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Rui-Qi Guo

Feng Wu

Xin-Ran Wang
1. Beijing Key Laboratory of Environmental Science and Engineering School of Materials Science & Engineering Beijing Institute of Technology Beijing 100081, China;2. Yangtze Delta Region Academy of Beijing Institute of Technology Jiaxing 314019, China;, wangxinran@bit.edu.cn

Ying Bai
1. Beijing Key Laboratory of Environmental Science and Engineering School of Materials Science & Engineering Beijing Institute of Technology Beijing 100081, China;, membrane@bit.edu.cn

Chuan Wu
1. Beijing Key Laboratory of Environmental Science and Engineering School of Materials Science & Engineering Beijing Institute of Technology Beijing 100081, China;2. Yangtze Delta Region Academy of Beijing Institute of Technology Jiaxing 314019, China;, chuanwu@bit.edu.cn

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Multi-Electron Reaction-Boosted High Energy Density Batteries: Material and System Innovation

Rui-Qi Guo[1,2], Feng Wu[1,2], Xin-Ran Wang[1,2*], Ying Bai[1*], Chuan Wu[1,2*]
(*1. Beijing Key Laboratory of Environmental Science and Engineering School of Materials Science & Engineering Beijing Institute of Technology Beijing 100081, China; 2. Yangtze Delta Region Academy of Beijing Institute of Technology Jiaxing 314019, China*)

Abstract: The continuous development of the global energy structure transformation has put forward higher demands upon the development of batteries. The improvements of the energy density have become one of the important indicators and hot topic for novel secondary batteries. The energy density of existing lithium-ion battery has encountered a bottleneck due to the limitations of material and systems. Herein, this paper introduces the concept and development of multi-electron reaction materials over the past twenty years. Guided by the multi-electron reaction, light weight electrode and multi-ion effect, current development strategies and future trends of high-energy-density batteries are highlighted from the perspective of materials and structure system innovation. Typical cathode and anode materials with the multi-electron reactions are summarized from cation-redox to anion-redox, from intercalation-type to alloying-type, and from liquid systems to solid-state lithium batteries. The properties of the typical materials and their engineering prospects are comprehensively discussed, and additionally, the application potential and the main challenges currently encountered by solid-state batteries are also introduced. Finally, this paper gives a comprehensive outlook on the development of high-energy-density batteries.

Key words: high energy density; lithium-ion batteries; multi-electron reaction; solid-state batteries; electrode material system

1 Introduction

As the global promotion of "dual carbon" plan (peak carbon dioxide emissions and carbon neutrality), rapid development in energy harvesting, conversion and storage has been achieved and accordingly attracted both scientific and commercial attentions. Nowadays, it has become the mainstream to accelerate energy transition from fossil fuel to renewable ones, such as solar and wind power. Regarded as the most successful benchmark for renewable energy storage, lithium-ion batteries (LIBs) have received intensive exploration for decades[1]. Its application range has expanded from consumer potable electronics, power tools to emerging fields, such as electric vehicles, electric aircraft, large-scale grid regulation, and so forth. Unfortunately, the energy density offered by current electrode materials and systems has been handicapped approaching to 300 Wh·kg^{-1}, which cannot fulfill the rapid growth of requirements on energy density-sensitive implementations[2,3]. In this regard, the original concept of "multi-electron reaction materials" has been declared by Wu et. al. in 2002, providing fundamentals to break through energy density limits and significantly promoting the progress of LIBs[4, 5]. Herein,

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Received: 2022-09-21; Revised: 2022-10-25. * Corresponding author, Xin-Ran Wang: Tel: (86-10)68918766, E-mail: wangxinran@bit.edu.cn; Ying Bai: Tel: (86-10)68912528, E-mail: membrane@bit.edu.cn; Chuan Wu: Tel: (86-10)68912676, E-mail: chuanwu@bit.edu.cn

this review has illustrated the principle of "multi-electron reaction materials" and "multi-ion effect", and summarized the development of multi-electron reactions materials and systems innovations.

