Developing New Force Field Models Li Ion Movement

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Overview

Timeline

- Start: Oct.1 2019
- End: Sept. 31, 2022
- Percent complete: 50%

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
- Dr. Robert Kostecki
- Dr. Haimei Zheng
- 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	Milestones06/2021
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	Lithium charge density fitting in electrolyte, to fit the long-range Coulomb interaction
03/2021	Study of electrolyte behaviors, including their stability problems
06/2021	Incorporation of Coulomb interaction in the local energy calculation: ML-FF fitting
09/2021	Further study of Li-S cathode with polymer, to study electric conductivity in such systems

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 grand canonical fixed potential density functional theory approach to study the electron transfer and chemical stability of the electrolyte
- 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.

A fixed-potential algorithm for electro-chemistry calculations

Potential dependent reactions, as the one in battery, are often simulated with constantcharge. We have developed a fix-potential method for potential-dependent reactions, in which the total number of the electron in the system was floated to match the "applied voltage'. We have overcome the self-consistent convergence problem during the simulation. We have used single atom water catalyst problem as a example to develop this method. Now, the fix-potential method allow us to realize atomic relaxation, NEB and *ab inito* molecular dynamic at a given constant potential U.





EC decomposition on the electrode via Fix-potential method

The formation of solid electrode interface in battery is still too complex to be understood. Here, we combine the fix-potential method with ab initial MD to investigate the EC decomposition on the electrode. First, we found that when the Li metal electrode voltage is high enough, the EC molecule will be reduced and broken up. In the pure Li electrode, the EC will be decomposed into a chain with one edge oxygen diving into the inner layer of Li. With LiF terminated Li electrode, the EC will be decomposed into a chain the electrode decomposed into on $CH_2=CH_2$ and CO_3^{-2} and the CO_3^{-2} will bind with Li on the surface to form Li_2CO_3 .



Li⁺ diffusion in polymer and vulcanized polymer

We have studied Li⁺ diffusion in polymer and vulcanized polymer in a confined space. This is interesting because in many battery systems, polymer, especially vulcanized polymer is wildly used as a electrode materials. We have used ab initio molecular dynamics to investigate this problem, and found that in pure polymer, the Li+ prefer to bind with oxygen in DMC electrolyte molecule, while the Li+ will form small cluster with S in the vulcanized polymer. The formation of Li_nS_m reduces the diffusion of Li significantly.



Large scale traditional classical force field simulations of DEC electrolyte: the difference with different Li(PF₆) concentration

In collaboration with TEM group, who found phase separation in low temperature DEC electrolyte with different $Li(PF_6)$ concentration, we have simulated large systems with tens of thousands of atoms. OPLS-AA classical force field is used with Gromacs code. We found That when there is a 4M $Li(PF_6)$, the DEC molecules have short range order, which is observed in TEM diffraction pattern. On the other hand, for the 1M case, there is no such short range Order.



A 4M Li(PF6) in DEC simulation with 35664 atoms. The temperature is 240K.





The back bond of DEC molecules connected by two Li ions, forming the short range order, extracted from snapshot in the left panel. Inter-molecule O-C pair distribution function for cases where Li(PF6) concentration is 1M and 4M

A new density-based ML-FF to deal with nonbonding interaction

For nonbonding interaction in electrolyte, the most important thing is the electrostatic interaction. The classical force field uses point charges to describe such interaction. However, that ignores the dipole effects, as well as short distance exchange interaction. We have developed a new force field based on molecule electron charge. Fitted spherical charge on each atom can be used to represent the molecule charge, which can describe the charge on different molecule configurations.



Nonbond molecule-molecule interactions

Accurate nonbond interaction energy can be obtained from the total charge density of the system as a sum of the molecular charge density. For system without chemical bonding, such approximation is rather accurate. The electrostatic interaction can be calculated using conventional Fourier transformation method on the charge grid. Furthermore, due to molecule charge overlap, there are exchange interaction, as well as repulsing energy. These energies cannot be obtained from point charge approximaitons.

Intramolecule energy and force using ML-FF

The bonding energy of each molecule (intramolecule energy) can be fitted with conventional machine learning force field (ML-FF). Here we have used two-body and three-body features. Since the molecule movement is close to its equilibrium positions, ML-FF can provide accurate energy and force. Different ML-FF regression models can be used. Here, we only used the linear fitting model, which is good enough for our purpose.

Density based ML-FF for EC/DEC system simulations

We have finished the program to carry out molecular dynamics (MD) based on the density-based ML-FF for multiple molecules. The calculation is not as fast as the pure classical force field without charge, but it is hundreds of times faster than DFT MD.

The result of ML-FF MD and compared with DFT MD

The ML-FF MD results have been compared with DFT MD result. These are for their pair distribution function and the molecule-molecule binding energy. For the binding energy, for DEC+EC solvent, the averaged binding energy per molecule is -0.46 eV and -0.60 eV for ML-FF and DFT results respectively. The ML-FF binding energy is smaller by 0.14 eV. We believe this is because we have not included the polarization effect in our model.

Collaborations

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

Dr. Gao Liu, LBNL on polymer with S attachment

Dr. Robert Kostecki on block copolymer S cathode

Dr. Haimei Zheng on TEM imaging of DEC/Li(PF₆) phase separation

Prof. Feng Pan, Peking University on solid electrolyte materials

Remaining Challenges and Barriers

- Polarization effect of the electron charge
- Balance the accuracy of the ML-FF versus the range of applicability to different systems
- Possible complex structure of Li-S cathodes, difficult to determine the most plausible structure
- Systems with chemical bond formations, e.g, Li-S bonds
- 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

- Introduce the polarization effects.
- Include the Li⁺ and PF_6^- ions in the system.
- Improve the speed of the calculation, perhaps implement the code on GPU.
- Develop the density based ML-FF for polymer and polymer with S.
- Use the developed ML-FF for Li diffusion in various types of systems (e.g., with space confinement).
- Use fixed potential calculation to study the EC, DEC decomposition mechanism.

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 the EC decomposition at the Li surface and the mechanism for SEI formation. Developed an stable algorithm for constant potential calculations. Studied the Li diffusion in polymer S-cathode with EC electrolyte molecules. Developed an electron density based machine-learning force field (ML-FF) to describe the long range Coulomb interactions and molecule-molecule nonbonding interactions. Used this ML-FF to simulate the EC and DEC liquid electrolyte.
- **Collaboration and Coordination**: Yi Cui, Stanford; Liu Gao, Robert Kostecki, 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.