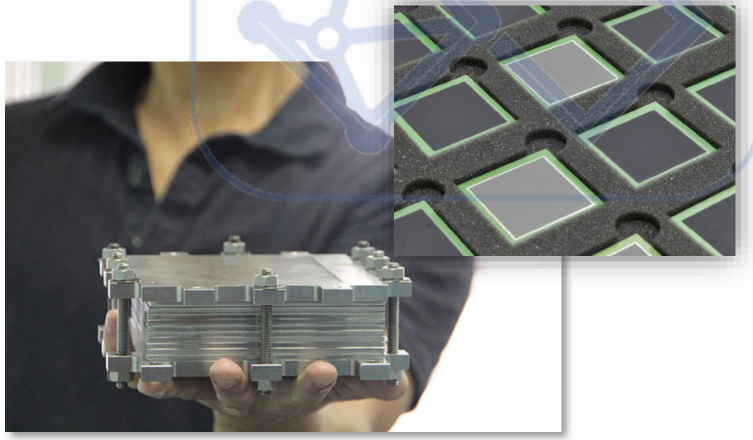




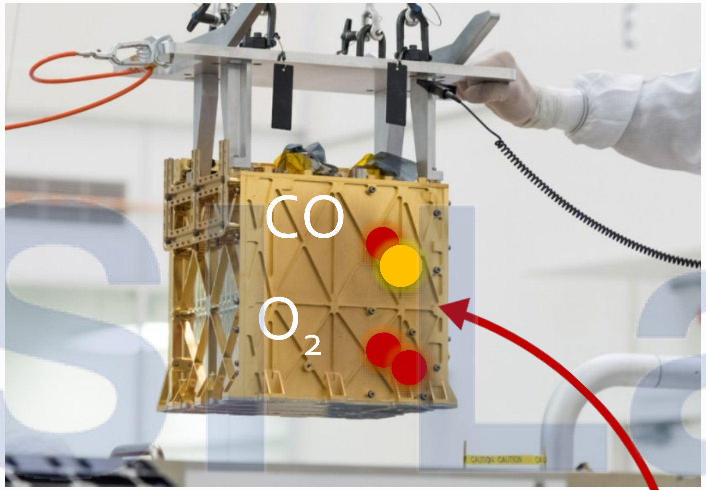


Solid Oxide Fuel/Electrolysis Cells (SOFC/SOECs)

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)

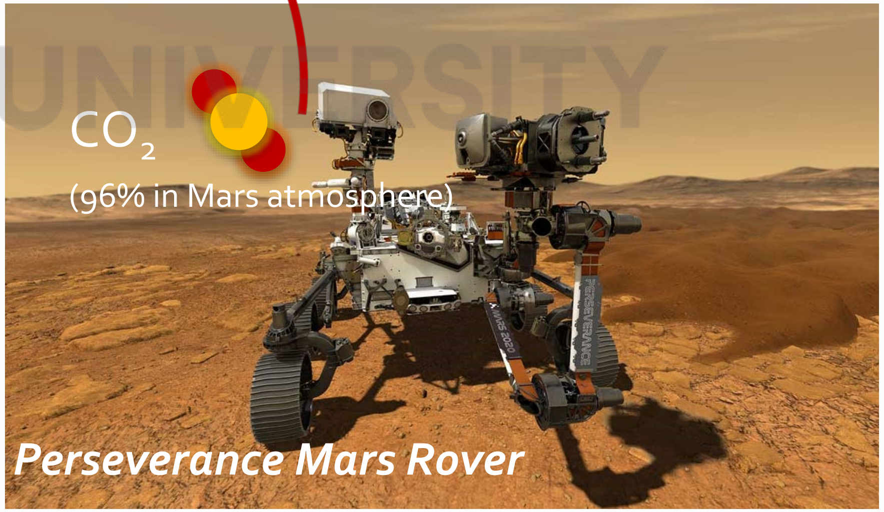


MOXIE unit on ***Perseverance*** **Mars rover**

CO_2

+ Renewable Energy

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



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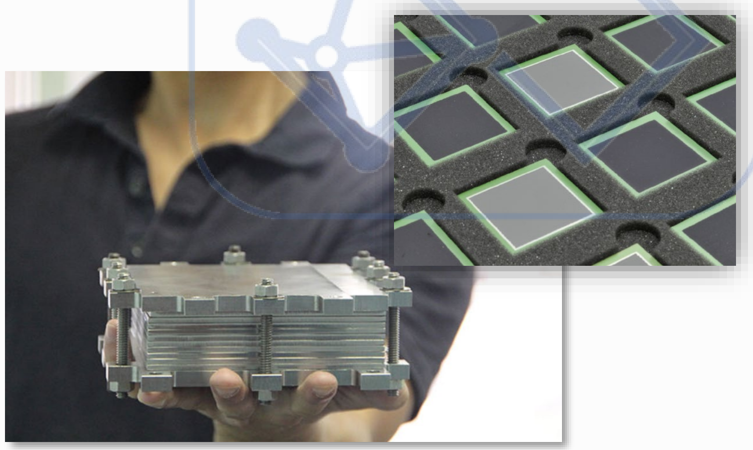
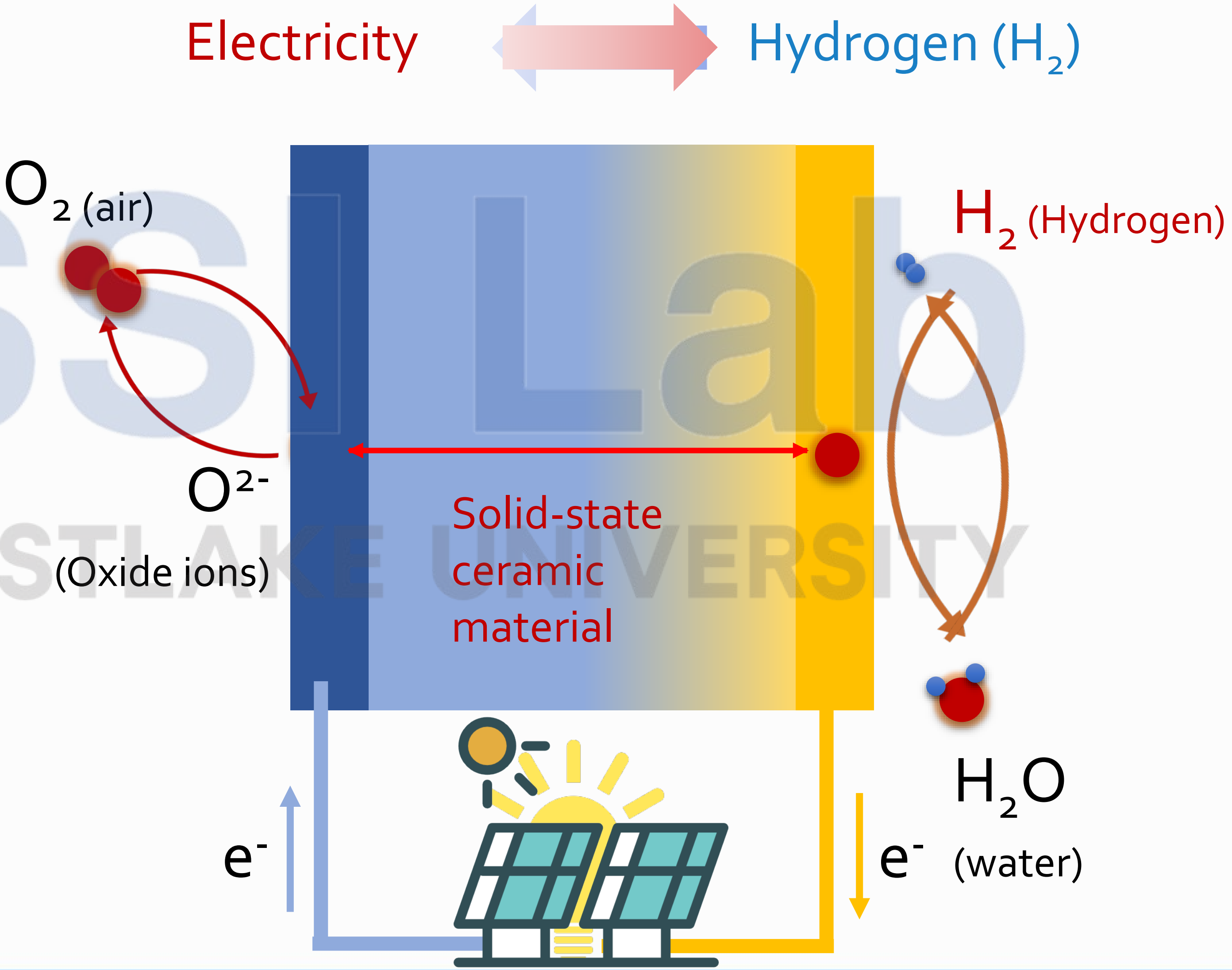
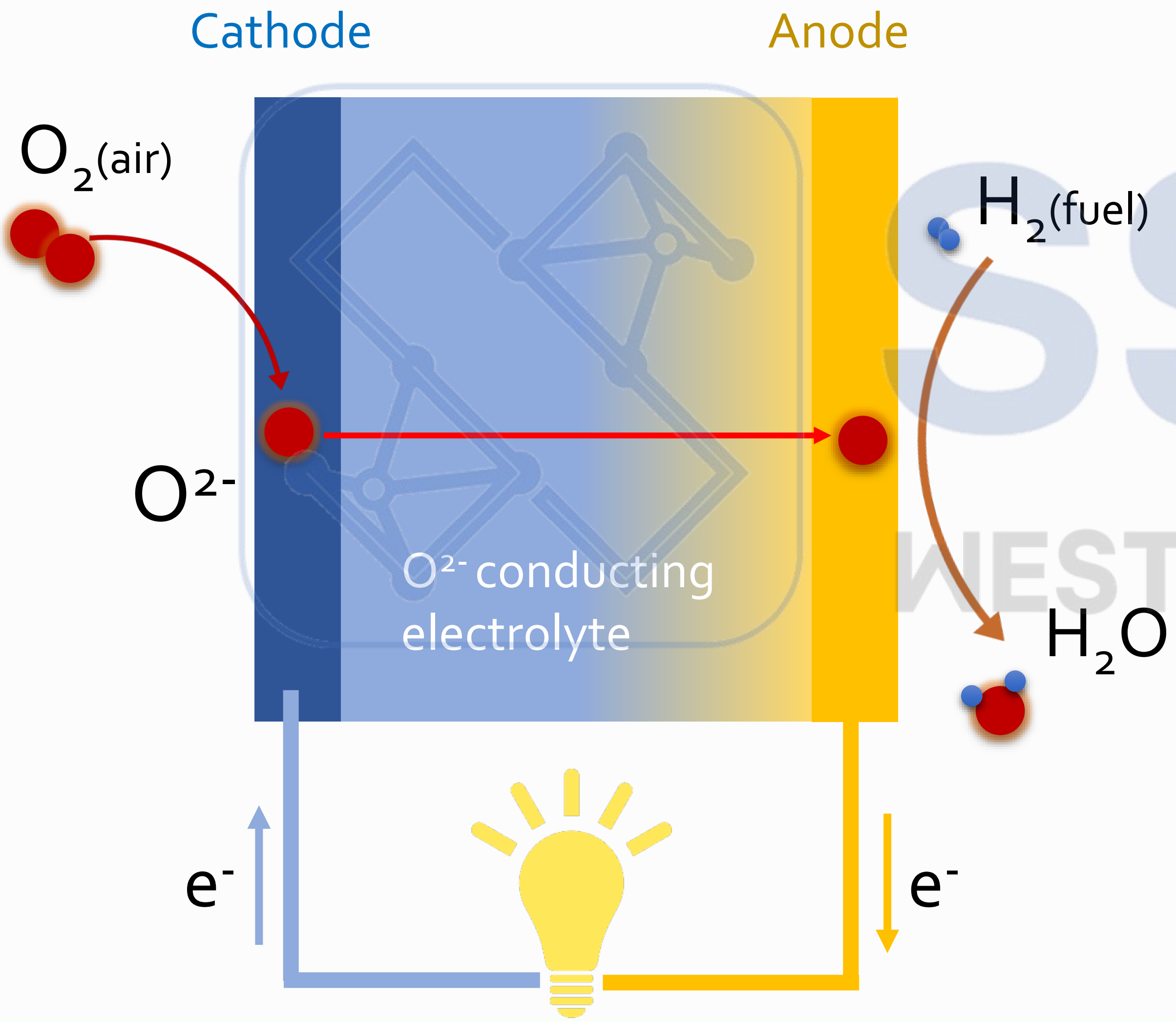