2 Multi-Electron Reaction Mechanisms for Electrode Material Design

The specific energy density is determined by the Gibbs free energy of certain redox reactions under standard conditions. Taking the gravimetric energy density (E_g) as an example, it can be expressed by the following equation:

$$E_g = -\frac{nFE}{\sum M_g} \tag{1}$$

in which $\sum M_g$ is the total weight of reactants ($mol \cdot g^{-1}$), n represents the charge transfer number, E is the voltage (V), and F is the Faraday constant. According to Equation (1), three strategies can be concluded to increase the overall energy density: (1) higher E, (2) multi-electron reaction transfer ($n > 1$) and lighter weight (lower M_g). By comparison, it seems promising to establish multi-electron reaction materials or select light weight but redox-activated elements since there is not much space for optimizing operating voltage. The connotation of such concept has been expanded due to the intensive exploration of multi-electron reaction materials, where the multi-ion effect has been defined as follows:

$$E_g = \frac{-nFE}{\sum M_g}\eta \tag{2}$$

where η means the activity of charge carriers, including both cations and anions that participate during the redox ("multi-ion effect")[6]. Figure 1 depicts the origin and development of multi-electron reaction materials. Funded by the National Basic Research Program ("973" project, 2002-2008), the "fundamental research on new green secondary batteries" project conducted by Wu et al. has focused on the basic multielectron reaction materials, such as ferrates, delivering three-electron transfer per Fe atom[7]. The second "973" project in 2009-2013 has achieved a huge leap in practical energy densities by transferring from aqueous to organic systems, highlighting multi-electron reaction materials with light weight, such as metal borides, fluorides, silicon/silicon oxides, sulfur and oxygen. The third "973" project in 2014-2019 has particularly introduced the concept of multi-ion effect, describing the development in multivalent charge carrier and lattice oxygen redox contributor in LIBs, sodium-ion batteries and alumina-ion batteries[7]. Three "973" projects have built up theoretical foundations for the construction of multi-electron reaction battery system toward high energy density. Since 2019, the active materials of the battery system represented by LIBs have been particularly optimized under the guidance of multi-ion effect. For cathode

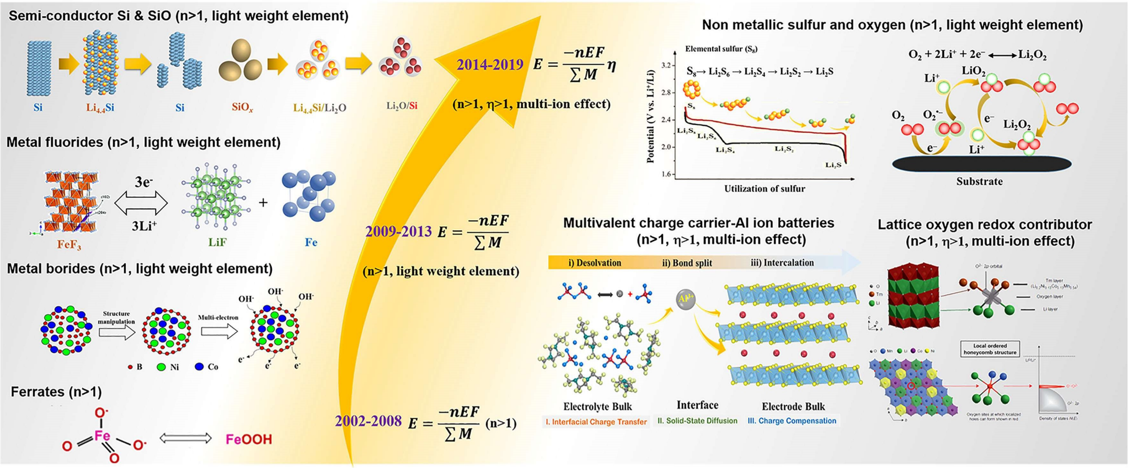

Figure 1 Schematic diagram showing the main periods of development of the multi-electron reactive material project. Reproduced with permission of Ref. 6, copyright 2021, Springer. (color on line)

materials, the research trend has shifted from cation-redox to anion-redox. While for anode materials, rather than intercalation-type candidates, alloying-type and conversion-type electrochemistry and materials have become the main focus. In addition, multi-valence charge carriers have played an important role in building up multi-electron reaction systems, such as zinc-ion battery, magnesium-ion battery, aluminum-ion battery, dual-ion battery and so forth. In the following sections, we mainly focus on the development trend of electrode active materials based on the multi-electron reaction theory. The corresponding design strategy and electrochemical performance of representative electrode active materials are summarized in Table 1.

