Understanding Interfacial Resistance in Batteries by Atomic-Scale Modeling

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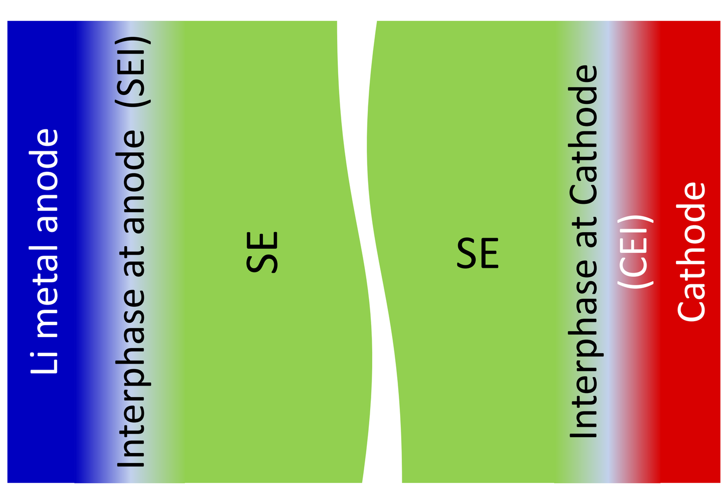
Atomic-Scale Simulations for Battery Cell Engineering

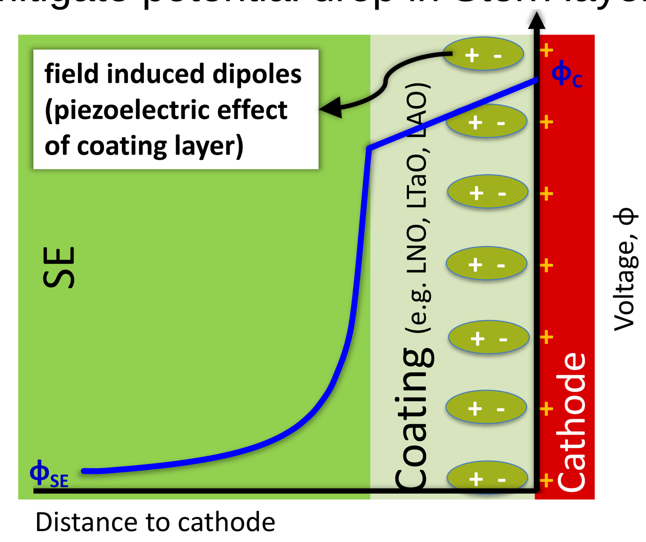
Simulations with the MedeA® software suite provide property data and atomic-scale understanding for the design of battery materials

- ▶ High energy density: electrode materials for cells with capacities ≥ 200 Ah/kg and voltages of 4-5 V
- ▶ Fast charging: high ion conductivity in electrolytes, electrodes, coatings, and across interfaces
- ▶ Safety & performance: understand and control electrochemical processes at interfaces
- ▶ Long life time: improve mechanical and kinetic stability during cycling

All Solid State Battery Challenges

- Formation of interphases between electrodes and solid electrolytes (SE)
  - Li rich phases in SEI
  - Li poor phases in CEI
- Design of oxidation stable, piezoelectric & ductile cathode coatings
  - prevent formation of charge carrier deficient interphases
  - mitigate potential drop in Stern layer

