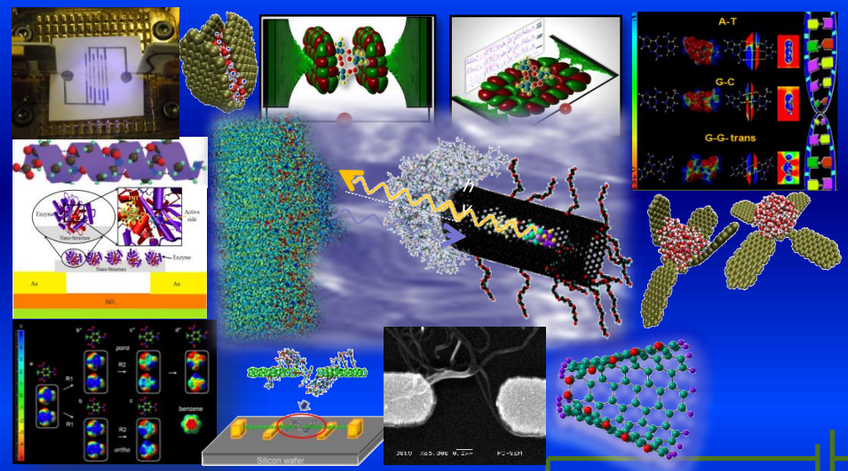
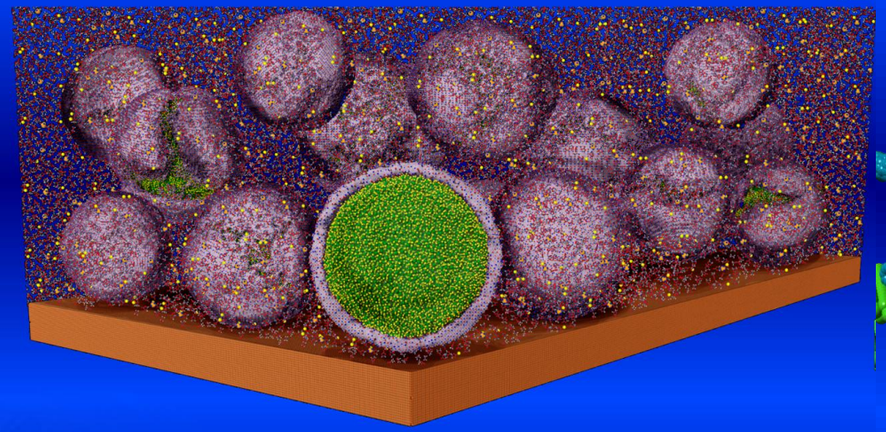
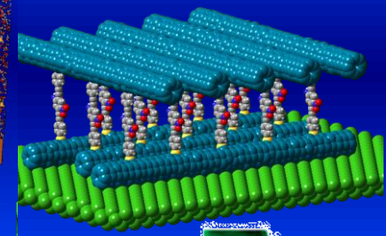
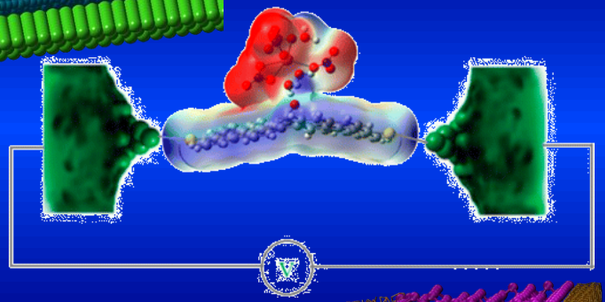
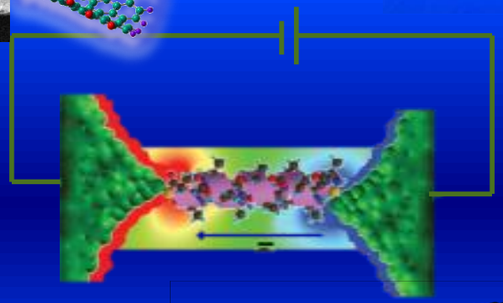
Atomistic Classical and Quantum Simulations of Nanobatteries – Part 1

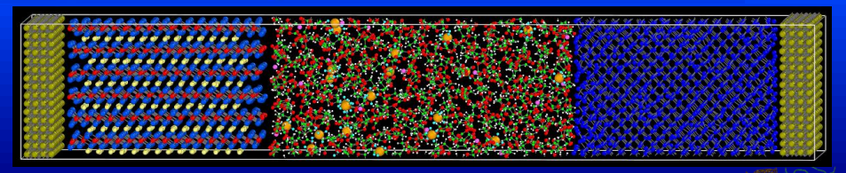


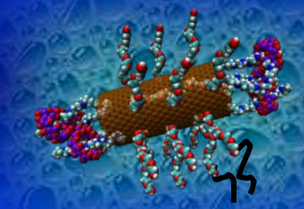


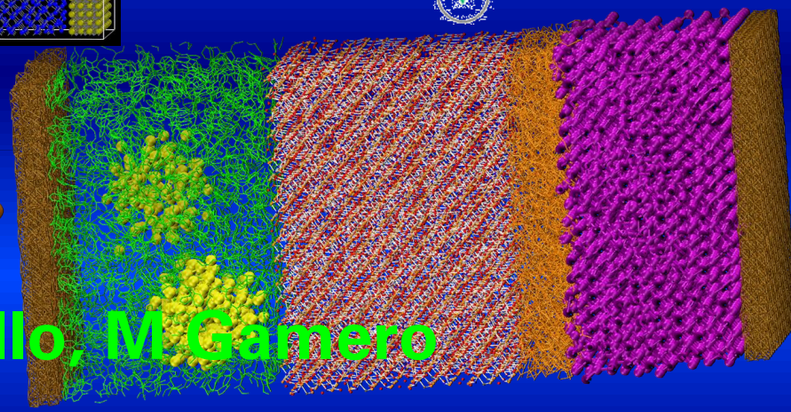












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Analysis of Solid-State Electrolytes for Li-metal Batteries using a Multiscale Molecular Dynamics Approach

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- Metal lithium anodes are excellent alternatives for Li-ion batteries
- nonuniform plating, swelling of anode causes growth of Li-dendrites
- atomistic multiscale quantum and classical MD simulations
- a full nanobattery to determine properties of the SEI
- speciation of interfaces with Li-metal anodes
- Electrolytes: sulfides, halogenated phosphor-sulfides, halogenated nitrates, few others
- full nanobatteries, thus, a cathode: sulfur and spinel structures are also potential alternatives

Background Information

- Vehicles move our economy
- Vehicles transport 11 billion tons of freight/year
- Vehicles move more than $35 billion of goods each day
- Vehicles move people more than 3 trillion vehicle-miles/y

- Economy grow requires transportation
- Transportation requires energy

- Transportation accounts for
- 30% of total U.S. energy needs
- 70% of U.S. petroleum use

- Oil price volatility affects:
- National economy
- Commercial enterprises
- Household budgets.

- U.S. household spends 20% of family expenditures on transportation
- The most expensive spending category after housing

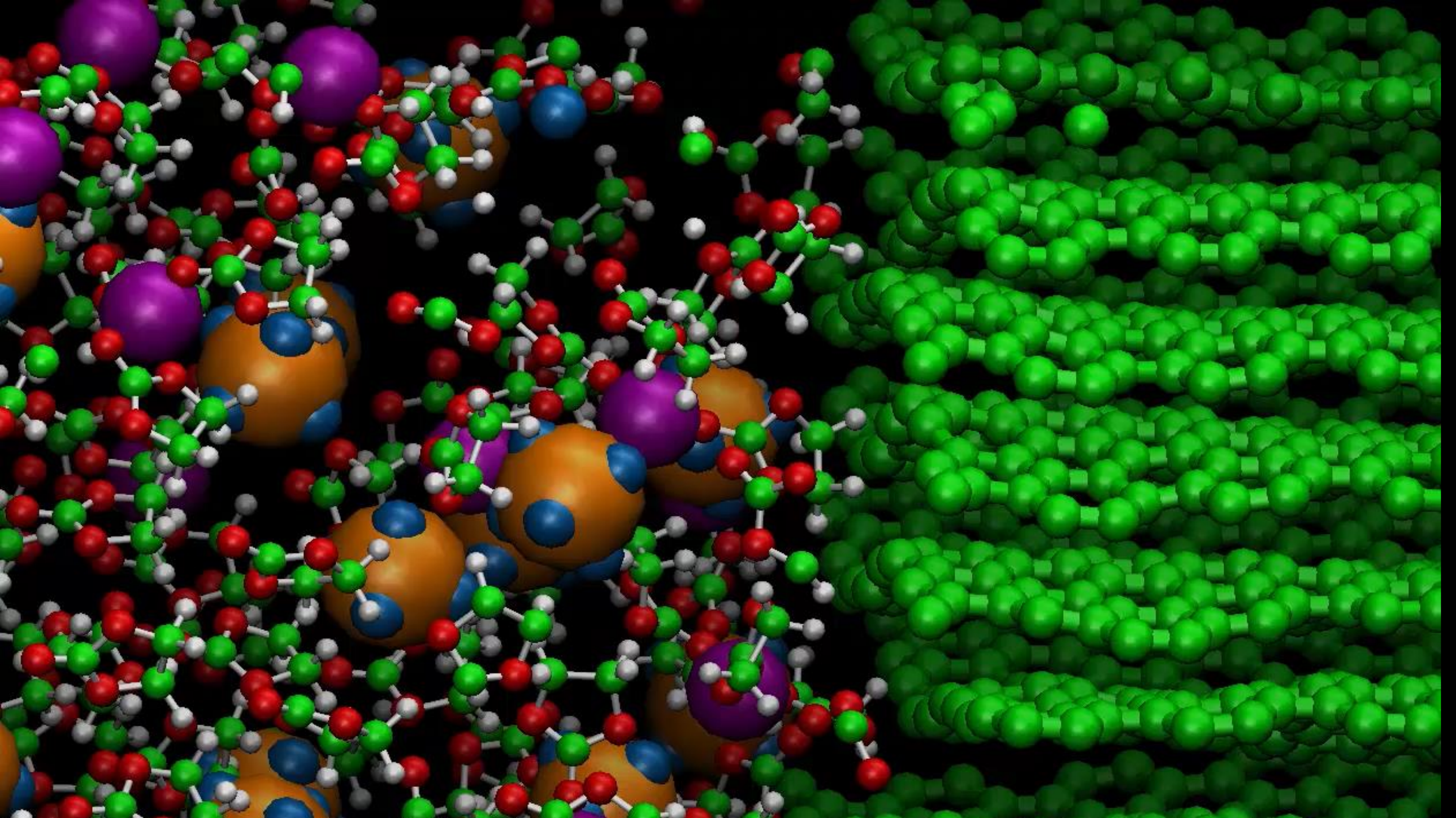
- To enable future economic growth
- Increase transportation affordability

Lithium-ion batteries have made tremendous progress in the last two decades
Created worldwide demand for electric vehicles (EVs)

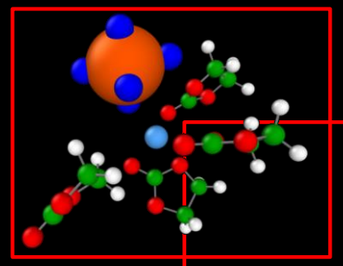
Problems
Liquid organic electrolyte is highly reactive and flammable

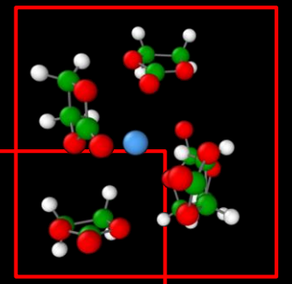
Solution: Solid State Batteries
Solid Li-ion conducting materials in place of liquid electrolytes
Solid electrolyte materials are nonflammable
Allow more robust cell operation
Integration of metal-based anodes
Improve: cost, energy density, cycle life

Challenges
low conductivity,
poor voltage stability
inadequate mechanical properties

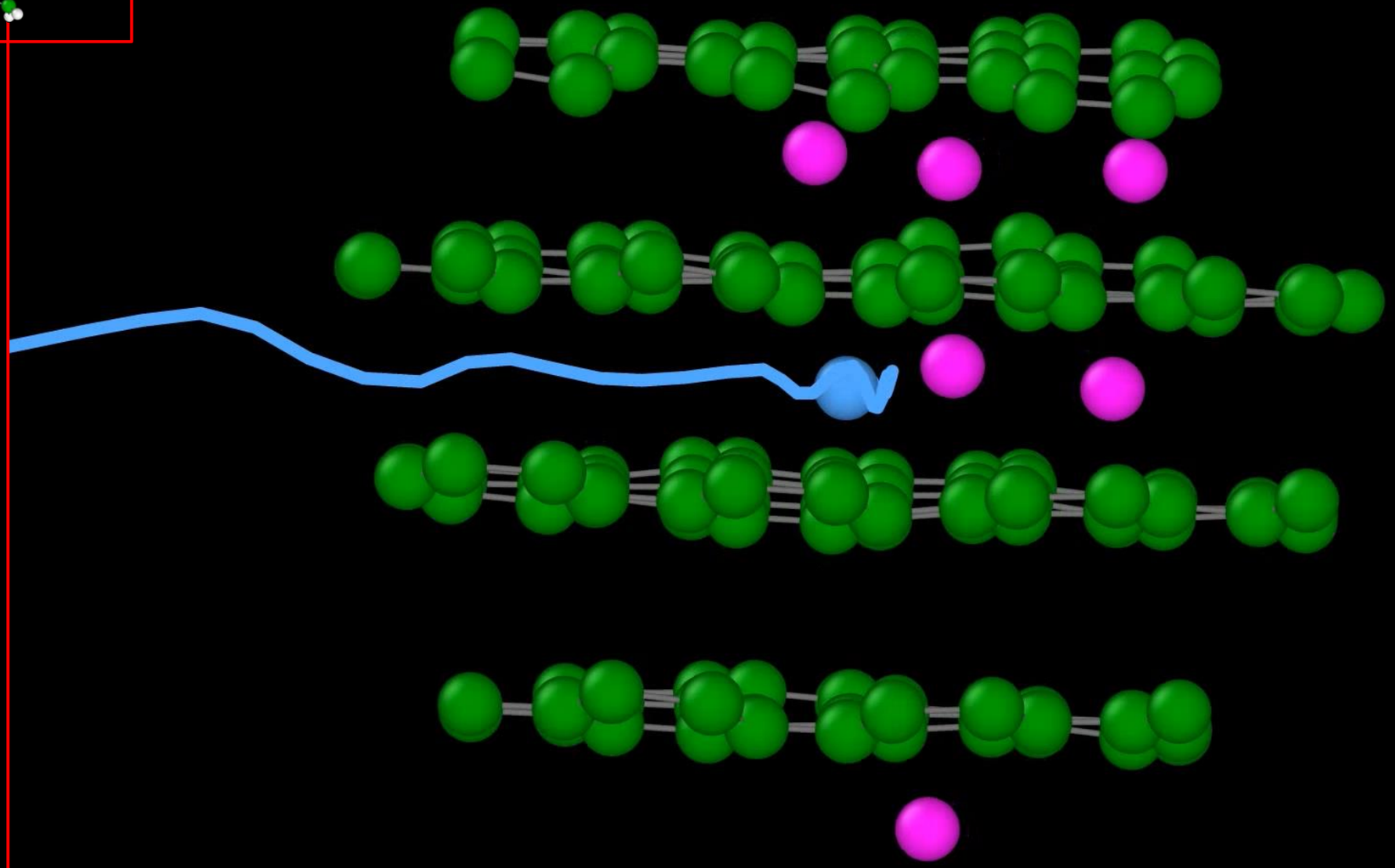


Simulations of the First Charging cycles of Nanobatteries

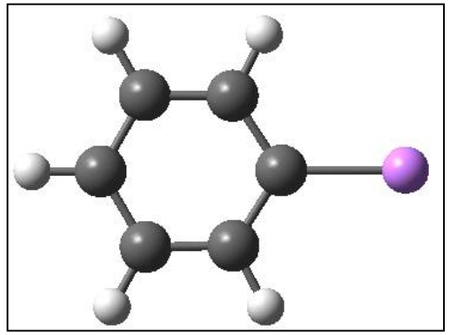




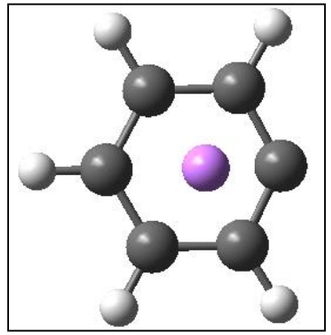
Learning from trajectories of Li-ions



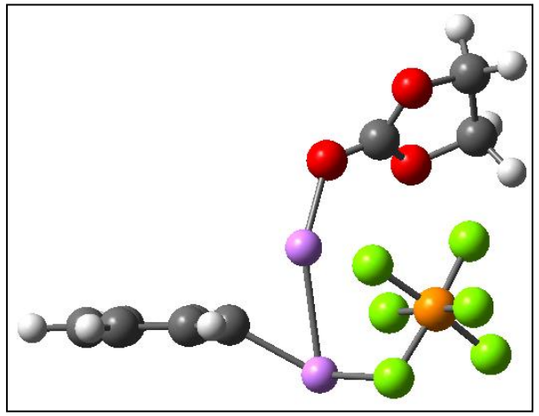
Li Capture by Graphitic C



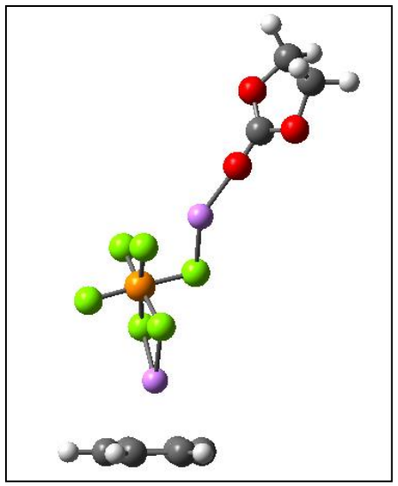
q = 0, m=1
C–Li = 1.98 Å
E = -239.03445 a.u.



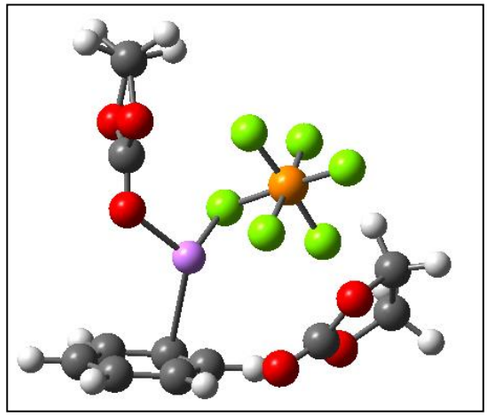
q = 1, m = 2
C–Li = 2.38 Å
E = -238.80736 a.u.



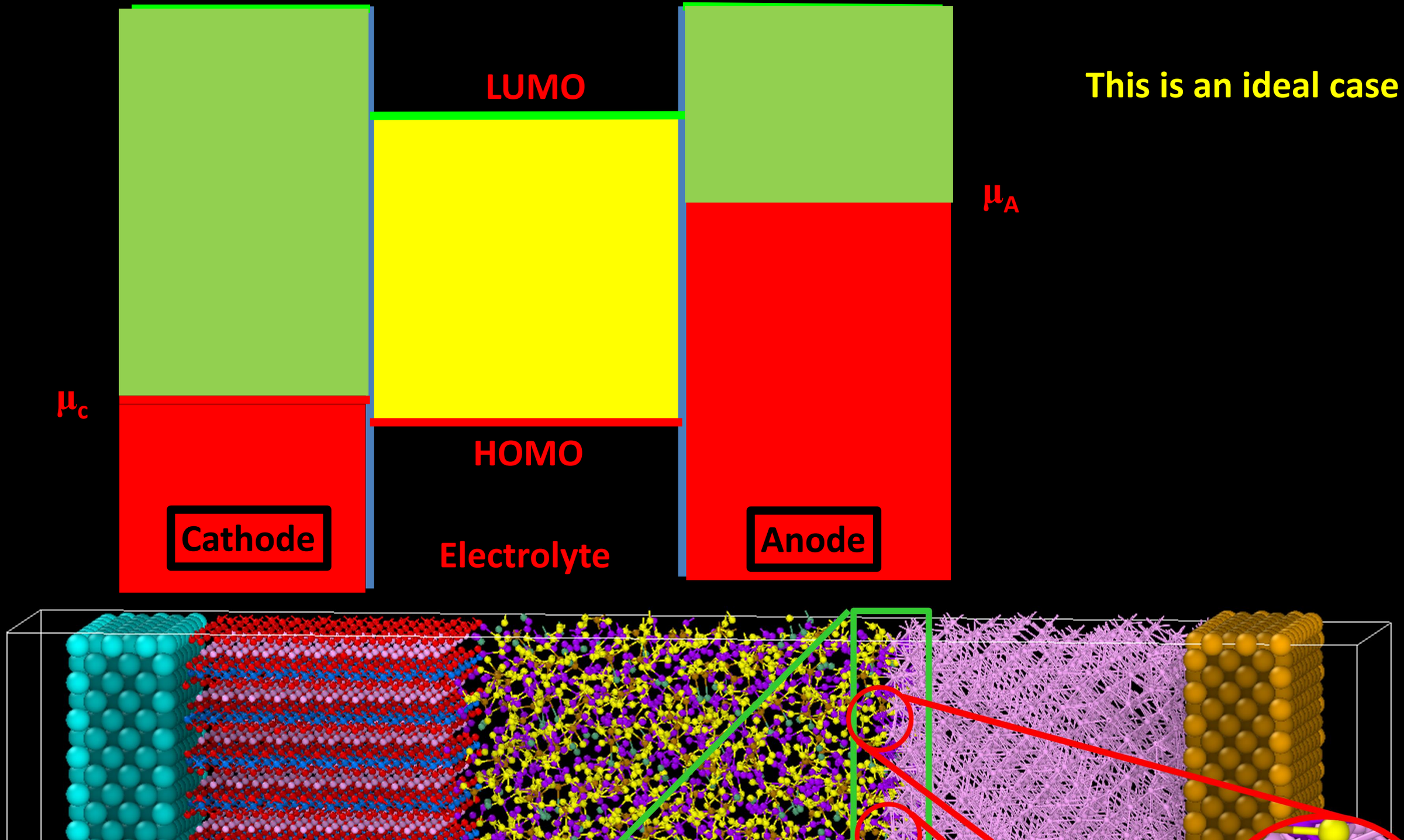
q = 0, m = 1
C–Li = 2.08 Å
E = -1529.30186 a.u.

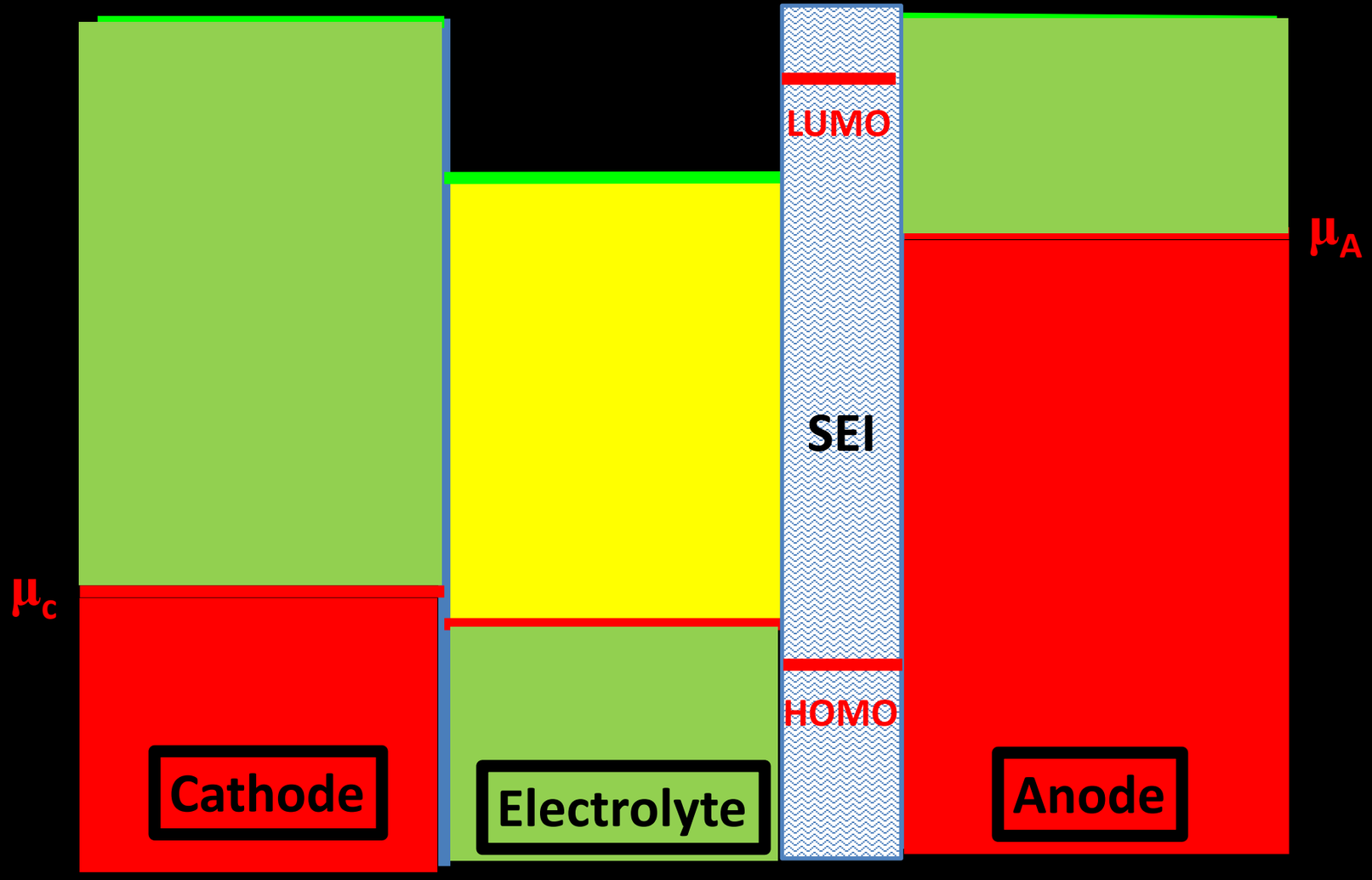


q = 1, m = 2
C–Li = 2.47 Å
E = -1529.08439 a.u.