3 From Cation-to Anion-Redox Cathodes $n > 1$, $\eta > 1$): structure, stability and safety

According to Equation (1) (high E), the ternary cathode ($LiNi_xCo_yMn_{1-x-y}O_2$, NCM) has exhibited high operational voltage and theoretical capacity (~280 mAh·g^{-1}), thus fulfilling high specific energy density for LIBs. The crystal structure of the ternary material is α-$NaFeO_2$ type layered structure, which belongs to the hexagonal crystal system with the R-$3m$ space group. As shown in Figure 2a, Li and O atoms occupy the 3a and 6c sites in the lattice, while transition metal (TM) atoms randomly occupy the 3b positions to form a MO_6 octahedral structure[8]. In fact, high Ni-content ($x > 0.8$) in crystal will increase specific capacity and in turn produce severe Li/Ni mixed arrangement since the radius of Li^+ (0.76 Å) is similar to that of Ni^{2+} (0.69 Å). During cycling, a large number of vacancies produced by Li^+ extraction from the interlayer will accelerate Ni/Li mixing, which aggravate the structure transformation to spinel and rock-salt structures with serious capacity attenuation[9]. Introducing guest ions in lattice has been reported to minimize such problems, which can form strong bonds with host ions to suppress cation-mixing (Figure 2b)[10]. More promisingly, designing a full concentration gradient (FCG) NCM allows for both high capacity and long cycle life[11]. Being steadily protected

Table 1 Corresponding design strategy and electrochemical performance of representative electrode active materials

Electrode type	Material type	Designing strategy	Cycling performance	Capacity retention or voltage hysteresis (Li|Li cells)	Ref.
Cathode	$LiNi_xCo_yMn_{1-x-y}O_2$	"Pillar ions" doping	162.5 mAh·g^{-1} at 1 C after 100 cycles	96.2%	[10]
		Concentration gradient regulation	158.7 mAh·g^{-1} at 1 C after 100 cycles	92.7%	[12]
	Li- and Mn-rich based	Surface modification	202 mAh·g^{-1} at 1 C after 100 cycles	94.0%	[18]
		Doping modification	222.2 mAh·g^{-1} at 1 C after 200 cycles	89.2%	[19]
Anode	Silicon-based	Nano-crystallization by vapor phase growth	3500 mAh·g^{-1} at 0.2 C after 20 cycles	/	[28]
		Coating by dual-carbon shell	~1350 mAh·g^{-1} at 0.2 C after 1000 cycles	75.2%	[29]
	Li metal	Composite with carbon fiber and Ag coating	Cycled over 400 h at 1 mA·cm^{-2} with an area capacity of 1 mAh·cm^{-2}	80 mV	[33]
		PVDF-HFP coating	Cycled over 1600 h at 1 mA·cm^{-2} with an area capacity of 1 mAh·cm^{-2}	20 mV	[34]

by the outer Ni-deficient layer, the inner Ni-rich portion enables high reversible capacity and cycle stability (Figure 2c)[12]. Towards more commercially-friendly strategies, preparing single-crystalline NCM is highlighted due to the isotropic crystal orientation for expansion accommodation and microcracks inhibition. The grain boundary-free characterization generally avoids the loss of effective contact, cracks, pulverization and cycle instability[13]. However, the debate on the safety of single- and poly-crystalline NCMs still exists. Wu et al.[14] explored the thermal-driven degradation behavior of single- and poly-crystalline NCMs through comprehensive thermodynamic analysis. It was proved that the single-crystalline one exhibited higher thermal decomposition rate and thus poorer thermal stability. The key parameters of thermodynamic degradation, such as activate factor, were quantitatively measured, also verifying the fact that single-crystalline NCM may not be as safe as we expected during thermal decomposition.

