Developing New Force Field Models Li Ion Movement

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bat425

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Overview

Timeline

- Start: Oct.1 2029
- End: Sept. 31, 2020
- Percent complete: 25%

Barriers

- Ability to simulate large realistic systems for Li electrolyte and Li-S cathodes
- Stable Li-S cathode material and design

Budget

- Funding for FY 20 $225K
- Funding for FY 21 $225K
- Funding for FY 22 $225K

Partners

- Prof. Yi Cui, Stanford
- Dr. Gao Liu, LBNL
- Prof. Feng Pan, Beijing Univ.

Objective and Relevance

- Li-S battery has a large theoretical capacity (2546 Wh/Kg), but dissolution, low electric conductivity have prevented its commercialization
- Need novel design of new Li-S cathode materials
- Real battery systems are often complex, need accurate, yet large scale simulations
- Ab initio methods might have the necessary accuracy, but cannot be used to simulate large systems
- Traditional classical force field is fast, but it is either not accurate enough, or does not exist for a given system
- Machine learning force field (ML-FF) can combine the ab initio accuracy with the speed of classical force field.
- The goal is to develop ML-FF to simulate Li-S system, and Li electrolytes

Milestones

Month/Year	Milestones06/2020
12/2019	Li-S cathode design, especially for S attached in polymers
03/2020	Preliminary results for ML-FF development, for S, Li.
06/2020	Ab initio simulation to study Li diffusion in confined electrolyte and charge transfer during Li-S cathode lithiation process.
09/2020	Long range electrostatic potential treatment for ML-FF development.
12/2020	Incorporate the ML-FF for critical interactions with conventional force field for the organic molecules.
03/2021	ML-FF for Li-S systems
06/2021	Complete ML-FF theory/simulation for Li transport in liquid electrolyte and combine it with classical force field
09/2022	Use ML-FF to simulate the Li-S cathode and electrolyte charge and discharge process

Approach

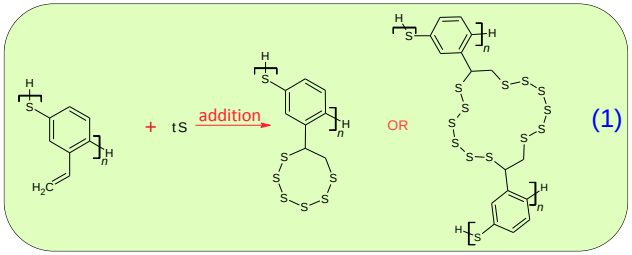
Using first principle simulation to design Li-S cathode systems, and combine machine learning model and ab initio data generation to develop ML-FF

- Use density functional theory (DFT) calculation to study Li-S attached to conductive polymer as cathode material
- Use time dependent density functional theory (TDDFT) approach to study the electron transport in S cathode lithiation process.
- Use ab initio molecular dynamics (AIMD) to study Li diffusion in electrolyte when it is close to the surface
- Use AIMD and special energy decomposition process to generate atomic energy data for ML-FF development
- Test different machine learning (ML) models to optimize ML-FF.
- Use charge fitting and extraction to separate out the long range charge interaction energy, hence to make the remaining energy short range, amenable for ML-FF model
- Develop ways to combine the ML-FF for critical interactions, and the traditional force field for organic molecules, simplify the ML-FF development.
- Using the developed ML-FF to simulate large realistic Li-S battery systems.

Accomplishments

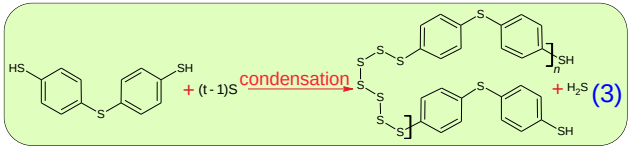
Vulcanize conductive polymer for Li-S battery cathode

Vulcanization is a process of adding S into polymer, to form cross links to increase the elastic constant of the polymer (to make it hard rubber). We propose to use similar processes to conductive polymer to make Li-S cathode materials. We theoretically investigated the feasibility of this approach.



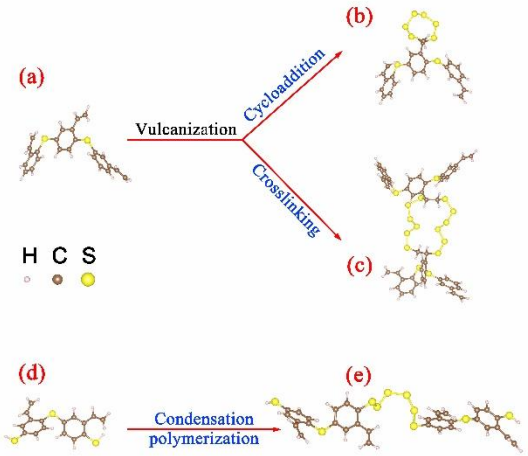
(1)

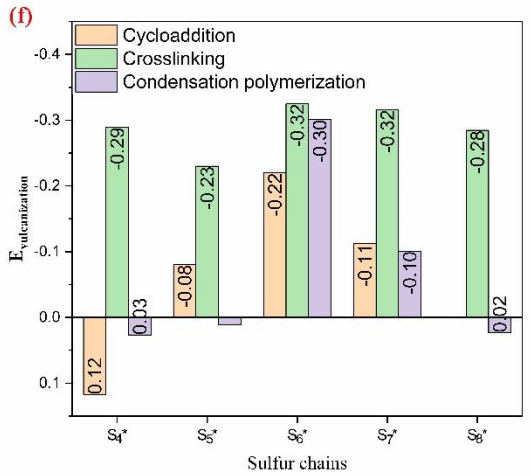
$$E_{vul} = E_{S_t^*} - t/8E_{S_8} - E_*$$ (2)



