



Li metal batteries and solid state batteries benefiting from halogen-based strategies



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ABSTRACT

Li-metal batteries are re-arising as the promising next-generation battery system due to its potential high energy density, as long as the issue of Li dendrite growth can be effectively addressed. Solid state battery architecture is a potential solution to dendrite free anode. However its high performance is still hampered by the low Li-ion conductivity of solid electrolyte and transport limitation at interface. In this review, we summary the recent progresses on Li dendrite inhibition at the anode side and conductivity enhancement at the solid electrolyte side from the viewpoints of halogen-based strategies. The methods based on electrolyte additive and artificial coating layer on anode are especially effective to construct F-rich solid electrolyte interface. Large-sized halogen as ligand modifier enables desired mineral phases of high Li-ion conductivity.

1. Introduction

Advanced electrochemical storage technologies are the driving force for multiple emerging fields varying from advanced robotics, autonomous aircraft, to hybrid electric vehicles and smart grids [1,2]. Since the Li-ion batteries (LIBs) commercialized from 1991, which have revolutionized the ways of communication and transportation, are getting into the bottleneck of energy density due to the inherent limitations of Li-ion chemistry and relatively low capacity of electrode materials. It is of high importance to develop advanced electrode materials with exceptional energy and power densities to meet the growing demand in the large scale application of cutting-edge electronic devices. Over the last 40 years, Li metal batteries (LMBs) have undergone highs and lows because of their superiority and inevitable imperfections. LMBs come to the eyesight of researchers now again mainly owing to the high energy requirements for future batteries. Of course, advanced materials and new (nano-)technologies play a great role in the reviving process of LMBs [1,2]. Li metal with the highest theoretical capacity (3860 mAh g^{-1} or 2061 mAh cm^{-3}) and lowest electrochemical potential (-3.04 V versus the standard hydrogen electrode) is thought to be the ultimate anode for a rechargeable battery as in the cases of Li–air and Li–sulfur (Li–S) batteries with ultrahigh theoretical energy densities [3–5].

Before LMB can become a viable application, however, formidable issues especially safety and cyclability need to be overcome due to the

high chemical and electrochemical reactivity of Li metal anode: (1) The formation and growth of Li dendrites caused by uneven deposition and stripping of Li anode could penetrate through the separator and reach the cathode, causing short circuit of a working cell and leading to a poor cyclic life and serious safety hazards [6]. Li dendrites could also be separated by the side reaction products of solid electrolyte interphase (SEI) from the current collector (or broken away from the electrode mass), and convert to electrochemically inert “dead Li”. It would also significantly shorten the cycle lifespan of LMBs [7]. (2) Li metal is interfacially instable, and it has a high Fermi energy level and can irreversibly reduce the liquid electrolyte, resulting in the formation of SEI film with increasing resistance and decrease of coulombic efficiency (CE) and cell life [8]. (3) The volume change of this hostless electrode during each plating/stripping process is huge, leading to cracking and repairing of SEI and further capacity fading [9]. In order to solve these issues, it is important to gain a profound comprehension of interfacial chemistry, Li deposition behavior and the correlations between them. As a consequence, various approaches have been proposed, involving the fabrication of host materials for Li injection, construction of artificial SEI layers, designing of electrolyte components and solid state electrolytes, and modification of separators [2,6–8].

Additive strategy is widely explored to improve the performance of Li anode, and it is considered as the potent weapon to facilitate the in-situ formation of SEI with high uniformity and stability and to regulate Li ion diffusion and plating behavior [10]. The presence of additive,