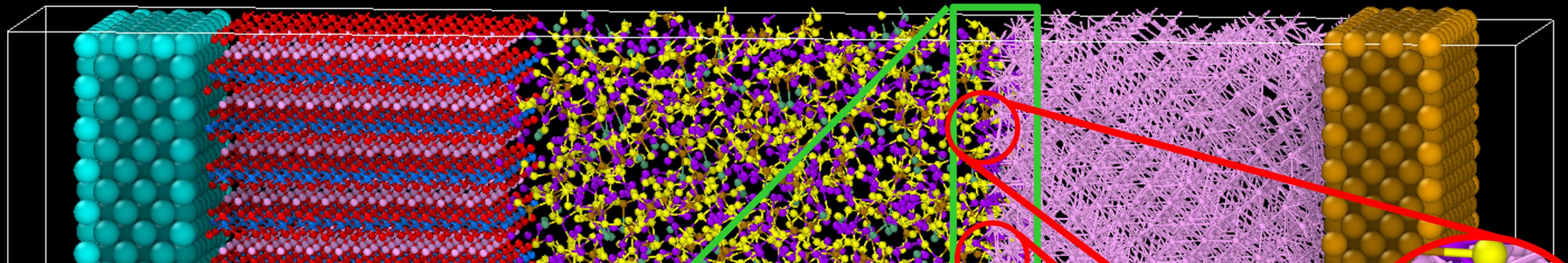


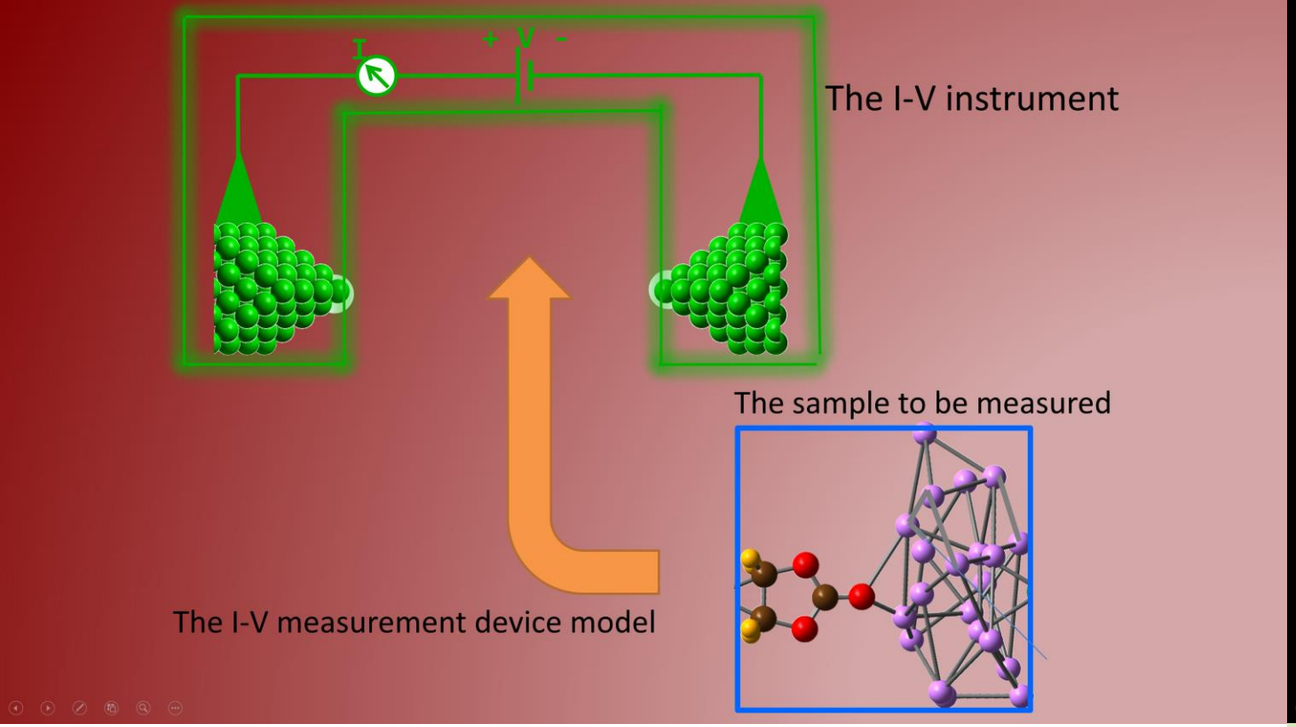
q = 0, m = 1
C–Li = 2.62 Å
E = -1863.95778 a.u.

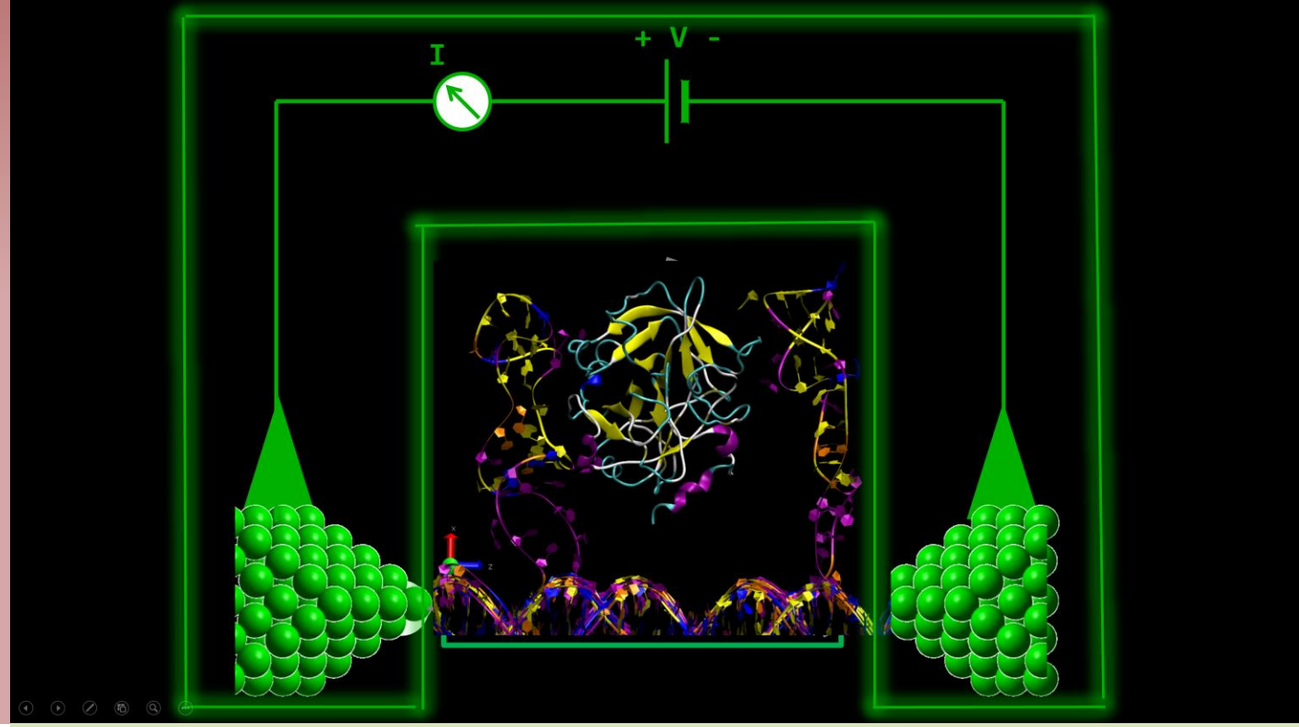

LUMO
HOMO
μ_c
μ_A
Cathode
Electrolyte
Anode
This is an ideal case

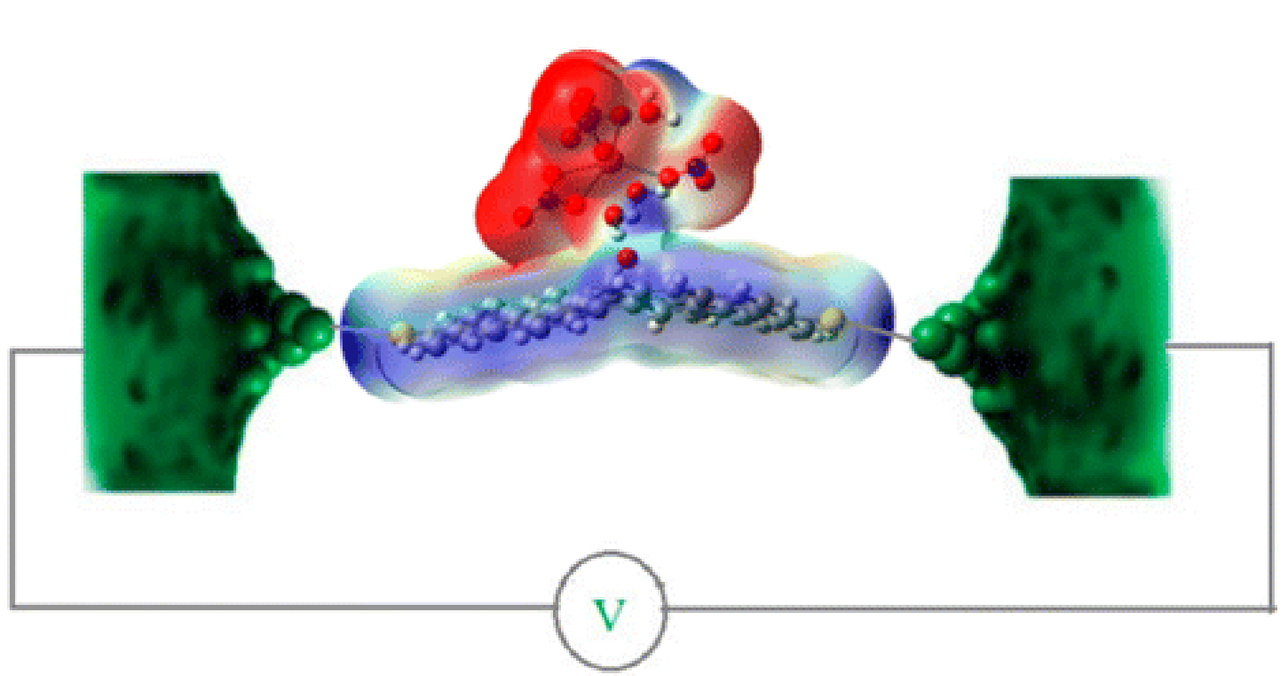


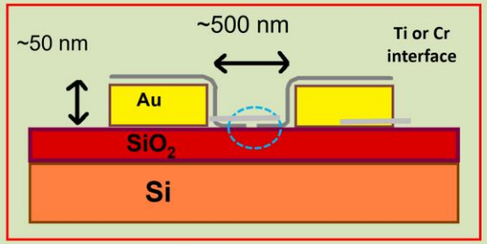
The lucky formation of a solid electrolyte interphase between the liquid electrolyte and the solid anode was of paramount importance for the success of present Li-ion batteries

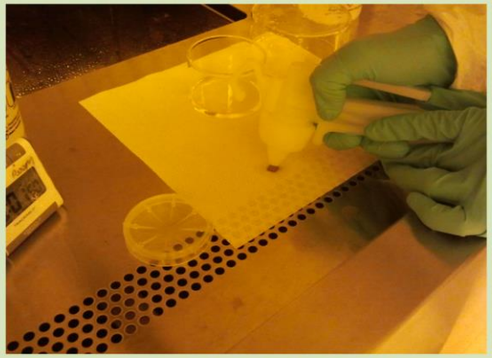


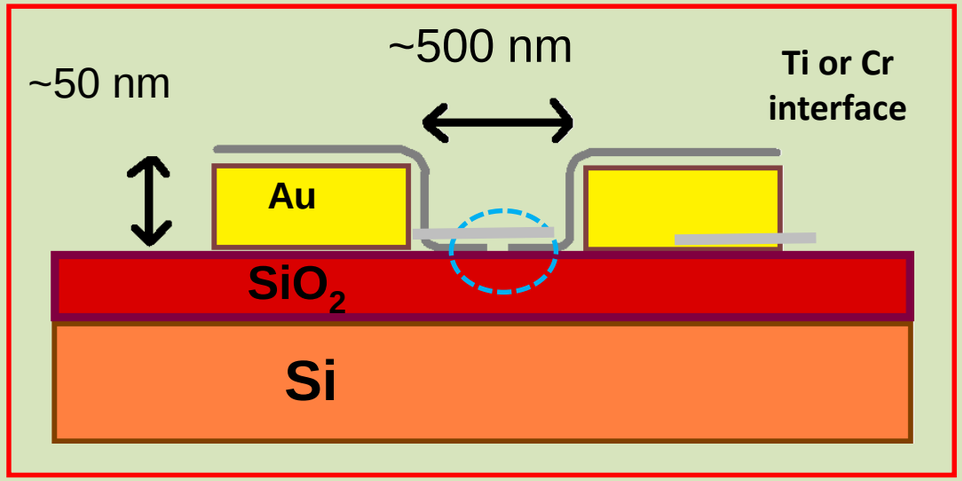

I
+ V -
The I-V instrument
The sample to be measured
The I-V measurement device model

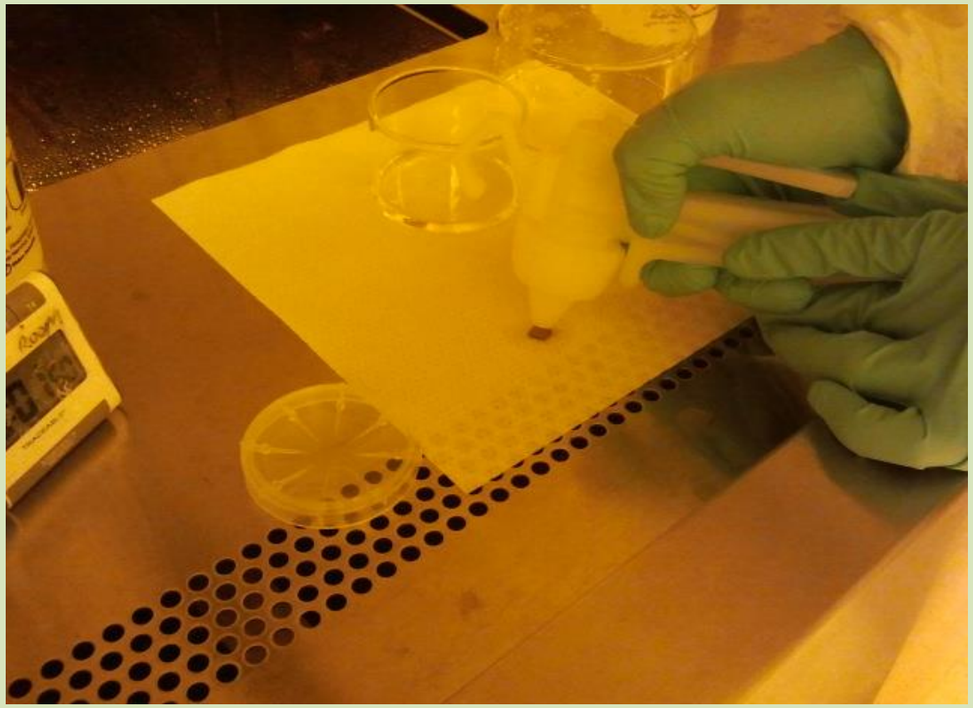

I
+ V -


V

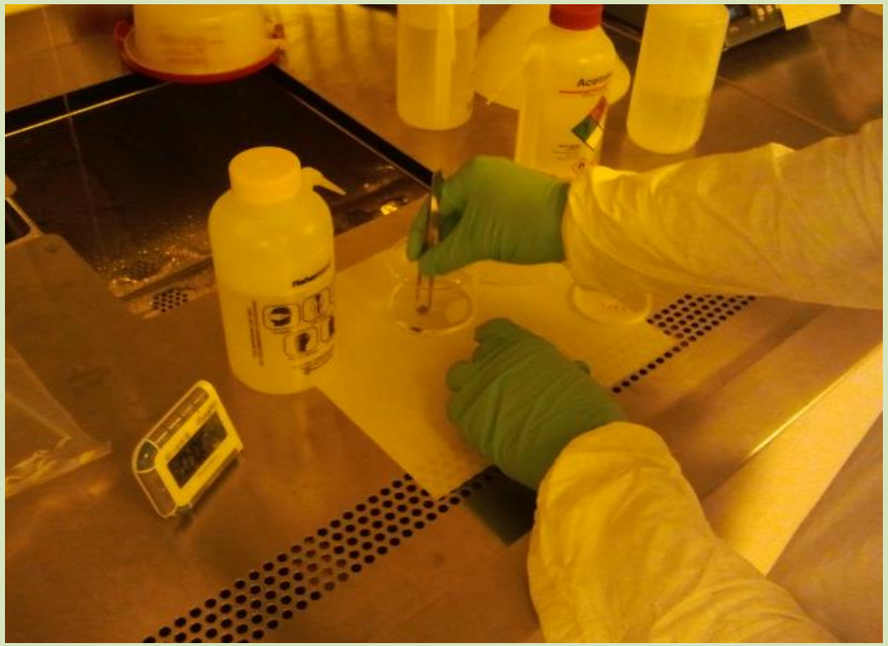

~50 nm
~500 nm
Ti or Cr interface
Au
SiO2
Si




~50 nm
~500 nm
Ti or Cr
interface
Au
SiO2
Si

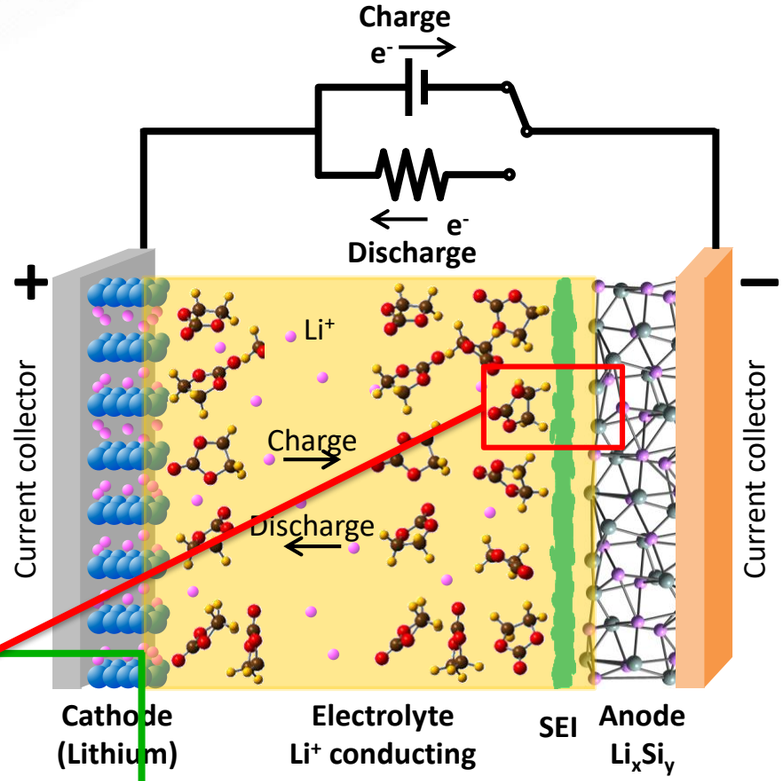


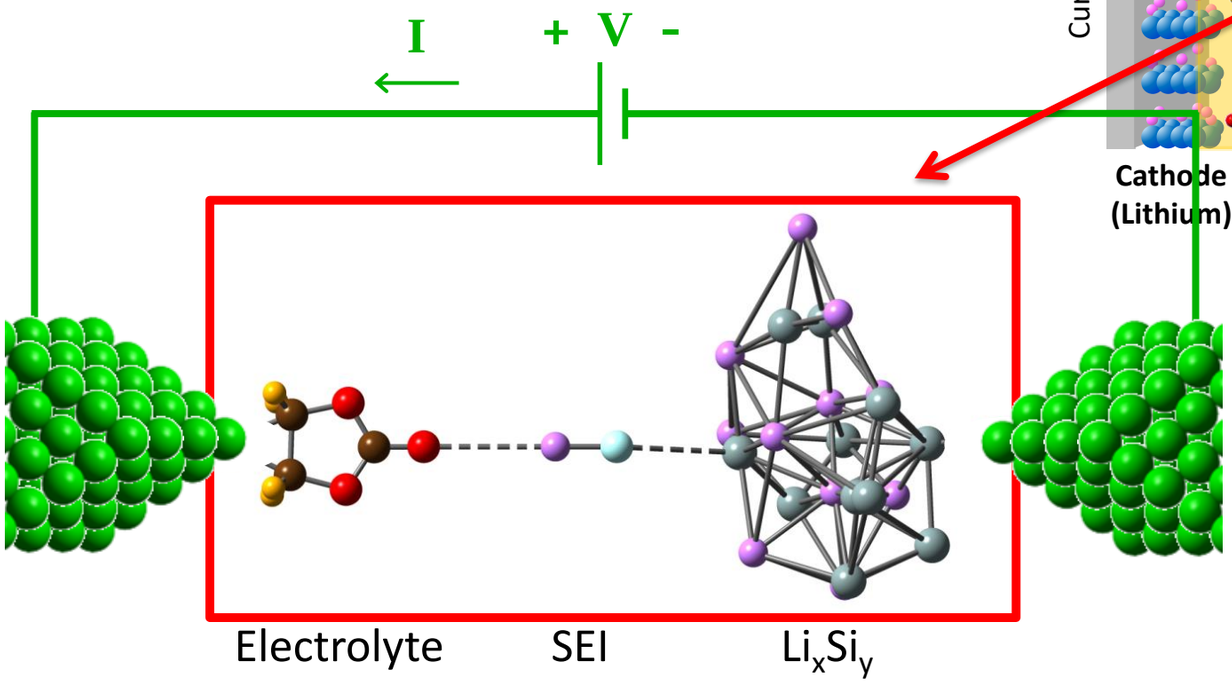

DO NOT ENTER
JEOL



GENIP

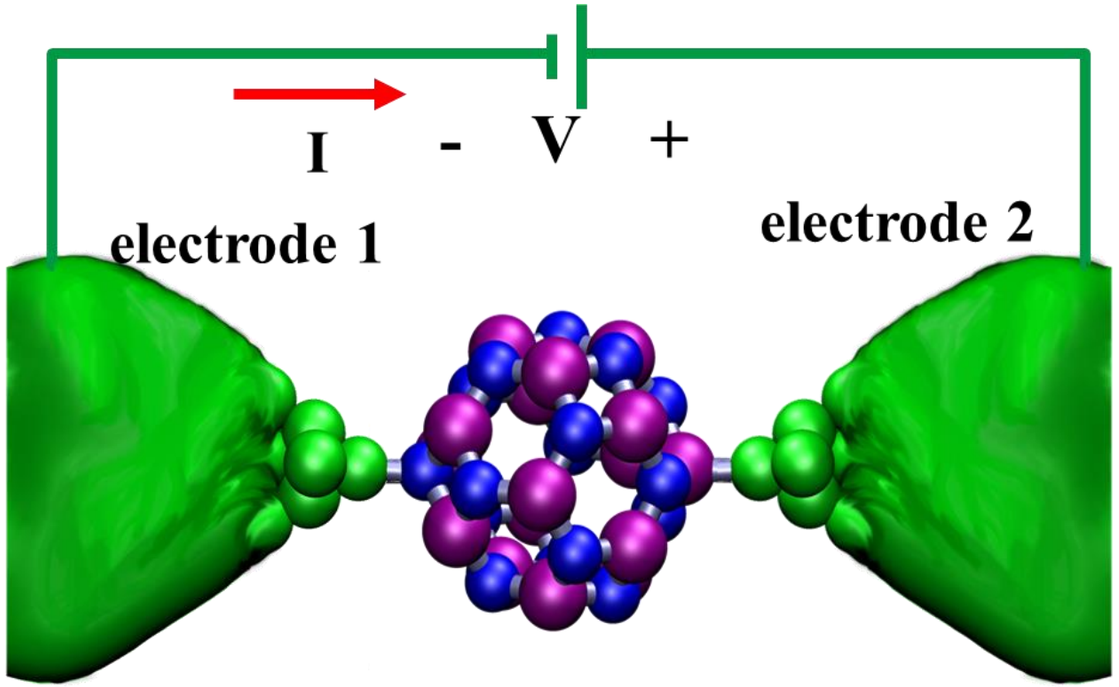
Benitez & Seminario, **Electron Transport and Electrolyte Reduction in the SEI of Rechargeable LIB Si Anodes**.
J. Phys. Chem. C **2016,** *120* (32), 17978-17988





