Molecular modelling, high performance computing, and the pursuit of better batteries

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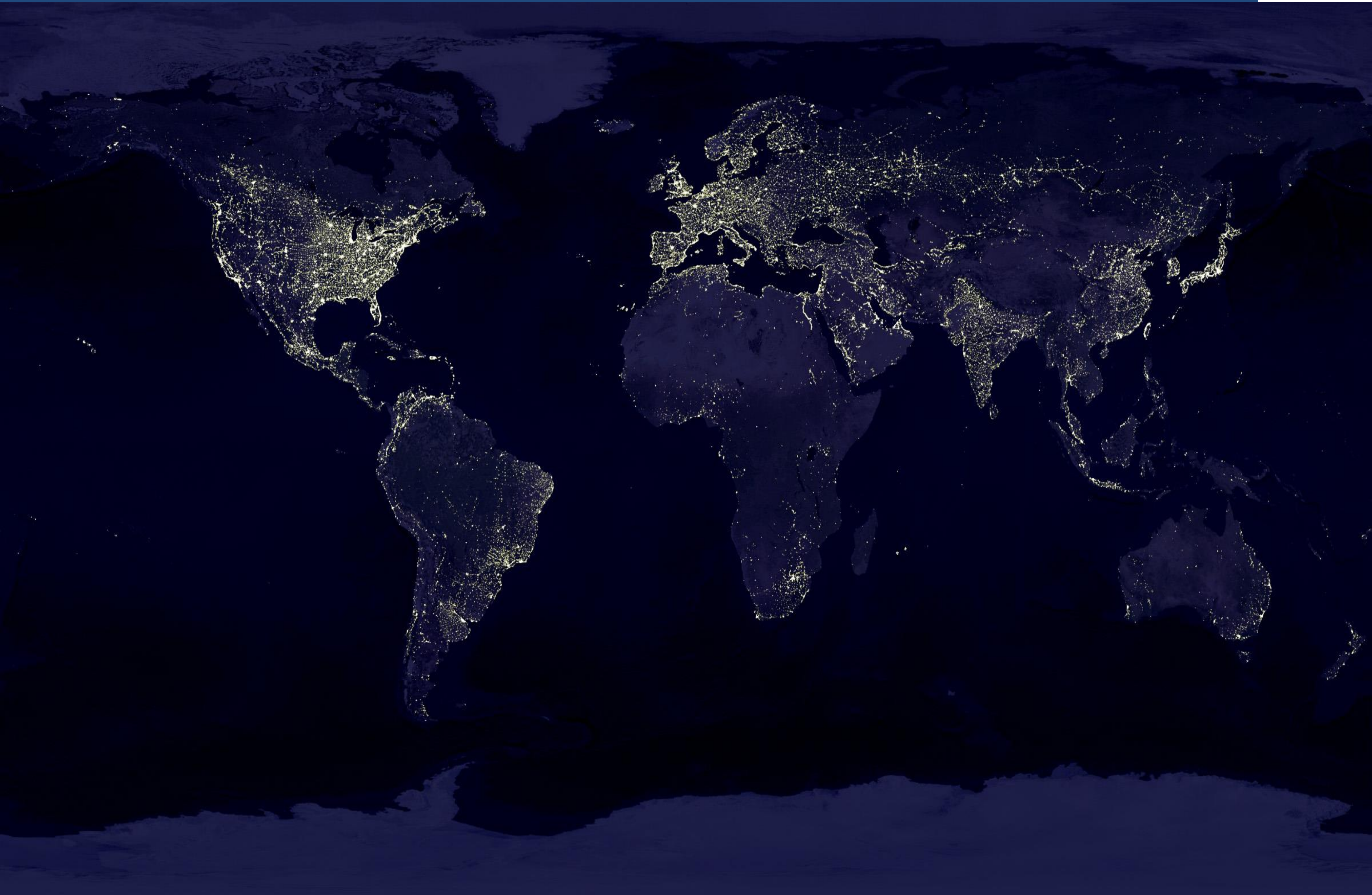
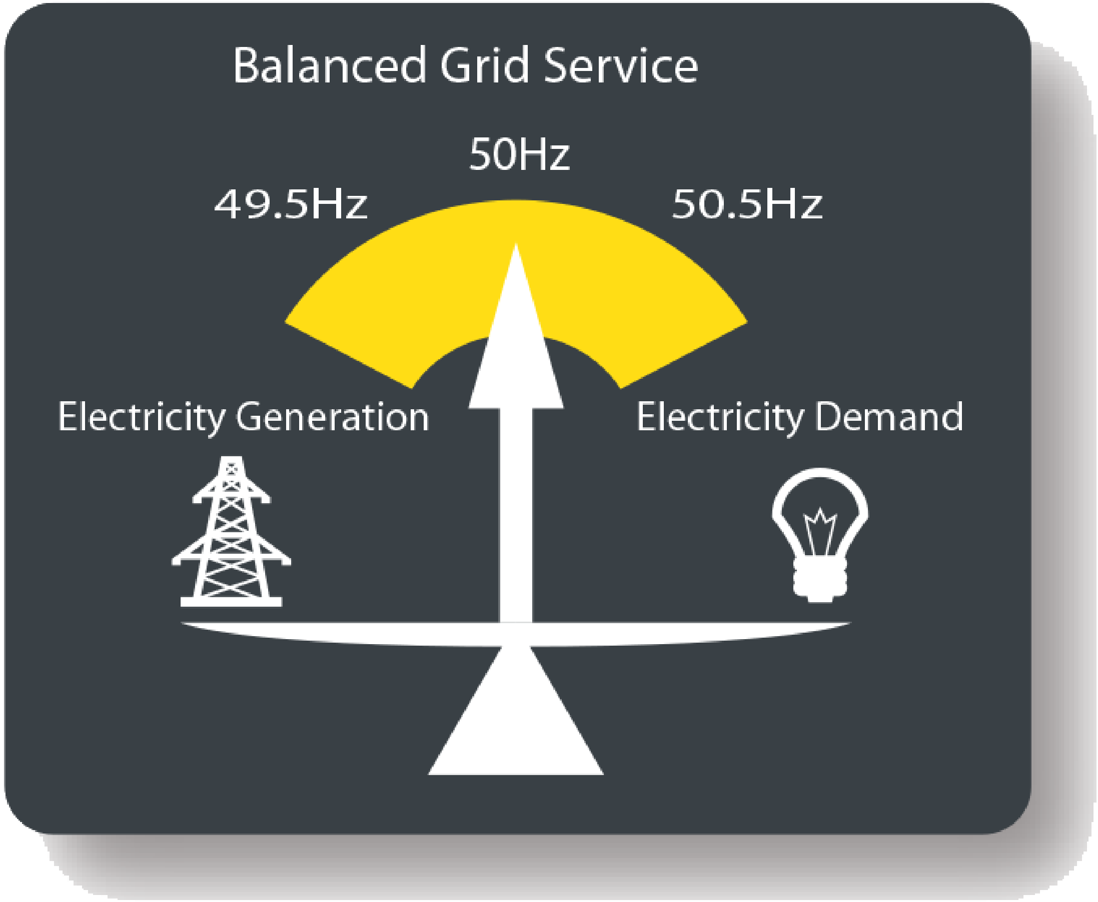
Electricity = modern society



