materials design

Li-Ion Batteries and Beyond:

Driving Next-Generation Energy Storage with *MedeA*®

Taylor Juran
Materials Design

Jan 2021

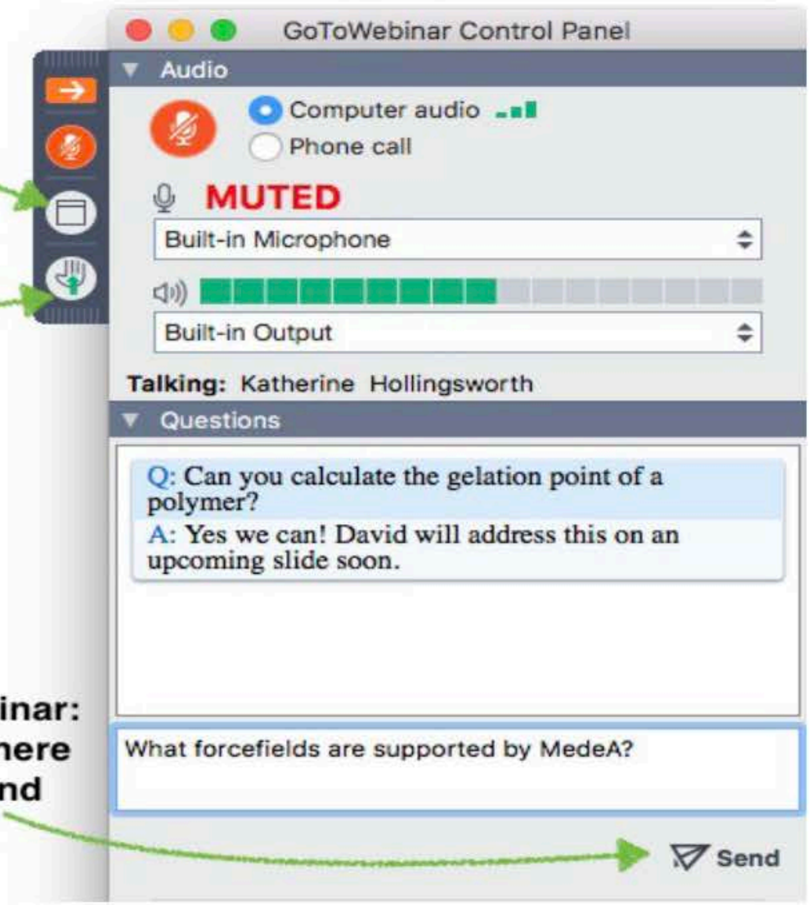
- **Share the webinar series with your colleagues!**
  - Registration details http://www.materialsdesign.com/webinars
- **We will be recording this webinar**
  - Watch any of our earlier webinars anytime
  - We will post upcoming webinars on the webinar page
- **Vote for the next webinar topic!**
  - Take a 2 minutes brief survey at the end of the webinar!

Materials Design Webinar Series

full screen

during discussion:

Use the raise hand icon to bring attention to your question



any time during webinar: type your question here and then press Send

Webinar Team

Katherine Hollingsworth
khollingsworth@materialsdesign.com

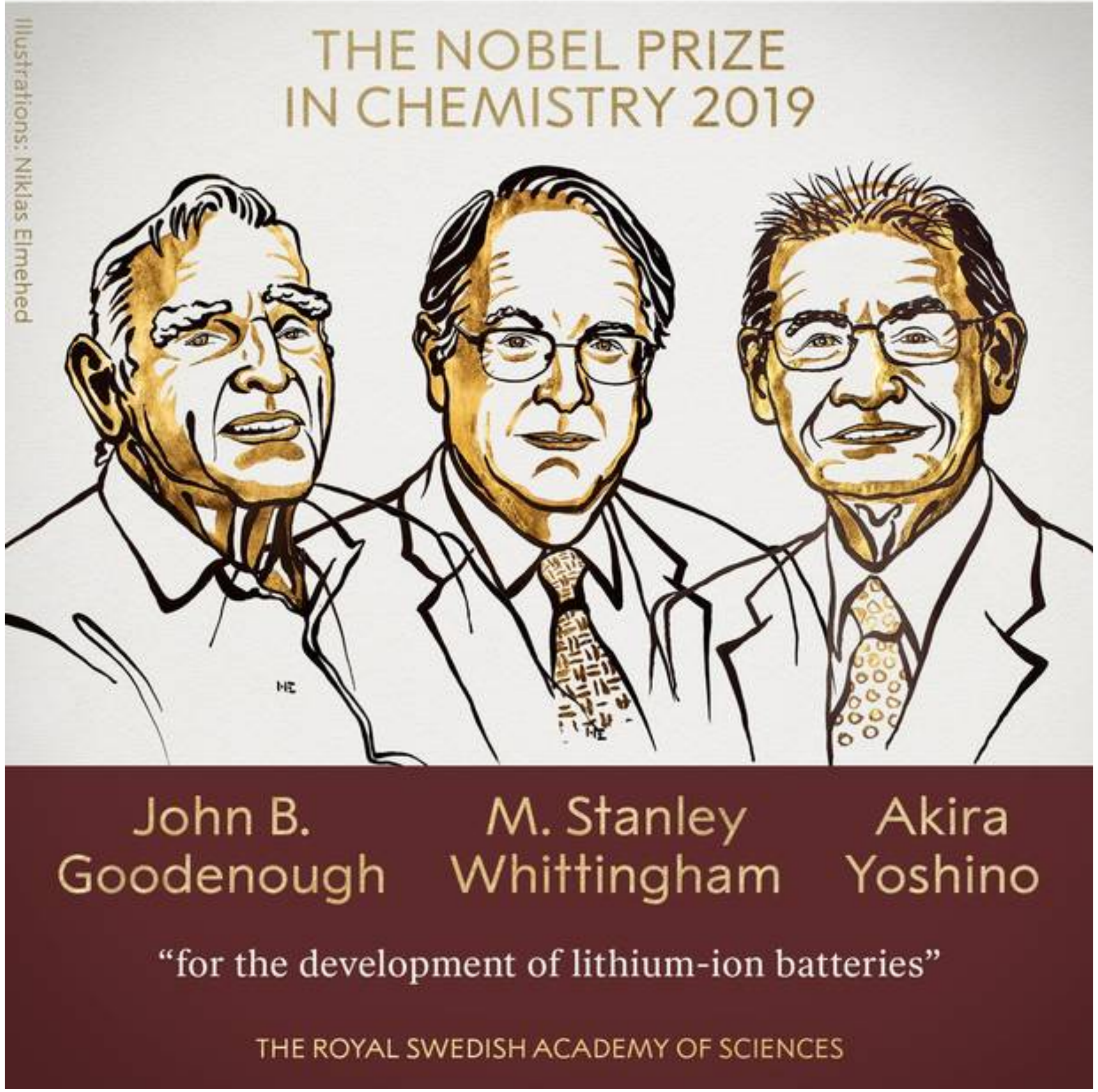
Dr. René Windiks
rwindiks@materialsdesign.com

Dr. Taylor Juran
tjuran@materialsdesign.com

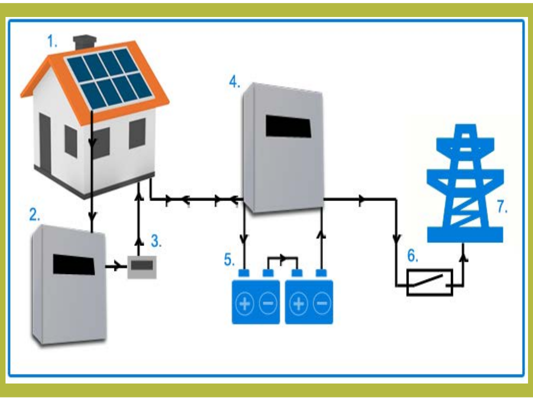
Outline

- Batteries Today
- Cluster Expansion of Li_xNiO_2
- Li_xNiO_2 Voltage Profile
- Multivalent Ion Batteries
- Intercalation Site Identification
- Electronic Properties
- Diffusion Barriers

Battery conversations become mainstream



Branches of batteries



- Vanadium-Redox Flow
- Zinc-Polyiodide Flow
- Organic Aqueous Flow
- Na-Metal Halide
- Na-ion
- Mg-ion
- Mg-Li Hybrid
- Zinc-Manganese Oxide

- Li-ion
- Li-S
- Li-Air
- Li-Metal
- Mg-ion
- Ca-ion

Toyota[1-3]

- Li-ion

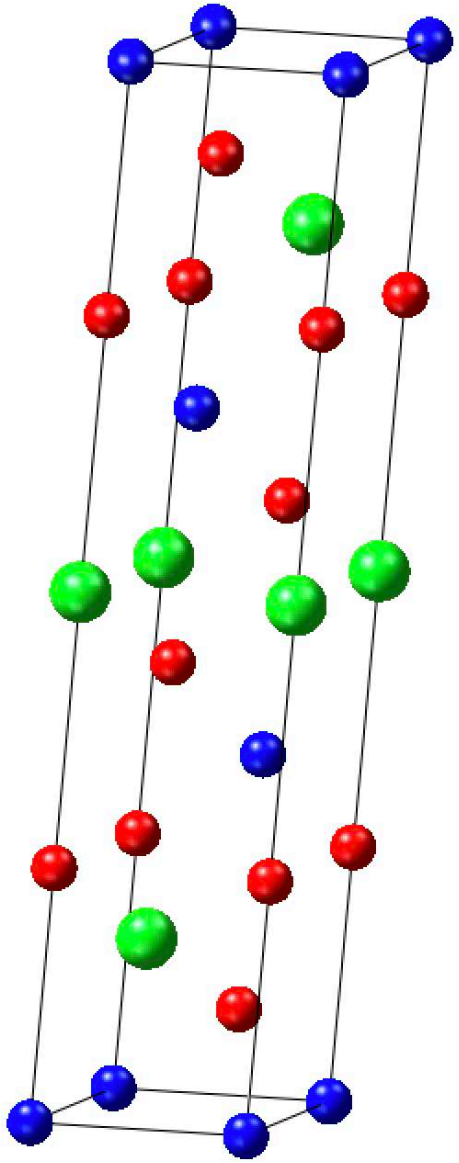
[1] Joule, Volume 3, Issue 3, P782-793, MARCH 20, 2019

[2] Nat Energy **5,** 1043–1050 (2020).

[3] Front. Chem., 20 February 2019

‘Li is the new oil’

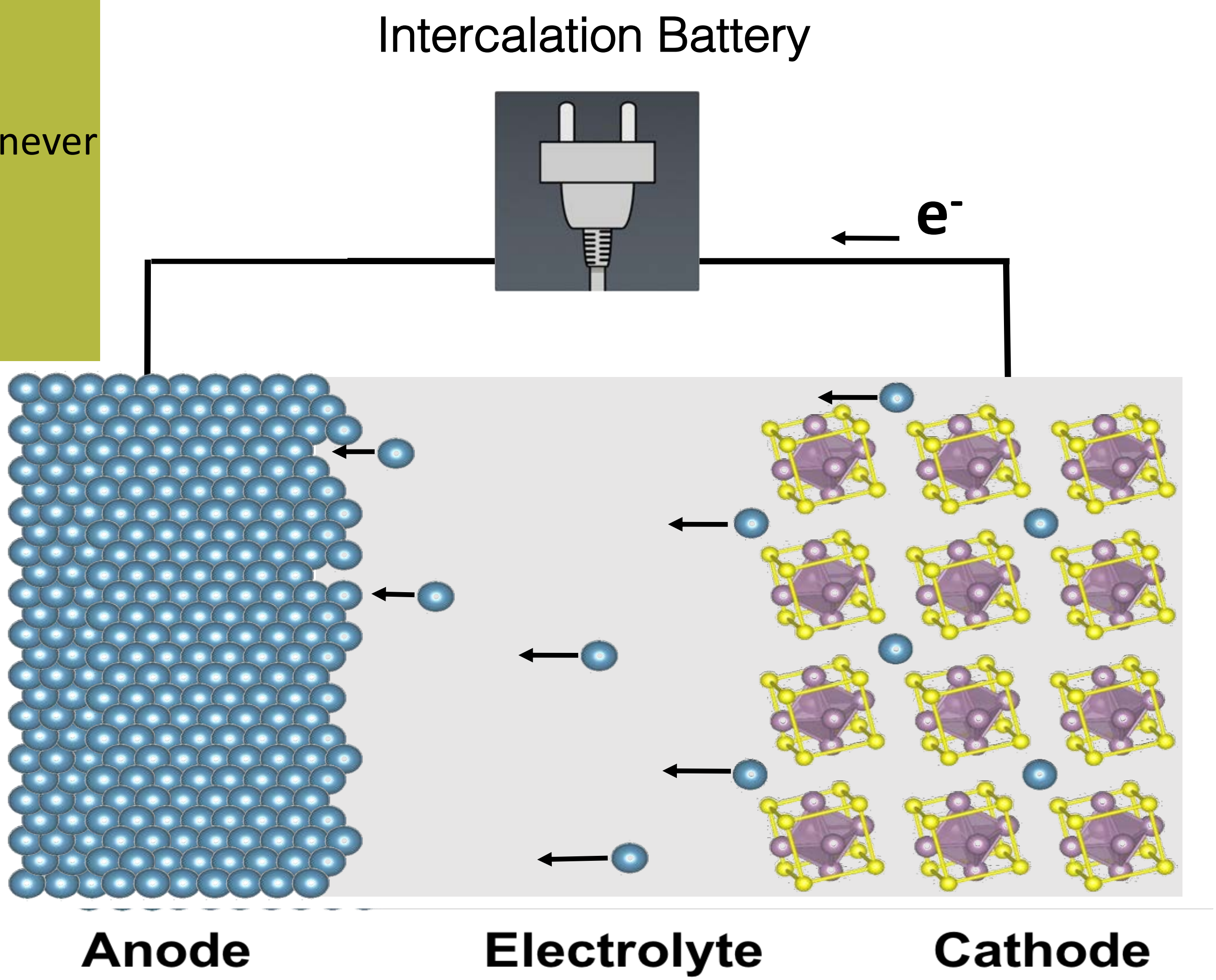
- Li is the lightest metal
- Most electropositive metal
- Energy density – 260 Wh/kg
- High cyclability – over 500 cycles
- Limited by the cathode
- $LiCoO_2$



We need new battery chemistries

“If you want something you've never had
You must be willing to do something you've never done.”

— **Thomas Jefferson**.



