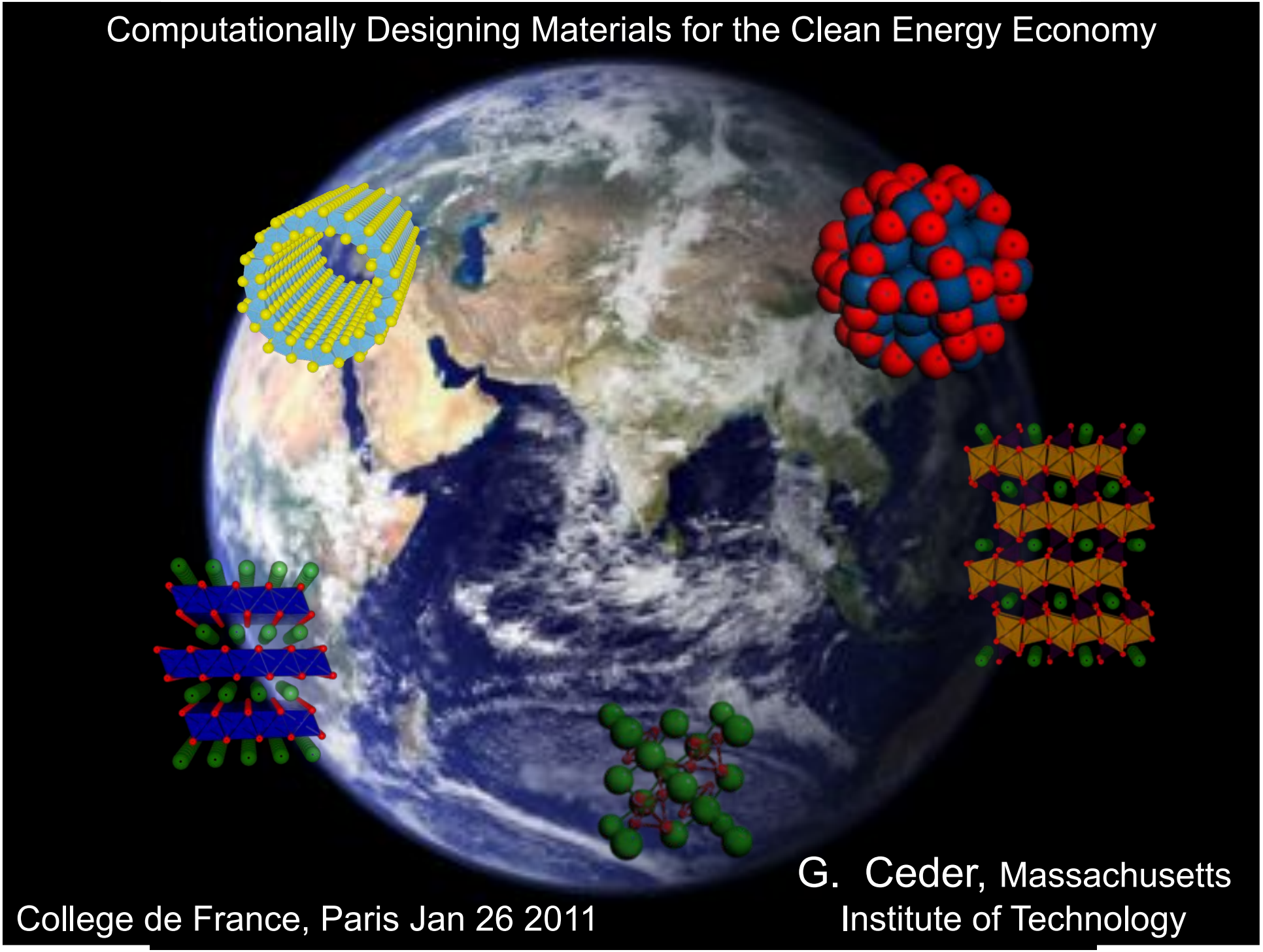
# Computationally Designing Materials for the Clean Energy Economy



G. Ceder, Massachusetts Institute of Technology

College de France, Paris Jan 26 2011

# 1973

# Materials Play a Strategic Role Today

**Sept 7, 2010**

Japan arrest Chinese boat captain

**Sept 22, 2010**

China blocks shipments of **Rare Earth Metals** to Japan

**Sept 24, 2010**


Japan releases captain

# From oil and coal to clean energy requires significant materials innovation

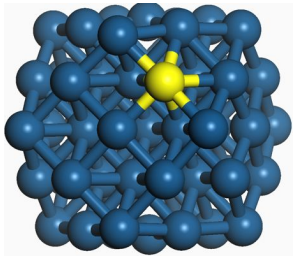
*Many promising energy technologies are limited by not having the right materials*

**Hydrogen Storage**

*Material needed that can absorb/desorb large quantity of hydrogen*

**Fuel cell electrocatalysts**

*Replace expensive Platinum. Find catalysts for more complex hydrocarbons*



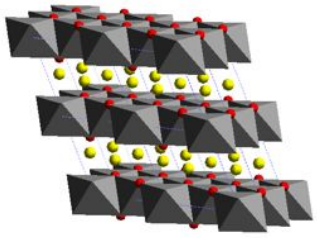
**Solid State Lighting**

**Thermoelectrics**

*Need higher ZT factor for efficient recovery of waste heat into electricity*

**Lighter/Stronger materials**

*Reduce weight in transportation sector: cars, airplanes, … e.g. Titanium*



**Solar cell materials**

**Battery materials**

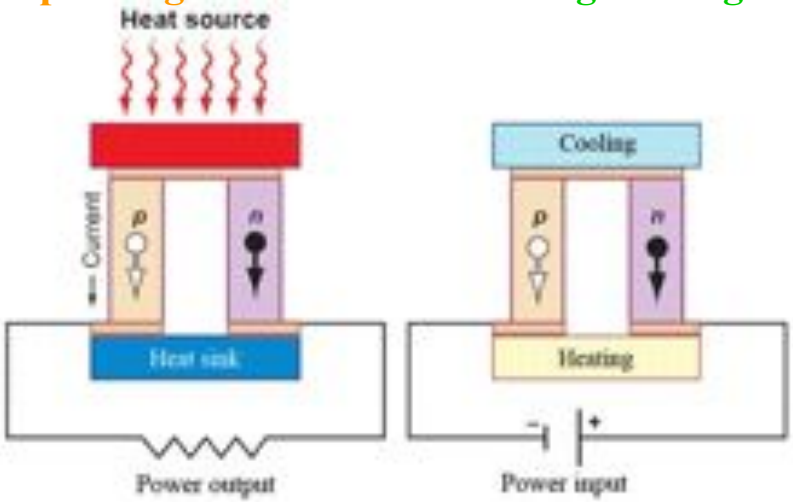
**Membrane materials (oxygen, protons, …)**

# Photovoltaics

- Efficiency of PV material is key as most of the cost is in making panels.
- Higher efficiency material reduces number of panels needed

# Example: Thermoelectrics: A real opportunity for materials design and engineering

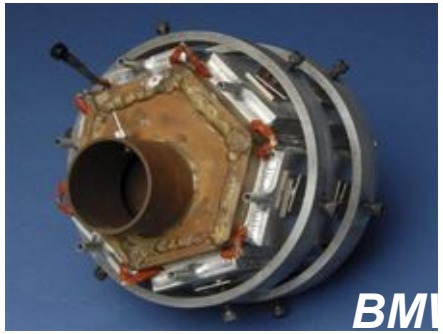
power generation




cooling/heating




## Waste heat conversion



reduce carbon emission by 8% (= remove 25% of all US cars)

- co-generation at home scale
- electricity in vehicles from engine waste heat (e.g. diesel engines)

## Materials need

high Seebeck coefficient

High electrical conductivity

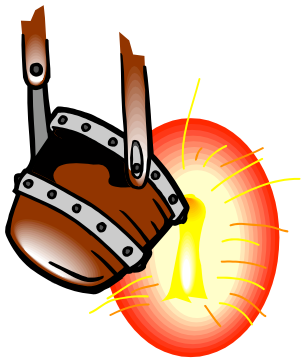
$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_{ph}} T$$

low thermal conductivity

## Many materials issues on the energy efficiency and $CO_2$ reduction side of the problem

- **cement** -> Production of CaO leads to large $CO_2$ emission. In China 9% of all $CO_2$ is from cement

*Can we make cement without CaO ?*



- **steelmaking** makes $CO_2$
- (½ kg C / kg Fe) x 1.3 billion tonnes
- 1/20 of primary energy use in the world is to make steel

*Can we make steel without $CO_2$ production ?*

# Materials Critical to Energy Innovation

**Hydrogen** | **Solar** | **Permanent Magnets** | **Construction (cement, steel …**

**Thermoelectrics** | **Energy Storage** | **Catalysis**

**Do we have this much time ?**

1930 1940 1950 1980 1990 2000

st IBM PC → Human Genome Mapped

invented → Teflon

Lithium ion ← Sony

Whittingham

Titanium

ond-like Thin Films

Polycarbonate

GaAs

Amorphous soft magnets

**Can we accelerate materials innovation ?**

**18 Years…from the average new materials discovery to commercialization**

*Materials Data from: Eagar, T.; King, M. Technology Review (00401692)* ***1995****, 98, 42.*

# The Materials Labyrinth

- 100,000 known inorganic compounds
- 2 Million known organic compounds
- Many substances still to be discovered
- How do we find the materials with good properties ?

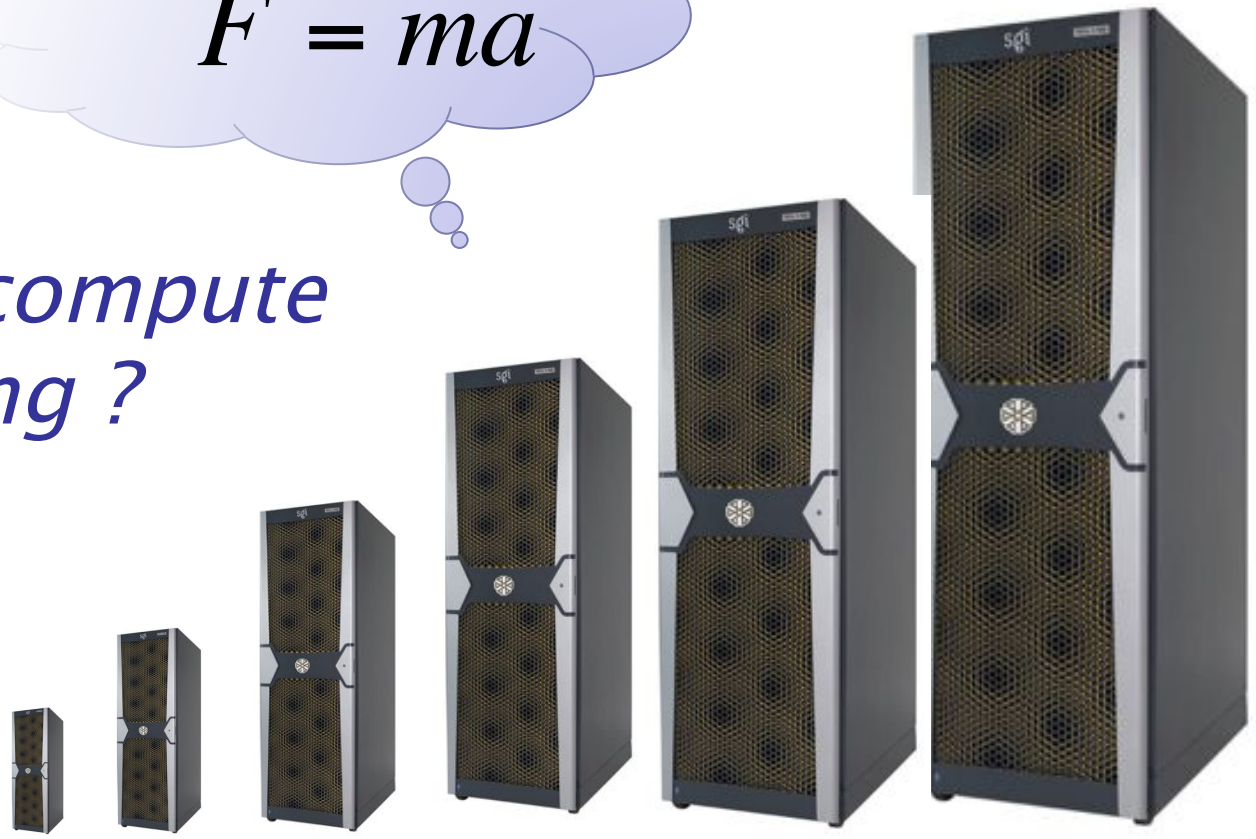
# The basic equations that describe matter are known …

$$H\Psi = E\Psi$$

$$E = mc^2$$

$$\vec{F} = m\vec{a}$$

*Can we compute everything ?*



# Quantum power: *Density Functional Theory*

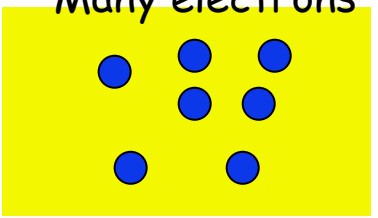
**Kinetic Energy**

**Interaction with nucleus**

**Interaction between electrons**

$$H = \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{nuclear}(r_i) + \frac{1}{2} \sum_{i}^{N_e} \sum_{j \neq i}^{N_e} \frac{1}{|r_j - r_i|}$$

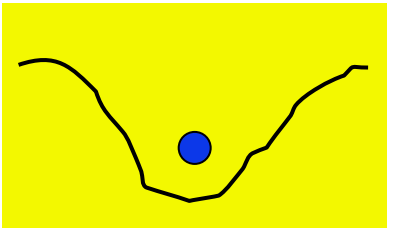
Many electrons



**Replace e-e interaction by average potential**

$$H = \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{nuclear}(r_i) + \sum_{i=1}^{N_e} V_{effective}(r_i)$$

