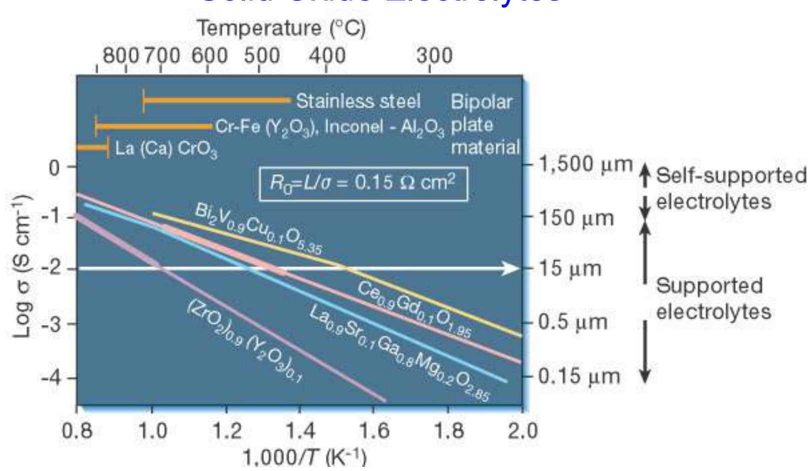
L11: Model Building-
Design of a Robust Solid Oxide Electrolyte

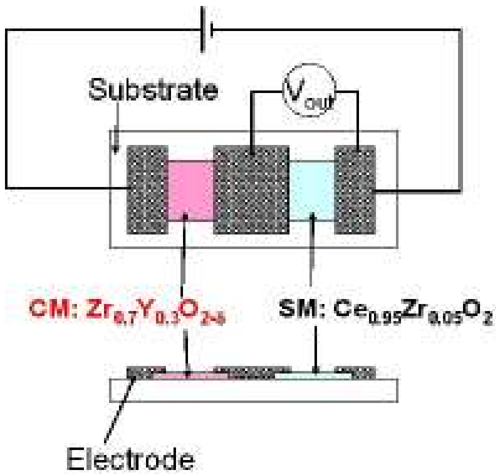
- Solid Oxide Electrolytes
- Oxygen Sensors
- Fuel Cells
- Competing Design Criteria- Temperature vs Lifetime
- Electric Fields and Diffusion
- Mechanical structure, stress and strain
- Electrodes and Interfaces
- The Materials Game, Applications of Multiscale Modeling

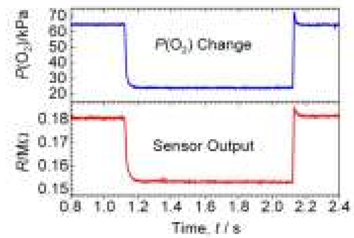
Solid Oxide Electrolytes

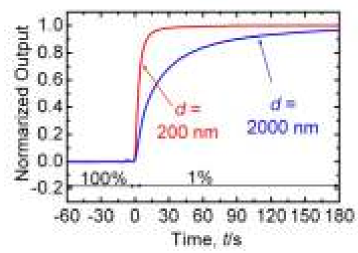


The target value for the area specific resistivity (ASR) of the electrolyte is set at 0.15 Ω-cm^2. Films of oxide electrolytes can be reliably produced using cheap, conventional ceramic fabrication routes at thicknesses down to approx15 µm. It follows that the specific conductivity of the electrolyte must exceed 10-2 S cm^{-1}. This is achieved at 500 °C for the electrolyte $Ce_{0.9}Gd_{0.1}O_{1.95}$, and at 700 °C for the electrolyte $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$. Although the electrolyte $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ exhibits higher conductivities, it is not stable in a reducing environment.

B. C. H. Steele, A. Heinzel, Nature 414, 345-352(2001)







For oxygen-sensor automotive applications, fast response and T insensitivity are needed. Thin-film resistive elements built from nanoparticle Zr-doped ceria with T-compensating YZO work better than conventional pressed powders.

unit.aist.go.jp/..

Left: Siemens 100kW Tubular Solid Oxide Power Plant

Right: Acumentrics' 5kW SOFCs anodes are made of nickel oxide and yttrium stabilized zirconia (YSZ). The tube is coated with and electrolyte layer made of yttrium stabilized zirconia. For the outer layer, a cathode of lanthanum manganite is applied.