Li- and Mn-rich cathode materials have received increasing attention due to their anion-redox (Equation (2), $n > 1$, $\eta > 1$) and high specific capacity (250 ~ 400 mAh·g^{-1})[15, 16]. Reversible crystal oxygen redox with additional Li$^+$ insertion contributes to the multi-ion effect. However, the voltage decay and irreversible releasing of oxygen constitute the major obstacles for their practical utilization, delivering low initial Coulombic efficiency (ICE), poor cycling stability, and low-rate capability[17]. Surface modification seems to be effective to control oxygen activation and prevent structural degradation. For example, Hu et al. [18] designed a compatible $La_{0.8}Sr_{0.2}MnO_{3-y}$ (LSM) coating layer through strong Mn—O—M bonding to suppress oxygen evolution, structural phase transition and the formation of surface nanopores during electrochemical processes (Figure 2e). In addition, doping ions (cations, anions, polyanions, etc.) in the bulk phase can affect the redox of anions, e.g., Yu et al. [19] introduced Te^{6+} by forming directional M—O bonds, prompting more non-bonded oxygen structures and improving anionic redox

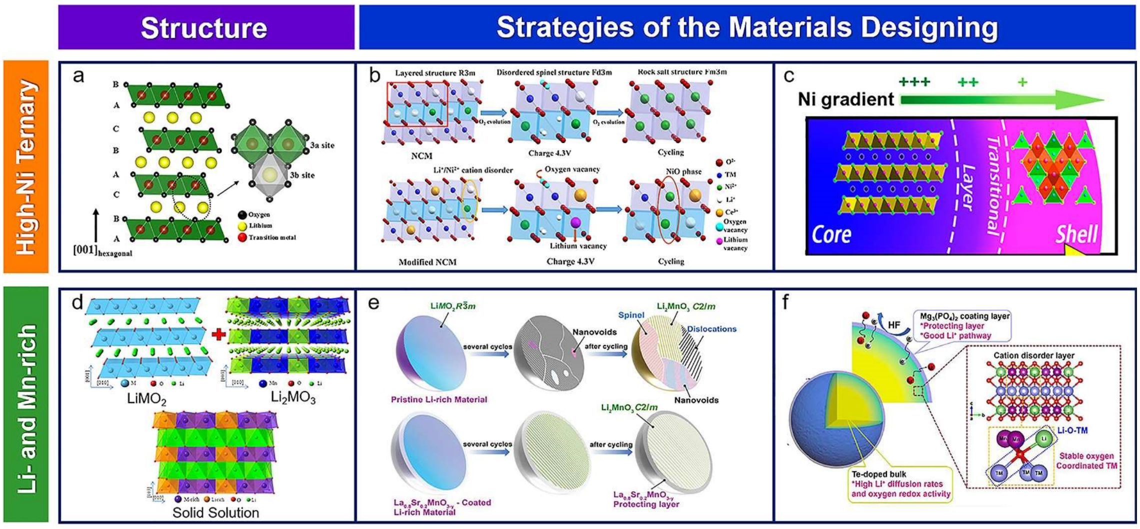

Figure 2 (a) Crystal structure of ternary materials. Reproduced with permission of Ref. 8, copyright 2021, Springer. (b) Schematic illustration of the cationic mixing and phase transition mechanism of NCM suppressed by doped "pillar ions". Reproduced with permission of Ref. 10, copyright 2021, American Chemical Society. (c) Illustration of a concentration gradient particle. Reproduced with permission of Ref. 12, copyright 2017, American Chemical Society. (d) Phase structures of $LiMO_2$, Li_2MnO_3 and Li- and Mn-rich solid solution. Reproduced with permission of Ref. 15, copyright 2013, American Chemical Society. (e) Schematic diagram of coating modification of Li- and Mn-rich material. Reproduced with permission of Ref. 18, copyright 2019, Wiley. (f) Schematic diagram of Te-doped Li- and Mn-rich layered oxides. Reproduced with permission of Ref. 19, copyright 2021, Elsevier. (color on line)

activity (Figure 2f). Xia has constructed an O_2-type Li- and Mn-rich cathode with a single-layer Li_2MnO_3 superstructure, which is not prone to metal migration and oxygen precipitation with a high reversible capacity of 400 mAh·g^{-1} [20].