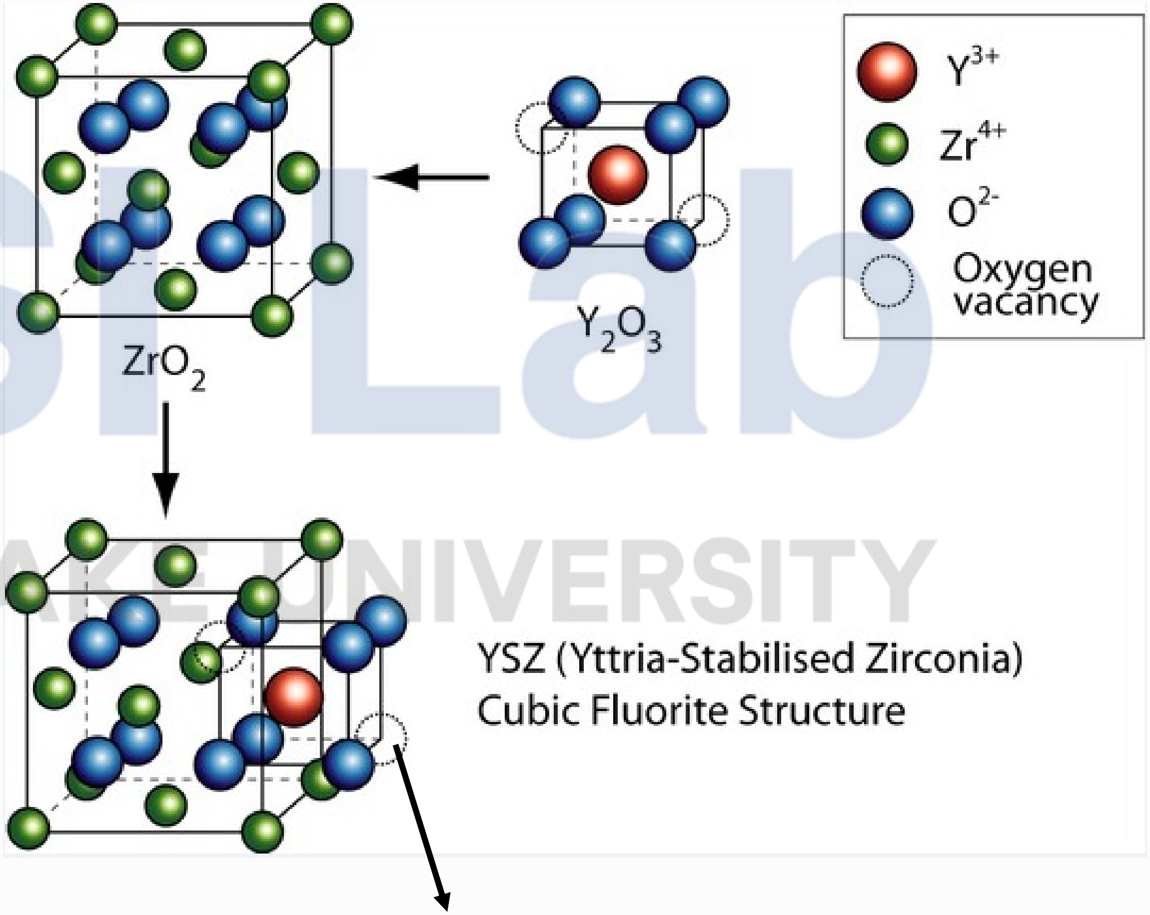
Solution
High-performance ***reversible*** solid oxide fuel/electrolysis cells (SOFC/SOECs)



