Multiscale modeling of lithium transport in solid and hybrid Li-ion electrolytes and their interfaces

Thesis topic submitted to the FOCUS program.

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Motivation

Energy storage is an essential component of a sustainable energy infrastructure based on intermittent renewable sources, such as photovoltaics or windmills. Among storage technologies, lithium-ion batteries are possibly the main current option for private electric vehicles. Replacing oil combustion vehicles by electric ones (ideally based on renewable sources) can reduce energy consumption by 20KWh/(day*person) in a country like the UK.[1] The adoption of electric vehicles, however, will be greatly facilitated if one can solve important challenges of the current *generation-3* Li-ion batteries: insufficient energy density and recharge speed, aging, and safety issues. The upcoming *generation-4*, based on Li-metal anodes and solid-state (SS) electrolytes, is expected to solve many of these issues: Li-metal SS batteries' theoretical energy densities approach those of oil[2]; solid electrolytes can be made very thin to further reduce battery size, and have been shown to improve safety by decreasing dendrite formation (which is a main cause for thermal runaway); addition of nanoparticles has been found to improve ion mobility in the electrolyte, enhancing recharge speeds. However, the physical mechanisms responsible for the solid-electrolyte/Li-metal system's advantageous qualities (i.e. nanoparticle-enhanced mobility, and dendrite inhibition) are still very poorly understood at the atomic level. To make *generation-4* batteries a reality, it is essential to elucidate and quantify these mechanisms. Predictive atomistic simulations, as proposed in this Ph.D. thesis project, may play a big role in this respect.

Research plan

The overall goals of this thesis are to *theoretically elucidate* the currently unknown transport mechanisms of Li in hybrid polymer/ceramic electrolytes, and *quantitatively predict* performance and aging properties related to these mechanisms.

State of the art

Hybrid solid electrolytes. The state of the art of hybrid **polymer/ceramic electrolytes** lacks in theoretical insights, especially at the atomistic level. Embedded nanoparticles have been shown to enhance experimental ionic mobility[3–5], but **the mechanism responsible for this enhancement is unresolved**[5]. **No atomic level modeling, nor multiscale ab initio modeling has yet been undertaken for these systems**. Experimental evidence suggests that Li flow is mediated by the interface between the matrix and the nanoparticles, favoring the hypothesis depicted on the right hand side of *figure 1*, over the alternative possibility schematized on the left hand side.

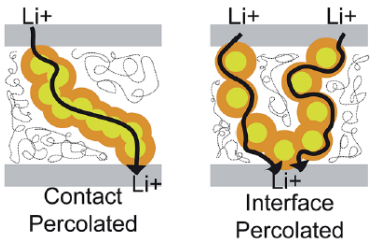

Fig. 1: Various hypothetical scenarios of mobility enhancement in hybrid electrolytes, from Zaman et al., *J. Mat. Chem. A,* 7, 23914 (2019).

But many unknowns still remain: Do the ions penetrate in the interior of the nanoparticles to some extent? Is the mobility enhancement due to chemical, or rather structural modifications? What is the typical thickness of the higher-mobility interphase? How is the Li-flow density distributed around the particles? What is the effect of the chemical (composition) and physical (size and shape) nature of the matrix and filler materials?

Our project aims at answering these questions via atomistic simulations, keeping close contact with experimental work that will be developed in parallel thesis projects. Both parameterized (effective) force fields and *ab initio*-trained machine-learning interatomic potentials will be implemented, in order to elucidate and predict the Li diffusion currents upon changing chemical and physical conditions of the electrolyte (see "*implementation*" below.)

Electrolyte/Li-metal interface. Current experimental know-how suggests that dendrite growth is largely inhibited in solid electrolyte/Li-metal systems[6,7]. Although continuum models have been used to simulate dendrite growth, such models remain highly semi-empirical, and are of limited use to estimate the likelihood and character of dendrite formation in systems with novel compositions. To be predictive, simulations must consider that "dendrite growth is a non-deterministic stochastic process"[8], such as those described by diffusion limited aggregation (DLA) models. However, to the best of our knowledge, only one such atomistic study exists for Li dendrites[8]. In the final part of the thesis project, we will therefore perform DLA simulations based on ab-initio obtained parameters, to understand and quantify dendrite formation as a function of temperature, isotopic mass, and electrolyte composition.

Implementation

We will start by employing empirical interatomic potentials to study Li-ion diffusion in PEO polymer matrix, with embedded SiO_2, Al-LLZO, and $(Li_2S)_x(P_2S_5)_{1-x}$ nanoparticles, . This will allow the student to get familiar with the simulation and statistical analysis methods of Molecular Dynamics. We expect to qualitatively elucidate the diffusion paths around or even through (if this happens) the

nanoparticles, and the role played by the structural modifications induced by the introduction of the latter. This will be performed by using the LAMMPS massively parallel simulation code.

In order to be predictive, we will train multi-element machine-learning potentials to replace the empirical force-fields used in the first stage of the thesis. We will employ the neural network approach previously developed in our group[9,10], together with the moment tensor potentials developed by the group of A. Shapeev[11,12].

During the third year, we plan to address the growth of dendrites, by implementing an atomistic diffusion-limited aggregation stochastic model. The different hopping probabilities for the bulk and Li-metal surface ionic diffusivity mechanisms, and the sticking coefficients onto the nucleating dendrite structures or electrolyte sections, will be obtained from MD simulations using our trained machine learning potentials.

Milestones

- 12 months: study of Li transport in electrolyte using empirical potentials completed.
- 24 months: study of Li transport in electrolyte using ab-initio-trained machine learning potentials completed.
- 36 months: study of Li-metal/electrolyte interface completed.

Main objectives

- Full understanding of mobility enhancement in hybrid solid-state electrolytes.
- New methods to optimize the enhancement.
- Quantitative prediction of the conditions for dendrite growth.
- New strategies to prevent dendrites in Li-metal/hybrid-electrolyte systems.

Relation to other "FOCUS" theses submitted in this call:

- *Etude de la dynamique du lithium dans des électrolytes « tout-solide ».* E. De Vito, T. Gutel, M. Bardet: Experimental measurement of the diffusion paths, via Focused Ion Beam tomography (FIB) with Li isotope tracking.
- *Simulation à l'échelle atomique d'hétérostructures pour des batteries solides.* Alain Chartier, Paul Fossati: use and validation of our machine learning potentials to simulate other types of solid electrolyte.
- *Characterisation operando de la microstructure et les interfaces …* S. Tardif, S. Lyonnard: Experimental information on the local, nanoscale and microscale morphology/structure of hybrid electrolyte/Li-metal system.

Potential impacts

- By optimizing the size, concentration, and composition of the particles embedded in the polymer matrix, our project may elucidate the relevant channels of Li mobility in hybrid electrolytes, without the need for lengthy trial and error experiments, with an impact on their efficiency.
- It will also explore novel strategies to prevent dendrite formation in *generation-4* systems, thus impacting aging and safety aspects.
- These hybrid electrolytes are part of the know-how of LITEN. By elucidating the mechanisms, and being able to predict ionic mobilities in a quantitative manner, this project can lead to

improve LITEN's current protocols for electrolyte synthesis, and possibly lead to patents and applications on Li-metal/hybrid electrolyte *generation-4* batteries.

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