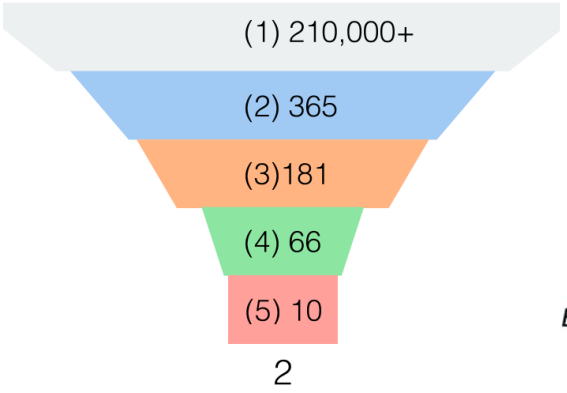
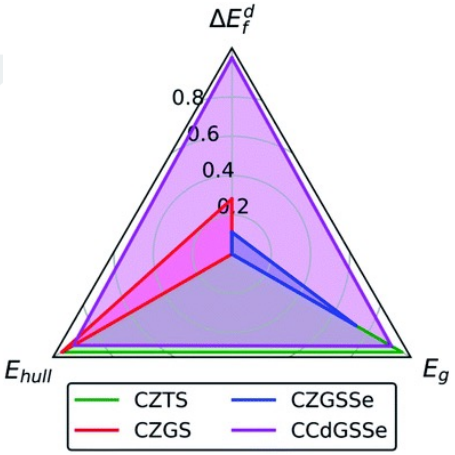




Theory-guided materials design for energy applications

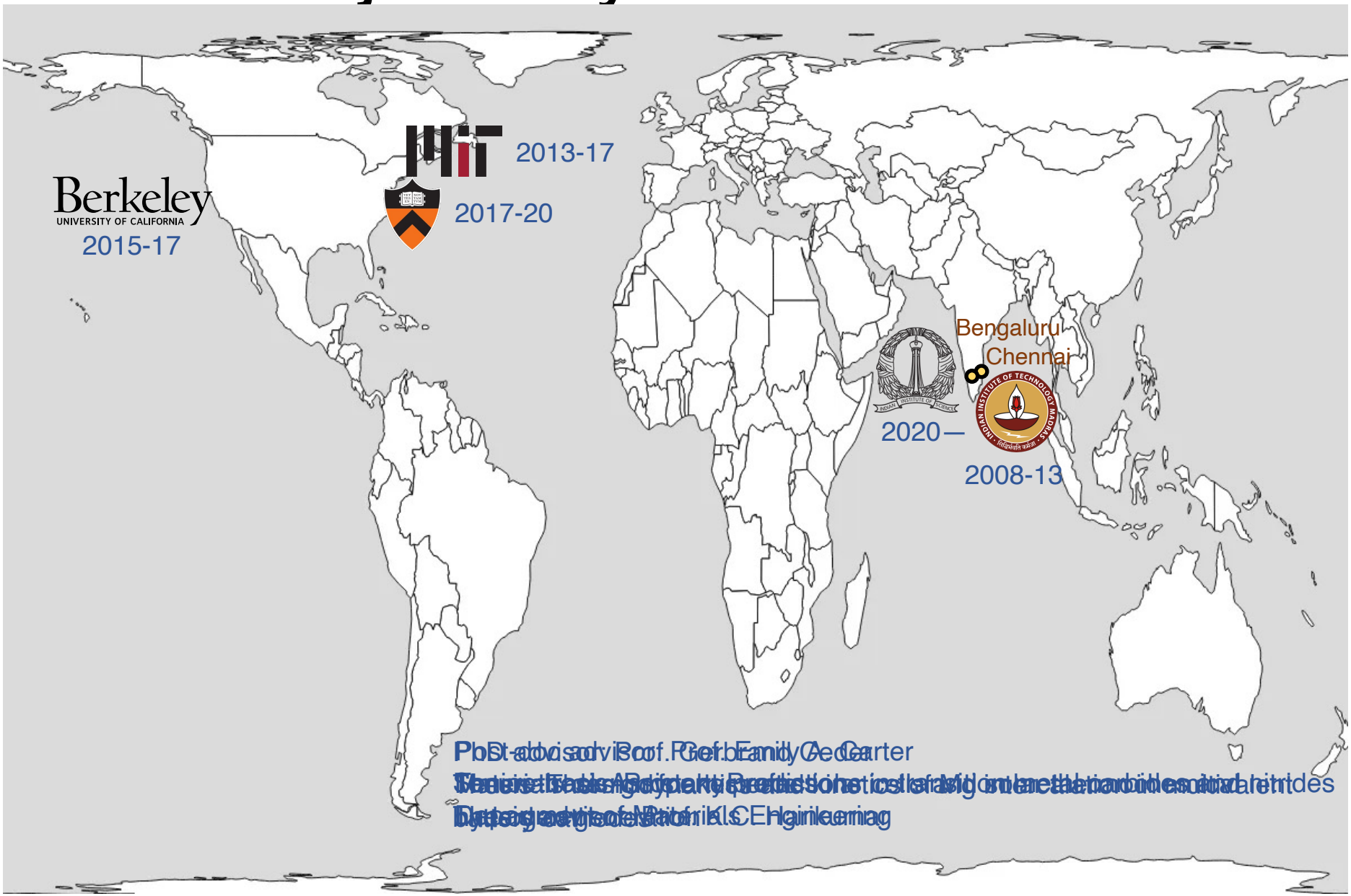
Sai Gautam Gopalakrishnan

Materials Engineering, Indian Institute of Science

saigautamg@iisc.ac.in; https://sai-mat-group.github.io

Seminar, Materials Advantage, National Institute of Technology Trichy
Sep 18, 2021

Scientific journey so far…



https://en.wikipedia.org/wiki/Gall%E2%80%93Peters_projection

Climate change is here

ipcc REPORTS SYNTHESIS REPORT WORKING GROUPS ACTIVITIES NEWS CALENDAR

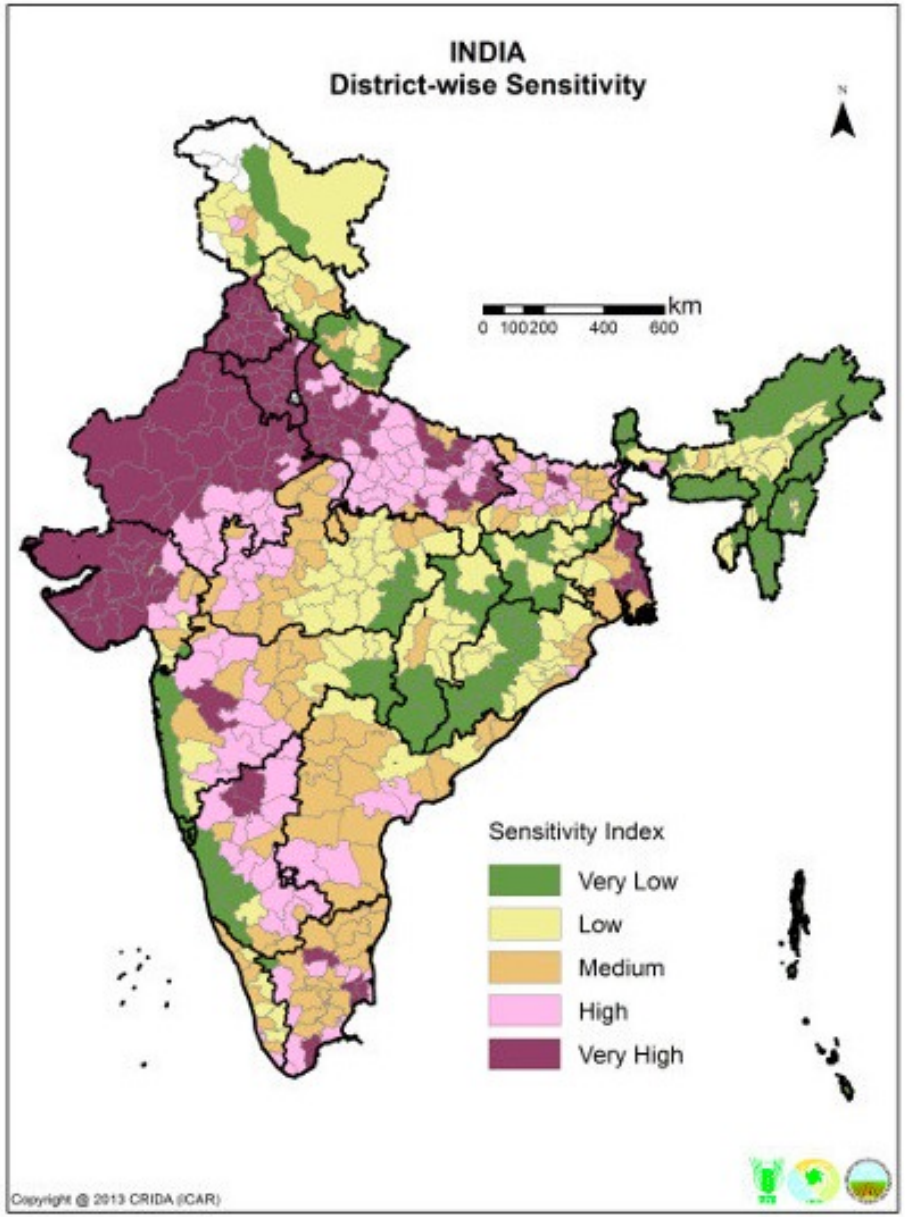
AR6 Synthesis Report:
Climate Change 2022

BACK TO REPORTS CORE WRITING TEAM

Code Red

Wildfire→
Fire clouds

Climate change's impact on India



Source: Indian council for Agricultural Research, 2013

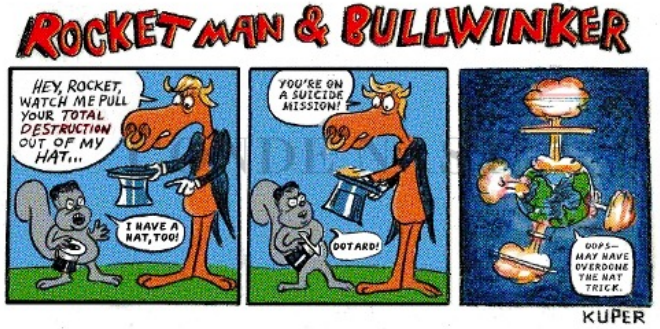
https://www.financialexpress.com/india-news/water-scarcity-to-cost-growth-spark-conflict-migration-world-bank/248179/

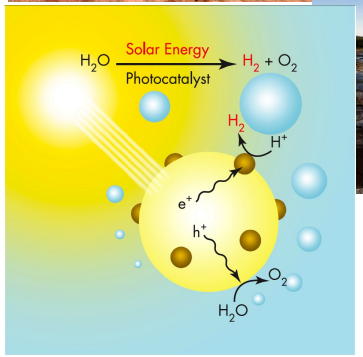
https://www.indiatoday.in/science/story/india-may-suffer-devastating-climate-change-impact-in-80-years-study-1685987-2020-06-05

Non-fossil-fuel options for mitigating climate change

"With great power comes great ~~responsibility~~ problem"
- Uncle ~~Ben~~ Zen

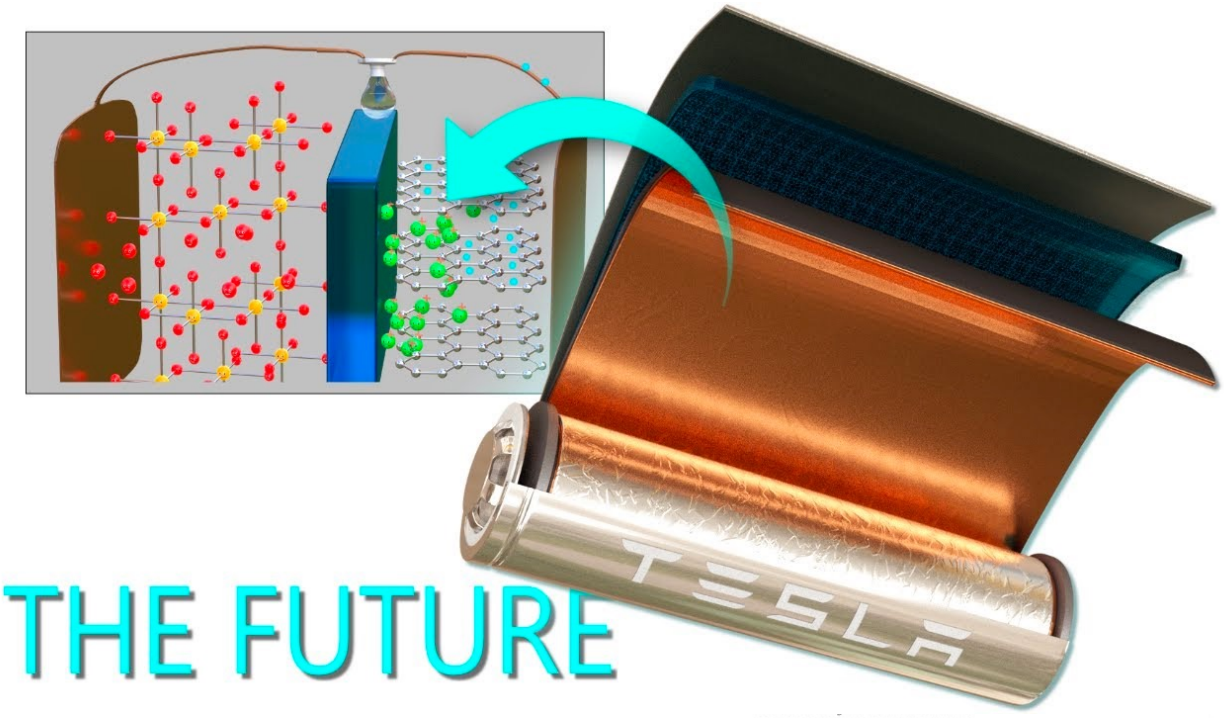
"But can they save themselves?"