One electron

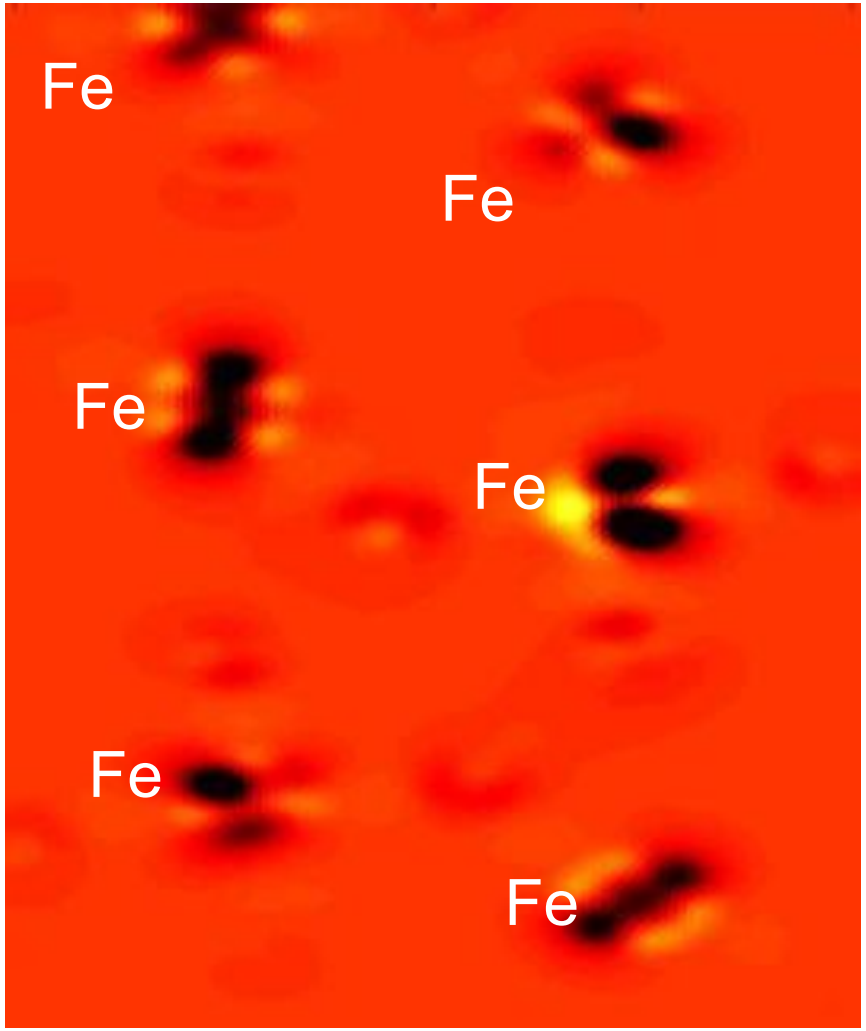


**Approximated in the Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA) to Density Functional Theory (DFT)**

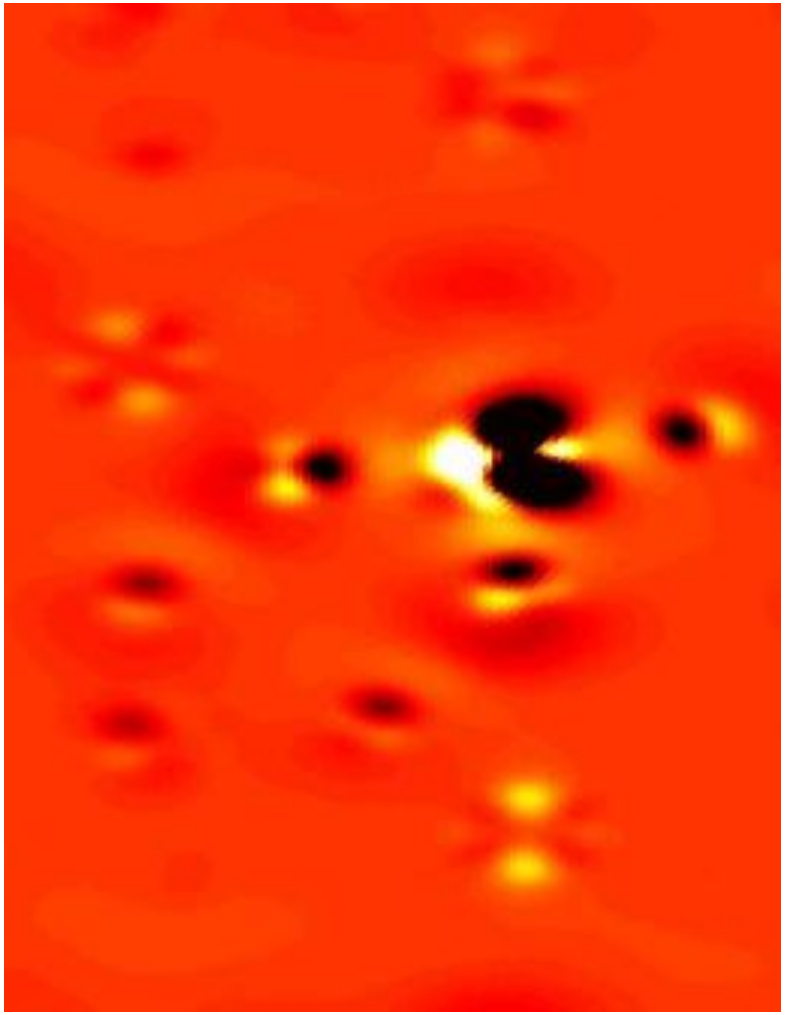
$V_{eff}$ = average electrostatic potential from other electrons + exchange effect (Pauli principle) + correlation effects

# Solving the equations of quantum mechanics let's us see inside materials

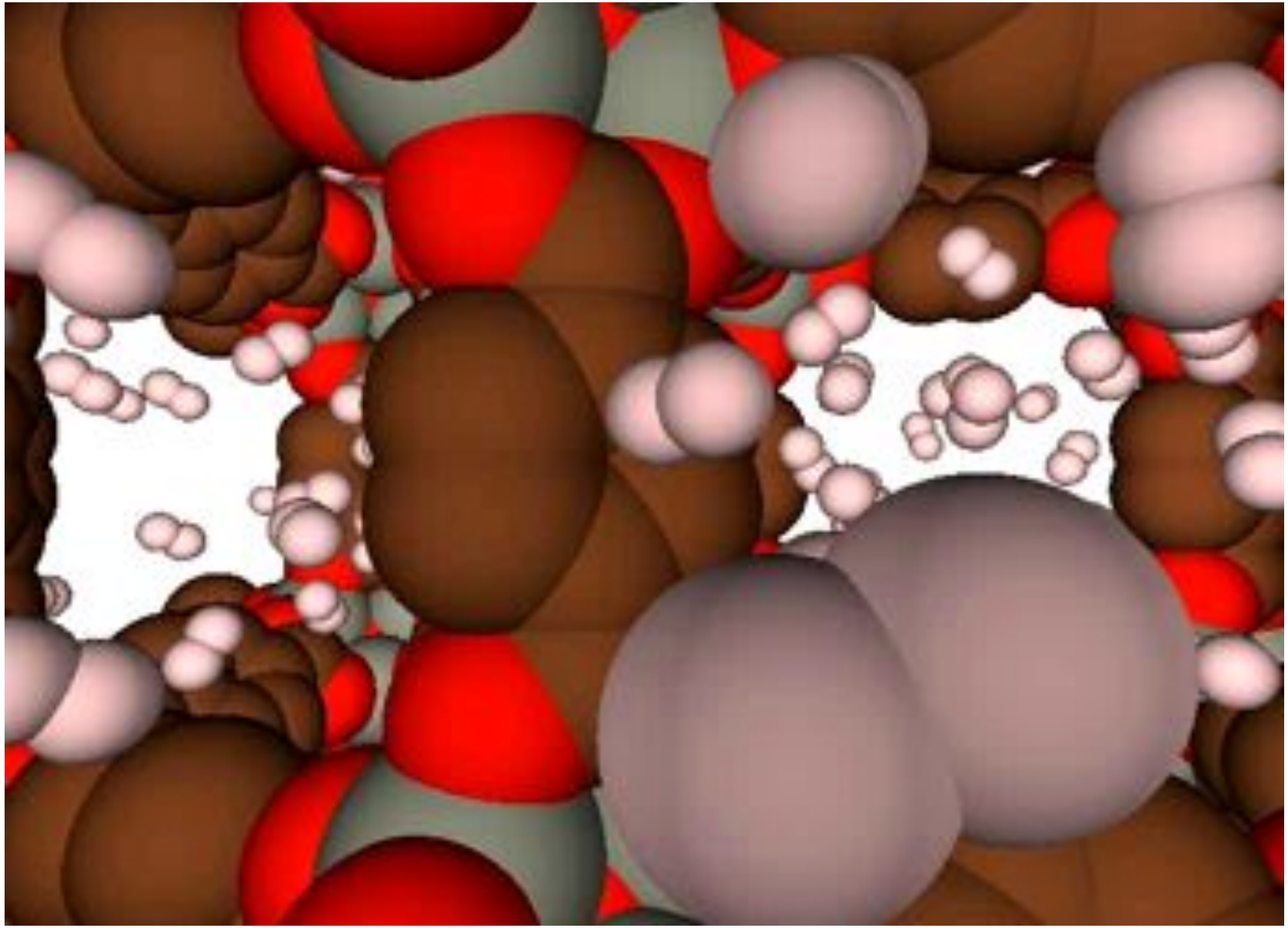
## Delocalized electrons



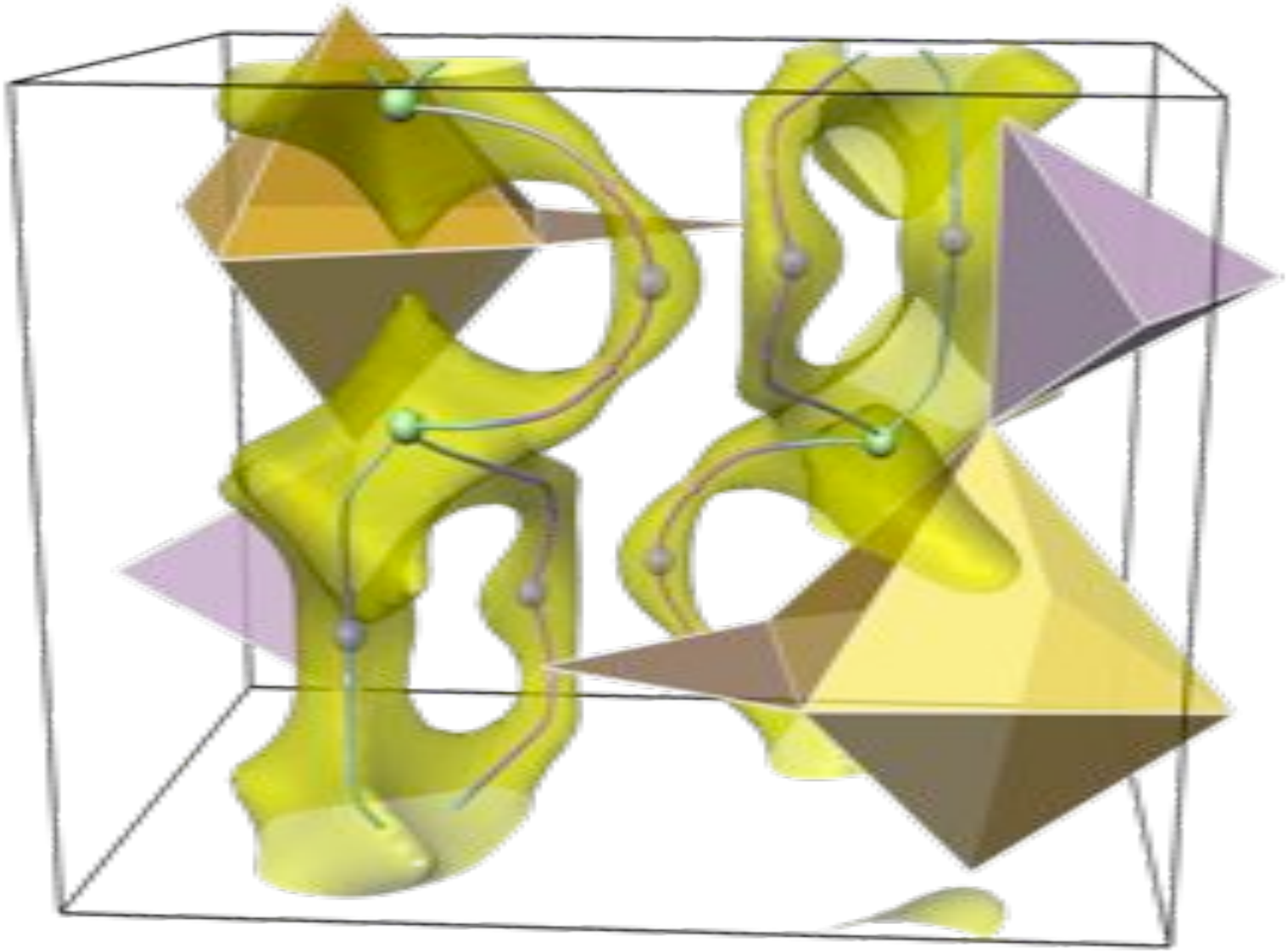

## Localized electrons



# Molecular Dynamics Simulation



# Diffusion channels inside of $LiMnBO_3$



# Storage of electrical energy
## Critical for a $CO_2$-free future

Transportation:  1/3 of $CO_2$ emissions in the USA

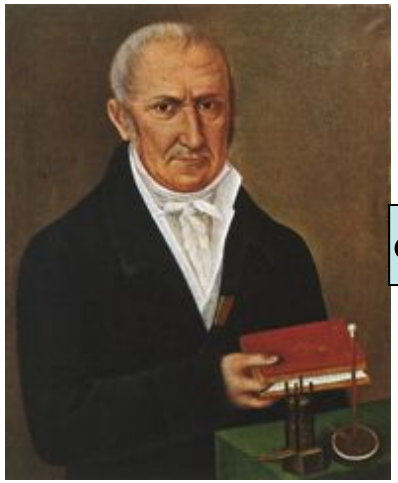
Grid Storage for renewables

# Some form of electrification is the solution

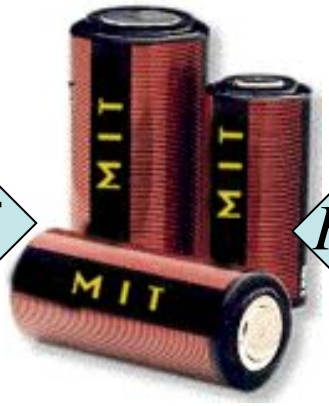
**Hybrid Electric Vehicles**

**Full Electric Vehicles**

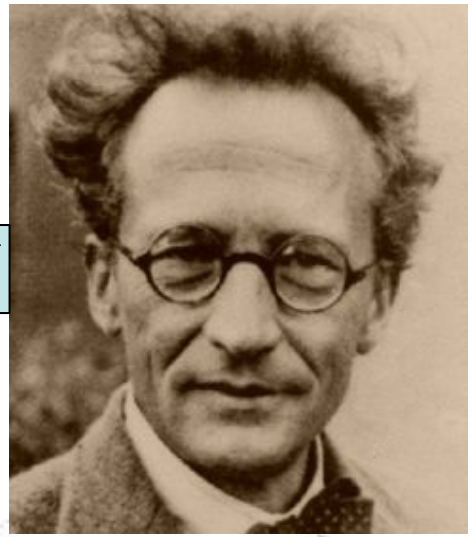
# Volta meets Schrödinger: Li-ion Batteries