CALCULATION OF CURRENT-VOLTAGE CHARACTERISTICS[1]

Green's Function Theory—Density Functional Theory Approach



$(LiF)_n$ and $(Li_2CO_3)_n$:
PBE&HSE06/6-311+G//B3PW91/6-31G(*d*)/LANL2DZ
Au DOS
Programs: Gaussian-09, CRYSTAL, GENIP

Hamiltonian H and overlap S

$$H_{KS}\Psi = \varepsilon S\Psi \quad H_{KS}S^{-1} \rightarrow H_T$$

$$H_T = \begin{pmatrix} H_1 & \tau_1 & 0 \\ \tau_1^\dagger & H_M & \tau_2^\dagger \\ 0 & \tau_2 & H_2 \end{pmatrix}$$

Green function

$$G_M = [E - H_M - \Sigma_1 - \Sigma_2]^{-1}$$

Self-energies and couplings of electrodes

$$\Sigma_k = \tau_k g_k \tau_k^\dagger \qquad \Gamma_k = i\left(\Sigma_k^- - \Sigma_k^+\right)$$

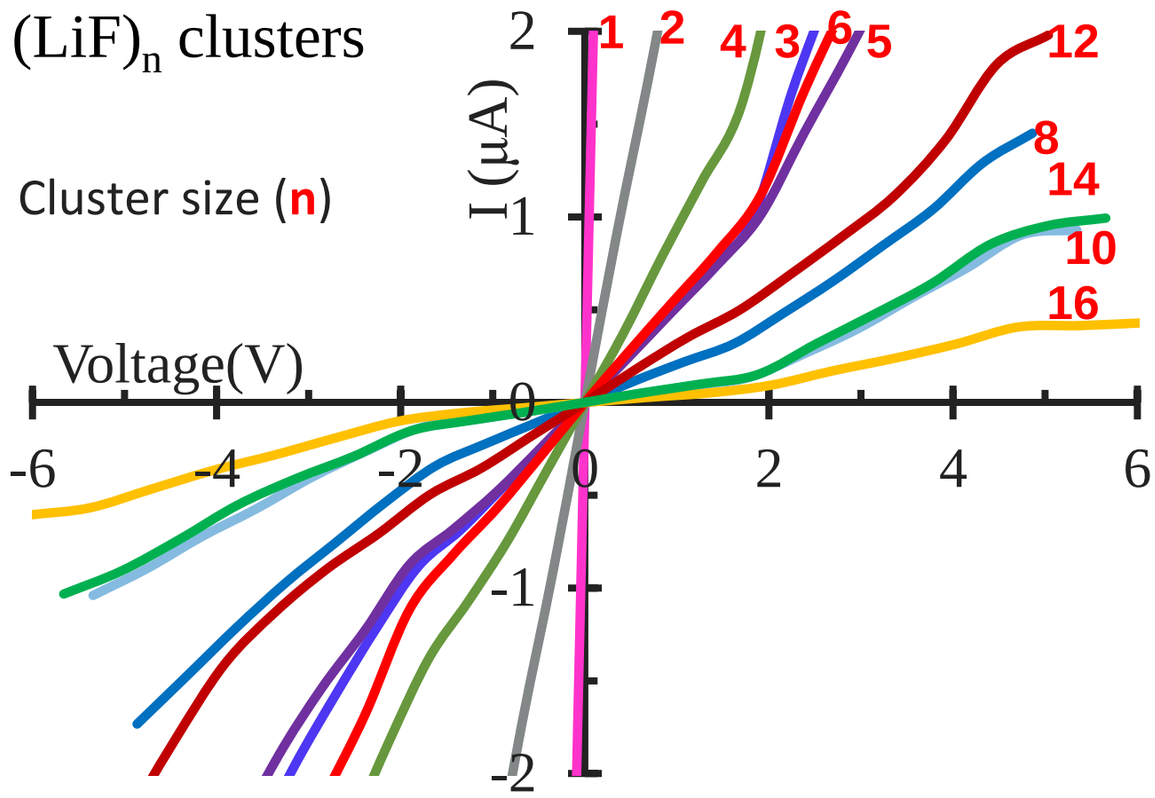
Transmission function *T* and current *I*

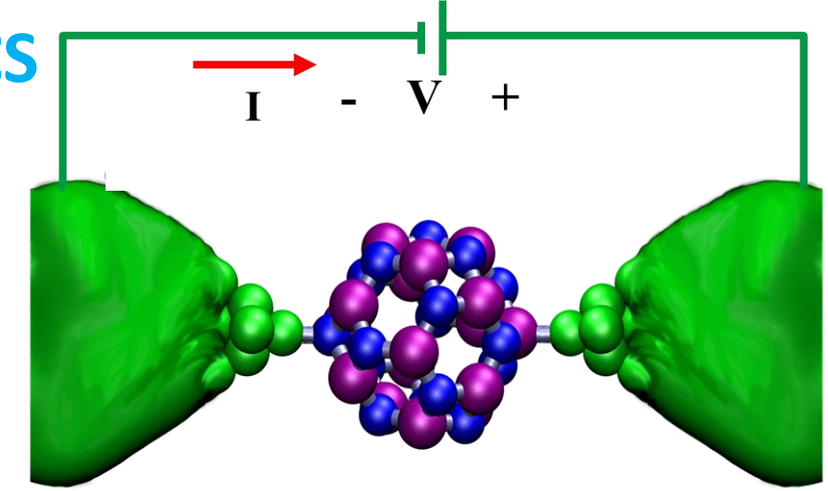
$$T(E) = Trace(\Gamma_1 G_M^R \Gamma_2 G_M^A)$$

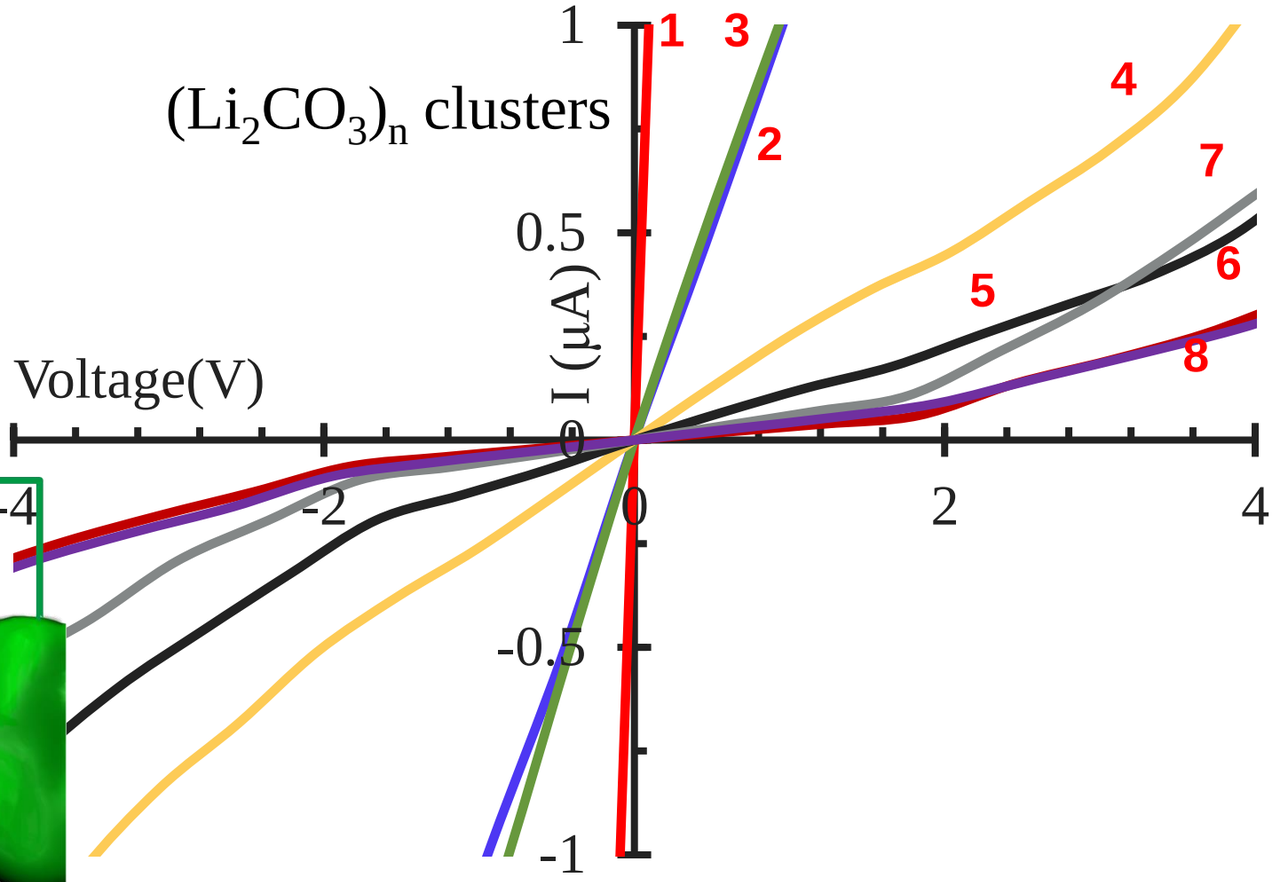
$$I \approx \frac{2e}{h}\int_{E_f+\mu_1}^{E_f+\mu_2} T(E)(f_1 - f_2)dE$$

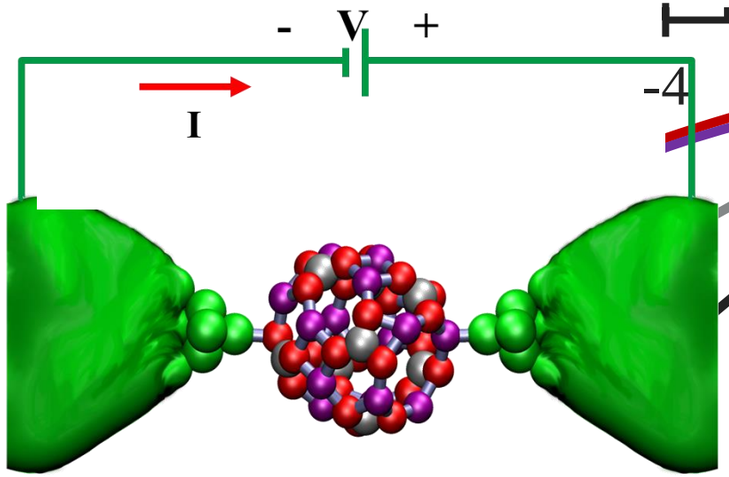
[1]Derosa & Seminario, Electron Transport through Single Molecules: Scattering Treatment Using Density Functional and Green's Function Theories. *JPC-B* **2001,** *105*, 471

CURRENT-VOLTAGE CHARACTERSITICS



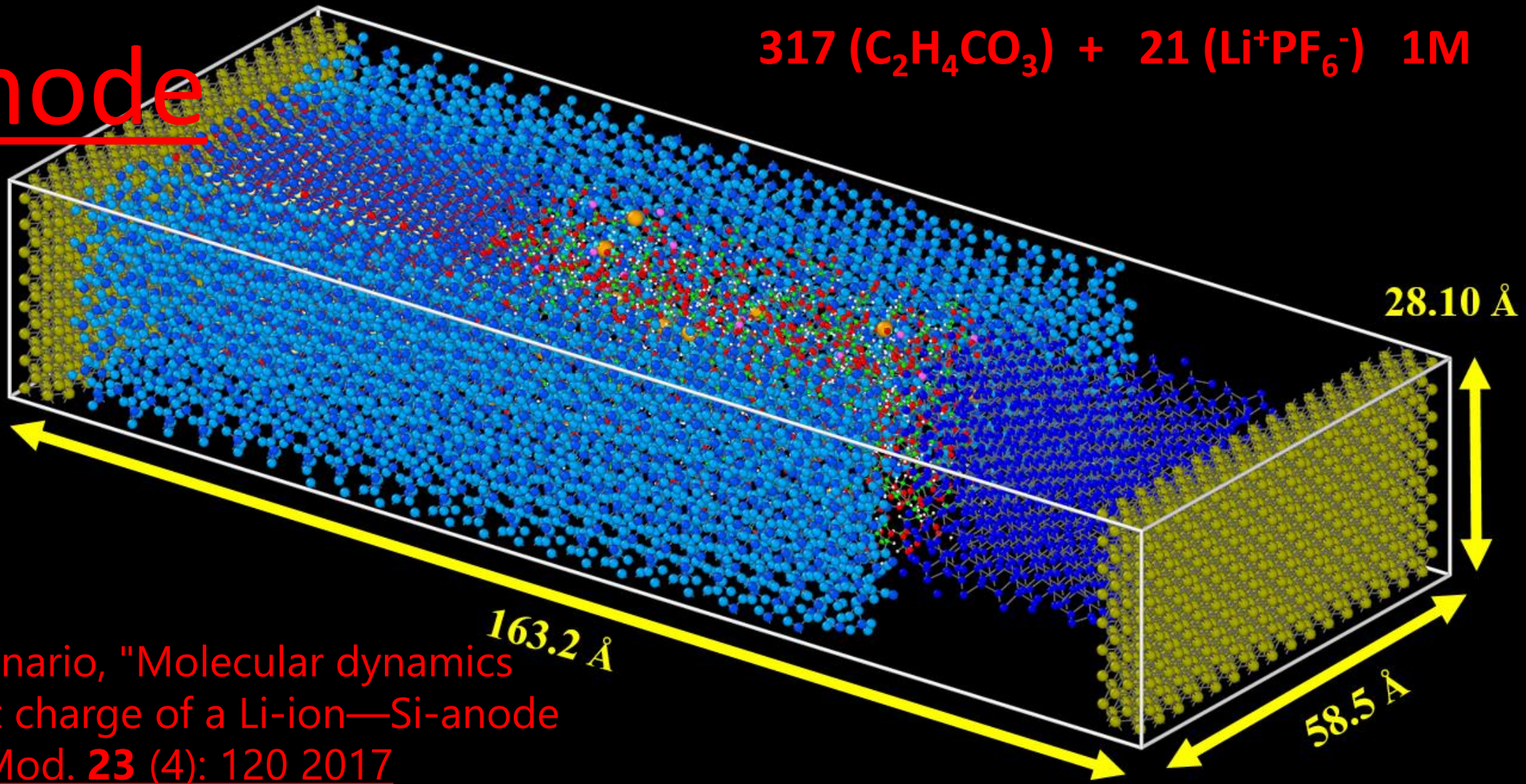




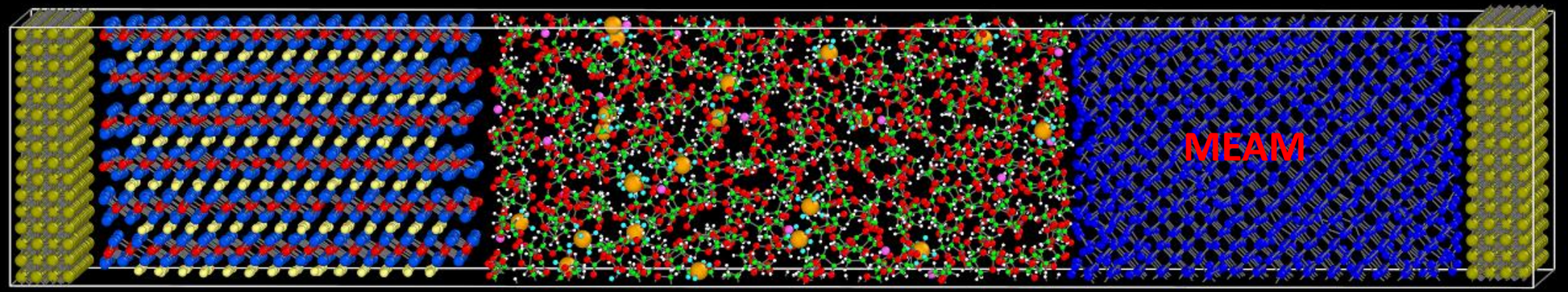


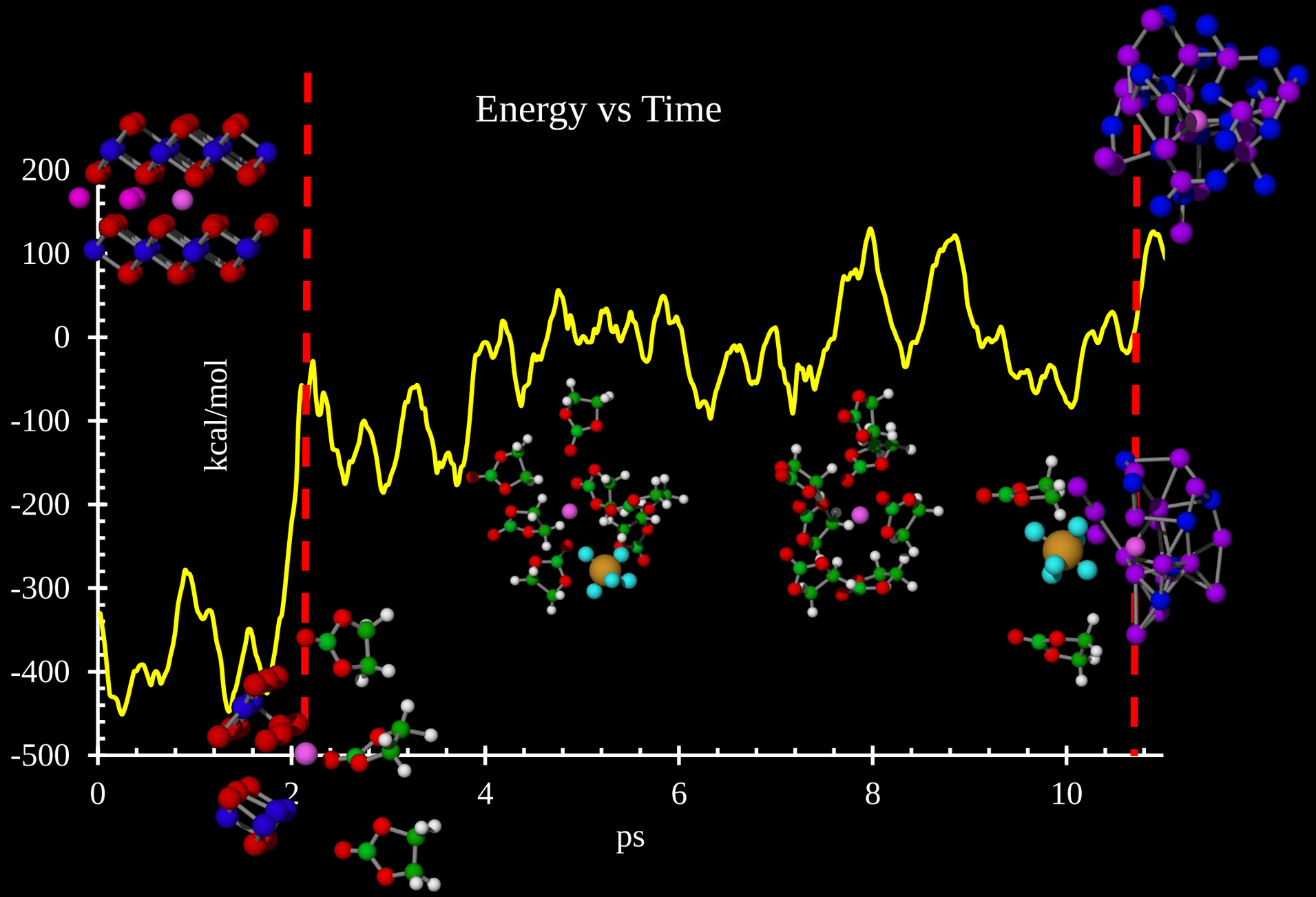
Silicon anode

317 ($C_2H_4CO_3$) + 21 ($Li^+PF_6^-$) 1M



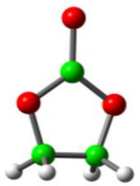
Galvez, Ponce, & Seminario, "Molecular dynamics simulations of the first charge of a Li-ion—Si-anode nanobattery." J. Mol. Mod. **23** (4): 120 2017



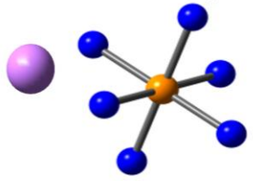

Energy vs Time
200
100
0
-100
-200
-300
-400
-500
kcal/mol
0
2
4
6
8
10
ps

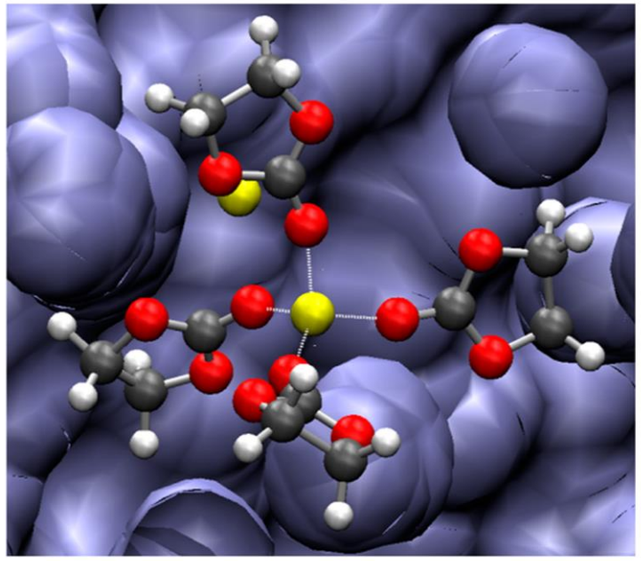
Electrolyte Solution 1M $LiPF_6$ in EC

Solvent: $C_2H_4CO_3$ (EC)