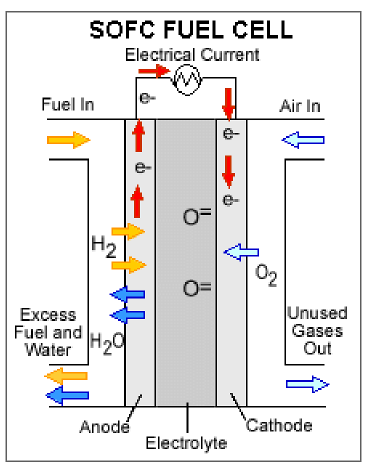
Want to put one in your car? 5kW = 6.7hp

Types of fuel cells

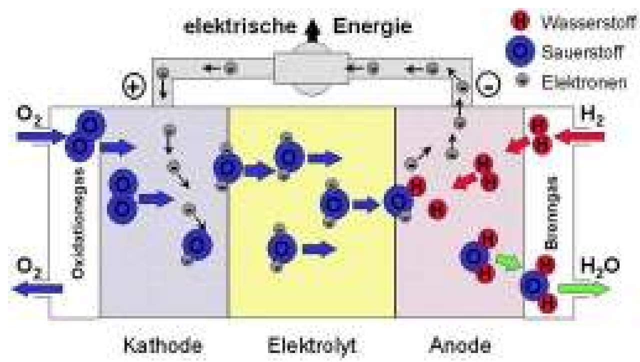
Solid Oxide Fuel Cell

Name	Electrolyte	Range	Working temp.	elec. eff.	Status
Reversible fuel cell					Learning kit
Blue energy	polyethylene membrane	Up to 250KW			Research
MFC - Biological fuel cell					
Zinc fuel cell ('Air' fuel cell)					
Redox fuel cell	Liquid electrolytes with redox shuttle and polymer membrane				Research
AFC - Alkaline fuel cell	alkaline solution	10 to 100 kW	under 80°C	Cell: 60–70% System: 62%	Commercial/Research
PEM FC - Proton exchange membrane fuel cell	polymer membrane (ionomer)	0,1 to 500 kW	70–200 °C,	Cell: 50–70 % System: 30–50 %	Commercial/Research
DBFC - Direct borohydride fuel cell	alkaline solution: NaOH		70 °C		Research
FAFC - Formic acid fuel cell	formic acid		90–120 °C		Research
DMFC - Direct methanol fuel cell	polymer membrane	mW to 100 kw	90–120 °C	Cell: 20–30 %	Commercial/Research
DEFC - Direct-ethanol fuel cell					Research
PAFC - Phosphoric-acid fuel cell	phosphoric acid	Up to 10 MW	200 °C	Cell: 55 % System: 40 %	Commercial/Research
MCFC - Molten carbonate fuel cell	molten alkaline-carbonate	100 MW	650 °C	Cell: 55 % System: 47 %	Commercial/Research
PCFC - Protonic ceramic fuel cell	ceramic		700 °C		Research
SOFC - Solid oxide fuel cell	oxide ceramic electrolyte	Up to 100 MW	800–1000 °C	Cell: 60–65 % System: 55–60 %	Commercial/Research

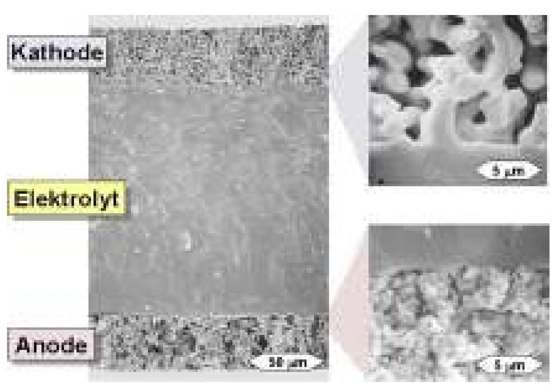
Basic ElectroChemistry of SOFC



Underlying Diffusion Processes



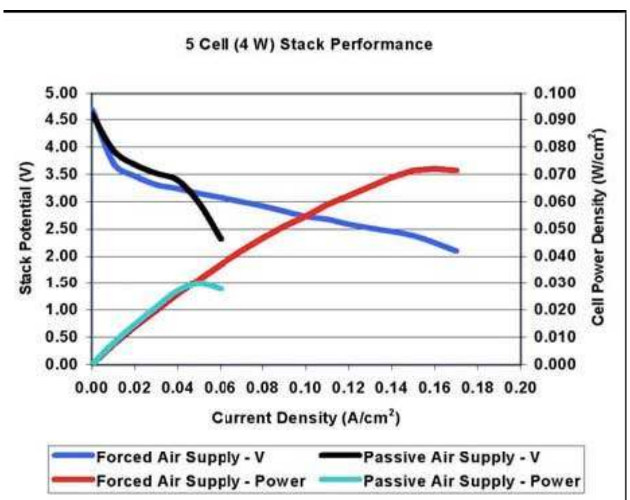
Micron Scale Microstructure



Oxide electrolyte is 150 micron thick, electron blocking; electrodes are screen printed, gas porous, electrically conductive.

