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Modeling and theoretical design of next-generation lithium metal batteries

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ABSTRACT

Rechargeable lithium metal batteries (LMBs) with an ultrahigh theoretical energy density have attracted more and more attentions for their crucial applications of portable electronic devices, electric vehicles, and smart grids. However, the implementation of LMBs in practice is still facing numerous challenges, such as low Coulombic efficiency, poor cycling performance, and complicated interfacial reactions. First-principles calculations have become a powerful technique in lithium battery research field, in terms of modeling the structures and properties of specific electrode materials, understanding the charge/discharge mechanisms at the atomic scale, and delivering rational design strategies for electrode materials as well as electrolytes. In this review, theoretical studies on sulfur cathodes, oxygen cathodes, lithium metal anodes, and solid-state electrolytes (SSEs) of LMBs are summarized. A brief introduction of simulation methods is offered at first. The next two chapters mainly focus on issues concerning cathodes of LMBs. Then the theoretical researches on the Li metal anode and SSEs are particularly reviewed. The current challenges and potential research directions in each field of LMBs are prospected from a theoretical viewpoint.

1. Introduction

Secondary lithium ion batteries (LIBs) are critical to a wide range of applications in our daily life, including electric vehicles, grid energy storage systems, and advanced portable devices [1,2]. However, the current techniques of LIBs cannot satisfy the energy demands in the future due to their theoretical energy density limits. Rechargeable lithium metal batteries (LMBs) based on multiple-electron reactions rather than ion-intercalations are expected to handle with this challenging issue for their higher theoretical energy densities [3–5]. Specially, lithium–sulfur (Li–S) batteries and lithium–oxygen (Li–O_2) batteries are strongly considered as the most promising candidates for next-generation energy storage devices for their ultrahigh theoretical energy densities (non-aqueous Li–O_2 battery: 3505 Wh kg^{-1}; Li–S battery: 2600 Wh kg^{-1}) [6–11]. Furthermore, solid-state LMBs can even deliver a much higher energy density in practice due to the decreasing of electrolyte mass. The introduction of SSEs is also expected to fundamentally solve the fatal defect on the flammability and limited electrochemical stability of organic liquid electrolytes as well as to stabilize the Li metal anode [5,12].

Unfortunately, the application of the rechargeable LMBs still faces numerous challenging issues, such as low Coulombic efficiency, poor cycling performance, and complicated interfacial reactions [4,13]. Each specific LMB also possesses respective issues. For example, the application of Li–S batteries is seriously hindered by some intrinsic issues: (1) the migration of soluble polysulfides driven by both concentration gradients and electric field, which is famous as shuttle effects, causes the side reaction between Li metal and polysulfides; (2) the significant volume fluctuation of 80% due to lower density of Li_2S (1.66 g cm^{-3}) than that of sulfur (α-phase, 2.07 g cm^{-3}) induces a distinct change of electrode structure; and (3) the low electrical conductivity of sulfur and solid product cause the low utilization of active materials [8,14–18]. Besides, the research about Li–O_2 batteries is still in primary stage, the actual energy density is far less than its theoretical energy density, and the capacity decay is also a critical trouble [19]. Particularly, Li metal anode is troubled by the uncontrollable growth of lithium dendrites, which can induce low Coulombic efficiency and severe safety hazards, and SSEs are challenged by the low ion conductivity and high interfacial resistance [20].

Tremendous efforts have been devoted to handling these intractable issues and promote the practical demonstration of LMBs with an ultrahigh energy density. Among various techniques, theoretical mod-

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eling methods based on quantum mechanics, such as DFT calculations and Hartree–Fock methods [21–23], play significant roles in these researches. Specially, they can provide a fundamental understanding of the physical and chemical properties of battery materials, such as geometrical structures, electronic interactions, ion diffusivities, phase transitions, and kinetic lithiation processes, a fruitful insight into the charge/discharge mechanisms, and thus rational design strategies of LMBs [24–26]. For example, Wang et al. [27] calculated the Li ion storage behavior at graphene/Li_2O interface through the DFT calculations and found the interface exhibits the synergistic effect resulting from the enhanced interface interactions induced by the Li ion insertion, which contributes to excess storage capacity of the graphene/metal oxide composites. The results explained the additional capacity of the metal oxide observed during the experiments and provided some insights into Li storage behavior via an electrostatic capacity mechanism.

Considering that the next-generation LMBs primarily composed of novel cathode (sulfur cathodes or oxygen cathodes), electrolyte (nonflammable aprotic electrolytes or polymer electrolytes), anode (nanostructured carbons or lithium-alloying metals) [28], an overview of major theoretical progresses in LMBs recently, in terms of sulfur cathodes, oxygen cathodes, Li metal anodes, and SSEs, need to be provided. All of the topics are considered as the key techniques for practical high-energy-density lithium-based rechargeable batteries and actually belong to the research field of next-generation lithium metal batteries, including Li–S batteries, Li–O_2 batteries and all-solid-state batteries. On the other aspect, these topics involve the new theories that are quite different from the traditional lithium ion batteries, and there are many similarities on the theoretical issues among them, such as the structure identification, the catalyst design, the interface properties and the kinetic reactions. Until now, many impactful and insightful reviews have focused on Li–S batteries [8,9,14–17,29], Li–O_2 batteries [30–32], Li metal anode [4,33,34], and SSEs [35–40], and there are also several excellent reviews summarizing the progress in LMBs, challenges and perspectives from an experimental viewpoint [19,41,42]. However, the systematic review on the theoretical work still lacks.