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sometimes even at ppm levels, can bring about remarkable effects on suppressing Li dendrite growth [1,2]. During the past several decades, many kinds of electrolyte additives have been proposed, such as fluoroethylene carbonate (FEC) [10,11], LiNO_3 [12], lithium halides [3,13,14], and highly concentrated electrolyte [15]. Considering the important role of a robust SEI layer playing, it is no wonder for researchers to design and construct artificial SEI layers or to modify the separators. The latter could not only indirectly engage in the formation of SEI, but also enhance the rigidity to prevent dendrites from penetrating through the separators. Liquid electrolytes are stuck with several safety issues including leakage, poor chemical stability and flammability. Compared with liquid electrolytes, solid-state electrolytes (SSEs) may deliver lots of advantages, including a wider electrochemical stability window against Li metal anode and effective suppression of Li dendrite growth. Solid-state battery (SSB) could fundamentally change the behavior of Li deposition and is expected to be an ultimate solution to the issues of Li-metal anode [6,16]. However, the application of SSBs is still retarded by the relatively low ionic conductivity of SSEs as well as the poor contact between SSE and electrode. These cause an increasing of interfacial resistance and a compromise of rate capability for most of the solid-state cells [17–19]. Additionally, the volume change of electrode material during (dis)charge may cause loss of contact between the particles of electrode and electrolyte, which could further decrease the wetting ability of solid-solid interface. Many efforts on designing new SSE materials have been made to improve their ionic conductivity, adhesion and mechanical stability. Current SSEs can be roughly divided into two categories: inorganic ceramic/glassy electrolytes (such as sulfides, oxides, nitrides, and phosphates) and solid polymer electrolytes (blending Li salt with polymer matrix) [2,6].

Recently, lithium halides and trace of water were reported as electrolyte additives to gain LiX-rich ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and stable SEIs, which successfully extend the cycling life of LMBs [3,13,14,20]. Utilizing halogen-rich precursors as additives or to synthesize coating layers on Li surface could also achieve robust SEI or strong Li host structure [9–11,21–23]. Besides, separator modified by halogen-rich material exhibited a significant mitigation in thermal shrinkage and an improved electrolyte uptake [24]. Additionally, the ionic conductivity and chemical/electrochemical stability of SSEs doped by halogen-contained components are greatly improved [17,19,25–28]. By taking a panoramic view, it can be discovered that halogen is a kind of indispensable component for many SEI and SSE materials used in LMBs. Herein, we summarize the recent progress on Li metal batteries and solid state batteries benefiting from halogen-based strategies and discuss the internal relationship of these halogen-based strategies and their mechanism of action. We do not intend to go into detail with respect to synthesis. Rather we wish to demonstrate the crucial characteristic features and results of these halogen-based strategies.

2. Defect chemistry and space charge effect of LiF

Typically, an ideal SEI should be ionic conductive and electronic insulated. That is that SEI should be stable enough to prevent electron transport from electrode to electrolyte and to allow Li-ion transfer to electrode [29–31]. If this passivation layer does not work well, cracks can form in SEI under large volume change during cell cycling. It can cause electron leaking from the underneath fresh Li, resulting in the decomposition of electrolyte molecules and Li consumption [29,31,32]. In most organic carbonate electrolytes, LiF is an indispensable component in the whole SEI layer, and it has good stability for electron isolation and low carrier concentration with relatively smaller ion conductivity than for other inorganic SEI compounds such as Li_2CO_3 and Li_2O [29,31,33,34]. In order to obtain a profound understanding of the ionic behavior in LiF, it is vital to study its defect thermodynamics, dominant diffusion carriers and transport pathways, on which the (electro)chemical properties (such as defect forming energy, diffusion

barrier and ionic conductivity) depend directly [29,33,35–38]. Theoretical calculation, such as by density functional theory (DFT) and nudged elastic band (NEB) method, was widely used to evaluate defect formation energy, diffusion barrier and so on [29,39].

LiF crystallizes into a rock-salt structure and is in the space group of $\text{Fm}\bar{3}\text{m}$ (no. 225) and its lattice parameter is calculated to be nearby 4.00 Å with a bandgap of 8.70 eV, which demonstrates that LiF is a strong electron insulator [29,39–41]. Yildirim et al. theoretically indicated that the vacancies of Li and F (V_{F}^{\cdot} and V_{Li}^{\cdot} , i.e. Schottky pairs) are the dominant defects according to their formation energies [29,34–36]. The formation energies of LiF Schottky pairs (V_{F}^{\cdot} and V_{Li}^{\cdot}) calculated by DFT are in a range of 2.24–2.94 eV, but the formation energy of a single vacancy of Li or F is about 0.76 eV, much lower than that of vacancy pairs [42]. Diffusion barrier is a pivotal indicator of transfer possibility. V_{Li}^{\cdot} is suggested to diffuse via a direct hopping mechanism with a diffusion barrier of 0.75 eV, exchanging its position with the lattice Li [29]. Considering these calculated values, it can be seen that the overall diffusion for dominant defects in bulk LiF is relatively slow. The contribution of ionic conductivity from these defects is found to be on the order of $\sim 10^{-7}$ – 10^{-13} S cm^{-1} .