Storage as enabler



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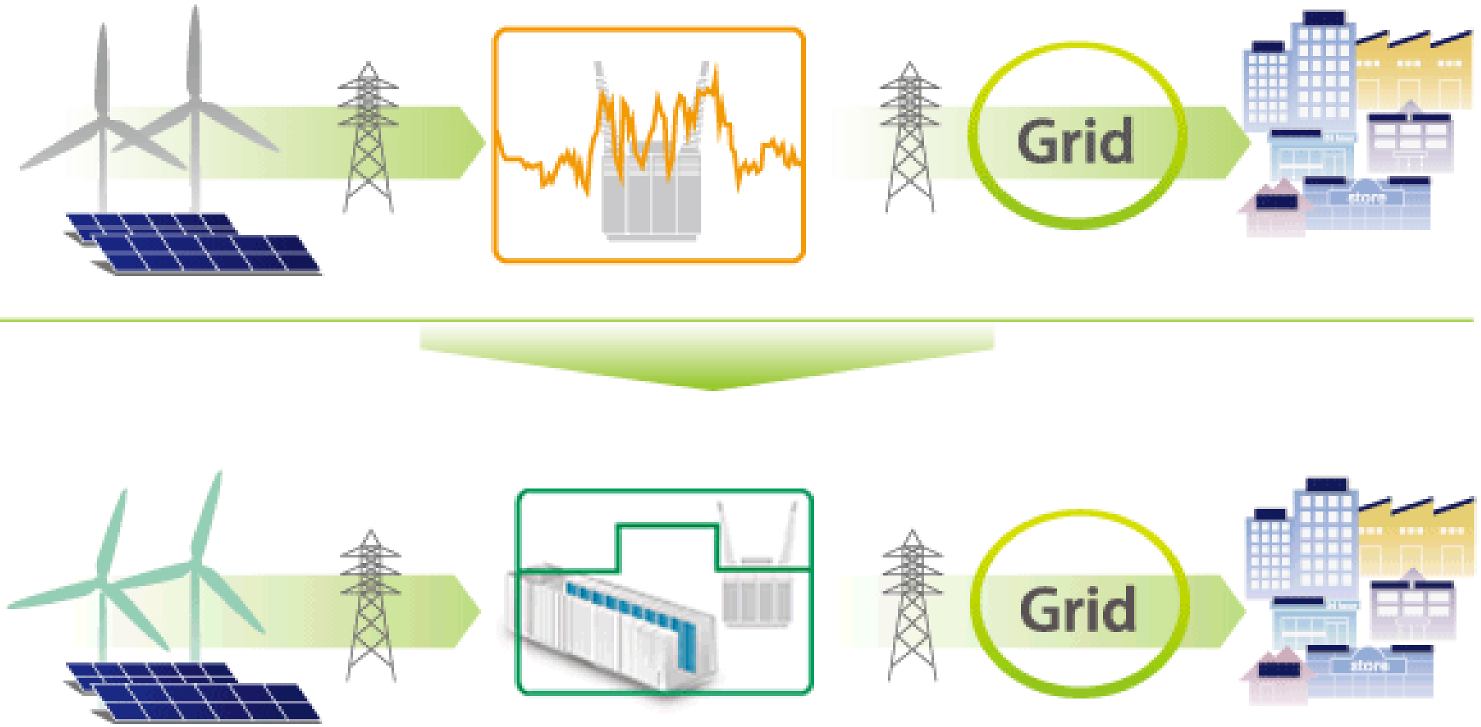
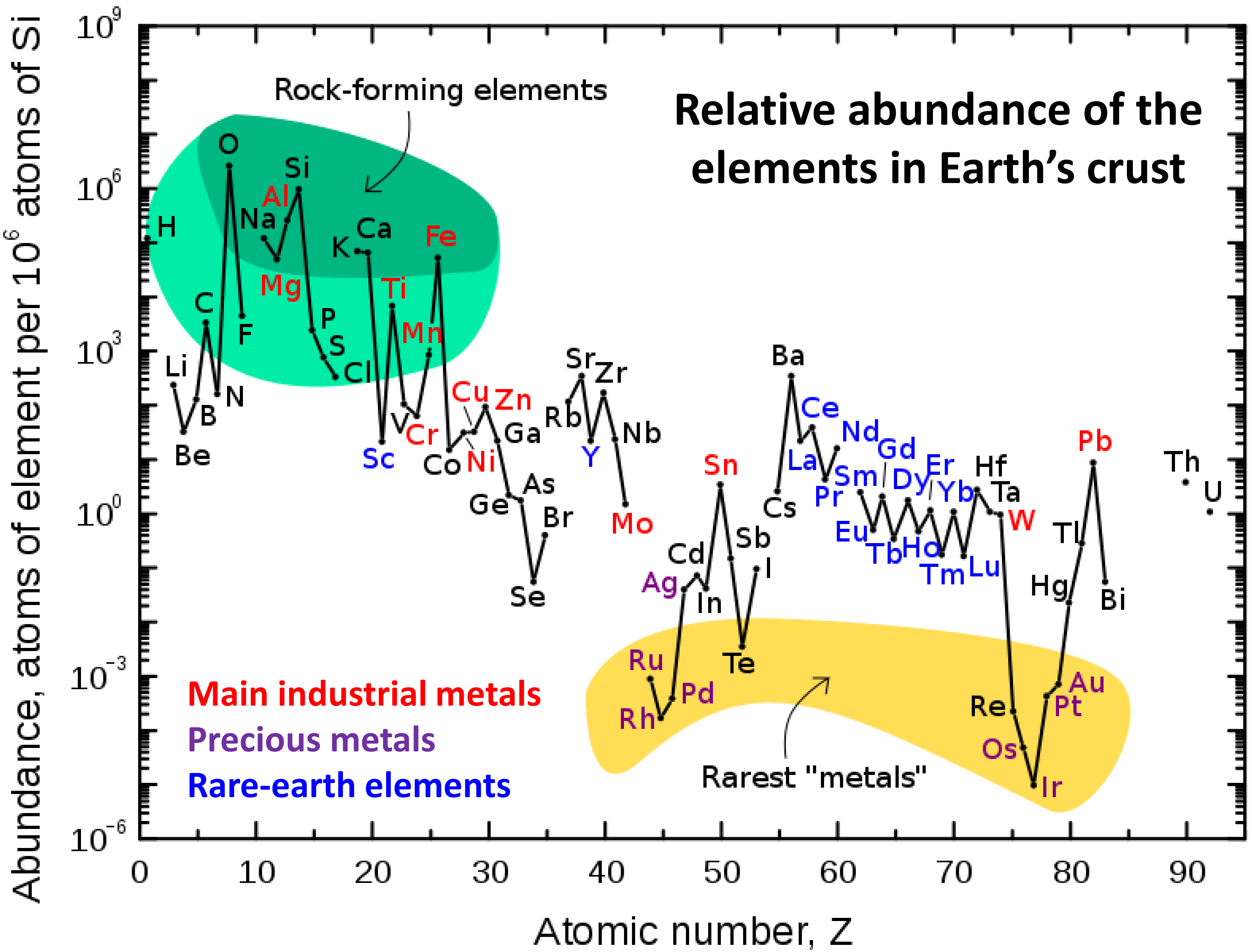


Energy storage mitigates intermittency of renewables (wind & PV solar)

Economic reality

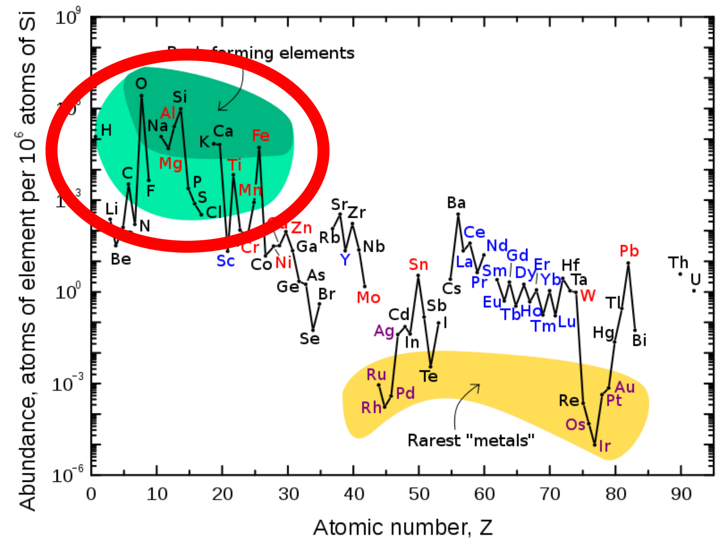
Invent cheap !

Cost-based discovery



Cost-based discovery

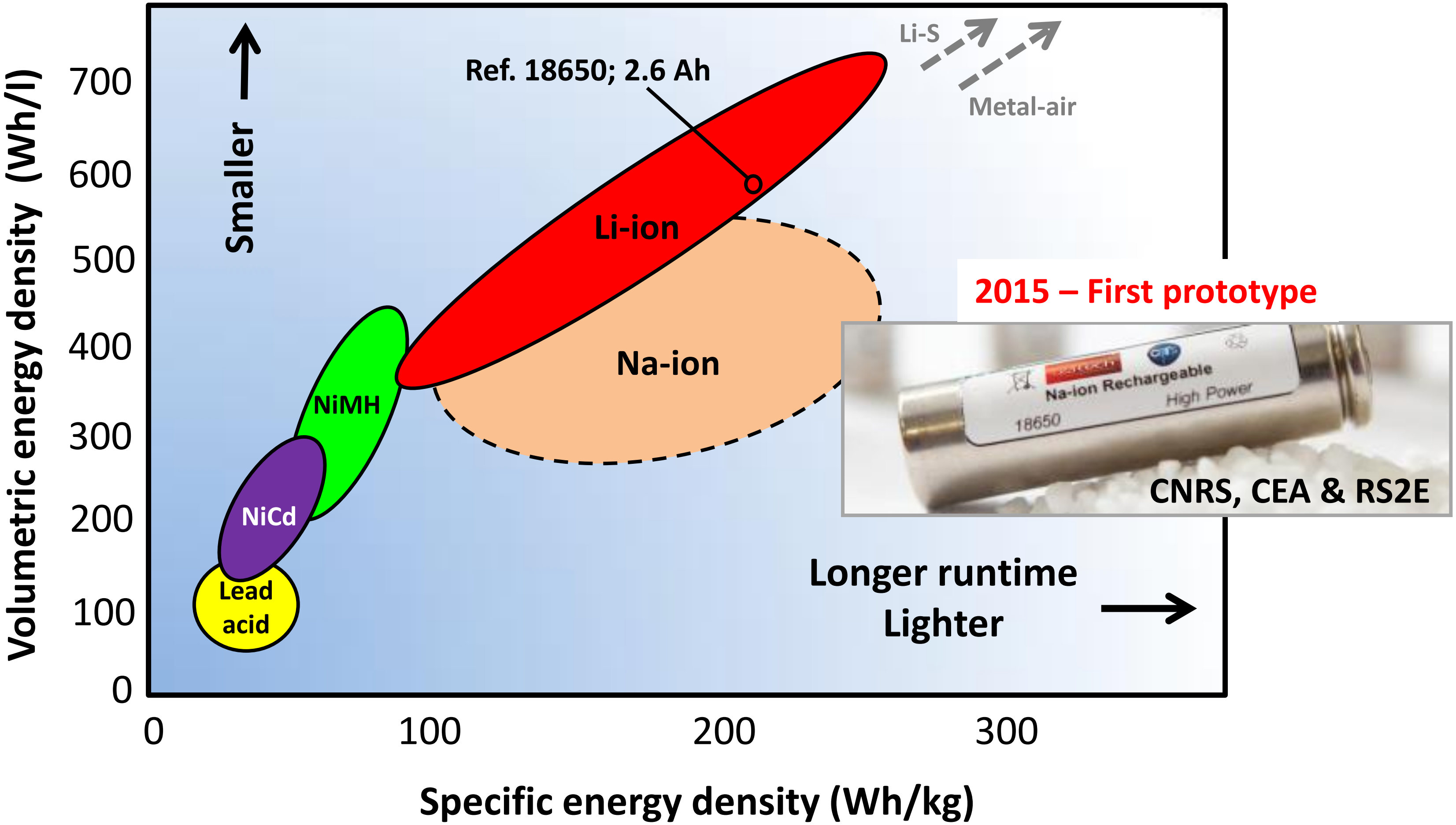
❑ **Confine chemistry to earth-abundant elements**