The metal oxide cathode materials containing Ni, Co, Mn and other transition metal elements have large atomic weight, which limits the increase of the energy density. The development of light-weight cathode materials with anionic redox effect has received extensive attention. Sulfur (S), as the representative of light-weight multi-electron reaction cathode, involves 16 electrons transfer for each S_8 and thus provides theoretical capacity of 1675 mAh·g^{-1}. Lithium sulfur (Li-S) batteries using S as a cathode has also made rapid development in recent years[21]. Yusheng Yang is a pioneer that makes great contribution to the development of Li-S batteries, the one who originally designed organic polymer sulfide cathodes (Figure 3a)[22], the mesoporous carbon/S composite cathodes and core-shell structure cathodes (Figure 3b and c)[23, 24]. A landmark study of DOL/DME binary electrolyte has been proposed by Yang's team, which is widely implemented in Li-S batteries[25, 26]. However, the poor electrical conductivity and shuttle effect of polysulfides lead to the poor cycling stability in practical. Therefore, Li-S batteries remain in the stage approaching to commercialization. Recent works showed that encapsulating S into nanomaterials for spatial confinement and introducing polar adsorption group into battery components are more feasible to suppress the shuttle effect of polysulfides (Figure 3d). At present, researchers are exploring the multi-electron reaction mechanism of S electrode to provide theoretical guidance for the commercialization of Li-S batteries.

4 From Intercalation to Alloy-Type Anodes (n > 1): Electrochemistry and Challenges

At present, graphite is still the main anode material for commercial LIBs. However, the theoretical specific capacity of graphite is limited due to the intercalation reaction mechanism. In order to further improve the energy density of battery, the new type of high-capacity anodes based on conversion reaction should be developed.

Alloying-type anode inherently enables multi-electron reaction and delivers several times higher capac-