The operation of SOCs relies on ionic point defects

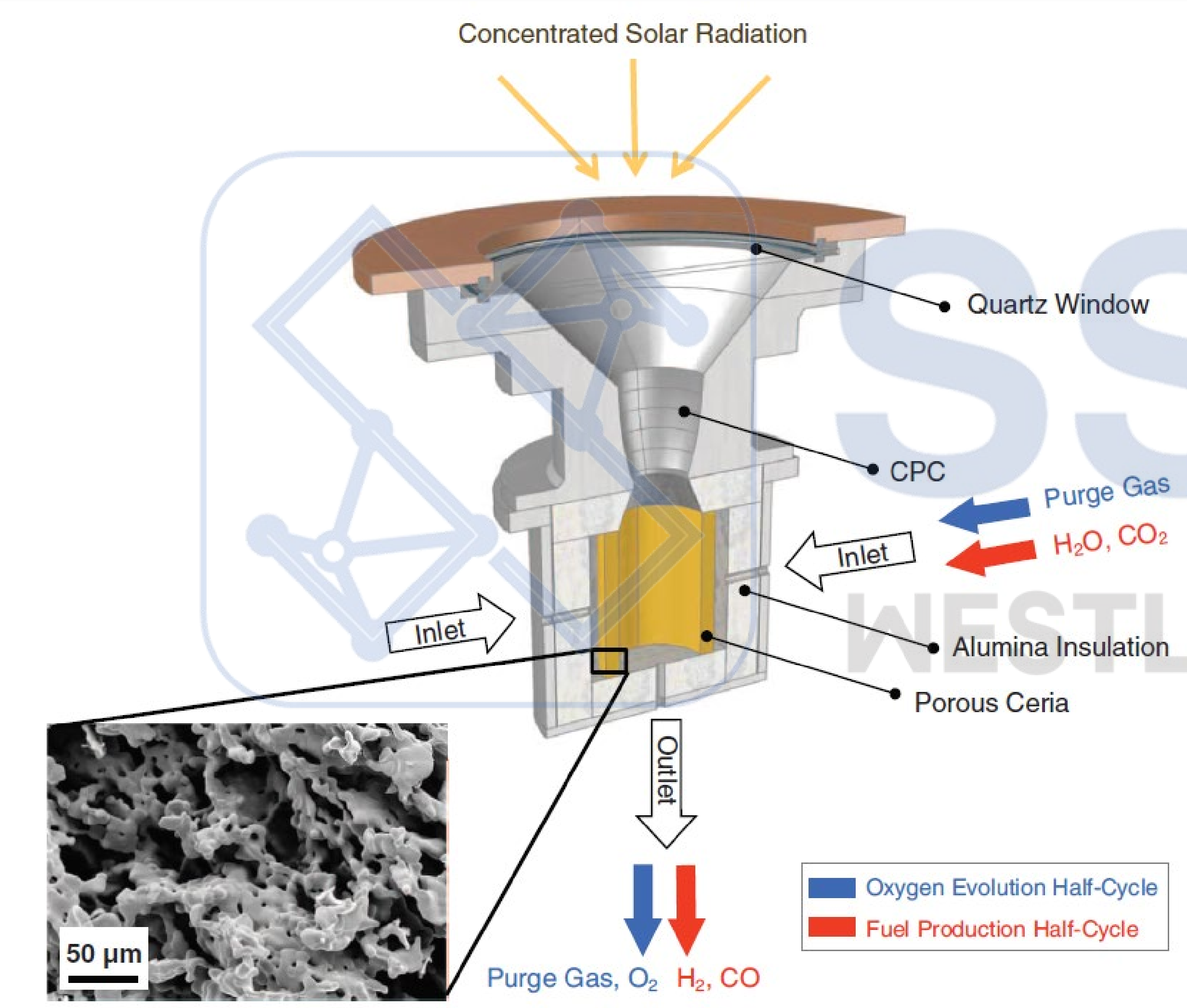


Y_2O_3-stablized ZrO_2 (YSZ) as electrolyte



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

CeO_2

Step 1: Reduction

$1/x\ CeO_2 \rightarrow 1/x\ CeO_{2-x} + ½\ O_2$

(High temperature)

Step 2: fuel generation

$1/x\ CeO_{2-x} + CO_2$

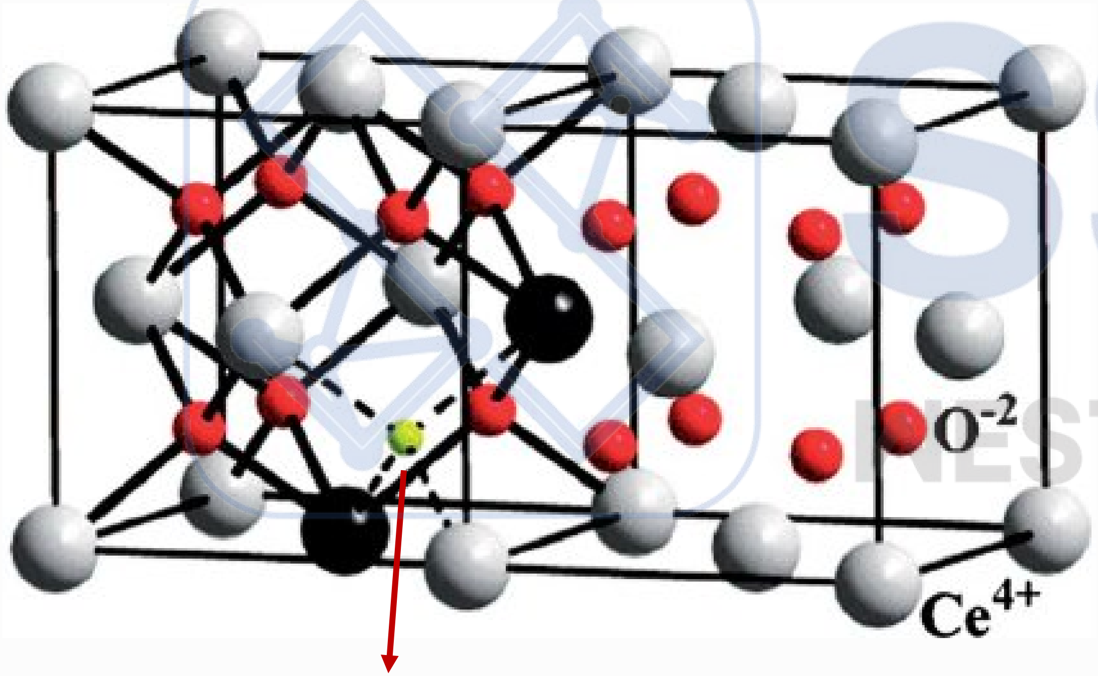
$\rightarrow 1/x\ CeO_2 + CO$

(Lower temperature)

CeO_{2-x}

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

CeO_2

Step 1: Reduction

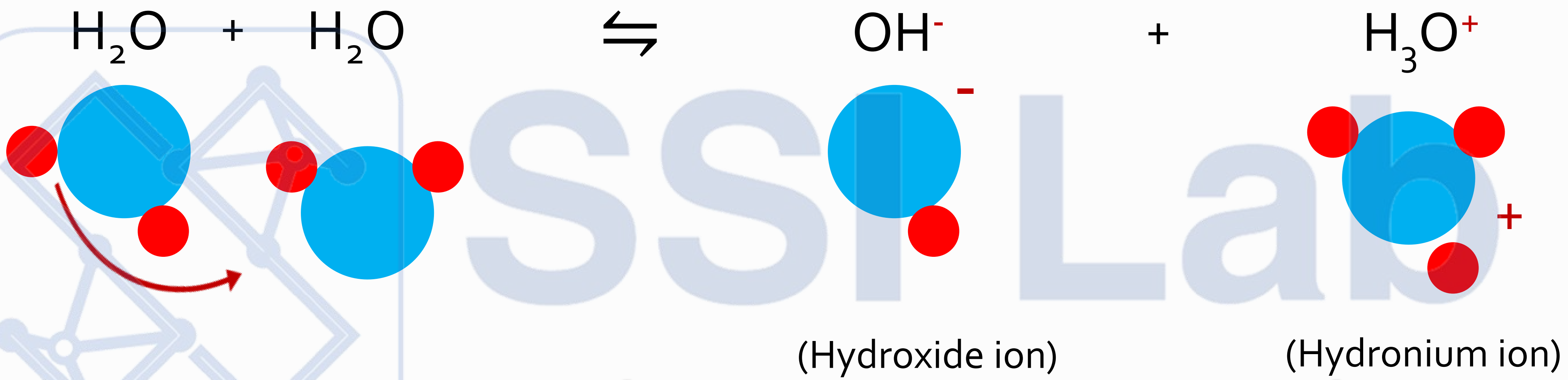
1/x CeO2 → 1/x CeO_{2-x} + ½ O_2
(High temperature)

Step 2: fuel generation

1/x CeO_{2-x} + CO_2
→1/x CeO2 + CO
(Lower temperature)