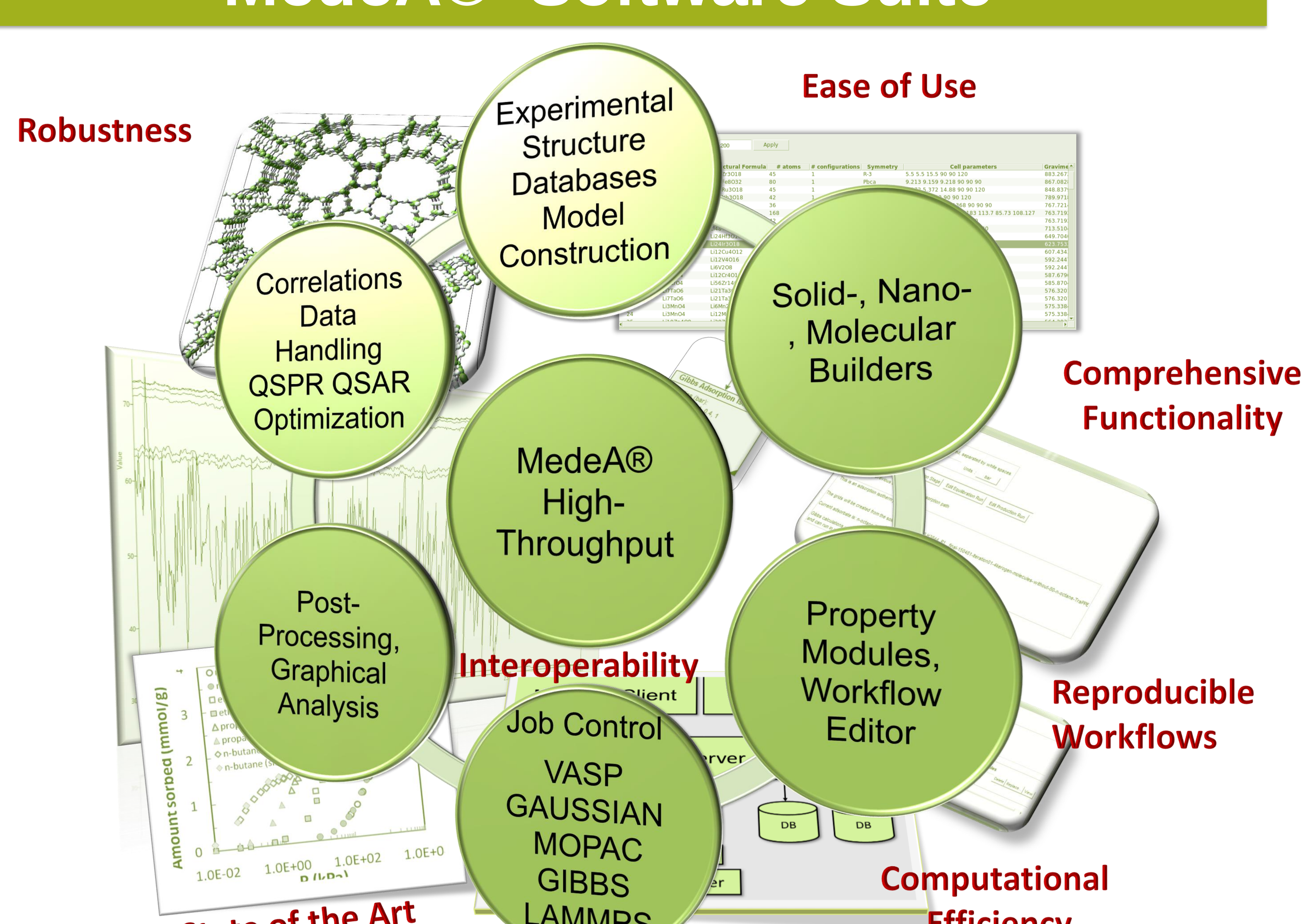




Properties from Calculations

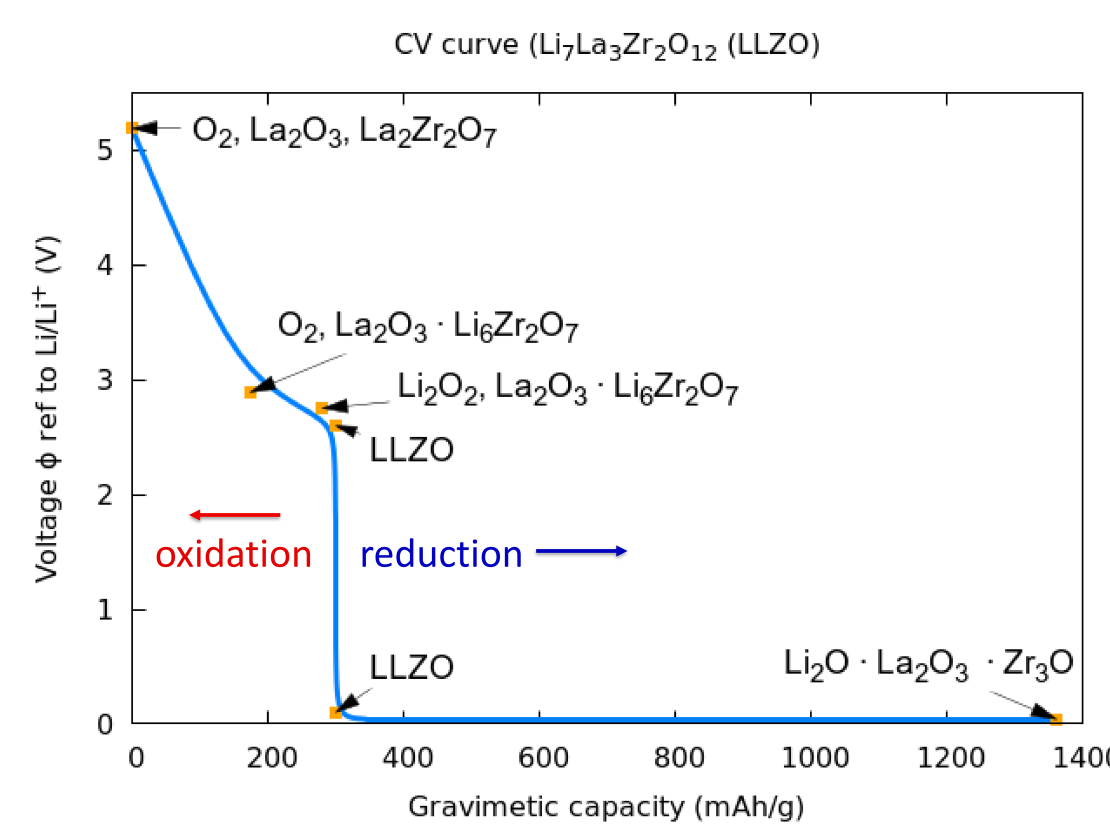
Materials Fabrication	Interfaces of Electrodes, Electrolytes, Coatings, Binders, etc.
▶ Phase diagrams: miscibility vs separation ▶ Elasticity: ductility, brittleness, hardness ▶ Permittivity Dielectric constants ▶ Piezoelectricity ▶ Ion conductivity ▶ Thermal conductivity ▶ Thermal expansion ▶ Heat capacity	▶ Interphase morphology ▶ Interfacial contact ▶ Current density ▶ Electrical conductivity ▶ Inter-diffusion & segregation ▶ Interfacial stabilities/delamination ▶ Potential profiles
Cycling Behavior, Fast Charging	**Diagnostics & Analysis**
▶ Electrochemical stability vs degradation ▶ Phase transformation ▶ Volume change of particles ▶ Metal plating	▶ IR & Raman Spectra ▶ UV-Vis Spectra ▶ XPS (core level shifts) ▶ Powder Diffraction Pattern

MedeA® Software Suite



Example: Behavior of Solid Electrolyte LLZO ($Li_7La_3Zr_2O_{12}$) Upon Cycling

Capacity vs voltage (CV) upon cycling



- ▶ LLZO is electrochemically stable between ~0.1 and 2.8 V Li/Li+
- ▶ above 2.9 V the oxidation of LLZO is irreversible due to O_2 release
- ▶ above 5 V interphase does not contain any charge carrier (Li^+ cations)
- ▶ below ~0.1 V LLZO is reduced to solid solution of the binary phases Li_2O, La_2O_3, and Zr_3O

