Electrochemical Devices: Nanostructured Electrodes, Electrolytes and Interfaces in Li-ion Batteries

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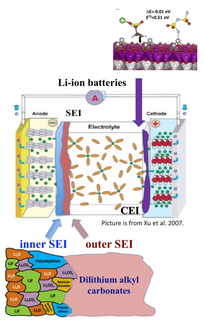
Research Area



•The coupling of electrochemical and mechanical processes inside electrodes, bulk electrolytes and at electrode/electrolyte interfaces is one of the key challenges that has to be addressed in order to provide efficient materials-by-design of novel batteries.

• We have focused on developing a set of multiscale modeling tools that allows us to couple the atomic, molecular and nanoscale electrochemical and mechanical processes to continuum level modeling. This approach substantially enhances the predictive capabilities for the modeling and the design of novel electrode materials and electrolytes.

•Specific focus is dedicated to understanding and design of electrode/electrolyte interfaces where key redox/oxidation reactions and formation of solid-electrolyte interphases (SEI) and cathode electrolyte interphase (CEI) layers occur.

Goals

The key materials research/design efforts in this topic are:

1) Understand the structure and the mechanisms of SEI and CEI layer formation and stability.
2) Predict mechanical properties and failure mechanisms of electrode and interfaces during charging/discharging processes
3) Predict transport and mechanical properties of SEI and CEI layers, their failure mechanisms.
4) Design system with optimal SEI/CEI structure and characteristics.

The key methods development efforts needed to facilitate this research include:

1) Enhancement of the *ab initio*–ReaxFF methods and their coupling to accurately capture redox reactions and mechanics in electrodes and at their interfaces with SEI and electrolytes.
2) Development of efficient coarse-grained models for electrolytes, SEI, and electrodes.
3) Coupling of fracture/damage models with continuum level modeling.
4) Development of methods that can deal with slow dynamic relaxations and rare events with high activation energy barriers.

Current State and Challenges

The key challenges for modeling methods in this area include:

-electrochemical/mechanical coupling (e.g., deformation and damage of electrodes during charging/discharging, formation and degradation of SEI/CEI layers upon cycling),

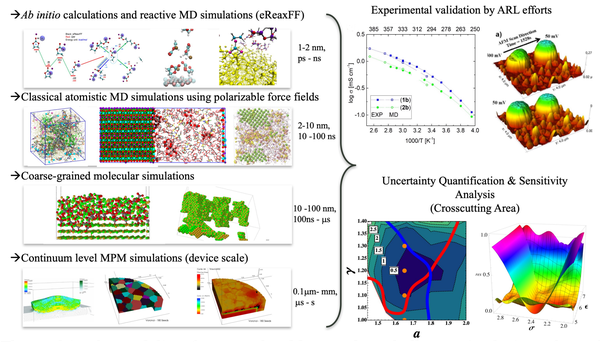
-dealing with the complexity of interactions in ionic systems (e.g., accurate and computationally efficient treatment of long-range electrostatic interactions, accurate models for induced polarization effects, parameterization of accurate coarse-grained models for electrolyte and electrode materials),

-redox reactions in ionic systems and at solid/liquid interfaces (e.g., reduction/oxidation reactions in bulk electrolyte, electrode/electrolyte interfaces, catalytic reactions),

-dealing with slow dynamic relaxations and events with high transitional state barriers (e.g., glassy behavior of SEI layer in batteries, chemical transformations and self-assembly of products of electrochemical reactions),

- necessity to efficiently navigate through a large space of materials design parameters (i.e., fast throughput of large data sets).

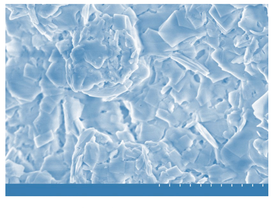
Strategy

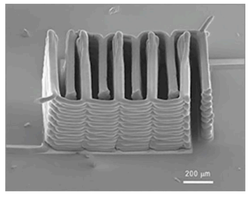


The multiscale modeling framework addresses key challenges in design of novel materials for Li-ion batteries. The approach couples:
1) ***ab initio* level calculations** allowing us to accurately capture electrochemical processes/reactions and the corresponding changes in materials properties,
2) **atomistic reactive and non-reactive molecular dynamics simulations** which are parameterized against the *ab initio* data and allow investigation of materials and interfaces on length scales of several nanometers,
3) **coarse-grained molecular simulations** that expand our length and time scales to allow modeling of self-assembly processes which are usually operative on multiple nanometers to micron length scales and time scales up to multiple microseconds, and
4) **mesoscale and continuum level simulations** allowing us to connect the molecular level features with macroscopic properties/behavior of materials