CeO_{2-x}

"Defects" in Liquid-phase Water



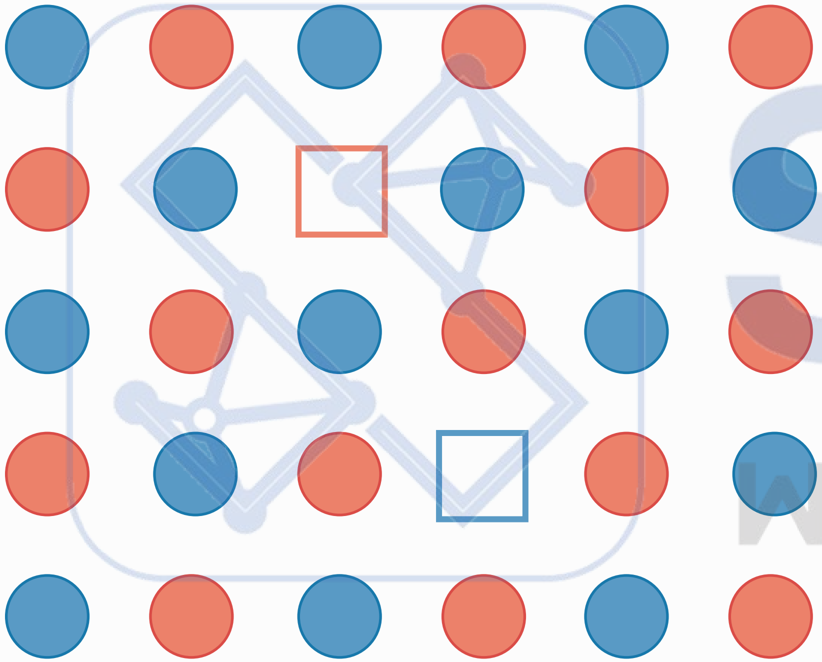
How many "defects" are we talking about?

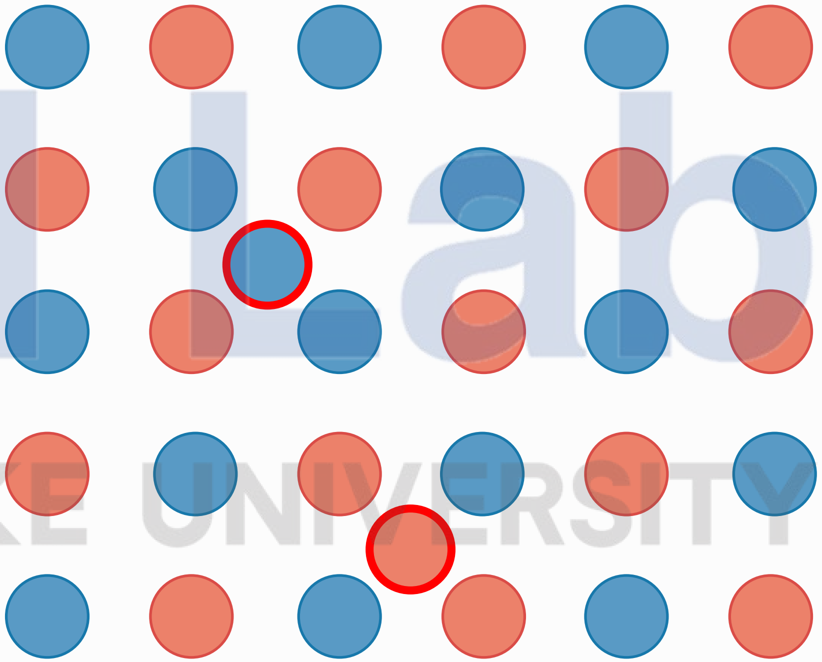
Chemical equilibrium (water self-ionization): $K = [H_3O^+]\,[OH^-]$

at RT, $K = 1 \times 10^{-14}$ → $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ mol/L (*i.e.* PH = 7)

1 L of water = 55. 6 moles → 1 pair of H_3O^+ and OH^- every ~3×10^8 water molecules (*i.e.* not many)

Vacancy and Interstitial Defect





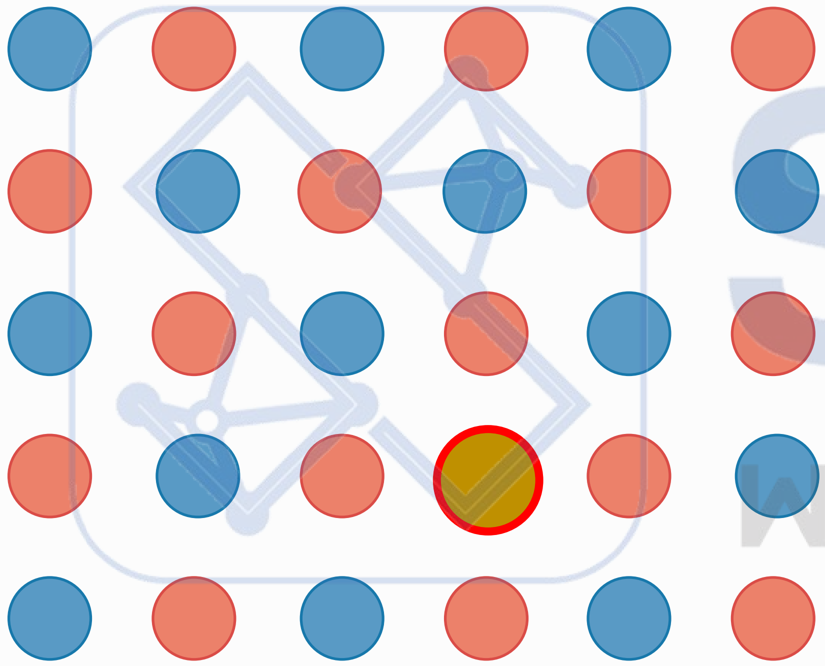
Cation Vacancy
Anion Vacancy

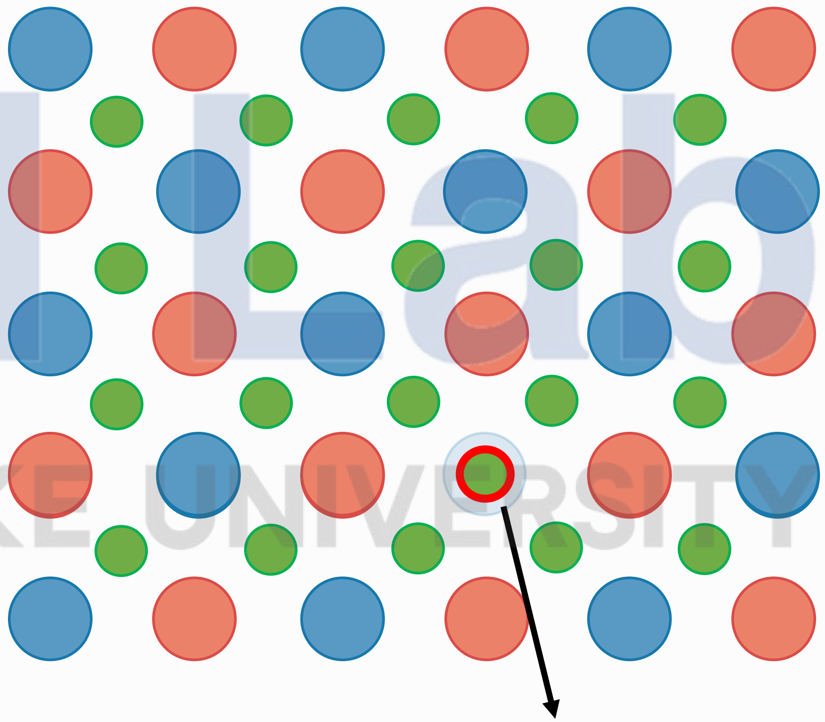
Cation
(e.g. Na^+)

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^{-})

Cation 2

Anti-site defect

Kröger-Vink Notation

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

$$A^{Chg}_{S}$$

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

$$A_S^{Chg}$$

E.g. 1:

Y_2O_3 doped ZrO_2 (YSZ)

$$Y_{Zr}'$$

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

$$V_O^{\bullet\bullet}$$

Oxygen(O^{2-}) vacancy

E.g. 2:

Schottky pair in NaCl

$$V_{Na}'$$

Sodium (Na^+) vacancy

$$V_{Cl}^{\bullet}$$

Chlorine(Cl^-) vacancy

Defect Reactions

$$H_2O + H_2O \leftrightharpoons OH^- + H_3O^+$$

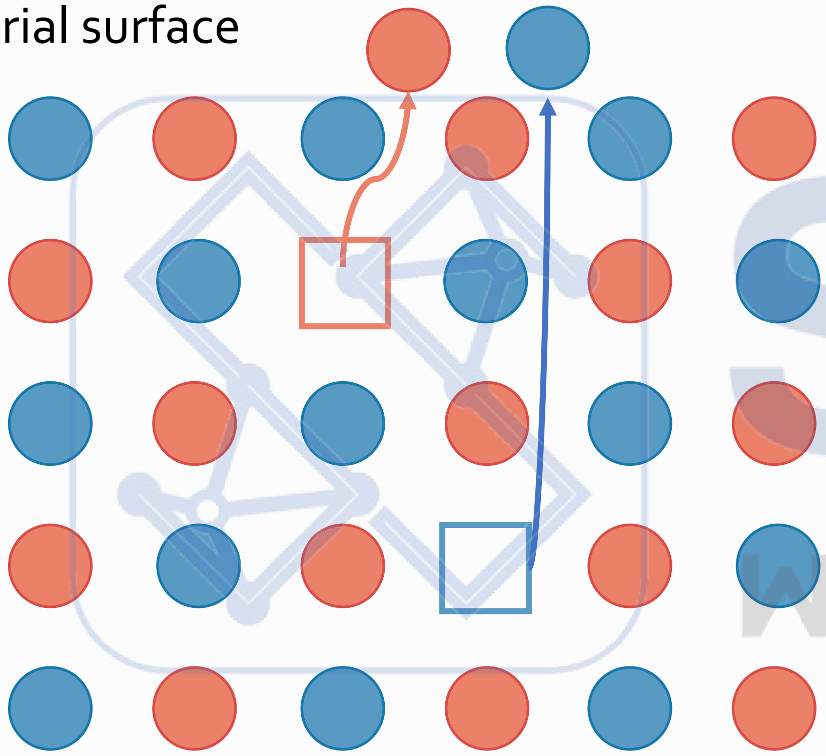
(Hydroxide ion) (Hydronium ion)

Let's go back to the example of "defects" in water.
What is the equivalent cases in crystalline solids?

Conservation rules of chemical reactions:

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

Schottky Reaction (or commonly Schottky Pair)



Cation (e.g. Na^+) Anion (e.g. Cl^-)

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

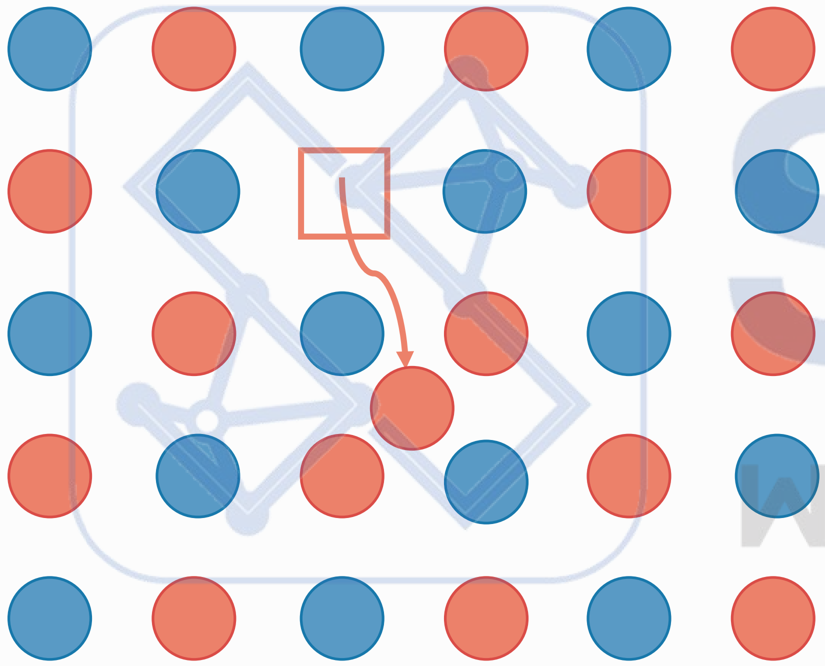
How to write the chemical formula for Schottky reaction?

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

Or more commonly:

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

Frenkel Reaction (or commonly Frenkel Pair)



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

How to write the chemical formula for Schottky reaction?

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

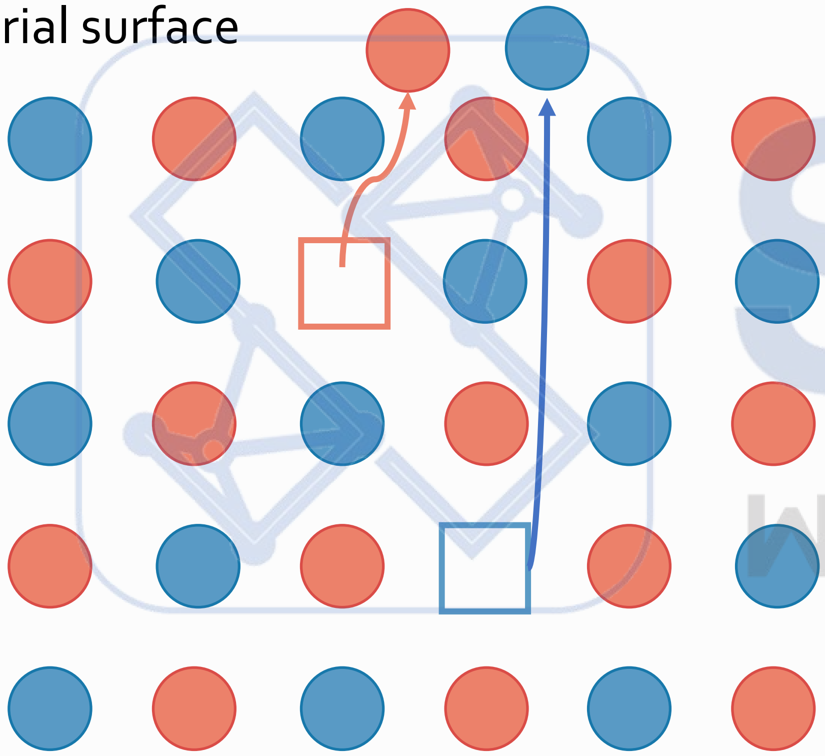
Or more commonly:

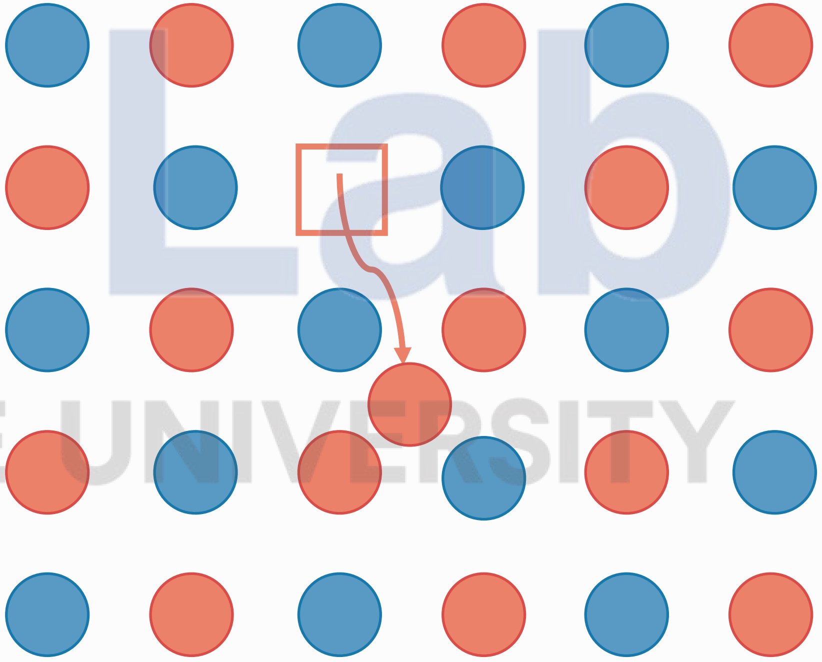
$$null \leftrightharpoons Cl_i' + V_{Cl}^{\cdot}$$

(*null* means the perfect lattice)

Defect chemical equilibrium

Question: How to predict defect concentrations at equilibrium?





Schottky Reaction

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

Frenkel Reaction

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

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:

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

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 $\mu_i = \mu_i^0 + RTlnc_i$

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:

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

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

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

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

Then why do defects form?