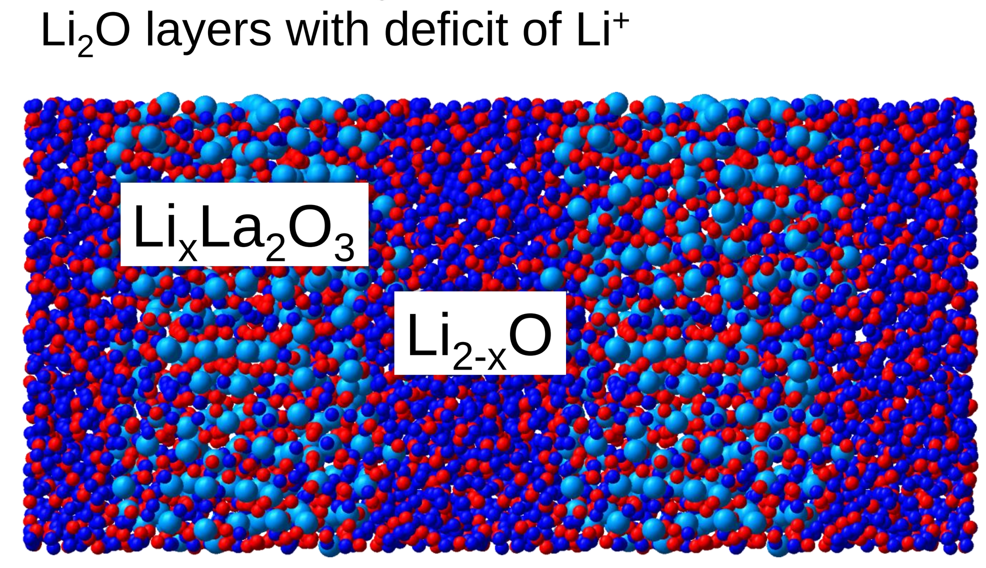
Interphase Properties

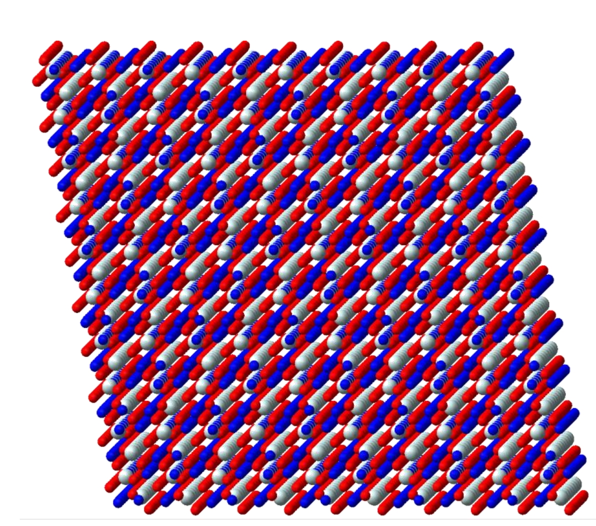
Phase	Bulk modulus GPa	Shear modulus GPa	Young's modulus GPa	Poisson ratio ≥ 0.3 → ductile		Pugh ratio > 1.75 → ductile		Ion conductivity Log (σ_{ion}) 300 K Log (S cm^{-1})	Max. thickness for current density of 1 Am^{-2} µm
LLZO	122	65	165	0.27	brittle	1.88	ductile	-3	2568
Interphase at anode side									
$Li_2O \cdot La_2O_3$	123	47	125	0.33	ductile	2.59	ductile	-6	10
Zr_3O	146	37	80	0.38	ductile	3.98	ductile		
Interphase at cathode side									
$La_2Zr_2O_7$	185	84	196	0.30	ductile	2.20	ductile	Zero Li^+	
Li_2O_2	77	54	130	0.22	brittle	1.43	brittle		
$Li_6Zr_2O_7$	116	74	183	0.24	brittle	1.57	brittle	-8	0.03

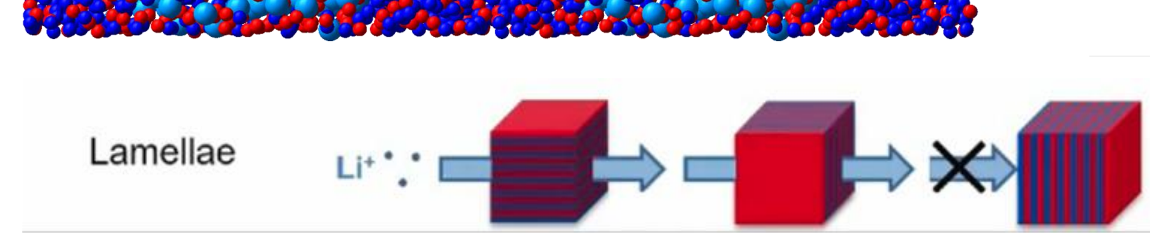
Nano-morphology of Interphases

▶ **$Li_2O \cdot La_2O_3 \cdot Zr_3O$**
Alternating layers of Li^+-enriched poly-crystalline La_2O_3 layers and amorphous Li_2O layers with deficit of Li^+

▶ **$Li_6Zr_2O_7 \cdot La_2O_3$**
Separated crystalline phases of $Li_6Zr_2O_7$ and La_2O_3







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