[1] Chem. Rev. 2017, 117, 5, 4287–4341
Publication Date:February 13, 2017

MedeA, take the wheel

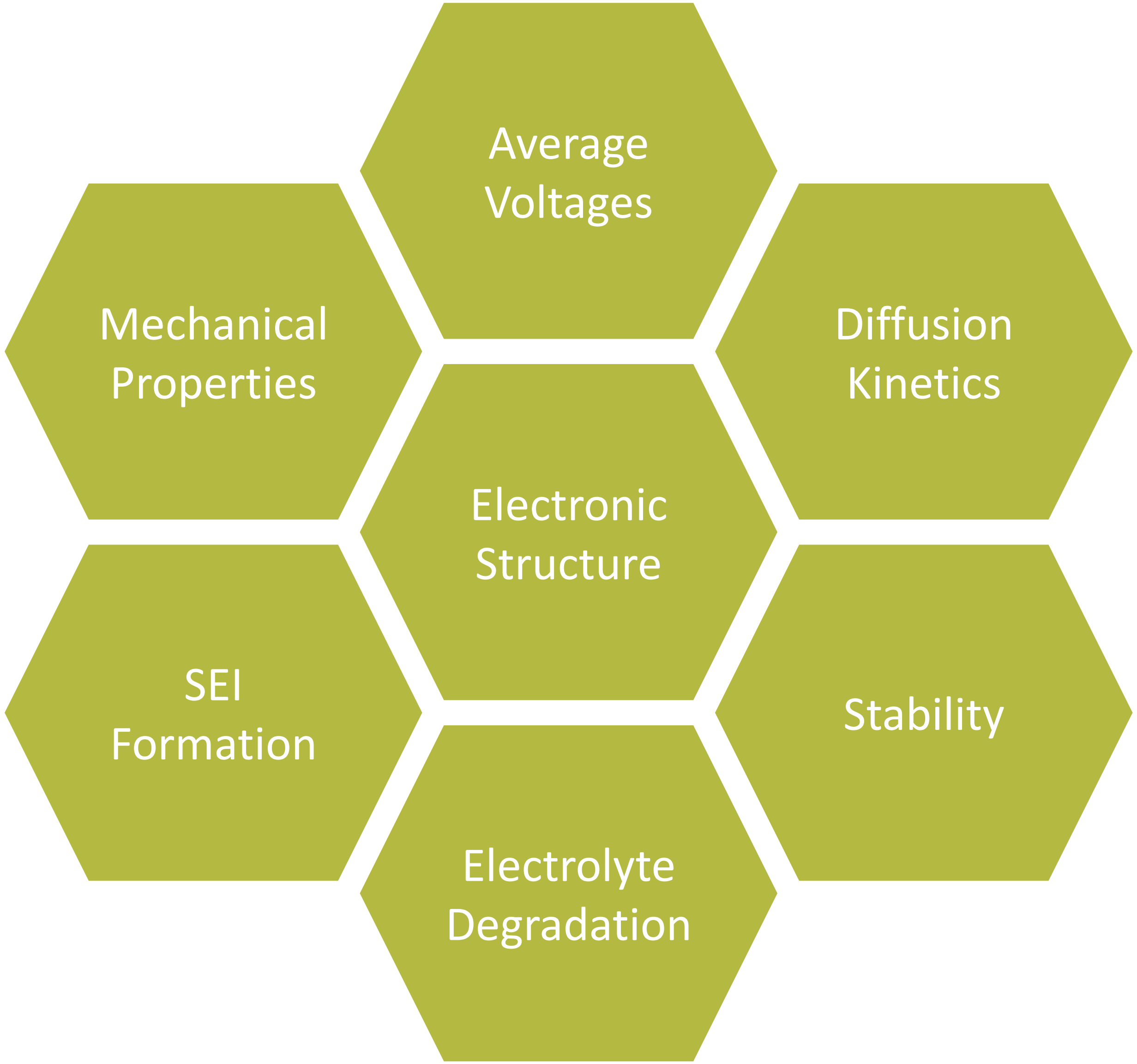
Drive the science forward, instead of spending valuable research time writing bad code

Modeling becomes more accessible

Study a broader range of batteries

Reserve experimental efforts for only the most promising battery candidates

Applying *MedeA* to battery material research



A computational study of anode/cathode pairs: The outline

Choose the material

MedeA® InfoMaticA

Convergence testing

MedeA® Automated Convergence

Intercalation site testing

MedeA® Empty Space Finder

Unit cell: electronic properties, average voltages, …

MedeA® VASP, Analysis Tools, …

Promising results?

No

Yes

Supercell studies: diffusion, voltage profiles,…

MedeA® VASP, Transition State Search, Analysis Tools, …

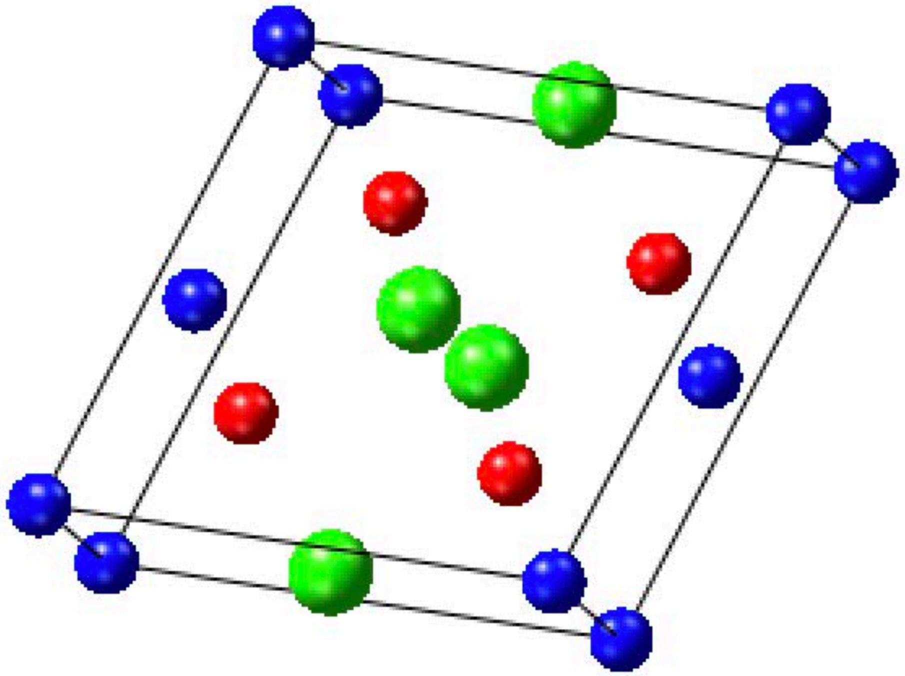
Change the material with doping or alloying

MedeA® VASP, MedeA® UNCLE

Call your favorite experimentalist

Li_xNiO_2

- $LiCoO_2$ is a commonly commercialized battery material - since the 1980's
- Mixing the transition metal *M* in Li*M*O_2 allows battery properties to be tuned
- Ni provides a favorable capacity
- Electrochemical properties are heavily dependent on cathode structural changes during cycling[1]



LiNiO2 structure: Li (blue), Ni (green), O (red)

[1] npi Computation Materials, volume 4, Article number: 60 (2018)

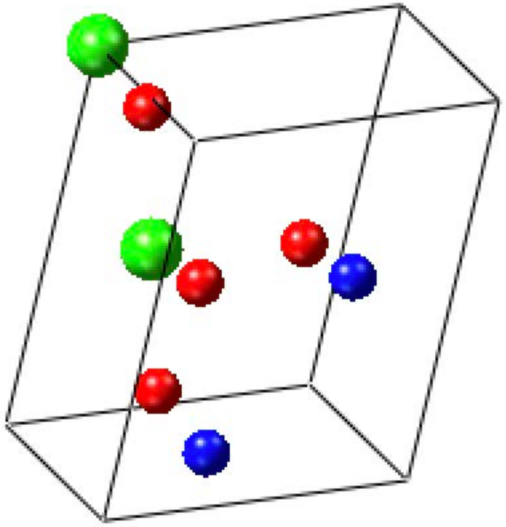
Li_xNiO_2 different phases, and ranges they are stable

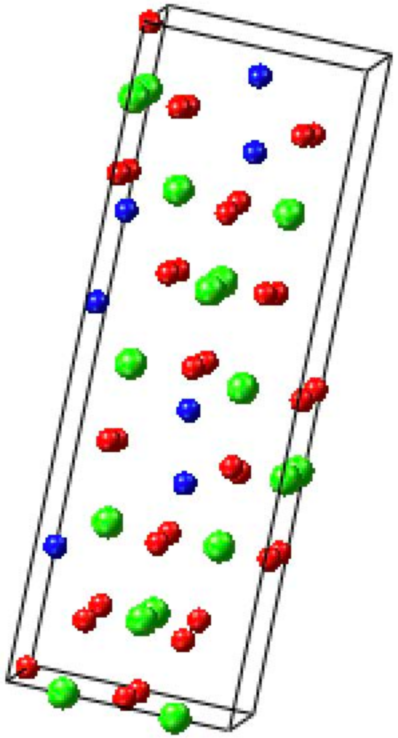
Rock Salt
Fm-3m
$0 \leqq x \leqq 0.5$

Spinel
Fd-3m
$0.5 \leqq x \leqq 0.6$

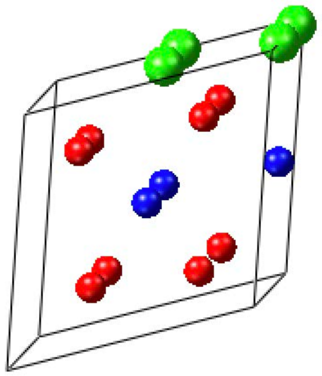
Layered
Hexagonal
R-3m
$0.4 \leqq x \leqq 1$

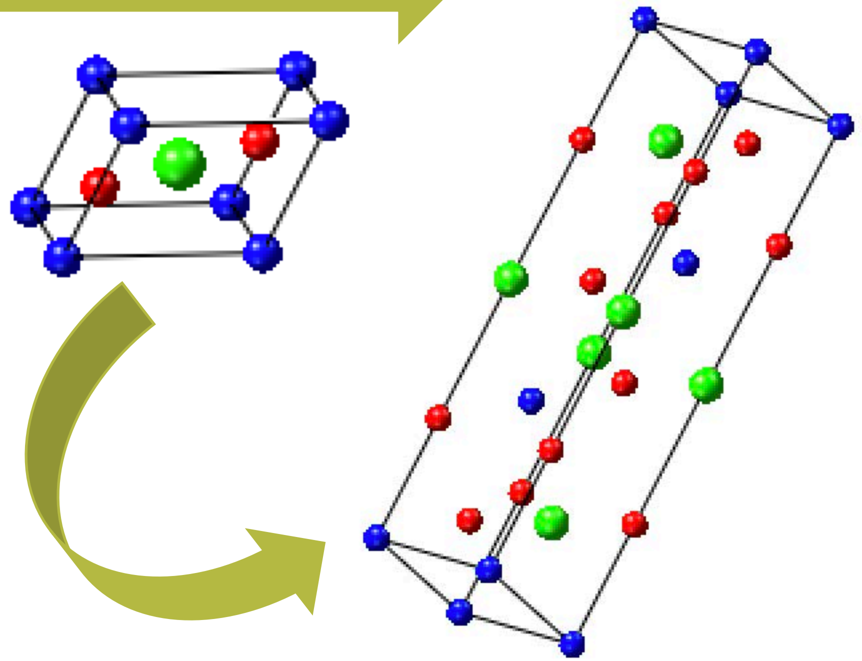
Increasing Li





Layered
Monoclinic
C2/m
$0.39 \leqq x \leqq 0.69$





Hexagonal primitive cell
to raised symmetry R-3m

LiNiO2 structure: Li (blue), Ni (green), O (red)

MedeA UNCLE – Identifying new cathode structures with Cluster Expansion

Model → Structures → Energies ← Automated

Model
- Crystal structure from a database
- Active sites
  - Elements
  - Vacancies
- Rank of CE (binary, ternary,…)
- Concentration ranges

Optimize Cluster Expansion
- Iteratively builds a training set
  - Max configuration size
- Cluster Expansion at each iteration
  - Max number of clusters within a fit

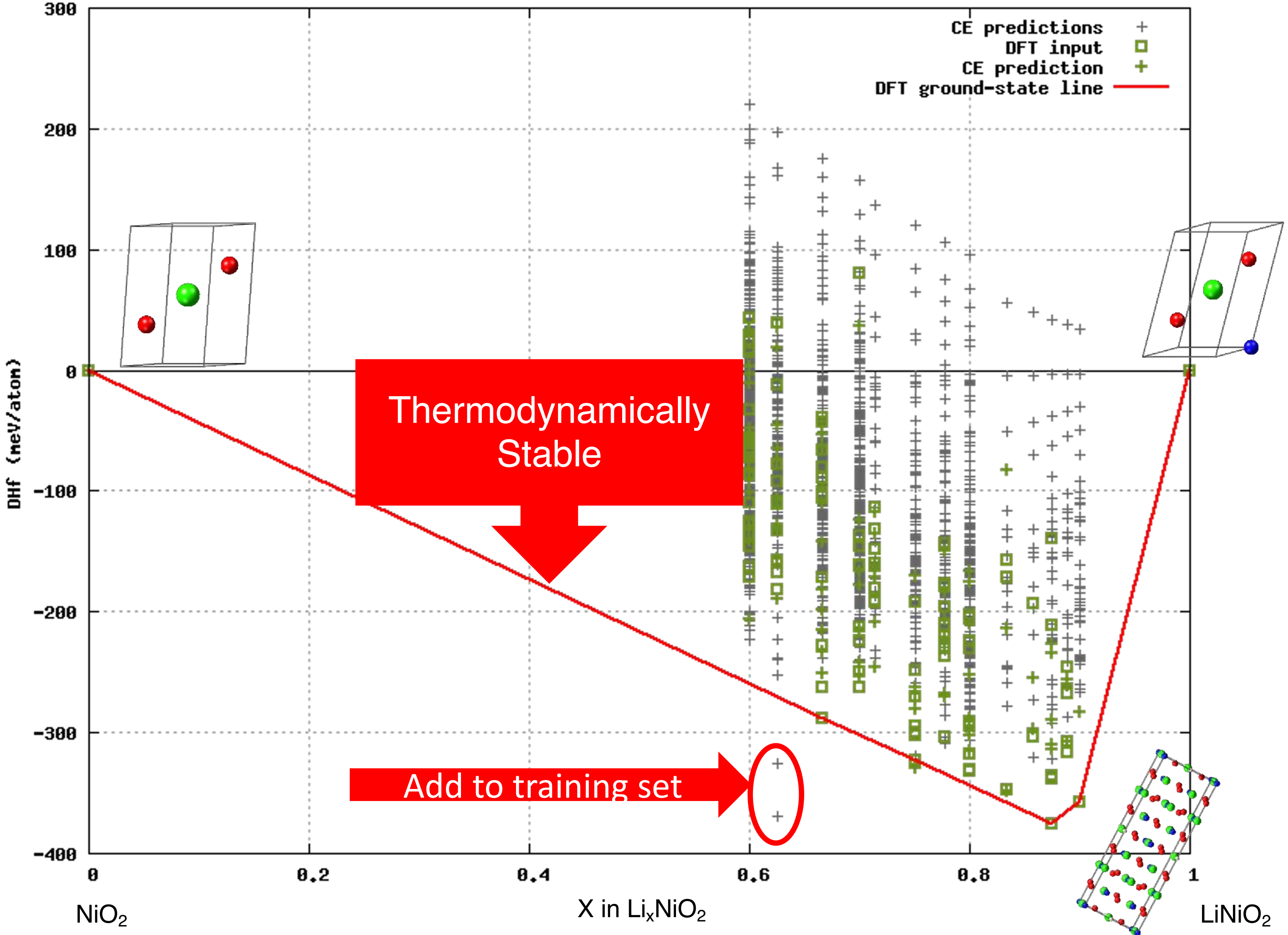
Energies of Training Set Structures
- Flowchart
- Optimize training set with ionic relaxations, or use an isotropic volume optimization
- Obtain energies