Competing Design Criteria- Temperature vs Lifetime

- Anion diffusion rate/current is exponential in T, current operating range 800-1000 C
- Anion resistivity ~thickness, current values of ~150 μm limited by mechanical strength, crack formation, pinholes,...
- Fabricating electrolyte from nanoparticles ~10-50nm is 'obvious' solution to improve surface diffusion flux. But, high T will lead to rapid coarsening and particle fusion.
- T- cycling during startup/shutdown induce interface stresses due to differential thermal expansion, leading to debonding of interfaces and cracking
- Thermochemical migration from electrodes into electrolyte and *vice versa* impact performance
- Operating lifetimes $t_L > 10^4$ hr needed for commericial applications; military and space applications have other timescales.
- Low output voltage per cell ~1V, leads to multiple serial piles: if one cell fails the stack fails, weight and bulk problems, interconnect, gas flow, and heat transport problems



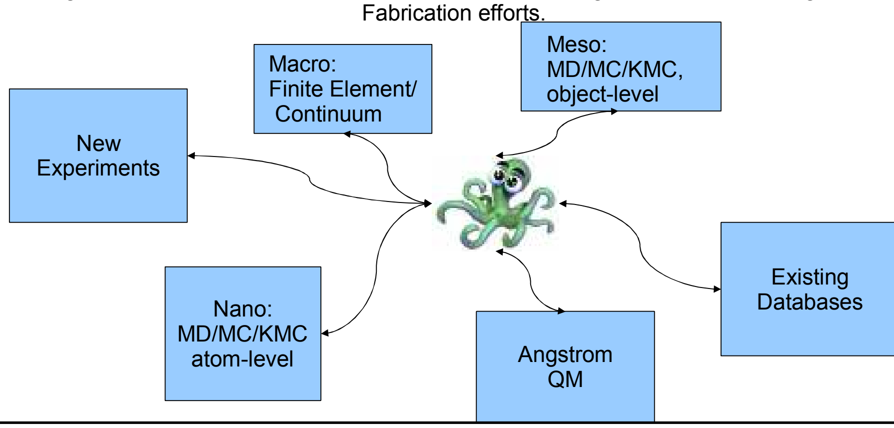
Performance of 4 Watt- 5 Cell PEM Educational Stack. Note power density!

www.tekstak.com/

General Principles of Multiscale Modeling

See MRS Bulletin, Vol 31, Dec 2006 dedicated to 'Materials Informatics' and in particular:
"Data-Mining-Driven Quantum Mechanics for the Prediction of Structure,
G. Ceder *et al.* , MRS Bull. **31**, 981 (2006)

How to iteratively link experimental data with modeling and simulation at several different length- and time-scales? A current world-wide effort and goal in Materials Design and Fabrication efforts.



One Part of the Multiscale (
Process:

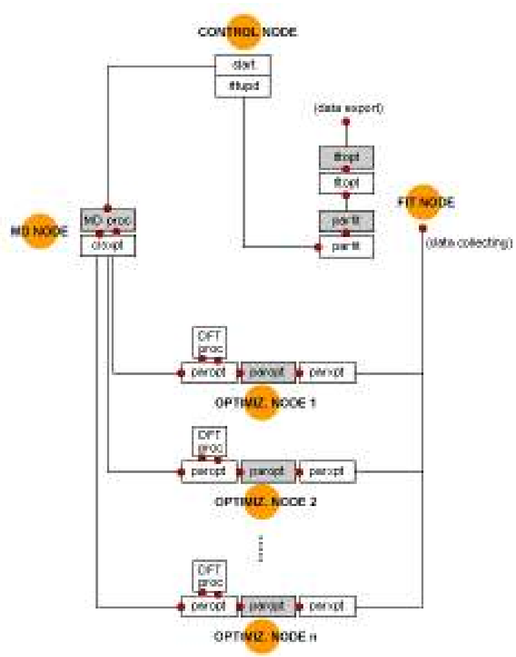
Control Node is asked to develop a potential U({**R**}), so initiates a series of MD processes.

MD spawns a series of QM processes, for selected {**R**}.

Each QM process finds electronic structure, energy and forces {**F**} which are fed to an Optimizer node.

Each Optimizer combines available and incoming data to update the database and potential parameters.

Control Node decides when fitting goal has been attained, and messages the Master Node.

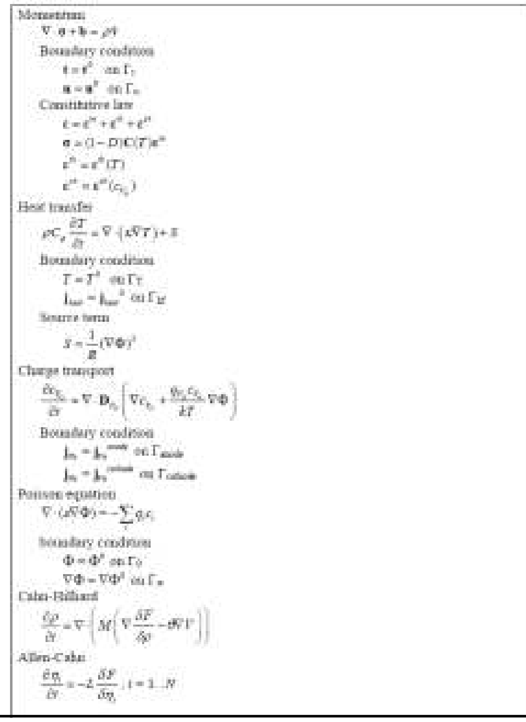


Getting down to brass tacks:

What equations have to be solved?