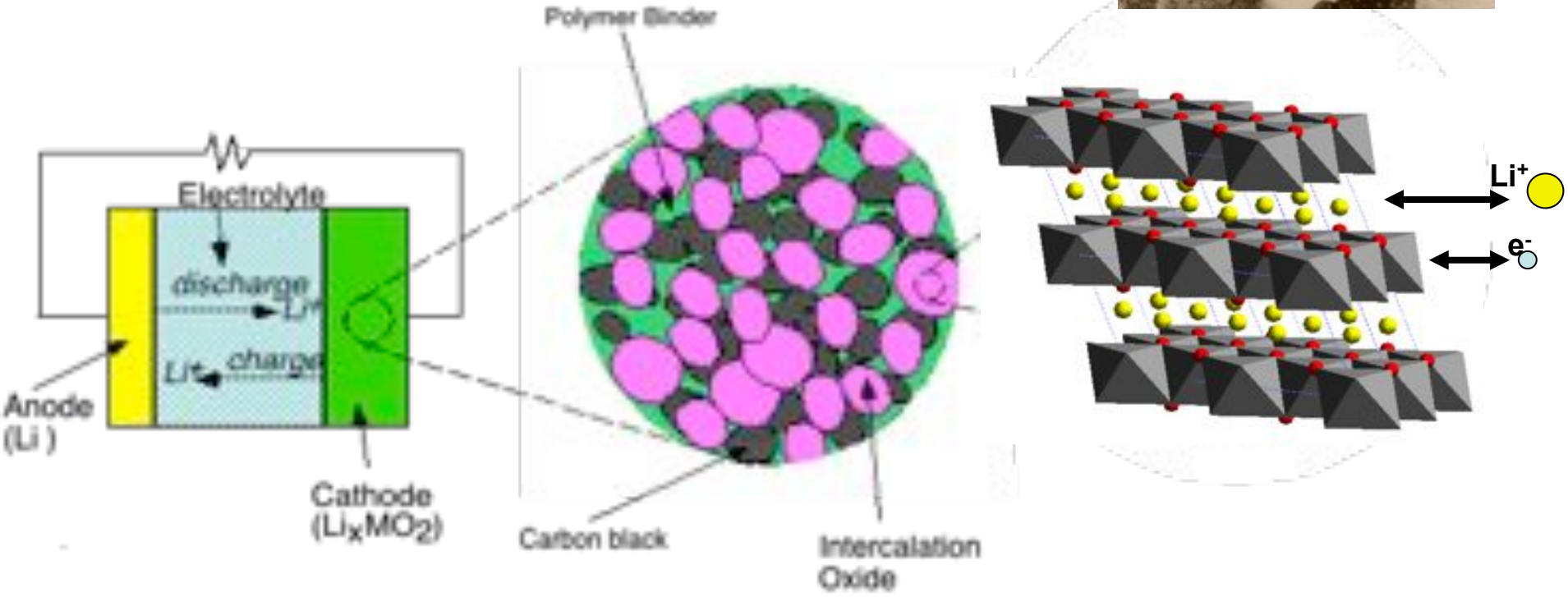


$\Phi = -\mu/zF$

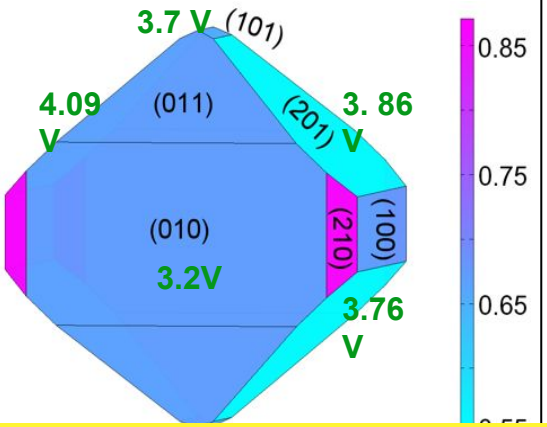


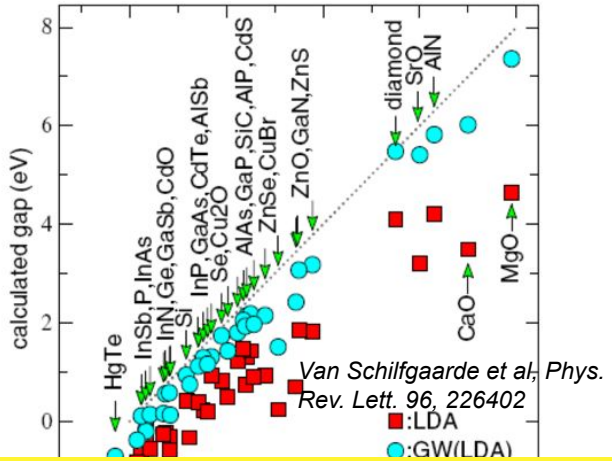

$H\Psi = E\Psi$



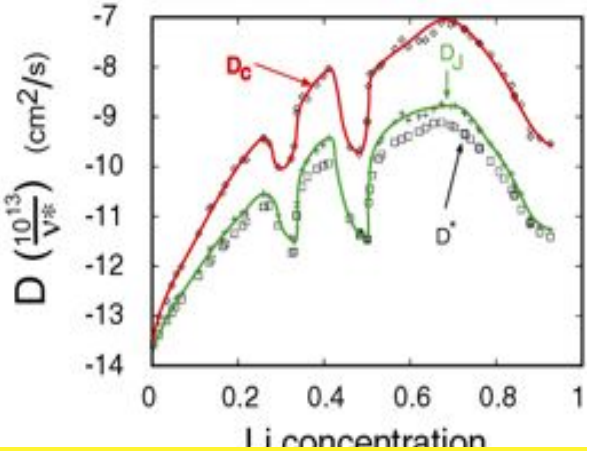


# Many properties of a material can now be predicted before a material is ever made

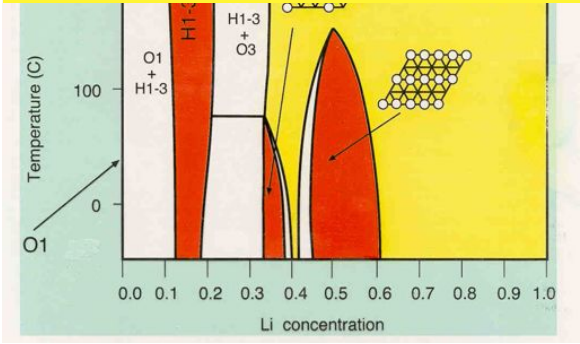


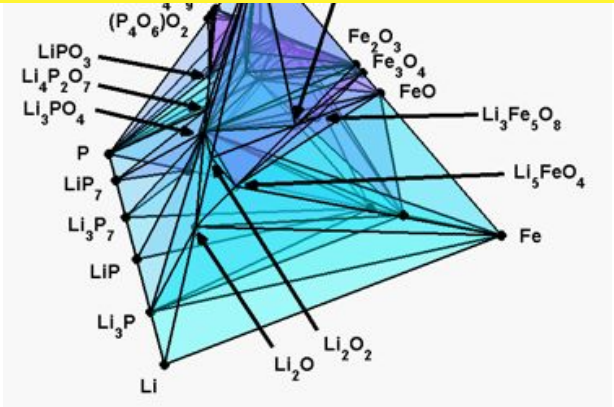




*Van Schilfgaarde et al, Phys. Rev. Lett. 96, 226402*




## Can we put all this together and design (and make) new materials ?

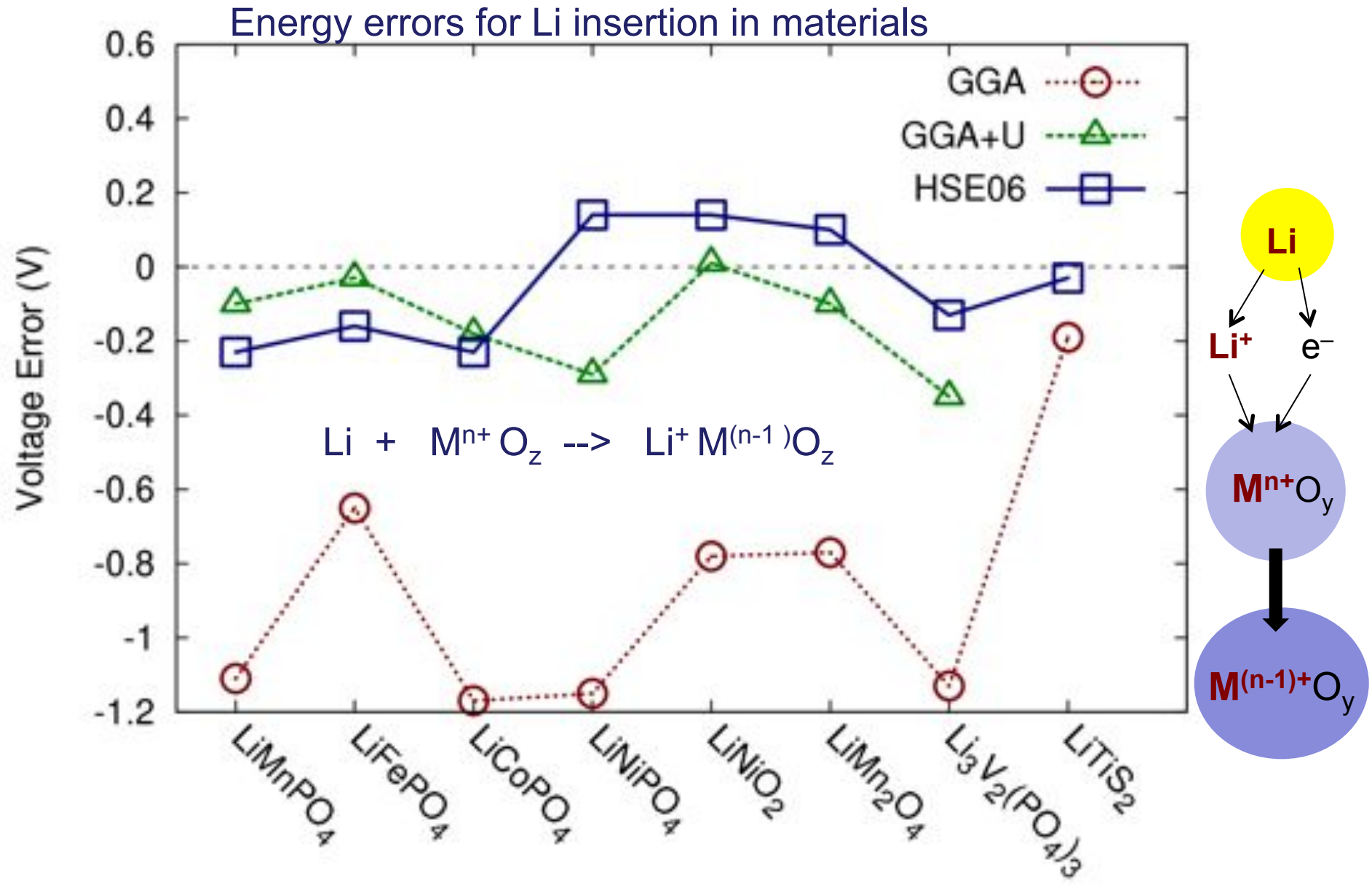


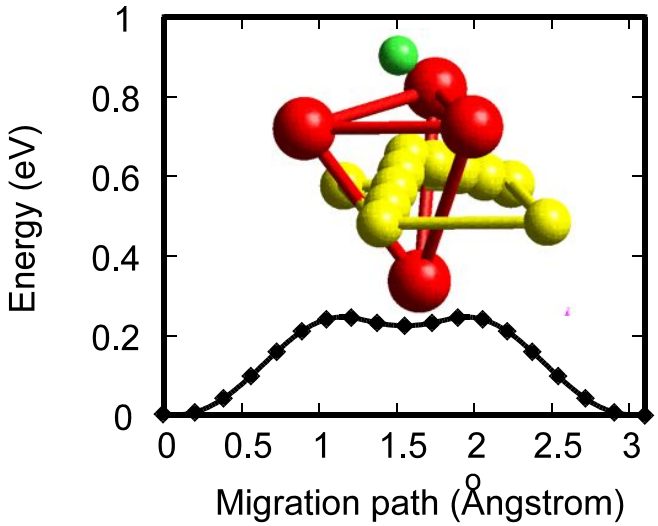

***But plenty of challenges left …***

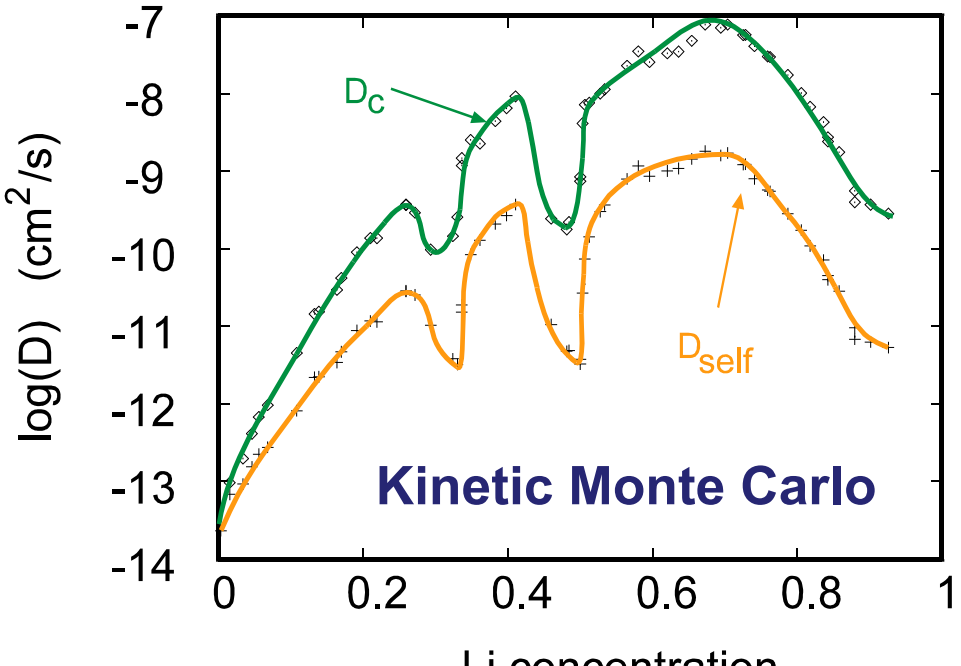
**Phase diagrams**

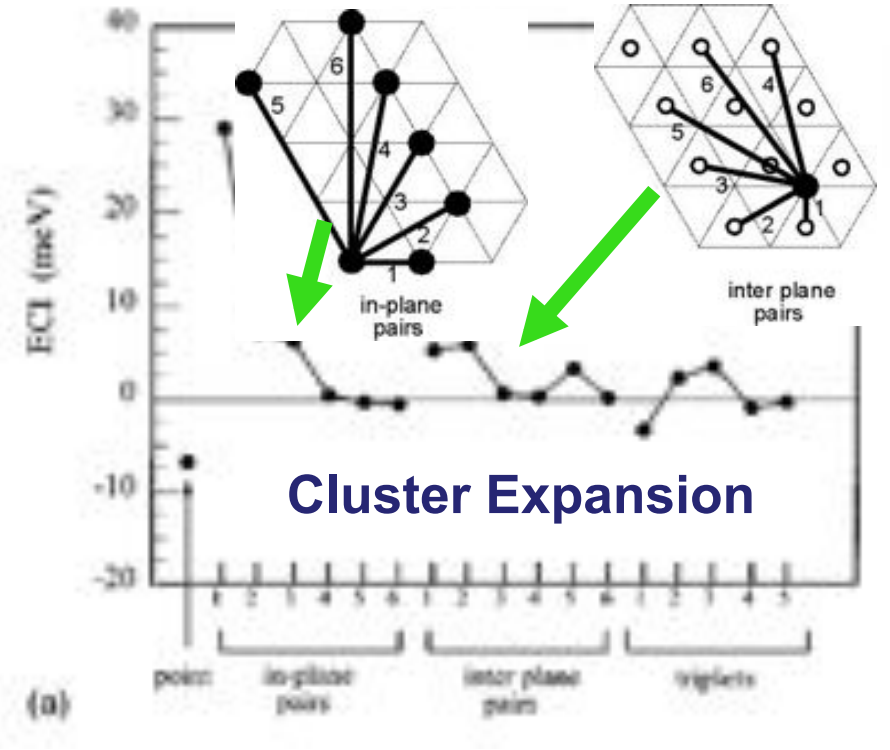
# How accurate ?
# Voltage of electrode materials

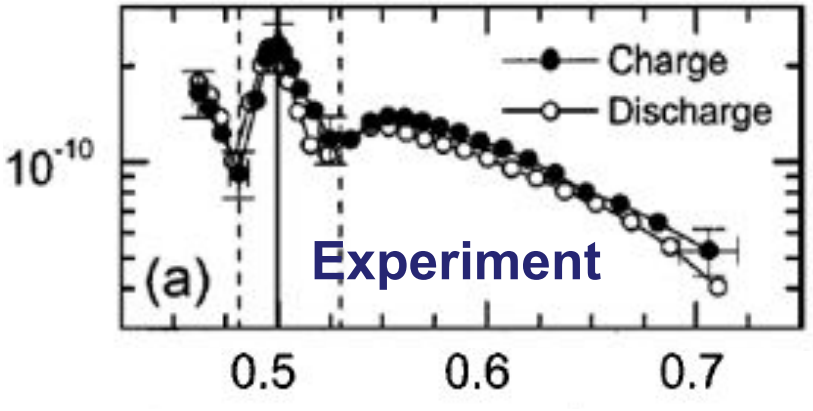


# Li mobility and diffusion ($LiCoO_2$)



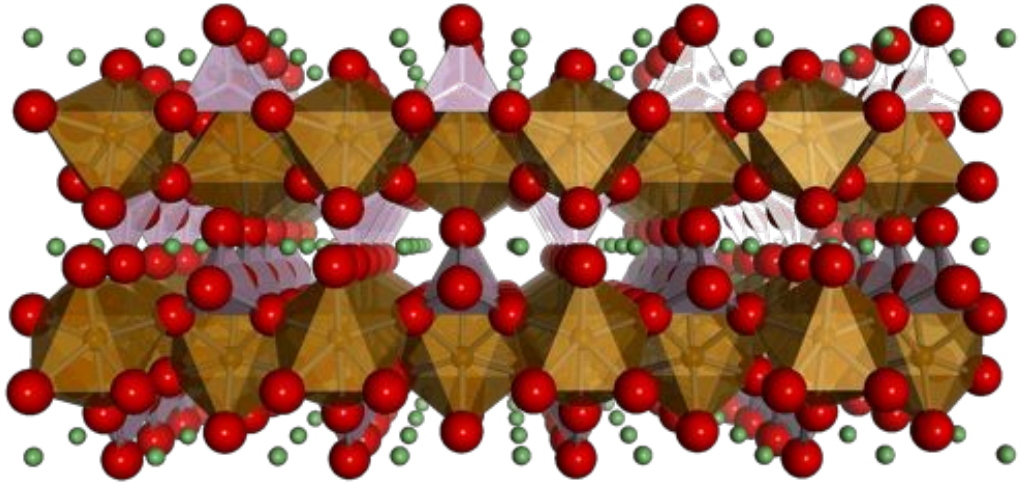




A. Van der Ven and G. Ceder, Electrochem. and Sol. St. Lett. **3** (7) (2000).

# Design Example:
# Optimization for Very High Charge Rate

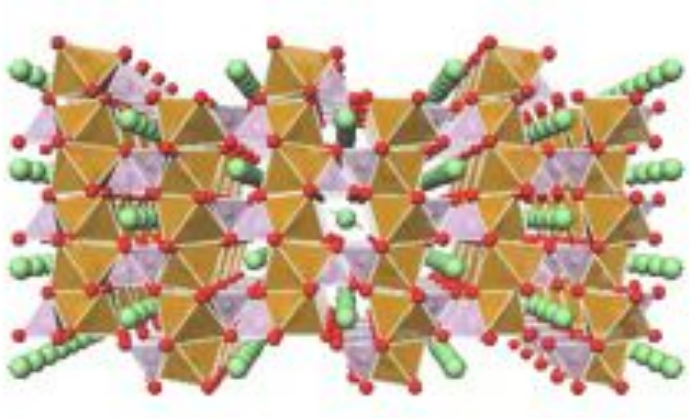
# $LiFePO_4$ : Low or High Rate ?

