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Application of theoretical computational simulations in lithium-metal batteries

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Abstract. In the area of high energy density batteries, lithium metal has attracted a lot of interest as an electrode material. But since lithium is so reactive, lithium metal batteries frequently have safety problems like thermal runaway, particularly under conditions such as overcharging, over-discharging, high temperatures, and mechanical impact. These safety issues can lead to dangerous situations such as battery explosion and fire. Furthermore, lithium-metal batteries are prone to dendrite development during the cycling process, which can pierce the separator and result in internal short-circuits, shortening the battery's cycle life. Lithium-metal battery use is strongly constrained by these important problems. To overcome these challenges, researchers are exploring various strategies, such as developing new electrolytes and additives, designing new battery structures, and exploring new anode materials. Computational simulations have emerged as a powerful tool to aid in this research. This review summarizes the recent applications of computational simulations in lithium metal batteries. Specifically, molecular dynamics (MD) and first-principles calculations have been widely employed to study key issues such as interface reactions, ion transport, and dendrite formation in lithium batteries. Additionally, this review discusses recent research directions in new types of ion electrolytes that can effectively address the safety concerns of lithium batteries and increase energy density, while still facing challenges in interface resistance and conductivity. The discussion of potential avenues for future research that will be pursued finishes this paper. These possibilities include multiscale simulations, the creation and manufacturing of new electrolyte materials, and the functional modification of lithium-metal anode surfaces.

Keywords: lithium-metal anode, computational simulation, solid electrolyte interface, ion transport.

1. Introduction

Due to their long cycle life, high specific energy, and high voltage, lithium-ion batteries have been intensively researched over the past four decades. The development of the electronics and automotive industries, particularly the popularity of new energy vehicles, has brought tremendous market opportunities to lithium-ion batteries. Nevertheless, the continuous enhancement of portable electronic products and electric vehicles requires greater energy density in energy storage systems [1]. The energy storage potential of lithium-ion batteries has reached its limit as research has advanced. Traditional graphite anodes have drawbacks such low initial coulombic efficiency and quick initial capacity degradation [2, 3], and they are getting close to their theoretical specific capacity of 372 $mAh \cdot g^{-1}$. The needs of the expanding industry can no longer be met by conventional lithium-ion batteries. In the realm of energy storage and applications, lithium batteries that use lithium metal as anodes have drawn more and more interest in recent years. Metallic lithium as an anode material has a higher theoretical specific capacity (3860 $mAh\cdot g^{-1}$) and a lower standard electrode potential (-3.04V, compared to the standard hydrogen electrode, than the graphite anodes now in use. Therefore, a straightforward and efficient way to increase battery energy density is to create high-performance lithium-metal anodes to replace graphite anodes used in lithium batteries. The creation of lithium dendrites, which can result in safety concerns, capacity loss, elevated internal resistance, and decreased battery life, is one of the difficulties that LMBs face. A thick SEI layer can form on the lithium surface that consumes both the electrolyte and the lithium metal due to the instability of the lithium anodes with the electrolyte, which can also lead to irreversible reactions between the lithium metal and the electrolyte. The SEI layer, the deterioration of the active components and electrode, and even battery swelling can all result from the volume variations of the lithium anodes [4-7]. Computational modelling is used to simulate and examine the battery's behavior in order to overcome these issues. The formation and effects of lithium dendrites [8, 9], as well as the intercalation, diffusion, migration, and reaction of lithium ions [10, 11], can all be simulated using computational simulations, such as molecular dynamics (MD) simulations and first-principles calculations based on density function theory (DFT). The development, destruction, and repair of the SEI layer, as well as electronic conductivity and ionic vacancies at the interface, may all be studied by looking at the interface structure and electronic characteristics of LMBs [12, 13]. The design, production, and optimization of LMBs may be guided by this, hastening the advancement and use of battery technology. Additionally, computer simulations can offer useful input for investigations, guiding and directing experiment design and analysis while increasing accuracy and efficiency. This paper provides an overview of current computer modelling applications in lithium-metal anodes.