❑ **Make it easy to manufacture**

Advances in battery technology

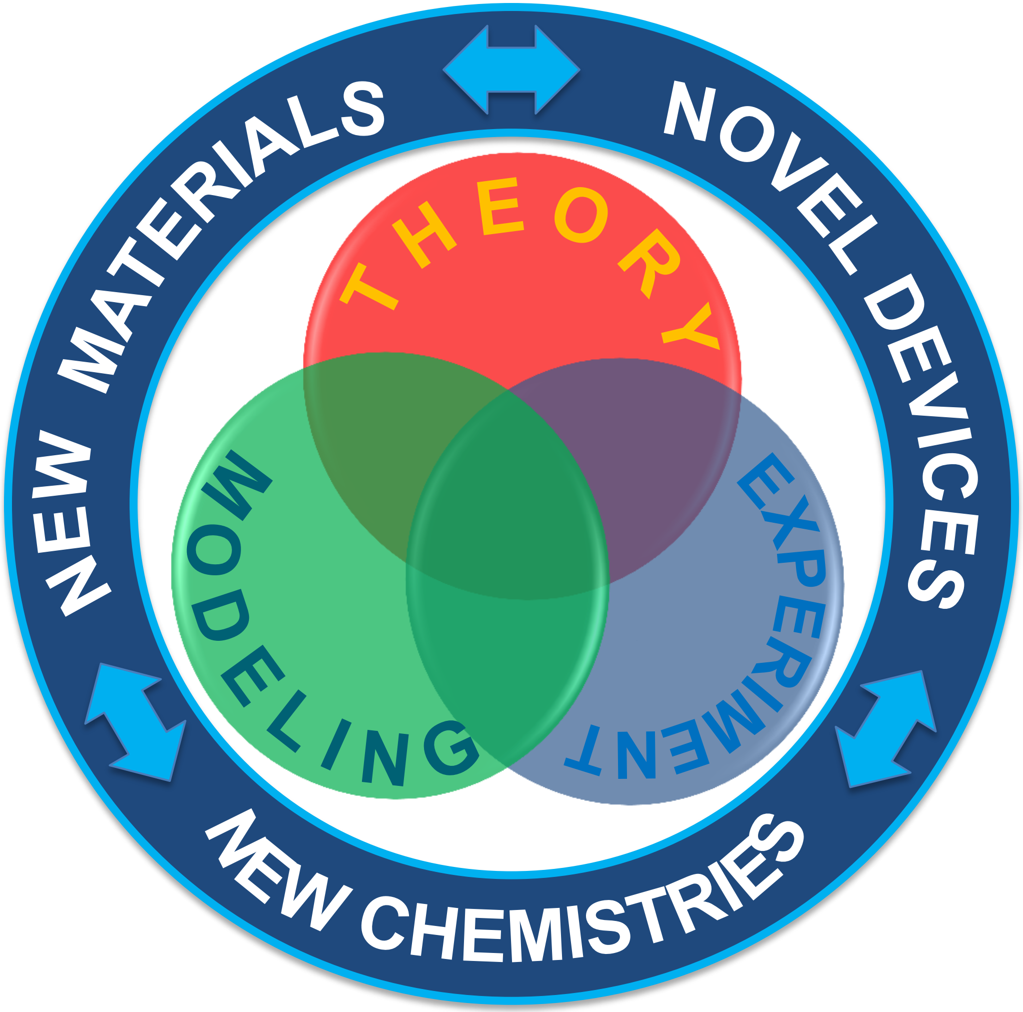
Primarily driven factor: Improvement in energy density



Na-ion technology is a **sustainable** alternative to Li-ion for **stationary storage**