+Tidal, biofuels, etc.

Non-fossil-fuel options for mitigating climate change



When the sun doesn't shine or the wind doesn't blow

Materials form the performance-bottlenecks of most renewable energy devices: **how do we understand and improve the material bottlenecks?**

- Look at what material properties govern energy devices first
- How can we improve the amount of energy stored (i.e., energy density) in a battery?
- How can we get better photovoltaics (solar cells)?

Energy technologies and how materials influence them

Solar Cells and Batteries

How does the modern Li-ion battery work?

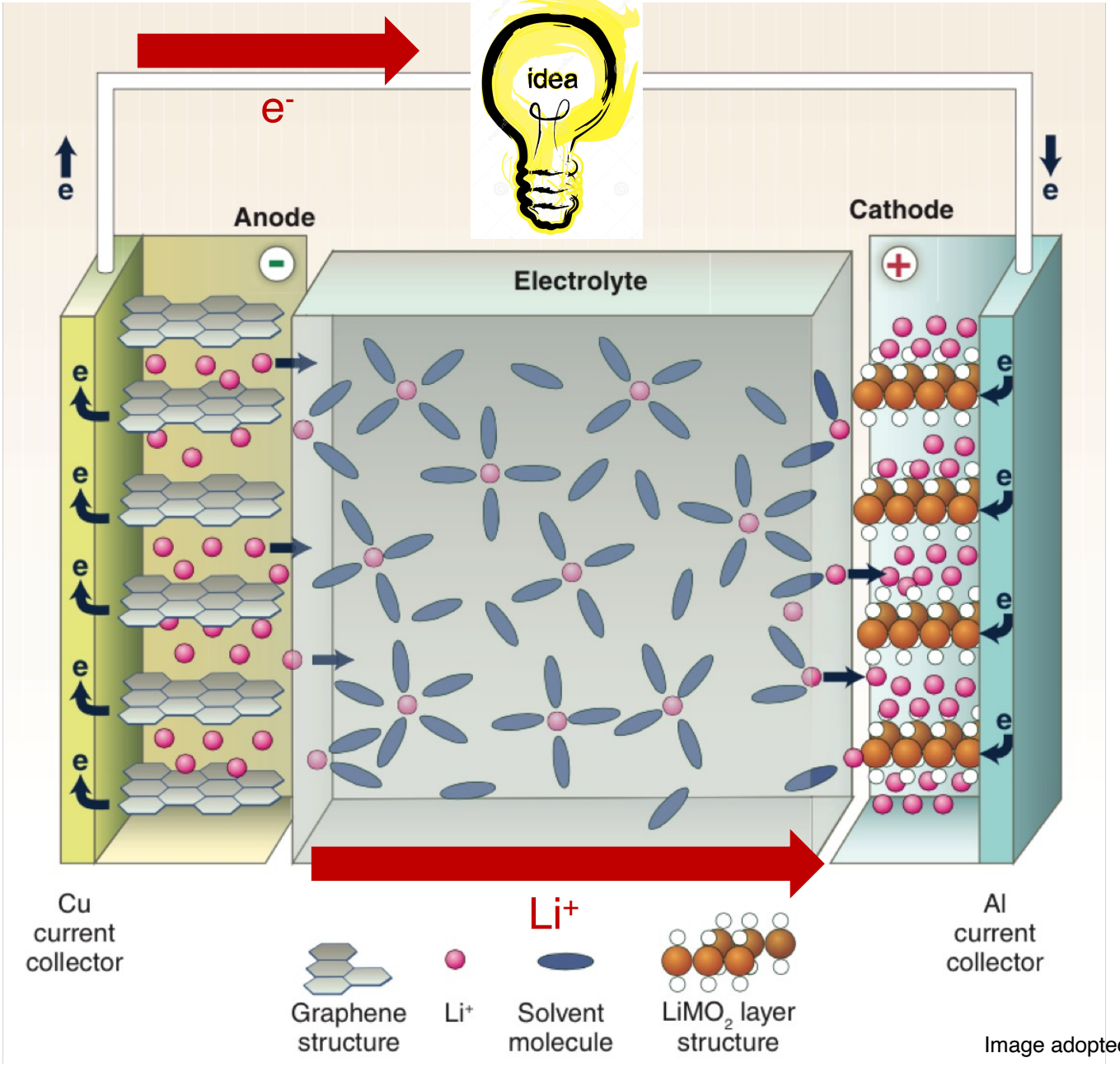
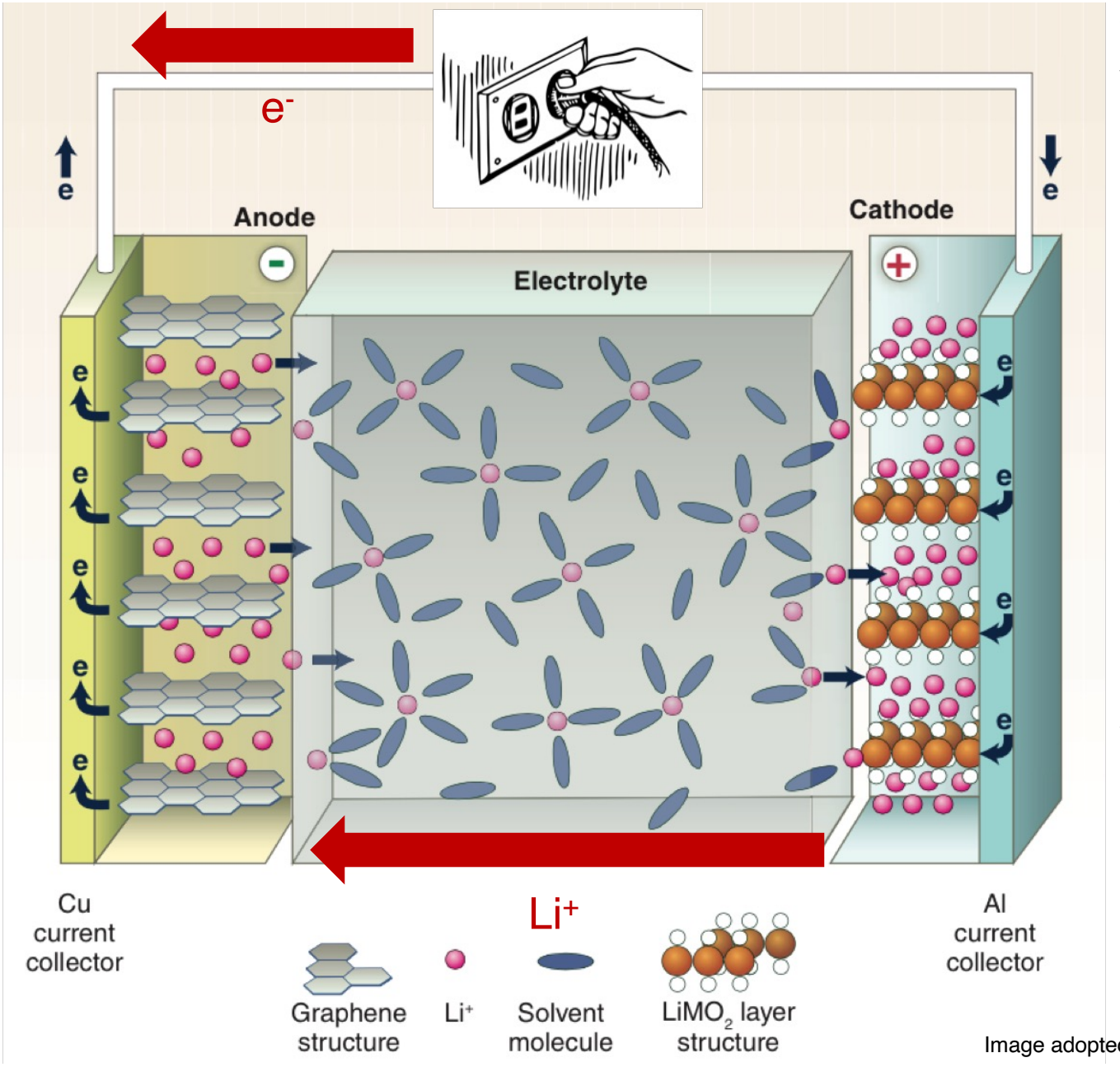


Image adopted from B. Dunn et al., Science 2011

How does the modern Li-ion battery work?



Voltage (V): Potential to do work

Capacity (mAh): Amount of charge stored

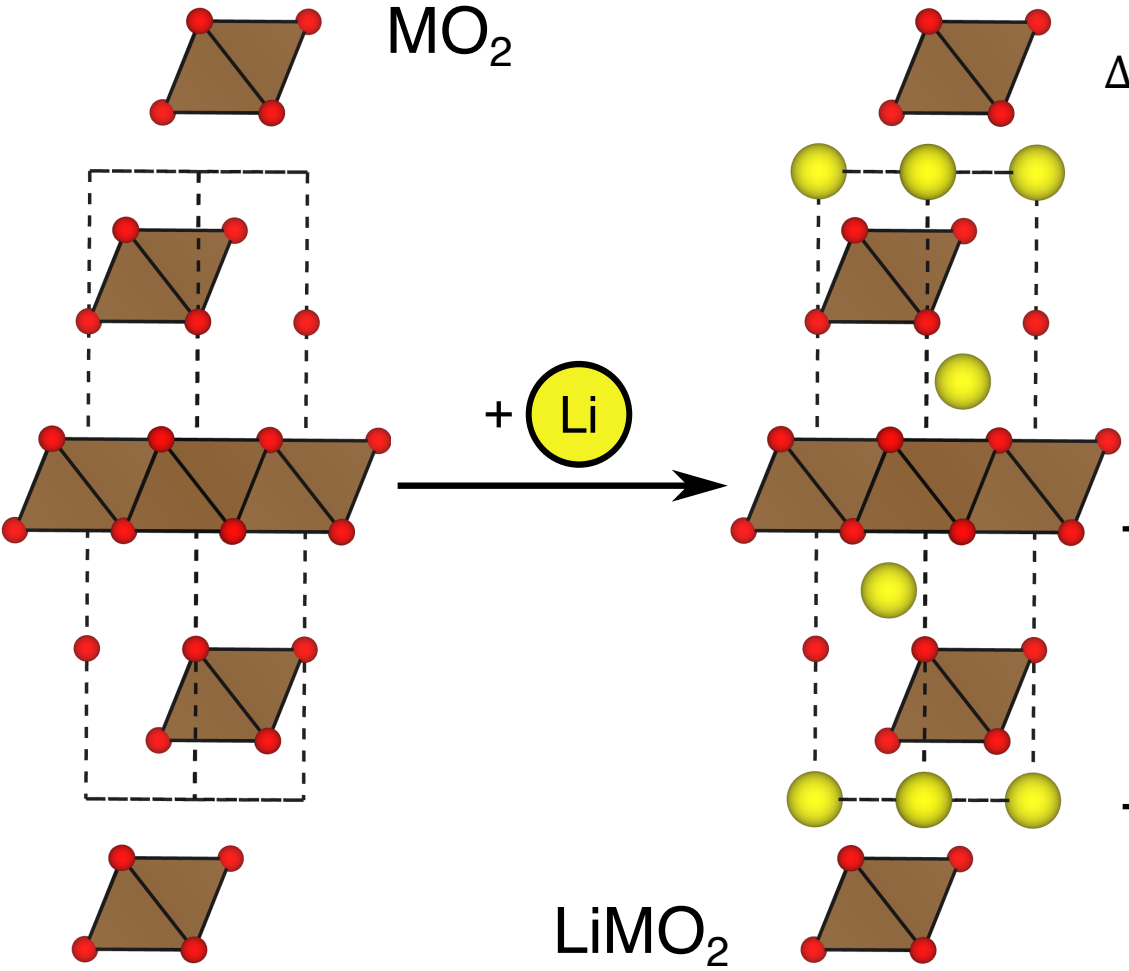
Voltage*capacity: Energy stored

Rate (C): How fast can a battery be charged and discharged?

All performance metrics of a battery system are **material dependent**: anode, cathode, and electrolyte

Image adopted from B. Dunn et al., Science 2011

Voltage, capacity, and rate



Charged cathode Discharged cathode

$$\Delta G_{intercalation} = G_{LiMO_2} - G_{MO_2} - G_{Li}$$

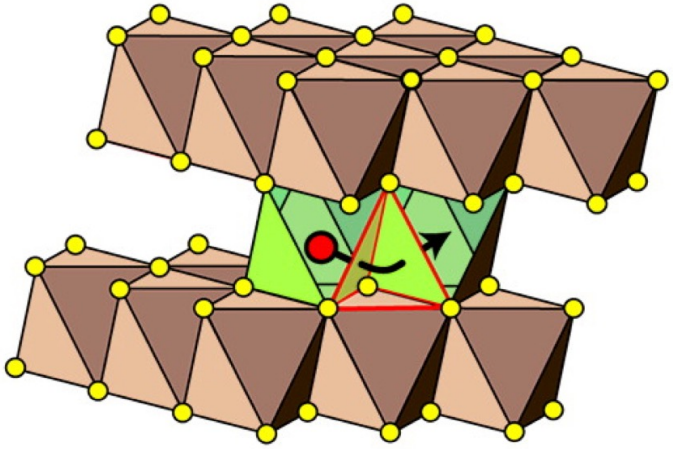
Nernst Equation

$$V = -\frac{\Delta G_{intercalation}}{nF}$$

(Do similar process for anode, take V difference!)