Although LiF layer exhibits excellent ability to insulate electrons, it seems that this component should hinder Li-ion migration and then cause increased interfacial resistance because of its high diffusion barrier and poor ionic conductivity. In fact, however, LiF plays an important role on promoting the whole ionic conductivity under the synergy effect of heterogeneous system [29,31,34]. A typical heterogeneous system is fabricated by addition of small oxide particles into ionic conductor, which likely shows increased defect concentration and enhanced ionic conductivity near the interface due to space-charge layer effect. For example, Liang et al. first discovered that the heterogeneous electrolyte of $\text{LiF}/\text{Al}_2\text{O}_3$ exhibited a conductivity enhancement close to two orders of magnitude as compared with pure LiF [43]. Because Li^+ was adsorbed to Al_2O_3 surface, the concentration of V_{Li}^{\cdot} was greatly increased in LiF.

Li_2CO_3 can provide a relatively high ionic conductivity ($\sim 10^{-8}$ S cm^{-1}) but it is not a good electron insulator [34,44], while LiF is a good electron insulator but has relatively low ionic conductivity. Neither one of them alone satisfies the desired properties of an ideal SEI [45], however, they may benefit from each other by forming a heterogeneous structure as they coexist in SEI to improve ionic conduction and electronic insulation at the side of negative electrode [34]. Recently, Pan and Zhang et al. have studied the synergistic effect of $\text{LiF}/\text{Li}_2\text{CO}_3$ system, providing a profound insight into the solid electrolyte interphase [31,34]. Space charge model was used to describe the defect behavior near the interface between LiF and Li_2CO_3 . The Li ion conduction is mainly limited by the concentration of diffusing carriers, because the defect formation energy in both materials is much larger than the migration barrier [31]. The dominant defect in Li_2CO_3 is positively charged Li interstitial (Li_i^{\cdot}) balanced by electron (e^-), while vacancies of Li (V_{Li}^{\cdot}) and F (V_{F}^{\cdot}) are the main defects in LiF. A lattice Li in LiF migrates to form a Li_i^{\cdot} in Li_2CO_3 , leaving a V_{Li}^{\cdot} in LiF, which can be expressed as $\text{Li}_{\text{Li}}(\text{LiF}) \leftrightarrow \text{Li}_i^{\cdot}(\text{Li}_2\text{CO}_3) + V_{\text{Li}}^{\cdot}(\text{LiF})$ [34]. As shown in Fig. 1a, chemical potential difference ($\Delta\mu$) leads to the accumulation of Li_i^{\cdot} in Li_2CO_3 near the interface and more V_{Li}^{\cdot} in the LiF side, causing a promotion of ionic conductivity of interface. This imbalance of charge caused by ionic carrier accumulation would create a space charge potential ($\phi(x)$) across the interface [31,33,35–37]. Fig. 1b shows the calculated defect distribution and electrostatic potential in the Li_2CO_3 side, indicating the space charge depletion of electron accompanied by Li_i^{\cdot} accumulation, which improves the Li ionic conductivity and the ability of blocking electron leakage. It should be noted that if the two-phase interface is parallel to the ionic conduction path, this structure can provide the maximum ionic flux from SEI to bottom electrode during lithiation (Fig. 1c).

Grain size of Li_2CO_3 and volume fraction of $\text{LiF}/\text{Li}_2\text{CO}_3$ are two important factors to influence ionic conductivity of this heterogeneous system [31]. The ionic conductivity in Li_2CO_3 can be increased by two

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