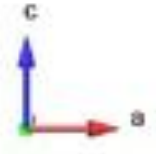


**First experimental paper about $LiFePO_4$ :**
**"*An excellent candidate for the cathode of a low-power, rechargeable lithium battery*"**

Padhi et al. *J Electrochem Soc* (1997), p.1188

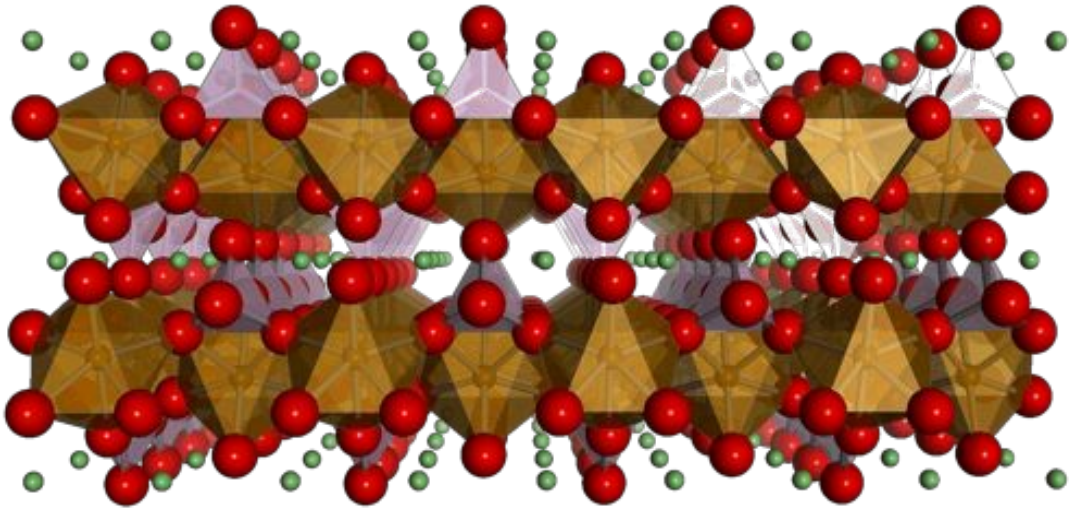
# Li diffusion paths





# Activation barriers for Li migration give good indication of kinetics

**Ab-initio theory** finds very **high diffusion** in b-direction and **strong anisotropy**



*Along the a-axis:* $E_a > 1$ *eV*

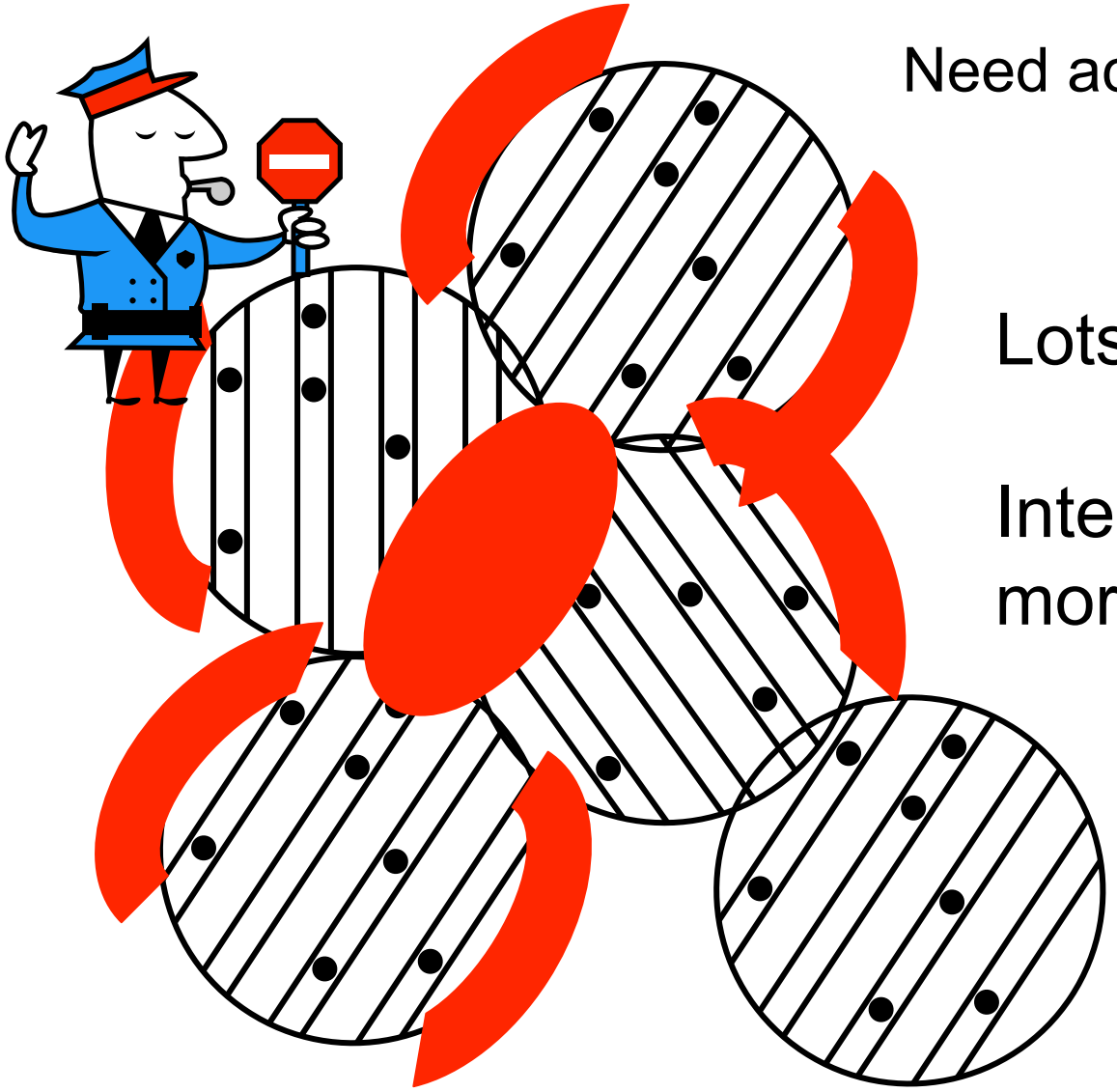
*Along the c-axis:* $E_a > 1$ *eV*

*Along the b-axis:* $\boldsymbol{E_a \approx 200\text{-}300meV}$

**D ≈ $10^{-7}$ to $10^{-8}$ $cm^2/s$**
diffusion length: **50 nm in about 1 ms**

D. Morgan et al, ESSL **7**, A30 (2004). AND M. S. Islam, et al. Chem Mat **17**, 5085 (2005).

# 1D diffusions is problematic $LiFePO_4$

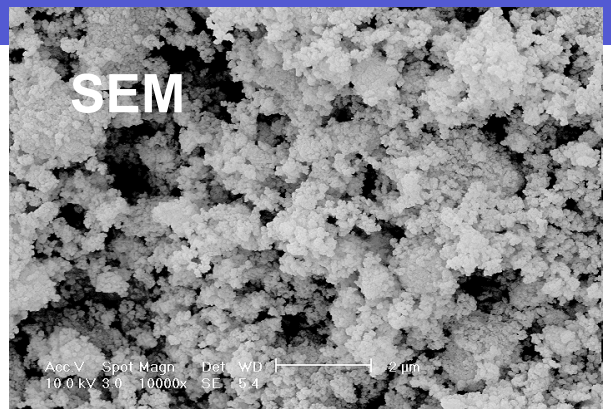


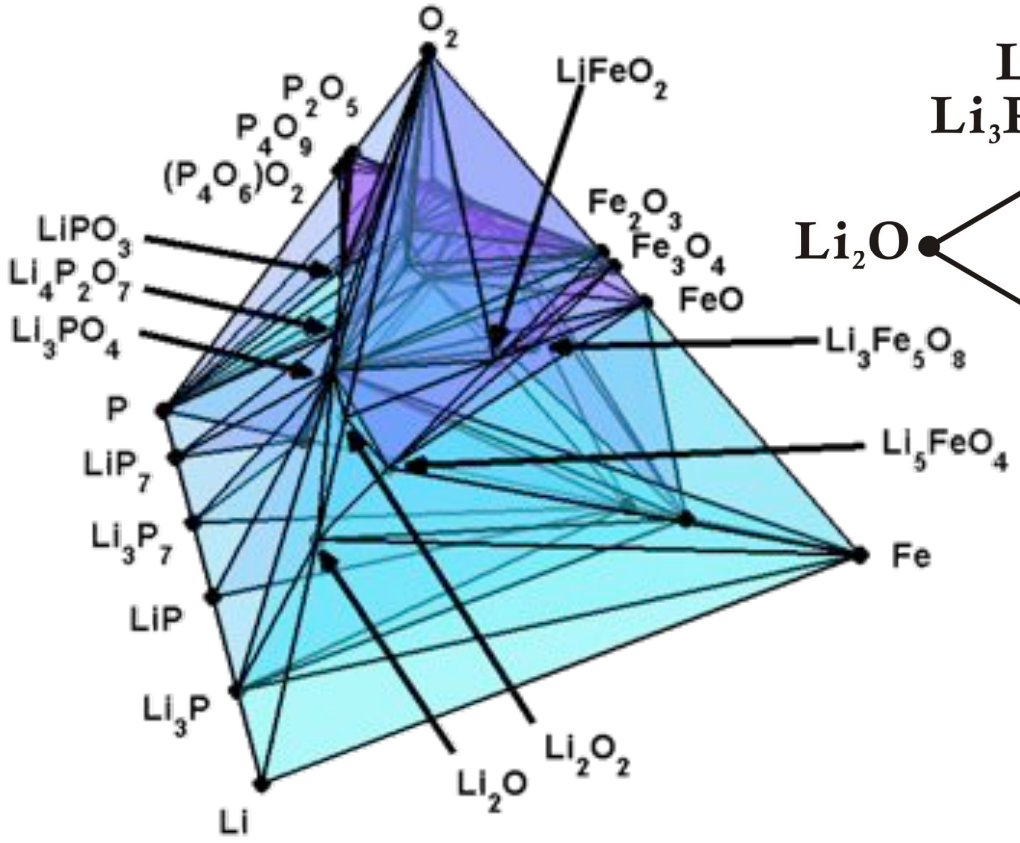
Need access to the (010) facet

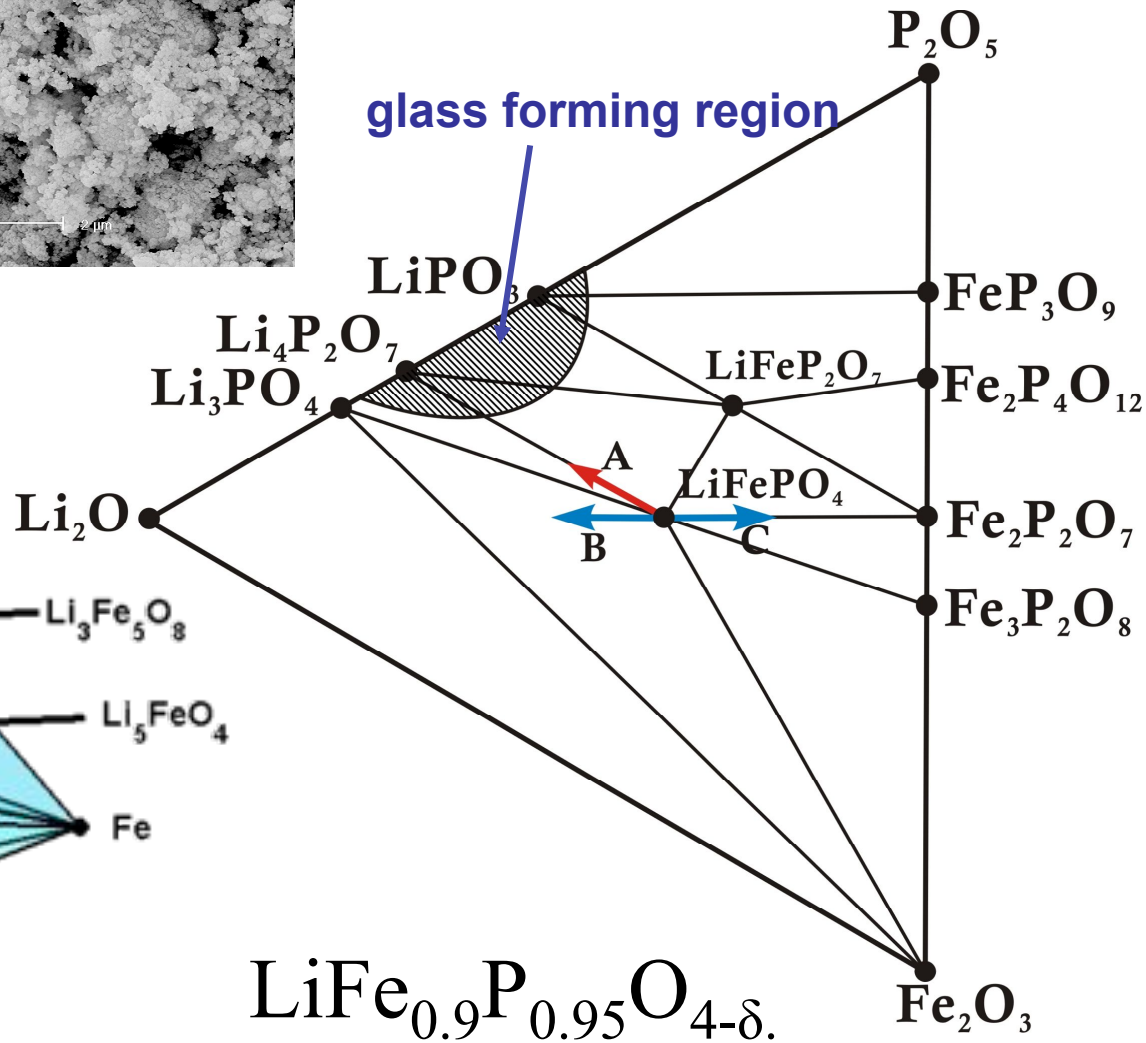
Lots of inactive surface

Intergranular contacts more difficult to access.