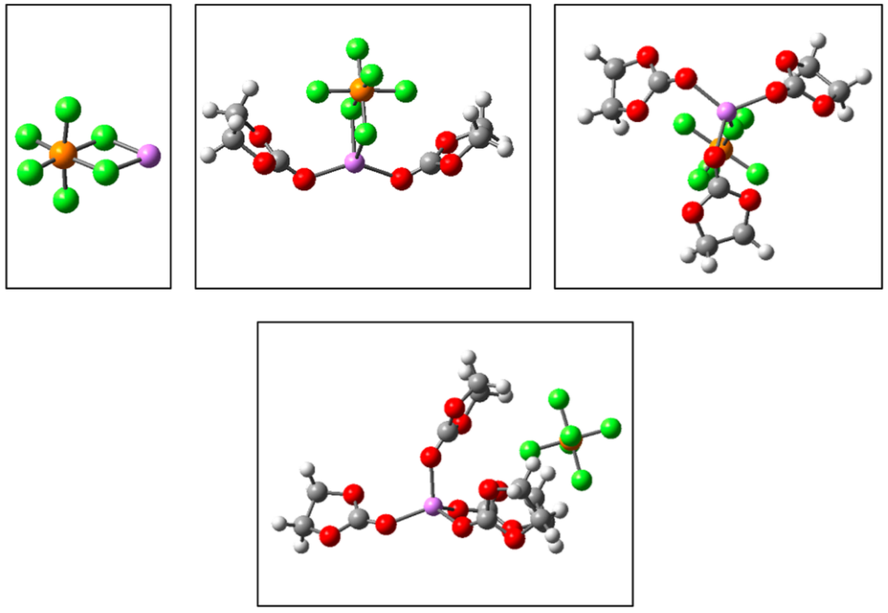


Salt: $Li^+ PF_6^-$

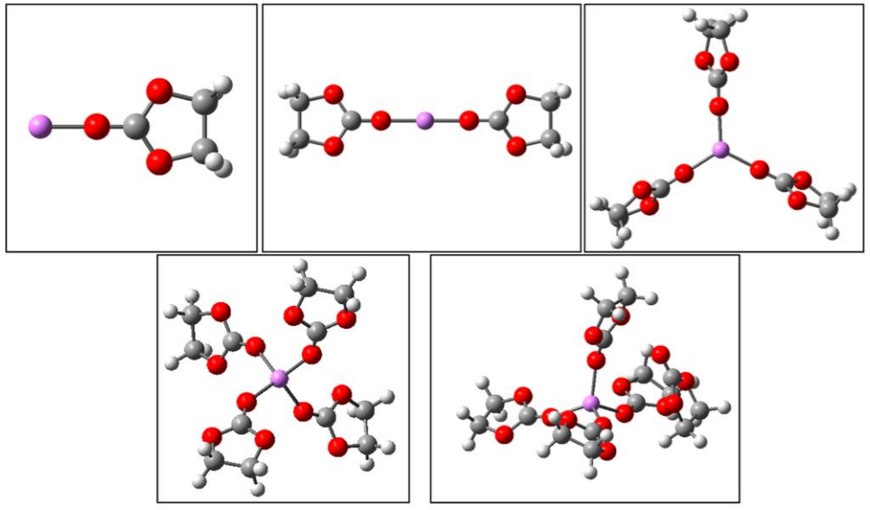




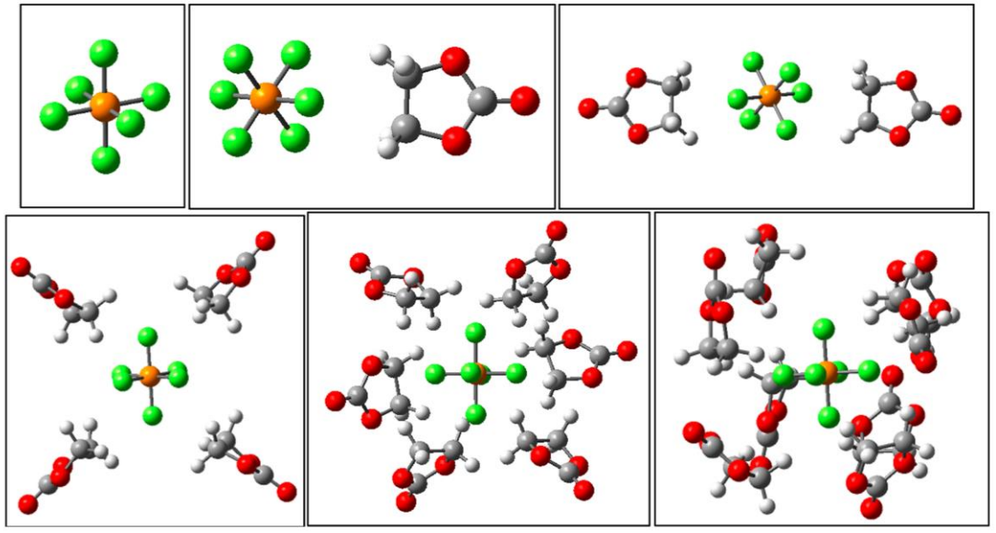
Typical structures in the electrolyte solution
PF_6^- & Li^+ & EC's



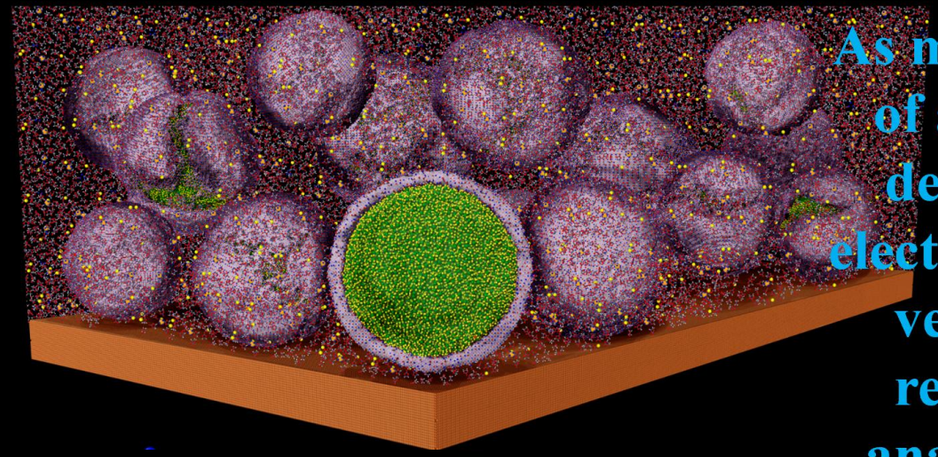
Typical structure in the electrolyte solution
Li^+ & EC's



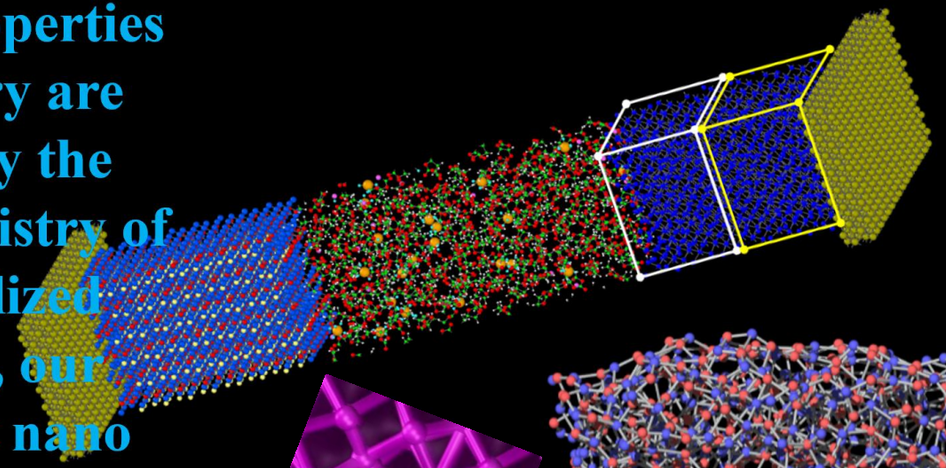
Typical structure in the electrolyte solution
PF_6^- & EC's



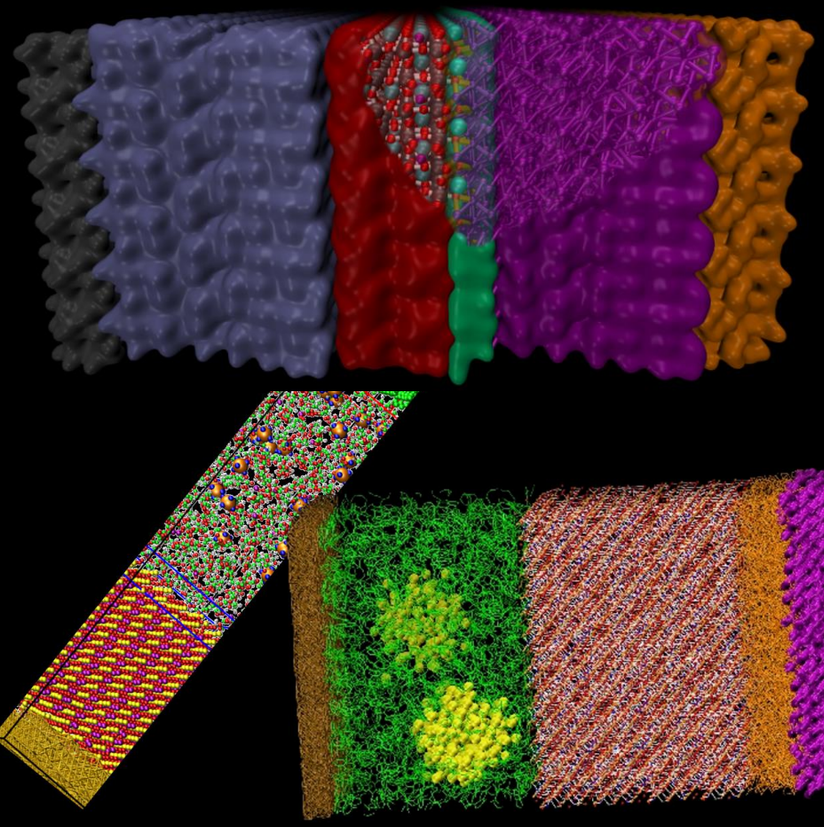
In Silico Foundry of Nanobatteries

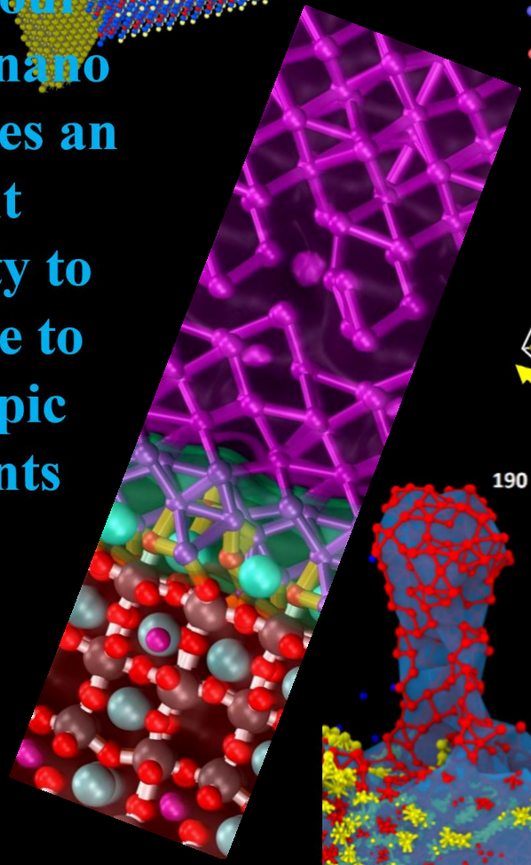


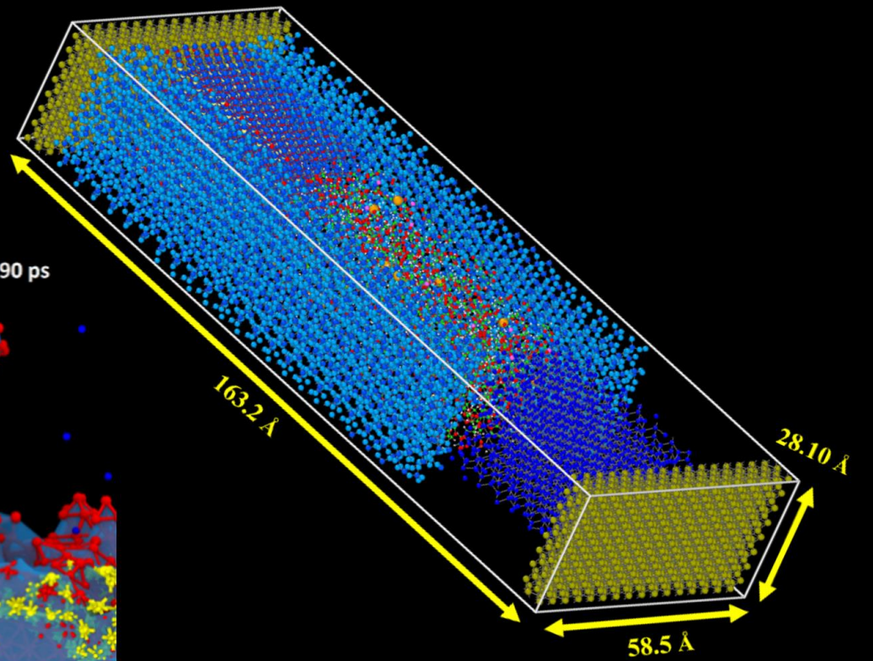
As most properties of a battery are decided by the electrochemistry of very localized reactions, our analysis at nano sizes provides an excellent opportunity to extrapolate to macroscopic components

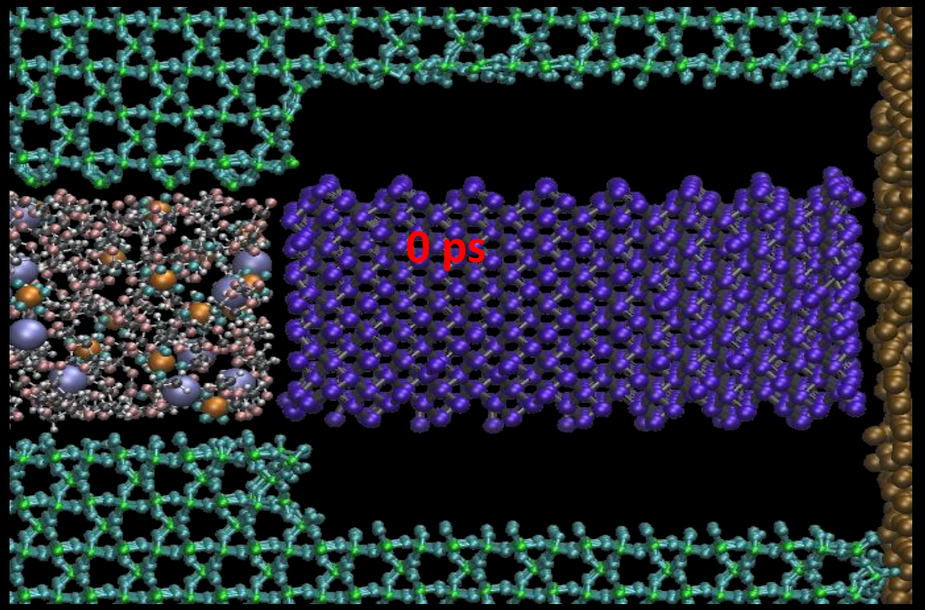


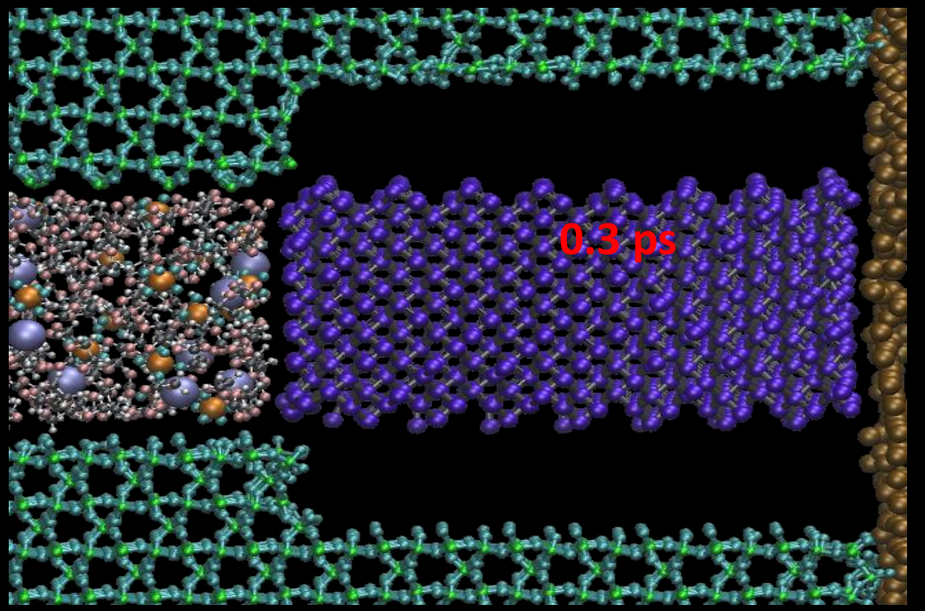
Software test-bed to analyze and simulate any type of nanomaterial components of a rechargeable battery

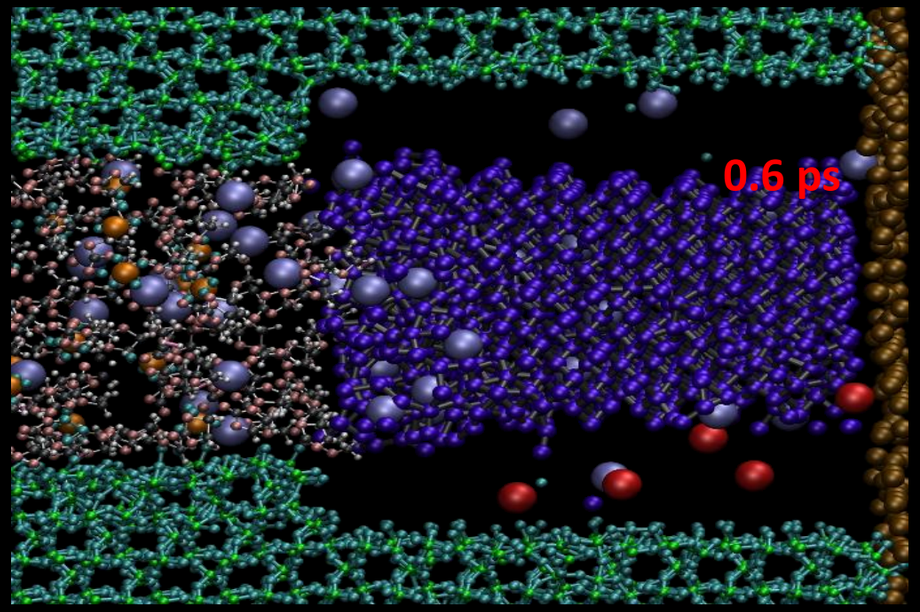


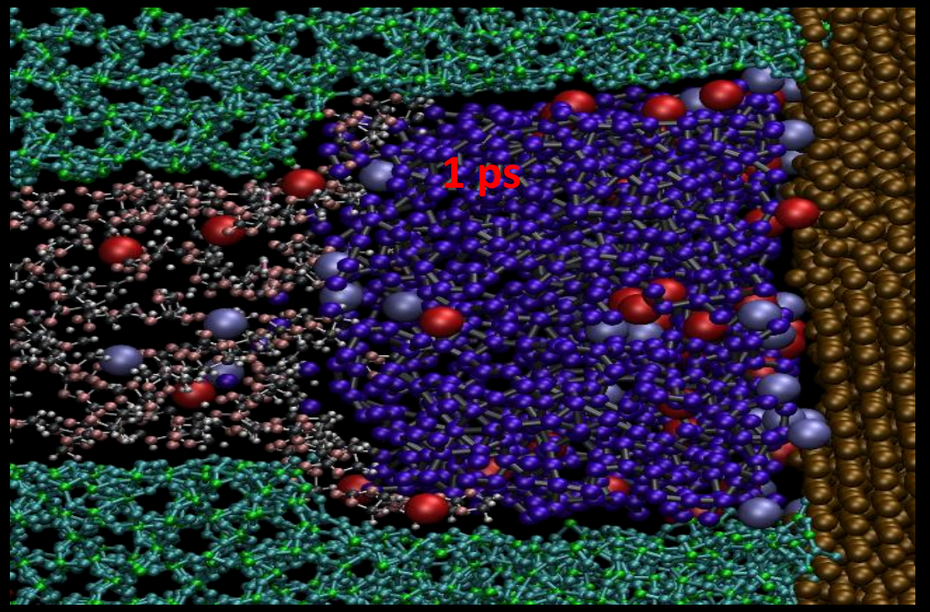










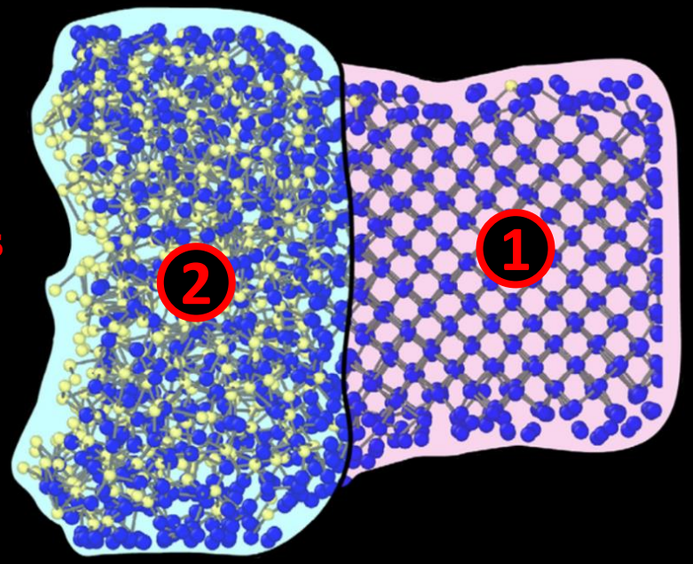


Swelling upon Lithiation

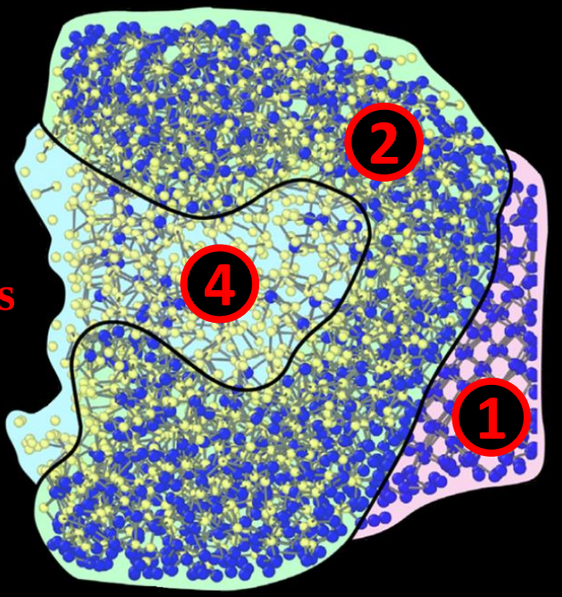
Silicon—ethylene carbonate interphase when an electric field of 4.5 Volt/Å is applied