(3)

$$E_{vul} = E_{S_t^*} + nE_{H_2S} - n(t-1)/8E_{S_8} - (n+1)E_{monomer}$$ (4)

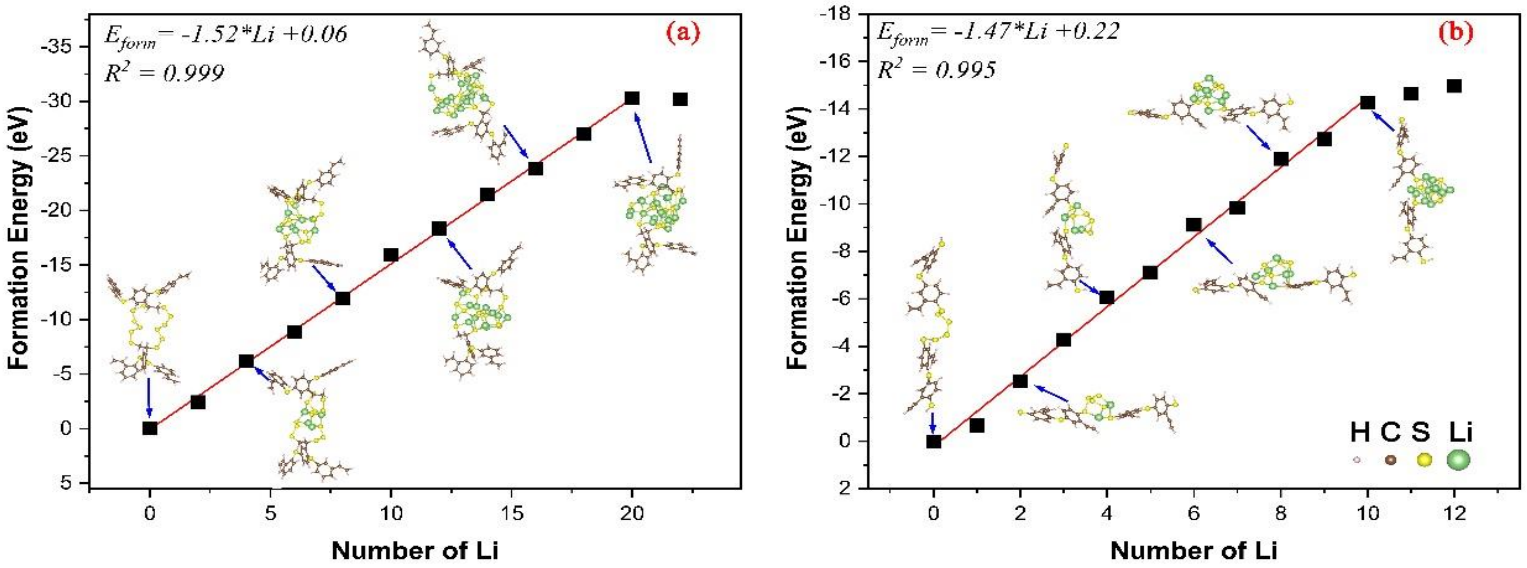




Different ways to adding S in polymers, and their vulcanization energies. (negative values mean the vulcanization is stable).

Accomplishments

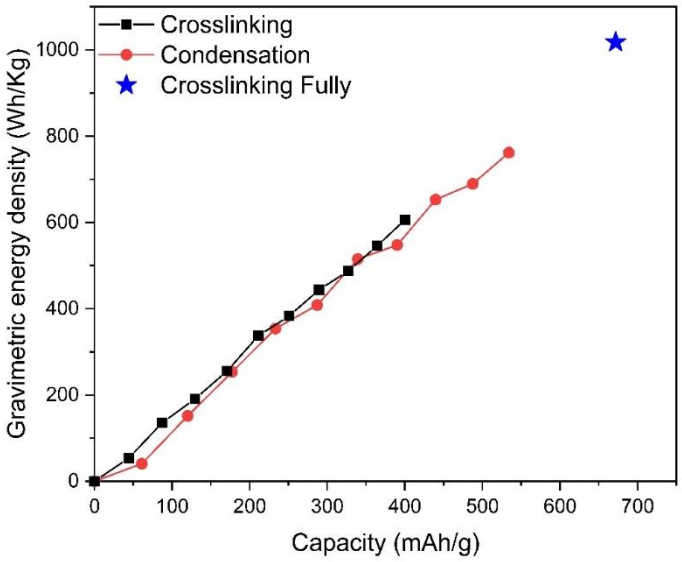
Vulcanize conductive polymer for Li-S battery cathode