2. Solid electrolyte interface reactions

To establish a stable interface, it is necessary to first understand the interface reaction mechanism between the electrolyte solvent and lithium-metal electrode. Currently, two major categories of organic solvents, esters and ethers, are widely used [14]. Due to their high redox potential and low electrochemical activity, esters solvents including propylene carbonate (PC), ethylene carbonate (EC), and diethyl carbonate (DEC) are frequently utilized in LMBs. Ether-electrolytes are usually composed of polyether (such as polyethylene glycol) and lithium salts (such as LiPF6, LiBF4, etc.), which typically have good ion transport properties and high conductivity [6, 15].

Yang et al. used first-principles calculations to show that the generation of SEI depends on the reaction products' ability to disperse in EC, DEC, and lithium metal. Lithium ethylene carbonate (LEC), produced when Li reacts with DEC, is easily dispersed in solution and cannot serve as a stable SEI component on lithium metal, whereas lithium ethylene dicarbonate (LEDC), produced when EC reacts with Li as a solvent or co-solvent, cannot be dispersed in the electrolyte. This research demonstrated how crucial product dispersibility is to SEI stability [16].

It has been demonstrated that the performance of lithium-metal anode batteries may be enhanced by using lithium salts such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium bis(fluorosulfonyl)imide (LiFSI) in combination with ether solvents as electrolytes [17, 18]. Beltran et al. used LiFSI/dimethoxyethane (DME) as an electrolyte to analyze the mechanism of SEI formation at low and high concentrations. At low concentrations, spontaneous disintegration of the inorganic LiFSI phase produced a variety of complexes including LiO, LiS, LiF, and LiN by cleaving FSI- anions and breaking S-O bonds. However, the complexes were too dispersed to form a continuous inorganic SEI phase. In computational simulations, the organic DME phase inhibited the dissolution of lithium metal, with only a few DME molecules being reduced to LiH complexes. At high concentrations, LiFSI rapidly decomposed and grew into an inorganic SEI, while DME was not reduced [19]. Li et al. proposed a dilution strategy, in which low concentration of lithium salts were combined with diluted nonpolar dipropyl ether (DPE) as the electrolyte. They discovered that by adjusting the decomposition sequence of solvation species using MD and DFT techniques, it was possible to encourage the breakdown of

Li^+/salt-derived anion clusters on free ether solvent molecules and produce a strong and stable SEI. This research offers a fresh approach for enhancing LMB performance at high voltages [20].

3. The ion transport mechanism

To increase the cycle life and safety performance of lithium-metal batteries, a homogenous and thick solid electrolyte interphase (SEI) layer must develop [21]. Understanding the lithium-ion transport process is crucial to achieving this aim. The interaction of organic compounds (and additives) in the electrolyte with active lithium metal during the initial charging and discharging process is what primarily creates the SEI layer on the lithium-metal anode surface. Common components include Li_2CO_3, Li_2O, LiOH, and LiF.

Angarita-Gomez et al. designed relevant models and discovered that the Li_2O- and LiOH-dominant SEI layers have different mechanism for Li^+ diffusion, with diffusion mechanism being dominant in Li_2O and substitution mechanism being dominant in LiOH. However, it is the same that Li^+ diffuses from lithium-metal anodes to the solution with less energy than the reverse process. This study provides new insights into ion transport and deposition in complex interfaces [22]. Simulating a ternary system of lithium metal, Li_2O, and LiF, Ramasubramanian et al. investigated the impact of the interface between the latter two on Li+ transport. LiF/LiF is the most stable on the surface of the lithium metal, which is best for ion transport, followed by Li_2O/Li_2O, and LiF/Li_2O is the least stable, according to the findings of DFT simulations. These papers offer fresh concepts for developing reliable SEI [23]. Tri(hexafluoroisopropyl)phosphate (THFP) was added to a triethyl phosphate (TEP) electrolyte by Sun et al. to make it non-flammable. According to DFT calculations, the strong interaction between THFP and PF_6^- decreased the amount of free solvent molecules, which effectively aided in the dissociation of LiPF6 and suppressed the formation of HF, significantly increased the number of Li^+ molecules that migrated, and enhanced the electrolyte's conductivity. Additionally, a significant portion of the CF_3 groups in the additive help to form an SEI layer that is rich in LiF, effectively inhibiting the breakdown of the electrolyte and the growth of lithium dendrites, and produce a rechargeable LMB with low overpotential, high current efficiency, and stable cycle performance [11]. Moreover, for the system where LiFSI decomposes in DME to form SEI, Kamphaus et al. demonstrated through theoretical calculations that SEI composed of LiF and Li_2CO_3 respectively had the best passivation effect, as they transferred fewer electrons to LiFSI for reduction. This promotes the development of a more stable SEI, increasing the battery's safety and toughness [24].