Concentrations during lithiation

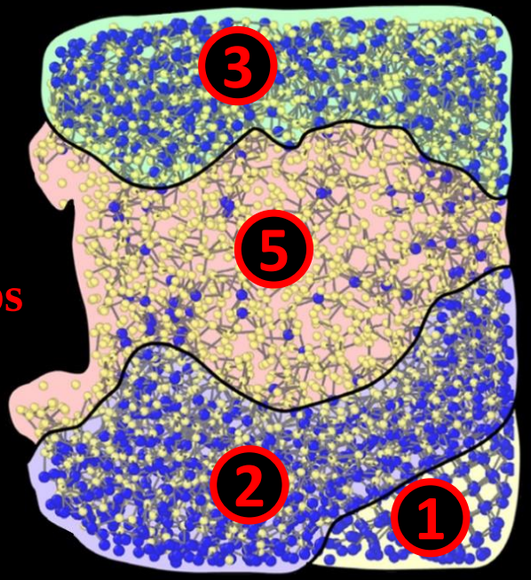
84 ps



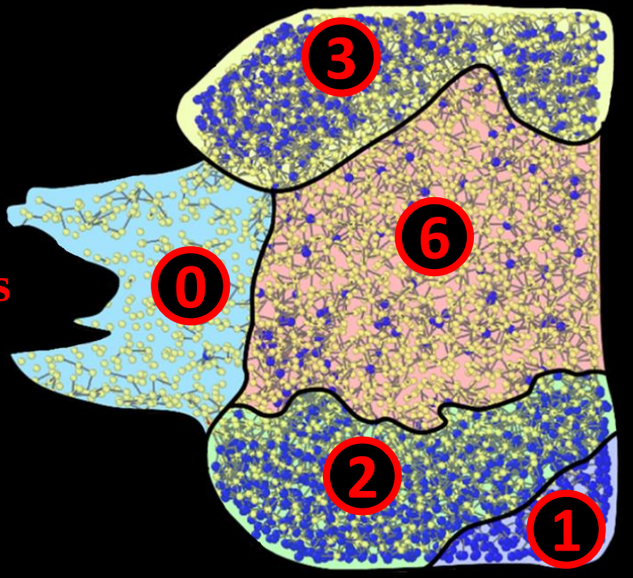
226 ps



336 ps

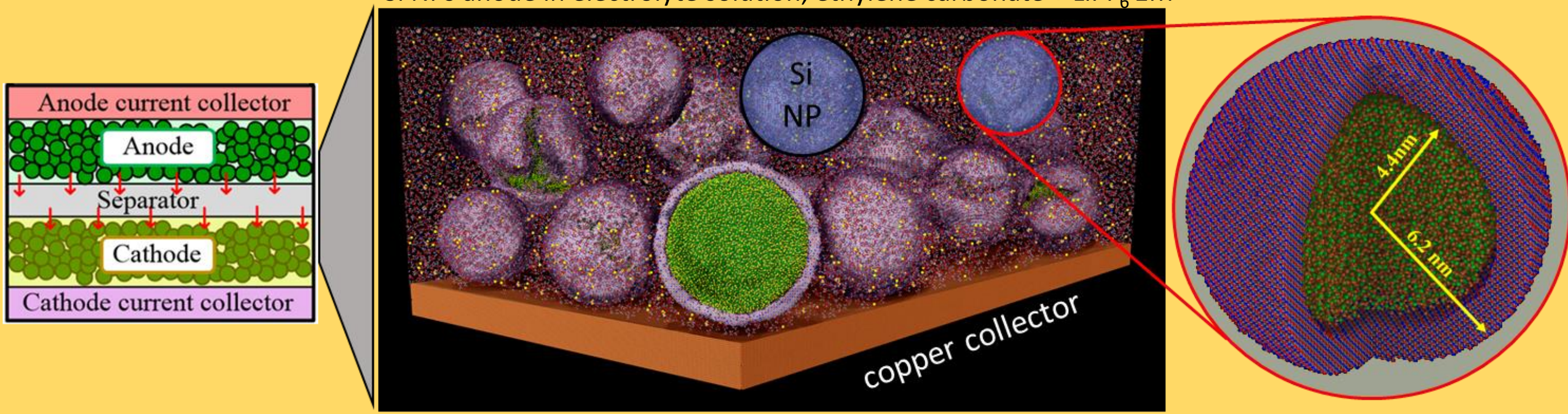


524 ps

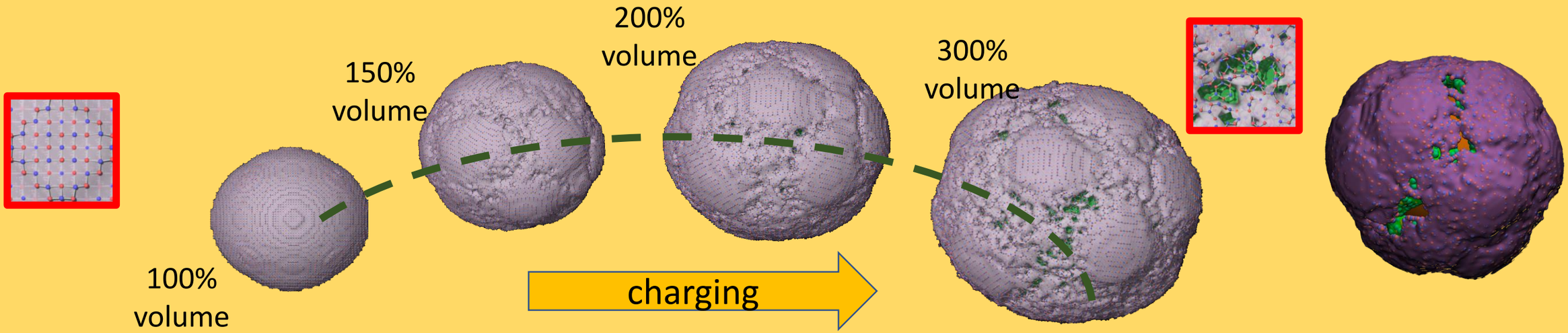


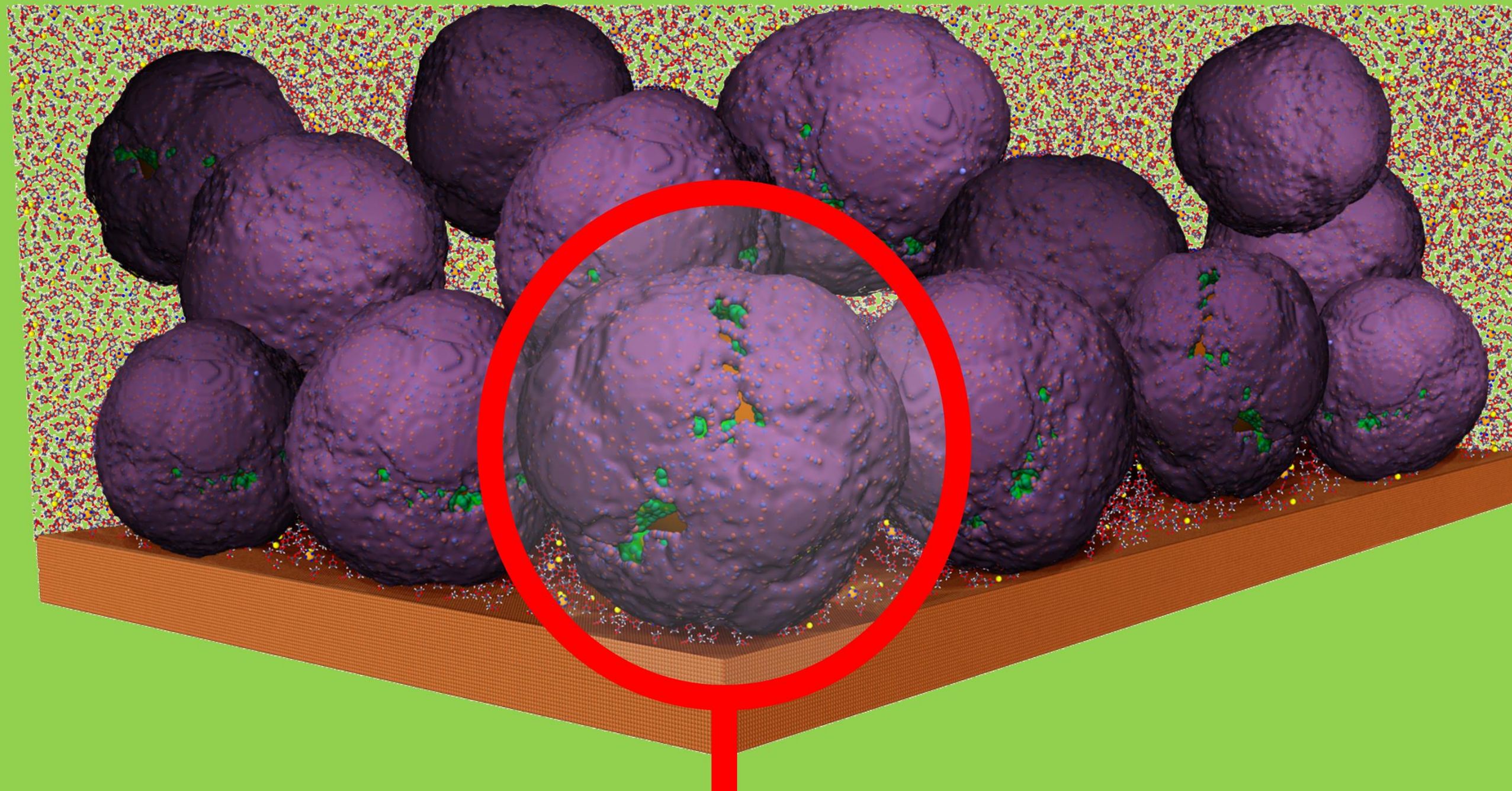
Electrode Expansion Due to Lithiation

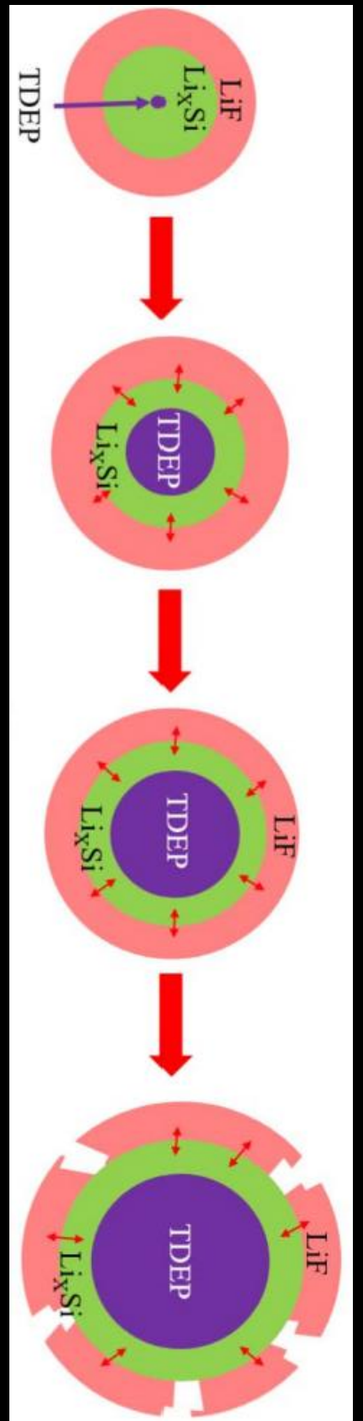
Si NPs anode in electrolyte solution, ethylene carbonate + $LiPF_6$ 1M



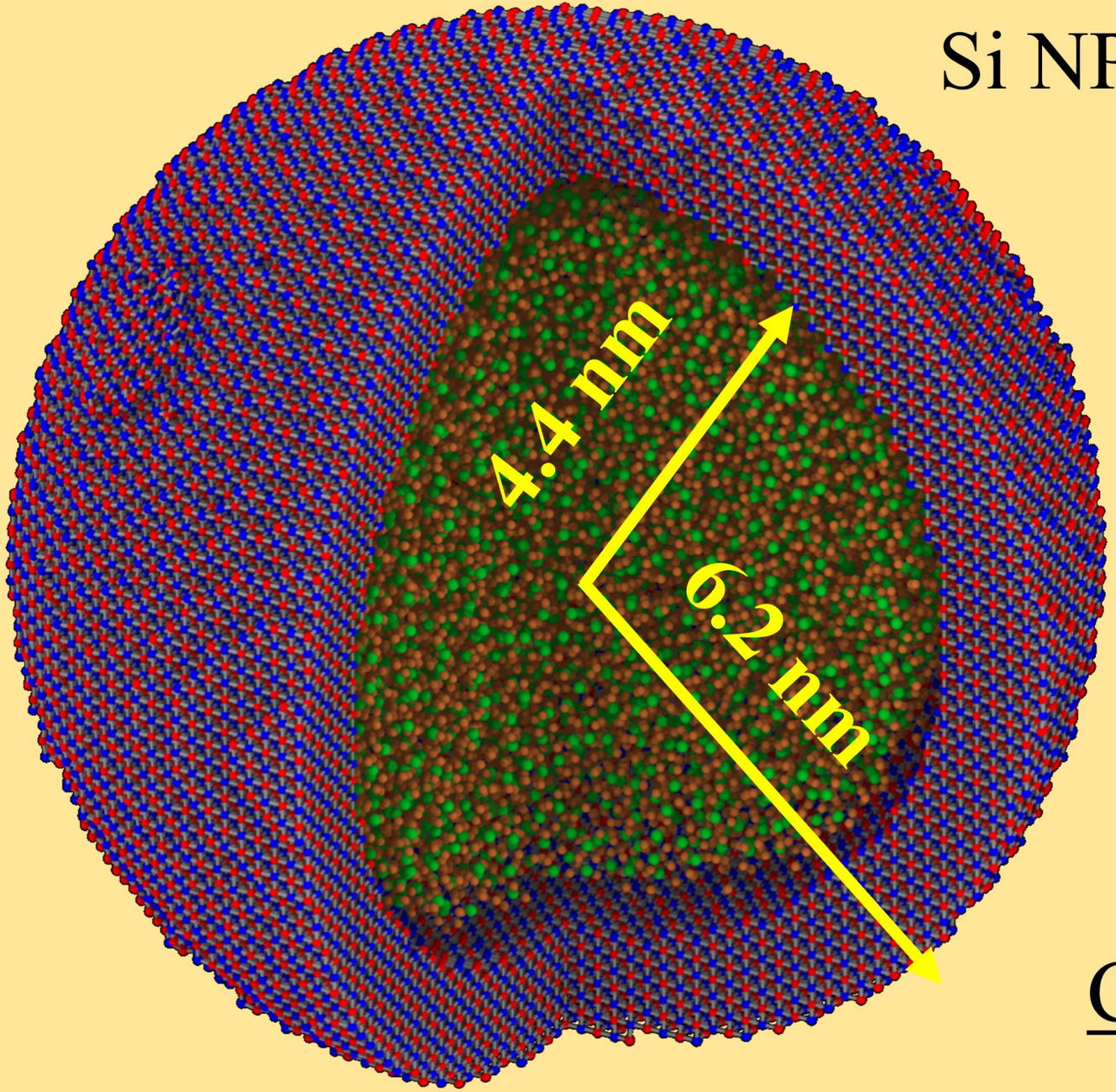
Questions for LIB: Si anodes: Li^+ diffusion in SEI film? SEI mechanics/Si expansion?
Li intercalation mechanical damage? Si-SEI interplay/cell performance?







Si NP coated with LiF SEI

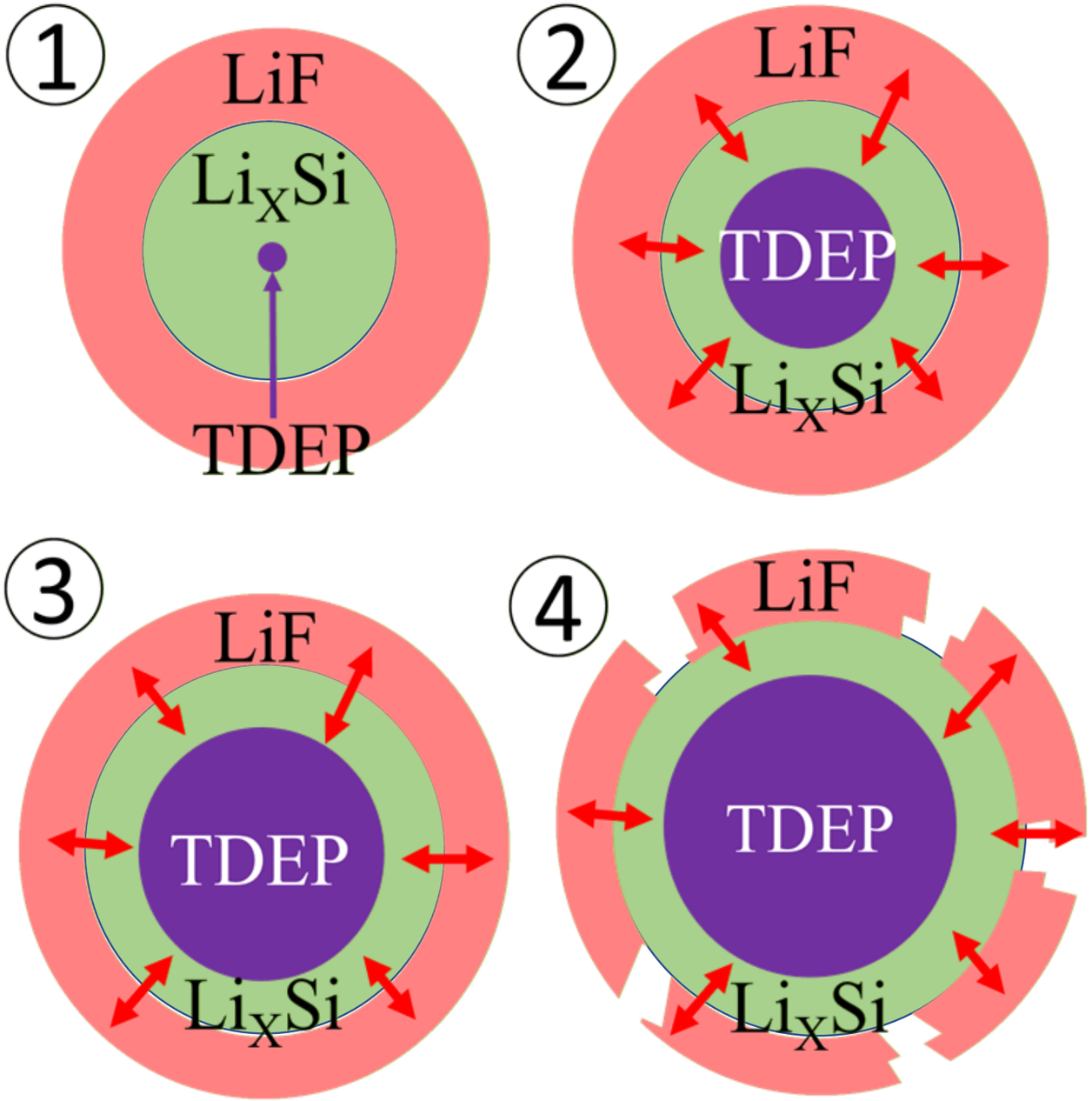


A TDEP, V(r), r = f(*t*) is centered in the NP

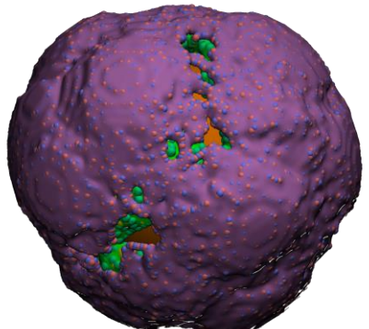
Composition

$$V[r(f(t)]^{TDEP}(Si_{5116}Li_{17996})^{core}(Li^{+}F^{-})^{SEI}_{28472}$$

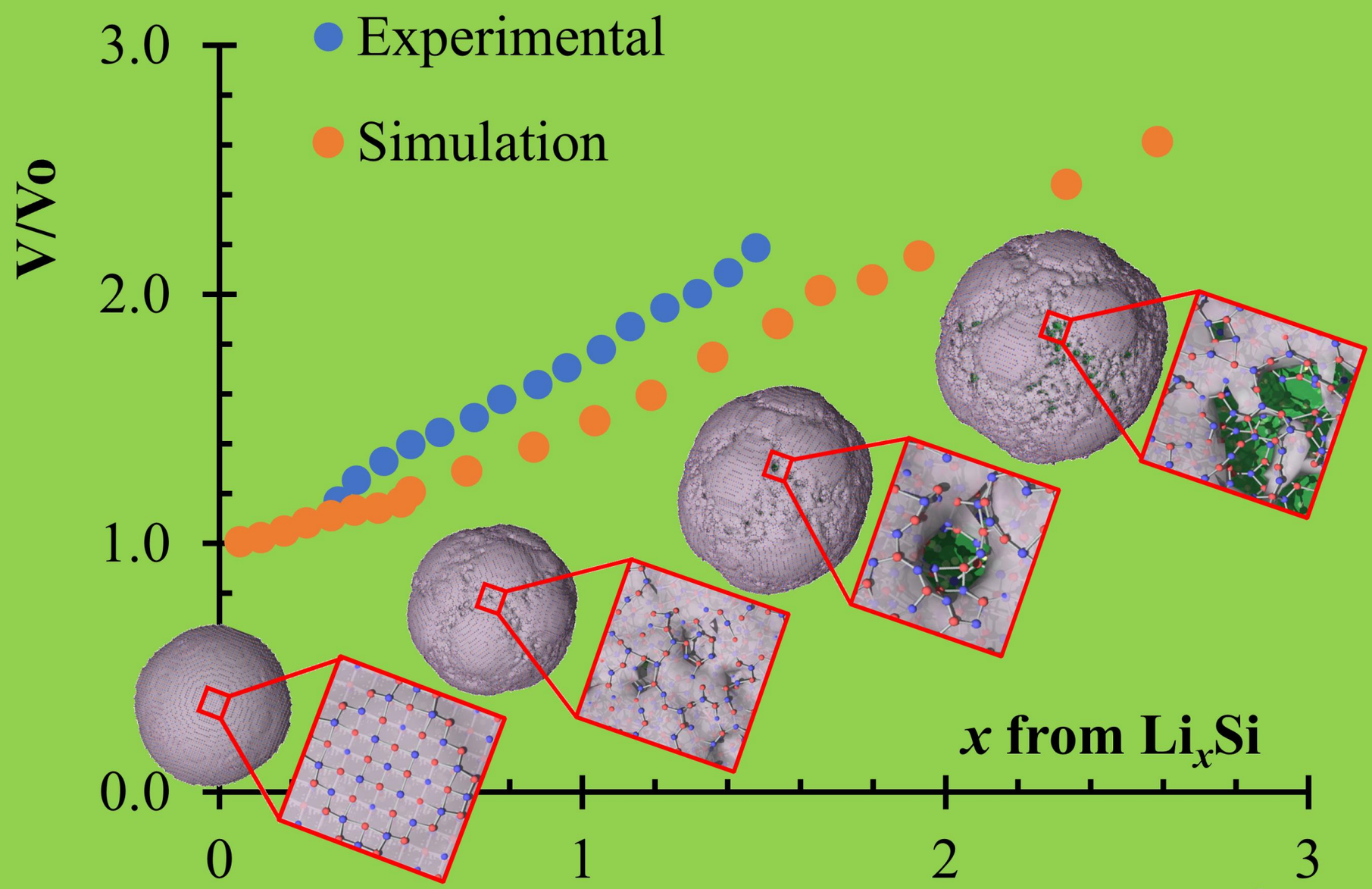
Time depending expanding potential (TDEP)



TDEP eliminates fast charging effects; only intrinsic expansion effects are considered.