1 Li moved = 1 electron stored

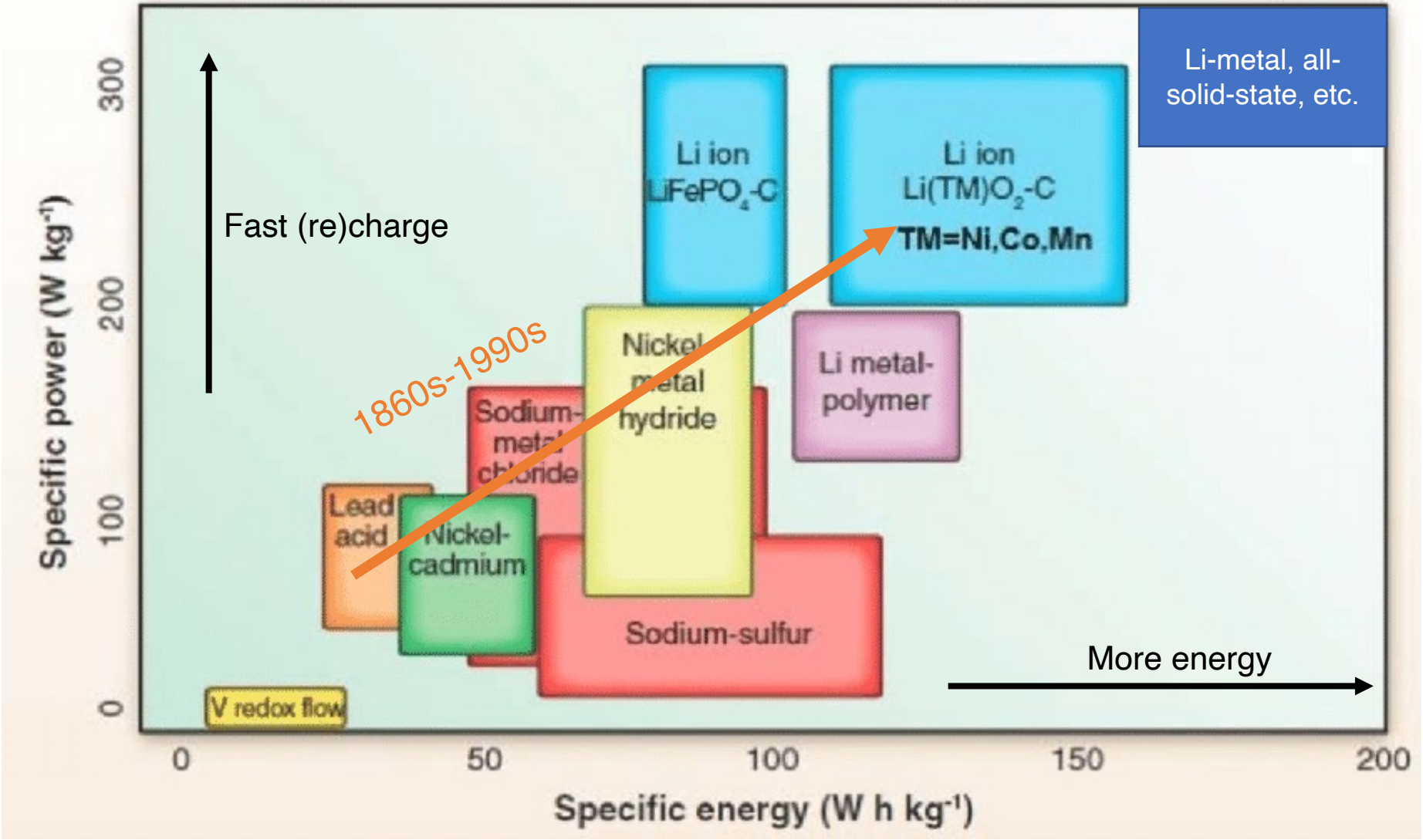
$$\text{Capacity} \propto \frac{\#\ Li\ moved}{\#\ 'Framework'\ atoms}$$



Rate: how fast can Li move (or diffuse) within electrode?

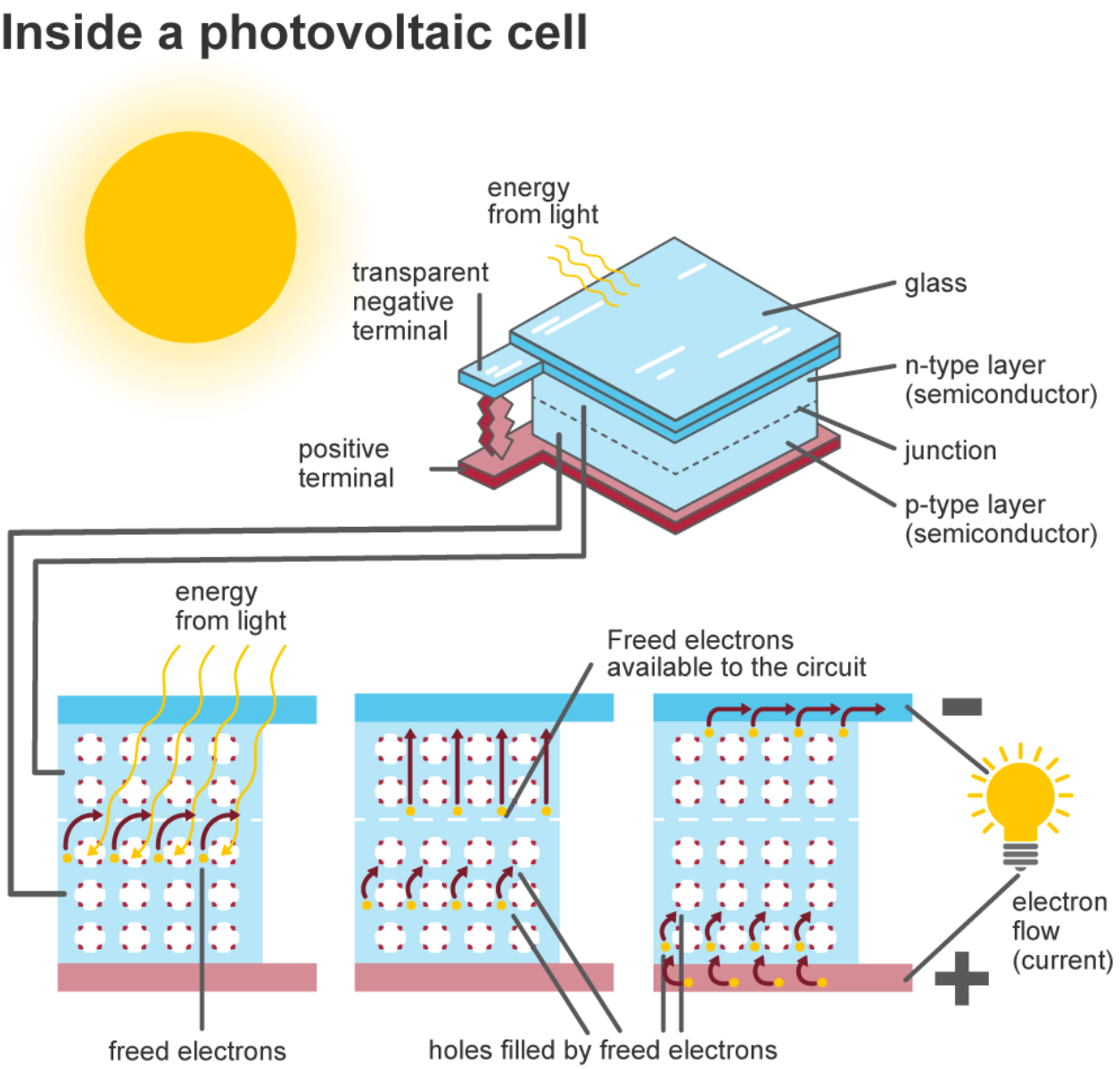
$$Rate \propto \exp\left(-\frac{E_m}{RT}\right)$$

We have made significant progress in batteries: but tremendous space left



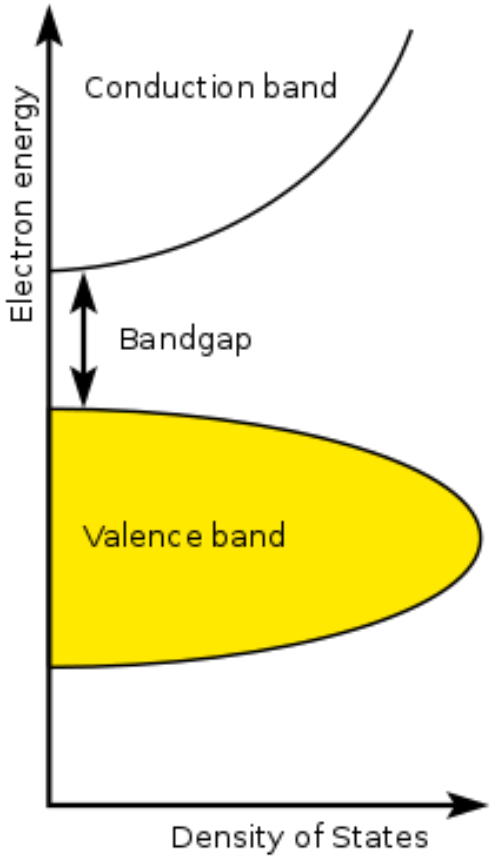
https://en.wikipedia.org/wiki/Ragone_plot

So how does a solar cell work?



Source: U.S. Energy Information Administration

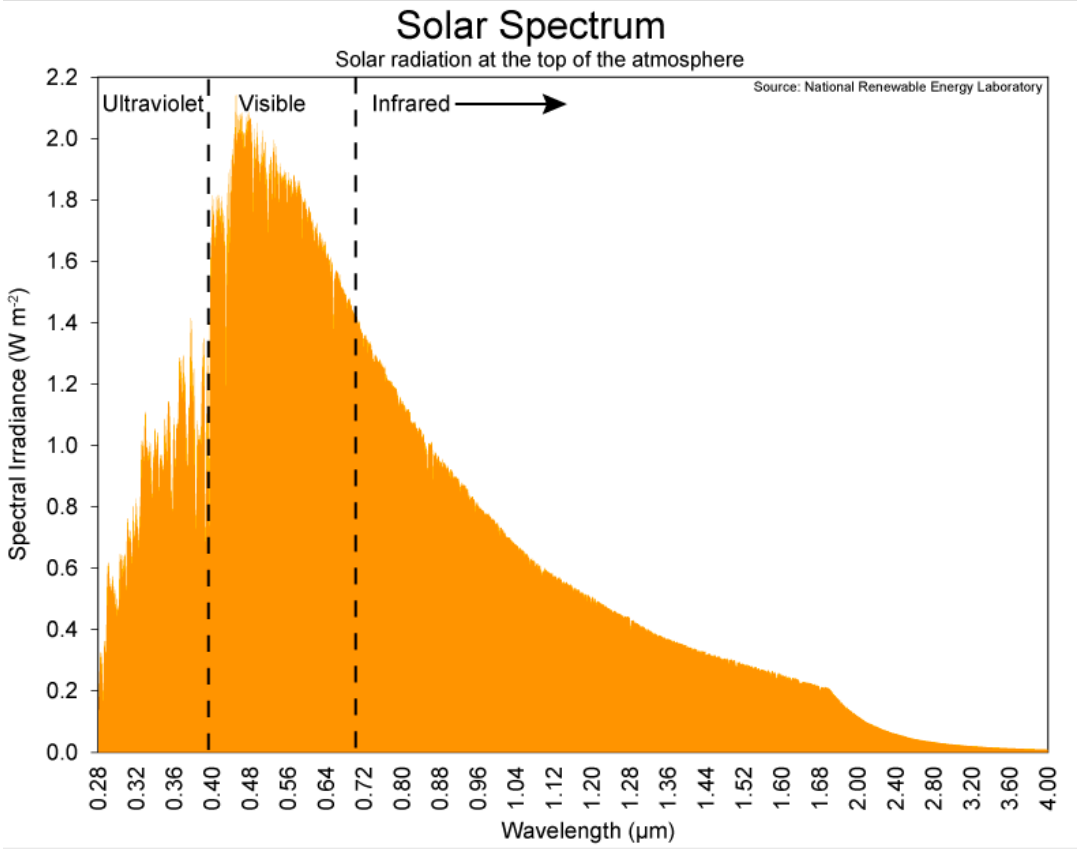
Voltage (V_{oc}) ∝ Band gap
Current (I_{sc}) ∝ # of states



"Curvature" of electronic bands → "mobility" of free carriers → do carriers escape into external circuit?