4. Enhancing ion transport effect

The cycle life and capacity retention of lithium-metal batteries will be improved if Li^+ can be transferred quickly, which will also help with the repair and stability maintenance of the SEI layer. Slow Li^+ transport, on the other hand, might result in an uneven distribution of ions on the electrode surface, which can promote the formation of lithium dendrites and create issues like reduced battery capacity and elevated internal resistance [25]. Therefore, it is necessary to address the issue of increasing lithium migration rate.

N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (C_3mpyrFSI), an ionic liquid, was introduced to the LiSFI/DME electrolyte by Pal et al. They utilised the MD method to discover that the diffusion rate of lithium ions dramatically increased when the mass ratio of the ionic liquid to DME was about 8:2. The connection between lithium ions and anions is weakened when DME is added because it disrupts their interaction network.; it also significantly reduces the viscosity of the solution. This method greatly promotes rapid ion exchange [26]. Kim et al. directly converted Li_2O into an electrolyte with suspended particles and added it to the electrolyte, which boosted the stability of Li^+ migration and markedly increased current efficiency. This method helps to obtain favorable SEI on the lithium anodes, in order to develop reliable LMBs [27]. Zhang et al. first introduced the diluent heptafluoro-1-methoxypropane (HM) into the LiFSI/DME electrolyte. HM synergistically deposits with anions to generate a uniform and dense SEI rich in LiF by releasing fluorinated species on the Li surface. This technique successfully prevents lithium dendrite development and addresses the instability issue of

LMBs at high pressure [28]. Similarly, Xia et al. demonstrated through MD calculations that the interaction between lithium ions and DME molecules as well as FSI- anions can be improved by adding 0.5 wt% potassium trifluoromethylborate (PTB) as an additive to the LiFSI/DME-1,1,2,2-tetrafluoroethyl- 2,2,3,3-tetrafluoropropyl ether (TTE) electrolyte. As a result, DME's antioxidant abilities are improved, and FSI- is reduced to produce a fluorine-rich SEI on the surface of lithium metal. This research offers guidance for the creation of novel electrolytes [29].

5. Conclusion

Currently, computational simulations have advanced lithium-metal battery research., providing many new insights for us to enhance the solid electrolyte interphase, comprehend the interactions between the electrolyte and the metal electrode better, and create composite electrode materials. However, due to various difficulties, many fundamental and important problems remain unsolved. On one hand, at the theoretical level, some basic problems such as the uneven deposition of lithium and the mechanism of interfacial reactions have not been thoroughly explored, and there is also a lack of experimental verification and feedback. On the other hand, the current cathode and electrolyte materials have certain limitations. The choice of cathode and electrolyte materials and their compatibility and synergy with the lithium metal anode is crucial and complicated. Only by further understanding these materials can we design better lithium metal batteries.

The potential research directions in this field are as follows.

5.1. Developing more applicable computational simulation methods

There are still certain errors in predicting ion transport and SEI layer formation in LMBs using existing computational simulation methods. Therefore, developing more accurate methods, such as machine learning methods, may help better understand the mechanism of ion transport and SEI layer formation in LMBs. Machine learning can be used to efficiently calculate and predict the electrochemical and physical properties of lithium battery materials on a large scale. Through extensive data analysis and modeling, performance indicators such as battery cycle life, charging efficiency, and energy density can be predicted, and the battery performance can be improved by optimizing algorithms.

5.2. Developing novel electrolytes

Developing new types of electrolytes is a promising direction in the field of LMBs. Current electrolytes used in LMBs are often based on organic solvents, which can lead to safety concerns due to their flammability and volatility. As a result, creating novel electrolyte types, such as solid-state or ionic liquid electrolytes, may enhance the stability and safety of LMBs.

A lot of research has been done on solid-state electrolytes because of their strong ionic conductivity, low flammability, and broad electrochemical stability window. A major challenge is creating solid-state electrolytes with excellent ionic conductivity and favorable electrode interfacial compatibility. Ionic liquid electrolytes are another promising alternative to traditional organic solvents. Ionic liquids have negligible vapor pressure, low flammability, and a wide electrochemical stability window, making them potentially suitable for high-performance LMBs.

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