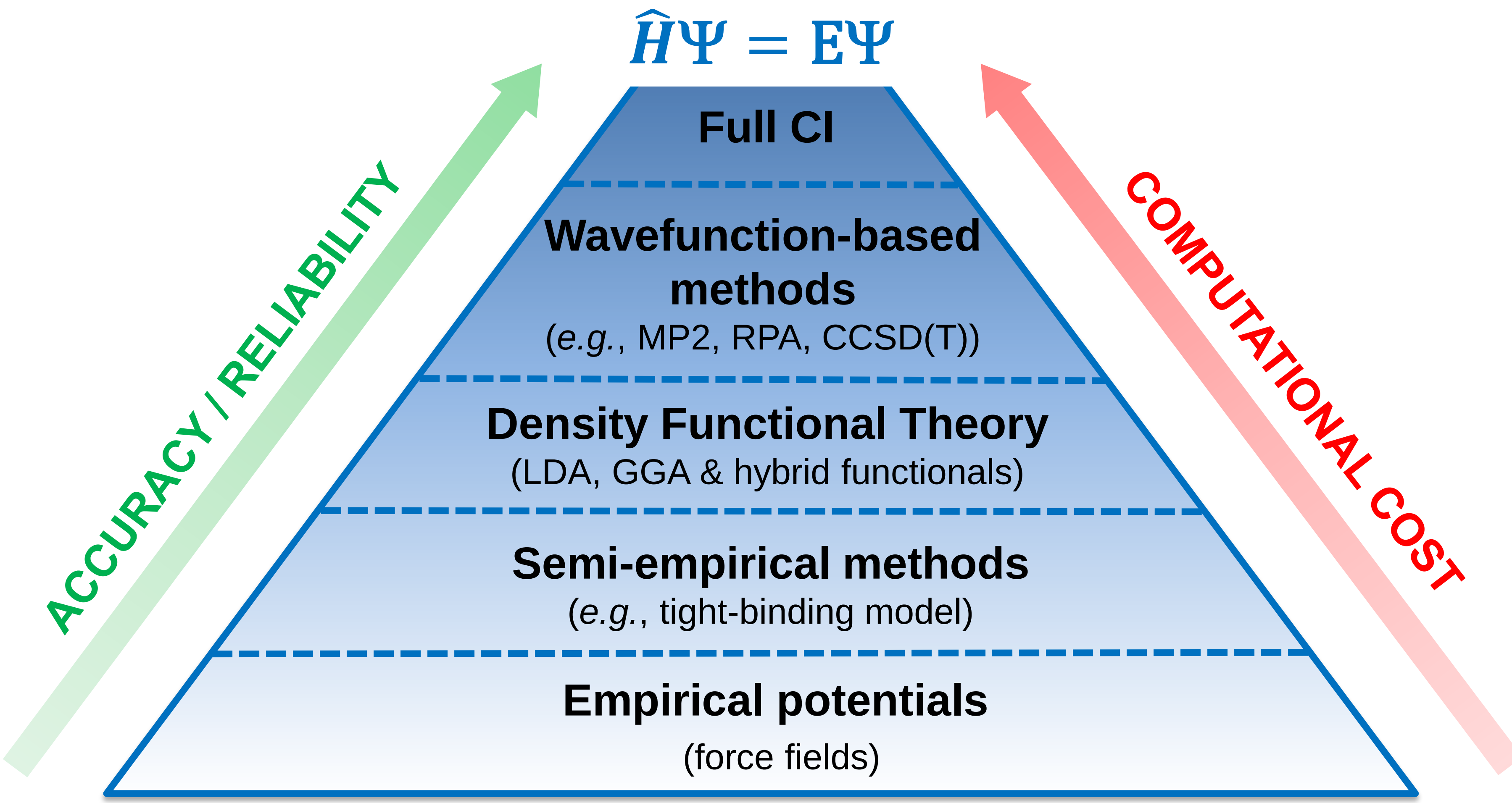
Materials' discovery

Impact of computer simulation



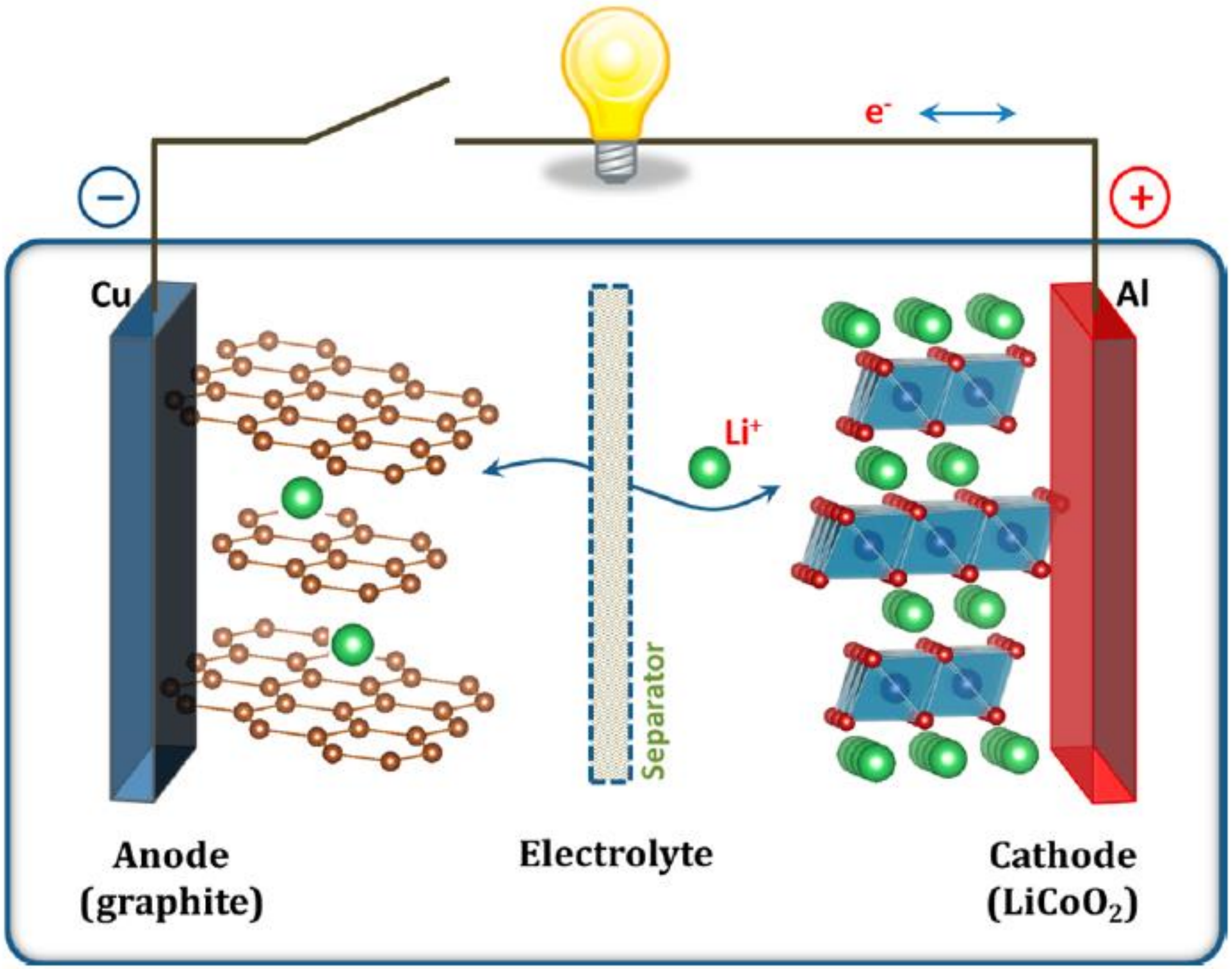
Atomistic modelling

DFT: A good trade-off



Rechargeable batteries

Main components

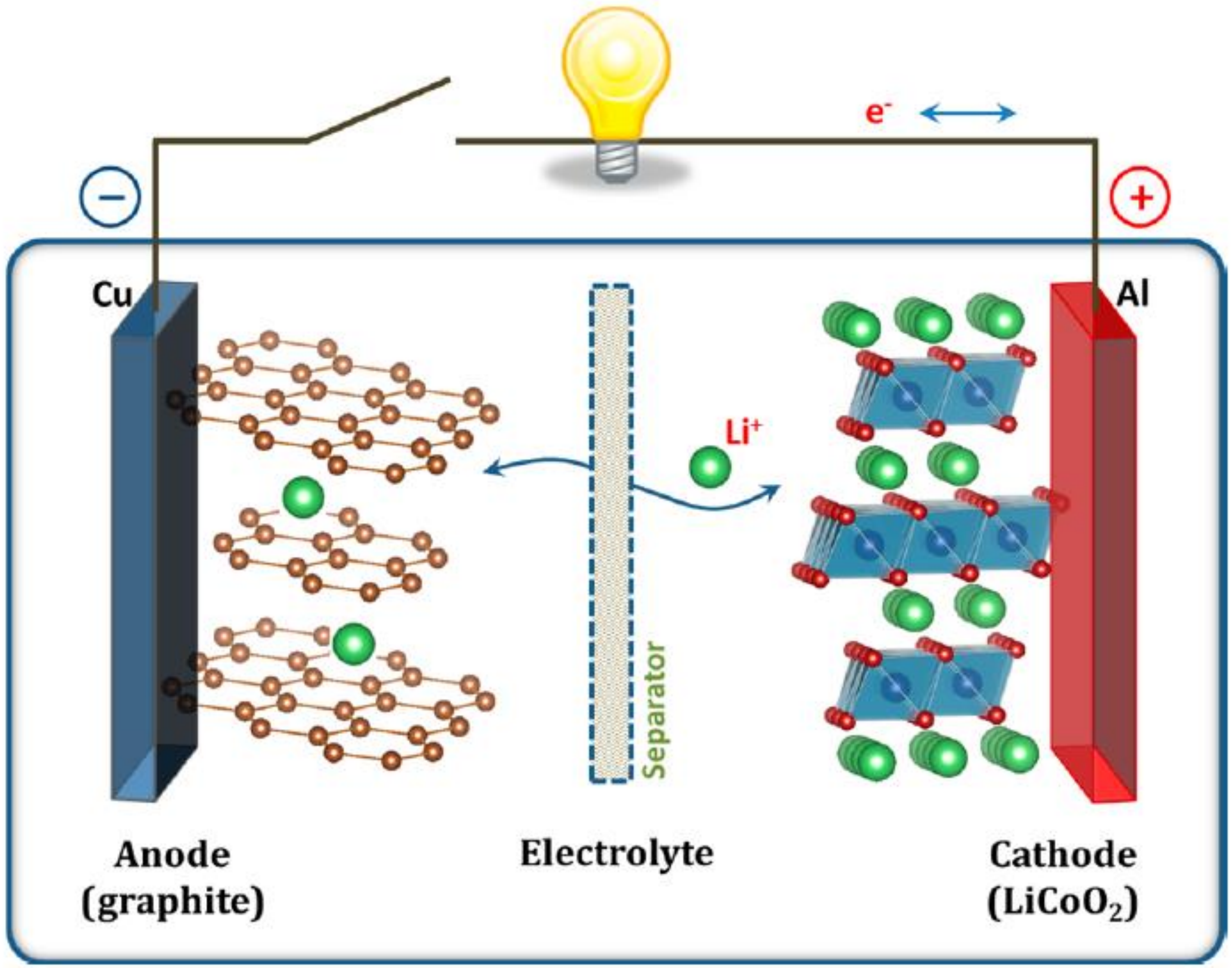


Source: J. B. Goodenough, K.-S. Park J. Am. Chem. Soc. **2013**, 135, 1167

Rechargeable batteries

Main components

- ❑ Anode
- ❑ Cathode
- ❑ Electrolyte
- ❑ Separator
- ❑ Binder
- ❑ Current collector