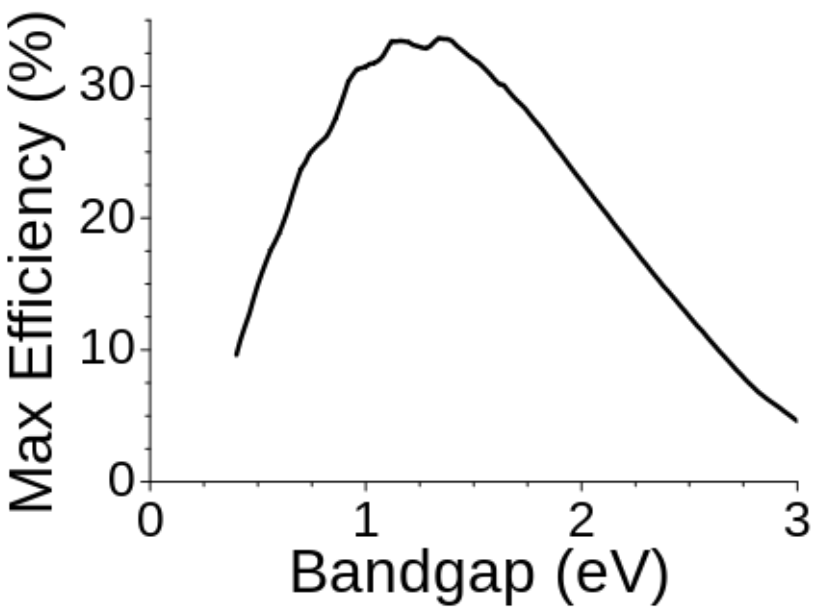
Point defects in solar cells→poor performance

The band-gap trade-off



http://sites.gsu.edu/geog1112/global-surface-temperature/

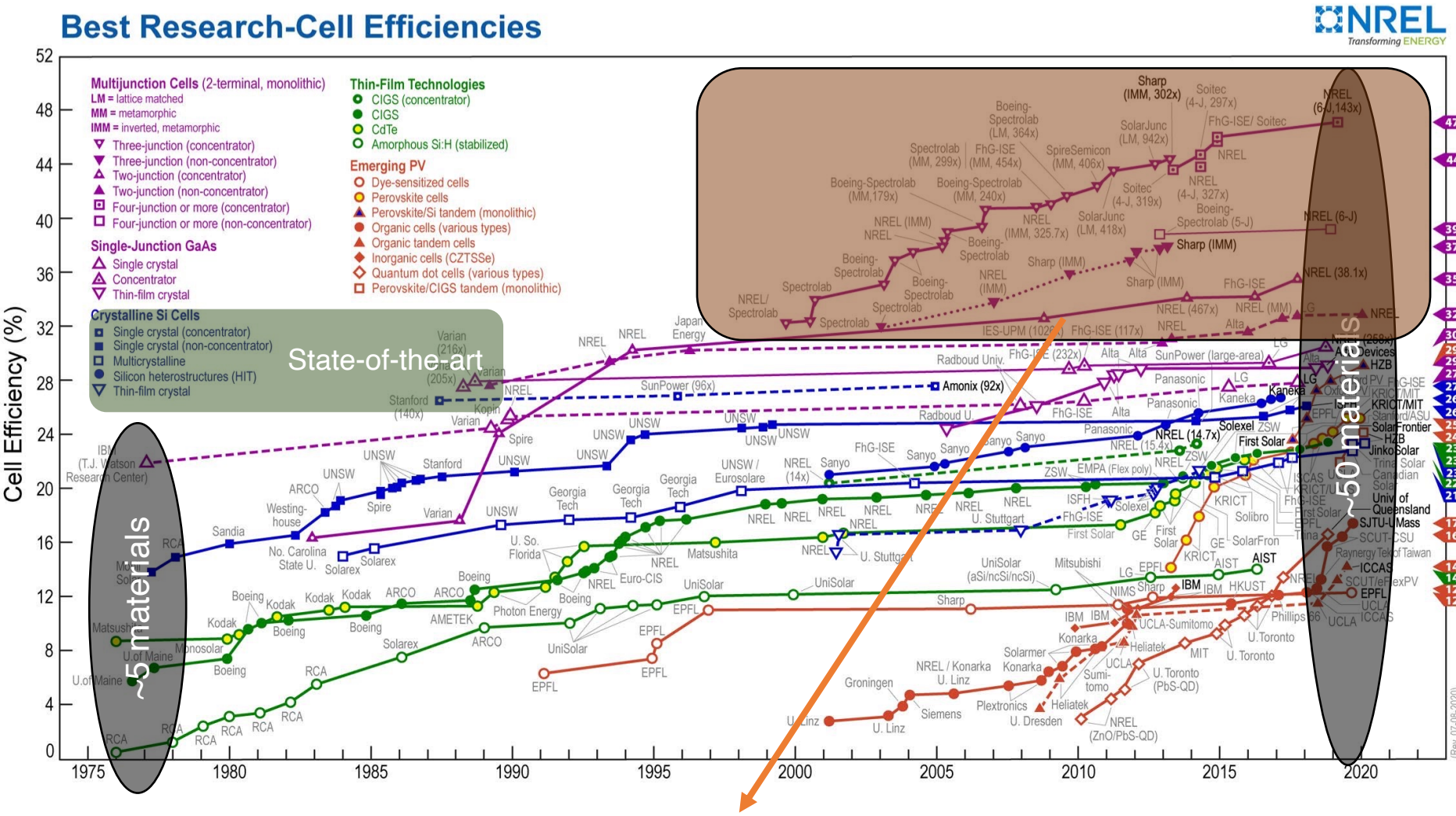
https://en.wikipedia.org/wiki/Shockley%E2%80%93Queisser_limit



Shockley-Queisser Limit

Solar spectrum: peaks at certain frequencies/wavelengths
Band gap of semiconductor: needs to match this peak frequency (**1.3-1.5 eV**)
Analogous to Carnot efficiency for a “simple”, single *p-n* junction semiconductor

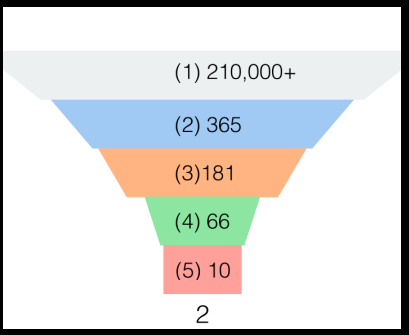
Several improvements in designing photovoltaics: still a long way to go



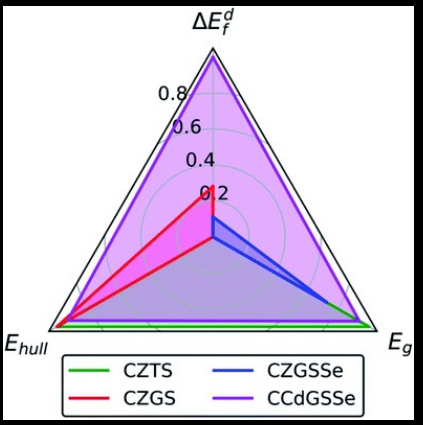
Going beyond the Shockley-Queisser limit via innovative device designs

https://www.nrel.gov/pv/cell-efficiency.html

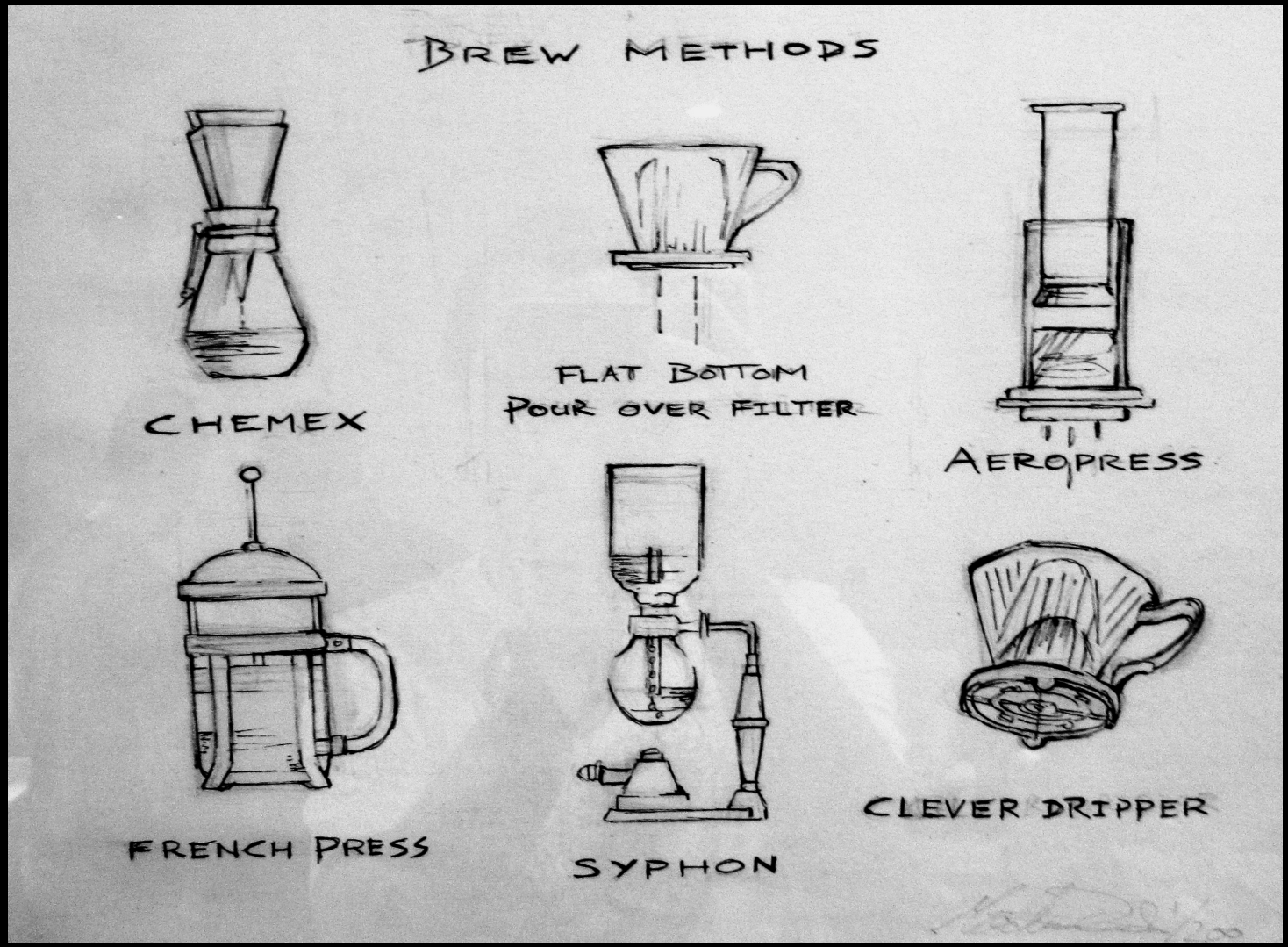
Objectives



How to design better materials (electrodes) for beyond-Li, multivalent batteries?

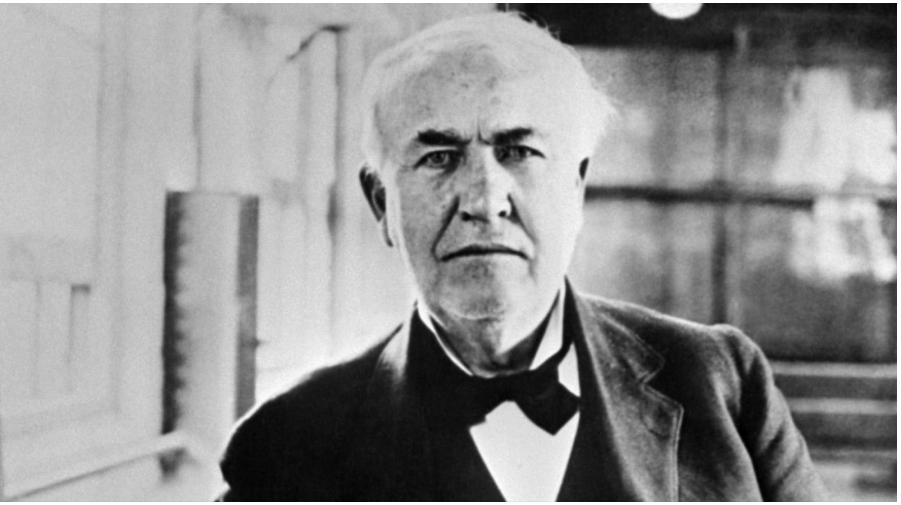


How to design better (defect-resistant) photovoltaics?