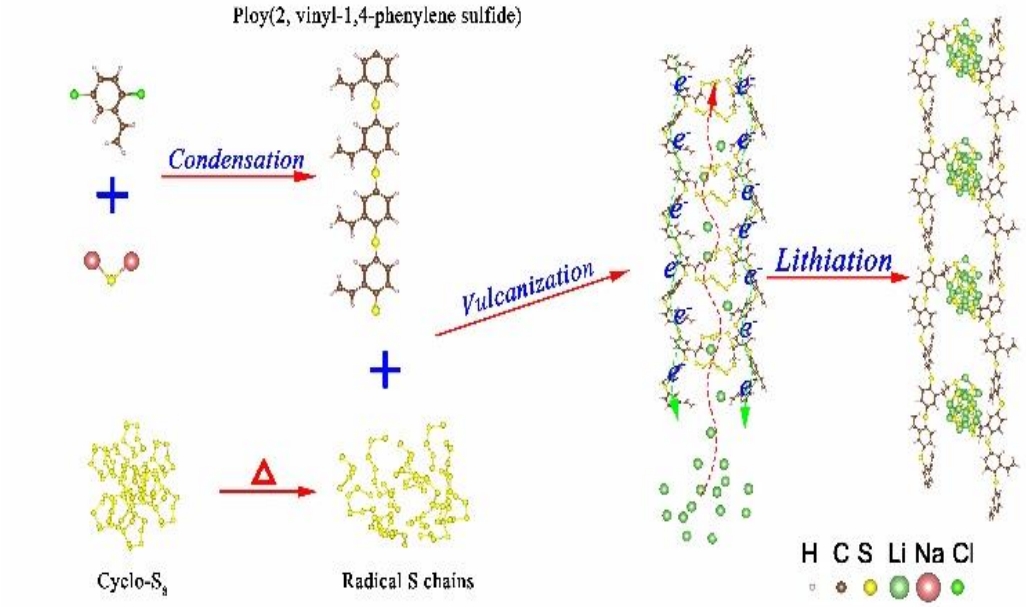
The lithiation processes and their formation energies for cross linked systems (a) and bridged chain (condensation) system (b). 20 Li atoms can be added to the cross linked system, with almost linear formation energy as a function of the Li atom number.

Accomplishments

Vulcanize conductive polymer for Li-S battery cathode



The gravimetric energy density for different degree of lithiation. The fully lithiated system corresponds to 20 Li atom for one crosslink.