Automated

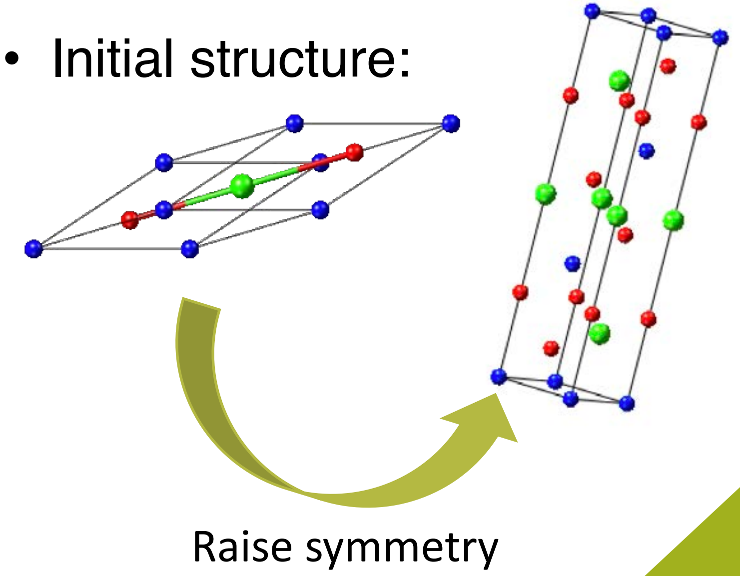
- Need new structures, which may not be available in current databases
- Efficient sampling of large configuration space and accurately obtaining energy values
- Candidate stable phase structures

https://www.materialsdesign.com/webinars/recorded/MedeA-UNCLE%3A-Atomistic-Studies-of-Crystalline-Systems-at-Higher-Scales

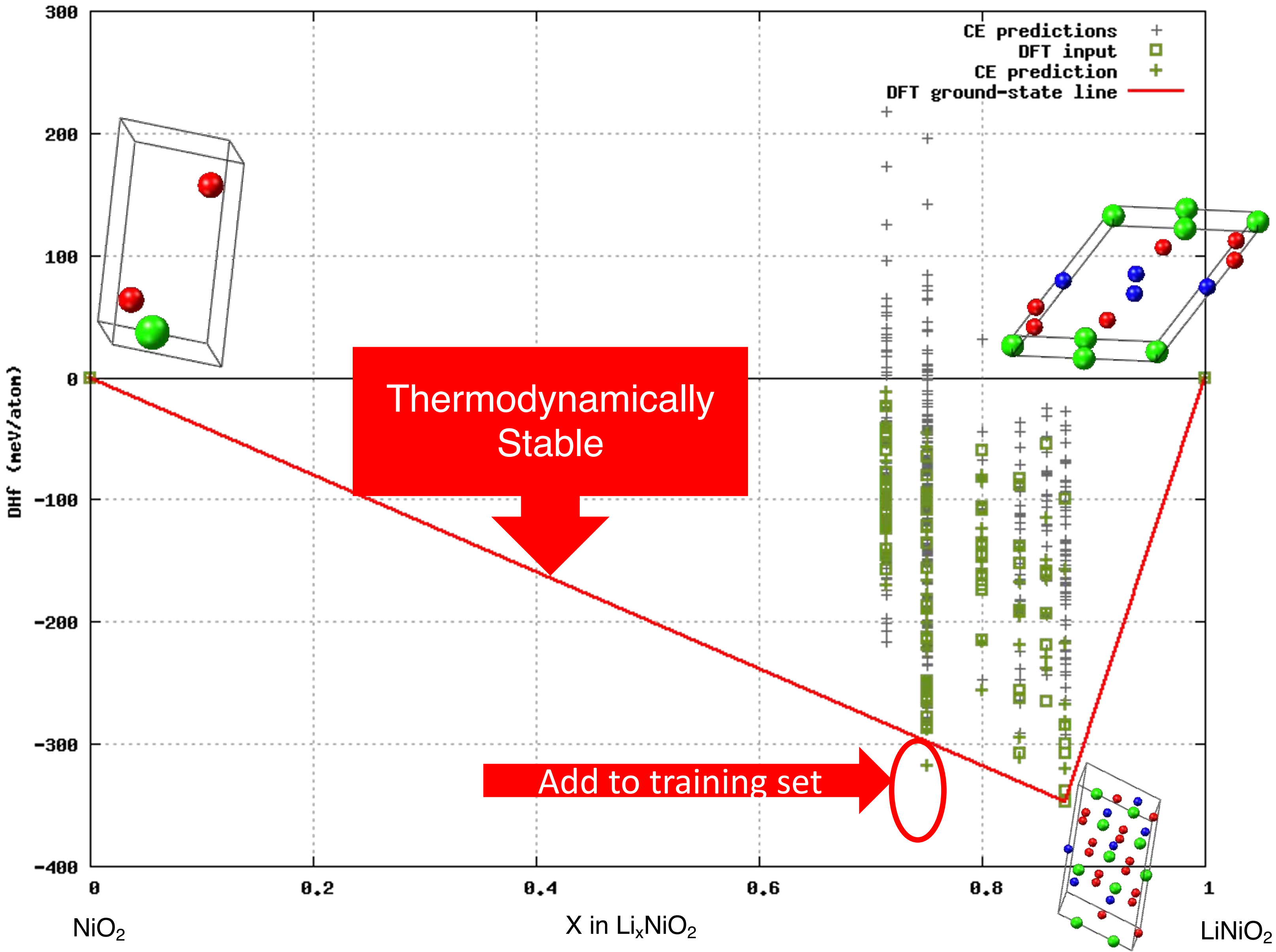
Li_xNiO_2 Layered Hexagonal (R-3m)



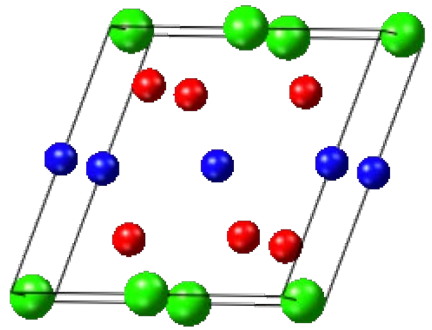
- Max generations = 200
- Max clusters in fit = 20
- Cross Validation Score (CVS) ≦7.7 meV/site
- Initial structure:



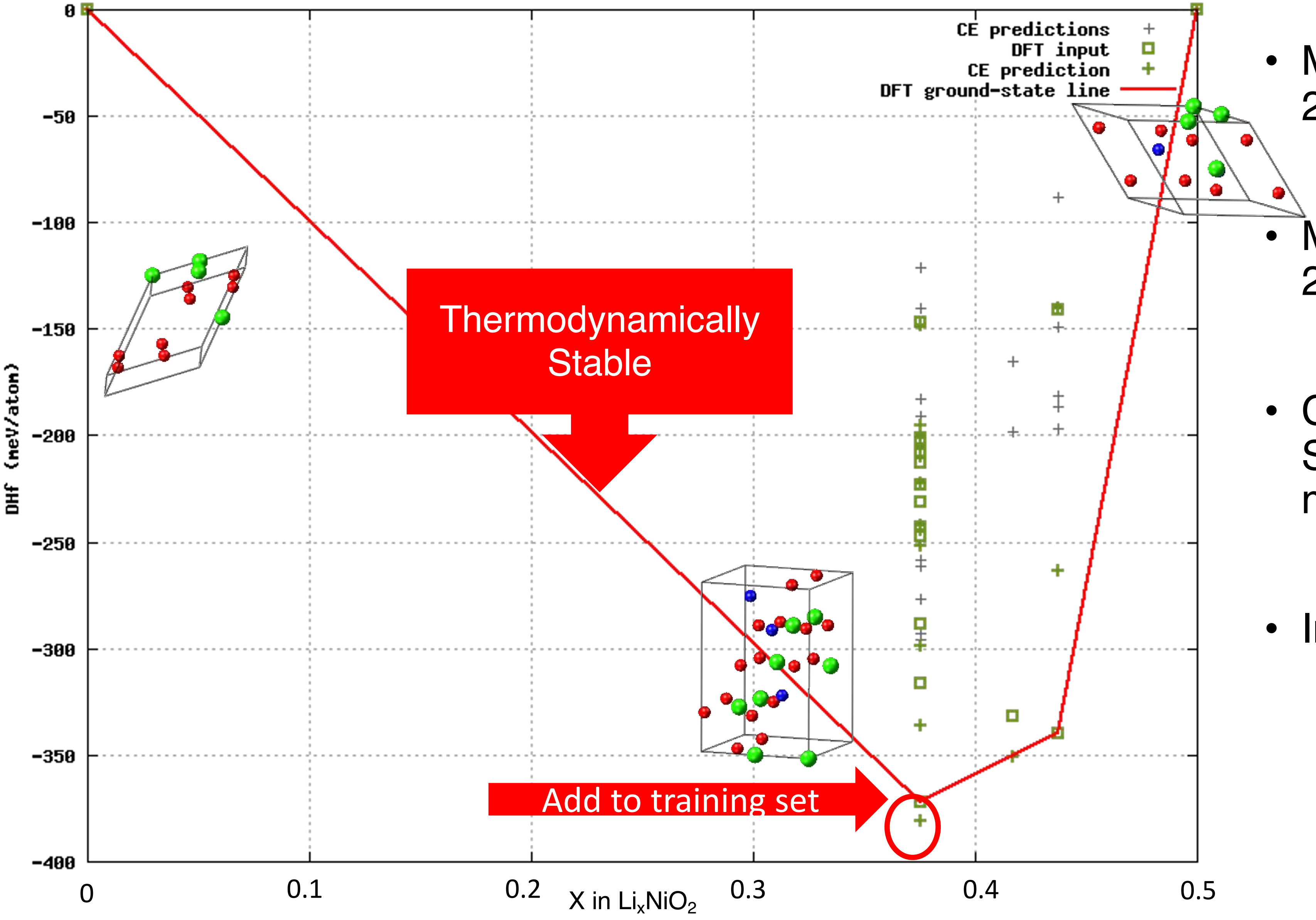
Li_xNiO_2 Layered Monoclinic (C2/m)



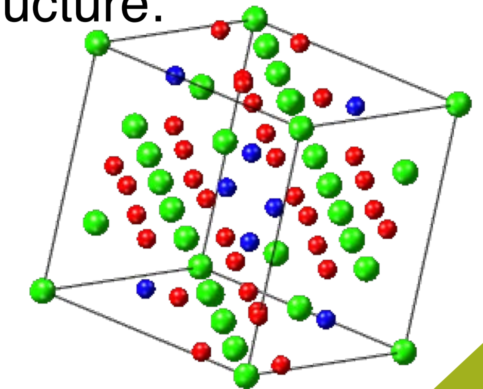
- Max generations = 200
- Max clusters in fit = 20
- Cross Validation Score (CVS) ≦35 meV/site
- Initial structure:



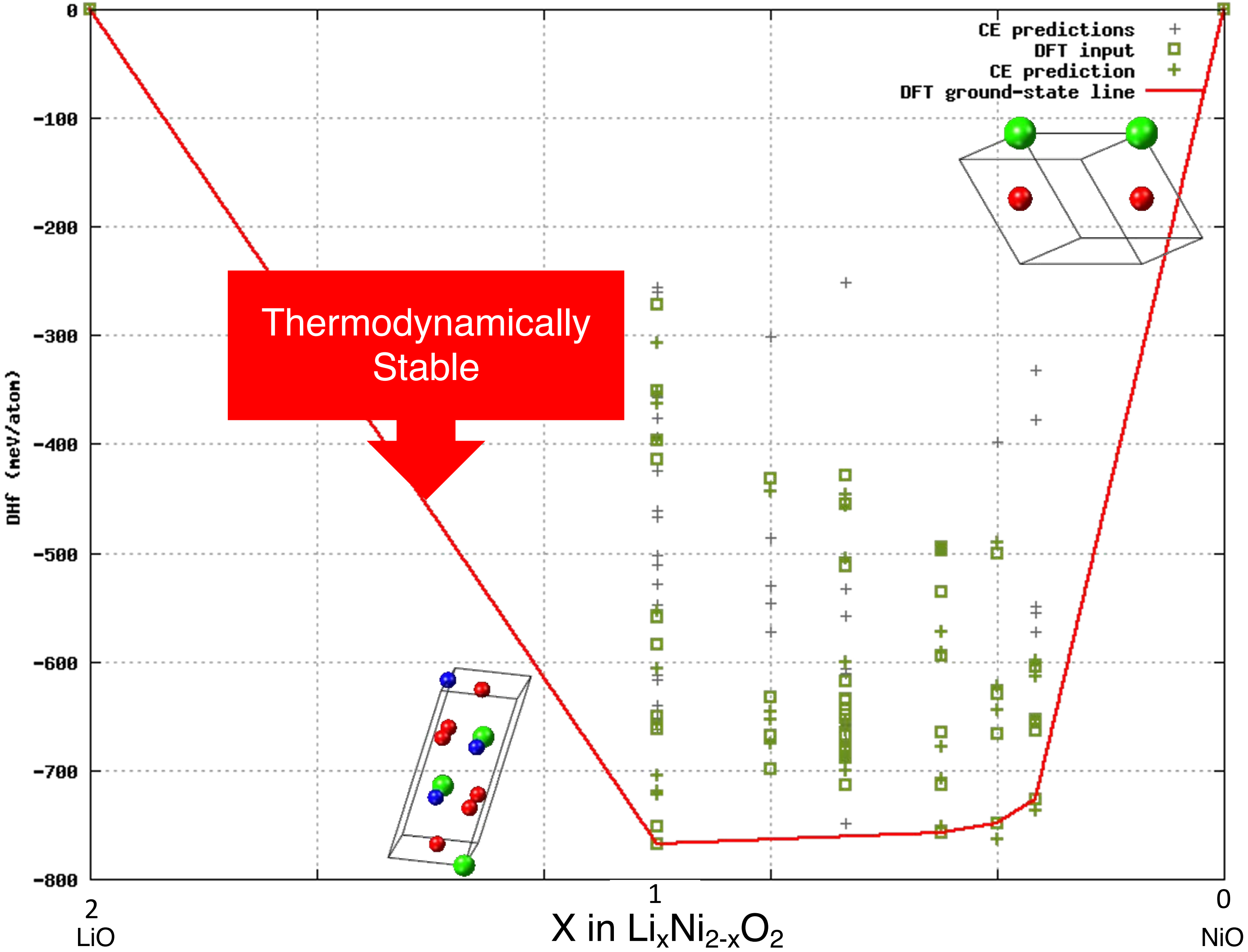
Li_xNiO_2 Spinel (Fd-3m)



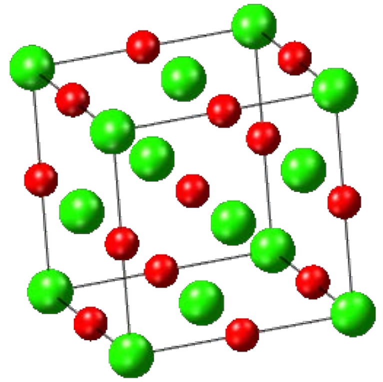
- Max generations = 200
- Max clusters in fit = 20
- Cross Validation Score (CVS) ≦ 22 meV/site
- Initial structure:



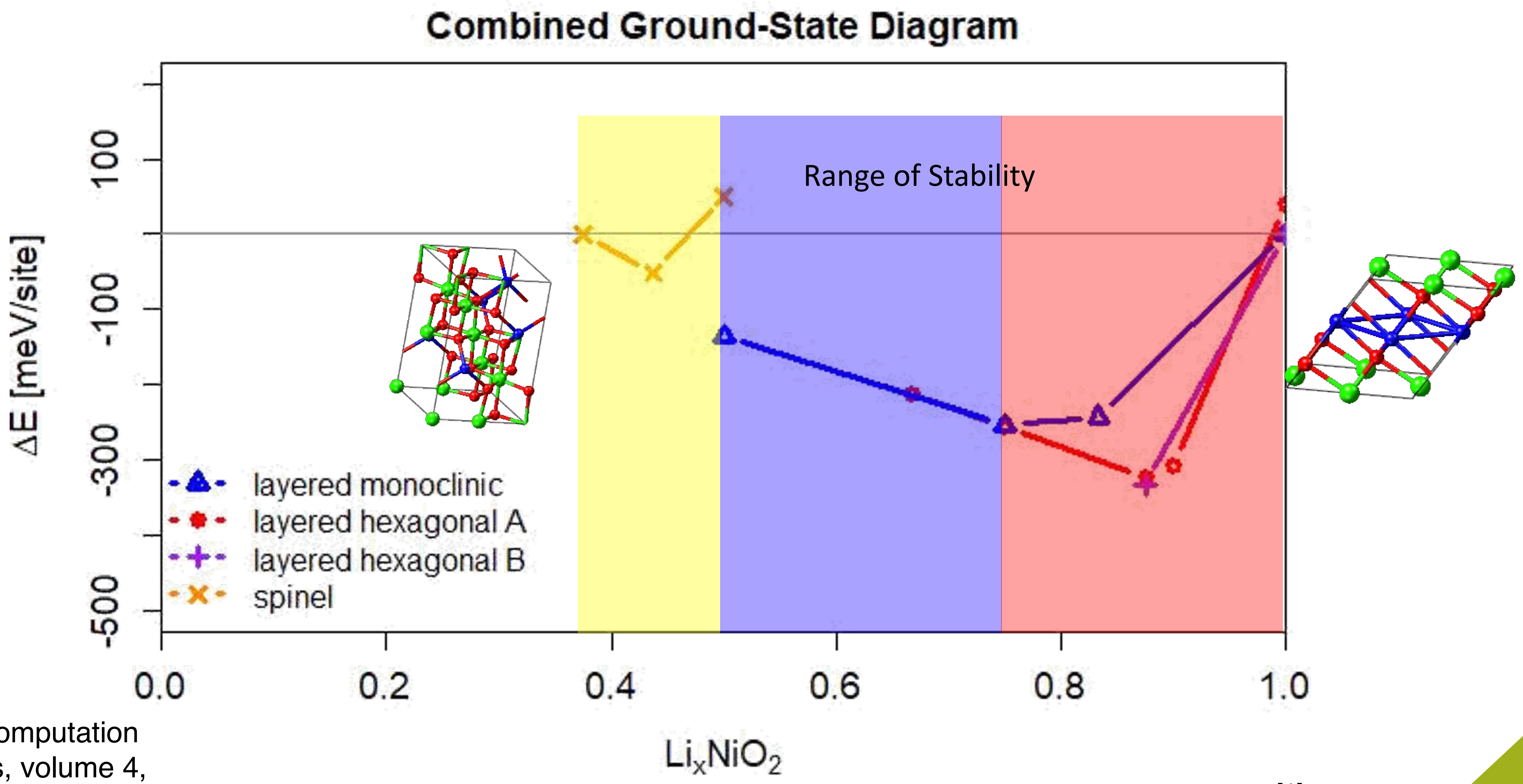
2 Phase Regime: X in $Li_xNi_{2-x}O_2$ Rock Salt (Fm-3m)



- Max generations = 200
- Max clusters in fit = 20
- Cross Validation Score (CVS) ≦ 26 meV/site
- Initial structure:



Li_xNiO_2 Combined Ground-State Diagram

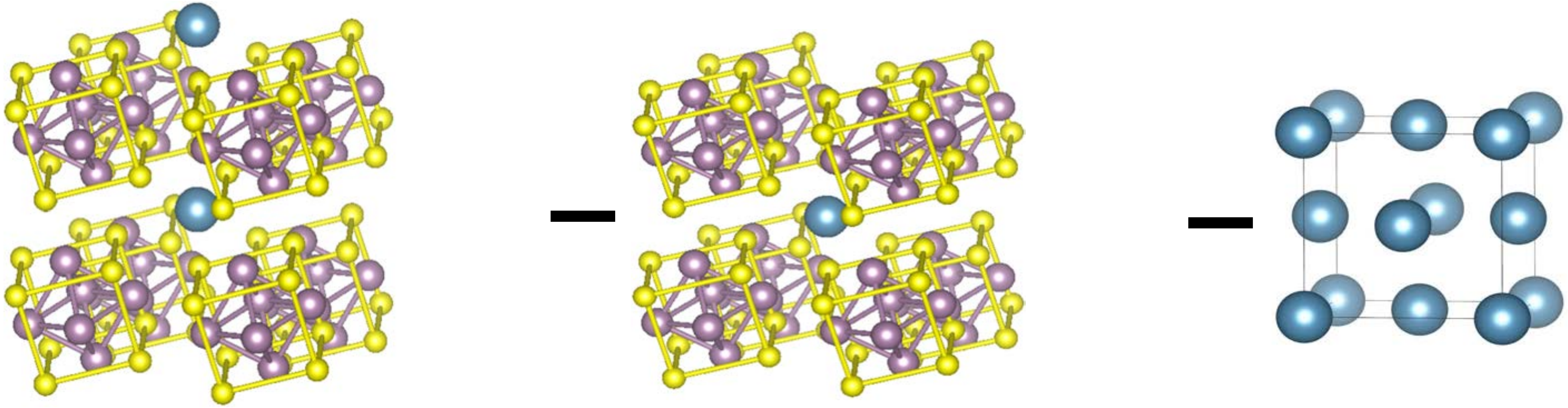


[1] npi Computation Materials, volume 4, Article number: 60 (2018)

The calculated stability ranges agree with the measurements.[1]

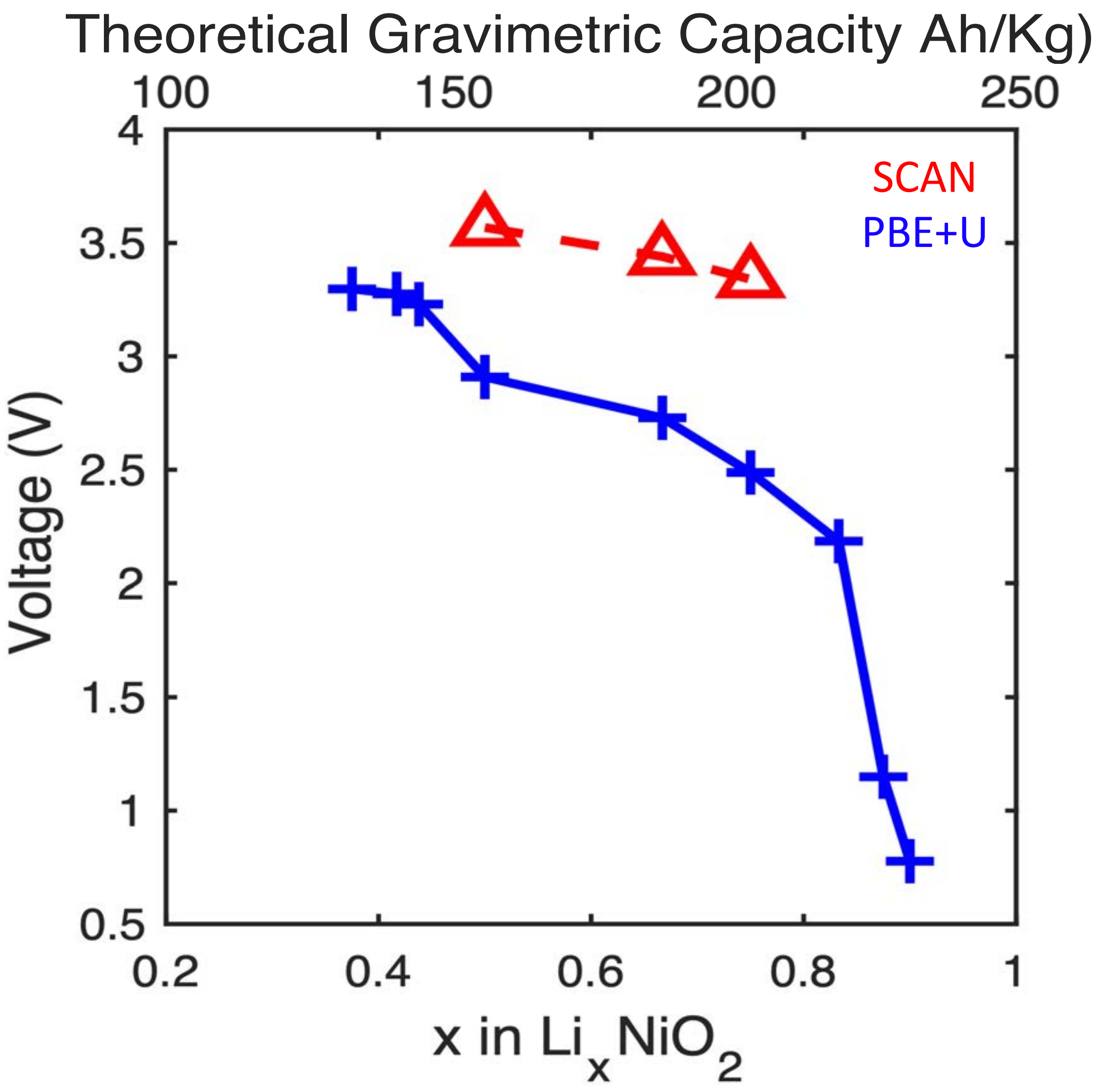
Voltage calculations

$$V = -\left(\frac{E(M_{x_2}\text{Cathode}) - E(M_{x_1}\text{Cathode}) - E((x_2 - x_1)\ \mu)}{N_{\text{electrons}}}\right)$$



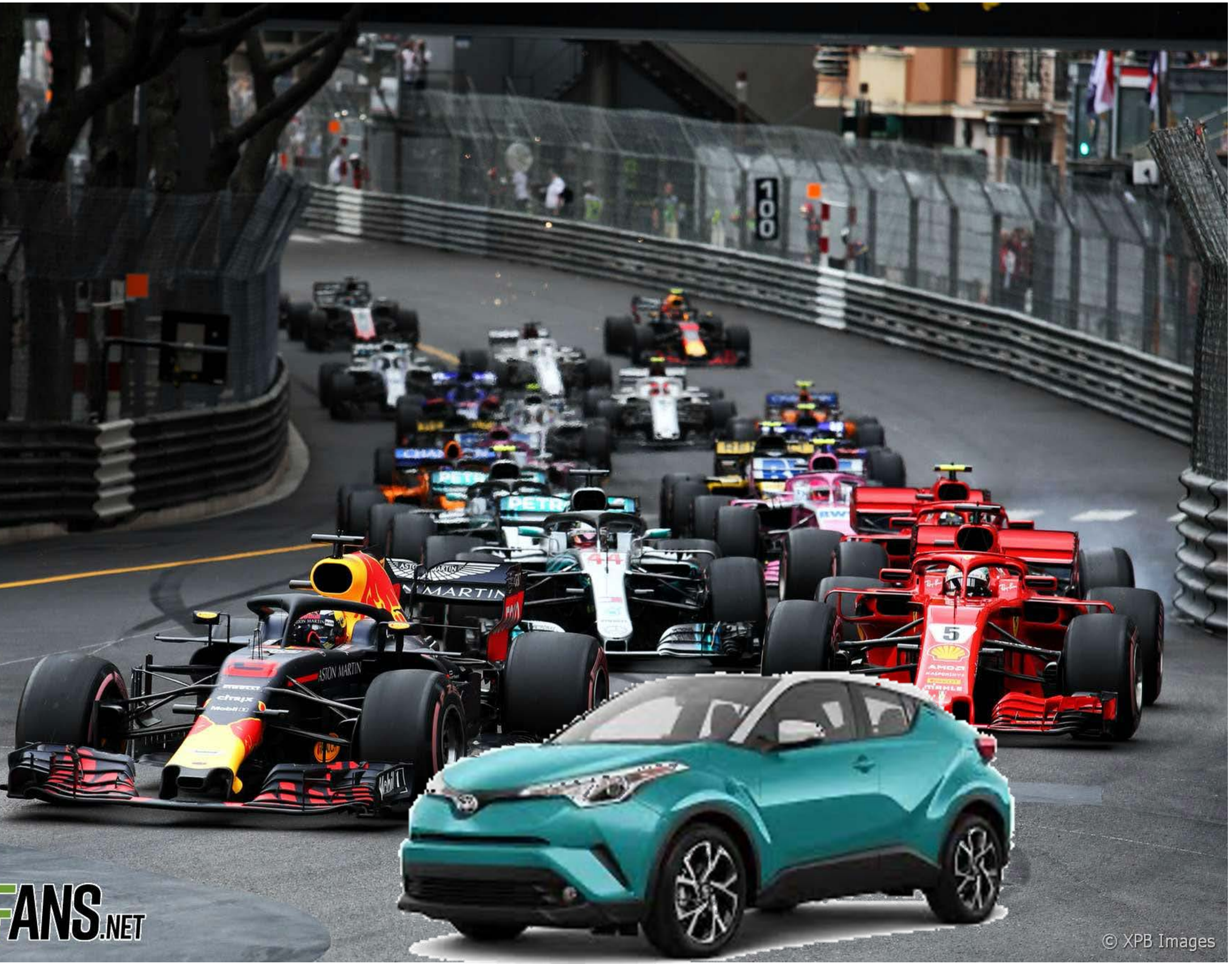
Voltages calculated for the previously identified stable structures

- PBE +U, U = 7.2
- Voltage is underestimated compared to experiment
- Voltages match those computed with PBE in a previous study
- SCAN should increase the voltage, and possibly lead to a better experimental match
- Compares well with other studies



[1] npi Computation Materials, volume 4, Article number: 60 (2018)

Functionals do matter, but we must work within our means



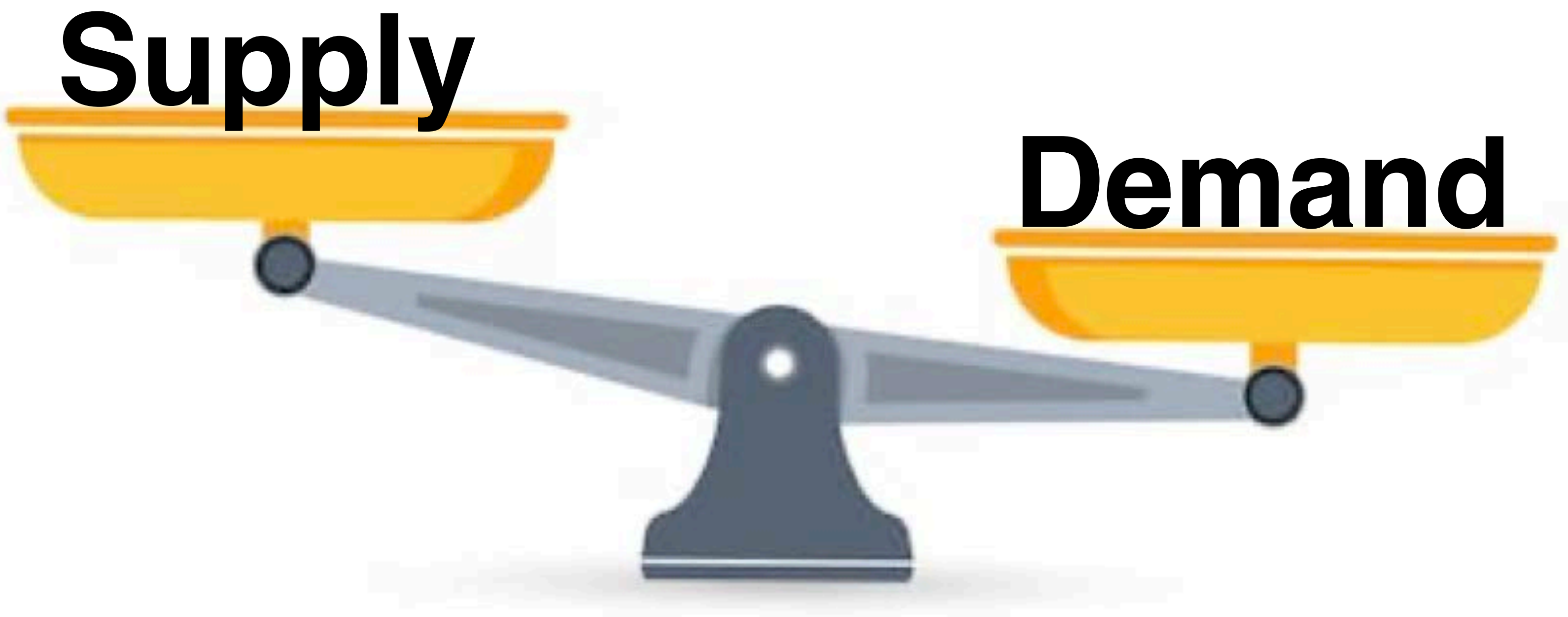
- Toyota and Honda: LDA and GGA
  - Local Density Approximation
  - Perdew-Burke-Ernzerhof (PBE)
  - PBE + Hubard-U (PBE+U)