Methods detour (and stability)

Methods: Edison vs. Iron Man



Trial and error of candidates in a lab

Simulate and identify candidates
(on a transparent touch screen preferably)

Density functional theory:
(Approximately) predict
material properties

Machine learning: learn
from predictions to make
better predictions

What is density functional theory (DFT)?

$$\left(\frac{p^2}{2m_e} + V(r)\right)\psi(r) = E\psi(r)$$

(kinetic energy+potential energy)*
(many-body-wavefunction)=
Total energy of system*
(many-body-wavefunction)

Analytical solution unknown for multi-electron system
Computational cost of numerical solution: $O(N^7\text{-}N^{10})$

$$(T_S[\rho] + E_{ne}[\rho] + E_H[\rho] + E_{xc}[\rho]) = E[\rho(r)]$$

(kinetic+nucleus-electron+electron-electron+
exchange-correlation) at given density
= Energy of system(at given density)

Electron density = Probability of finding electron

Computational cost of numerical solution: $\sim O(N^3)$

Variational principle → 0 K!
Total energy=Internal energy~Gibbs energy

Image: Lusk and Mattsson, MRS Bull. 2011

Use DFT: predict material properties

$$H\psi = E\psi$$

Total energy at 0 K ≈ Gibbs energy → Thermodynamics

Density of states + Band structure → Band gap

Energy to displace atoms → Phonon/vibrational

Barriers for atomic migration → Kinetics

Energy of defective structures → Defect thermodynamics

Density functional theory[1,2]: approximate electronic interactions into a non-interacting mean-field

- Approximation: exchange-correlation (XC) functional

DFT toolkit choice: Vienna ab initio simulation package (https://www.vasp.at/)

XC functionals: Jacob's ladder of increasing accuracy

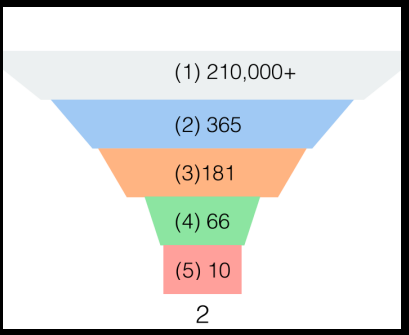
- Choice: strongly constrained appropriately normed (SCAN)[3]
- Or Hubbard *U* corrected generalized gradient approximation (GGA+*U*)[4]

Structural input: databases

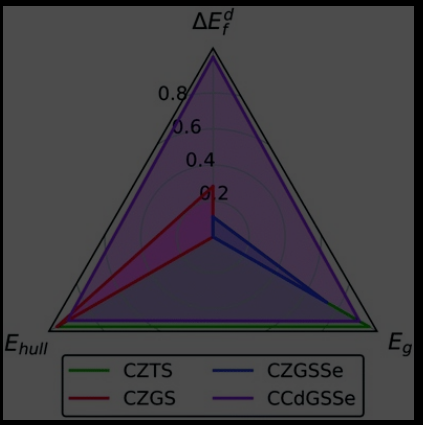
1. Hohenberg and Kohn, **Phys. Rev. 1964**, *136*, B864
2. Kohn and Sham, **Phys. Rev. 1965**, *140*, A1133
3. Sun et al., **Phys. Rev. Lett. 2015**, *115*, 036402
4. Perdew et al., **Phys. Rev. Lett. 1996**, *77*, 3865

Figure (above): Car, **Nat. Chem. 2016**, *8*, 820

Objectives



How to design better materials (electrodes) for beyond-Li, multivalent batteries?

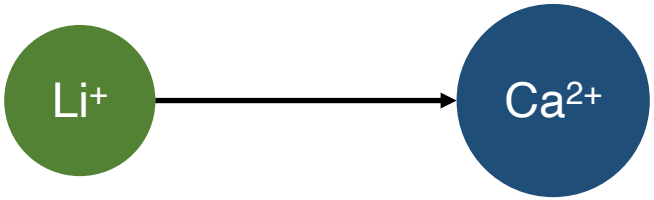


How to design better (defect-resistant) photovoltaics?

Why Multivalent or Ca batteries?

Next generation of electric devices will benefit from higher energy density storage systems

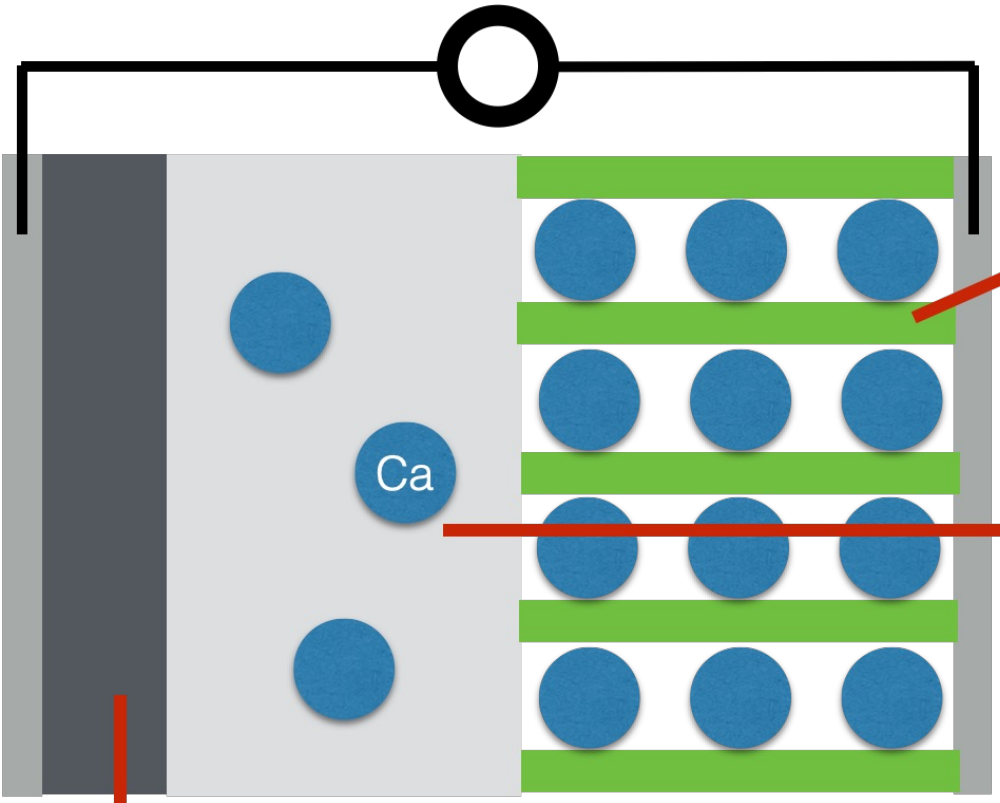
- Multi-valent == More electrons (Ca^{2+}, Mg^{2+}, Al^{3+}, etc.)
- Li-ion technology approaching fundamental limits
  - Safety, supply-chain constraints; limits on achievable energy densities
- Smaller batteries useful for portable electronics
- Lighter batteries favorable for electric vehicles



Why Ca?

- Superior volumetric capacity for Ca metal (~2077 Ah/l) than or Li in graphite (~800 Ah/l)
- Ca is safer than Li, less constrained geopolitically

Ca cathode design challenge



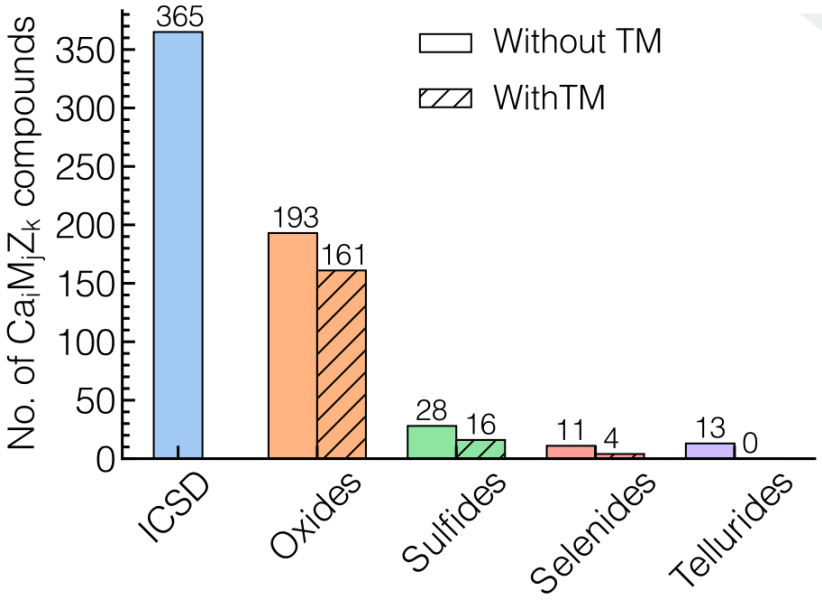
Intercalation Cathode:
High Voltage
High Capacity
High Mobility

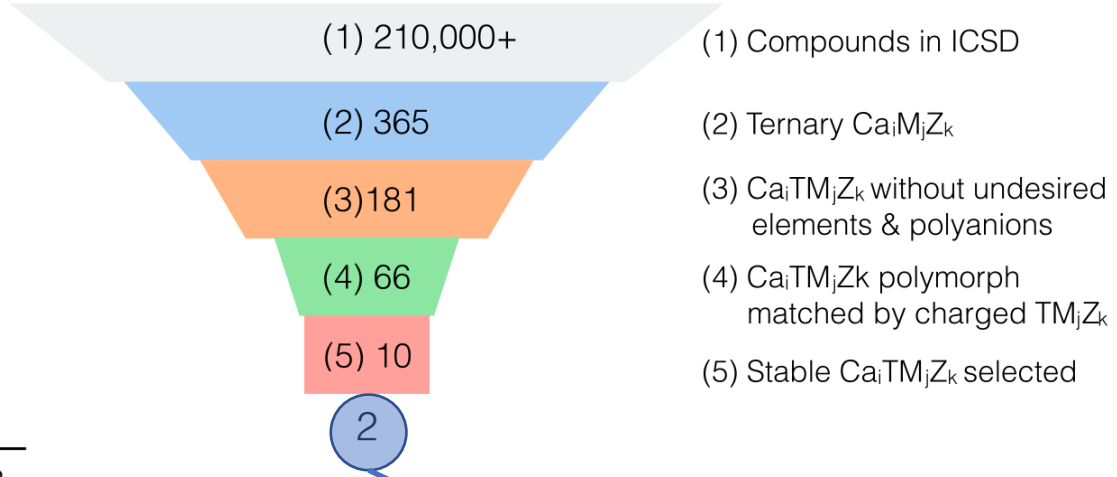
Electrolyte:
Stable electrolyte (at both electrodes) with good conductivity

Metal Anode:
Understand plating and stripping in organic electrolytes

Find new cathode materials that can yield **facile Ca diffusion**, reasonable voltage and capacity, and be thermodynamically stable

Let's look at ternary Ca-compounds





Inorganic crystal structure database (ICSD[1]): has > **210,000** compounds

- Only **365** are ternary compounds containing Ca
  - Compounds of composition $Ca_iM_jZ_k$; M, Z = elements other than Ca
- Let M = TM (i.e., transition metal) and Z = O, S, Se, or Te
  - Results in **181** unique compounds
- Charge-neutral charged compound (TM_jZ_k) available for $Ca_iTM_jZ_k$?
  - $CaMn_2O_4$-Mn_2O_4 is ok, $CaVO_3$-VO_3 not ok
  - **66** unique structures
- Either of $Ca_iTM_jZ_k$ or TM_jZ_k thermodynamically (meta)stable?
  - Decomposition energy ≤ 30 meV/atom (based on Materials Project[2])
  - **10** unique compounds → evaluate mobility

Final candidates!

1. https://icsd.products.fiz-karlsruhe.de/
2. https://materialsproject.org/

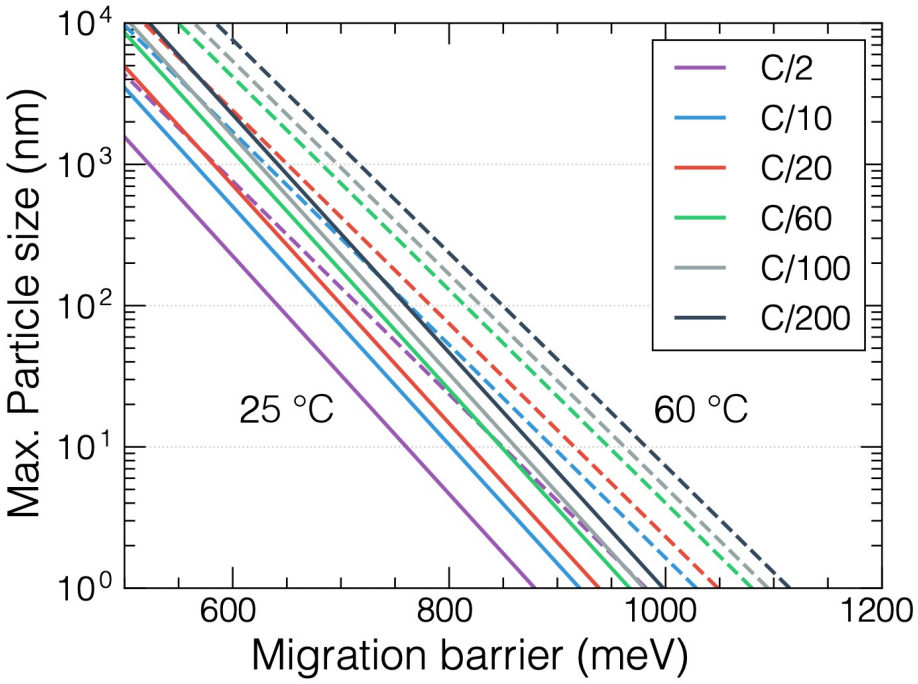
Ca diffusivity: nudged elastic band

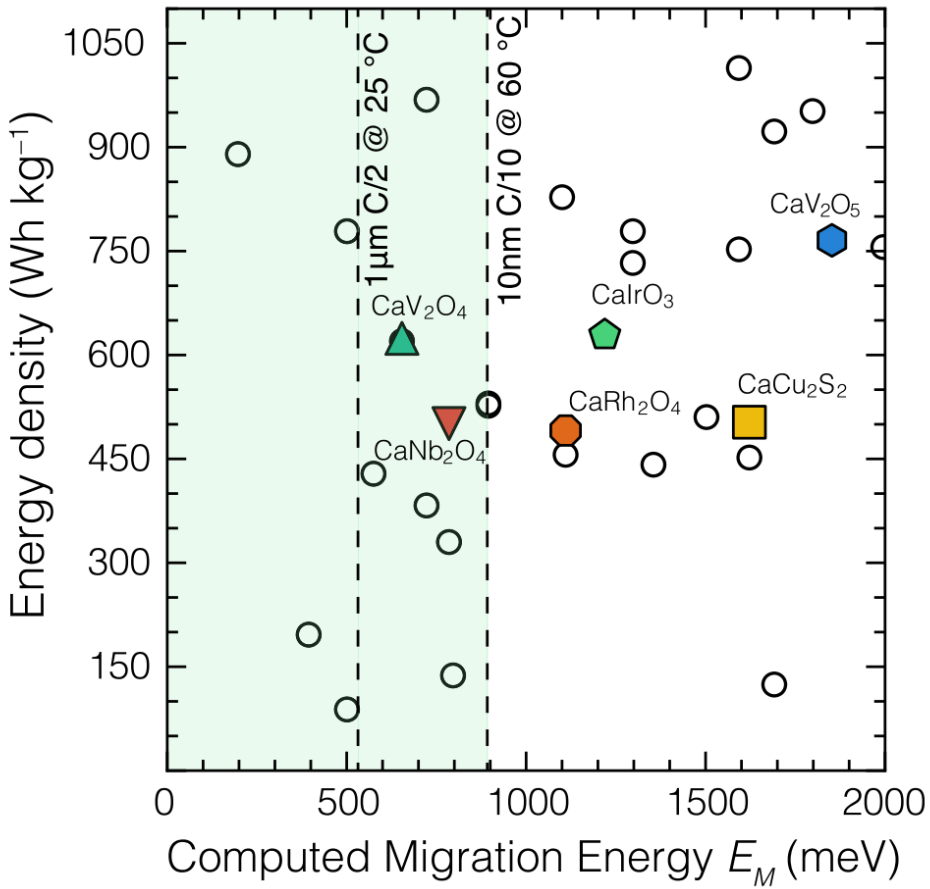
$$D \approx \frac{x^2}{t}$$ Electrode particle size