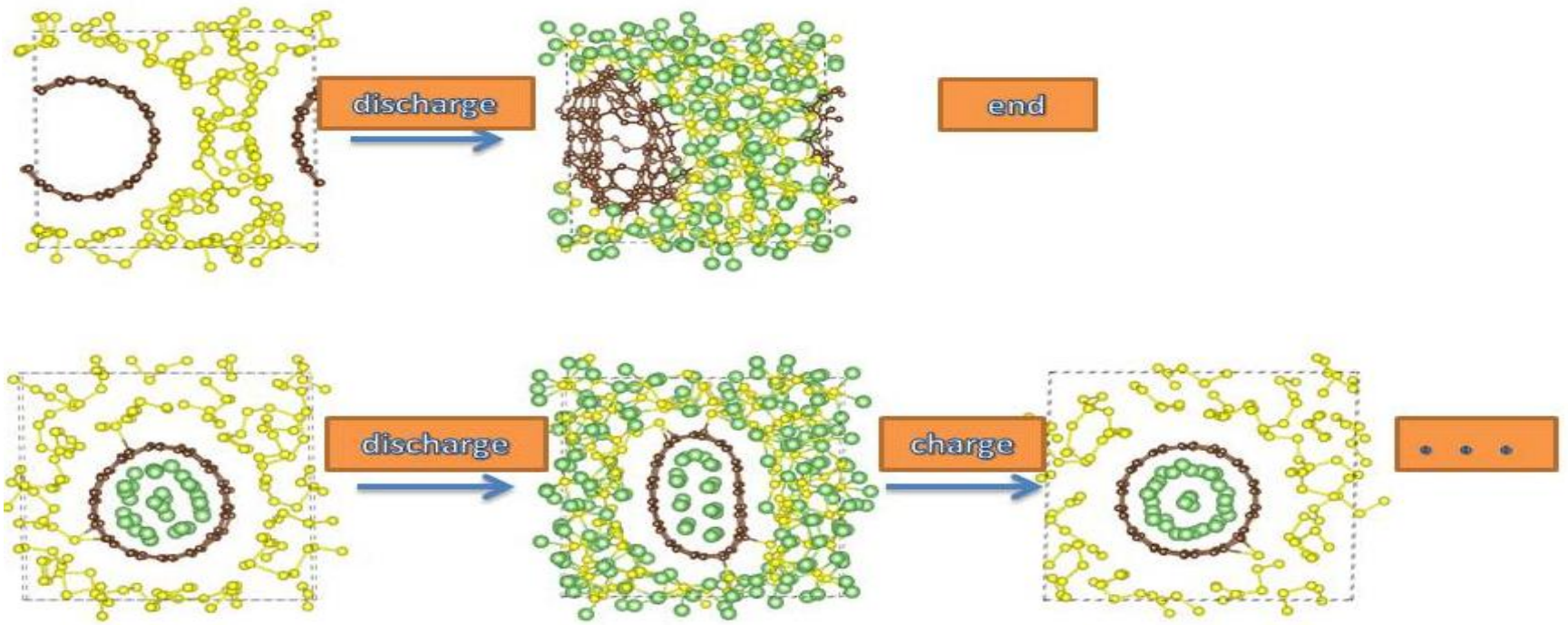


Possible synthetic routes to make the cross linked polymner

Accomplishments

Using S and ultra-fine black carbon as Li-S cathode material

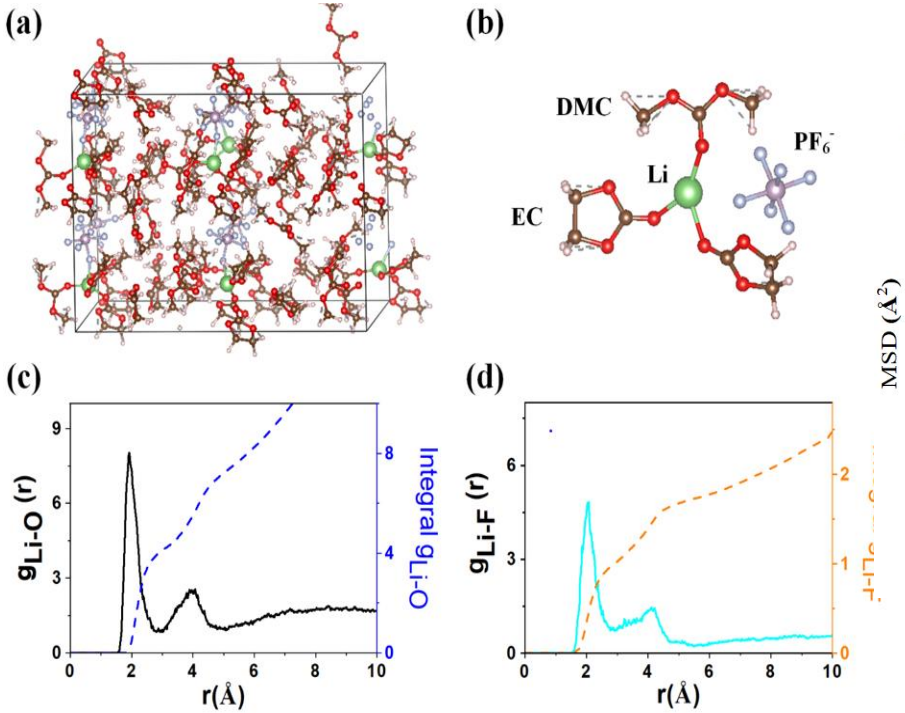
One interesting idea to make Li-S cathode material is to mix ultra-fine black carbon with solid sulfur, using carbon as electric conducting material, while S as Li binding material. We have used ab initio MD to study the possible systems, using a carbon nanotube to represent the black carbon. We found that, if the carbon nanotube is empty, upon lithiation, the carbon nanotube will collapse. On the other hand, if the carbon nanotube is filled with Li, the system will be stable during the lithiation cycle.



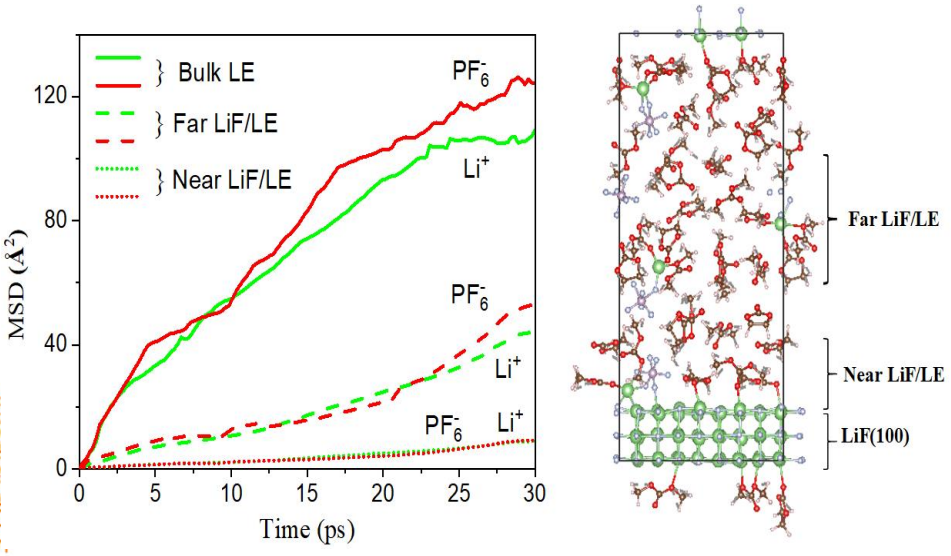
Accomplishments

Li^+ diffusion in electrolyte when close to a surface

It is interesting to study Li^+ diffusion in Li electrolyte, when the solvent is confined in a narrow space, this is because in many battery systems, the Li-electrolyte is intruded into small porous materials. We have used ab initio molecular dynamics to investigate this problem, and found that when it is close to a surface, its diffusion is significantly reduced.



EC/DMC electrolyte with $LiPF_6$ (a),(b), and Their Li-O, Li-F pair distribution function in MD.