- Mechanical stress-strain
- Heat transfer
- Charge and Mass Transport
- Free-energy driven response to applied gas pressure, mechanical clamping, electric fields

Courtesy: J-H Kim



Momentum:

$$\nabla \cdot \sigma + \mathbf{b} = \rho \ddot{u}$$

Boundary condition

$$\mathbf{t} = \mathbf{t}^0 \quad \text{on } \Gamma_t$$
$$\mathbf{u} = \mathbf{u}^0 \quad \text{on } \Gamma_u$$

Constitutive law

$$\varepsilon = \varepsilon^{el} + \varepsilon^{th} + \varepsilon^{ch}$$
$$\sigma = (1 - D)\mathbf{C}(T)\varepsilon^{el}$$
$$\varepsilon^{th} = \varepsilon^{th}(T)$$
$$\varepsilon^{ch} = \varepsilon^{ch}(c_{Li})$$

Heat transfer

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + S$$

Boundary condition

$$T = T^0 \quad \text{on } \Gamma_T$$
$$\mathbf{j}_{heat} = \mathbf{j}_{heat}{}^0 \quad \text{on } \Gamma_H$$

Source term

$$S = \frac{1}{R}(\nabla \Phi)^2$$

Charge transport

$$\frac{\partial c_{Li}}{\partial t} = \nabla \cdot \mathbf{D}_{Li}\left(\nabla c_{Li} + \frac{q_{Li} c_{Li}}{kT}\nabla \Phi\right)$$

Boundary condition

$$\mathbf{j}_{Li} = \mathbf{j}_{Li}{}^{anode} \quad \text{on } \Gamma_{anode}$$
$$\mathbf{j}_{Li} = \mathbf{j}_{Li}{}^{cathode} \quad \text{on } \Gamma_{cathode}$$

Poisson equation

$$\nabla \cdot (\varepsilon \nabla \Phi) = -\sum_i q_i c_i$$

Boundary condition

$$\Phi = \Phi^0 \quad \text{on } \Gamma_\Phi$$
$$\nabla \Phi = \nabla \Phi^0 \quad \text{on } \Gamma_n$$

Cahn-Hilliard

$$\frac{\partial \varphi}{\partial t} = \nabla \cdot \left(M\left(\nabla \frac{\delta F}{\delta \varphi} - \theta \nabla \Gamma\right)\right)$$

Allen-Cahn

$$\frac{\partial \eta_i}{\partial t} = -L \frac{\delta F}{\delta \eta_i}, \; i = 1 \ldots N$$

General Equations of Diffusion

The particle flux ***j*** is driven by its concentration gradient, and the locally varying diffusion coefficient D.

$$\vec{j} = -D(\phi)\,\nabla\,\phi(\vec{r}, t)$$

The equation of continuity is satisfied if no particles are created/destroyed:

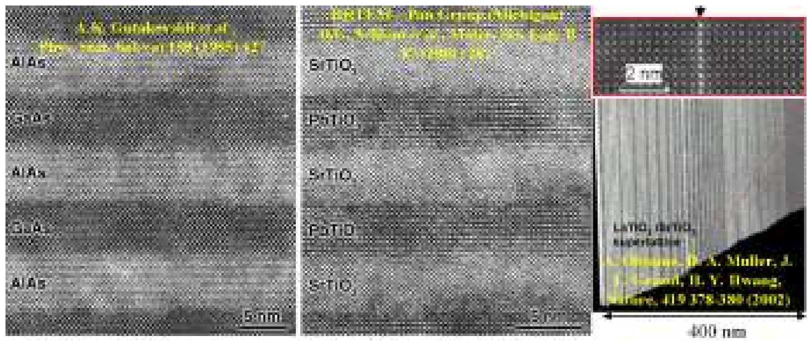
$$\frac{\partial \phi}{\partial t} + \nabla \cdot \vec{j} = 0$$

Finally giving the second order PDE:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \Big(D(\phi, \vec{r})\,\nabla \phi(\vec{r}, t)\Big),$$

D(φ,r) contains granularity, surface and volume rates, varying chemical composition

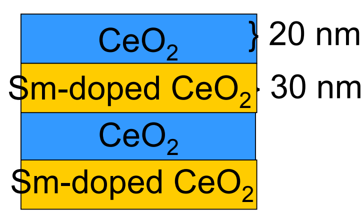
The Materials Game



Multilayer fabrication technology for oxides is approaching that developed for III-V semiconductors. As in the semiconductor industry, this is an essential step for realizing oxide-materials by design.