Diffusion time (rate of operation)

$$D = \nu a^2 f g x_D \exp\left(-\frac{E_m}{k_B T}\right)$$

Diffusivity mainly governed by barrier
Required diffusivity → maximum of E_m
Variables: size, time, and temperature





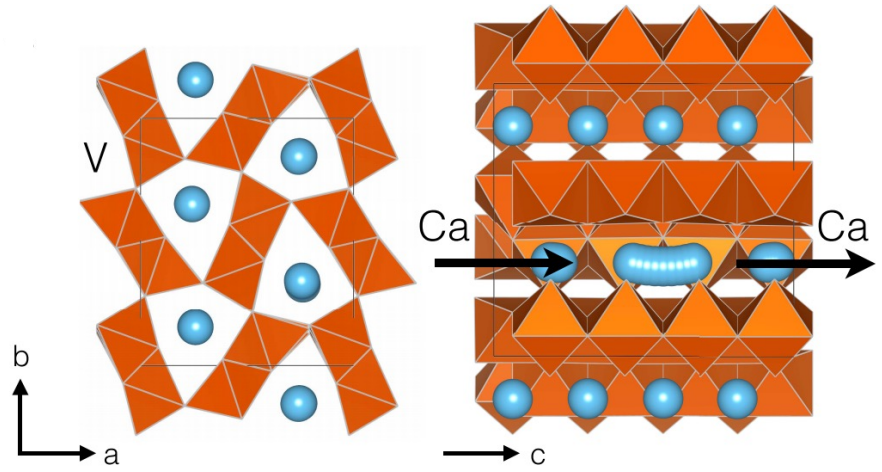
Max. tolerable barrier ~ 980 meV

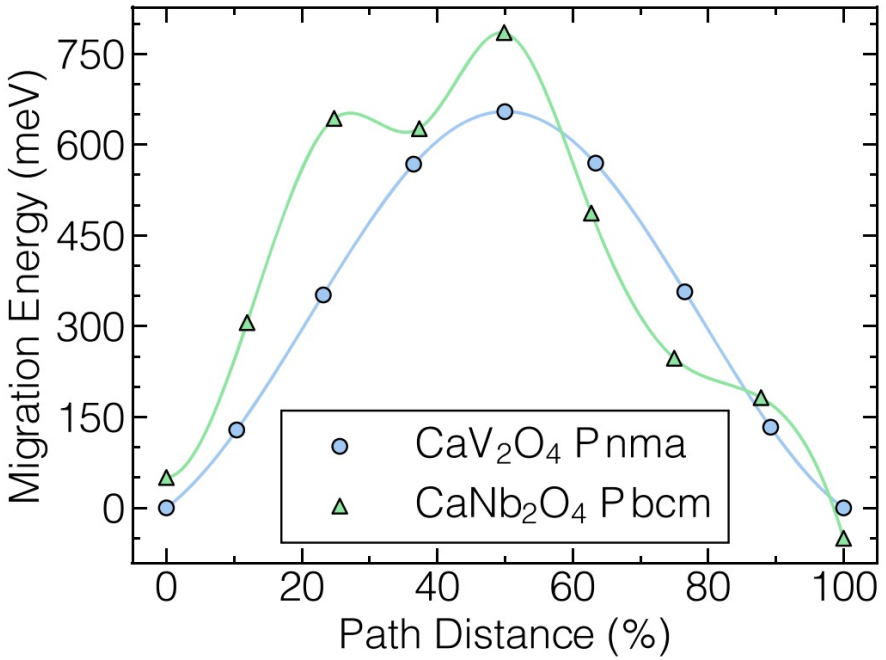
2 candidates display reasonable E_m

- CaV_2O_4: 654 meV
- $CaNb_2O_4$: 785 meV

Nudged Elastic band: Sheppard et al., **J. Chem. Phys. 2008**, *128*, 134106

Migration pathways of candidates

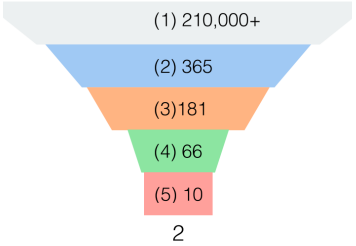




CaV_2O_4: 8→3→8 $CaNb_2O_4$: 6→4→6→4→6

2 promising candidates!

Summary

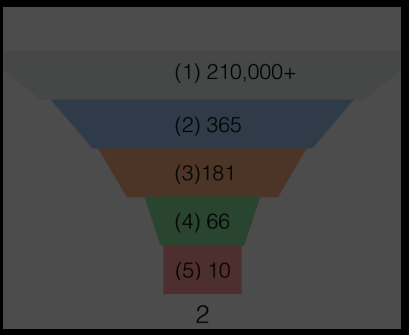


- Ca (or multivalent) batteries form an important type of high-energy-density, beyond-Li systems
  - Chief challenge is to find (positive) electrodes with facile Ca-diffusion

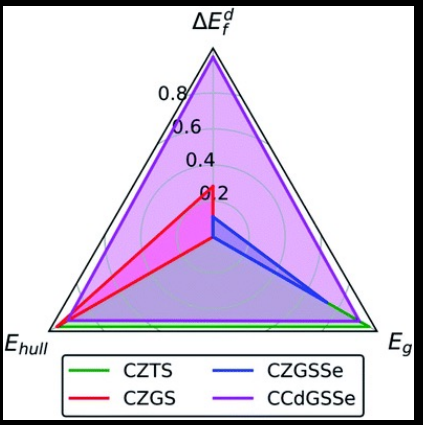
- Screening through ICSD for redox-active, charge-neutral and thermodynamically (meta)stable ternary Ca oxides/chalcogenides yielded 10 possible candidates
  - Evaluated using density functional theory calculations

- 2 promising candidates: CaV_2O_4 and $CaNb_2O_4$

Objectives

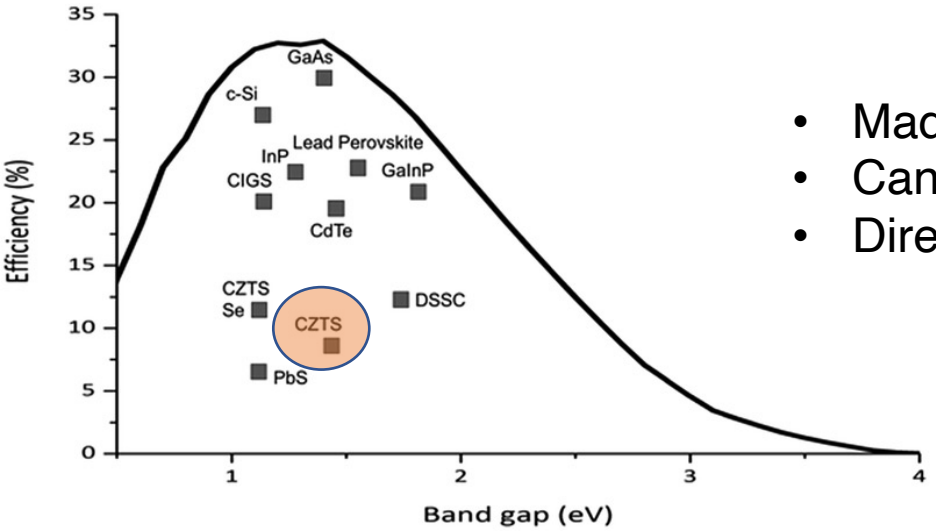


How to design better materials (electrodes) for beyond-Li, multivalent batteries?



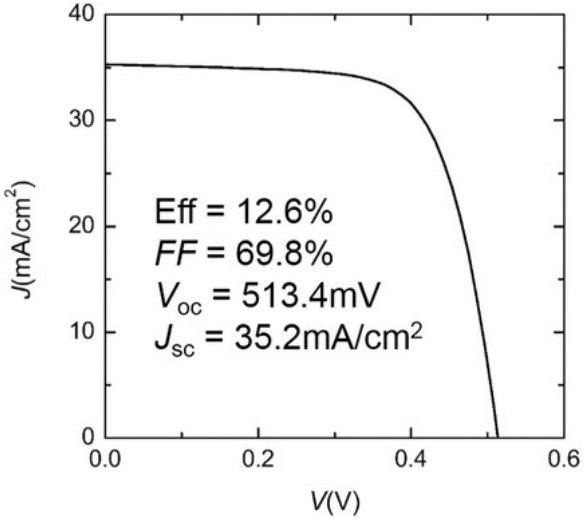
How to design better (defect-resistant) photovoltaics?

Cu_2ZnSnS_4 (CZTS) is a promising candidate for beyond-Si solar cells



Mathews et al., *Chem. Sci.* **8**, 4177 (2017)

- Made of abundant elements
- Can be synthesized through wet chemistry
- Direct band gap, 1.4-1.6 eV



Wang et al., *Adv. Energy Mater.* **4**, 1301465 (2014)

Often suffers from low efficiencies (~12%)

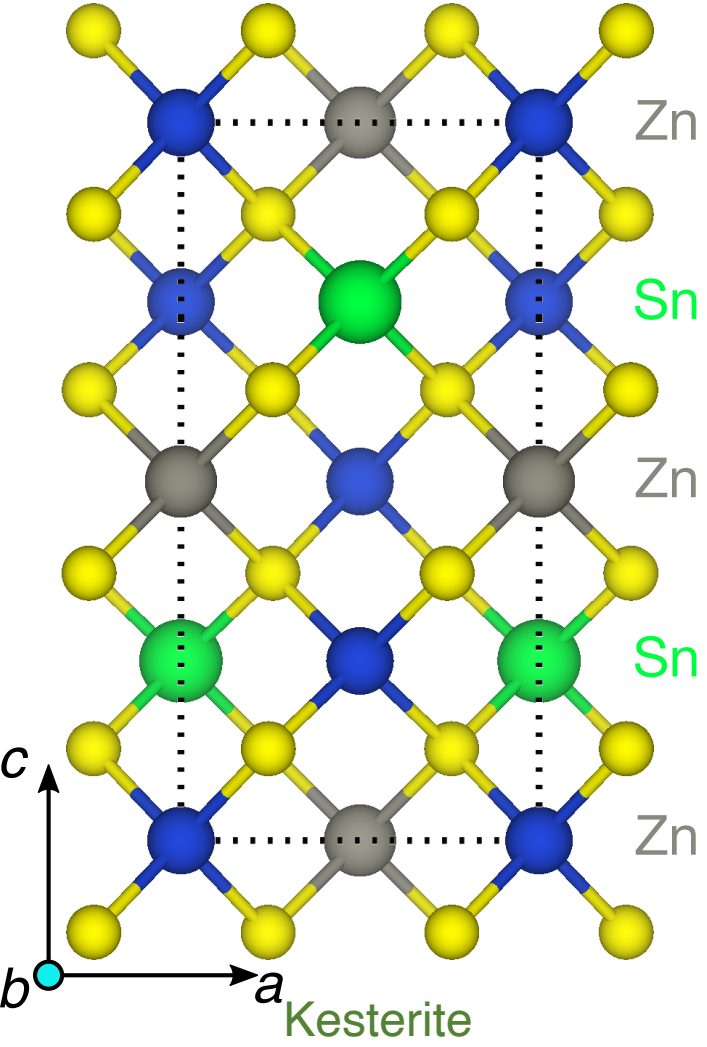
- Si is > 20%
- Due to disorder in Cu-Zn sub-lattice