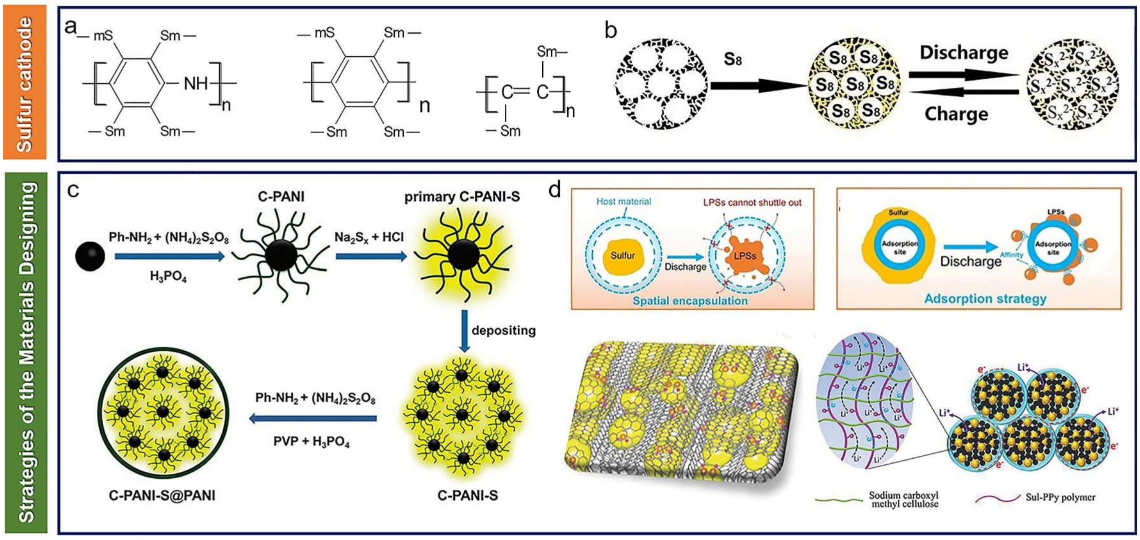

Figure 3 Schematic diagrams of organic polymer sulfide cathode (a) and mesoporous carbon and S composite cathode (b). (c) Synthetic route of C-PANI-S@PANI. Reproduced with permission of Ref. 23, copyright 2013, Royal Society of Chemistry. (d) Schematic illustration of various routes to inhibit the shuttle effect of polysulfides. Reproduced with permission of Ref. 21, copyright 2022, Wiley. (color on line)

ity than the conventional intercalation-based counterparts, e.g., silicon (Si)-based anode gives rise to an ultra-high theoretical capacity ($4200\ \mathrm{mAh\cdot g^{-1}}$ for pure Si anode). Actually, due to the multi-electron transfer, alloying-type anode inevitably suffers from severe volume expansion, e.g., 300% for Si. The huge volume change may lead to the accumulation of internal stress and the generation of cracks in the electrode, resulting in the pulverization of active materials. The pulverization leads to the instability of the solid electrolyte interface (SEI) on the Si surface, and the continuous fragmentation and regeneration process, leading to the consumption of electrolyte and the attenuation of reversible capacity (Figure 4a). Accompanied with low electronic conductivity (10^{-5} ~ $10^{-3}\ \mathrm{S\cdot cm^{-1}}$) and ionic diffusion coefficient (10^{-14} ~ $10^{-12}\ \mathrm{cm^2\cdot S^{-1}}$), pure silicon anodes have not yet been successfully commercialized[27]. At present, multiple trade-off directions have been produced, including: (1) nanostructured Si. It can support 100% silicon anode with acceptable volume expansion, but low density, relatively high cost and intensive SEI forming (Figure 4b)[28]; (2) Si/C composite. Apparently, the capacity of Si/C (with limited Si less than 10%) delivers much reduced capacity than that of pure Si, yet it is the most commercialization available forms. Regulating Si/C structure is widely accepted, such as core-shell structure, yolk-shell structure, etc. Typically, Yu's team proposed a Si/C anode with two carbon cladding layers (Figure 4c). The internal carbon shell provides a limited internal void to allow a large number of changes in Si nanoparticles inside the internal carbon shell, while the static external shell helps to form a stable SEI. The space between shells can be reserved to buffer volume changes and reduce the mechanical stress generated by the internal carbon shells. This dual-shell concept can also be used to synthesize other electrode materials with large volume changes in cycles[29]. (3) SiO_x. As a mixture of oxygen-containing Si compounds, SiO_x is with restrained volume expansion and thus better cycle stability. Pre-lithiation is required for all the Si-containing anode systems due to the low initial Coulombic efficiency (CE), where current pre-lithiation technology