- BMW and Mercedes-Benz: Meta-GGAs
  - Strongly Constrained and Appropriately Normed semi-local density (SCAN)
  - Modified Becke-Johnson (mBJ)

- Rolls Royce – Hybrids
  - Hyde-Scuseria-Ernzerhof (HSE)

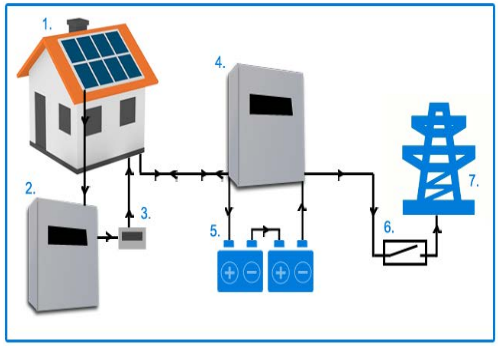
Li is ‘the new oil’, but Ca might fill in the gap

- Range of battery chemistries to select from
- Better batteries:
  - Energy density – Capacity and voltage
  - Charge/Discharge Rate – mobility of charge carriers
  - Lifetime – stability, phase transitions, swelling and cracking

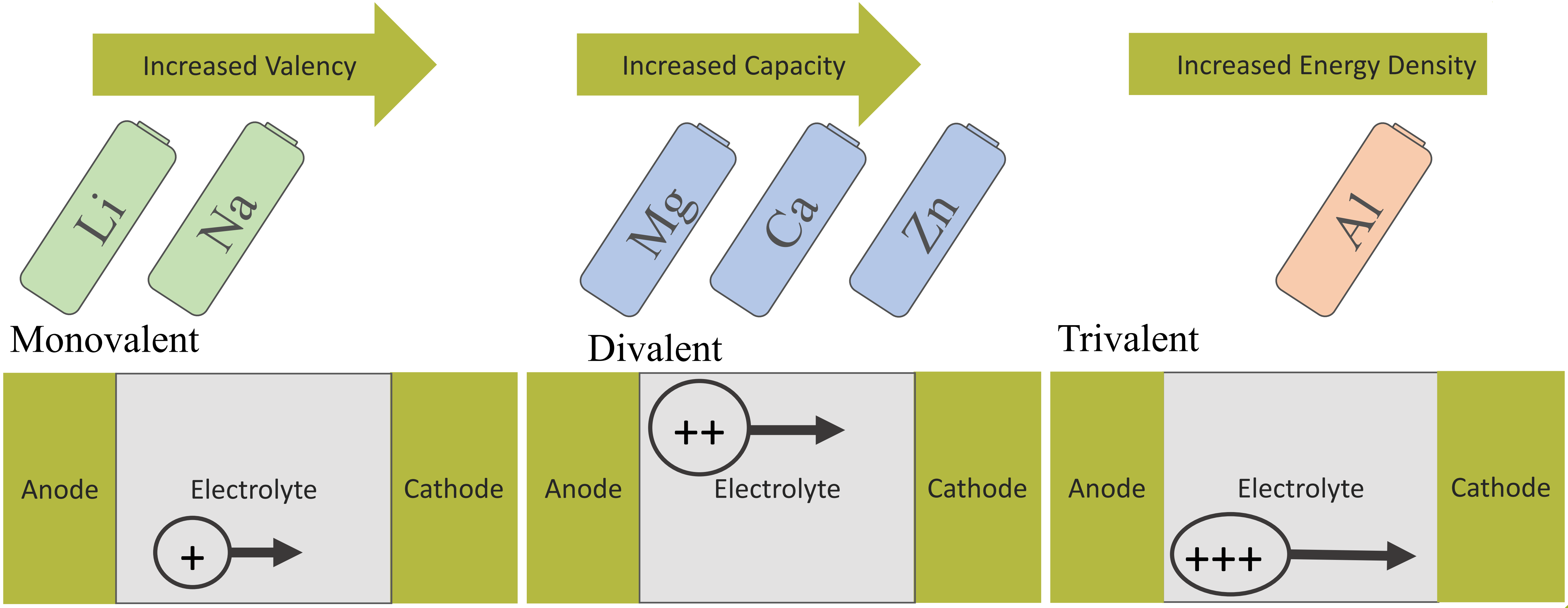


An alternative – when portability is not a concern

- Multivalent Ion Batteries
  - Reduced cost
  - Low environmental impact
  - Improved safety

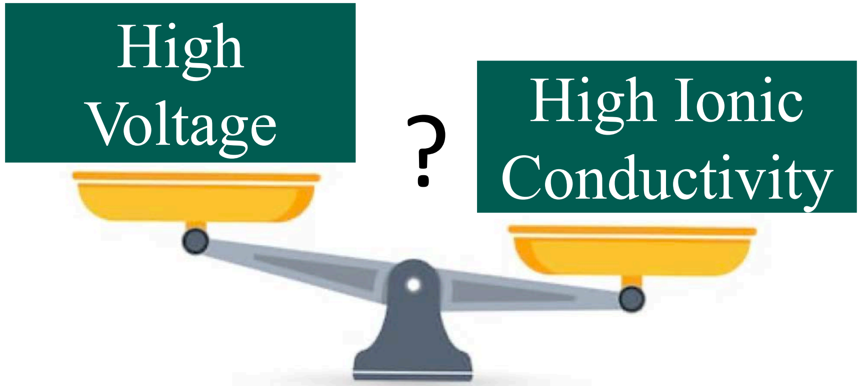


Are two better than one?



Major drawbacks of multivalent ion batteries

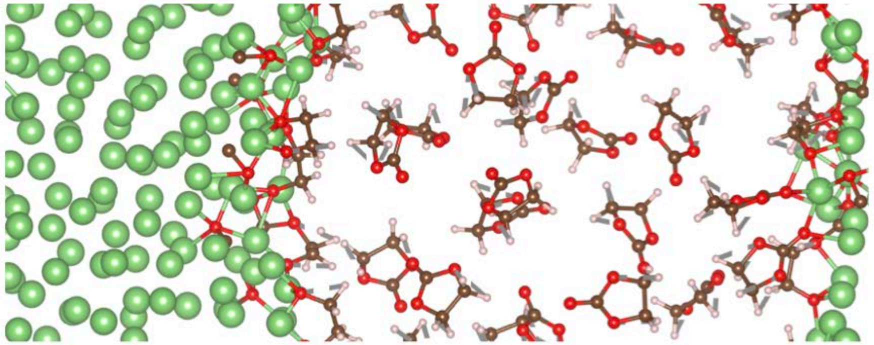
- Primarily limited by the cathode
- Desired cathode qualities:
  - High energy density
  - Cyclability
  - Good diffusion kinetics
- Lack of information regarding the impact of valency on electrolyte and SEI

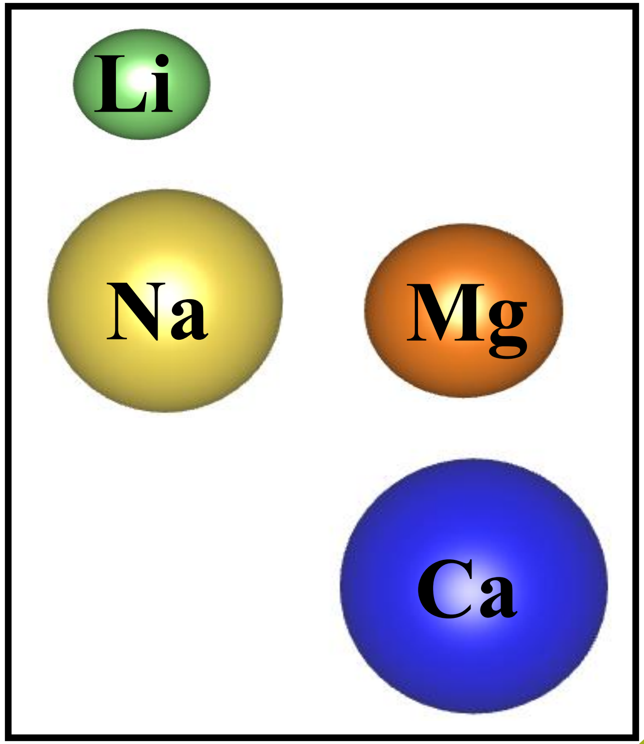


Impact of valency on:

SEI ?

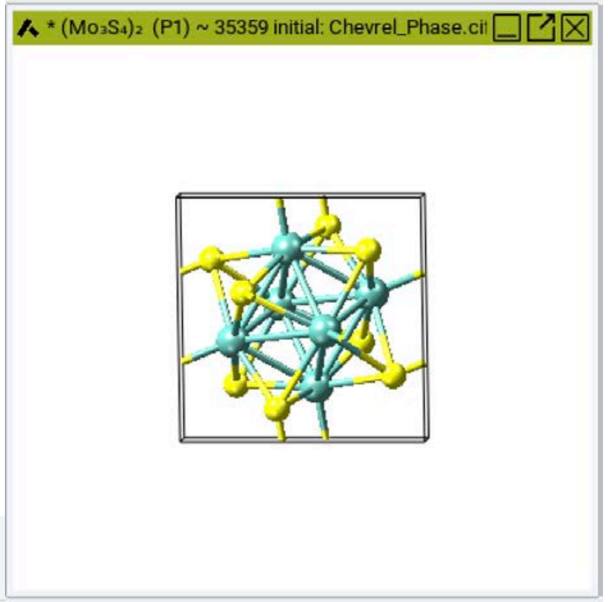
Electrolyte Decomp?

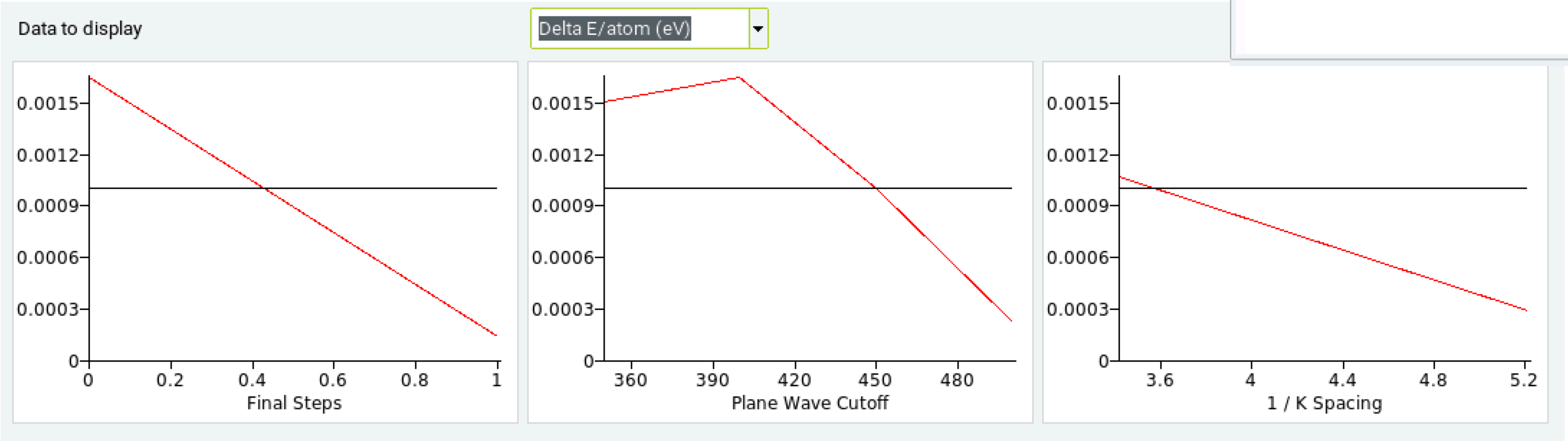




The building block of a DFT study: Automated Convergence to obtain accurate energy values

- Test for a range of energy cutoff and k-mesh values
- Convergence: 450 eV and 5x5x5 k-mesh
- Matches well with previous non-automated computational studies[1]