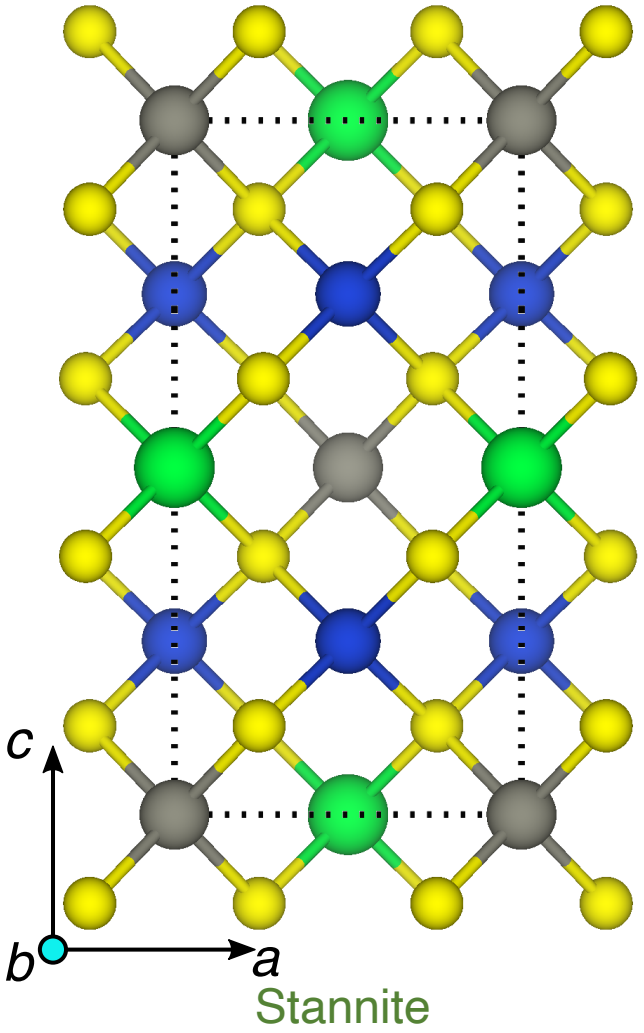
Se frequently added to tune band gap

High temperature annealing to improve crystal size

- Often leads to elemental loss and defect production

Disorder ≡ Antisites ≡ Defects

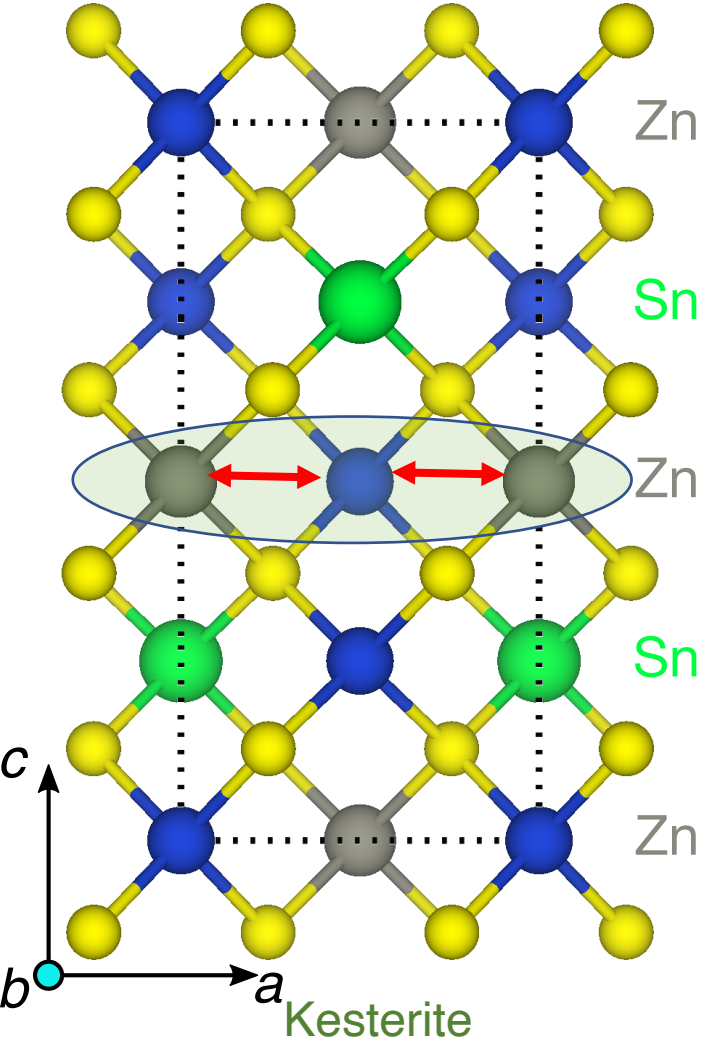




Cu-Zn: similar atomic radii
Kesterite-Stannite near degeneracy (~3 kJ/mol)

G.S. Gautam et al., *Chem. Mater.* **2018**, *30*, 4543; Yu and Carter, *Chem. Mater.* **27**, 2920 (2015)

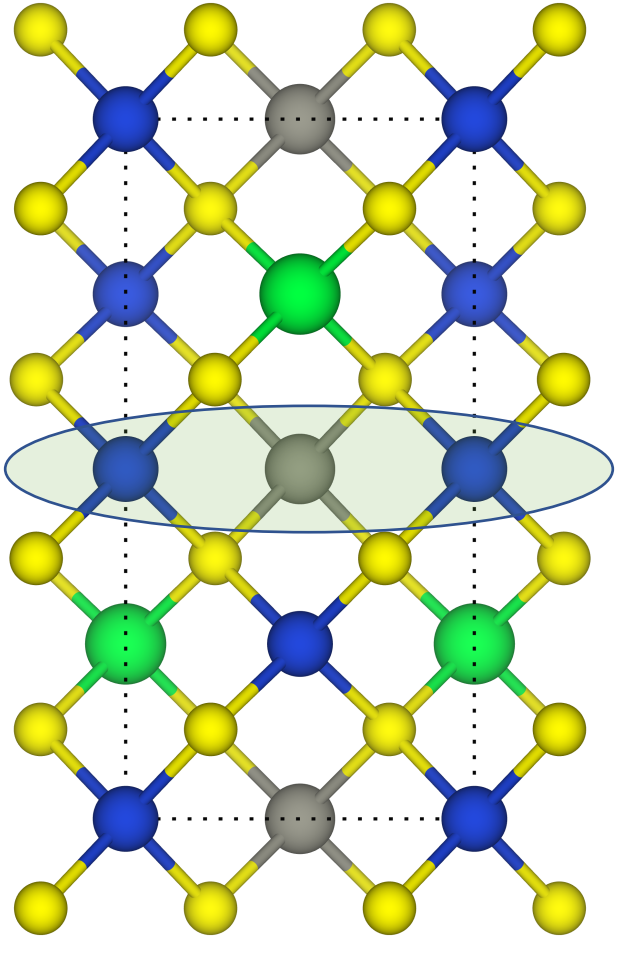
Disorder ≡ Antisites ≡ Defects



Kesterite

Anti-site formation

$Cu_{Zn} + Zn_{Cu}$



Disordered-Kesterite

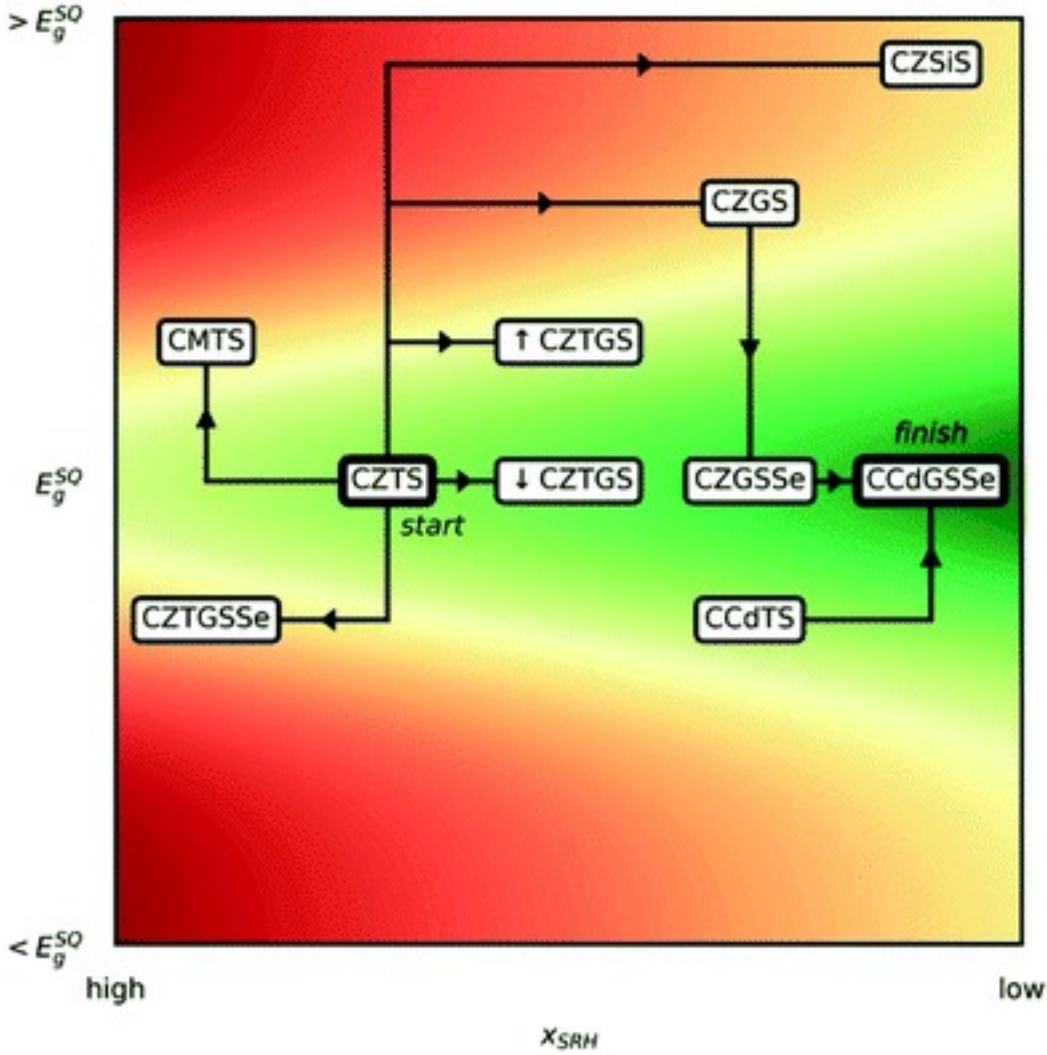
Cu-Zn: similar atomic radii
Kesterite-Stannite near degeneracy (~3 kJ/mol)

Other defects:
$Sn_{Zn}+2Cu_{Zn}$ (electron traps)
V_{Cu} (reduce band edge fluctuations)

G.S. Gautam et al., *Chem. Mater.* **2018**, *30*, 4543; Yu and Carter, *Chem. Mater.* **27**, 2920 (2015)

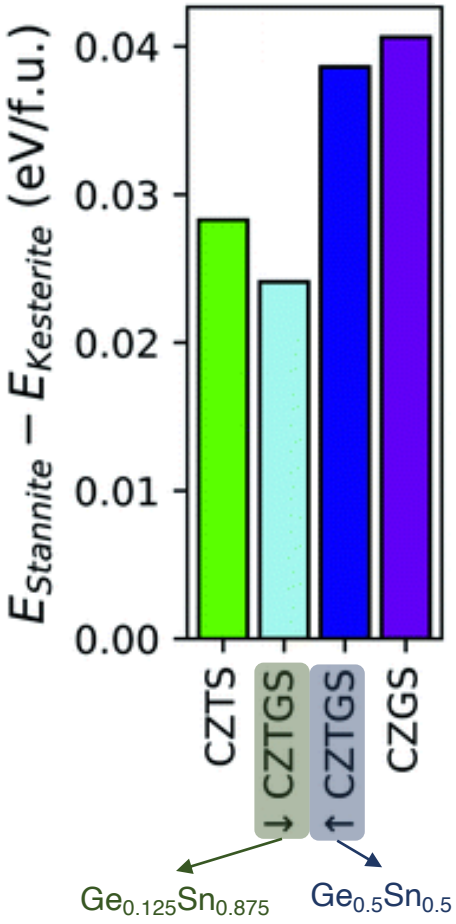
Objectives and roadmap

- Optimal band gap (1.3-1.5 eV)
- Thermodynamic stability (less than 25 meV/atom decomposition energy at 0 K)
- High defect formation energy for Cu_{Zn}+ZnCu and Sn_{Zn}+$2Cu_{Zn}$ (at least higher than CZTS)
- Low defect formation energy for V_{Cu}



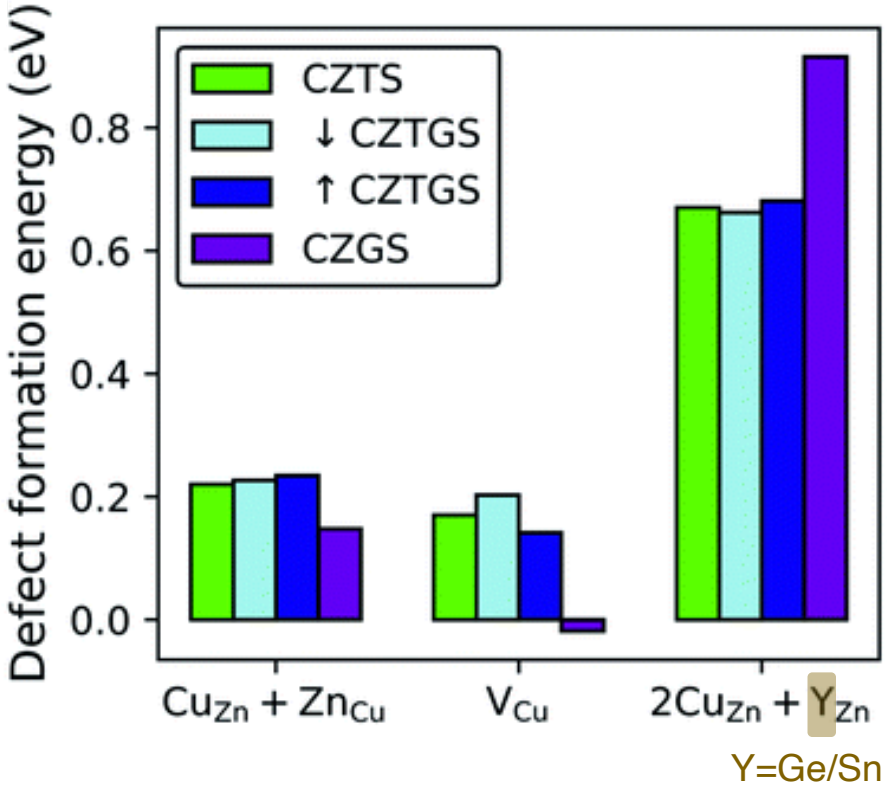
Elements explored (apart from CZTS):
M=Mg, G=Ge, Si=Si, Se=Se, Cd=Cd