Volume expansion due to lithiation

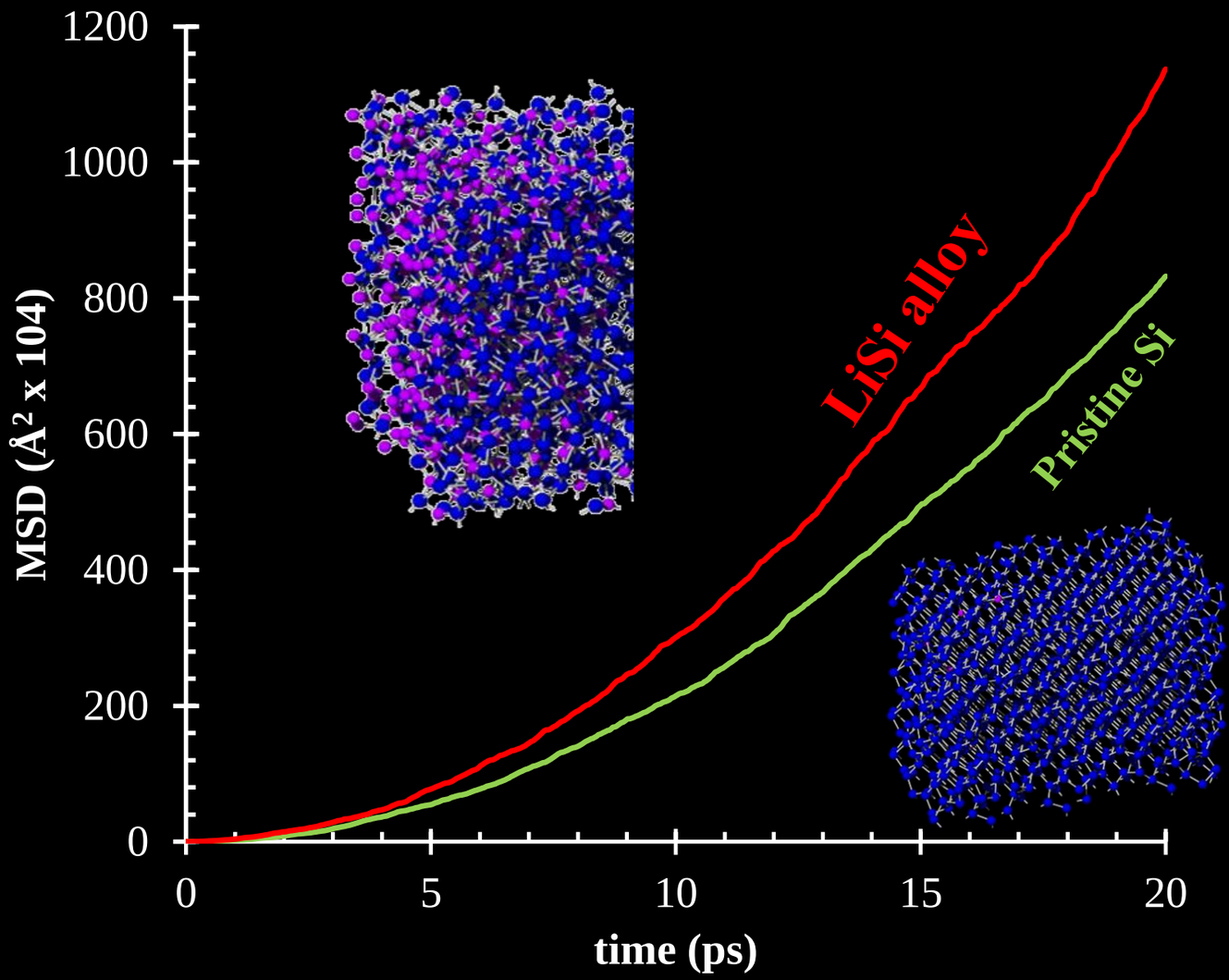


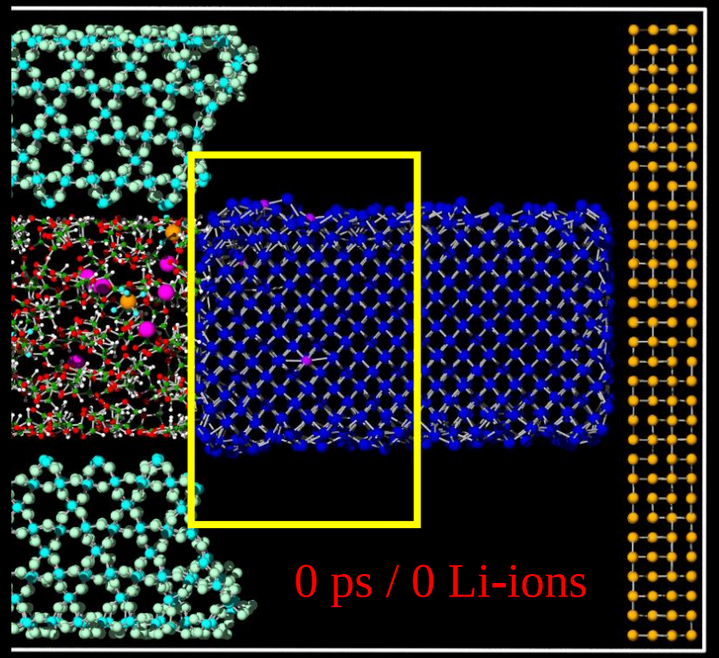
6

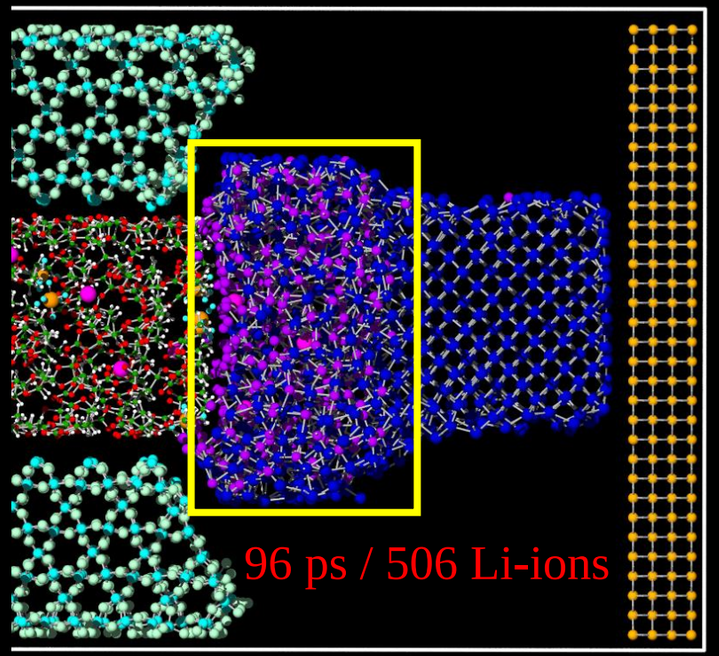
Li-diffusion in the silicon anode during charging

Diffusion of Li-ion through amorphous LiSi alloy seems greater than in a silicon crystal

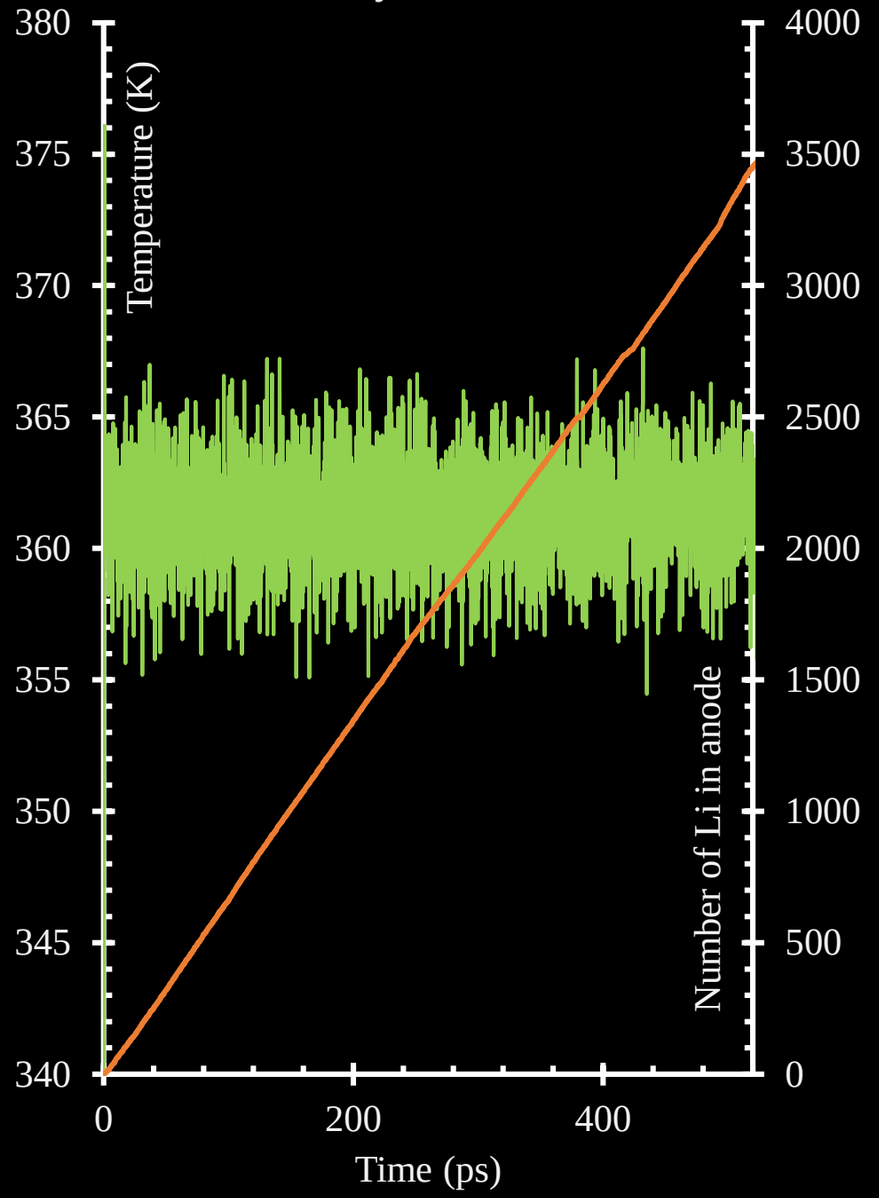
The MSD for same region (yellow squares) at 0 ps (pristine Si) and at 96 ps (SiLi alloy)



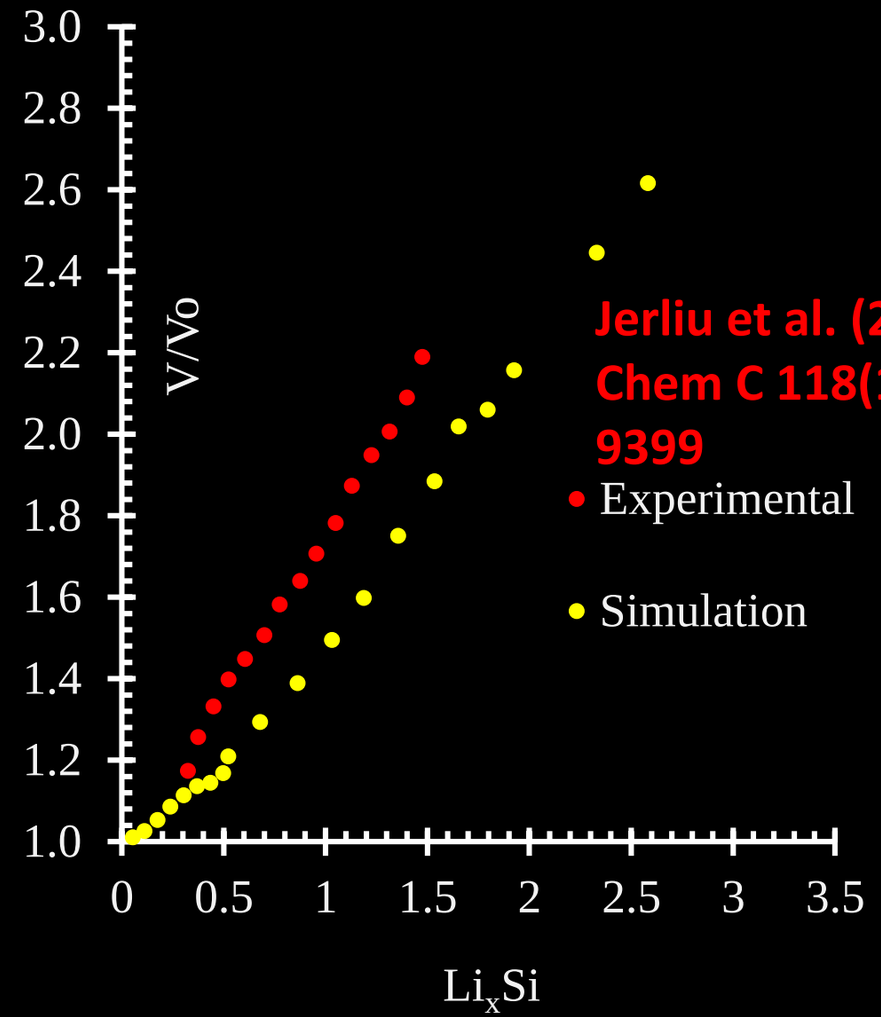


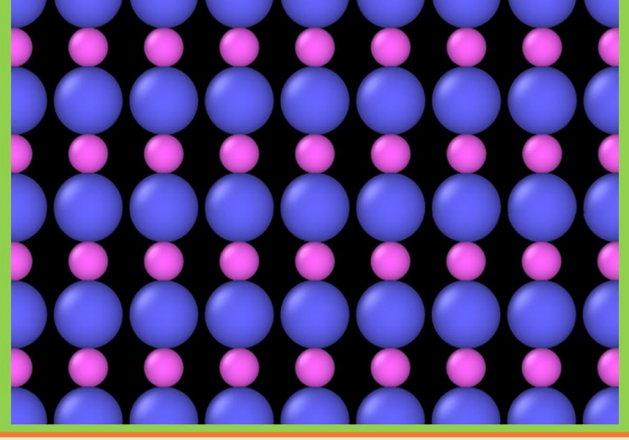


- Number of Li in anode increases linearly with time
- Volume ratio (V/Vo) shows a linear behavior with number lithium.
- Volume increases linearly with time. This behavior is simulated in the next work, in which we study the cracking due to SiLi expansion.



Volume expansion during charging



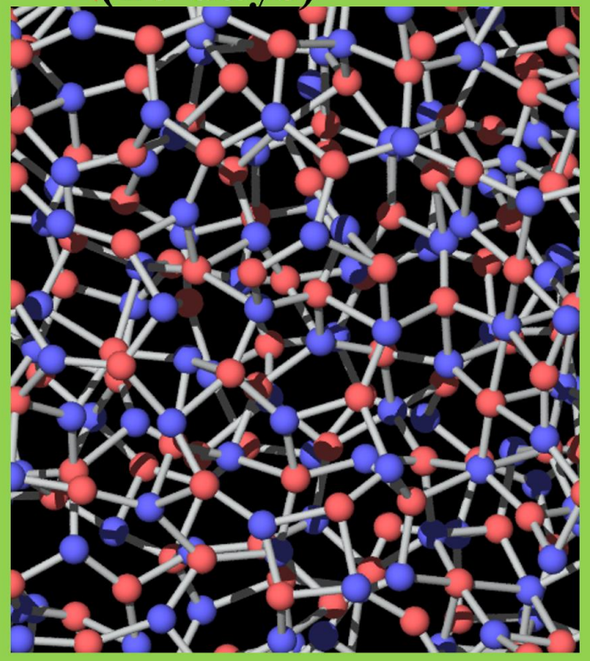


Charging current effects

(and wall times)

current (mA)

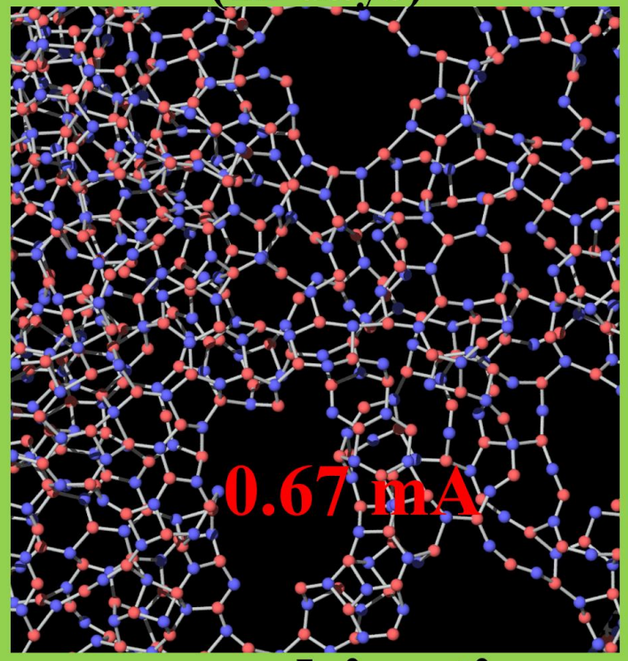
(16 days)



2.66 mA

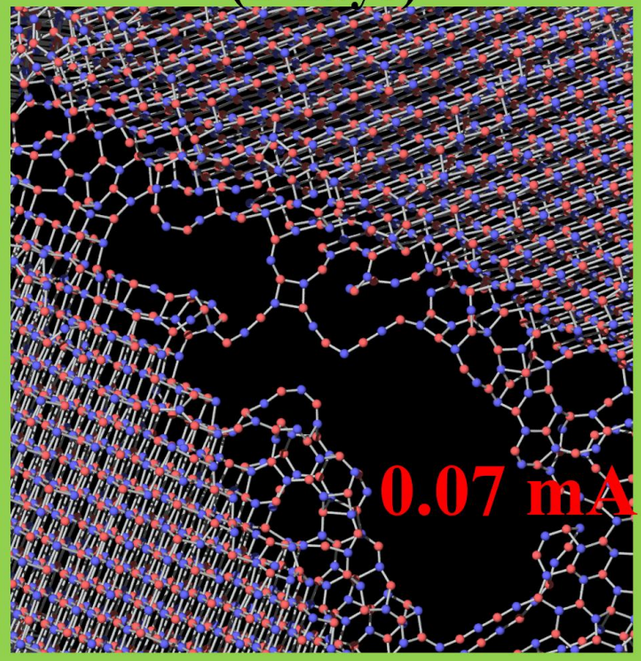
amorphization

(11 days)



amorphization + cracking

(2 days)

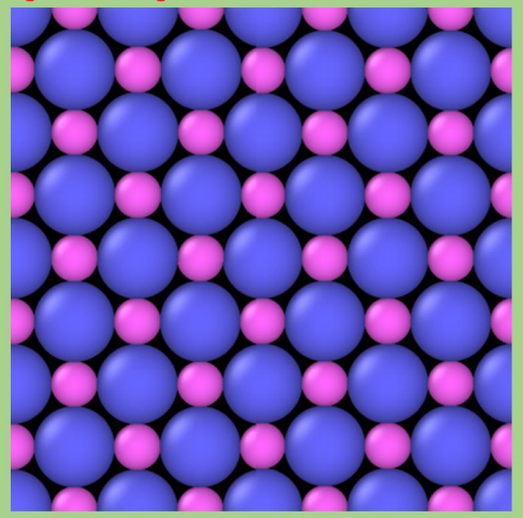


cracking

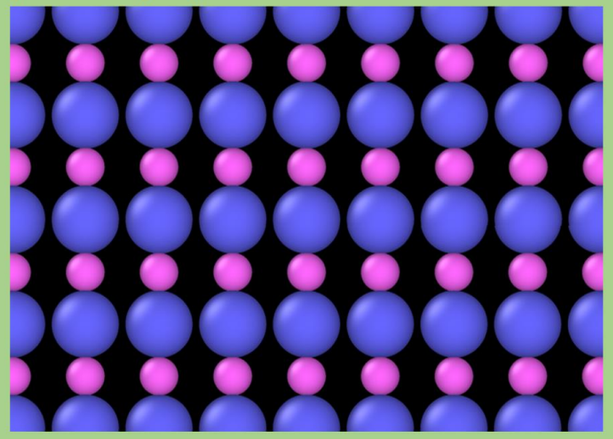
Charging current effects

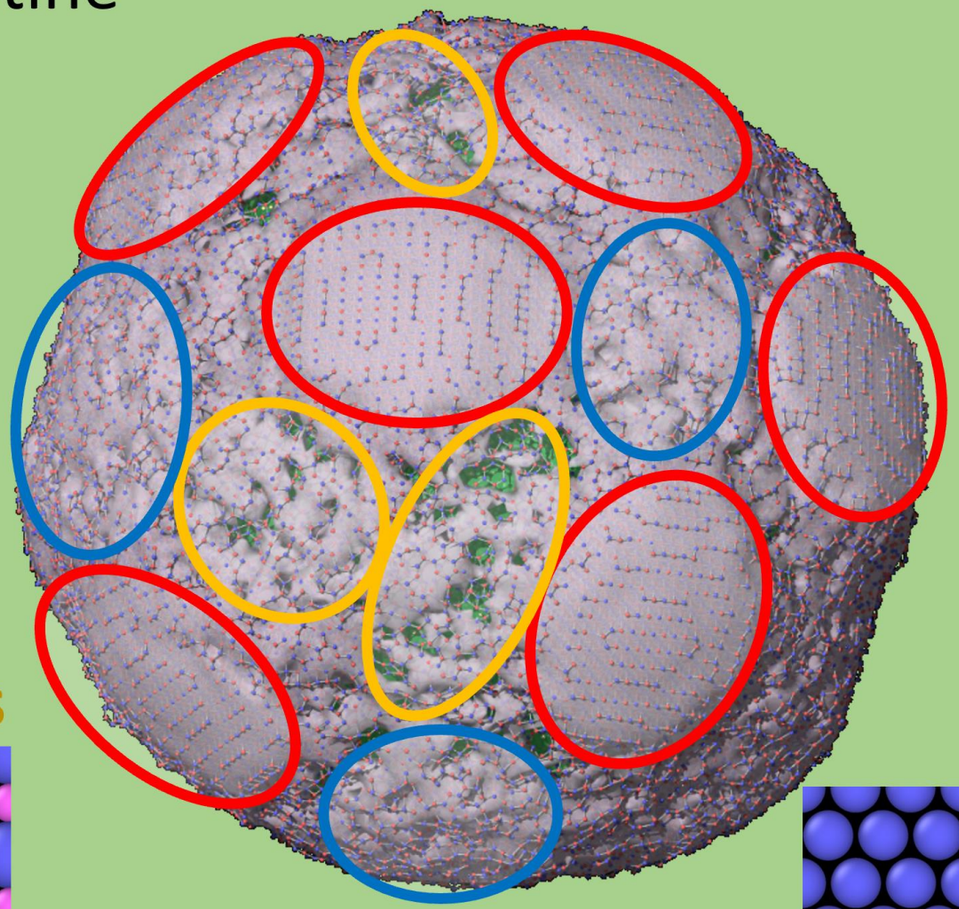
Cracking take place on planes (111) and (110), the (100) planes remain pristine

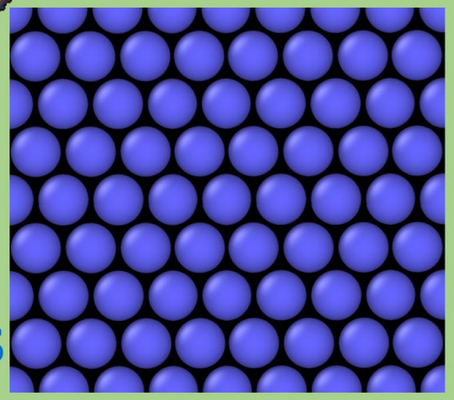
(100) red circles



(110) yellow circles

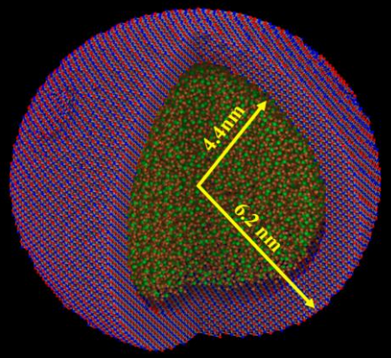






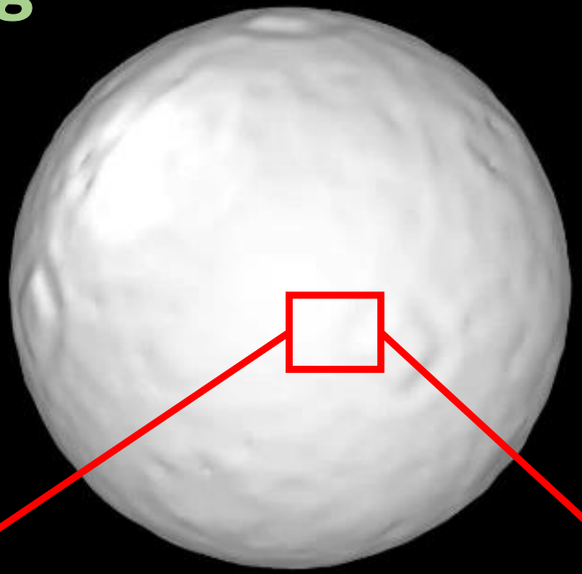
(111): blue circles

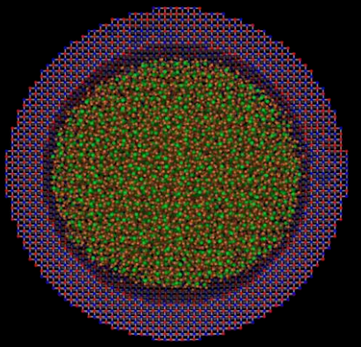
SEI Cracking



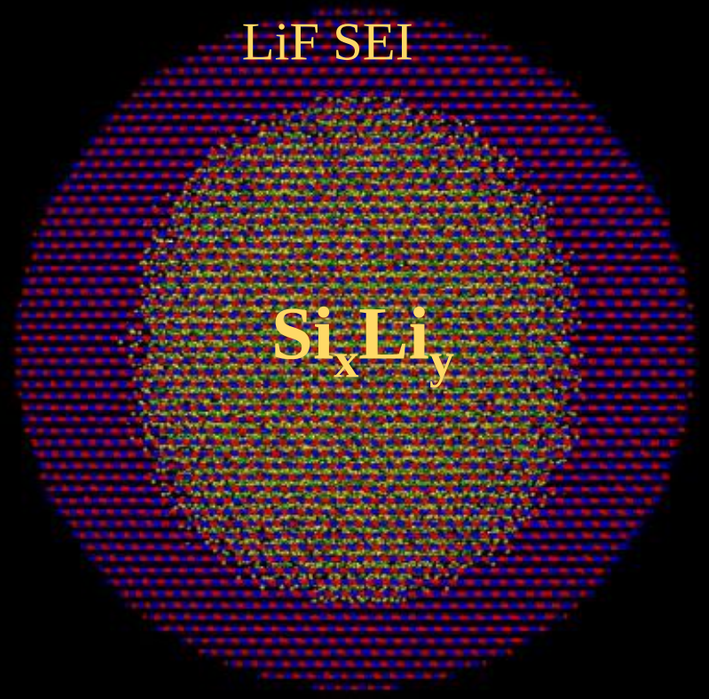
core sphere radius

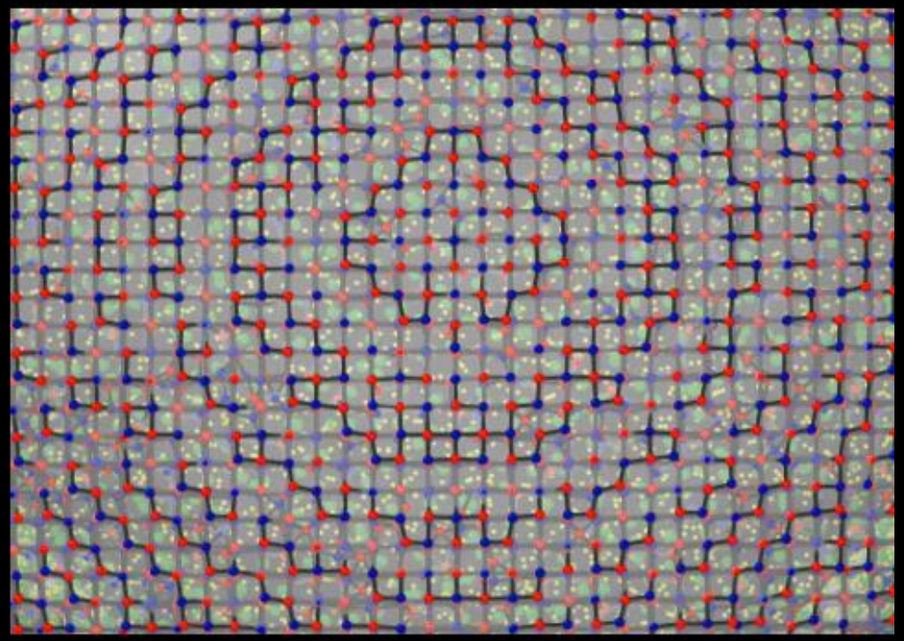
0.00 Å





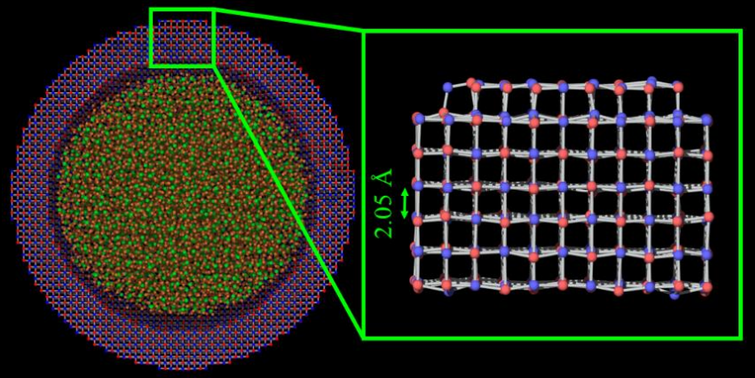
LiF SEI





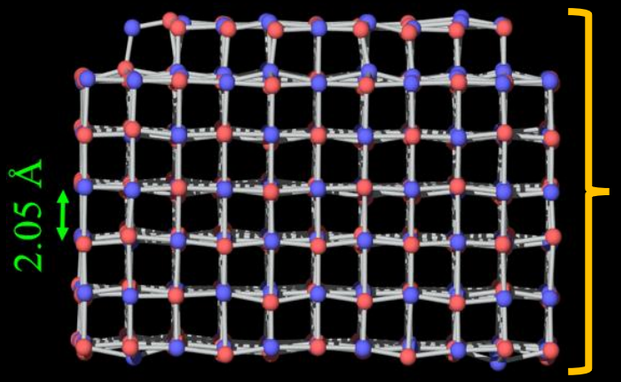
Cracking (by an expanding core) of Si_xLi_y covered by a SEI of LiF. Core expanding sphere radius goes from 0 to 56 Å