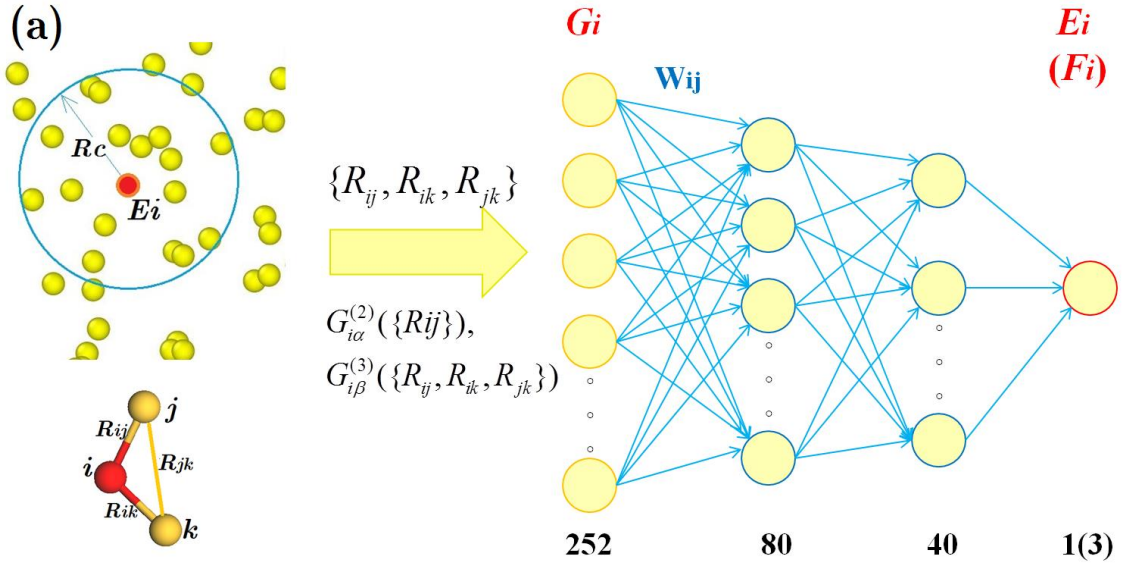


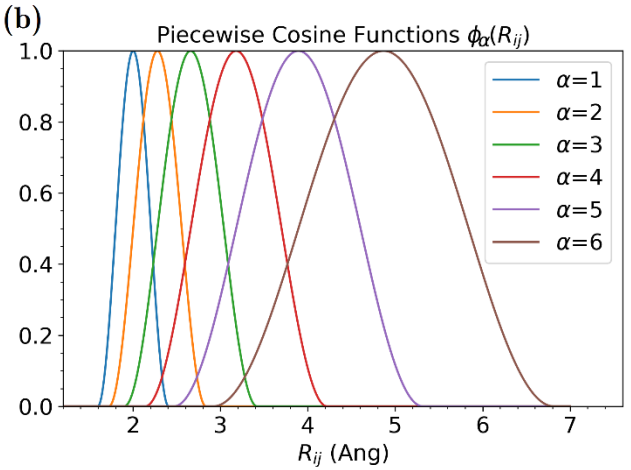
The mean square distance (MSD) as a function of time, when the Li^+ and PF_6^- are at difference distance from a LiF surface.

Accomplishments

Machine Learning Force Field (ML-FF) development

We develop ML-FF for Li, S and Li-S systems, as well as Li electrolytes





Atomic positions $\{R_j\}$ within Rc

Features $G_{i\alpha}(2)$, $G_{i\alpha\beta\gamma}(3)$

ML model to fit Ei

$$E_{tot} = \sum_i E_i$$

$$G_{i\alpha}(2) = \sum_j \phi_\alpha(|R_j - R_i|)$$

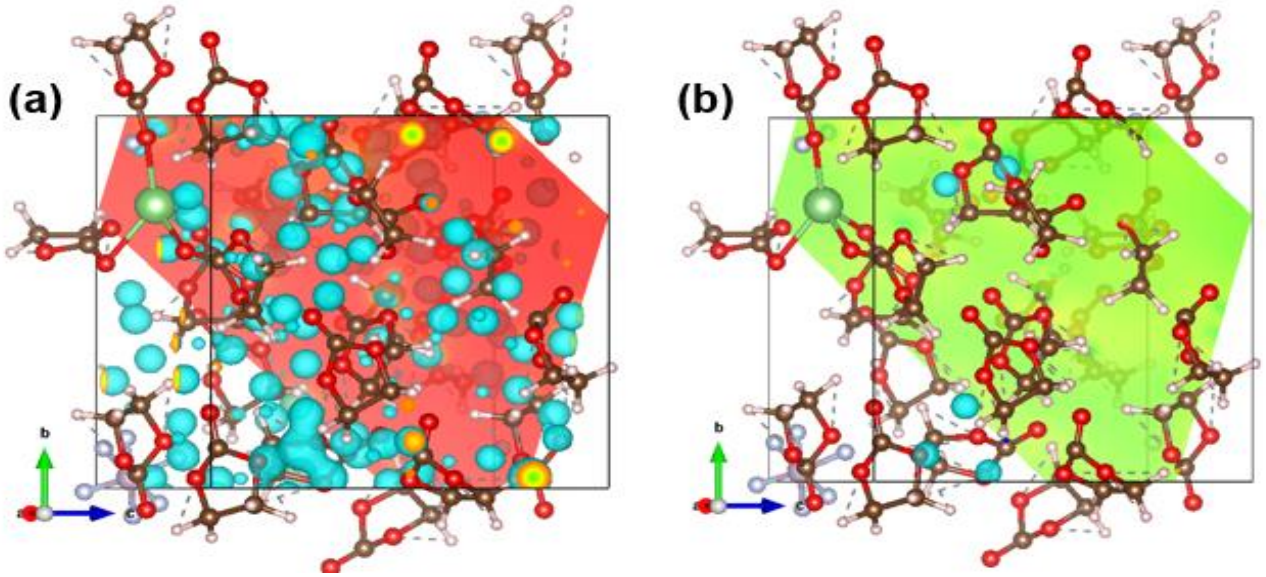
$$G_{i\alpha\beta\gamma}(3) = \sum_{j,k} \phi_\alpha(|R_j - R_i|)\phi_\beta(|R_k - R_i|)\phi_\gamma(|R_j - R_k|)$$

We have used neural-network, Gaussian process regression, and linear fitting methods for ML models

Accomplishments

Machine Learning Force Field (ML-FF) development

Long range Coulomb interaction fitting: ML-FF can only describe the local dependence of E_i on its nearby atomic positions (within the cut-off Rc). But the Coulomb interaction is a long range interaction, needs to be treated differently. We have fitted the ionic charges using spherical models, then subtract the corresponding electrostatic energy from the total energy Etot, hence only use ML model to fit the remaining energy.