$-T\Delta_{\text{defect}}S$, *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*)

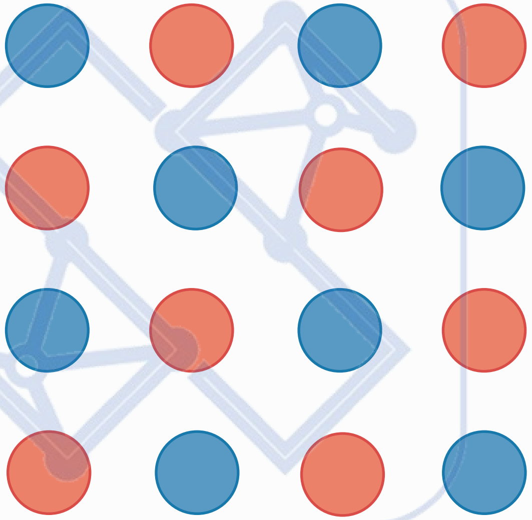
More complicated dependence on # of defects
The main source of entropy term

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

$$\Delta G = n_D(\Delta_{\mathrm{defect}}H - T\Delta_{\mathrm{vib}}S) - T\Delta_{\mathrm{cfg}}S(n_D)$$

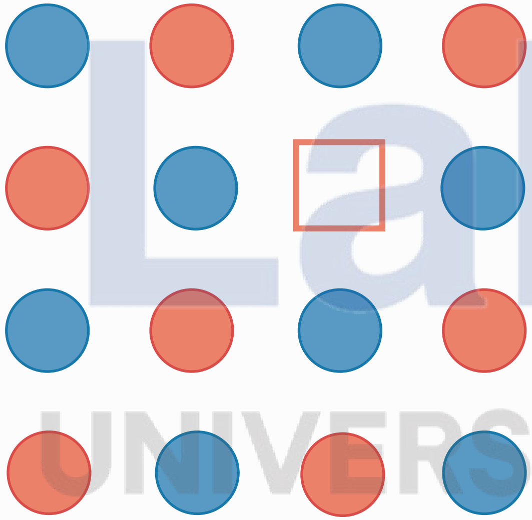
Configurational Entropy

Perfect Crystal



Only 1 way to configure the lattice

Real Crystal with one vacancy



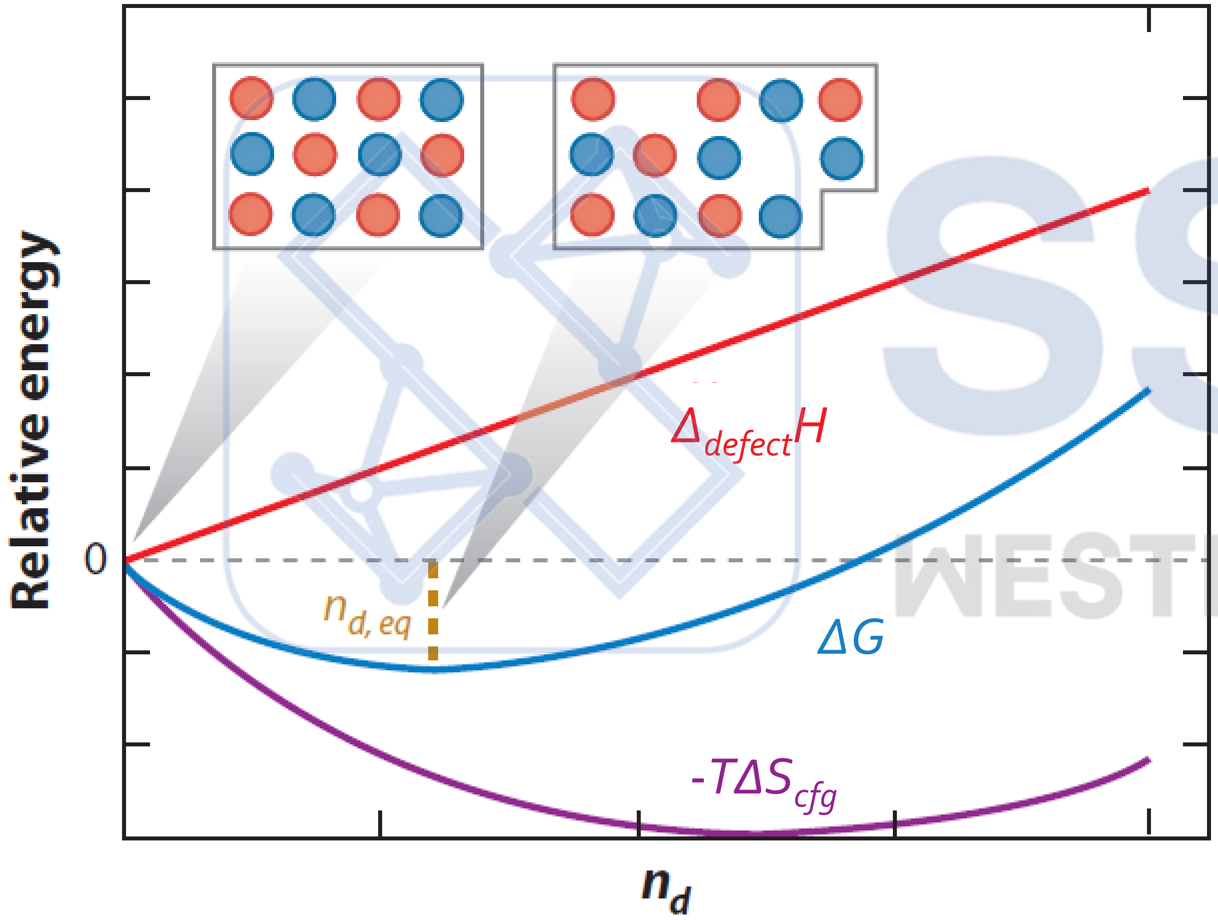
8 different ways to configure the lattice

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

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

Defect concentration at equilibrium

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



$$\Delta G = n_D(\Delta_{\mathrm{defect}}H - T\Delta_{\mathrm{vib}}S) - T\Delta_{\mathrm{cfg}}S(n_D)$$

If one solves for defect concentration at equilibrium, we have: (derivation skipped)

$$n_{D,eq} = N\exp\left(\frac{\Delta_{\mathrm{vib}}S}{R}\right)\exp\left(-\frac{\Delta_{\mathrm{defect}}H}{RT}\right)$$

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

Defect chemical equilibrium

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

From any given chemical reaction *a*A + *b*B → *c*C + *d*D

We have:

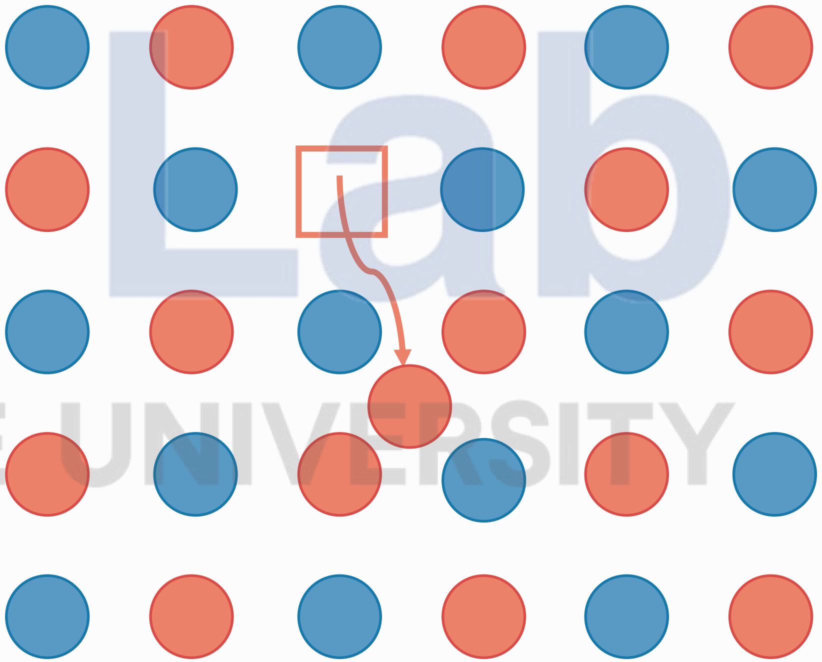
$$\Delta G^0_{rxn} = \Delta H^0_{rxn} - T\Delta S^0_{rxn} = -RT ln\ K$$

$$= -RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

rxn: reaction
K: equilibrium constant

If we apply the same treatment to Frenkel reaction:

$$\Delta G^0_{Frk} = \Delta H^0_{Frk} - T\Delta S^0_{Frk} = -RT \ln([Cl_i'][V_{Cl}^{\cdot}])$$