Application of Multiscale Modeling to Enhance Oxide Electrolyte Conductivity

- $(Sm/Ce)O_2$ Superlattices have been shown to exhibit enhanced Oxygen conductivity*.



- Goal: To study interface thermodynamics in this system to help understand the origin of this enhanced conductivity.

*I. Kosackia, T. Christopher, M. Rouleau, P. F. Becher, J. Bentley, D. H. Lowndes, Solid State Ionics 176, 1319 (2005) and I. Kosacki, C.M. Rouleau, P.F. Becher and D.H. Lowndes, in press.

General Approach

Ab initio calculations

Electrostatic Model

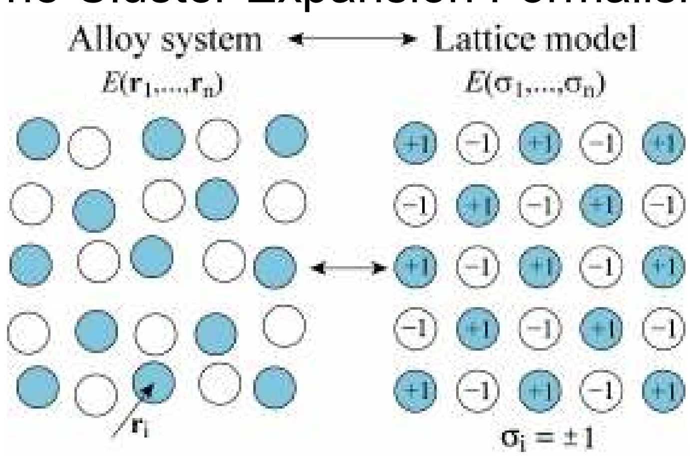
Lattice-gas Hamiltonian
(Cluster expansion – generalized to multicomponent & coupled-sublattice)

Lattice-gas Monte Carlo simulation
(Hybrid canonical/grandcanonical)

Equilibrium composition profile across interface

http://cms.northwestern.edu/atat

The Cluster Expansion Formalism



$$E(\sigma_1,\ldots,\sigma_n) = \sum_{\{i,j\}} J_{ij}\,\sigma_i\sigma_j + \sum_{\{i,j,k\}} J_{ijk}\,\sigma_i\sigma_j\sigma_k + \ldots$$

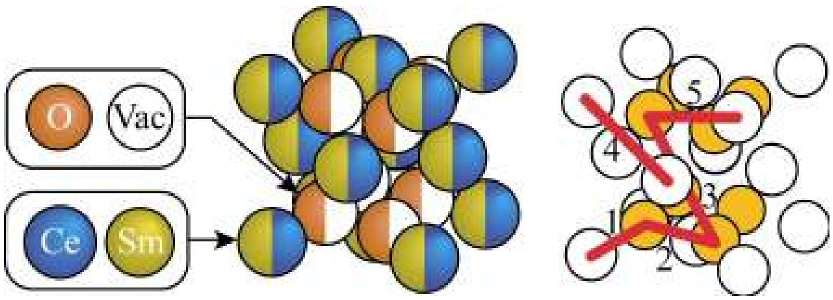
$$= \sum_{\alpha} J_\alpha\,\sigma_\alpha$$

Sanchez, Ducastelle and Gratias (1984)

Coupled Sublattices Multicomponent Cluster Expansion

Same basic form: $E(\sigma_1,\ldots,\sigma_n) = \sum_{\{i,j\}} J_{ij}\, \sigma_i\sigma_j + \sum_{\{i,j,k\}} J_{ijk}\, \sigma_i\sigma_j\sigma_k + \ldots$

Occupation variables: N_i *(0,1) on Lattice i=1,2*



Tepesch, Garbulski and Ceder (1995); Sanchez, Ducastelle and Gratias (1984)

Hybrid Canonical/Grandcanonical Monte Carlo

- To stabilize interface, two options:
  - keep some species completely fixed (cations)
  - keep composition of at least one specie fixed (Here the cation composition).
- For oxygen, two alternatives:
  - Oxygen is free to exchange with environment. (constant O chemical potential)
  - System remains "charge-balanced".