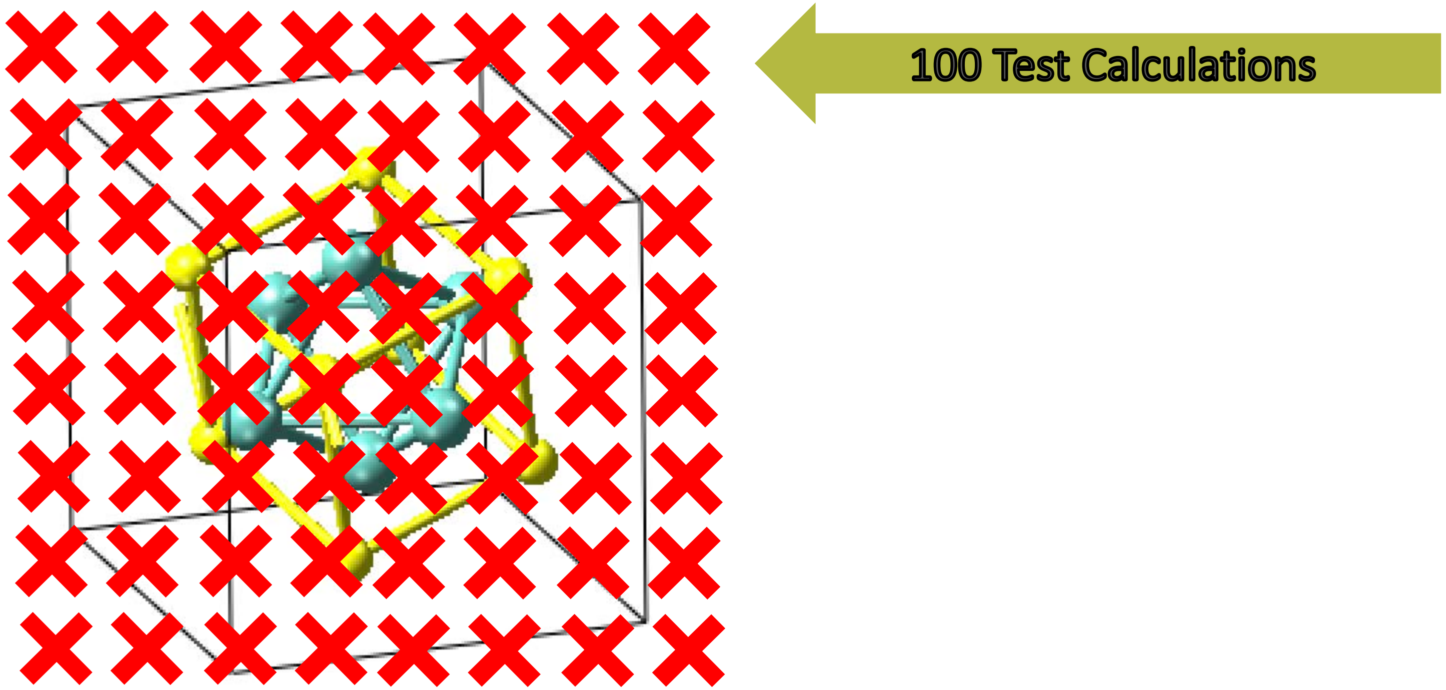




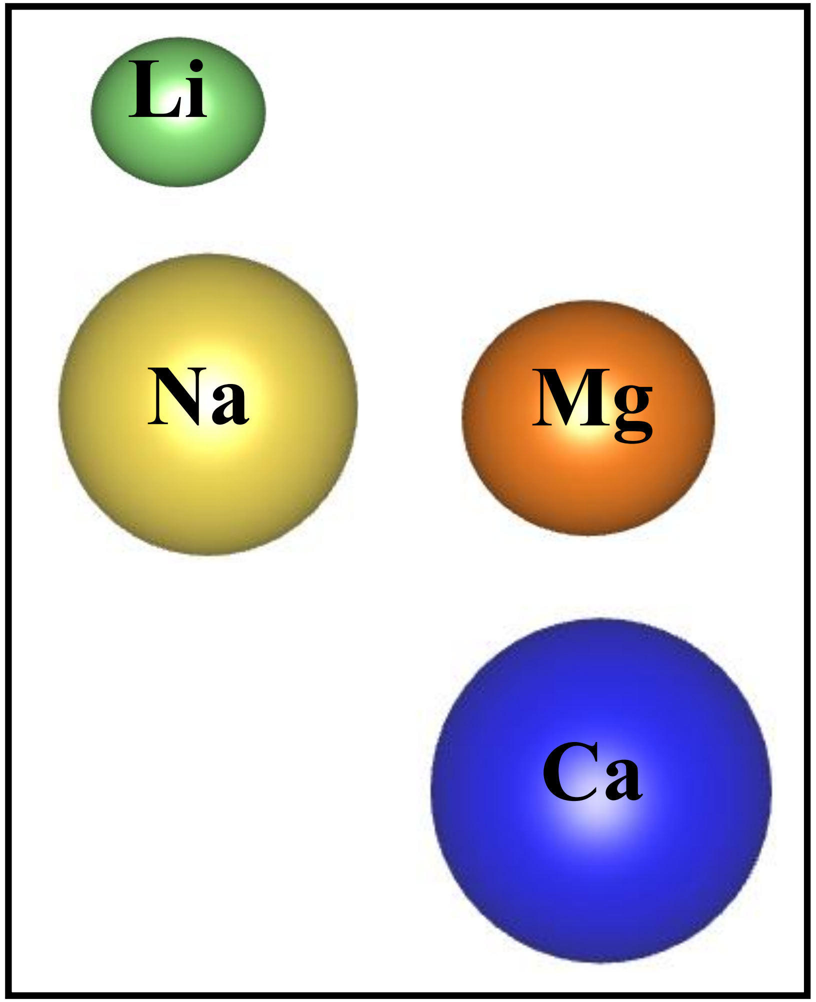
[1] *Phys.Chem.Chem.Phys.*,2017,19,20684-20690 I 20685

Intercalation site identification is a common problem with MVIBs

- Intercalation ion size differences lead to different intercalation sites
- Instead of waiting on costly NMR we can use modeling to identify sites

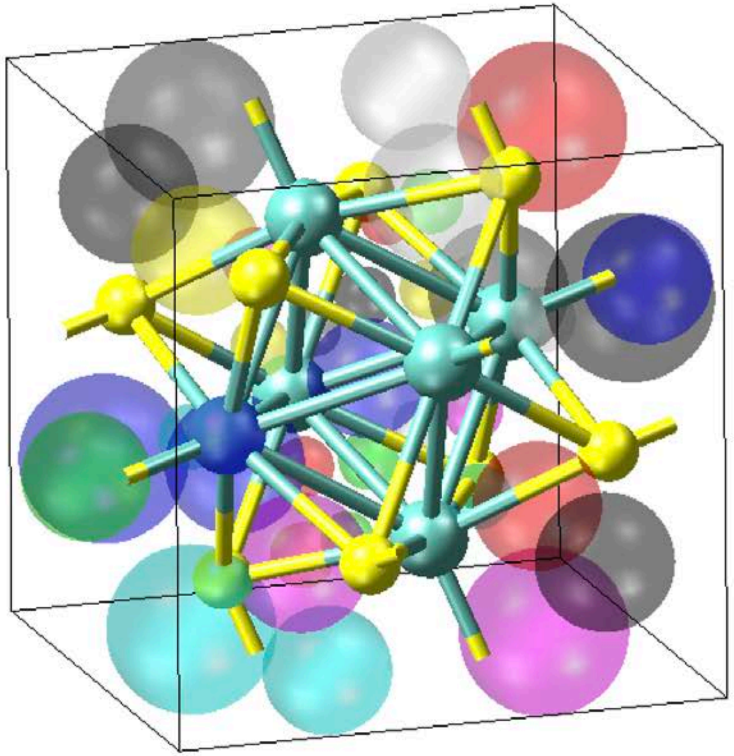


Mo_6S_8: Mo (teal), S (yellow)



Automated intercalation site testing: Empty space finder

* $(Mo_3S_4)_2$ (P1) ~ 35358 minimized: CP_Spiedie

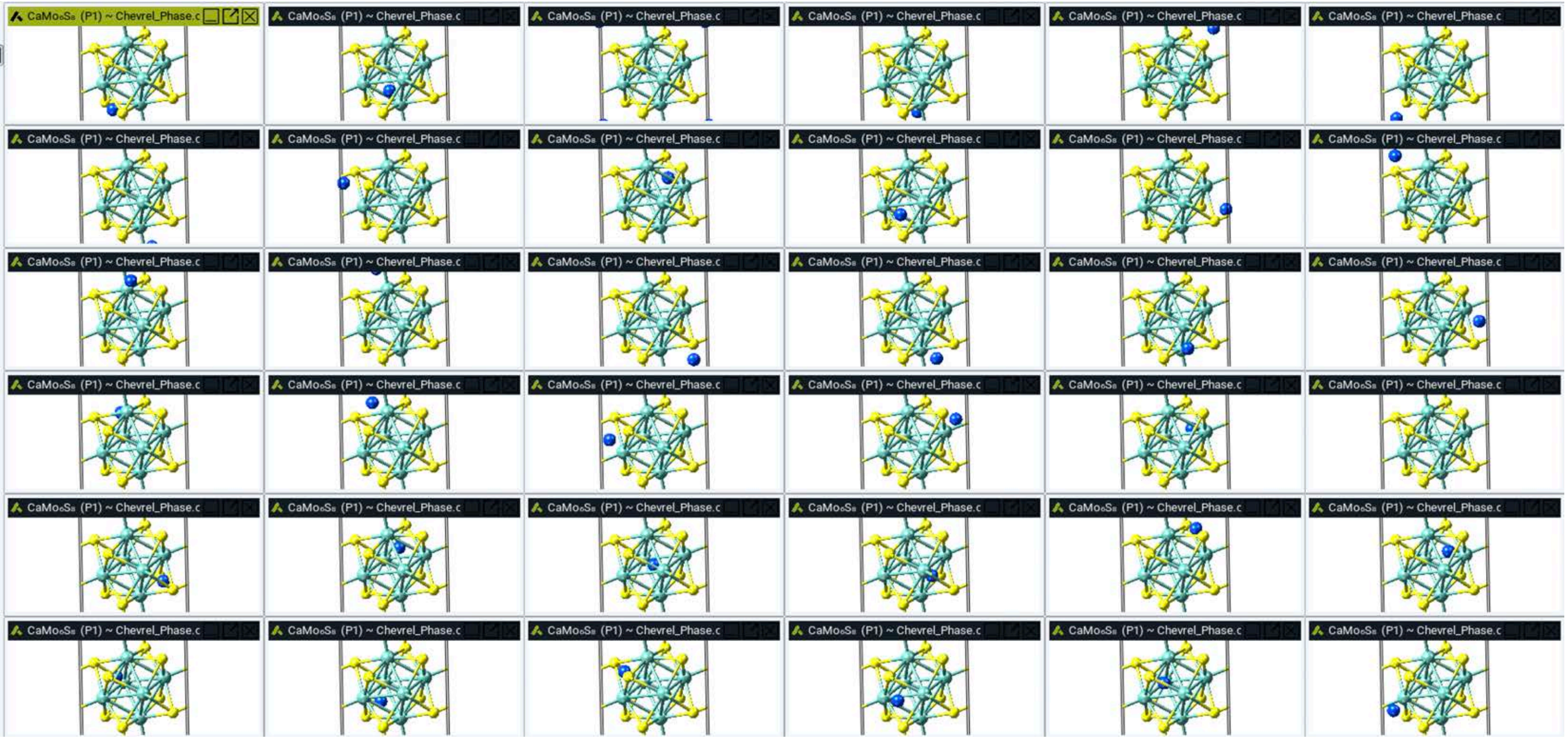


Id	Radius	Site	Coordination	X	Y	Z
4	0.345	1a	3	0.3984	0.5477	0.6625
5	0.376	1a	2	0.3444	0.3813	0.7749
6	0.376	1a	2	0.2250	0.6556	0.6185
7	0.292	1a	3	0.3675	0.3676	0.3676
8	0.345	1a	3	0.3375	0.6017	0.4522
9	0.292	1a	3	0.6325	0.6324	0.6324
10	0.308	1a	2	0.7042	0.8433	0.5229
11	0.345	1a	3	0.6625	0.3983	0.5478
12	0.683	1a	6	0.5000	0.5000	0.4999
13	0.345	1a	3	0.5477	0.6625	0.3983
14	0.376	1a	2	0.7750	0.3444	0.3815
15	0.345	1a	3	0.6016	0.4523	0.3375
16	0.376	1a	2	0.6556	0.6186	0.2251
17	0.973	1a	1	0.8867	0.7084	0.1362
18	0.801	1a	1	0.0731	0.5124	0.1288
19	0.974	1a	1	0.2917	0.8640	0.1130
20	0.376	1a	2	0.3815	0.7750	0.3444
21	0.801	1a	1	0.9269	0.4876	0.8712
22	0.376	1a	2	0.6185	0.2250	0.6556
23	0.974	1a	1	0.7083	0.1360	0.8870
24	0.972	1a	1	0.8637	0.1134	0.2919
25	0.742	1a	2	0.3357	0.9744	0.3729
26	0.800	1a	1	0.4879	0.8710	0.9268
27	0.972	1a	1	0.1363	0.8866	0.7081
28	0.742	1a	2	0.9743	0.3729	0.3357
29	0.743	1a	2	0.3730	0.3354	0.9744
30	0.743	1a	2	0.6270	0.6646	0.0256
31	0.742	1a	2	0.0257	0.6271	0.6643
32	0.742	1a	2	0.6643	0.0256	0.6271
33	0.801	1a	1	0.1288	0.0730	0.5123
34	0.801	1a	1	0.8712	0.9270	0.4877
35	0.800	1a	1	0.5121	0.1290	0.0732

Minimum radius: 0.2 Maximum radius: 1 Recalculate

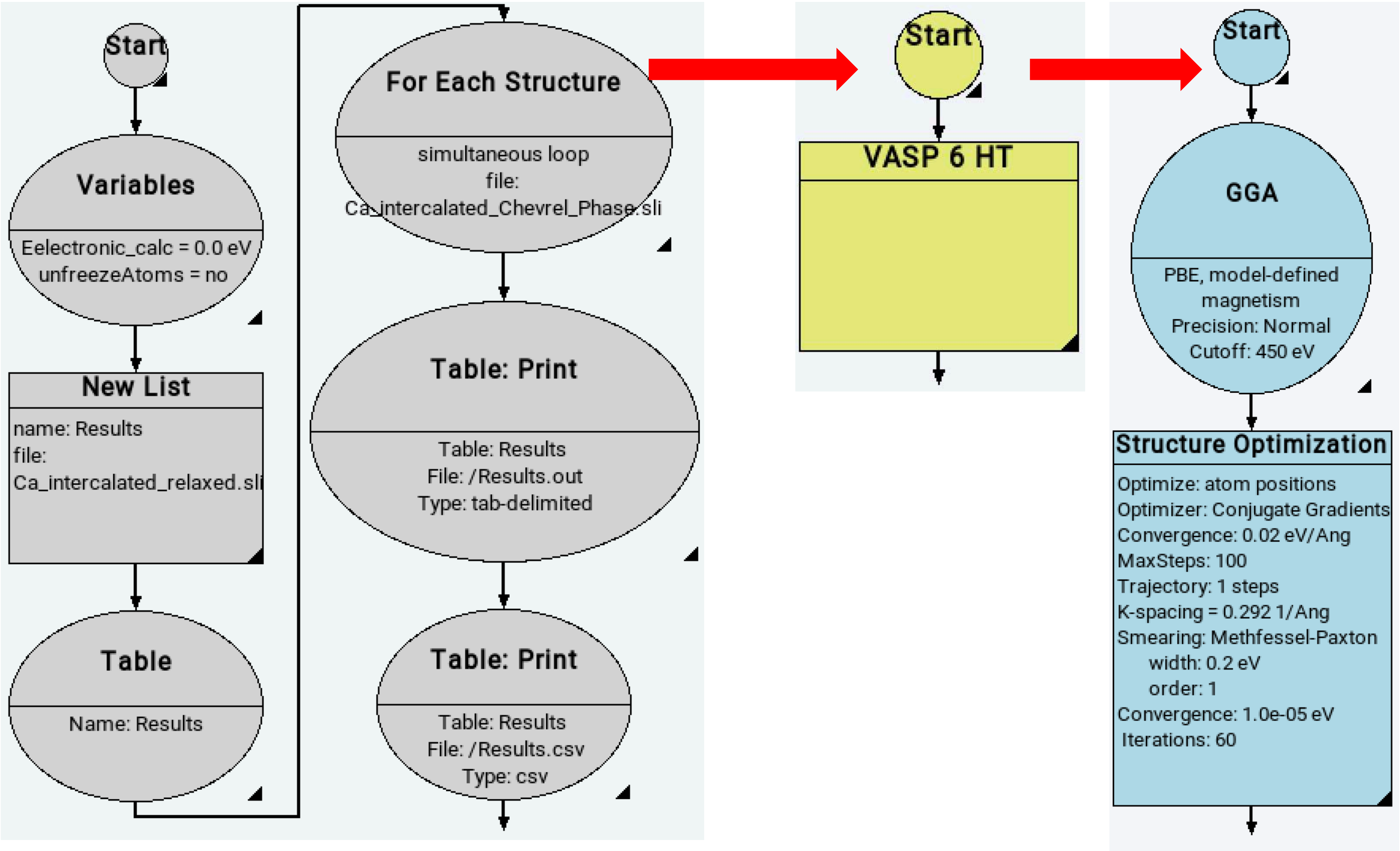
- Reduce number of calculations from 100 to 35

Automated intercalation site testing: Move a Ca to each of the 35 possible intercalation sites



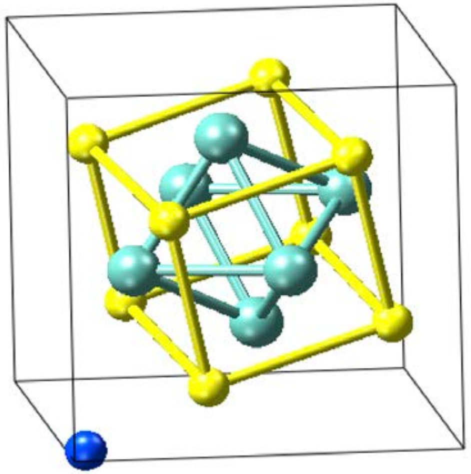
- Start with placing a Ca atom at a random position withing the empty CP and moving it to each void
- Structure list containing 36 structures is created