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Our efforts

Anodes
- New Na intercalation materials
- New Na alloys

Cathodes
- New Na intercalation materials

Electrolytes
- New Na/Li salts
- New solvents
- New solid electrolytes

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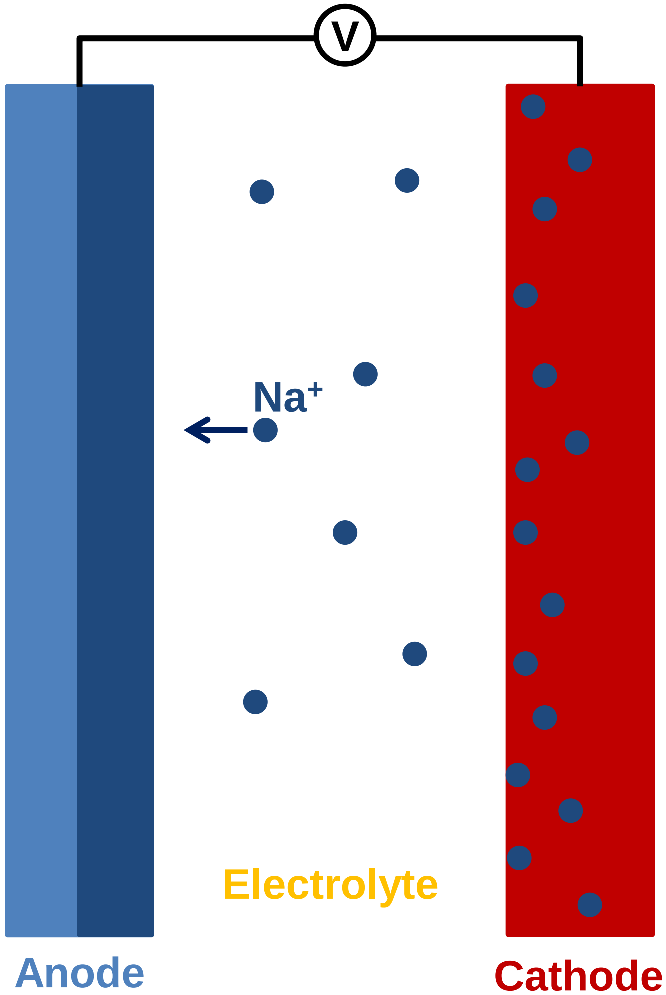
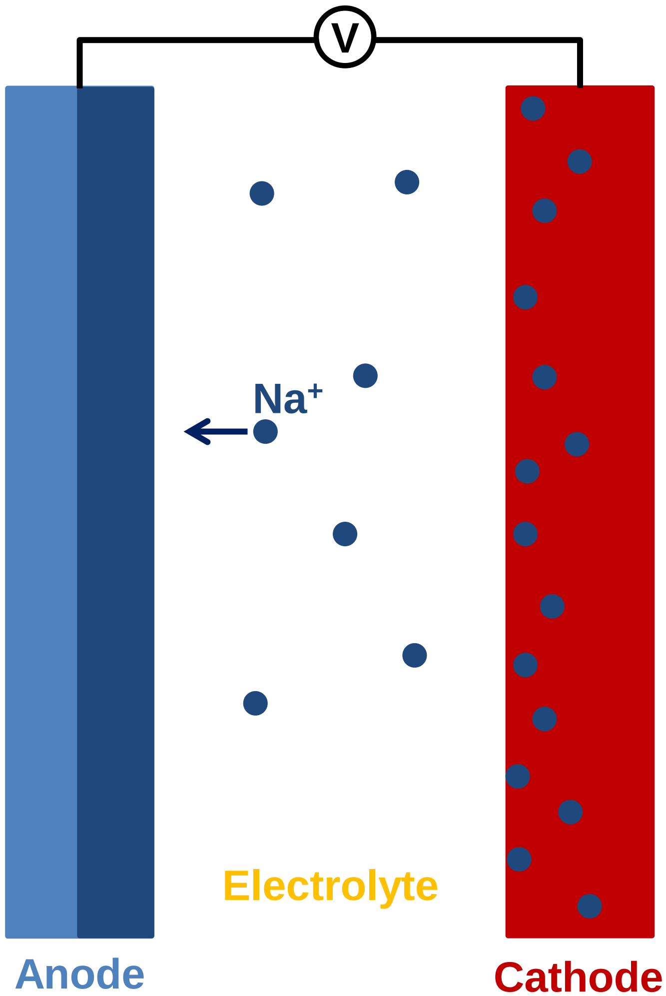
Na metal as anode



Ideality: Uniform growth

Na metal as anode



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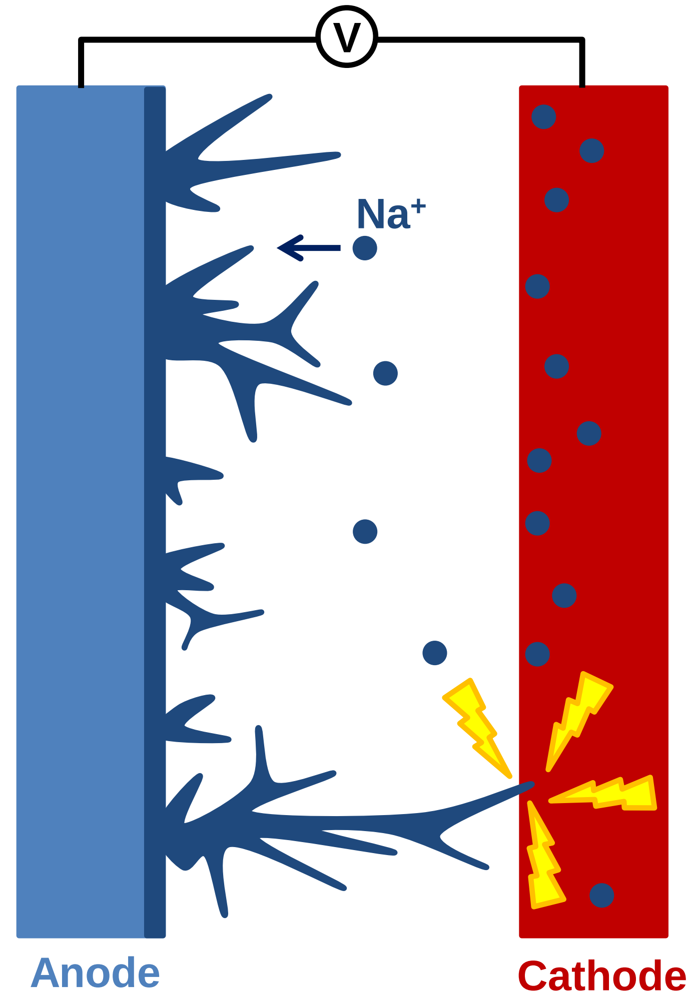
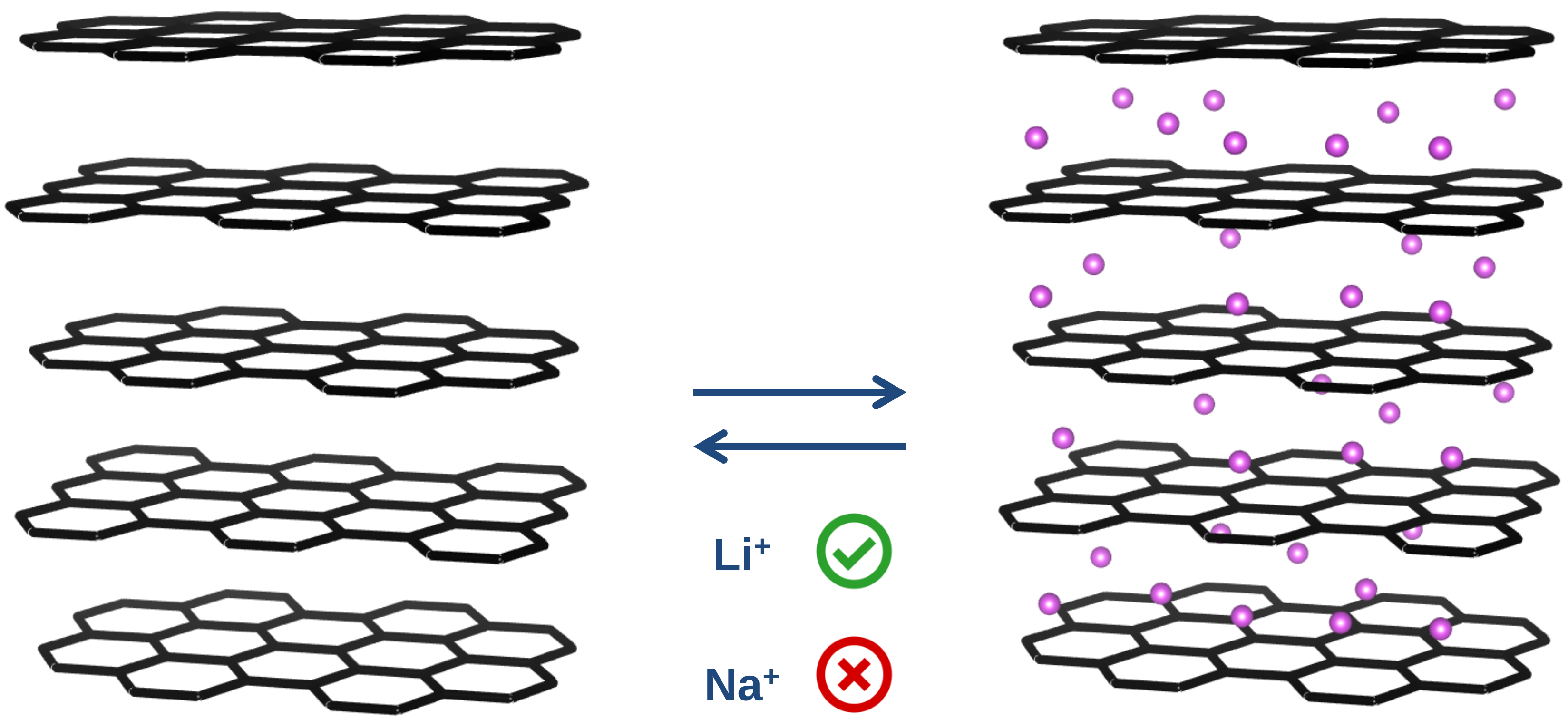