Frenkel Reaction

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

Defect chemical equilibrium

Recall the conservation principles of chemical reactions

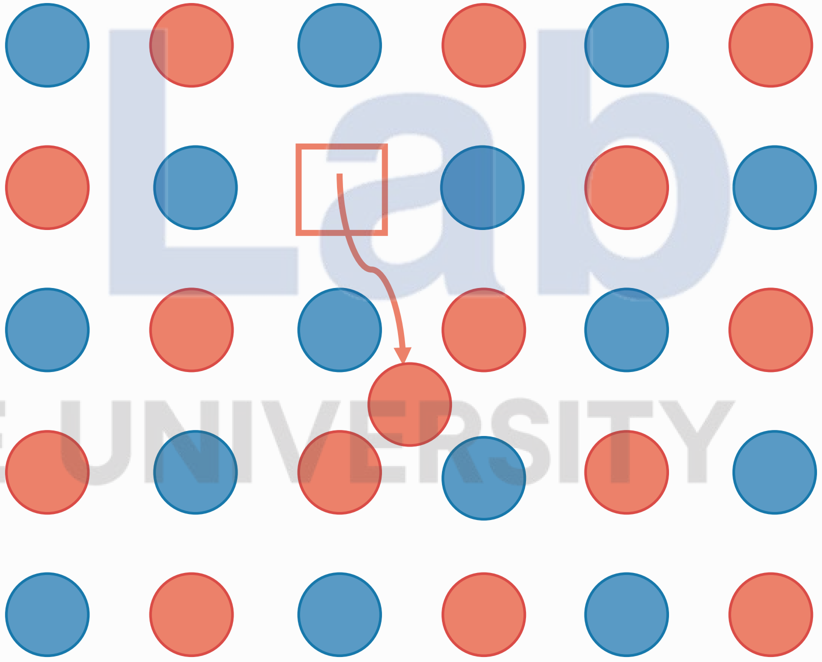
$$\Delta G^0_{Frk} = \Delta H^0_{Frk} - T\Delta S^0_{Frk} = -RT\ln([Cl_i'][V_{Cl}^{\cdot}])$$

Conservation rules of chemical reactions:

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

These means: $[Cl_i'] = [V_{Cl}^{\cdot}]$, therefore:

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



Frenkel Reaction

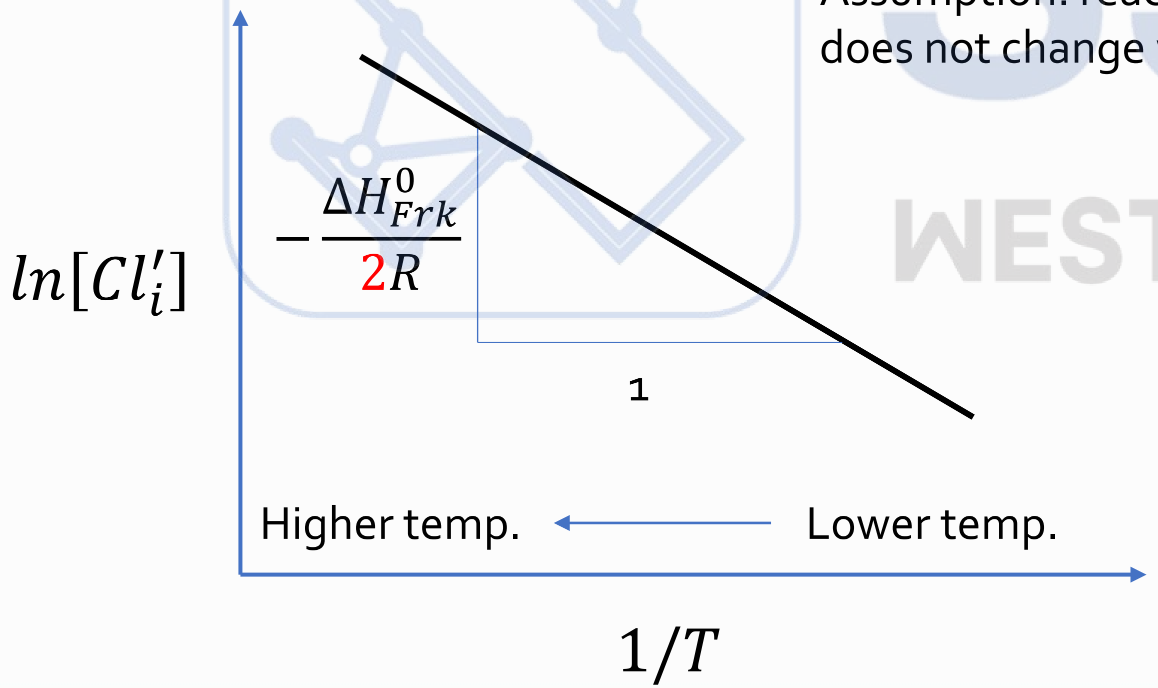
$$null \leftrightharpoons \mathrm{Cl_i'} + \mathrm{V_{Cl}^{\cdot}}$$