Cracking on LiF Shell

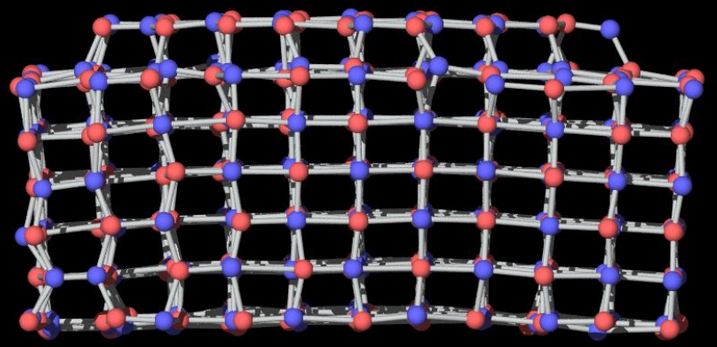


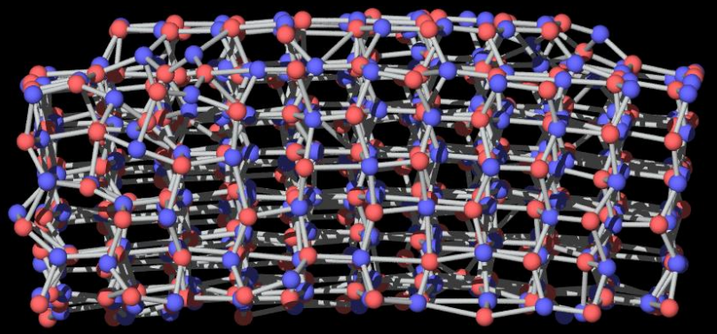
A piece of the LiF is extracted from the whole shell to study the cracking mechanism.