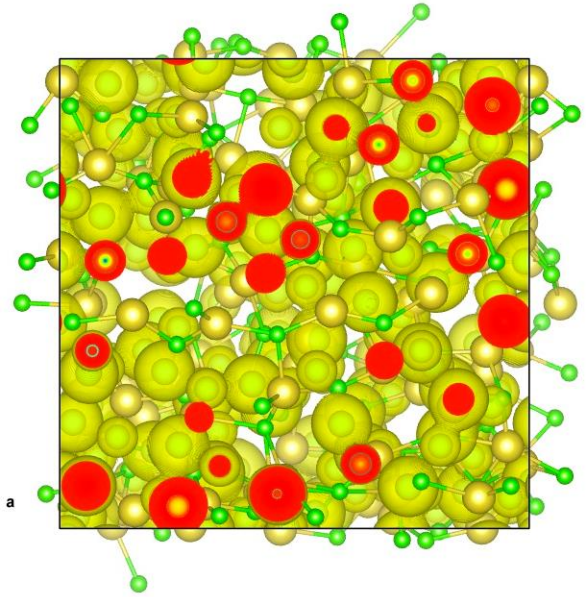


the electrostatic potential in a ethylene carbonate (EC) electrolyte with $LiPF_6$ salt. The Li^+ and PF_6^- can induce long range electric field. (a) is the full electrostatic potential, while (b) is the electrostatic potential after removing the fitting charge density electrostatic potential.

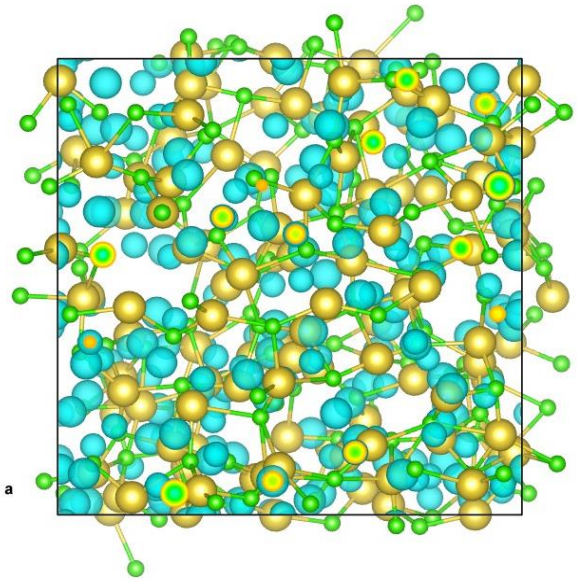
Accomplishments

Machine Learning Force Field (ML-FF) development

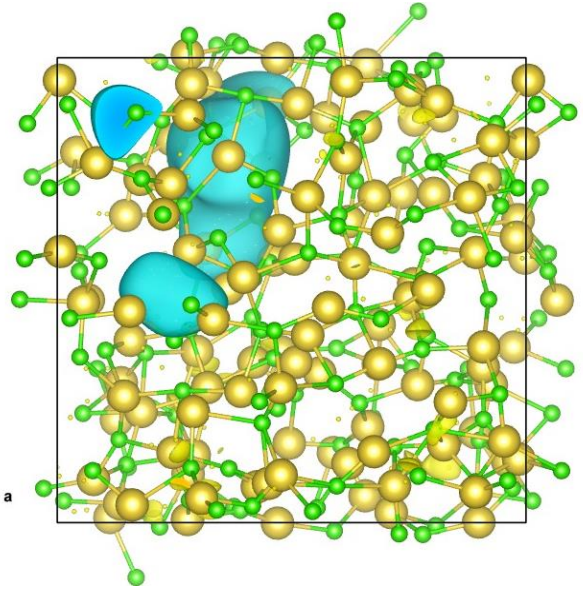
NaCl electrostatic potential problem.