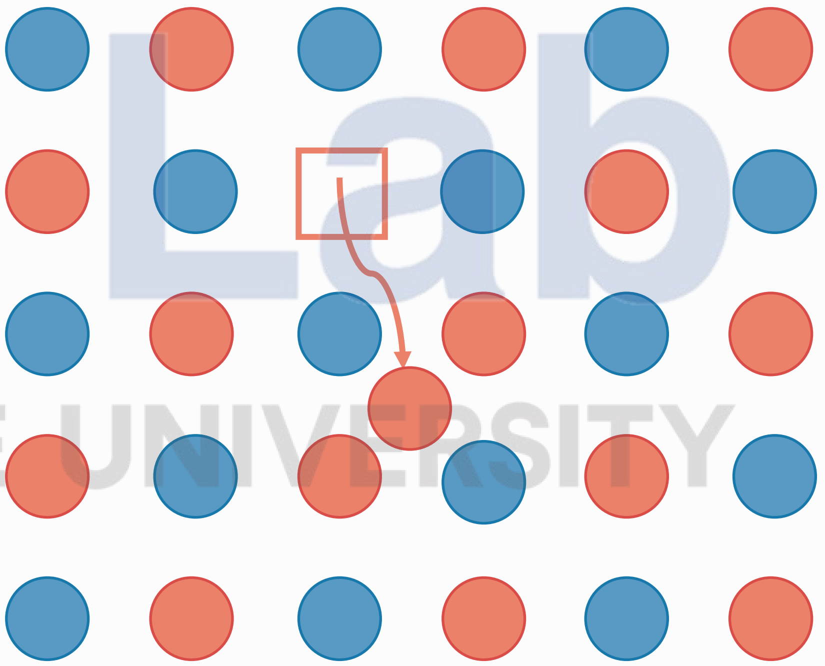
Defect chemical equilibrium

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*

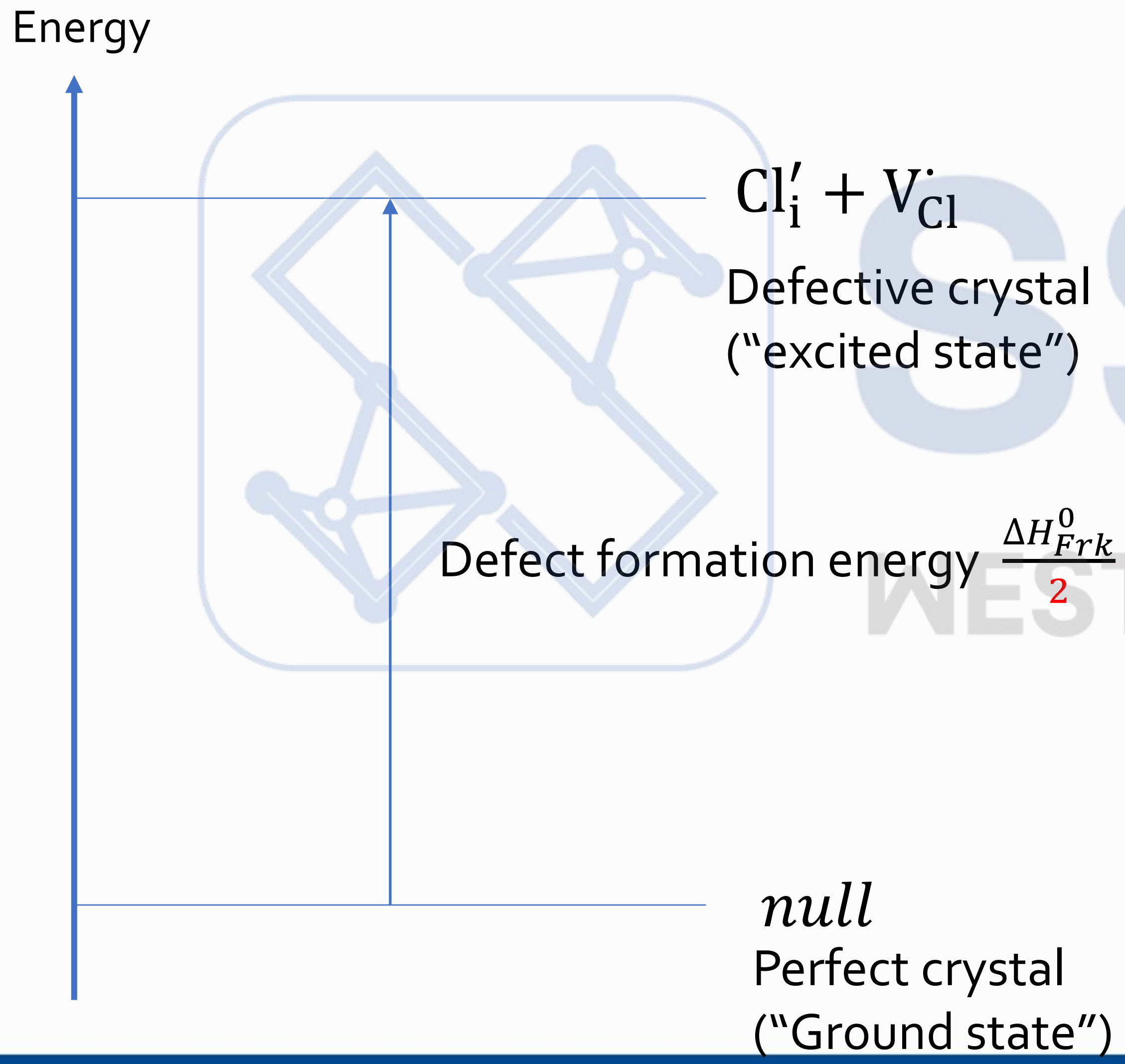




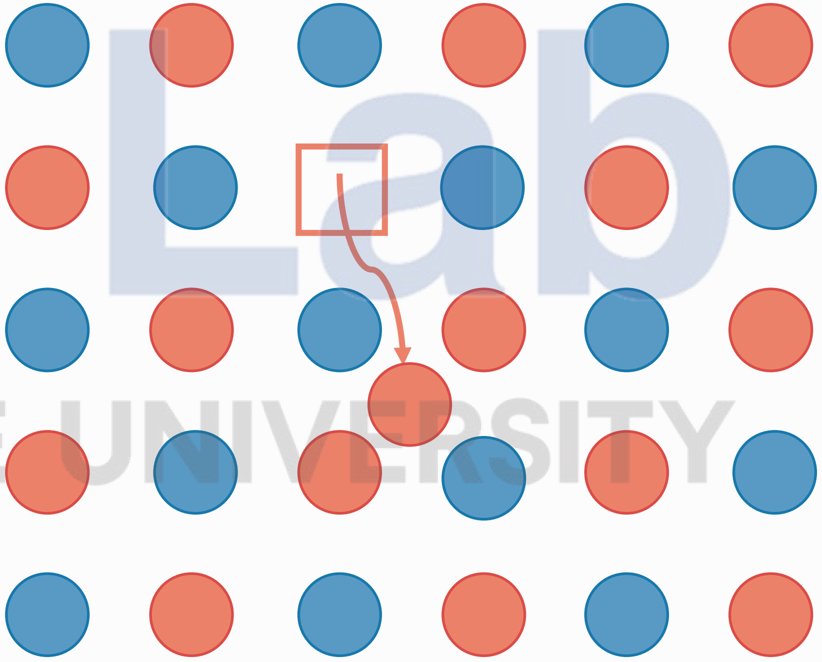
Frenkel Reaction

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

Another way to look at this problem



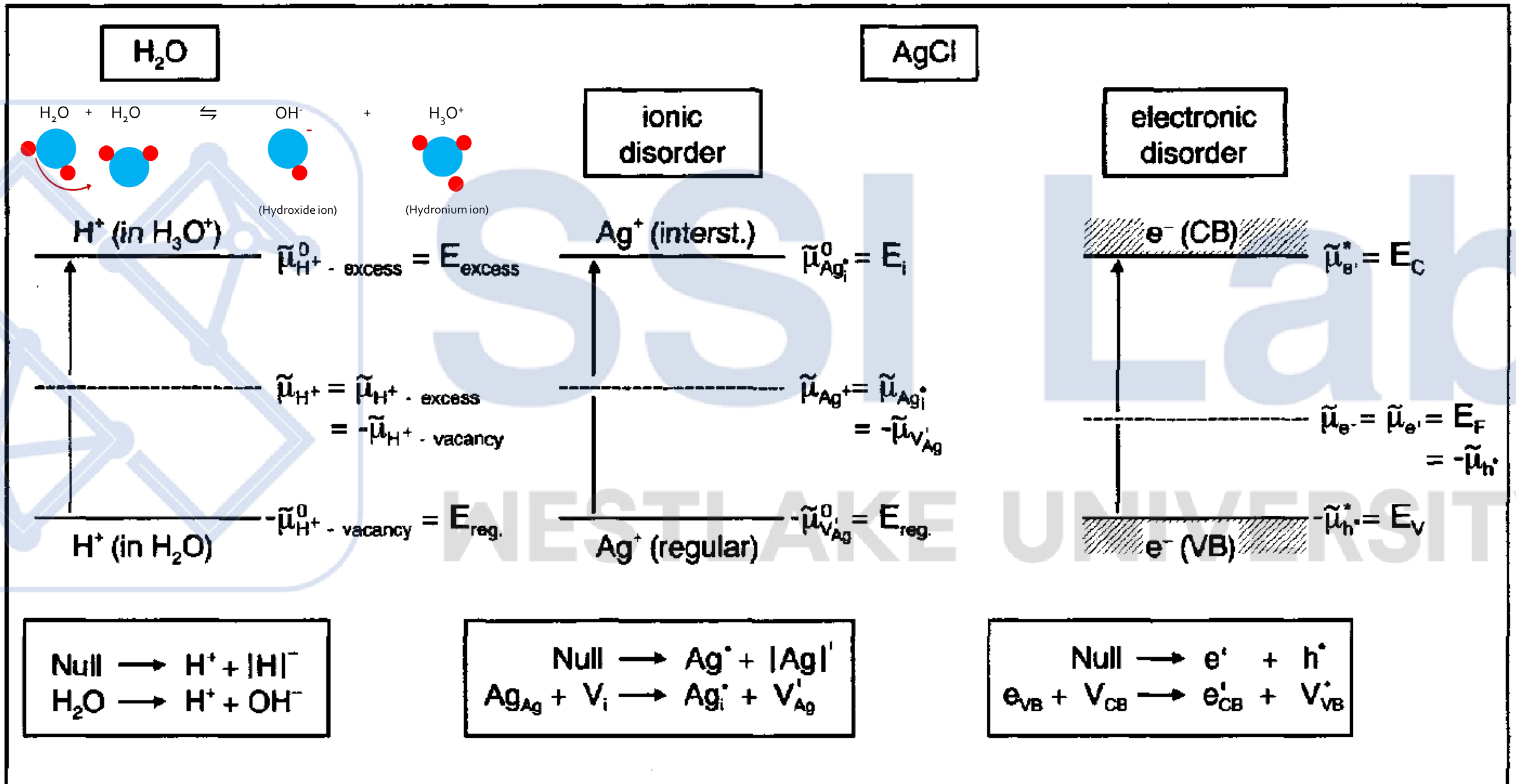
$$[Cl_i'] = [V_{Cl}^{\cdot}] = \exp\left(\frac{\Delta S_{Frk}^0}{2R}\right)\exp\left(-\frac{\Delta H_{Frk}^0}{2RT}\right)$$



Frenkel Reaction

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

Link to the case of water and electronic defects in semiconductors



$$\tilde{\mu}_i \equiv \mu_i + z_i F\phi = \mu_i^0 + RT\ln[i] + z_i F\phi = \tilde{\mu}_i^0 + RT\ln[i]$$

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

End of Lecture 1
Solid State Ionics Fall 2022

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