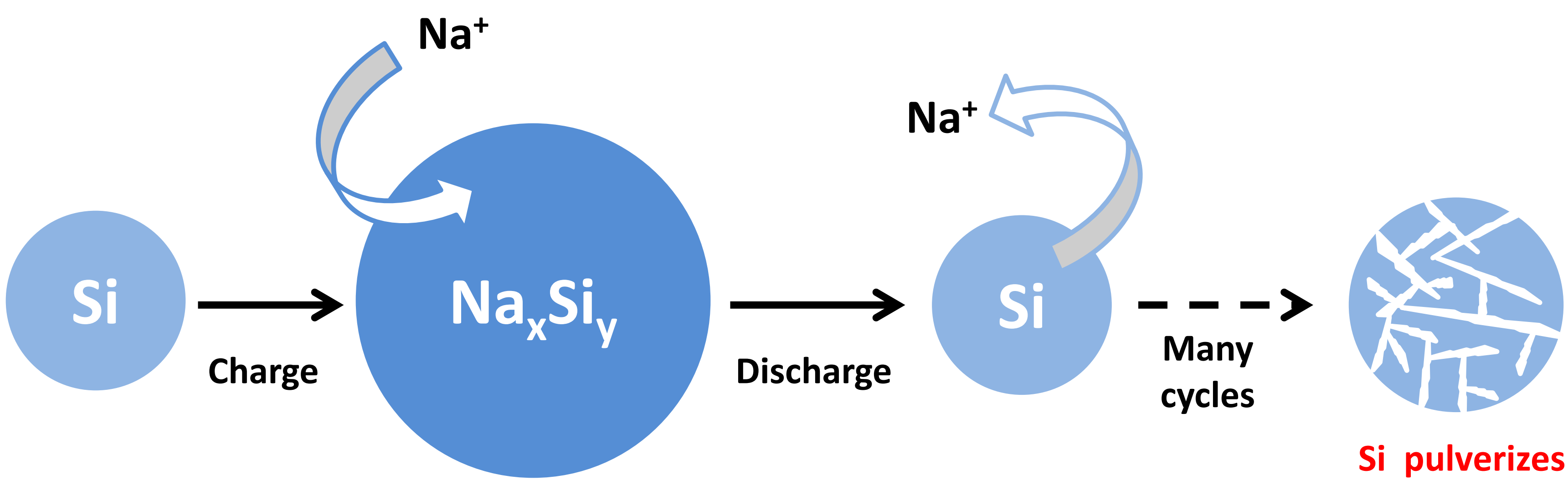
Reality: Dendritic growth

Graphite-based anodes



Graphite **doesn't intercalate** Na

Silicon-based anodes



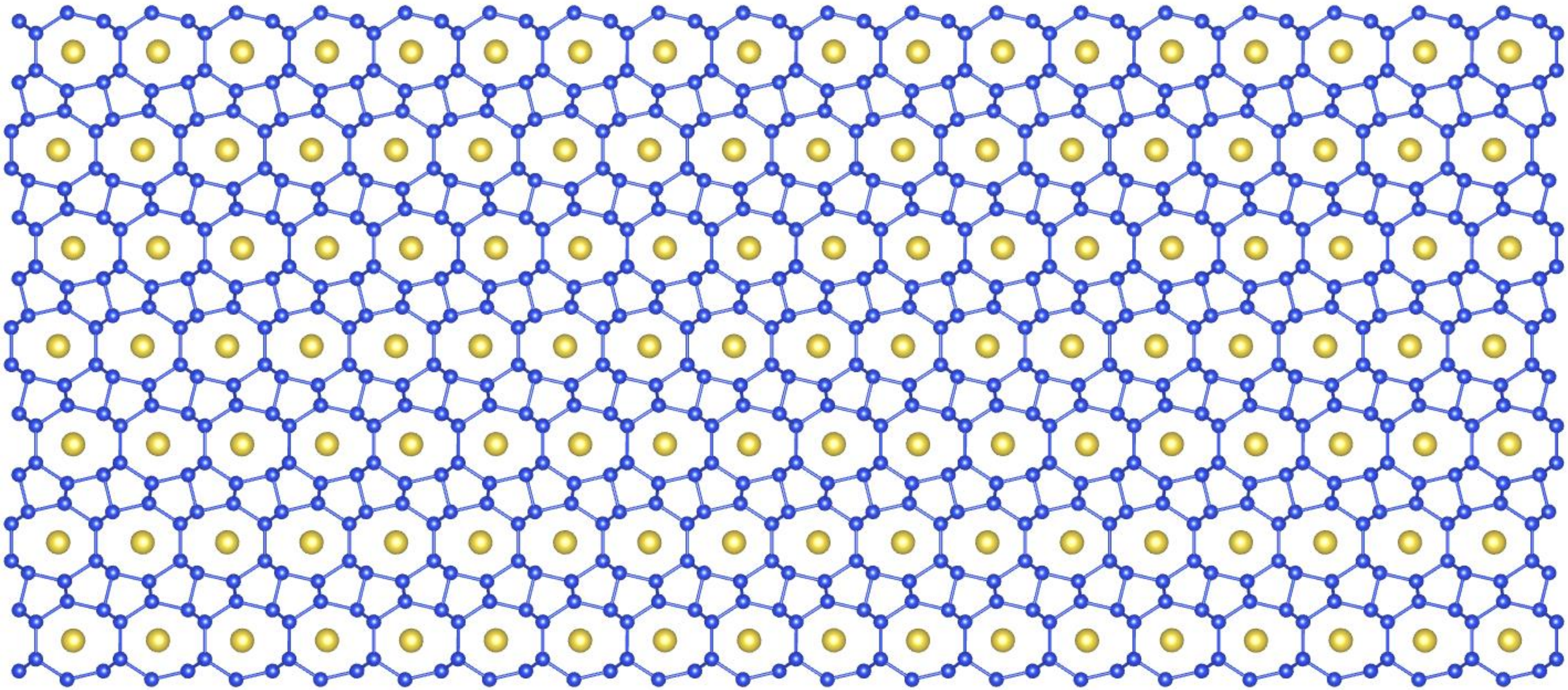
α-NaSi (%υ = 230%)

α-$Na_{0.76}Si$ (%υ = 114%)

Amorphous Si suffers from **large volume changes** upon Na insertion/extraction

Crystalline Si_{24}

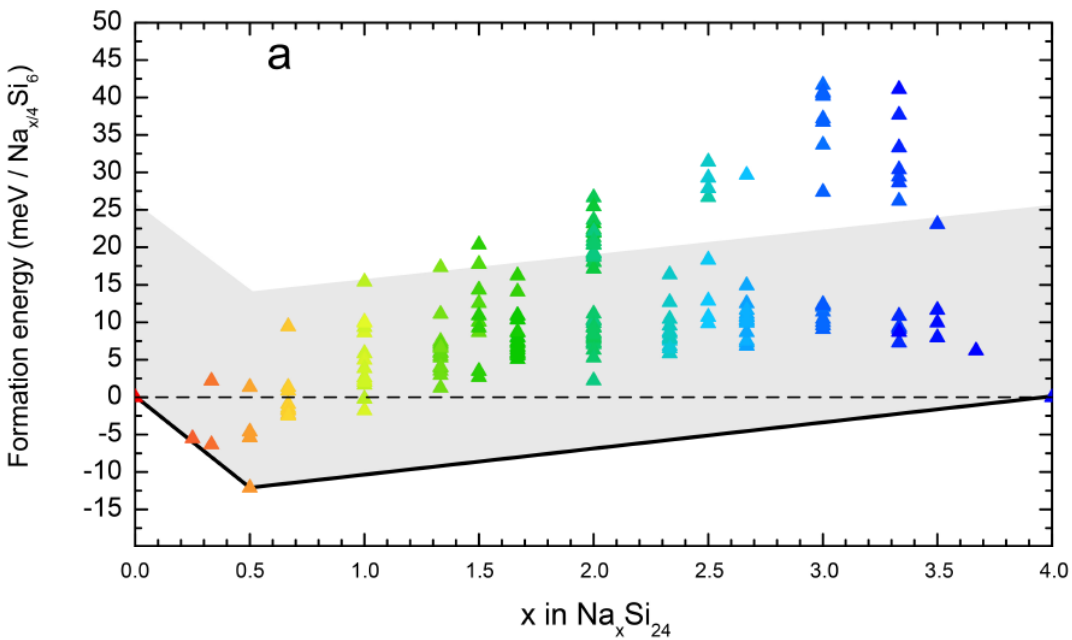
D. Kim *et al.*, Nat. Mater. **2014**, 14, 169

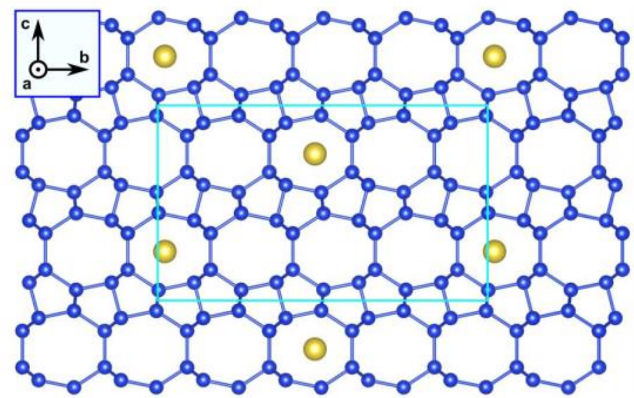


$4Na + 24\ Si \xrightarrow{\sim 8\ GPa} \boxed{Na_4Si_{24}} \xrightarrow{400\ K} \mathbf{Si_{24}} + 4Na(g)$