Ge: suppresses Sn_{Zn} but increases band gap



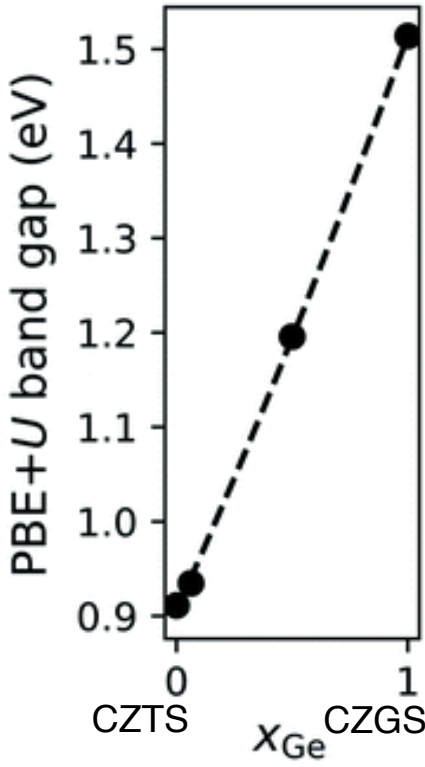
Stabilizes kesterite

Stability: Good



- Ge suppresses Cu_{Zn}+Zn_{Cu} only at intermediate concentrations
- Largely favors V_{Cu} formation
- Suppresses Sn_{Zn}+$2Cu_{Zn}$ only at large concentrations

Defect thermodynamics: Not great



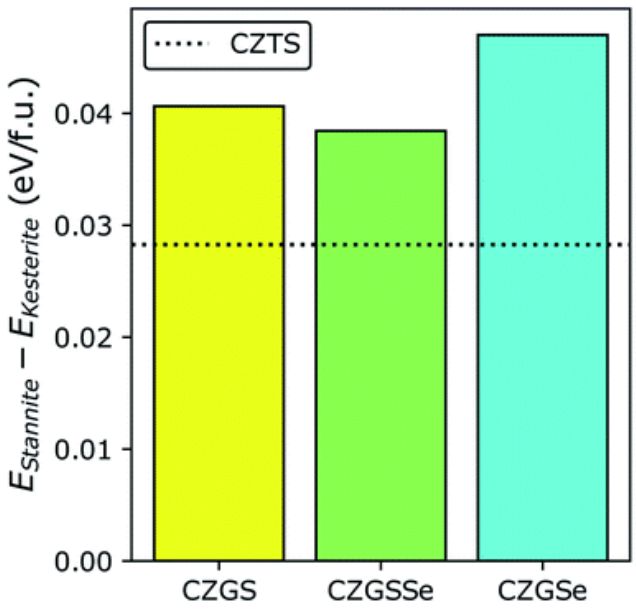
Increases band gap

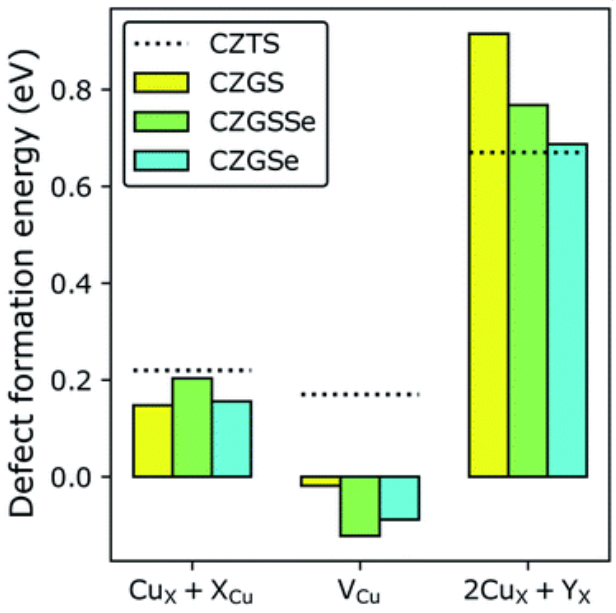
Theory: 1.5 eV

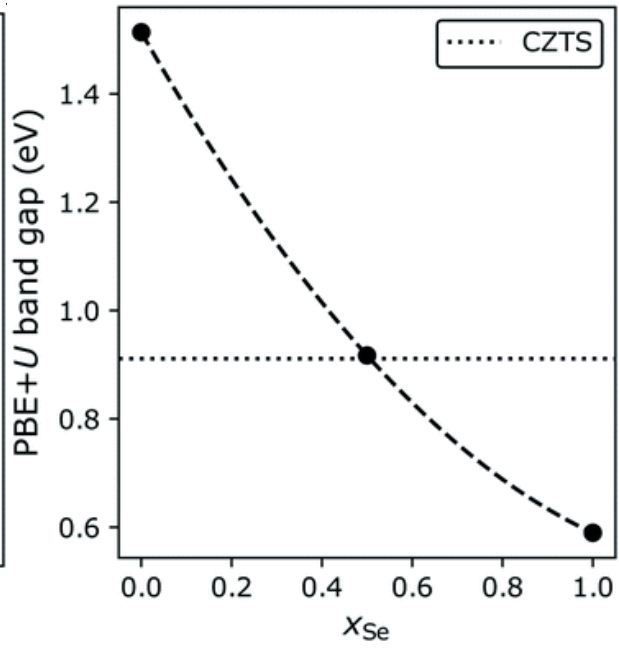
Experiments: 2.1 eV

Band gap: Bad

Ge+Se: defects form more readily







Stabilizes kesterite better than CZTS/CZGS

Stability: Good

- Cu_{Zn}+Zn_{Cu}: more favored than CZTS
- V_{Cu}: more favored than CZTS
- Sn_{Zn}+$2Cu_{Zn}$: similar to CZTS

Defect thermodynamics: Bad

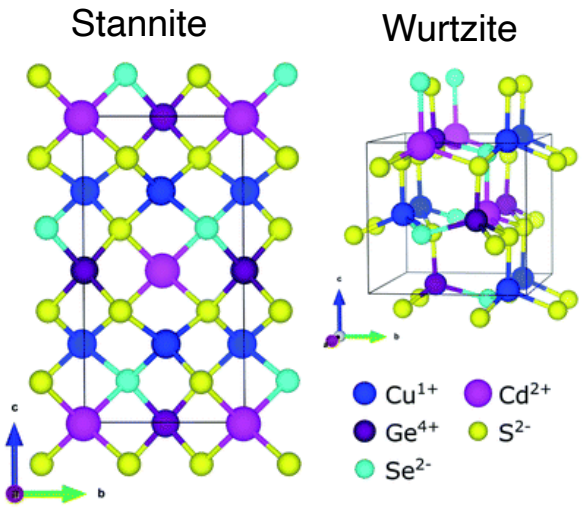
Predicted band gap: similar to CZTS

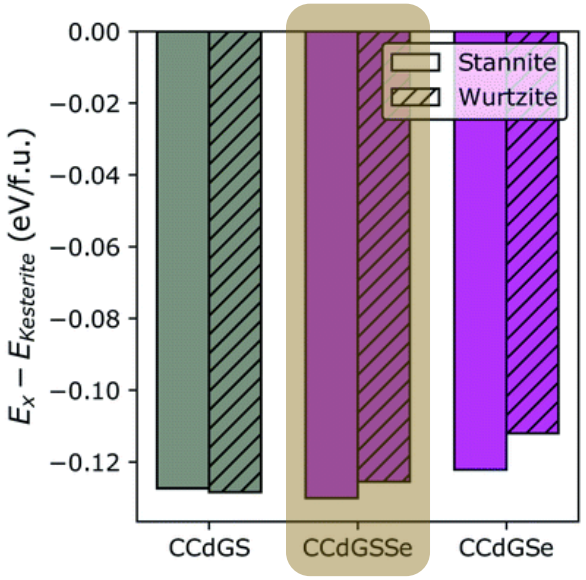
Band gap: Excellent

Overall, Ge or Ge+Se addition does not provide better photovoltaic candidate than CZTS

Any other dopants or substituent elements?

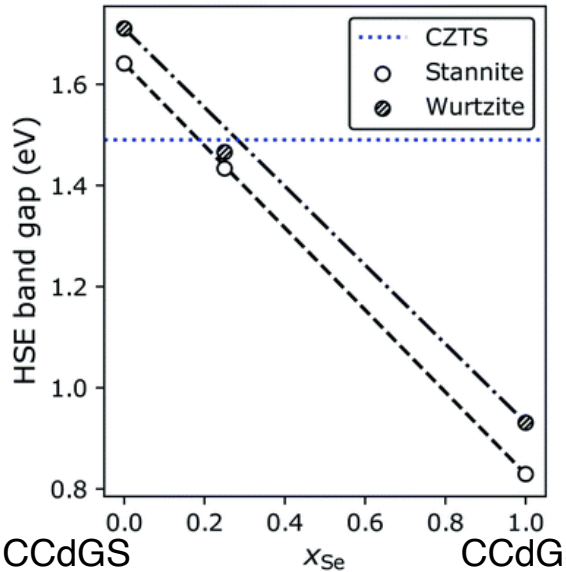
Ge+Cd+Se: optimal composition, new photovoltaic candidate

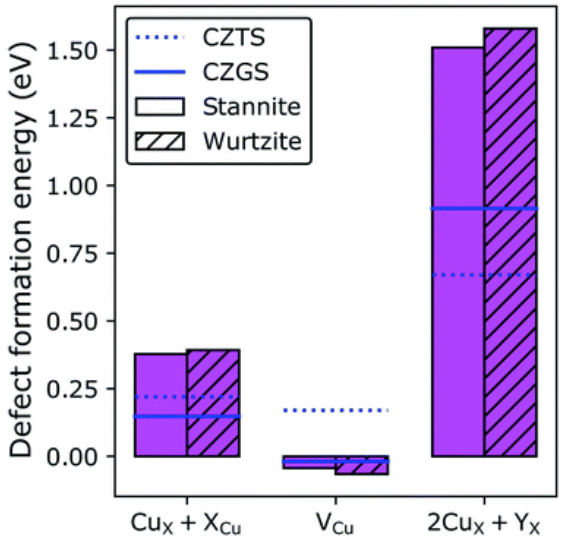




- Stable polymorph of Cu_2CdGeS_3Se: stannite, not kesterite
- Wurtzite's stability similar to stannite
  Stannite/Wurtzite could still be beneficial

Stability: Ok





- $Cu_{Zn}+Zn_{Cu}$ and $Sn_{Zn}+2Cu_{Zn}$: better suppressed than CZTS/CZGS
- V_{Cu} formation: more favored than CZTS

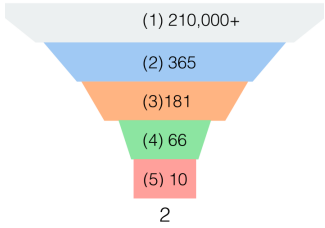
Defect formation: Excellent

- Predicted band gap: similar to predicted gap for CZTS
- HSE functional: typically agrees with experiments for S^{2-}/Se^{2-}

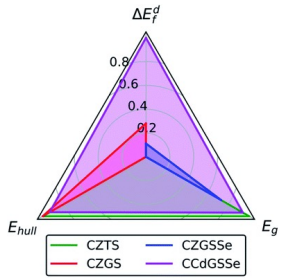
Band gap: Excellent

Conclusions and Acknowledgments

- Removing material bottlenecks is important for improving performance of energy devices
  - Need better batteries (Ca vs. Li)
  - Need better photovoltaics (sulfides vs. silicon)



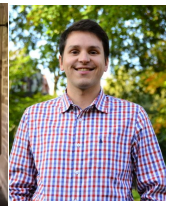
- Ca-containing ternary compounds from ICSD screened
  - Screening criteria: redox-activity, charge-neutrality, and thermodynamic stability
  - 2 possible candidates: CaV_2O_4 and $CaNb_2O_4$



- Computational search for chalcogenide semiconductors that exhibit optimal band gap with higher defect formation energy for detrimental defects and better structural stability
  - Optimal candidate is Cu_2CdGeS_3Se (CCdGSSe)

Ca-batteries:
"Searching ternary oxides and chalcogenides as positive electrodes for calcium batteries", W. Lu, J. Wang, G.S. Gautam, and P. Canepa, **Chem. Mater. 2021**, *33*, 5809-5821

Photovoltaics:
"Optimizing kesterite solar cells from Cu_2ZnSnS_4 to $Cu_2CdGe(S,Se)_4$", R.B. Wexler, G.S. Gautam, and E.A. Carter, **J. Mater. Chem. A 2021**, *9*, 9882-9897



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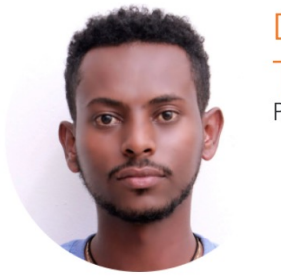

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