The charge density of a melt NaCl liquid



The Coulomb potential of the system

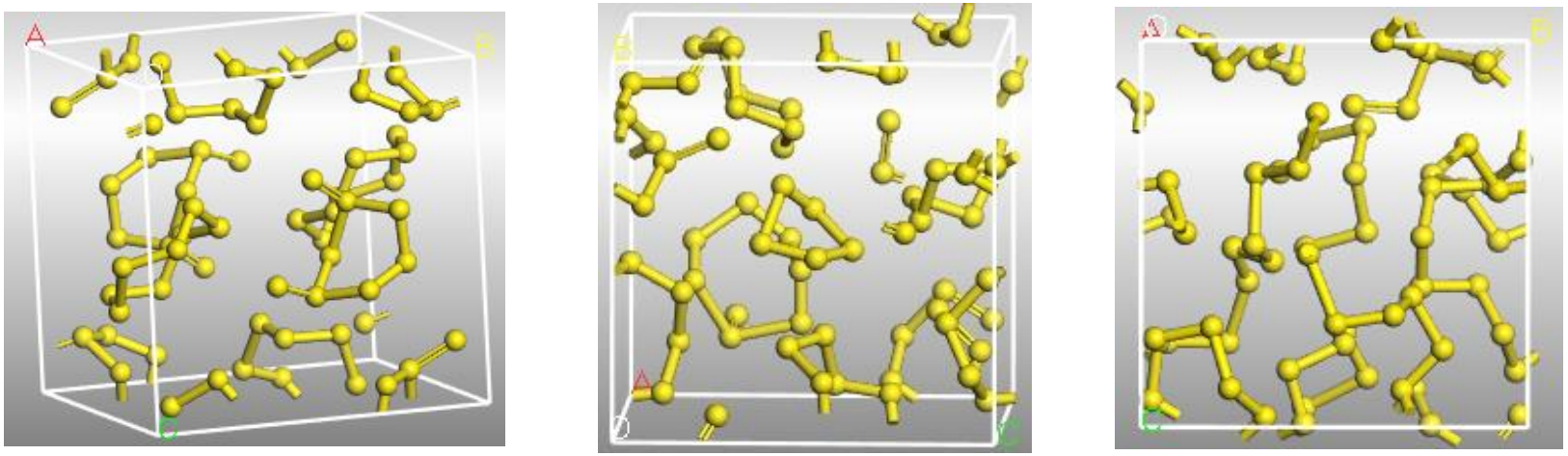


The residual Coulomb potential after a fitting of the charge density

Accomplishments

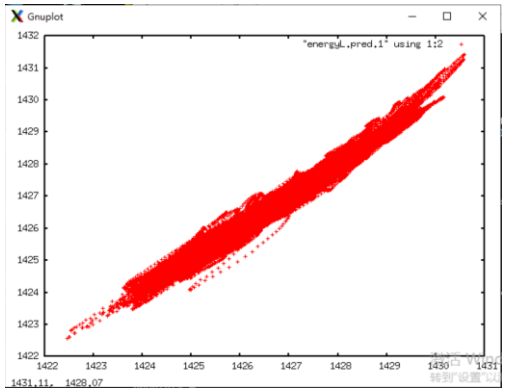
Machine Learning Force Field (ML-FF) development

S systems ML-FF preliminary results



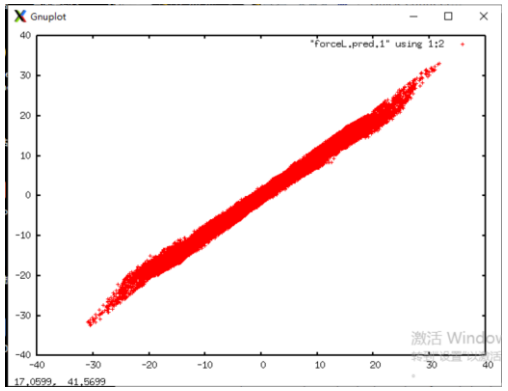
The surface phases from ab initio MD at different temperatures

ML-energy

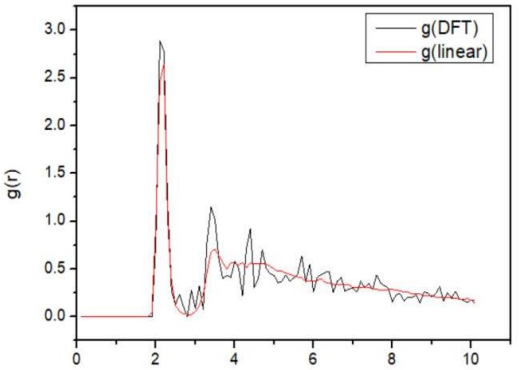


DFT energy

ML-force



DFT force

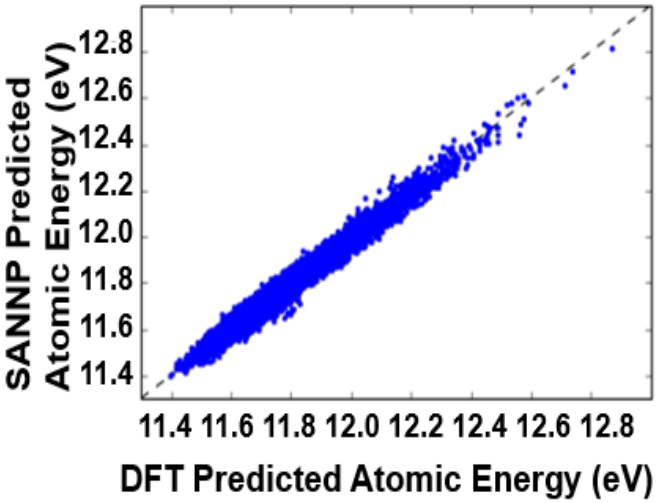


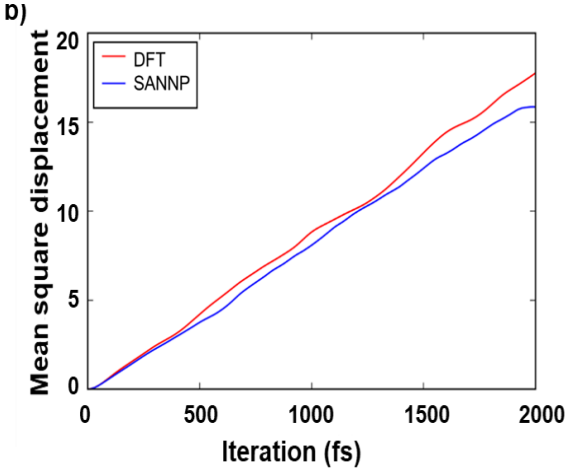
Pair distribution function
ML and DFT results

Accomplishments

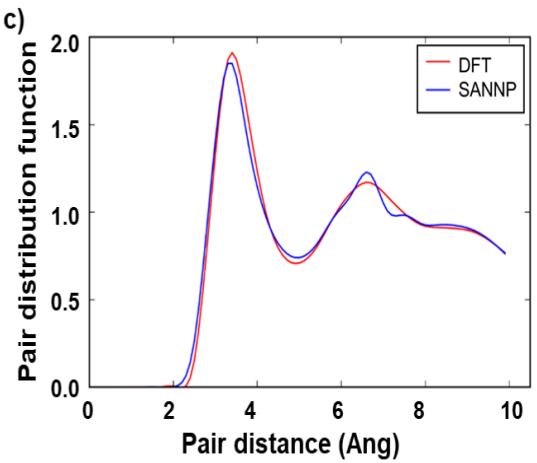
Machine Learning Force Field (ML-FF) development

Na systems ML-FF results. We have not done Li system yet, but we have developed a ML-FF for Na (SANNP), and it is better than the Na embedded atom force field.