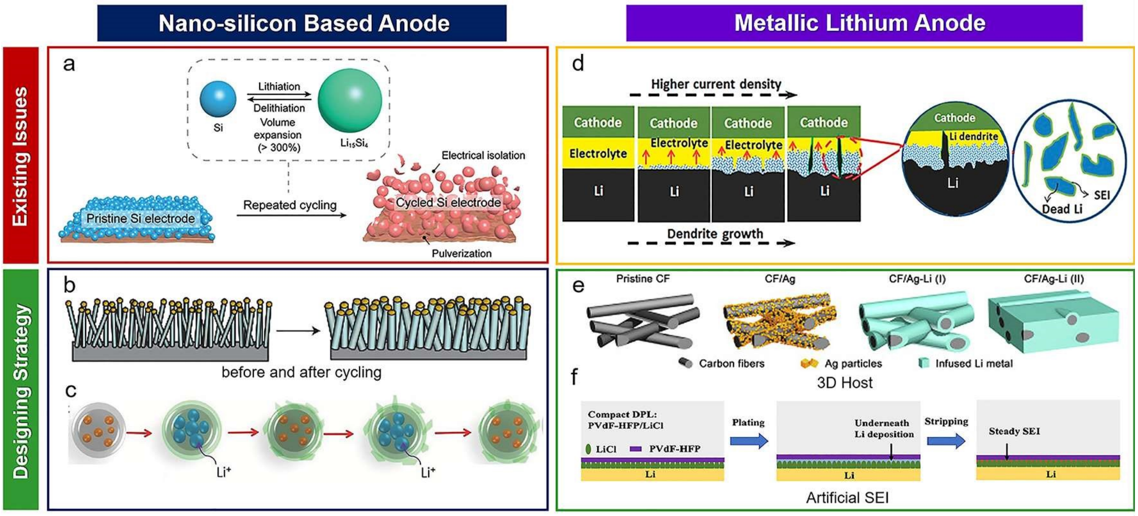

Figure 4 (a) schematic diagram of failure mechanism of silicon-based anode. Reproduced with permission of Ref. 27, copyright 2021, Wiley. (b) Schematic of morphological changes that occur in Si nanowire during cycling. Reproduced with permission of Ref. 28, copyright 2008, Nature. (c) Schematic illustration of the morphology evolutions of Si-C with double layers during cycling. Reproduced with permission of Ref. 29, copyright 2017, Wiley. (d) Failure mechanism of metal lithium anode. Reproduced with permission of Ref. 30, copyright 2020, American Chemical Society. (e) Schematic diagram of preparation process of 3D host composite metal lithium anode. Reproduced with permission of Ref. 33, copyright 2018, Cell. (f) Schematic diagram of the artificial SEI-stabilized lithium metal interface. Reproduced with permission of Ref. 34, copyright 2021, Elsevier. (color on line)

remains challenging to achieve the balance among safety, cost and environment requirement.

Lithium metal is regarded as one of the most attractive choices for anode due to its high theoretical capacity of 3860 mAh·g^{-1} and the lowest reduction potential (−3.04 V vs. SHE). It can theoretically provide a specific energy exceeding 400 Wh·kg^{-1} when paring with S or high-Ni NCM cathodes. However, the application of metallic lithium anode is still in the very initial stage due to its obvious defects (Figure 4d), such as the uncontrollable growth of Li dendrites. In addition, the unstable SEI is easily broken during cycling, resulting in direct contact and the consumption of electrolyte, thereby shortening the cycle life. Moreover, the active Li is also easily detached from the current collector to form "dead Li", which reduces the CE and further deteriorates the cycle performance[30]. In order to solve these problems, a number of carbon host have been implemented, being supposed to buffer the volume expansion[31, 32]. Moreover, they also have the ability to regulate the transports of electron and Li$^+$ so that Li can be uniformly deposited inside the host in the absence of dendrites. As shown in Figure 4e, Zhang et al.[33] designed a Li-infused carbon fiber composite, where the surface of carbon framework (CF) was modified with a lithiophilic silver coating (CF/Ag). By comparison, the CF/Ag-Li exhibits no dendrite and "dead Li" during cycling, thereby obtaining excellent electrochemical performance. Furthermore, the flexible-rigid artificial SEI is also important to achieve better electrochemical performance. For example, Wu et al.[34] designed an organic/inorganic bilayer protection interface containing lithium chloride (LiCl), polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP). *In-situ* grown LiCl inorganic inner layer provides high mechanical strength (Young's modulus 6.5 GPa) and low diffusion barrier (0.09 eV), which can suppress dendrite growth from both mechanical stress and chemical diffusion. The coated PVDF-HFP organic layer has good flexibility and ion permeability to buffer the volume change of Li metal, and suppress the dissolution of the LiCl layer and interfacial side reactions (Figure 4f).

5 From Liquid to Solid-State Lithium Batteries: High Safety and Energy Density

High levels of energy density and safety are requisite for the development of LIBs. Solid-state lithium batteries (SSLBs) are expected to inhibit safety hazards and better implement the multi-electron reaction materials. As shown in Figure 5, current SSBs can be divided into polymer and oxygen group inorganic compounds (oxide, sulfide, etc.) according to the type of materials.