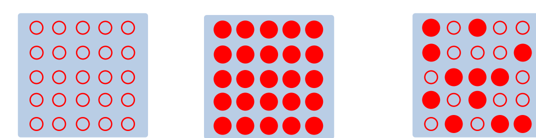
Example case

Na intercalation in crystalline Si_{24}





$(1-x)\ Si_{24} + x\ Na_4Si_{24} \rightarrow Na_xSi_{24}$



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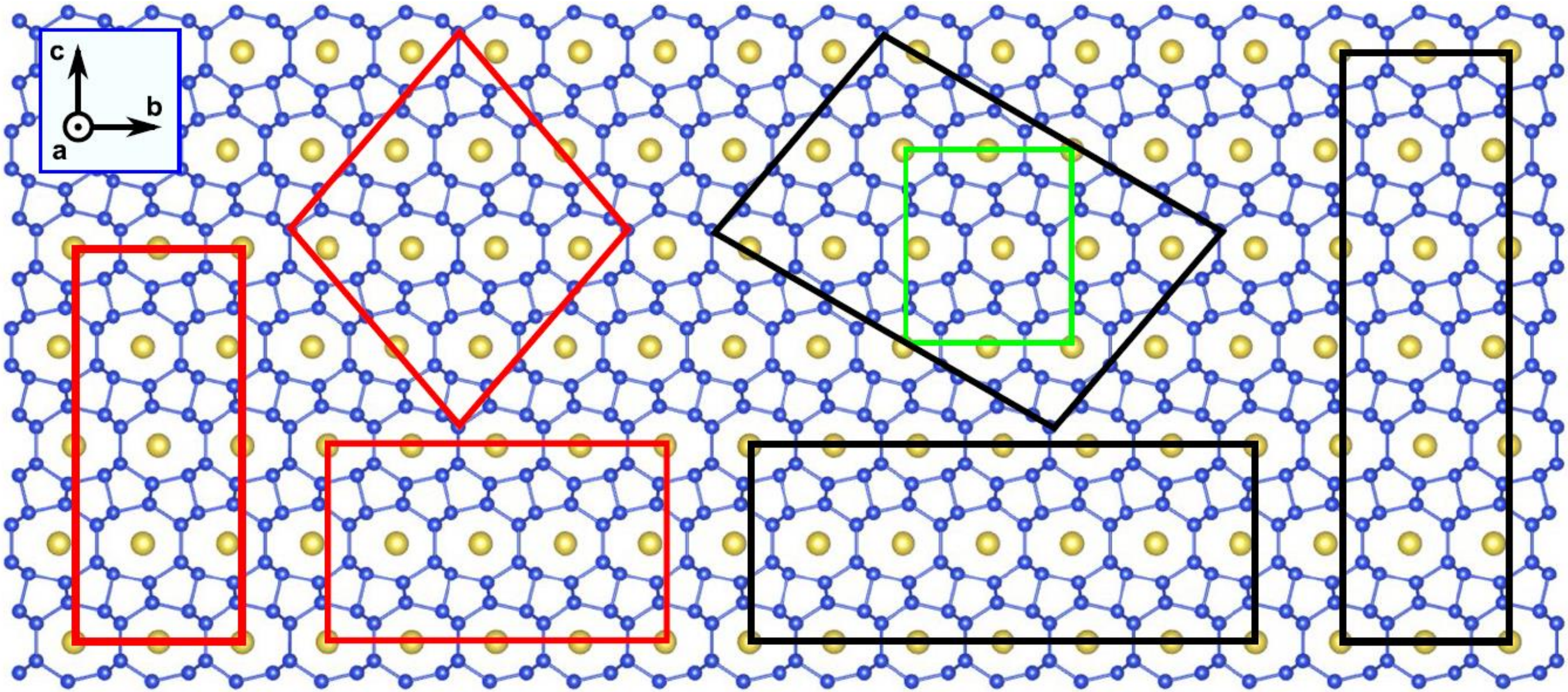

- Na_xSi_{24} ($0 \leq x \leq 4$) systems using **supercells** containing up to 16 formula units ($Na_{x/4}Si_6$)
- CASM code to generate all of the possible **Na and Na vacancy arrangements**
- Only 235 configurations at DFT level; selection: fitting procedure using a **cluster expansion**

Example case

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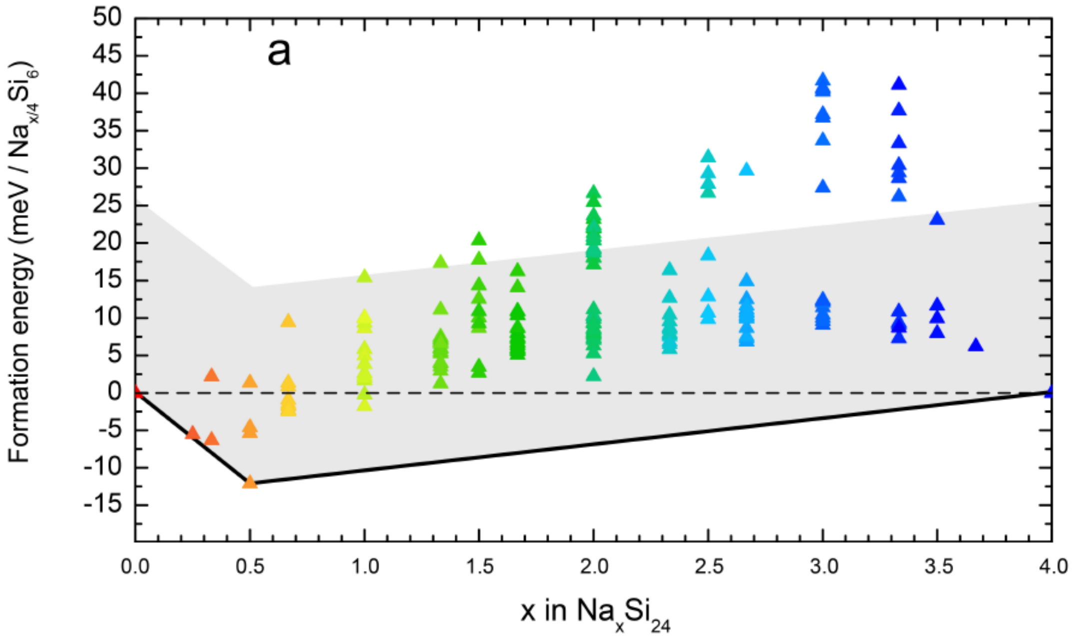

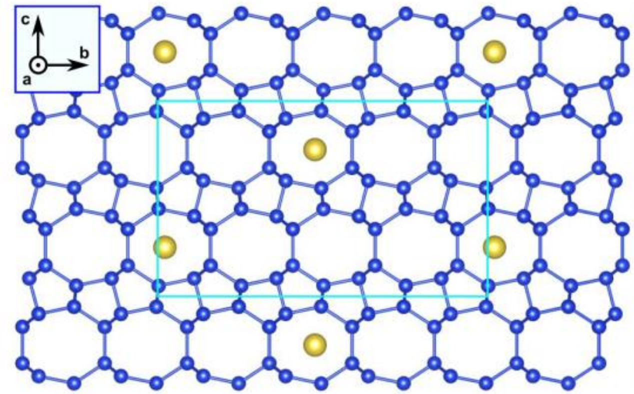

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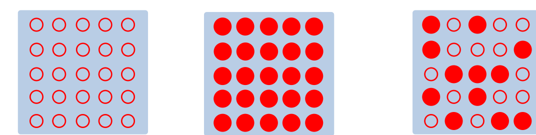