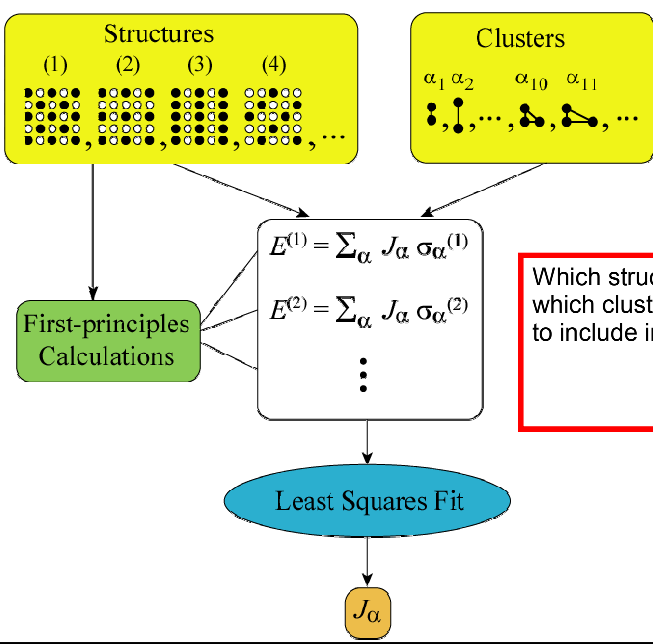
A General Approach

Implementation of the method is very general:

- Can impose any type of linear composition constraints (the code automatically finds the appropriate MC moves).
- Can handle any number of components on any number of sublattices for any spacegroup.

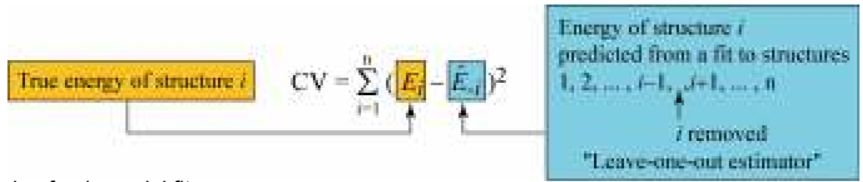
Available at http://cms.northwestern.edu/atat

Cluster expansion fit

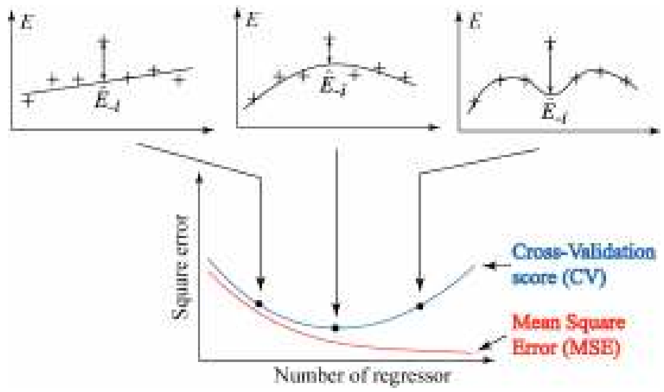


Which structures and which clusters to include in the fit?

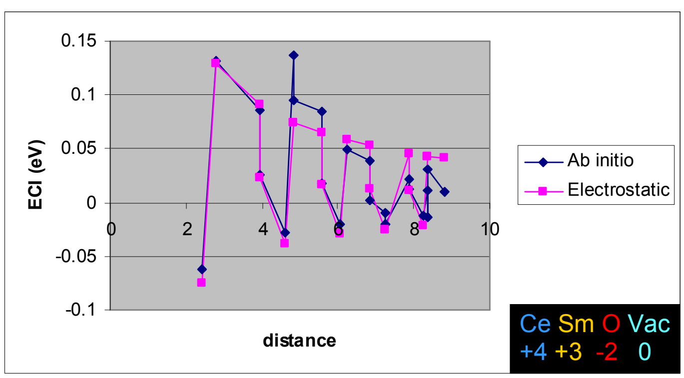
Cross-validation



Example of polynomial fit:



Effective Cluster Interactions



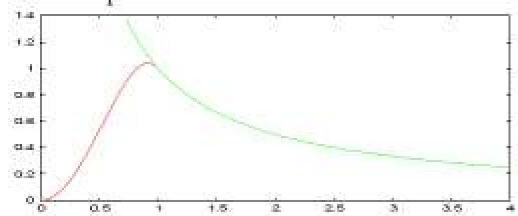
Model interactions as:

Electrostatic contribution (calculated analytically)	+	Chemical & elastic contribution (fitted from *ab initio* data)

(effective ε fitted to ab initio data)

Efficient handling of long-range electrostatic interactions in MC

- Electrostatic energy calculated entirely in reciprocal space
  - Trick: Smooth cutoff as $r \to 0$ in real space, since short distance never sampled in lattice model.