# Calculate Phase Diagrams

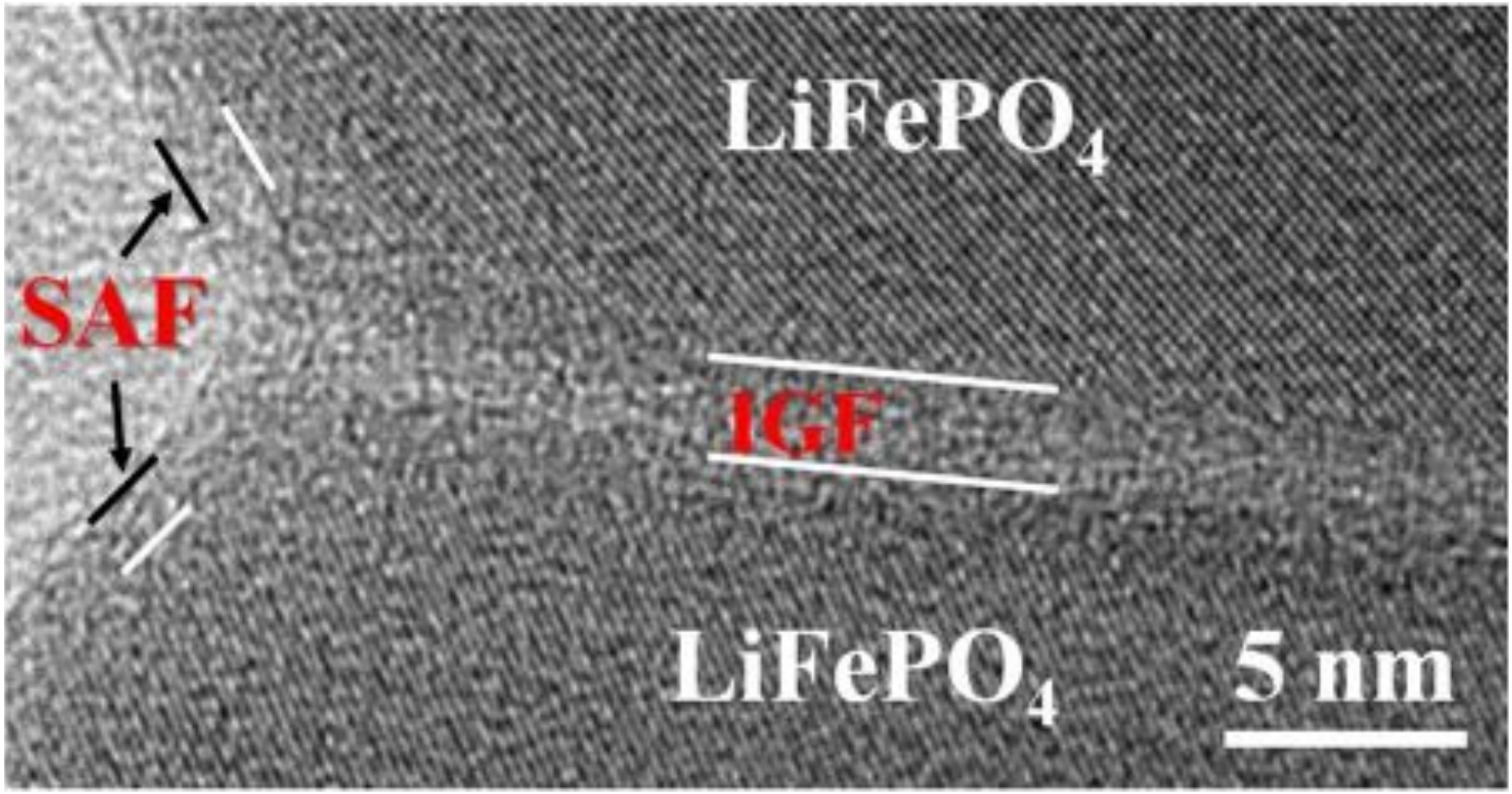


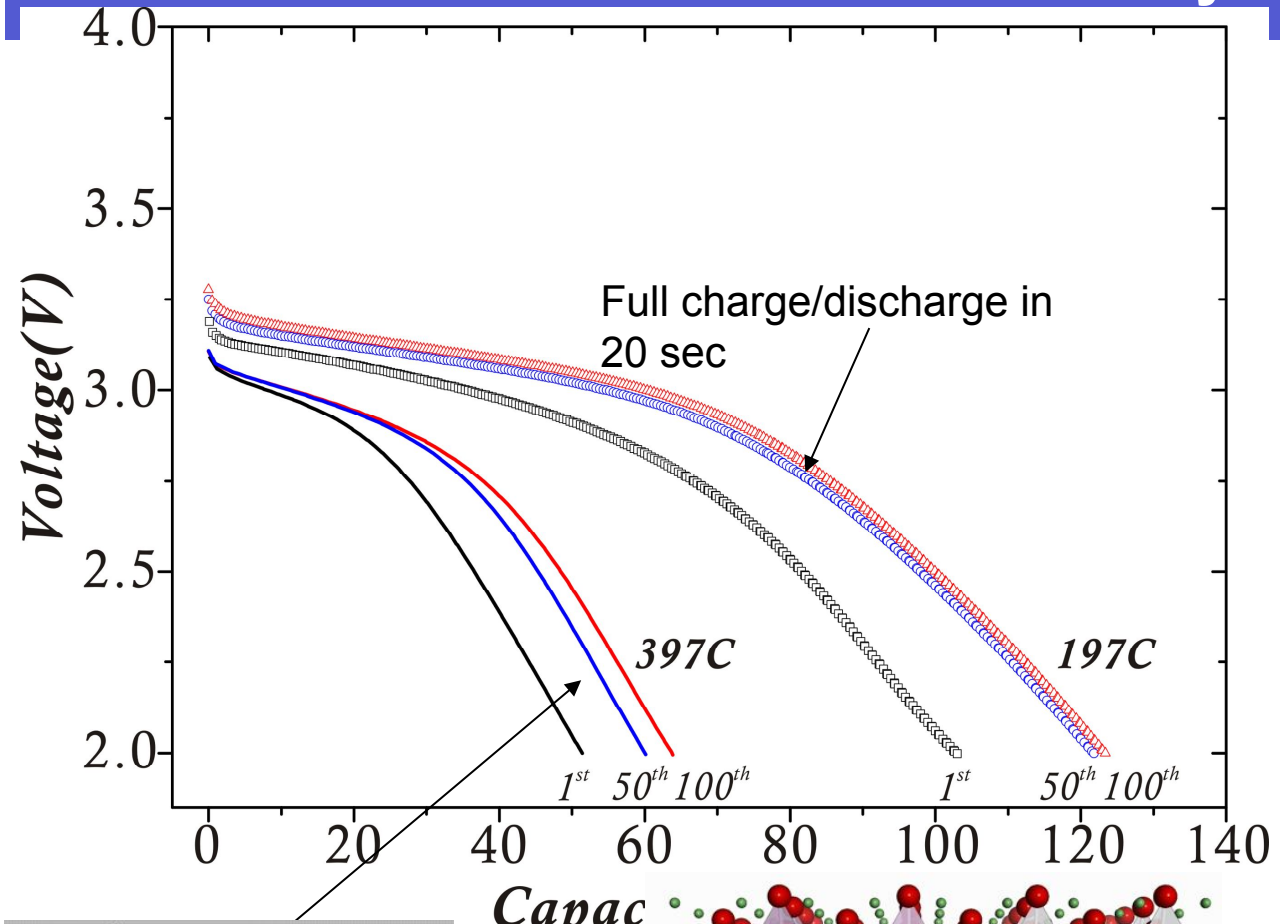

$LiFe_{0.9}P_{0.95}O_{4-\delta}$.

# Intergranular and Surface Films in $LiFePO_4$




Kayyar, Qian & Luo, *Appl. Phys. Lett.* 95: 221905 (2009)

# With some electrode modification can obtain highest rate ever observed in a battery material

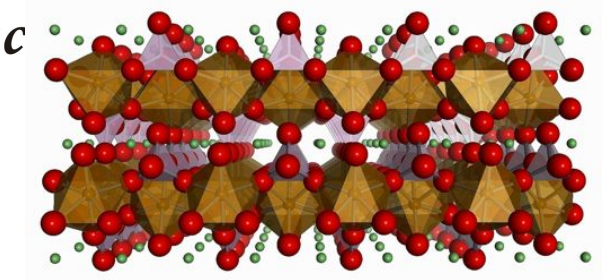



400 C is full battery charge/discharge in **9 seconds**

Power density:

**175 kW/liter**
**90kW/kg**

+



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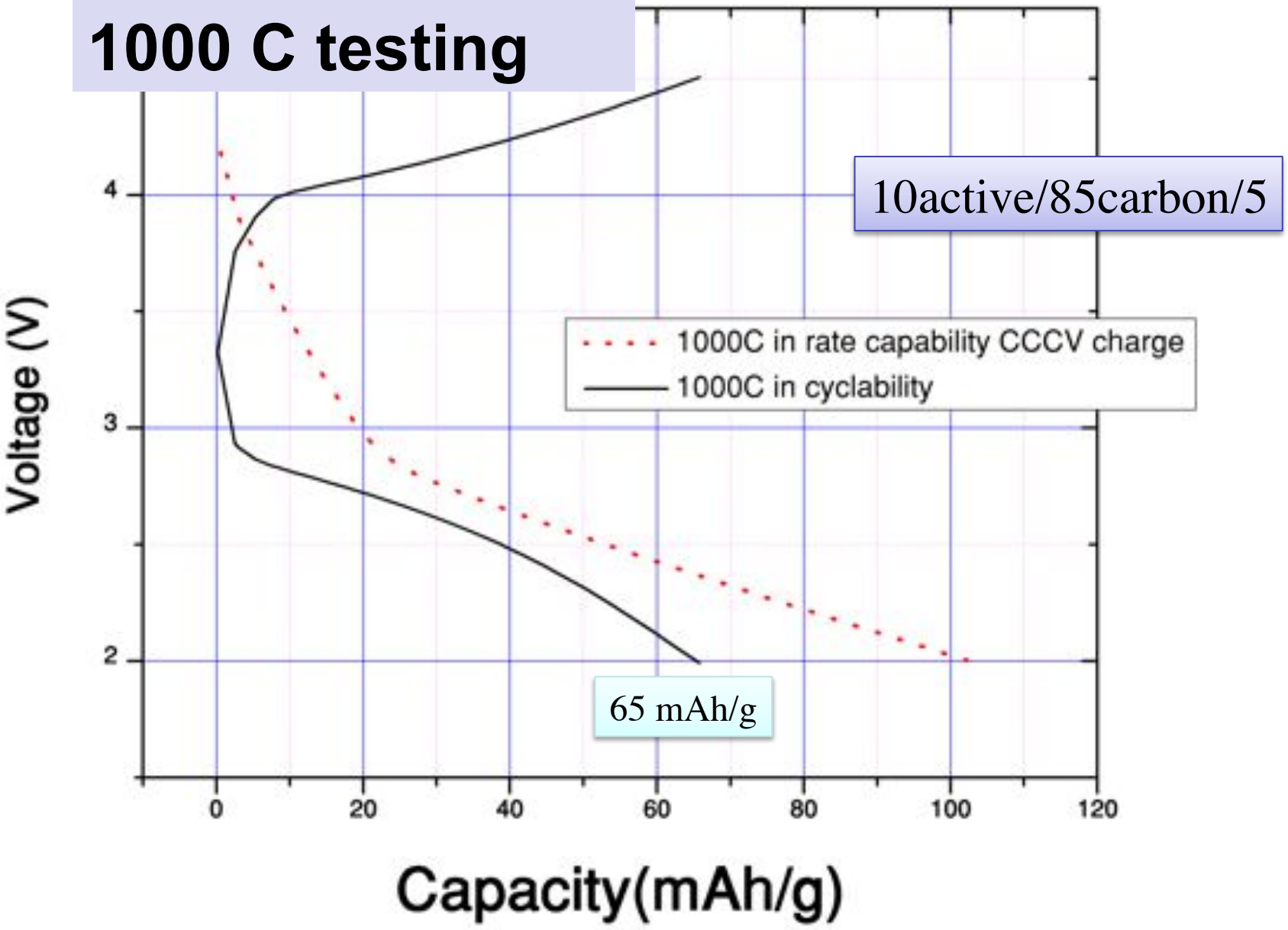
# Dilute further to find rate limit of the material

## 1000 C testing



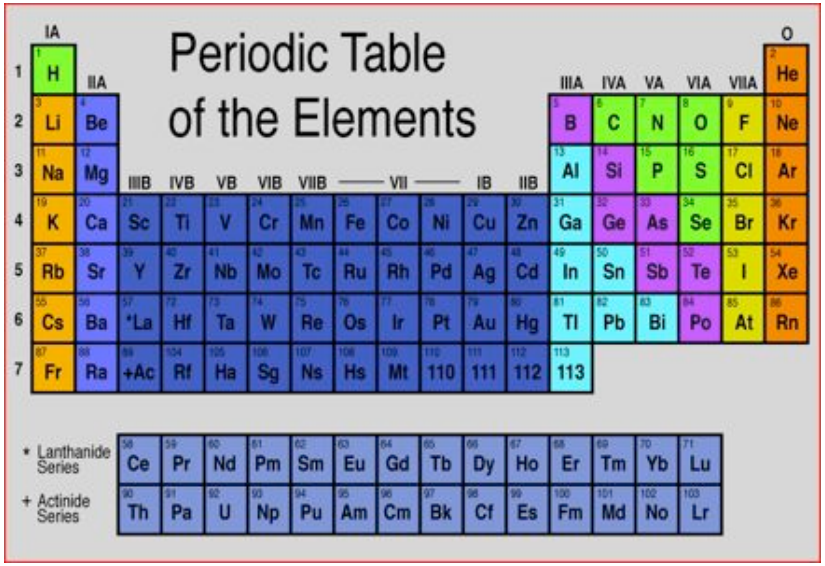
*Computing is scalable*

# The game changer for new materials design: High-Throughput Computing and the Materials Genome Project

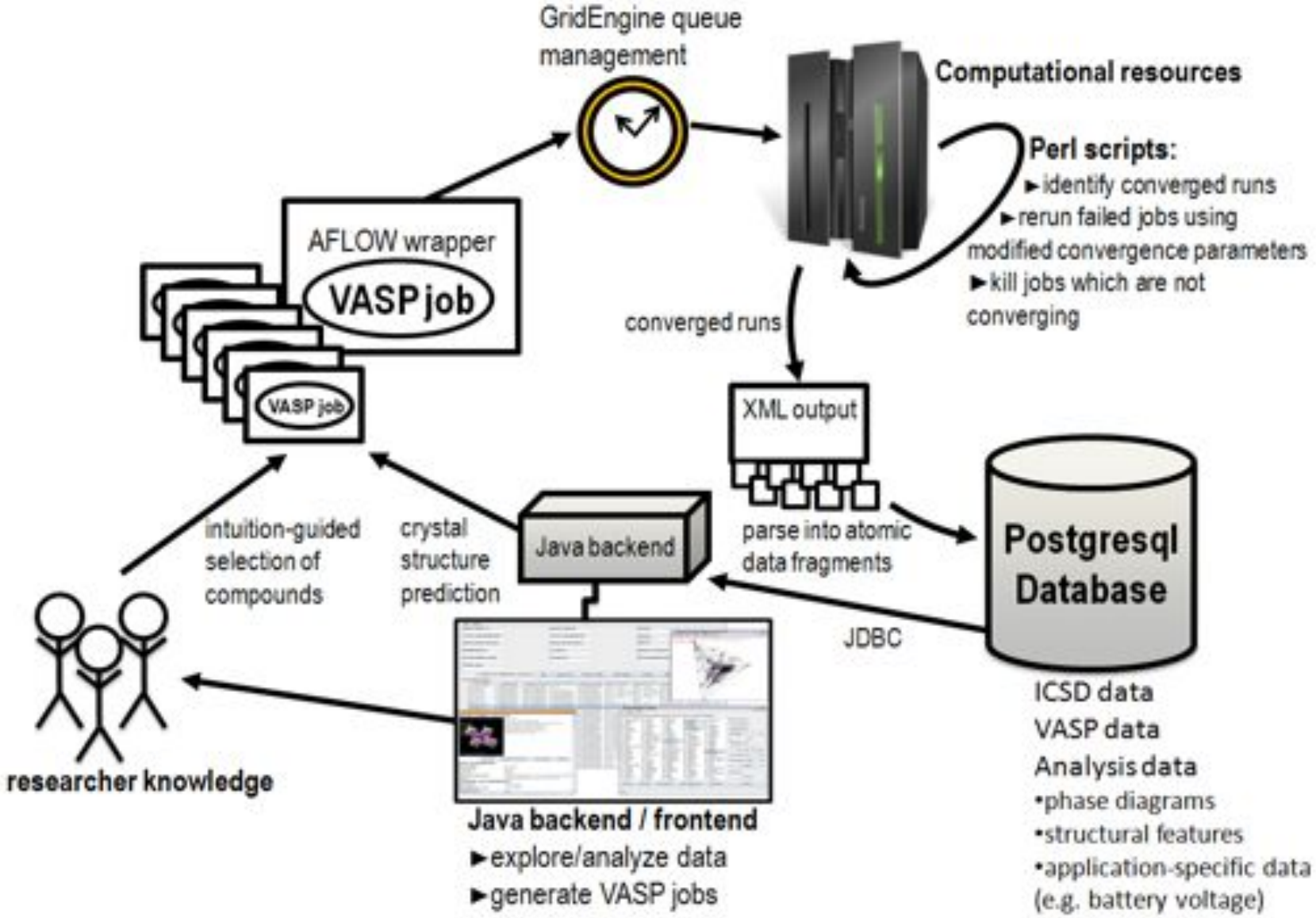
*Do for materials what genomics is trying to do for biology, what Google does for information*