Automated intercalation site testing: *MedeA VASP* high-throughput calculations



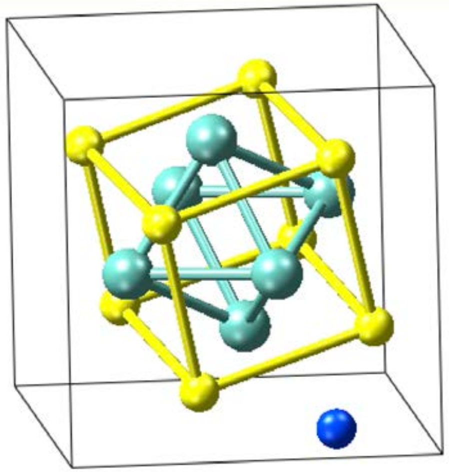
- You do not need know how to code to achieve fully automated complex multi-step calculations
- Pseudo coding is enough, and is conveniently guided by visualization tools

Automated intercalation site testing: sites identified

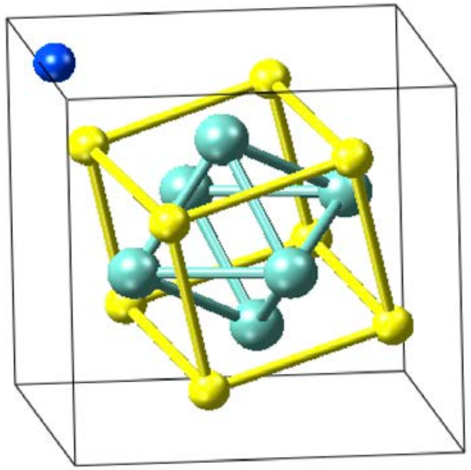


Cavity 1

Metal	Cavities
Li	1, 2
Mg	1,2,3
Ca	1,3
Al	1,2,3



Cavity 2



Cavity 3

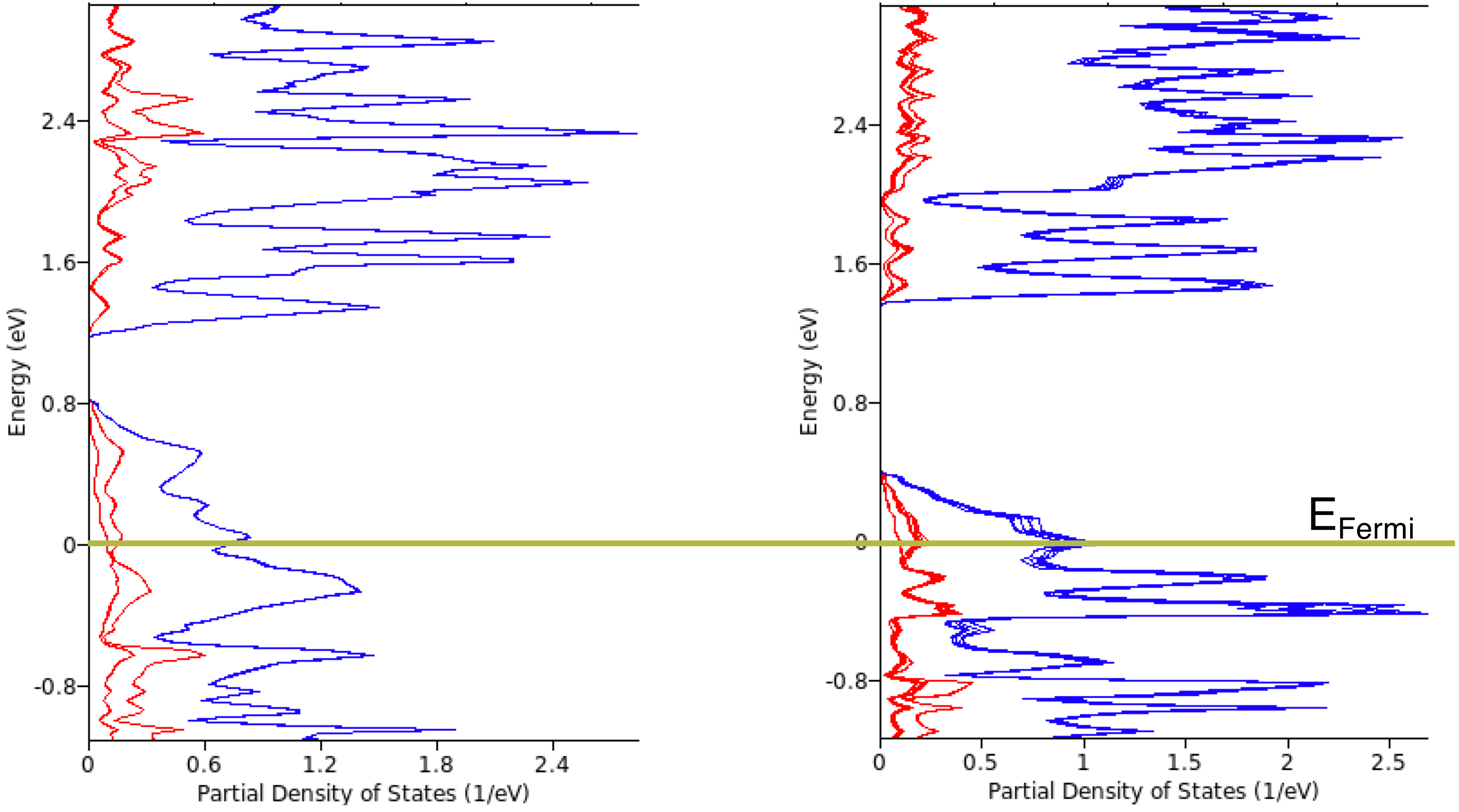
Mg (blue), S (yellow), Mo (teal)

[1] *Journal of Power Sources*, Volume 306, 29 February 2016, Pages 431-436

[2] *ACS Appl. Energy Mater.* 2018, 1, 2, 440–446

[3] Phys.*Chem.Chem.Phys.*,2017,19,20684-20690 l 20685

Electronic structure – without external visualization codes – DOS



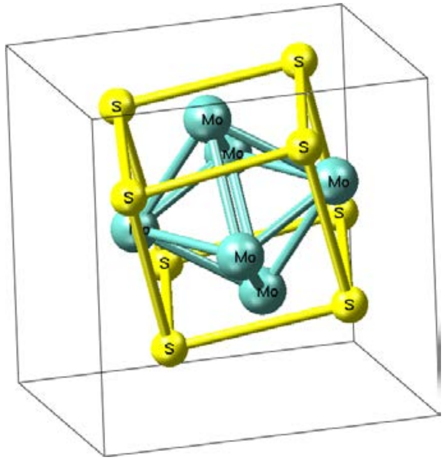
Mo 4d (blue), S 3p (red)

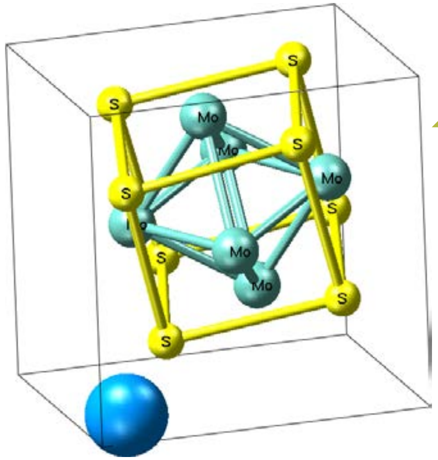
- Finer k-mesh and type of smearing are automatically tailored to the DOS calculation
- Mo_6S_8 and $CaMo_6S_8$ are both metals
- Mo 4d-orbitals are hybridized with S 3p–orbitals near the Fermi level
- $CaMo_6S_8$ has higher conductivity
- Matches well with previous non-automated computational studies[1]

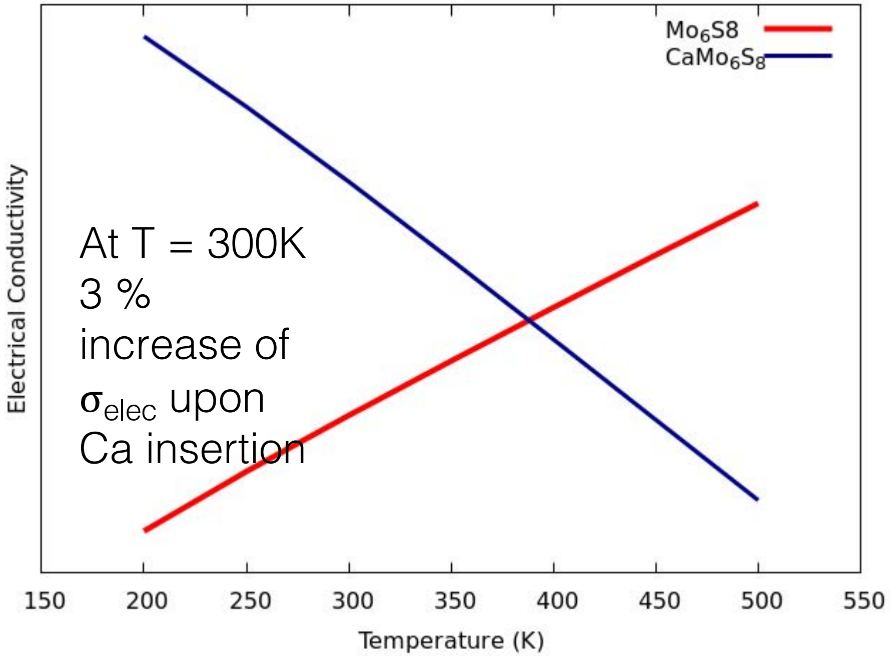
[1] *Phys.Chem.Chem.Phys.*,2017,19,20684-20690 I 20685

Calculated Electrical Conductivity (σ_{elec})

Band Structure → Electron Velocity and Effective Mass → Electronic Conductivity







- MedeA® Electronics
- Prediction of trends
- σ_{elec} of Mo_6S_8 increases with temperature whereas decreases in case of $CaMo_6S_8$
- At 300 K Ca insertion into Mo_6S_8 causes an increase of σ_{elec}
- In agreement with DOS, and gives a more in depth and temperture dependent analysis

Charge Analysis: Spatial distributions of electrons around each atom

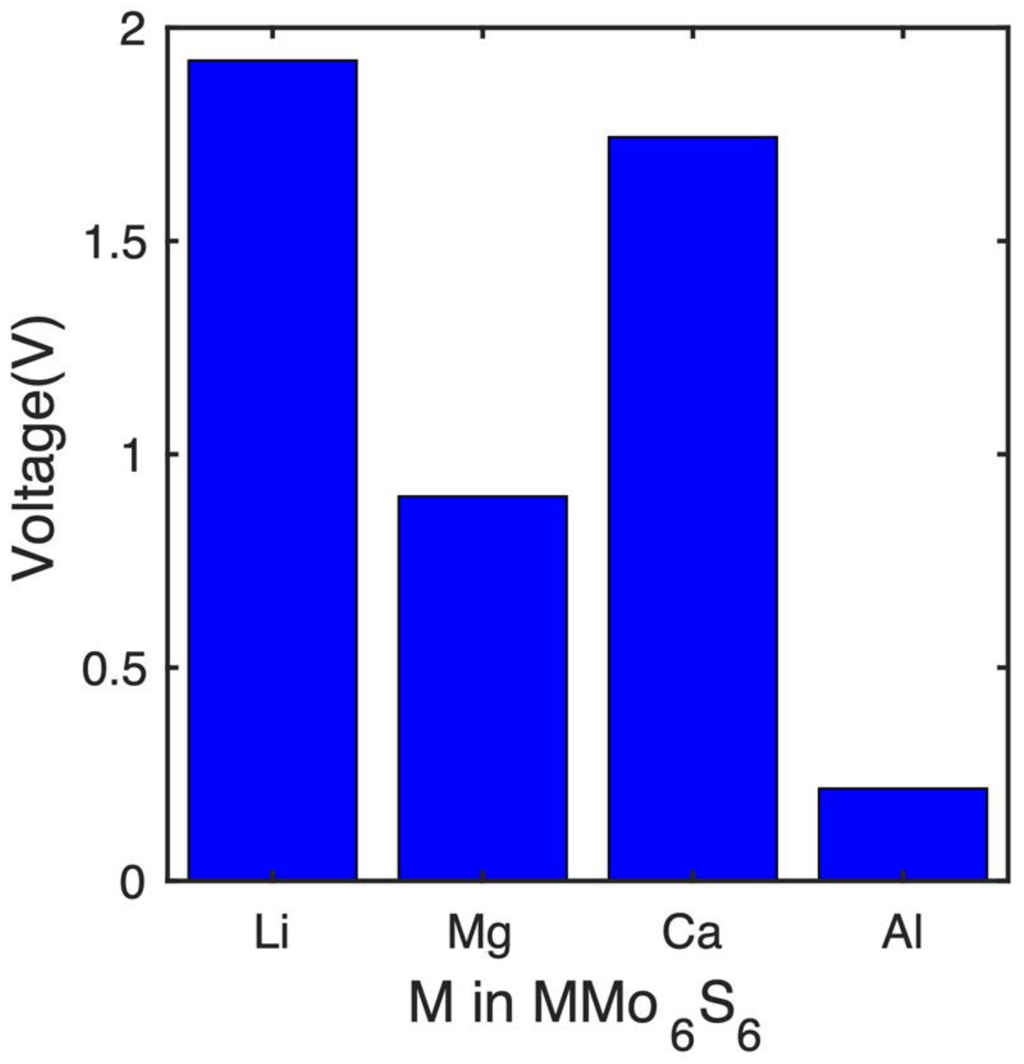
Atom	Mo6S8 Charge Difference (e)	CaMo6S8 Charge Difference (e)
Ca	-	1.49
Mo	0.99	0.93-0.95
S Type 1	-0.77	-0.85 - -0.94
S Type 2	-0.67	-0.87- -0.88

- MedeA® VASP Bader Charge Analysis
- Two types of S atoms
- The majority of the charge redistribution occurs on S atoms
- Matches well with previous non-automated computational studies[1]

[1] *Phys.Chem.Chem.Phys.*,2017, 19,20684-20690 I 20685

Average voltage for a MMo_6S_8 unit cell

- Ca is significantly higher than Mg
- Matches well with previous non-automated computational studies[1] and several experimental studies
- <1% volume change upon intercalation