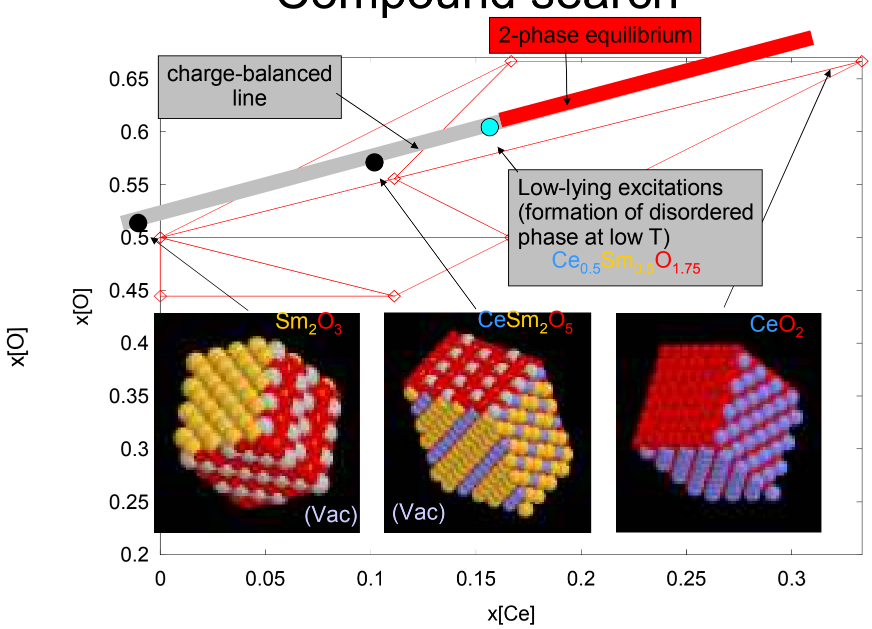


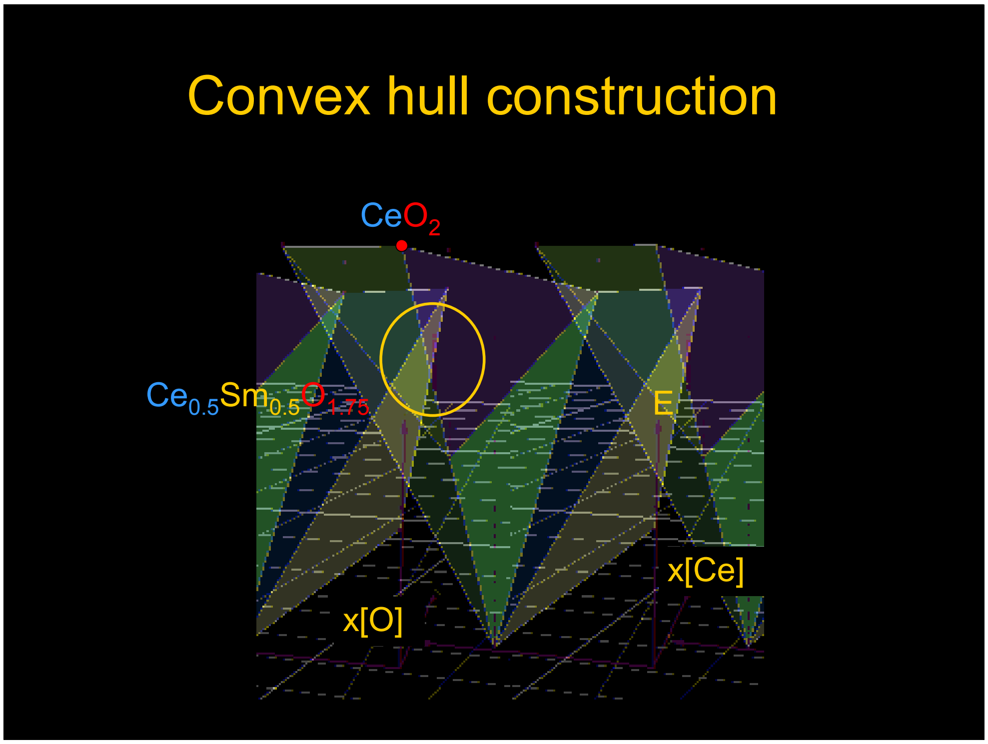
Smoothness $\Rightarrow$ fast decay of Fourier transform