*... but better*

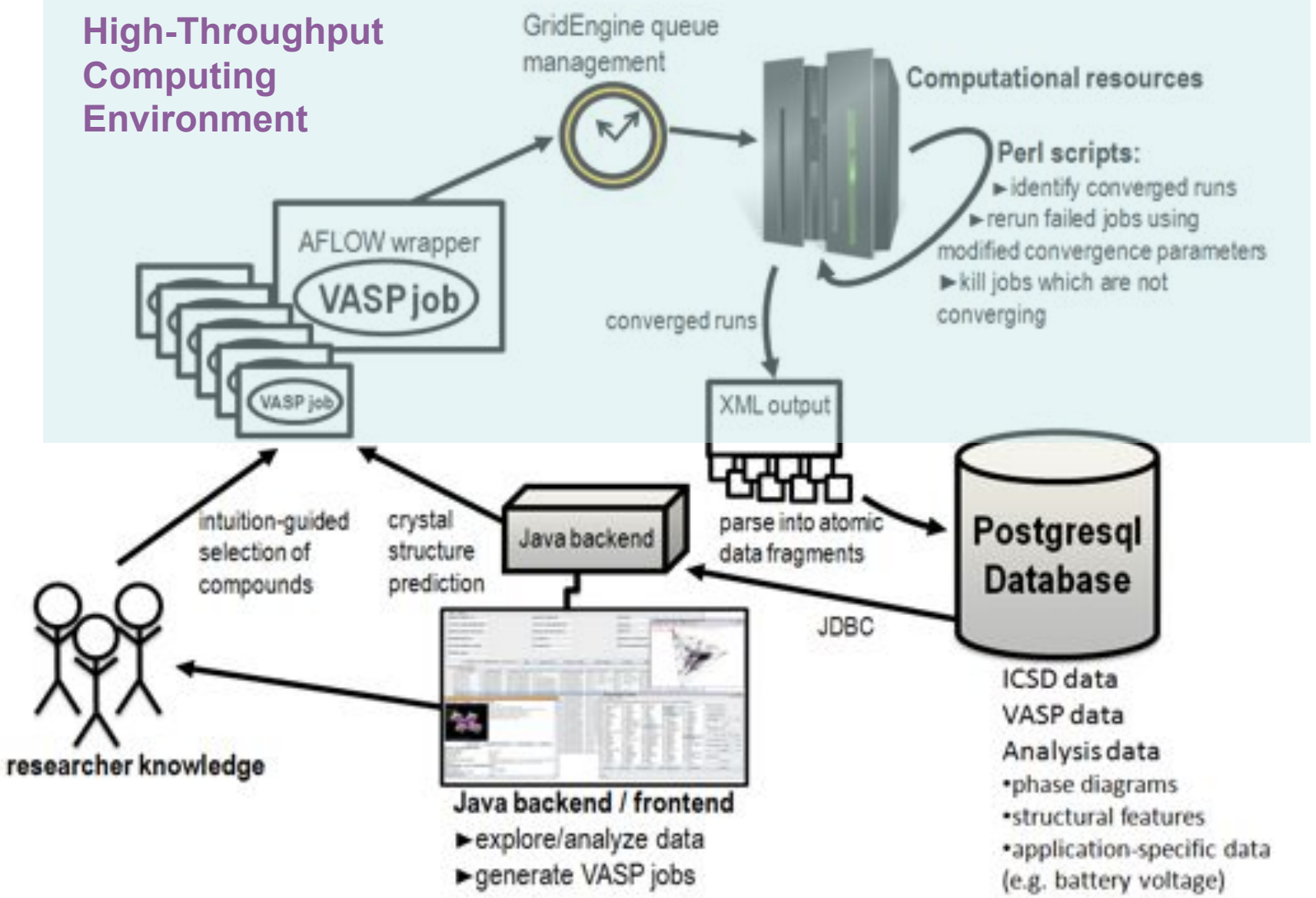
*There are somewhere between 50,000 and 200,000 known inorganic crystalline compounds*



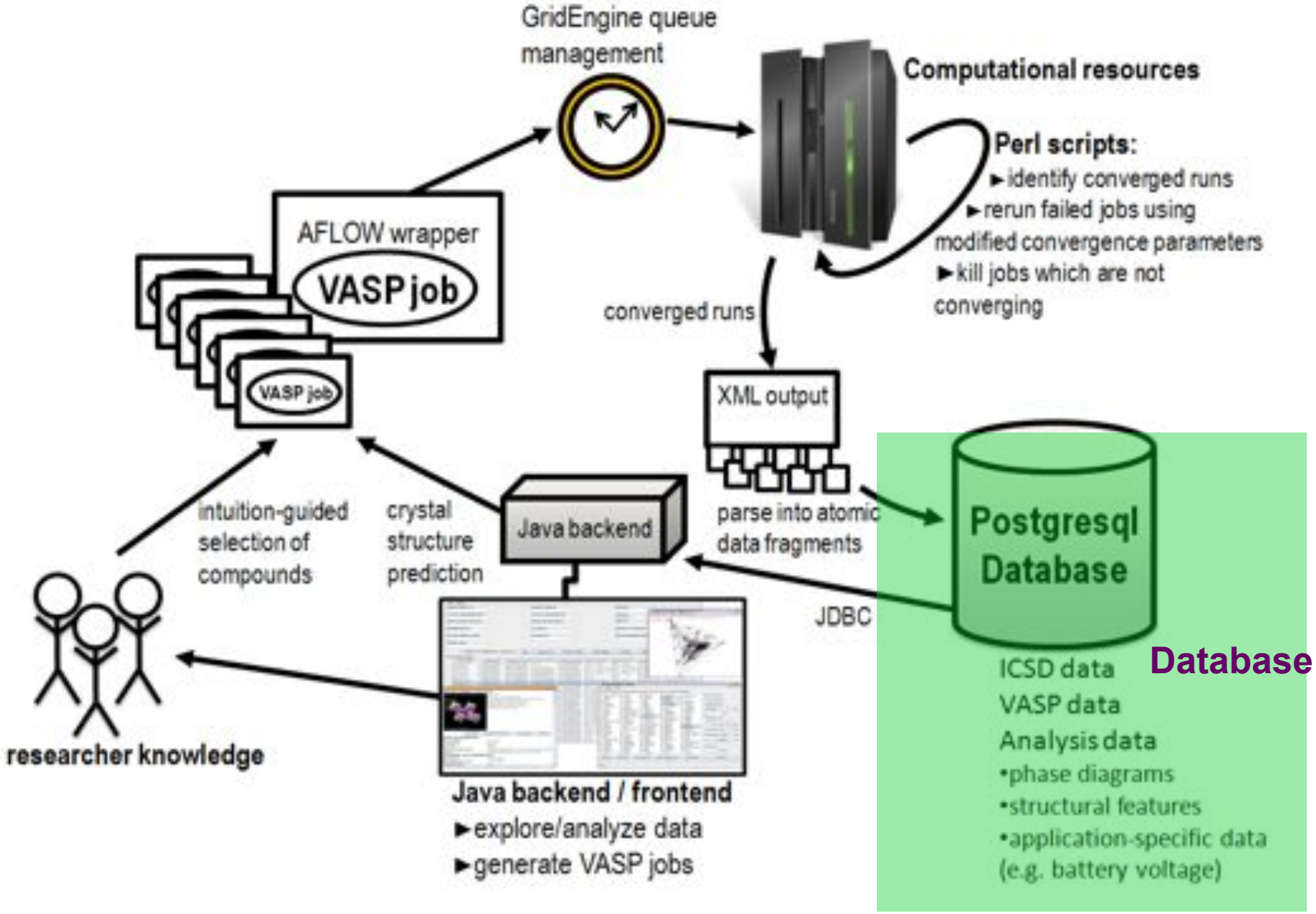
# **The Materials Genome**:
## High-throughput materials computation



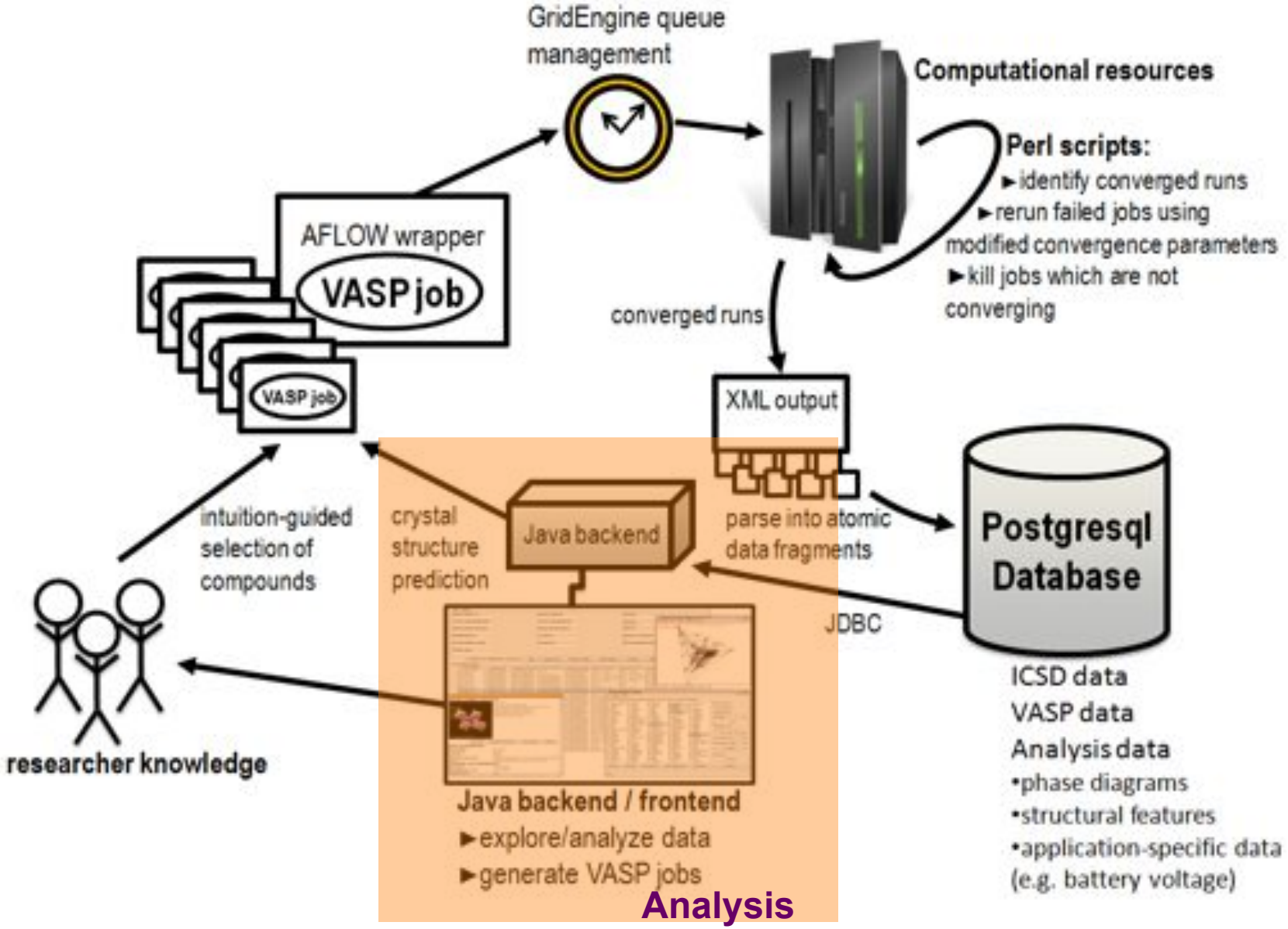
# **The Materials Genome**: High-throughput materials computation



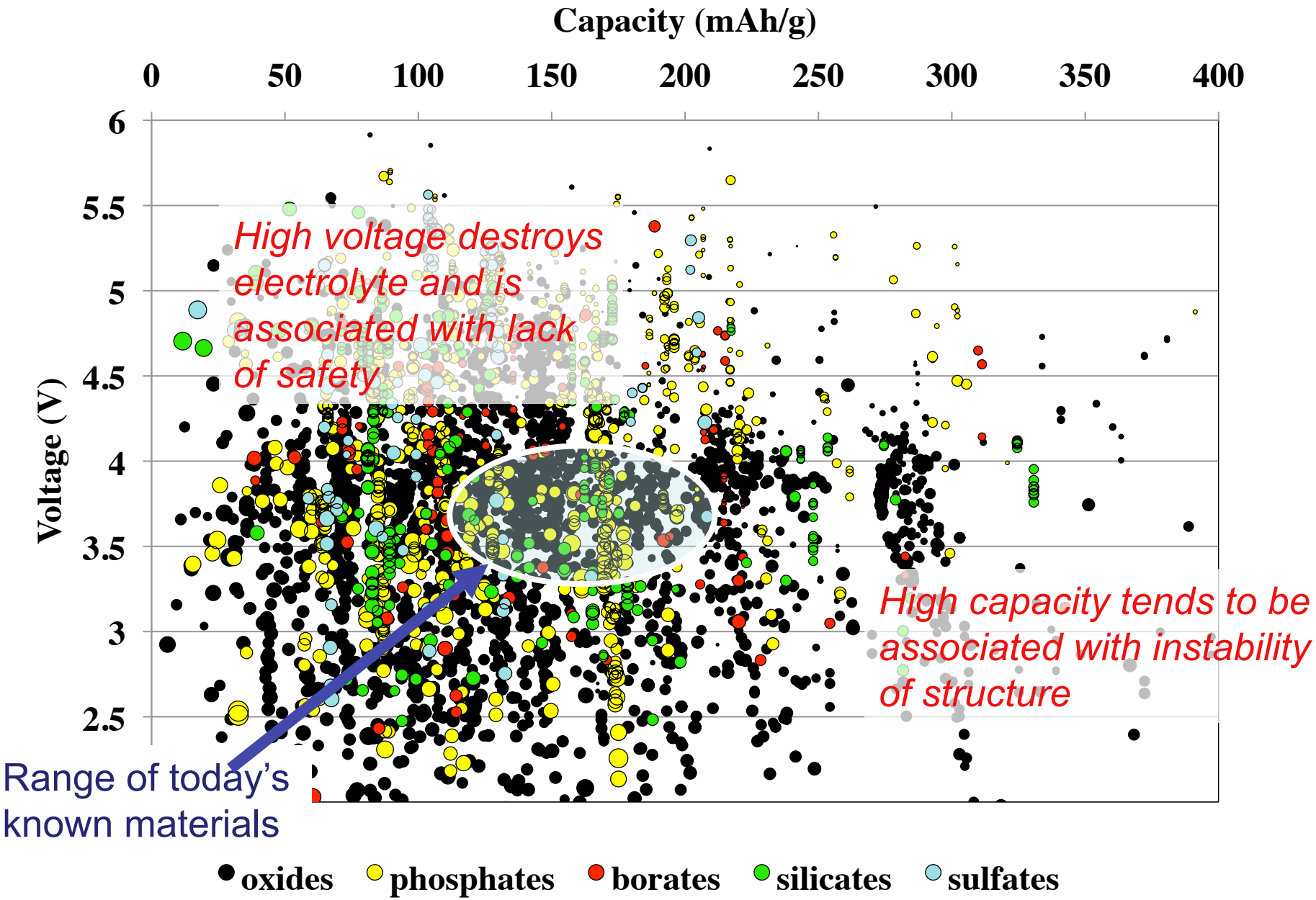
# The Materials Genome: High-throughput materials computation



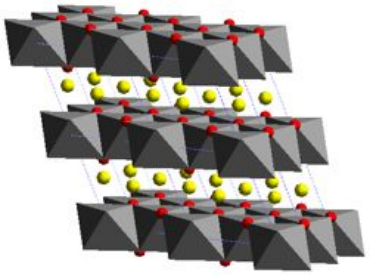
# **The Materials Genome**: High-throughput materials computation



# High-throughput voltage calculations

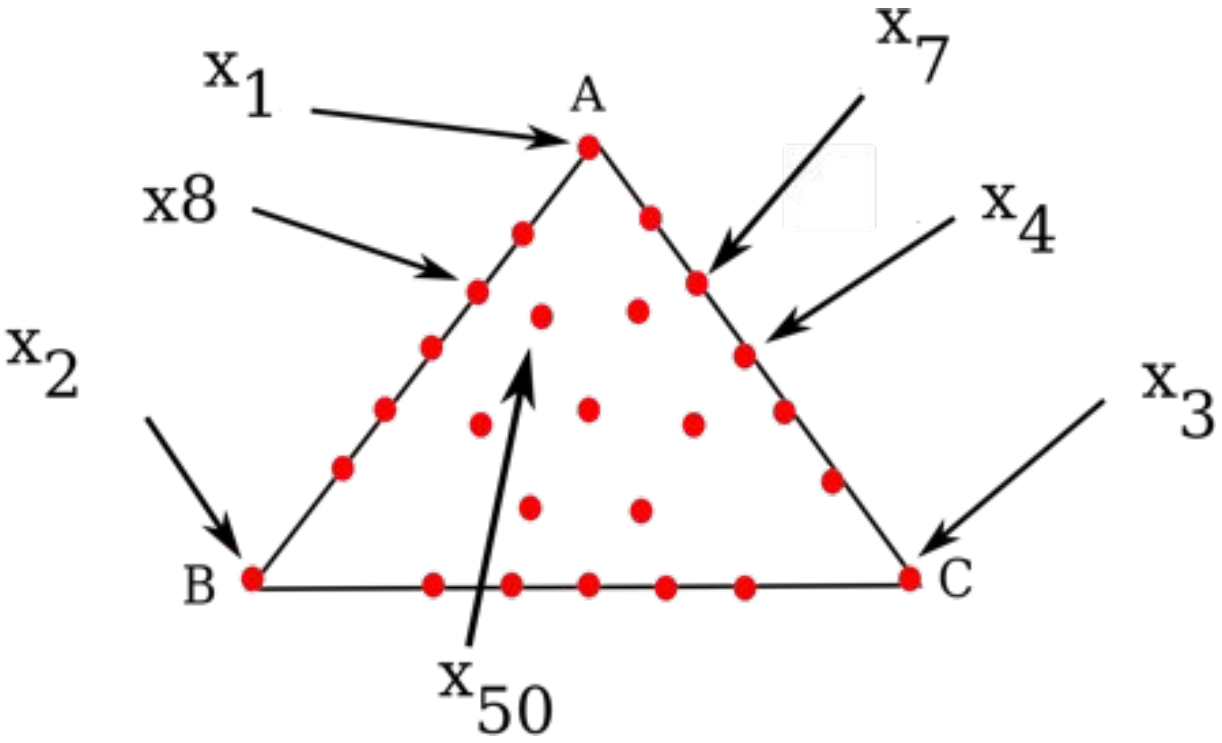


# What does one need to “design” ?

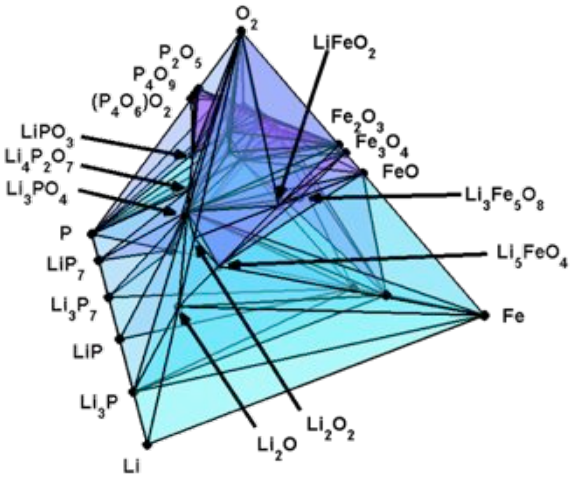


- Methods to predict multiple properties: *voltage, Li diffusion, stability, etc.*
- Method to predict crystal structure/stability
- Ideas
- An idea of what can be synthesized and how