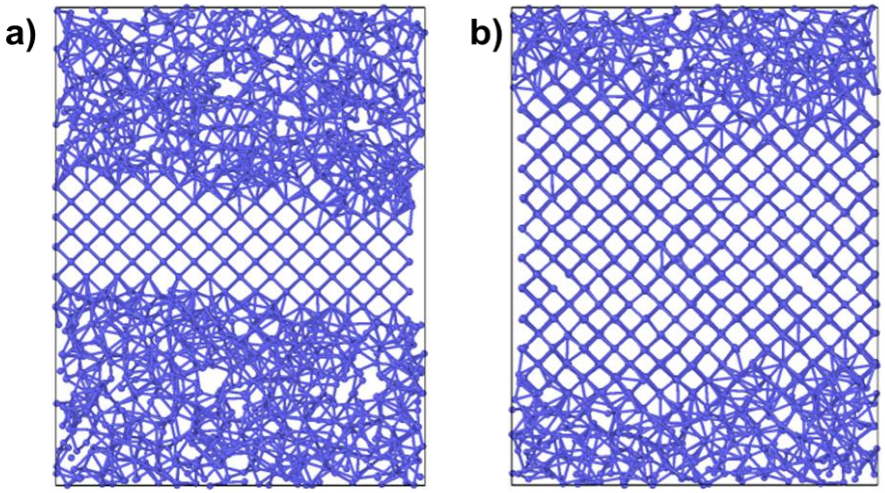




Mean square disance



Pair distribution function



Melted liquid to crystal growth simulation using the ML-FF.

Collaborations

- Prof. Yi Cui, Stanford University
  on S attachment on metal and graphene surfaces

- Dr. Gao Liu, LBNL
  on polymer with S attachment

- Prof. Feng Pan, Peking University
  on various types of battery materials

Remaining Challenges and Barriers

- Accurate ML-FF for Li-S systems, for large system calculations
- Balance the accuracy of the ML-FF versus the range of applicability to different systems
- Reliable description of the long range Coulomb interaction, e.g., not affected by the polarization screening
- Possible complex structure of Li-S cathodes, difficult to determine the most plausible structure
- A design of Li-S cathode, with sufficient gravimetric and volumetric capacity.
- Direct large scale simulation based on ML-FF for different Li-S cathode designs

Proposed future work

- Continue study of S + ultrafine carbon mixture as Li-S cathode, especially for electric conductivity, Li diffusion and stability.

- Continue development of ML-FF for Li-S systems, test the development procedure and protocol, thus we can develop a specific ML-FF for a given system quickly.

- Select one system (e.g., Li-S-C) for an demonstrative study using ML-FF for large scale and long time simulations, to establish the usefulness of the ML-FF

- Using time dependent density functional theory to study possible charge transfer bottleneck during lithiation process for Li-S cathode.

Summary

- **Objective and Relevance**: using ab initio simulations to understand the underlying mechanism in Li-S reaction process; to design new Li-S cathode materials; and to develop machine learning force field (ML-FF) for large scale simulations with ab initio accuracy.

- **Approach**: ab initio density functional theory based simulations; large ab initio data, ML-FF development, and use ML-FF to carry out large scale simulations.

- **Technical Accomplishments**: Studied vulcanize conductive polymer as Li-S cathode material. Studied mixture of S and ultrafine black carbon as Li-S cathode material. Investigated Li+ diffusion in the Li electrolyte when the ion is close to a surface. Developed preliminary S-S interaction ML-FF. Developed Na metal ML-FF, and its procedure can be readily extended to study Li metal. Tested different methods to describe the long range Coulomb interactions.

- **Collaboration and Coordination**: Yi Cui, Stanford; Liu Gao, LBNL; Feng Pan, Peking Univ.

- **Remaining Challenges and Barriers**: Accurate and reliable ML-FF for Li-S-C systems.

- **Proposed Future Work**: Continue the development of ML-FF for Li-S-C systems; study the electron transfer bottleneck during lithiation process for Li-S battery.

Publications

- G. Zhou, A. Yang, Y. Wang, G. Gao, A. Pei, X. Yu, Y. Zhu, L. Zong, B. Liu, J. Xu, N. Liu, J. Zhang, Y. Li, L.W. Wang, H. Hwang, M. Brongersma, S. Chu, Y. Cui, "Electrotunable liquid sulphur mircodroplets", Nat. Comm. 11, 606 (2020).
- B. Zhang, Z. Lin, H. Dong, L.W. Wang, F. Pan, "Revealing cooperative Li-ion migration in Li1+xAlxTi2-x(PO4)3 solid state electrolyte with high Al doping", J. Mat. Chem. A 8, 342 (2020).
- G. Gao, F. Zheng, L.W. Wang, “Solid 3D Li-S battery design via stacking 2D conductive microporous coordination polymers and amorphous Li-S layer”, Chem. Mater. 32, 1974 (2020).