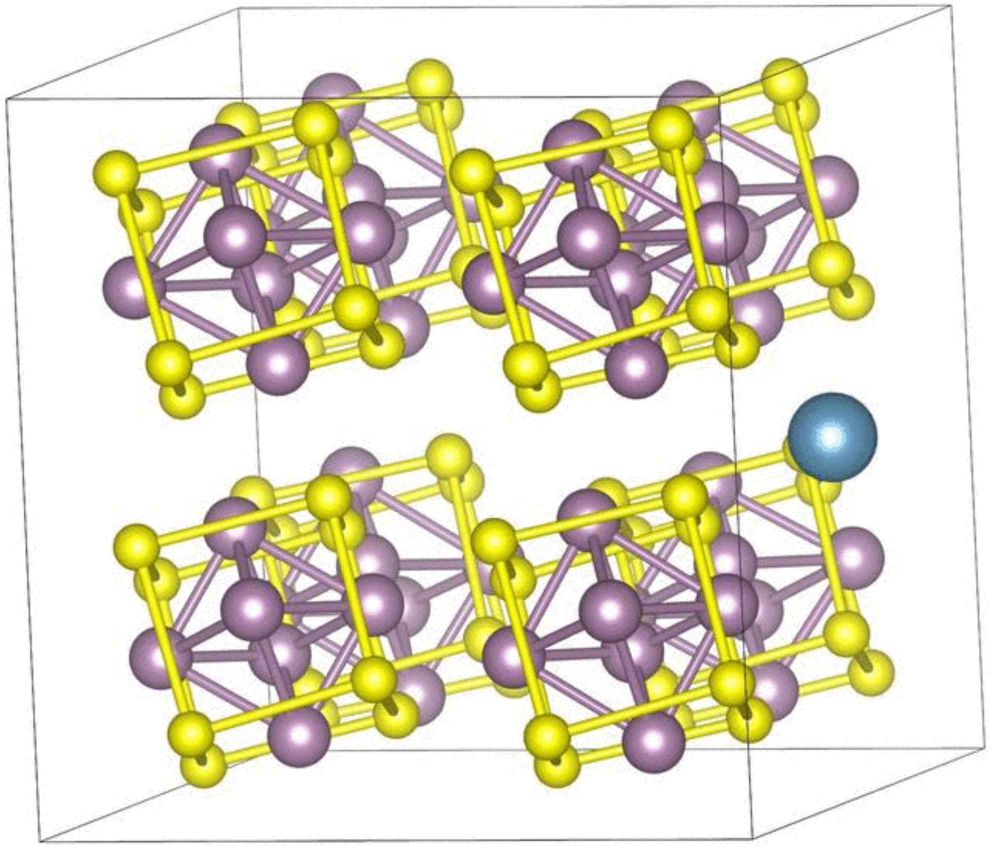


[1] *Phys.Chem.Chem.Phys.*,2017,19,20684-20690 I 20685

Diffusion kinetics – especially important with bulky MVIBs

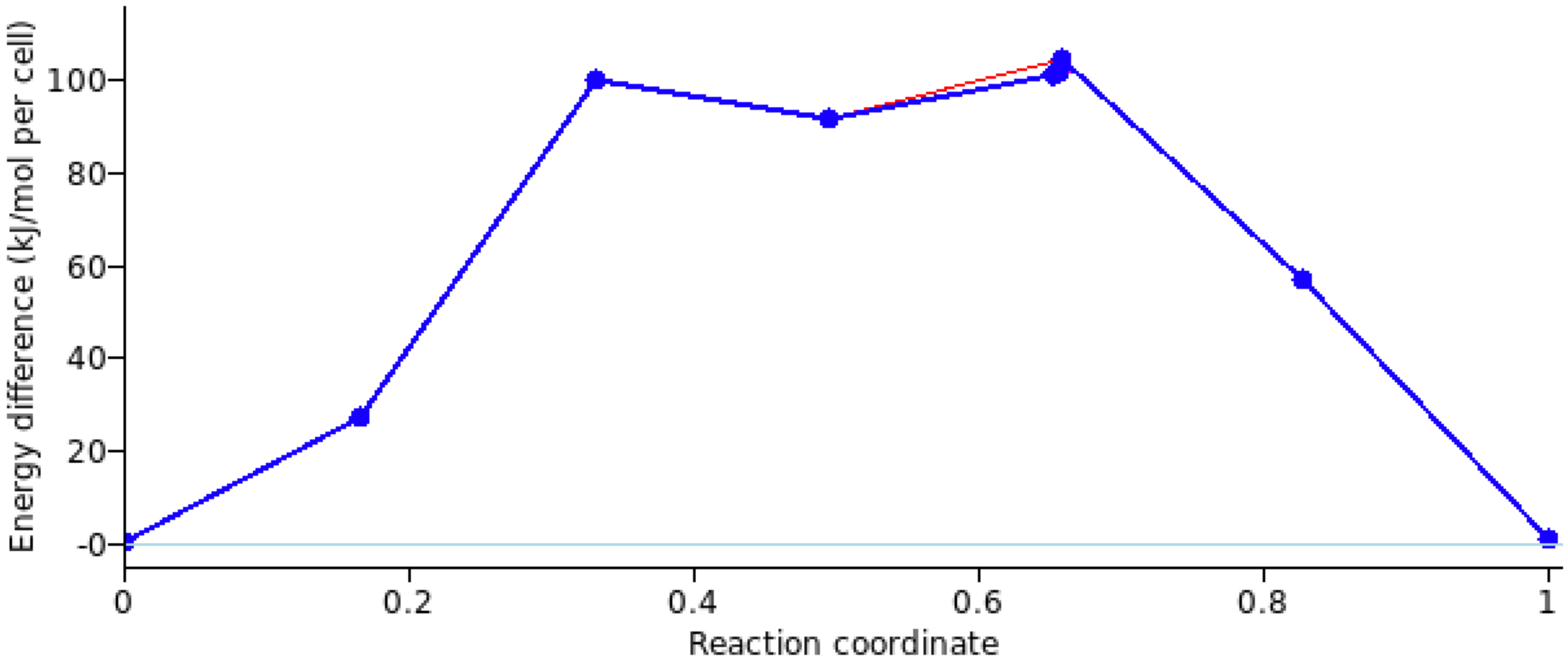
- Cations experience an energy barrier as they transition from one intercalation site to the next

- MedeA® Transition State Search
  - Map reaction path and find transition states
  - Transition states in random directions
  - View images
  - Make movies



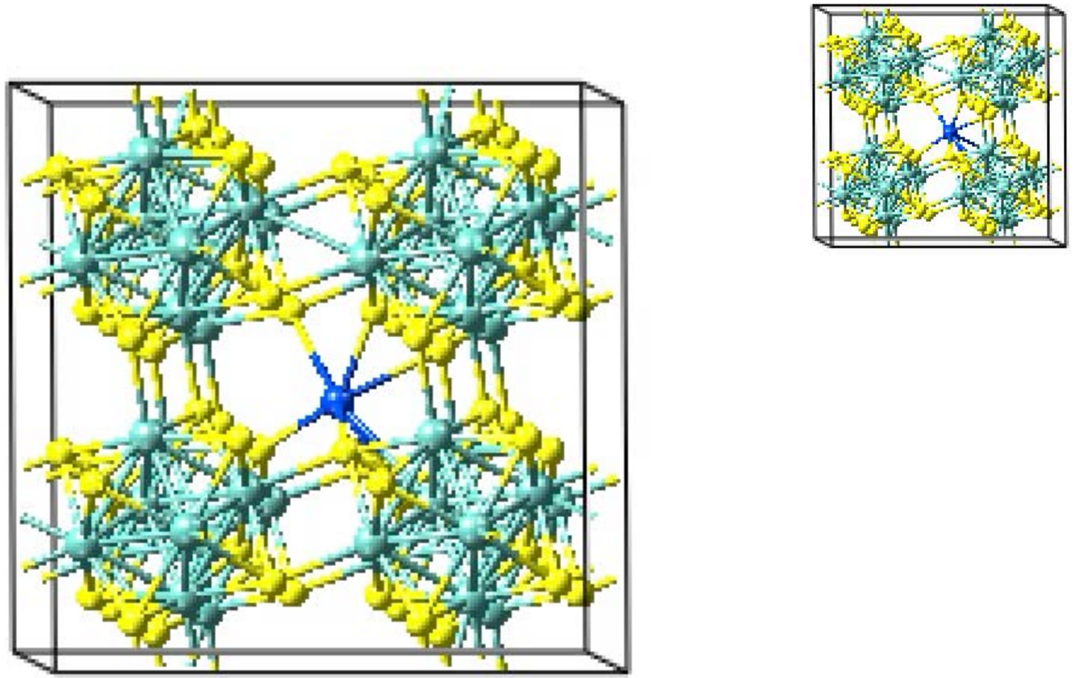
Energy barrier for Ca diffusion through a Mo_6S_8 supercell

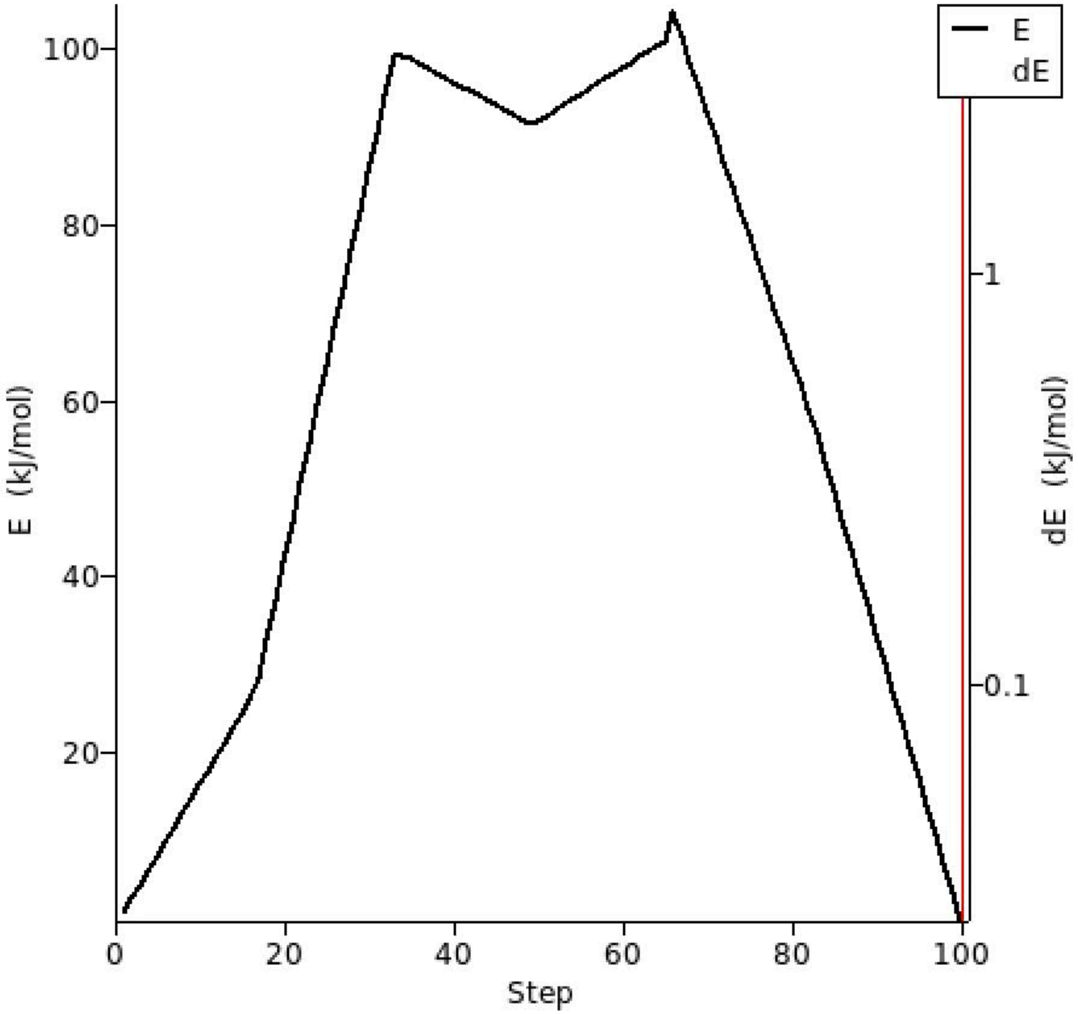
- 1 eV energy barrier
- Matches well with previous computational studies[1]



[1] *Journal of Power Sources*, Volume 306, 29 February 2016, Pages 431-436

Energy barrier for Ca diffusion through a Mo_6S_8 supercell





Conclusion

The demand for next- generation batteries is at an all time high

We can design battery materials that cater to desired electrochemical properties

Ca-ion batteries are a phenomenal contribution to next-generation batteries

MedeA is a comprehensive tool for investigations of next-generation batteries

materials design®

Acknowledgements


Jason Aubry
Development Engineer


Boris Belin
Research Scientist in Contract Research & Development


Laetitia Cheguillaume
Director of European Operations


Mikael Christensen
Research Scientist


Anna McNair
Financial Manager


Benoit Minisini
Pre-Sales Application Scientist


Steve Mumby
Chief Business Development and Commercial Officer


David Reith
Application & Research Scientist


Naida Lacevic
Director of Academic Engagement


Benoit LeBlanc
Software Architect


Alexander Mavromaras
Commercial Director, EMEA


Jessica Coll
EMEA Academic Account Manager


Brian Dron
Commercial Director, Europe


Volker Eyert
Senior Scientist


Laura Foster
Financial Assistant in Finance & Operations


Dave Rigby
Senior Scientist


Ken Roberts
Head of Marketing Operations


Xavier Rozanska
Research Scientist


Ray Shan
Director of Support


Walter Wolf
Senior Scientist


Marianna Yiannourakou
Director of Product Management


Clive Freeman
President & CEO


Clint Geller
Senior Advisor Scientist in Contract Research & Development


Jörg-Rüdiger Hill
Senior Software Engineer in Contract Research & Development


Katherine Hollingsworth
Marketing & Communications Manager


Reynald Takchi
Financial Assistant


Siwen Wang
Support & Application Scientist


Erich Wimmer
Chief Scientific Officer & Chairman of the Board


Rene Windiks
Senior Scientist, Battery Specialist

Key properties for batteries, that can be attained from atomistic modeling…

Materials Fabrication

•Free energies and phase diagrams: miscibility vs separation
•Elasticity: ductility, brittleness, hardness
•Permittivity Dielectric constants
•Piezoelectricity
•Diffusivity
•Thermal expansion
•Heat capacity
•Electronic structures

Cycling Behavior, Fast Charging

• Ion conductivity
• Electrical conductivity
• Thermal conductivity
• Electrochemical stability vs degradation • Phase transformation
• Volume change of particles

Interfaces of Electrodes, Electrolytes, Coatings, Binders, etc.

• Interphase morphology • Interfacial contact
• Current density
• Overpotentials
• Inter-diffusion & segregation
• Interfacial stabilities/delamination • Potential profiles

Diagnostics & Analysis

• XPS (core level shifts)
• NMR (chemical shifts, field gradients, paramagnetic shifts)
• Powder diffraction patterns • IR & Raman Spectra
• UV-Vis Spectra

Online Training and Demo

Li-Ion Batteries and Beyond: Driving Next-Generation Energy Storage with *MedeA*

Next Tuesday, January 26, 2021

USA/EUROPE:

10:00 am PST/1:00 pm EST

7:00 pm CEST

Register for the training:

https://www.materialsdesign.com/webinar-register/li-ion-batteries-medea-jan-2021

*Training open to everyone

Upcoming Webinar

Machine Learning Meets Quantum Chemistry: Using Theory, Data, and Experiments to Design Catalysts

Presented by Dr. Siwen Wang

February 2nd 3rd, 4th

Register www.materialsdesign.com/webinars

Li-Ion Batteries and Beyond

- ***MedeA* modules mentioned in today's webinar**
  - https://www.materialsdesign.com/compute-engines
  - https://www.materialsdesign.com/analysis-tools

  - *MedeA Environment*
  - *MedeA VASP*
  - *MedeA HT*
  - *MedeA UNCLE*
  - *MedeA Electronics*
  - *MedeA Transition State Search (TSS)*

- **Webinar: Live and Recorded**
  - https://www.materialsdesign.com/webinars
- **Publications**
  - https://www.materialsdesign.com/Publications
- **Application Notes**
  - https://www.materialsdesign.com/application-notes
- **For questions or comments contact**
  - Katherine Hollingsworth
    - khollingsworth@materialsdesign.com

Question and Answer Session

Dr. René Windiks

Materials Design

Dr. Taylor Juran

Materials Design

Questions about Materials Design Webinars

Katherine Hollingsworth

khollingsworth@materialsdesign.com

materials design

info@materialsdesign.com

www.materialsdesign.com

MedeA

Innovation by Simulation