Future Directions

- **Multiscale modeling of SEI**: formation, self assembly, structure-transport correlations.
- **Novel electrolytes**: high salt concentrations, aqueous, polymer.
-**New electrode chemistries:** Zn, Li metal, organic cathodes, etc.
- **3D interdigitated anode/cathode nanostructures:** geometry optimization





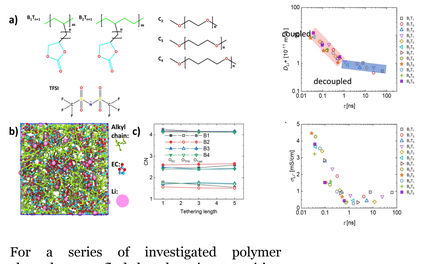
Nature Materials **2018**, *17*, 543-549

CMSME | Center for Multi-Scale Multidisciplinary Modeling of Electronic Materials

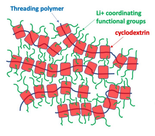
Significant Accomplishments

Optimization of Li⁺ transport in bulk electrolytes

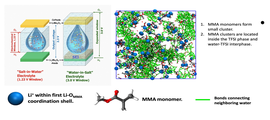
Coupling/decoupling transition between Li+ transport and segmental motion in polymer electrolytes.



- For a series of investigated polymer electrolytes we find that there is a transition between regimes where Li⁺ motion is coupled to polymer segmental motion and where it is insensitive to changes in polymer dynamics
- We also found macromolecular architectures that can allow to decouple optimization of Li⁺ transport and mechanical properties of electrolyte.

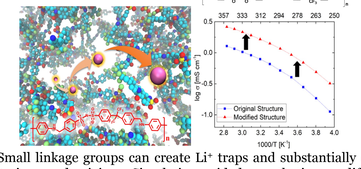


Design of Water-in-Salt-Electrolyte (WiSE)+polymer gels



- Addition of PMMA polymer to WISE electrolyte has little influence on Li⁺ conductivity, but results in a non-leaking gel with good mechanical properties.
- Simulations show that MMA monomers incorporate inside the salt-rich domains and can be efficiently polymerized in WiSE electrolyte.

Small groups, big impact: Eliminating Li+ traps in single-ion conductor polymer gels



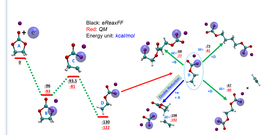
- Small linkage groups can create Li⁺ traps and substantially reduce ionic conductivity. Simulation-guided synthetic modification allowed gel electrolyte with the highest so far conductivity for this class of materials.

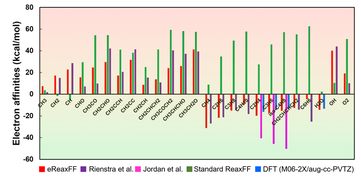
J. Am. Chem. Soc. **2020**.

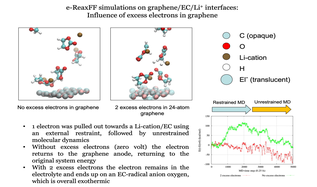
Modeling electrolyte decomposition in bulk and at electrode surfaces

e-ReaxFF advancement

- Explicit electron e-ReaxFF model has been significantly enhanced to describe redox reactions in electrolytes

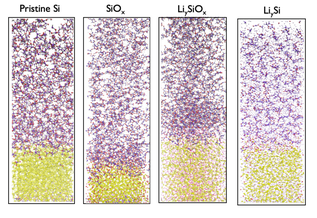


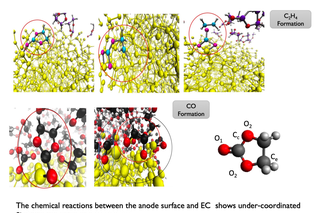


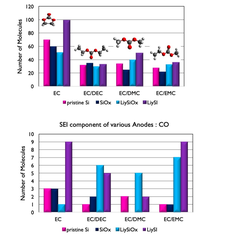


- 1 electron was pulled out towards a Li-cation/EC using an external restraint, followed by unrestrained molecular dynamics
- Without excess electrons (zero volt) the electron returns to the graphene anode, returning to the original system energy
- With 2 excess electrons the electron remains in the electrolyte and ends up on an EC-radical anion oxygen, which is overall exothermic