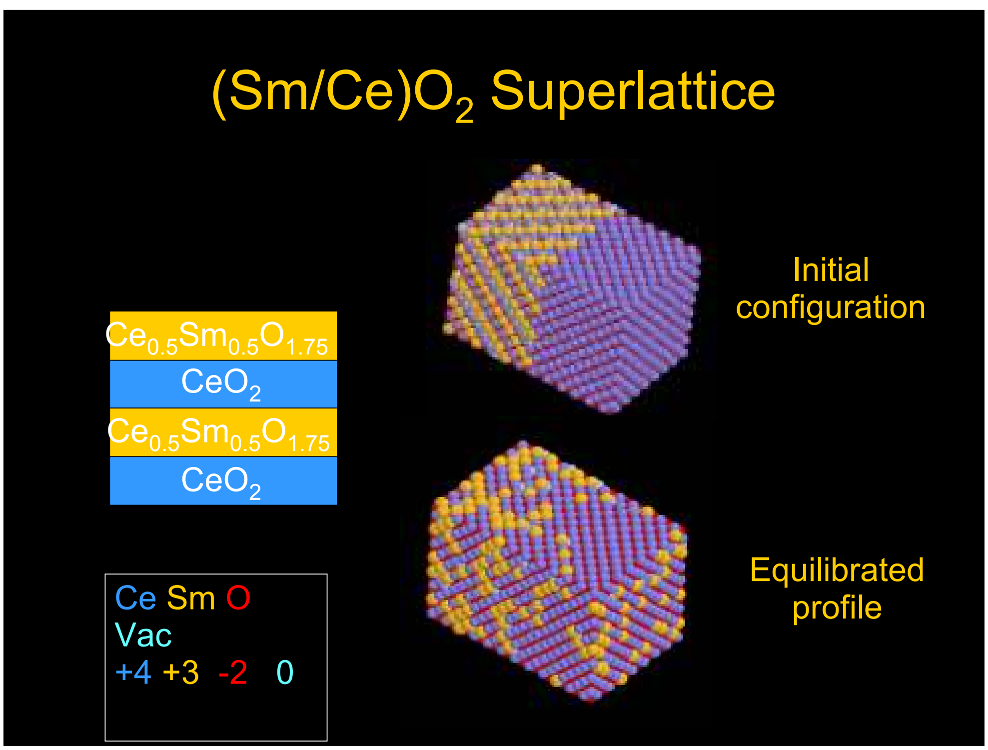
- Use efficient mixed-basis method* to update energy at each MC step.

*Lu Z W, Laks D B, Wei S-H and Zunger A 1994 *Phys. Rev.* B **50** 6642

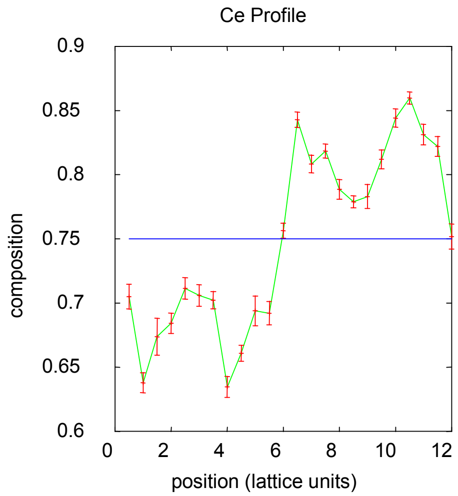
Compound search

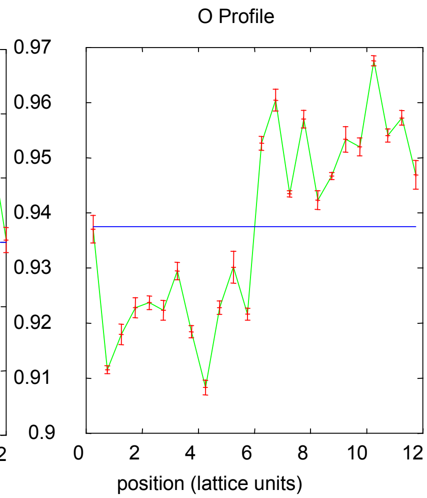



Convex hull construction
CeO_2
$Ce_{0.5}Sm_{0.5}O_{1.75}$
E
x[Ce]
x[O]

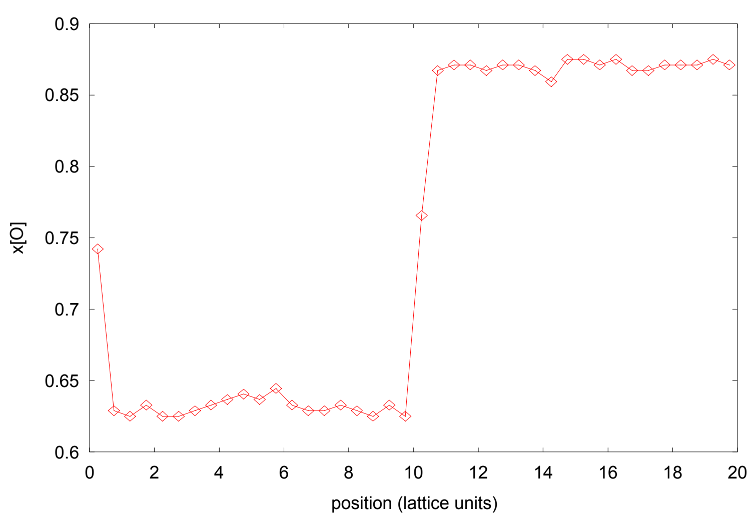

$(Sm/Ce)O_2$ Superlattice
$Ce_{0.5}Sm_{0.5}O_{1.75}$
CeO_2
$Ce_{0.5}Sm_{0.5}O_{1.75}$
CeO_2
Ce Sm O
Vac
+4 +3 -2 0
Initial configuration
Equilibrated profile

Interface composition profile





O composition profile across interface within the frozen cation approximation



Composition profile samples