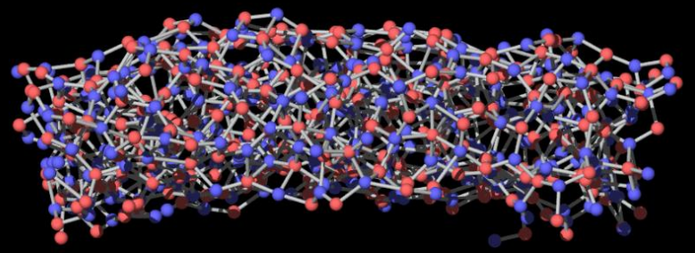
Initially the shell has a width 12.3 Å



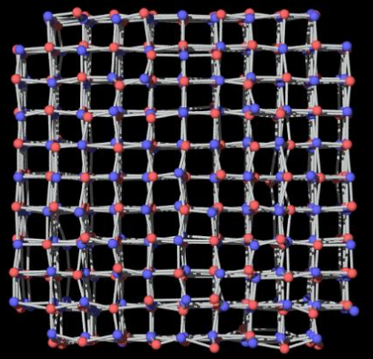
Front view of the extracted LiF Shell

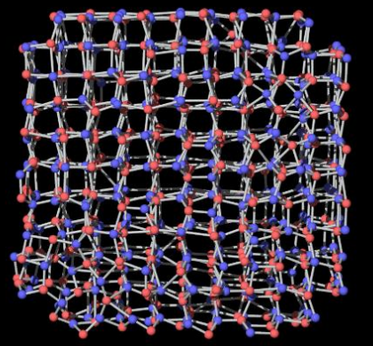


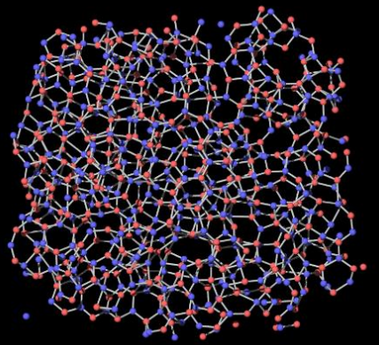




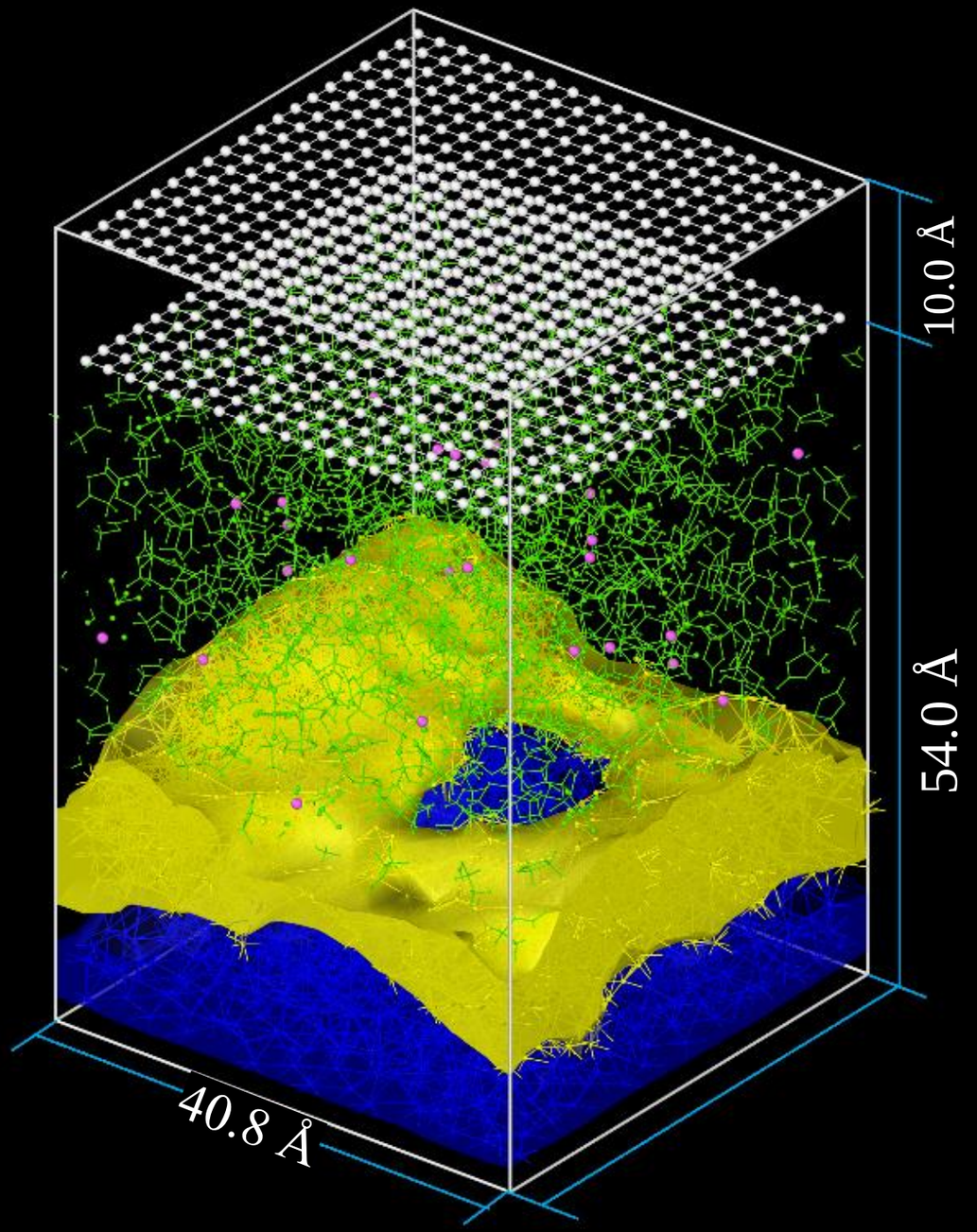
Top view of the extracted LiF Shell

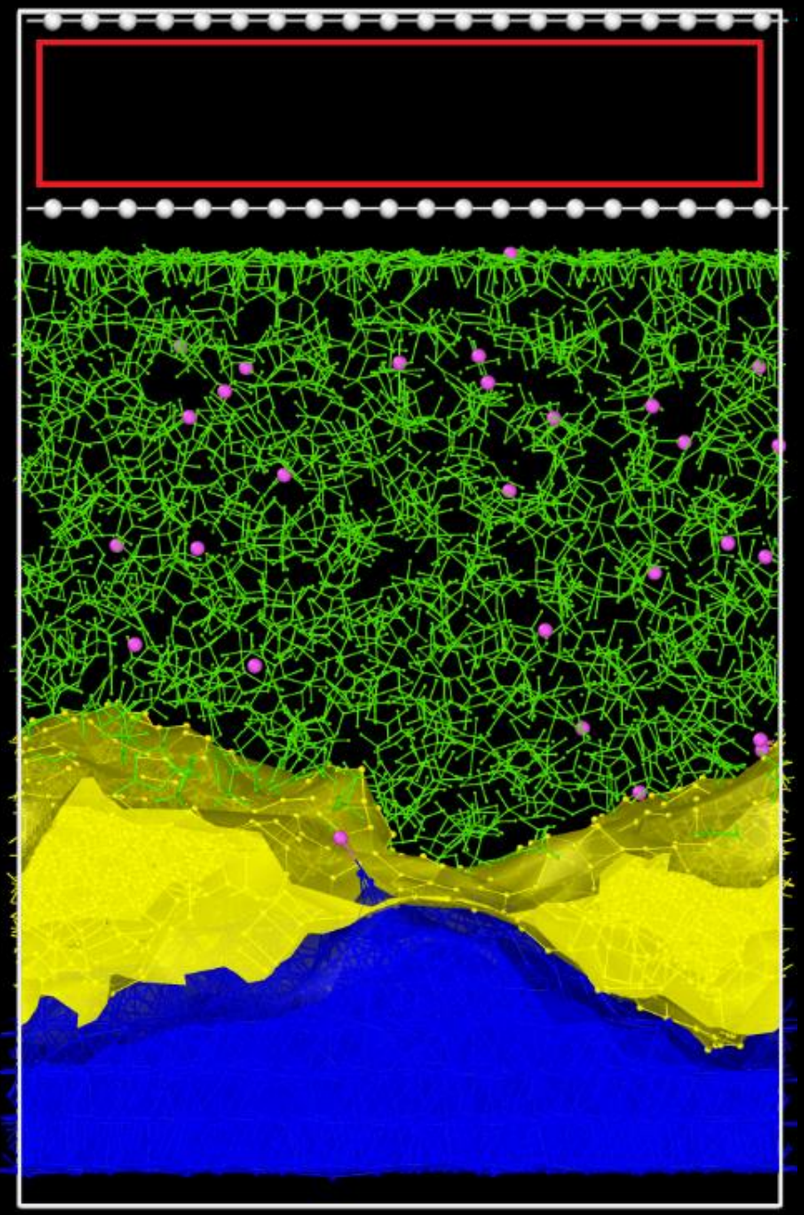


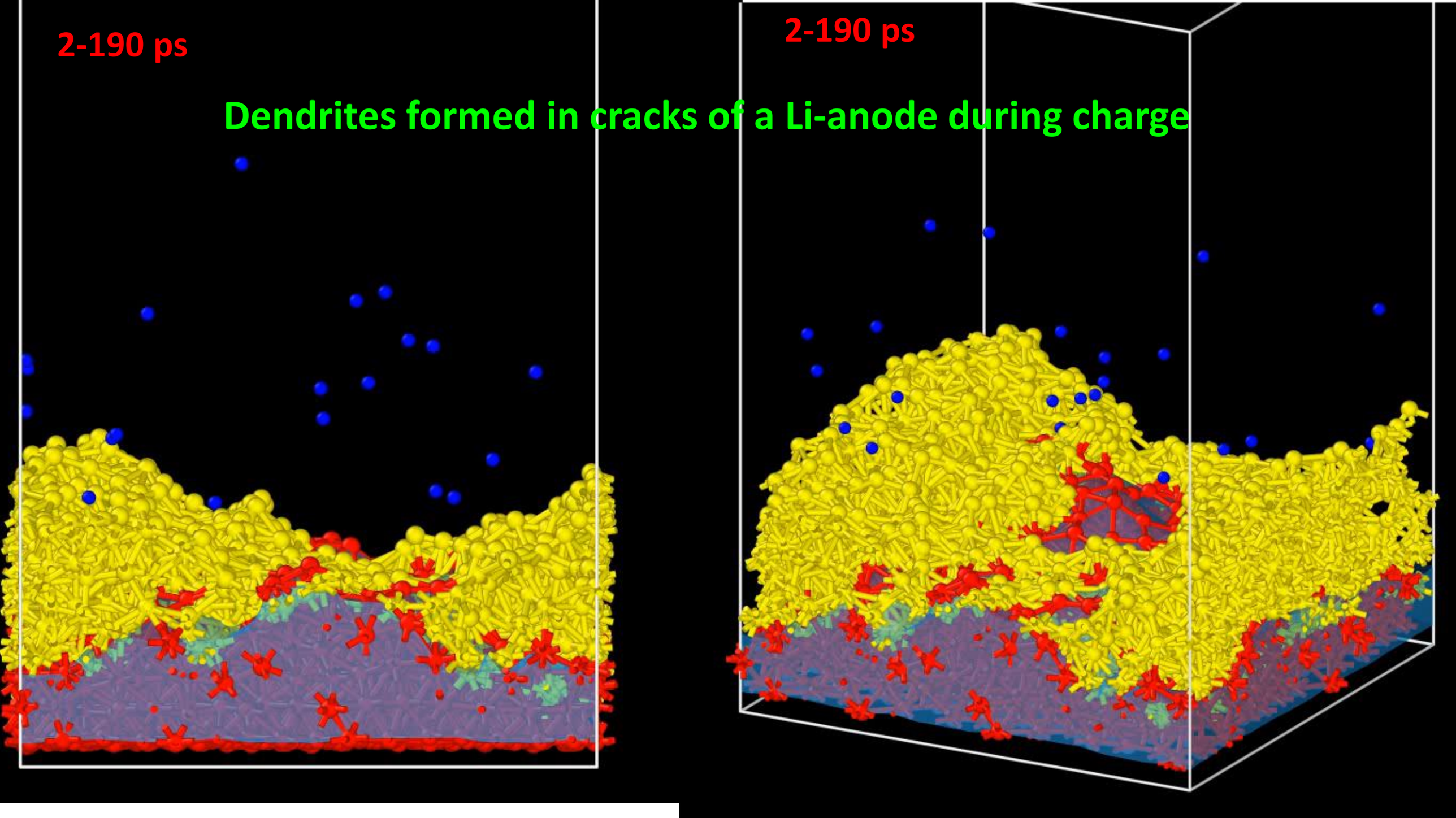


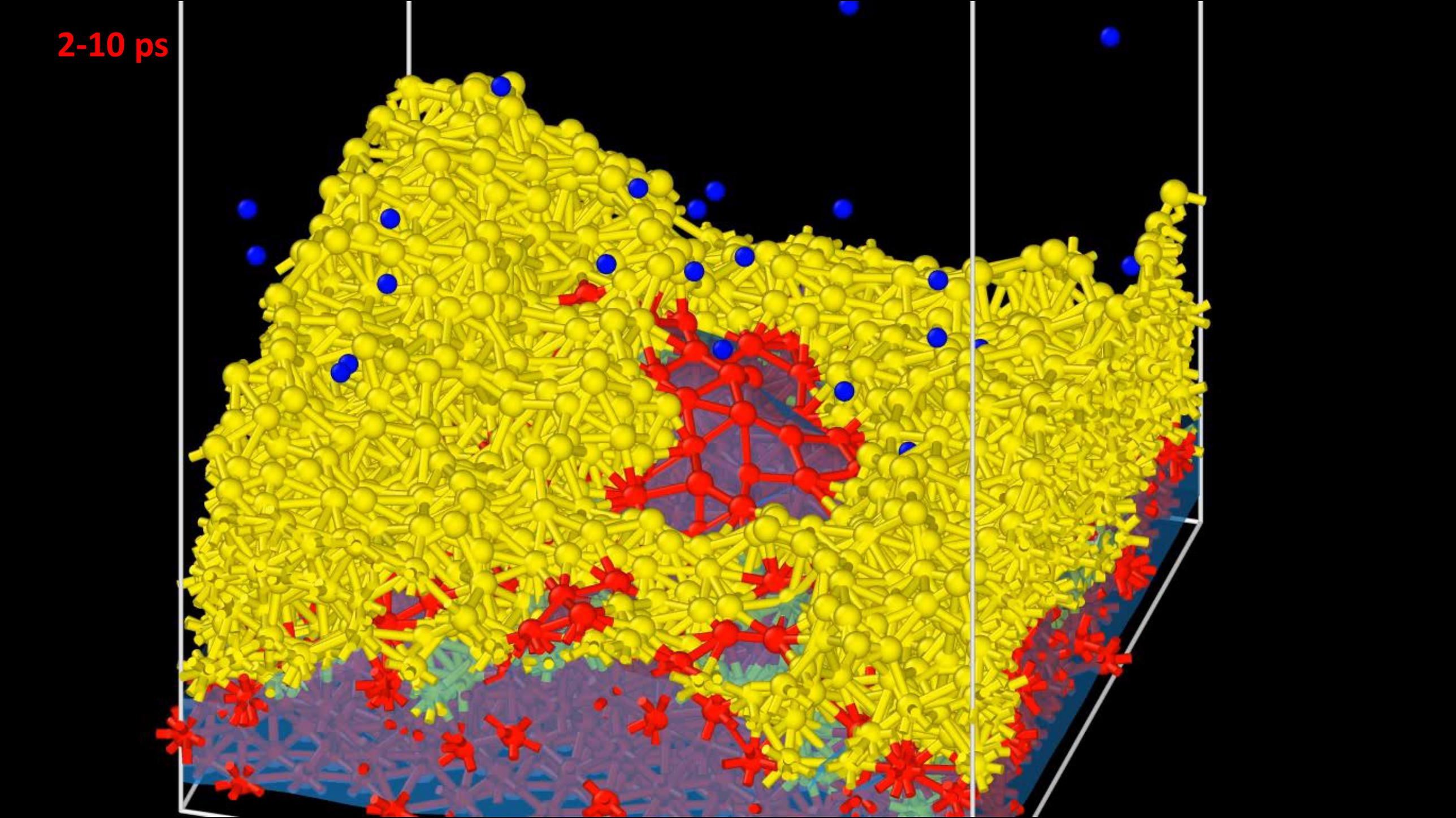


Dendrites formed in cracks of a Li-anode during charge

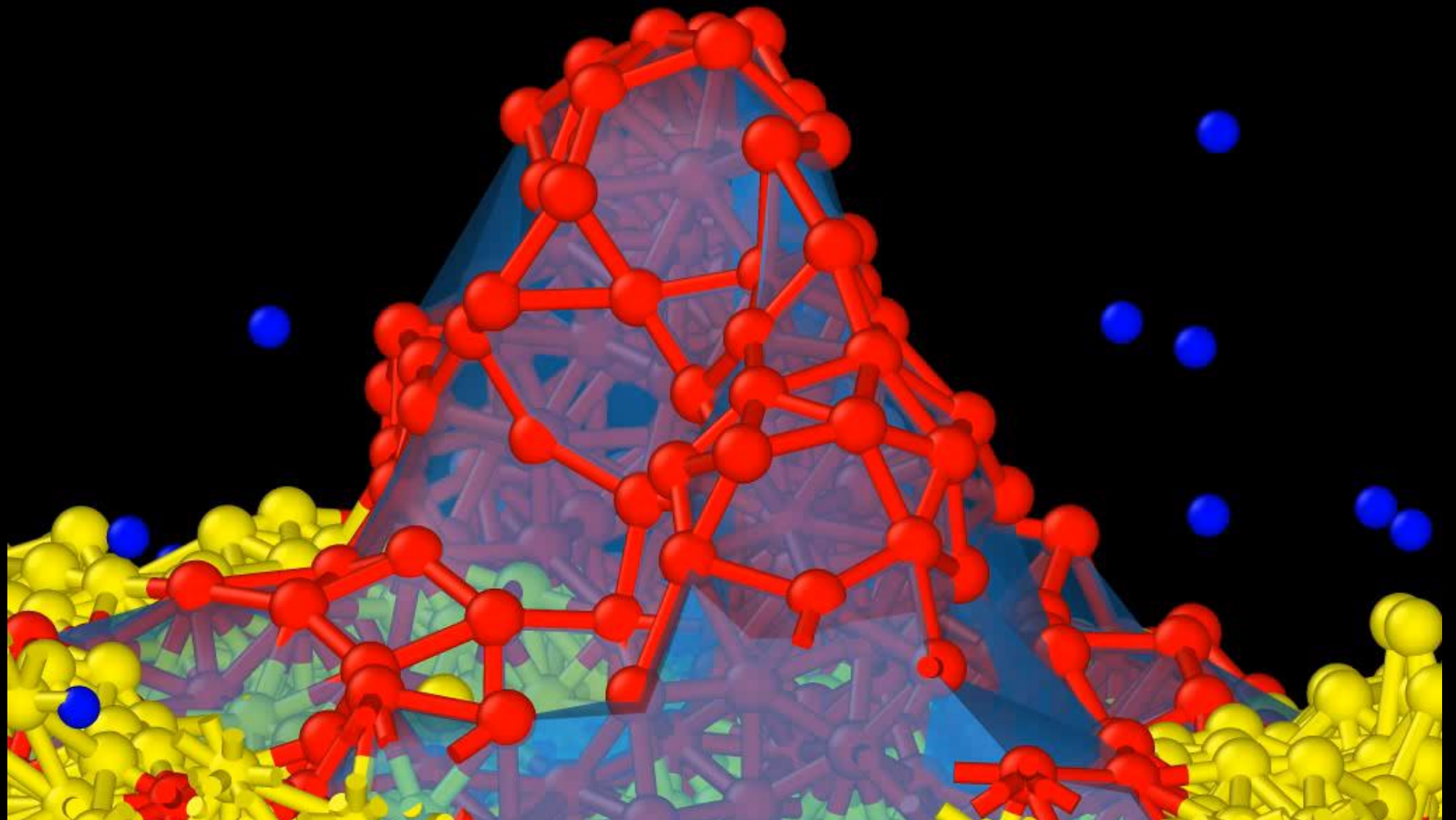




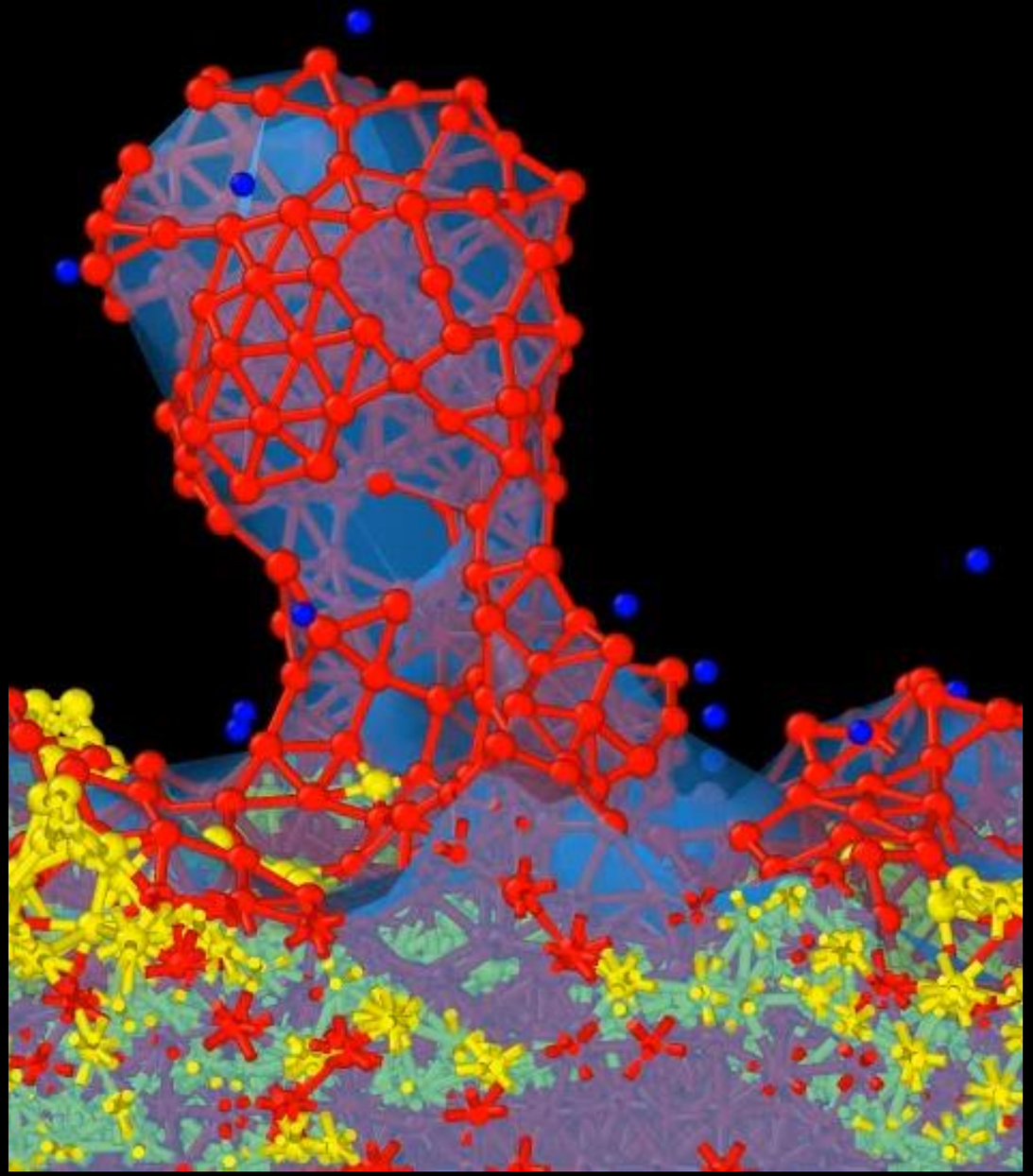

2-190 ps
2-190 ps
Dendrites formed in cracks of a Li-anode during charge

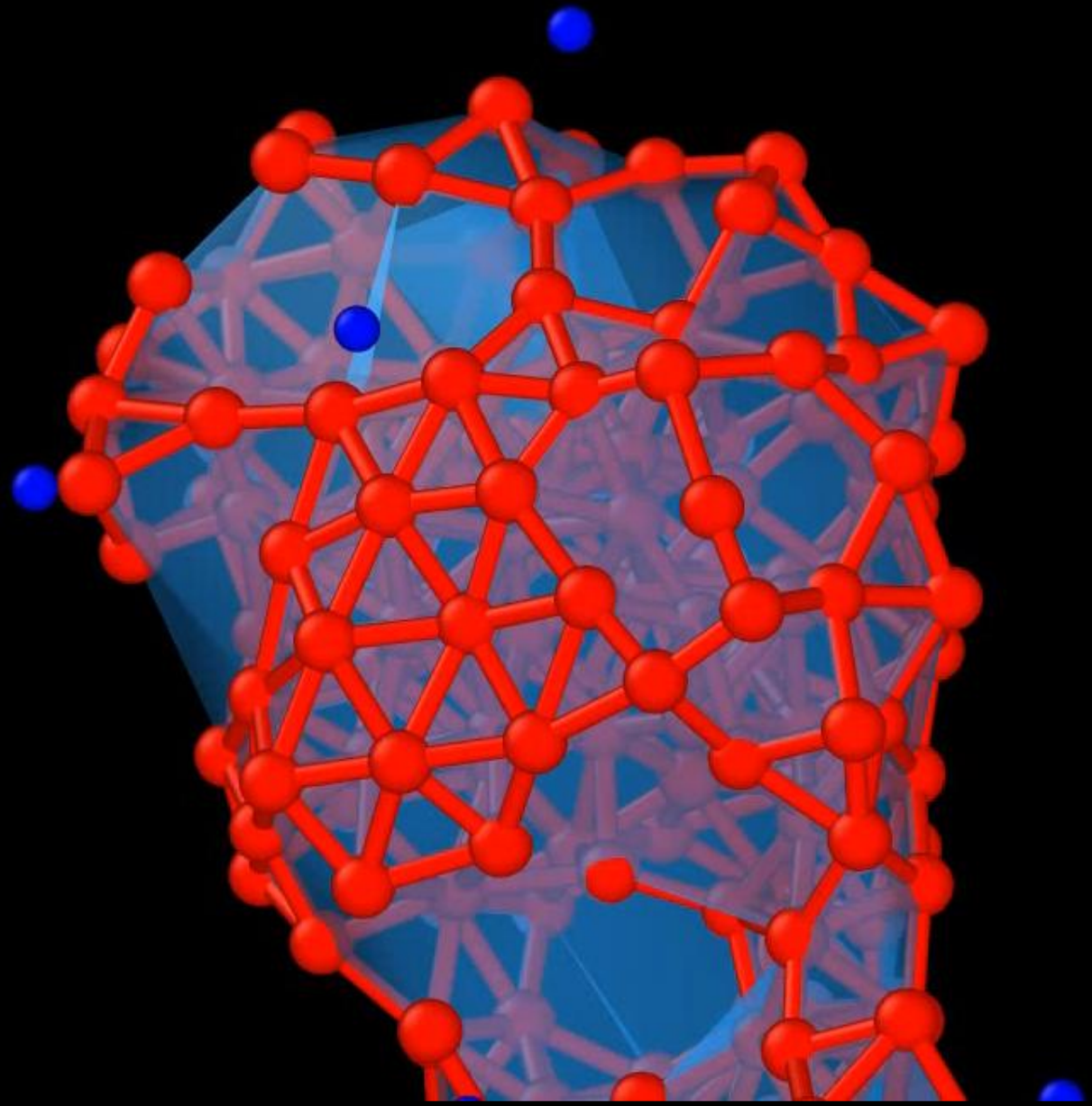

2-10 ps

80-85 ps



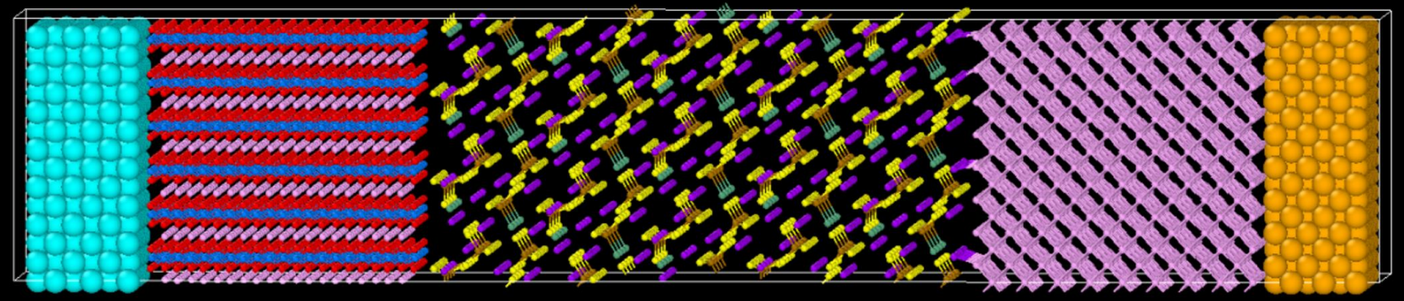
170-175 ps



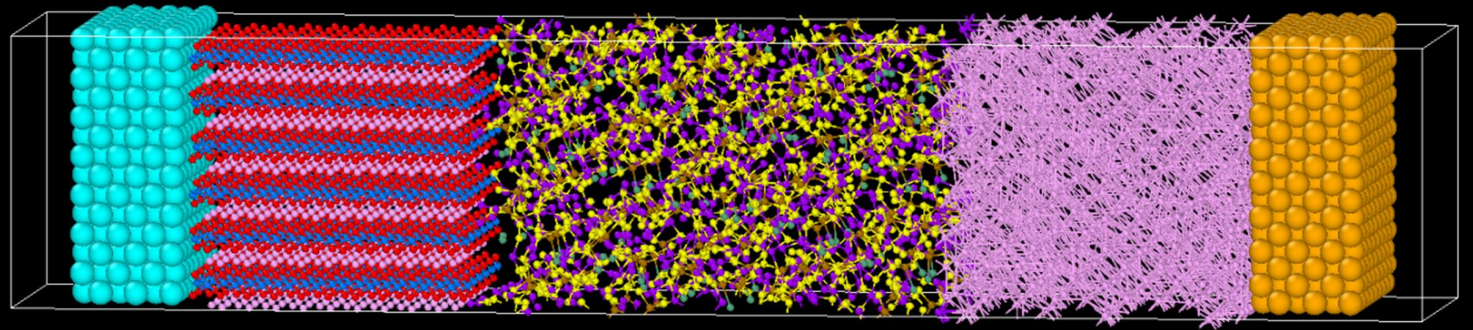


$Li_{840}P_{240}S_{960}I_{120}$ SSE battery

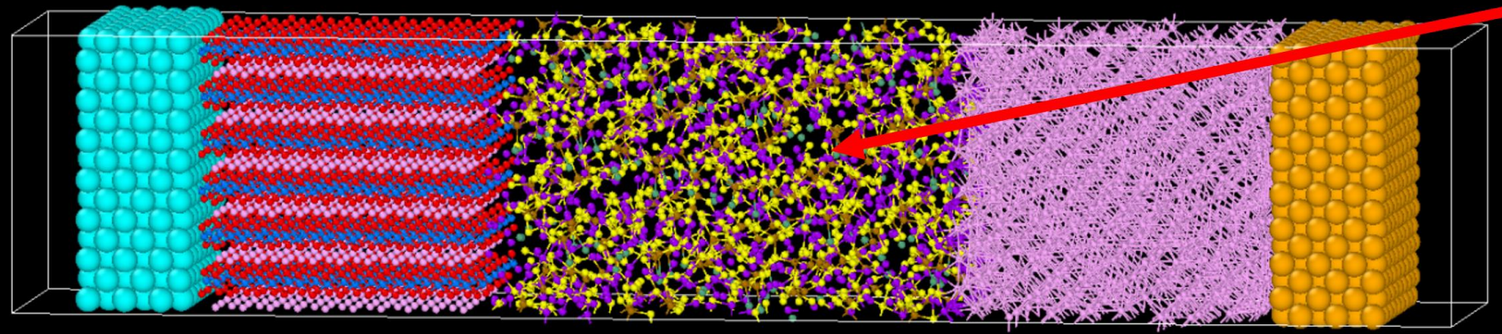
Initial geometry

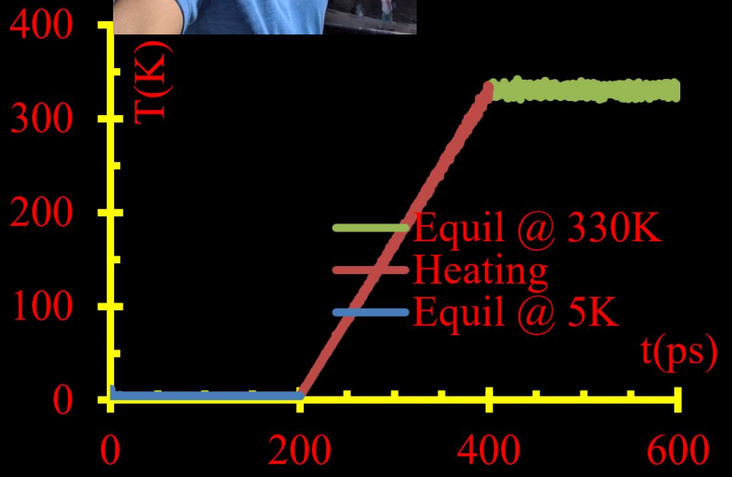


After equilibration at 5K



After heating from 5K to 330K





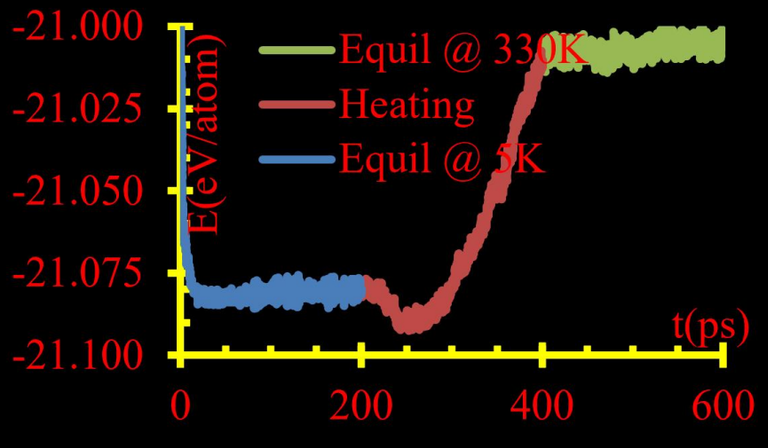
collectors
Al
Cu

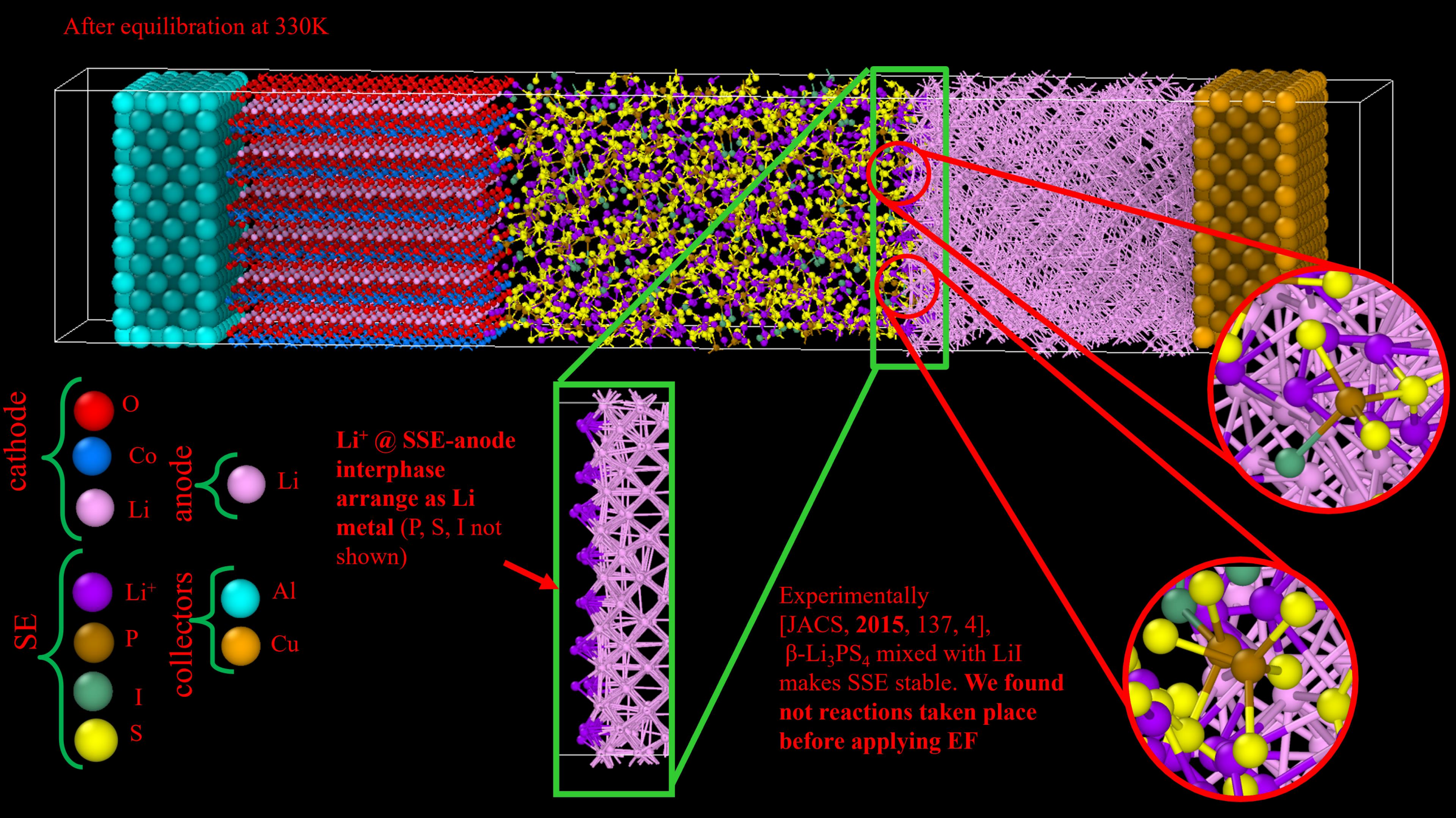
cathode
O
Co
Li

SE
Li^+
P
I
S

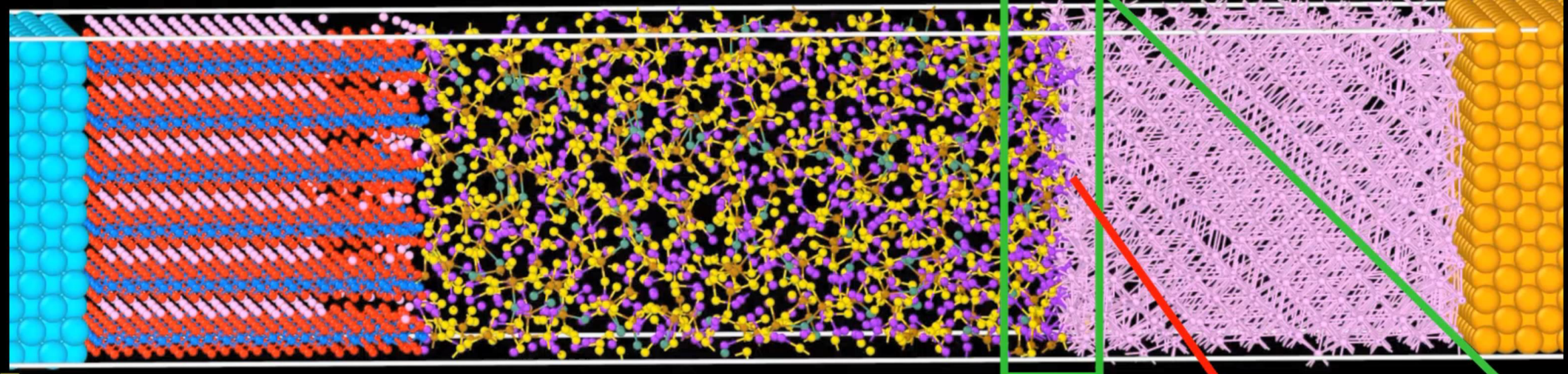
anode
Li

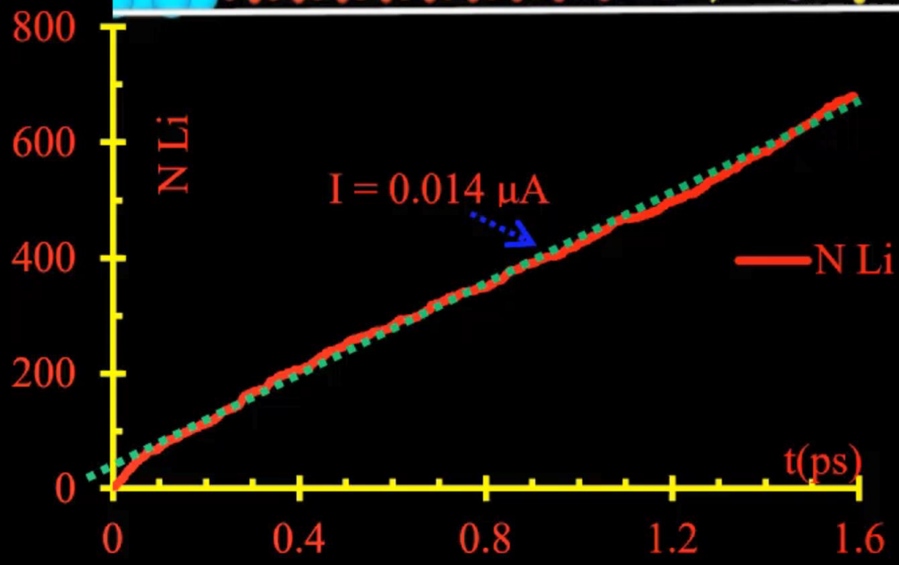
PS_4 and PS_3I do not dissociate without EF




After equilibration at 330K
cathode
O
Co
Li
anode
Li
SE
Li+
P
I
S
collectors
Al
Cu
Li+ @ SSE-anode interphase arrange as Li metal (P, S, I not shown)
Experimentally [JACS, 2015, 137, 4], β-Li3PS4 mixed with LiI makes SSE stable. We found not reactions taken place before applying EF

$Li_7P_2S_8I$ SSE battery under EF = 1 V/Å



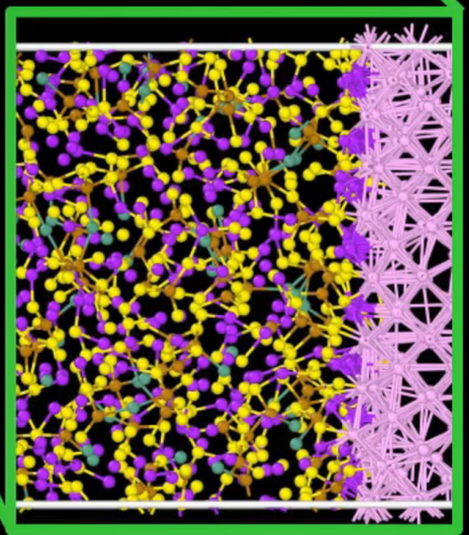


$I = 0.014 \mu A$

$\sigma = 0.16\ S/m$

$\sigma_{exp} = 0.063\ S/m$

Li metal growing



cathode: O, Co, Li

SE: Li^+, P, I, S

anode: Li

collectors: Al, Cu

Experiment: JACS, **2015**, 137 (4)

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