# Predicting Crystal Structure

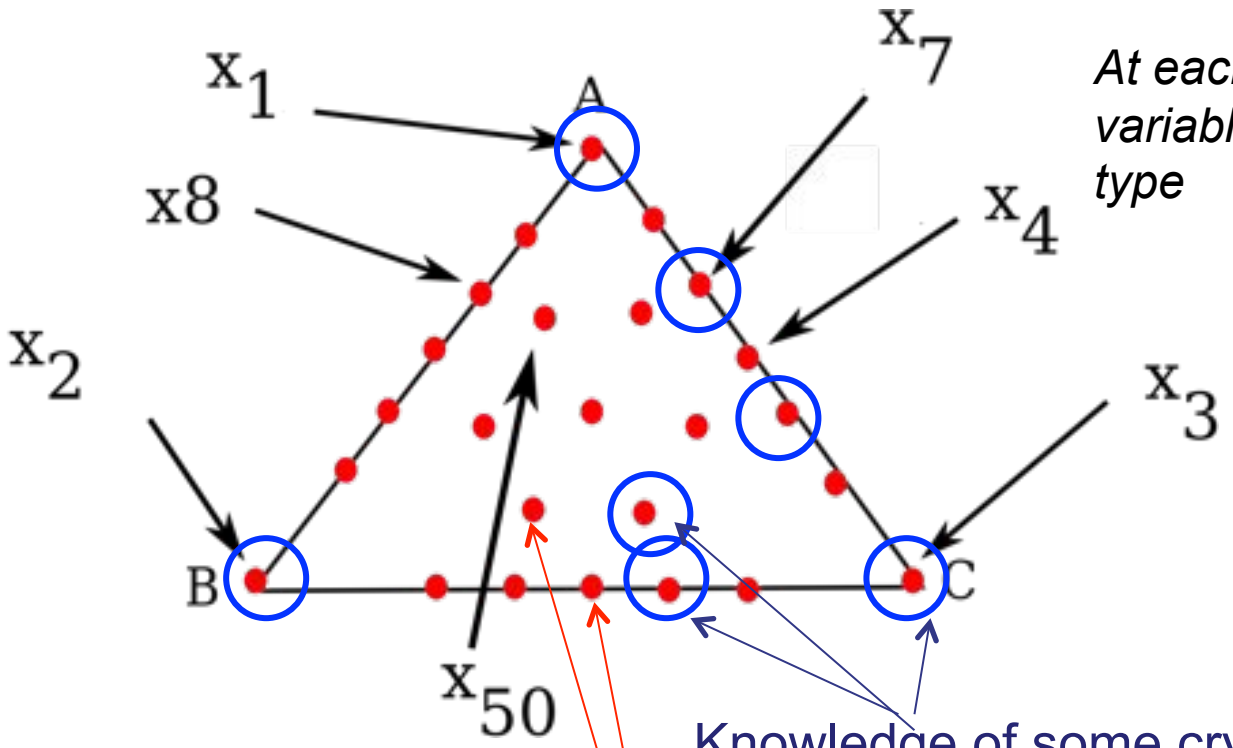



- *Any undiscovered ternary oxides ?*
- *Need ability to predict possible structures at a given composition*




Geoffroy Hautier, et al., ***Finding Nature's Missing Ternary Oxide Compounds Using Machine Learning and Density Functional Theory. Chemistry of Materials 22 (12). pp. 3762 - 3767 (2010).***

# Concept of Probabilistic Structure Prediction Approach




*At each composition, variable $x_i$ to give structure type*

Knowledge of some crystal structures in a system

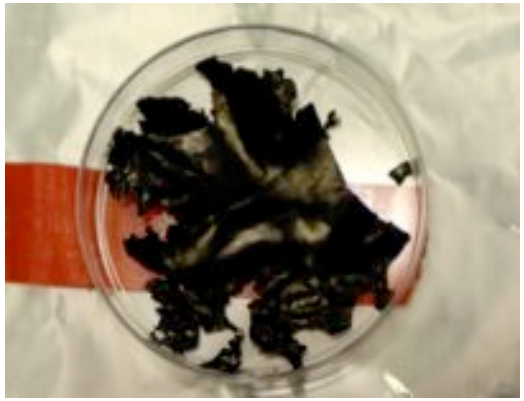
**X**= ( $x_1$, $x_2$, $x_3$, … , $x_n$ )

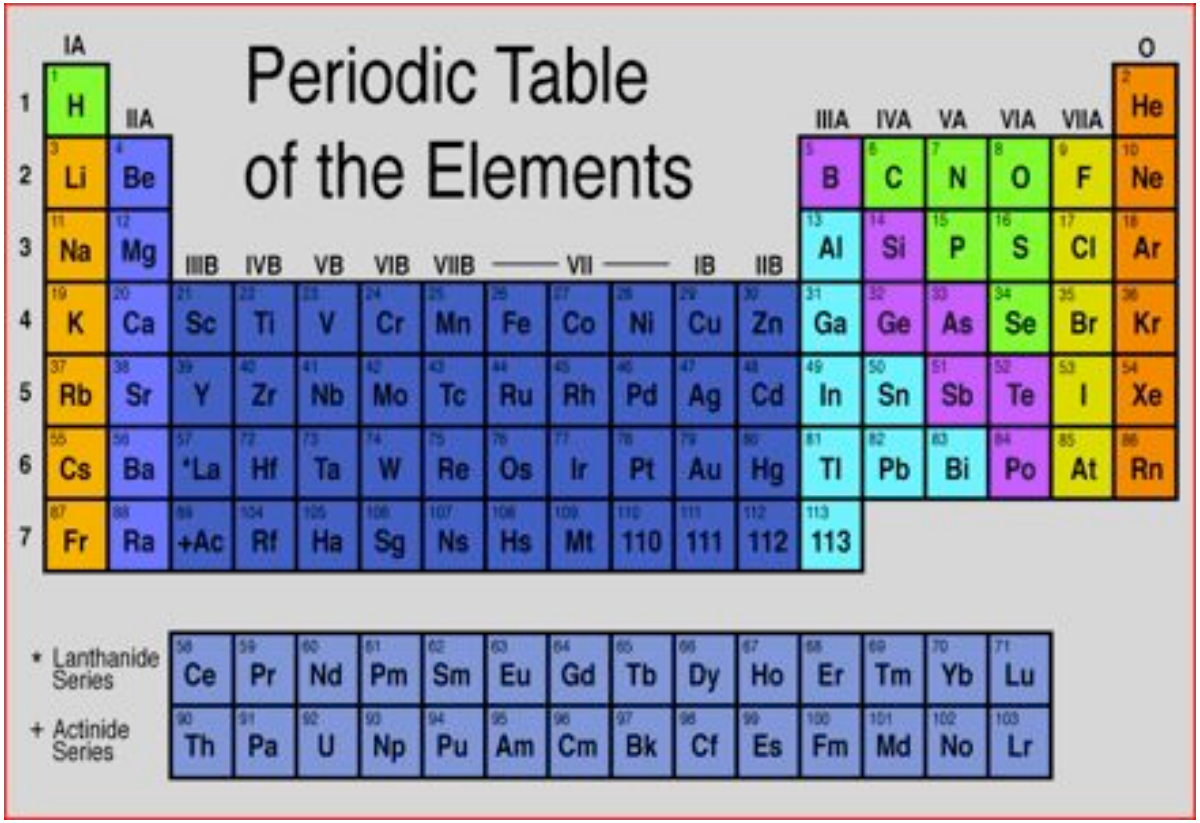
P(**X**) = probability that series of structures coexist

Can we predict other ones present ?

# Example: Look for “undiscovered” compounds in A-B-oxides

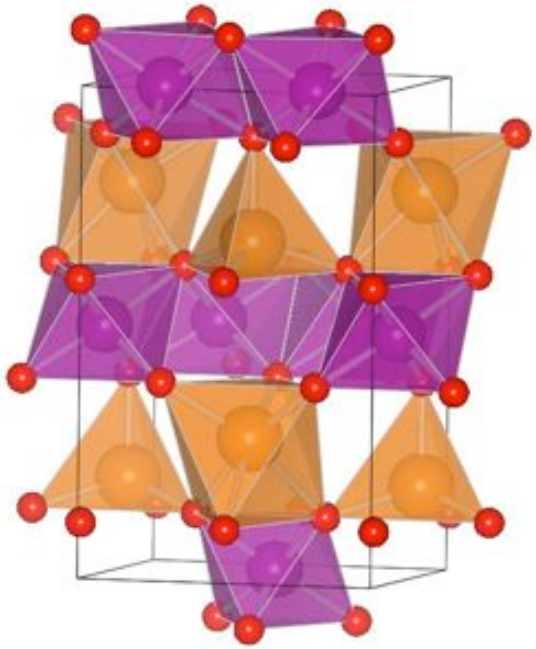
A and B can be any metal in any ratio
Oxygen





# Searching for new Ternary oxides (model trained on ICSD)

- Today there are about 5,000 known ternary oxide compounds (A-B-O)  (source: ICSD)
- We searched in all A-B-O systems for possible new compounds
- **366 new compounds confirmed** by DFT + datamining



$Mg_2Mn_3O_8$

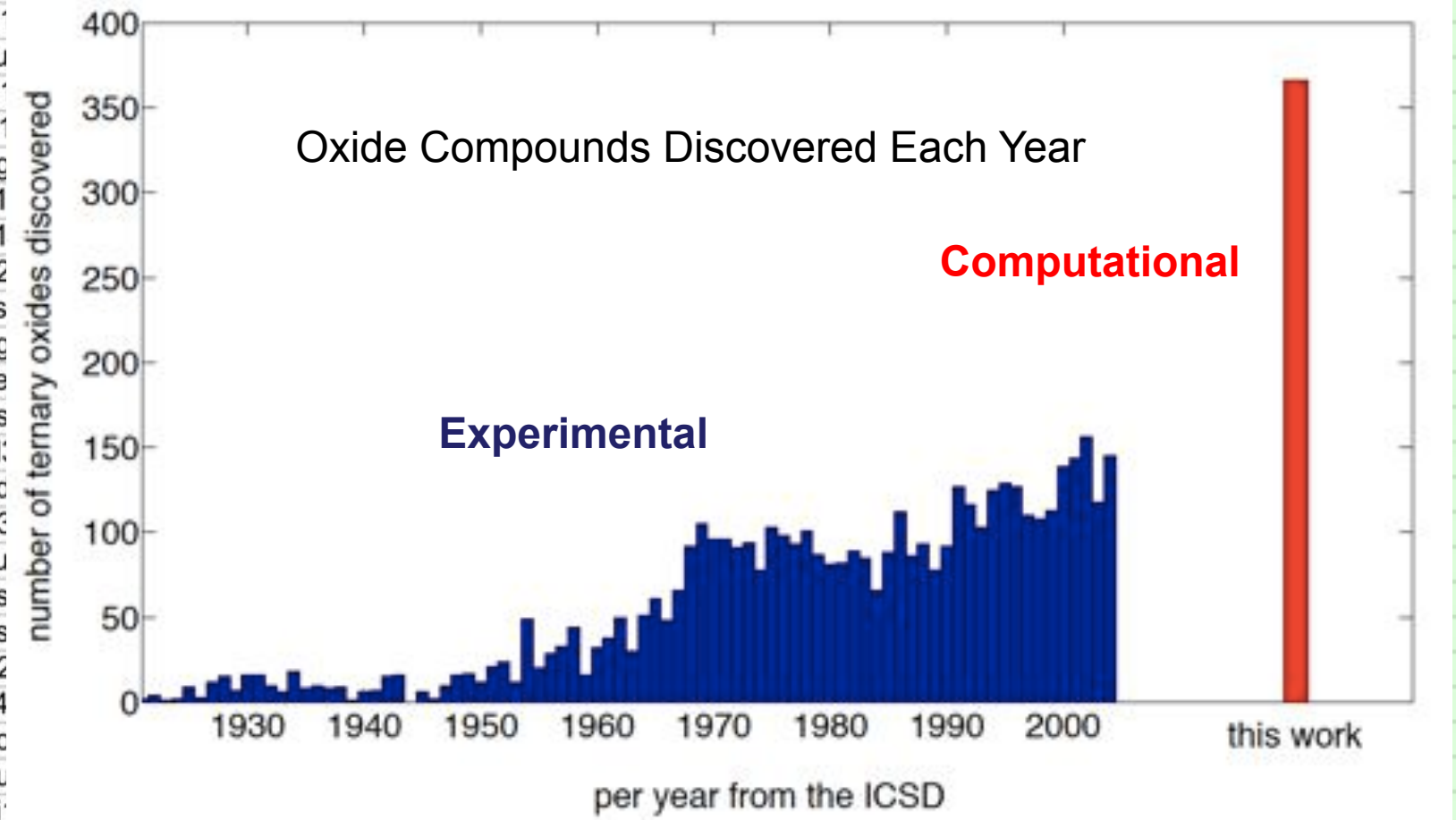
G. Hautier, C.C. Fischer, A. Jain, et al., Chemistry of Materials, 22 (12), 3762-3767 (2010

# Some example of newly predicted compounds

| | |
|---|---|
| Ag1Cs1O2 | Cs1Cu1O2 |
| Ho2O12Se3 | O12S3Sc2 |
| Cd1O4Se1 | Cd1Cr1O4 |
| Eu4Mo2O11 | La4Mo2O11 |
| O4Rb4Sb1 | Ge1O4Rb4 |
| Cu2Lu1O4 | Cu2La1O4 |