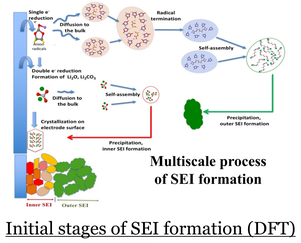
Reaction pathways for CO and C_2H_4 evolution at Si-based electrodes





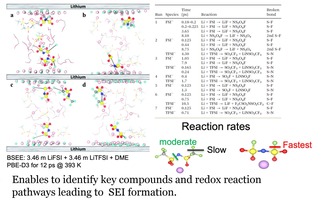


Solid electrolyte interphase (SEI) properties



Multiscale process of SEI formation

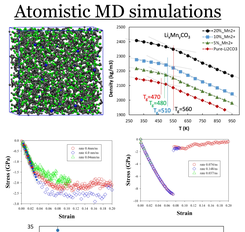
Initial stages of SEI formation (DFT)



- Enables to identify key compounds and redox reaction pathways leading to SEI formation.

Ener. Env. Sci. **2019**, 12, 780-794

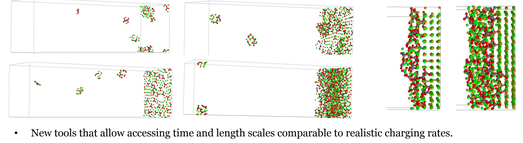
Atomistic MD simulations



- Structural, transport, and mechanical properties of different SEI phases are obtained from non-reactive MD simulations (impractical to obtained from experiments)
- Enables in-silico characterization of different SEI domains.

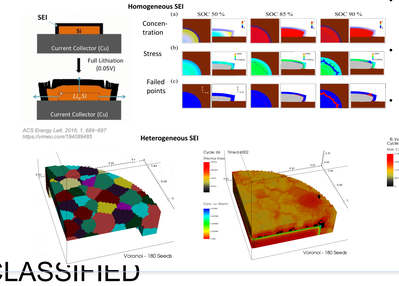
Crystals **2018**.

Coarse-grained simulations



- New tools that allow accessing time and length scales comparable to realistic charging rates.
- Enables studying SEI formation on much larger (domains) scale utilizing chemical mechanisms informed from DFT or ReaxFF simulations (i.e. reduction potential of all species, rate of reduction, radical recombination, etc.)

Continuum level MPM simulations



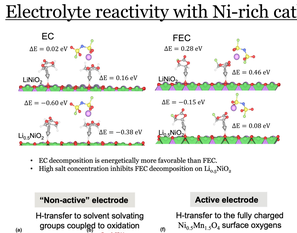
ACS Energy Lett. 2016, 1, 689−697
https://vimeo.com/194059455

- Material Point Method (MPM) enhanced to include mechanical/chemical coupling.
- Enables studying SEI deformation during charging and discharging processes.
- Allows to investigate influence of spatial heterogeneity of SEI domain structure.

ACS Appl. Ener. Mat. **2018**.

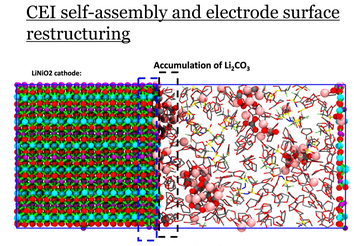
Cathode electrolyte interphase (CEI) formation

Electrolyte reactivity with Ni-rich cathode



- EC decomposition is energetically more favorable than FEC.
- High salt concentration inhibits FEC decomposition on $Li_{2/3}NiO_2$

CEI self-assembly and electrode surface restructuring



- Mechanisms electrolyte decomposition due to oxidation and initial stages of CEI formation investigated using state of the art DFT calculations at ARL.
- Atomistic MD simulation models are constructed to investigate CEI evolution at longer length and time scales with accurate representation of charge transfer/conversion events.

Materials Today **2018**, *21*, 341-353, *iScience* **2020**.