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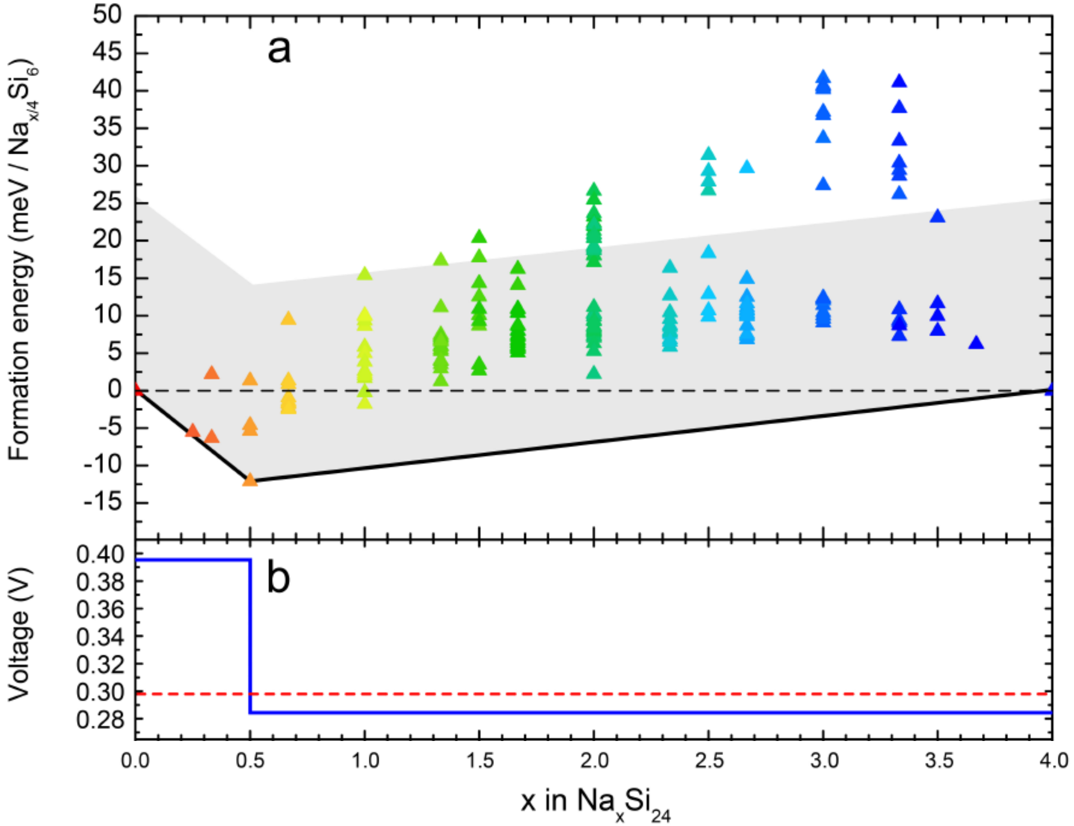
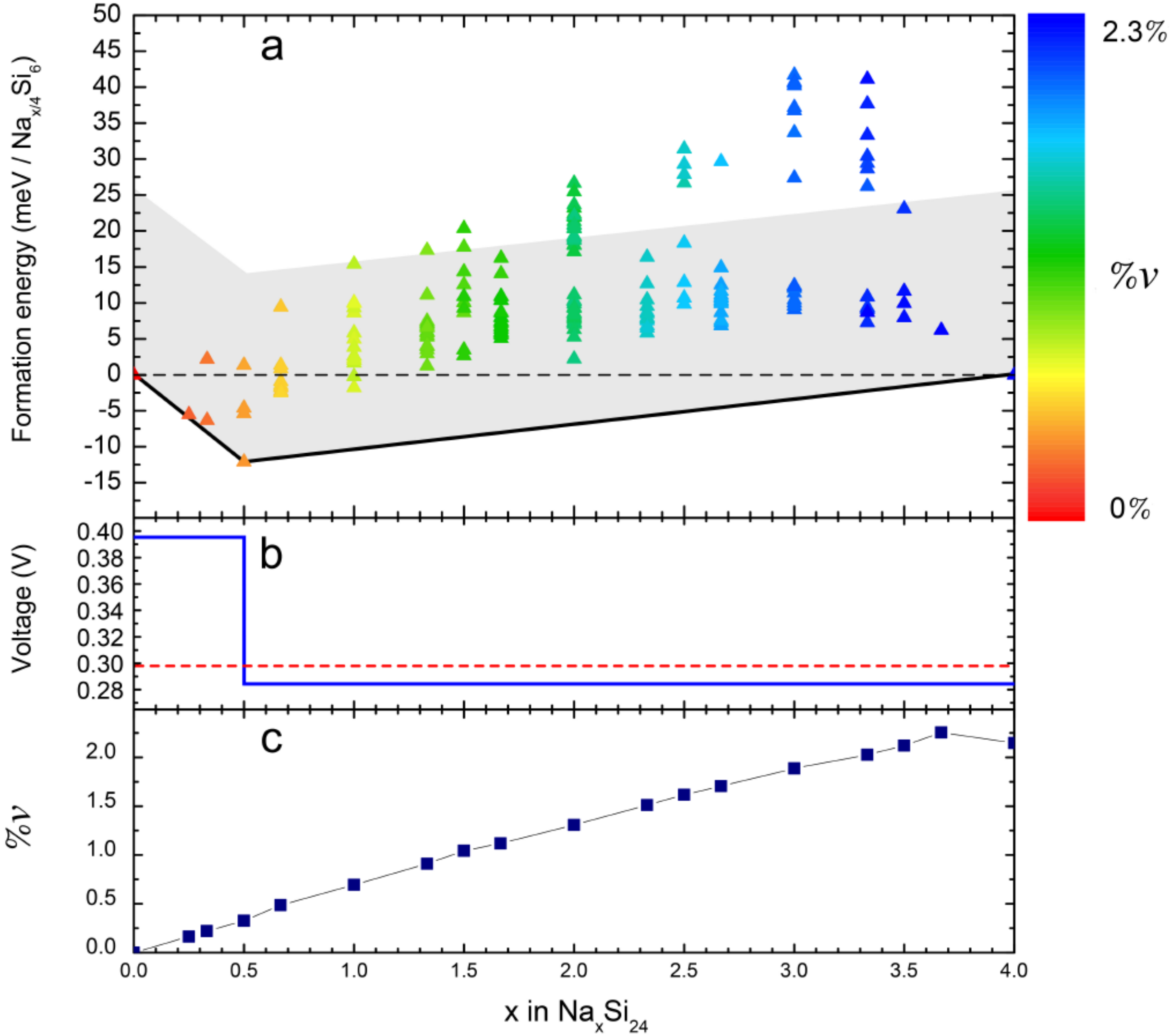


Average voltage

$$V(x) = -\frac{\Delta G^{ij}}{(x_j - x_i)F} \approx -\frac{\left[E_{Na_{x_j}Si_{24}} - E_{Na_{x_i}Si_{24}} - (x_j - x_i)E_{Na(s)}\right]}{(x_j - x_i)e}$$

Example case

Na intercalation in crystalline Si_{24}



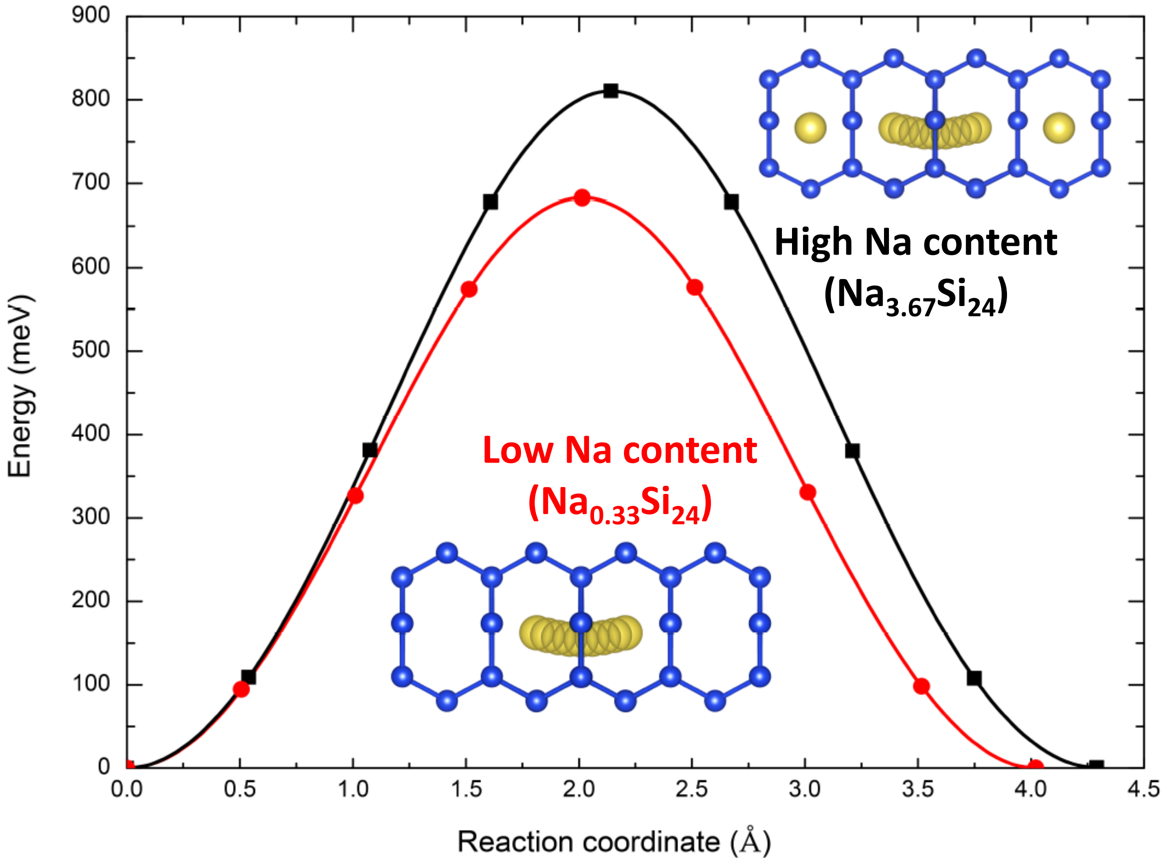
Volume change

$$\%v = 100 \cdot \frac{v_x - v_0}{v_0}$$

Example case

Na intercalation in crystalline Si_{24}

Na diffusion kinetics



$E_a(Na_{3.67}Si_{24})$ = **811** meV

$E_a(Na_{0.33}Si_{24})$ = **683** meV

Example case

Na intercalation in crystalline Si_{24}

Advantages

- Na_xSi_{24} forms a solid solution along the whole range of Na compositions
- Na_xSi_{24} shows negligible volume expansion upon Na insertion
- Its operating voltage versus Na/Na^+ is conveniently low

Limitations

- Need for enhancing Na mobility in bulk Na_xSi_{24}
- Moderate theoretical specific capacity of Si_{24} (159 mAh/g)
- The synthesis of Si_{24} is expensive (high pressures)

Conclusions

- **First-principles insight into electroactive materials is an effective tool to:**

  - ✓ Explore compositional and structural spaces
  - ✓ Understand novel energy storage mechanisms
  - ✓ Accelerate materials discovery
  - ✓ Design materials with better electrochemical performance

Acknowledgements

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❑ Team

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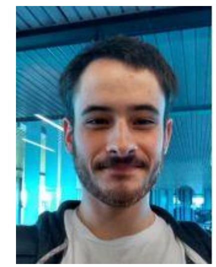

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