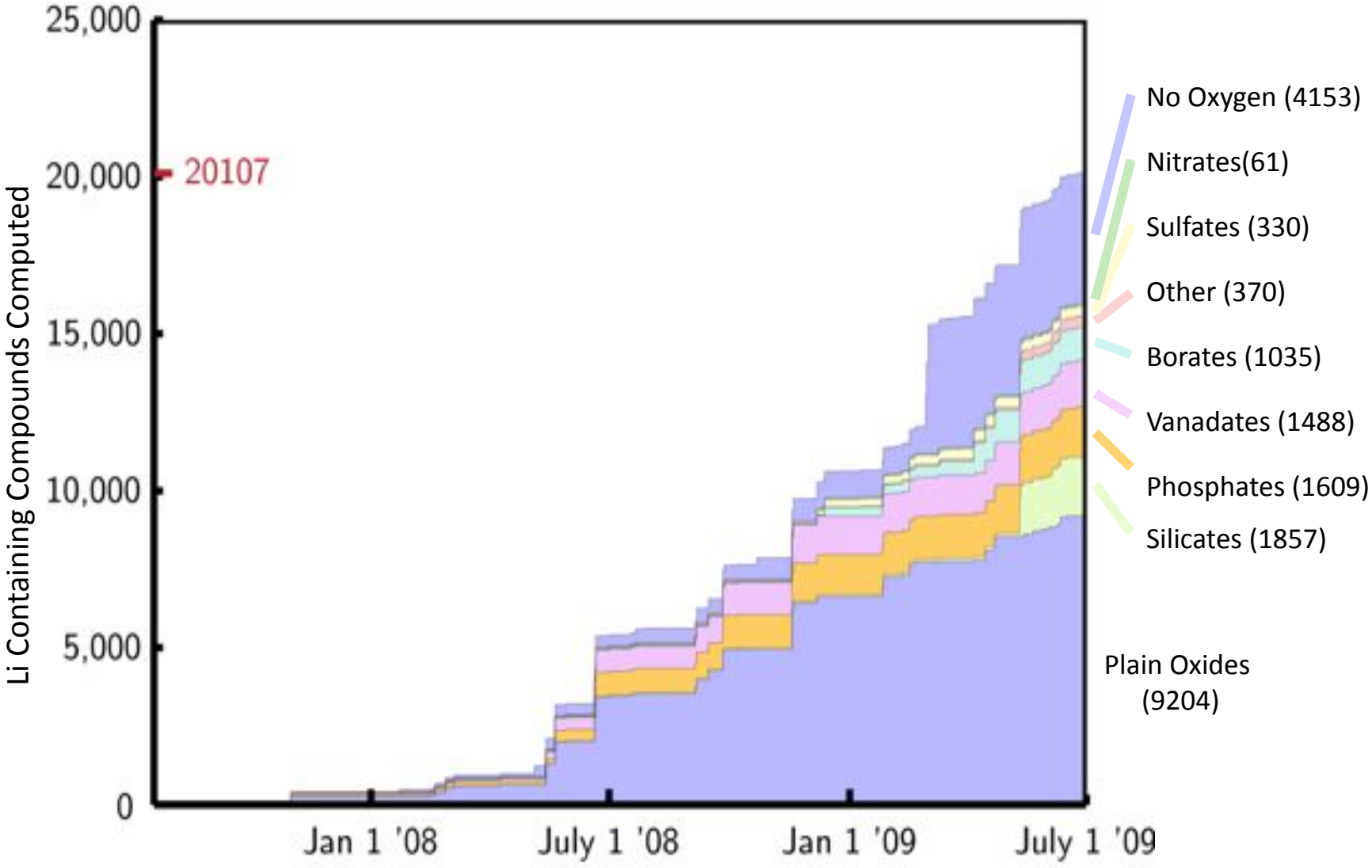
| | |
|---|---|
| Cs2O3Ti1 | O3Rb2Ti1 |
| Co2Cs6O7 | Cs6O7Si2 |
| Eu2Mn2O7 | Mn2O7Y2 |
| Ce1Cl4O16 | Cl4Hf1O16 |
| O4Rb4Si1 | K4O4Si1 |
| Ca2O5W1 | Ca2O5U1 |

| | |
|---|---|
| Br1Fe1O1 | Cl1Fe1O1 |
| K2O3Yb2 | Cd2K2O3 |
| Mo1Nb1O4 | Mo1Ni1O4 |
| Cs6Ge2O7 | Ge2O7Rb6 |
| Cr1O6Sb2 | Cu1O6Sb2 |
| Br4Cs6O1 | Br4O1Rb6 |

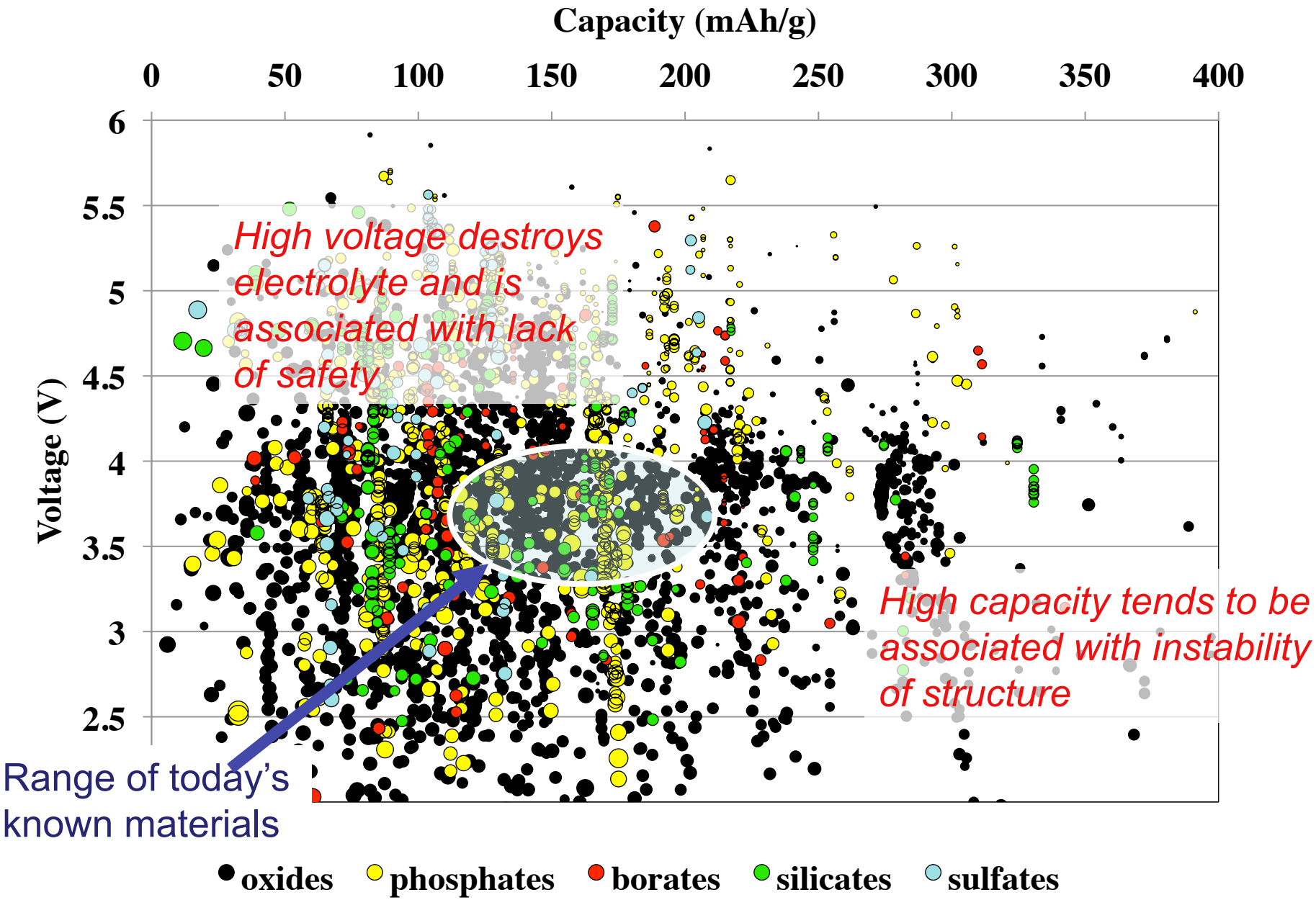


# *Lithium Batteries*

# About 25,000 battery compounds investigated so far



# High-throughput voltage calculations



**How do we learn from this ?**

**Example : Looking for Opportunity in Phosphates ($PO_4^{3-}$)**

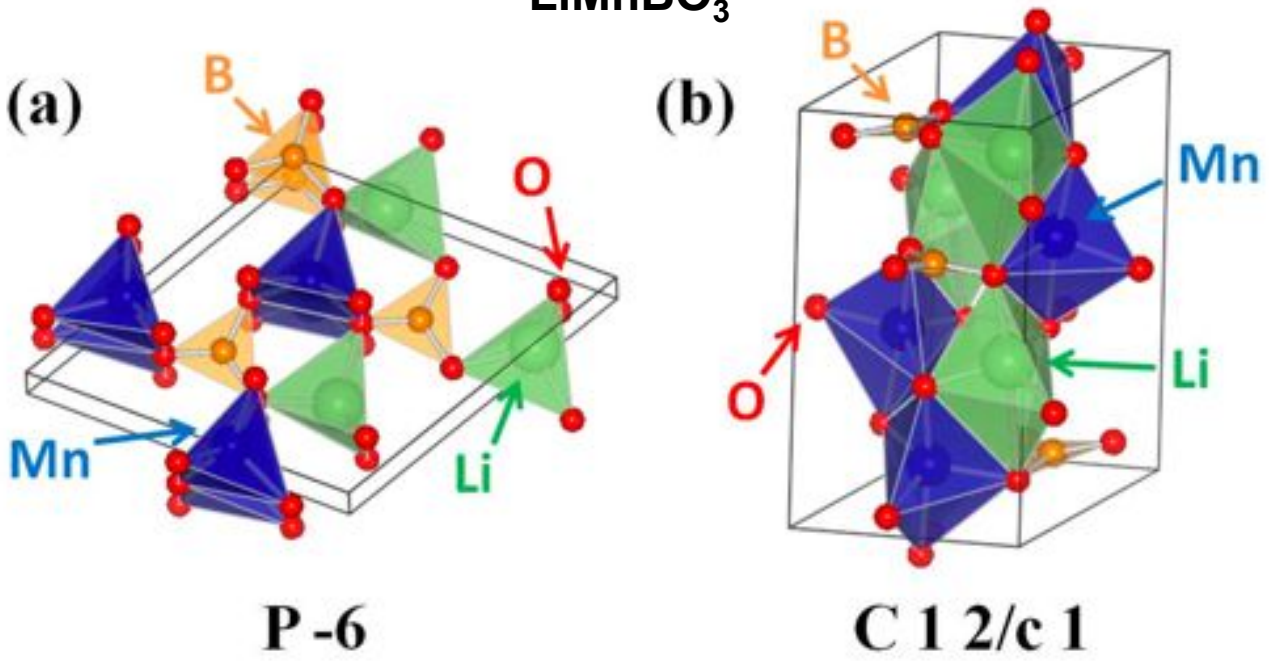
# Interesting “Light” and “safer” polyanions

***Molecular Weight***

| Polyanions | $(BO3)^{3-}$ | $(SiO4)^{4-}$ | $(PO4)^{3-}$ | $(SO4)^{2-}$ |
|---|---|---|---|---|
| **F.W.** | 58.8095 | 92.0831 | 94.9714 | 96.0636 |

**$LiMnBO_3$**

High-T hexagonal phase




Low-T monoclinic phase

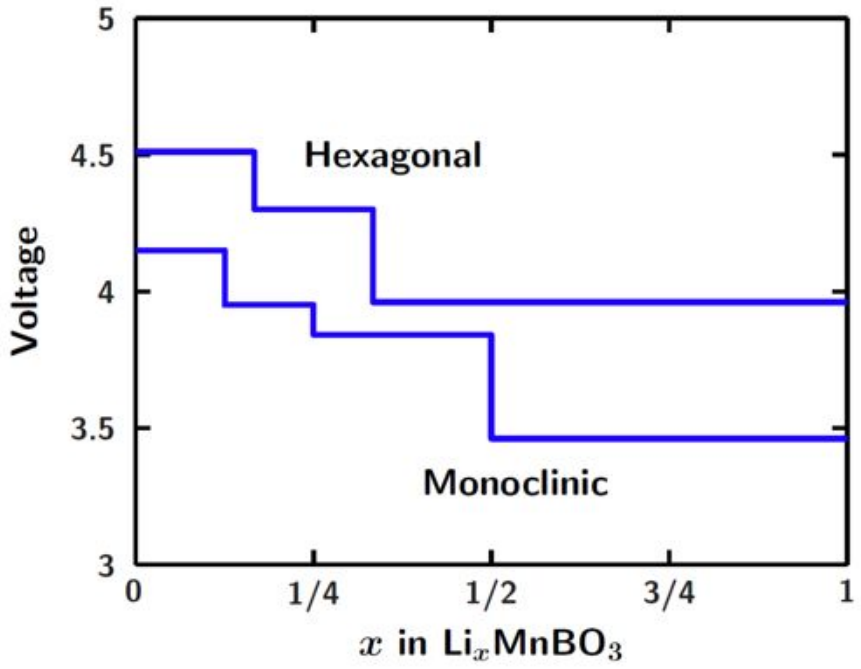
Tested by **Legagneur** et al. - **2001** - Solid State Ionics ≈ 6 mAh/g capacity

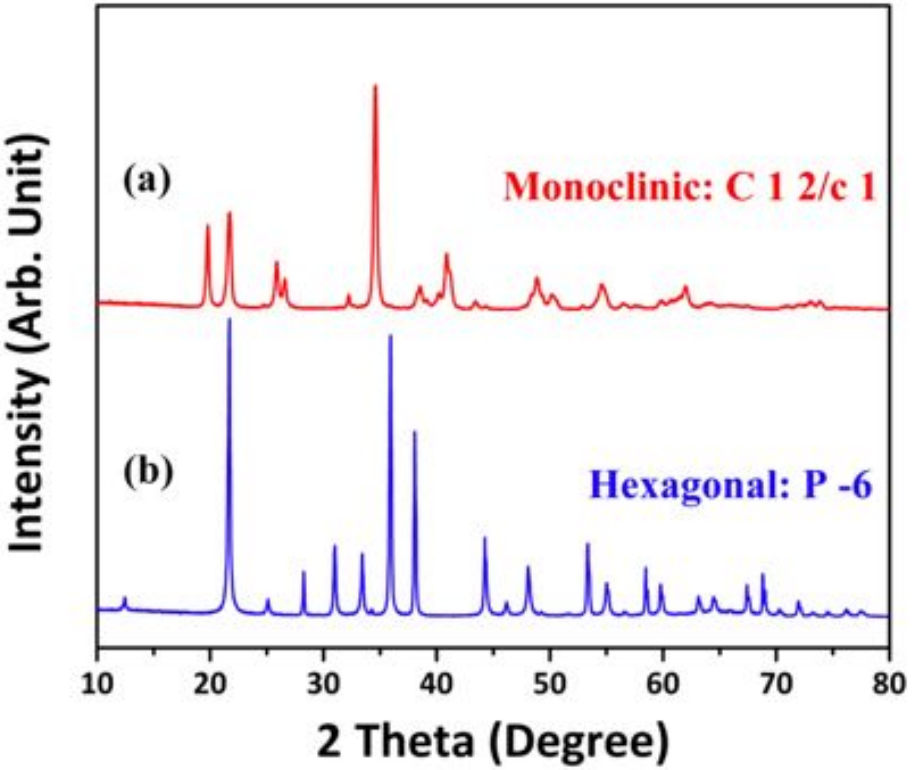
# $LiMnBO_3$: From calculation to synthesis

| Phase | Average Voltage | Theoretical Grav. Energy Density | Theoretical Vol. Energy Density | Theoretical Capacity | Lithiated distance to hull* | Delith. distance to hull* | Volume change** |
|---|---|---|---|---|---|---|---|
| Hexagonal | 4.11 V | 912 Wh/kg | 2922 Wh/l | 222 mAh/g | 0 meV/at | 216 meV/at | 0.6% |
| Monoclinic | 3.70 V | 822 Wh/kg | 2635 Wh/l | 222 mAh/g | 4 meV/at | 140 meV/at | 2.5% |

* Distance to hull stands for difference in energy from the computed ground state

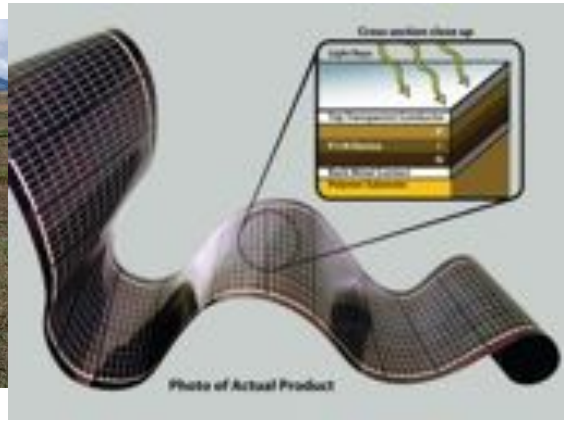
**Volume change is taken as a percentage of the Lithi

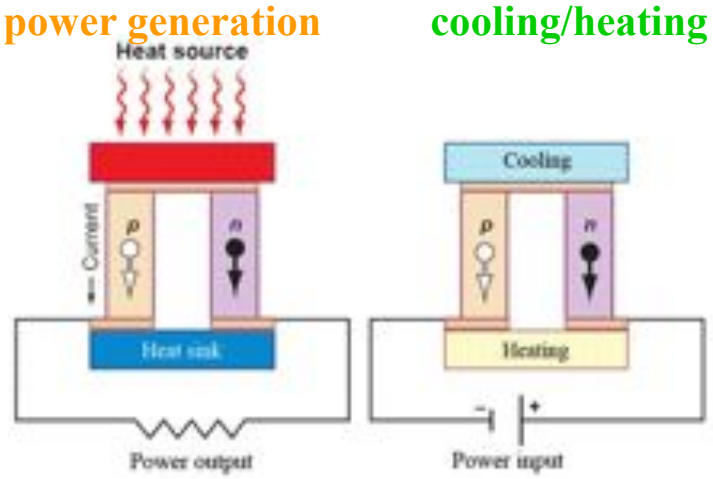


# Virtual design of Materials to save the planet

- Materials are the cornerstone of energy innovation
- Materials properties can be predicted **ab initio**.
- We will reach the point where properties of all materials are computed: **A Materials Genome**



# All the work is really done by …

**Umicore**

Robert **Bosch** Company

**Duracell**

BATT Program of **DOE**

BERKELEY LAB

umicore
materials for a better life

BOSCH

# Thank you