In the present review, the relevant theoretical studies for the four critical topics in LMBs are systematically reviewed. A brief introduction of simulation methods and the highlight of modeling and theoretical design of LMBs are provided in the first chapter. Then, the next two chapters mainly focus on issues concerning with cathodes of Li–S and Li–O_2 batteries respectively. Theoretical researches about the Li metal anode and SSEs are particularly discussed in the last two chapters due to their specializations, respectively. For each chapter, an introduction of current research conditions and the concerned major theoretical issues are provided, and the representative works concerning with these issues are reviewed in detail in the next step, then the summarization of the remaining problems and the potential of the solution method will be suggested. In the end of the review, current challenges and potential theoretical research directions in LMBs are summarized and prospected. We will see that although each topic exhibits its specific existing problem, there are still many issues that can be solved by the similar scheme from the theoretical viewpoint, and the study method can be shared among different systems (Fig. 1).

2. A brief overview of simulation methods

Most of the simulation researches in LMBs are performed based on the DFT calculations, which are free of the empirical fitting or adjustable parameters [47]. The history of DFT can be traced to early 20th century. In 1920s, Thomas and Fermi established Thomas–Fermi model, in which the system energy can be expressed as the function of electron density [48]. In 1964, Kohn proposed Hohenberg–Kohn theorem, strictly proving the exact dependence of molecular energy on electron density [49]. In 1965, Kohn and Sham [50] established the Kohn–Sham formalism, and clarified the relationship between the ground-state energy and the electron density [51].

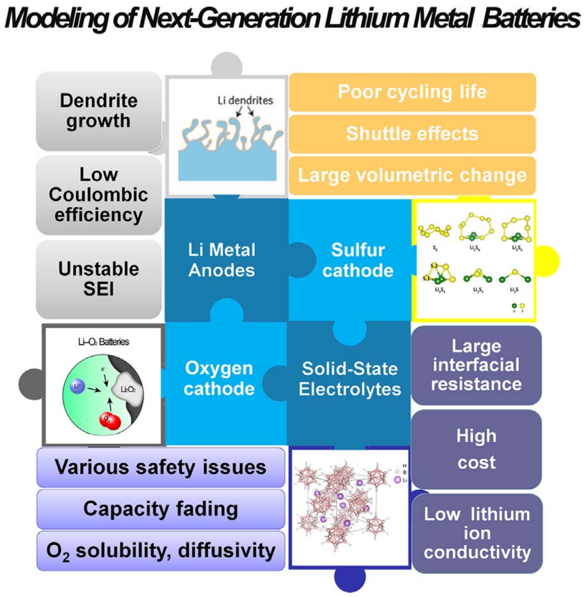

Fig. 1. Modeling of next-generation LMBs and the corresponding crucial challenges. Sulfur cathodes, oxygen cathodes, Li metal anodes, and SSEs are considered as the key techniques for next-generation LMBs and all of the four topics still face different challenging issues which have been shown in the figure above [43-46].

By self-consistently solving the Kohn–Sham one-electron equations, the ground state of a system composed of electrons and nuclei can be attained. Such first-principles calculations can provide total energies, stable atomic geometries and various electronic properties of molecular or crystalline materials. For lithium battery system, many physical or chemical quantities can be directly achieved through the computation of energies for the most stable conformation. For example, the phase stability can be predicted by calculating the formation energy and migration energy of material defects; thermodynamical stability can be determined by the formation enthalpy of compound [47,52,53]; the voltage can be attained by the energy evolution at different Li ratio [54,55]; the mechanical parameter can be achieved by the energy variance and loading force at different lattice parameters [46].

For treating the exchange–correlation energy and many-body potential, a number of exchange–correlation functionals were developed, including LDA (Local density approximation), LSDA (Local spin-density approximation), GGA (generalized gradient approximations), Meta-GGA, Hybrid GGA, Hybrid meta-GGA. Among them, LDA and GGA are most widely used in practice, while the other methods were developed to overcome the inaccuracy of conventional DFT methods, such as the underestimation of band gap [56]. To treat the system in which the electrons tend to be localized or strongly interact (transition metal or rare earth elements and their compounds), the DFT+U method was developed, and extended the functional approach to deal with self-interacting electron correlations. For lithium battery system, this method is required to treat the electrode or electrolyte materials that contain transition metal element or exhibit long-term magnetic order [57]. Recently, the van der Waals correction functionals are also considered into the exchange–correlation potential in order to accurately treat the long-range physical interactions [58]. It is extremely important for the physical adsorption systems, such as Li–S battery cathode, which involves the remarkable van der Waals interactions between sulfur species and host materials [44].

Molecular dynamics (MD) scheme can model the detailed microscopic dynamical behavior of various material systems in chemistry, physics or biology, which is one of the most powerful tools to study the