5.1 Organic Polymer Electrolytes.

Polymer-based solid electrolytes have received extensive attention due to their good safety properties, flexibility, easy processing into films, and excellent interfacial contact, such as polyethylene oxide (PEO), polycarbonate (PC), polyvinyl nitrile (PAN), polymethyl methacrylate (PMMA), polyvinylidene difluoride (PVDF), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (Figure 5a). Li$^+$ achieves polymer-to-salt solvation by coordinating with lone pairs of electrons on heteroatoms in the polymer chains[35]. The free volume is generated under the local segmental motion of the polymer chain, thereby realizing the conduction of Li$^+$ within and between chains[36]. The polymer electrolytes are restrained by the low room-temperature ionic conductivity, even though it is not expected, high temperature (60 °C) remains a necessity for practical implementation. In this regard, molecular design of novel polymer electrolytes paves the way to their commercialization. In particular, Wu et al. has synthesized novel hyperbranched polyether electrolytes with regional-condensed —OH groups, which constitutes "Li$^+$-solvation cages" to boost Li salts dissolution and Li$^+$ migration (Figure 5b). By further polypropylene skeleton compositing, the composite solid electrolyte (PHMP) synergistically achieves high voltage tolerance (4.6 V), high ion-conduction (25 °C, 1.26×10^{-4} S·cm^{-1}), and flexible-rigid mechanical properties. Furthermore, the first-principles calculation reveals the mechanism for the suppression of proton-induced high-voltage decomposition due to the 3D structure. As a result, high ionic conductivity over 0.1 mS·cm^{-1} at room temperature is achieved with 4.6 V stable voltage window, breaking through the inherent obstacles faced by polymer electrolytes[37]. More recently, Wu et al. has proposed an *in-situ* polymerization of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) inorganic and poly(ethylene glycol methacrylate) (PEGMA) based hybrid electrolyte system. The ionic conductivity was greatly improved to 2.37×10^{-4} S·cm^{-1} at room temperature. Furthermore, a solid-electrolyte-lithium integrated anode was synthesized thereafter, which can support the assembly of SSLBs in ambient condition (30% humidity) without any Li anode oxidation or capacity decay[38]. In order to achieve sufficiently high electrochemical window, Cheng et al.[39] utilized dual-salt components (LiBOB and $LiClO_4$) to enhance the electrochemical stability window of PEO-based composite electrolytes up to 4.7 V. The addition of the double salt component formed stable SEI and cathode electrolyte interface (CEI) at the anode and cathode interfaces, respectively. The multiplied polymer-ion interactions and formation of Li-B-O/C-O species originated from the (oxalato)borate group of LiBOB effectively promote the electrochemical stability of the PEO based composite electrolyte and its wetting properties with electrodes. As shown in Figure 5c, the dual-salt component can inhibit harmful non-conductive decomposition products and NCM particle breakage, thus improving the cycling stability.

5.2 Oxygen Group Inorganic Solid Electrolyte (Oxide- and Sulfide-Based)

Inorganic solid electrolytes mainly include oxide-based electrolytes and sulfide-based electrolytes (Figure 5d). Oxide-based electrolytes mainly include perovskite type ($Li_{3x}La_{2/3x}TiO_3$, LLTO), fast ionic conductor type (LISICON and NASICON), and garnet type ($Li_7La_3Zr_2O_{12}$, LLZO), which are promising for large-scale applications in SSLBs due to their stable existence in ambient condition. However, most of the oxide electrolytes are unstable to Li metals, and interfacial modifications are required[40]. Current researches generally adopt porous structures or coating layers on surface to stabilize the interface of Li metal[41, 42]. Theoretically, Li et al.[41] used first principles calculations to prove that the suitable coating layer can successfully prevent the electron transfer from lithium metal to SSE to inhibit the dendritic growth (Figure 5e). Experimentally, Zhu et al.[43] sprayed commercial boron nitride-based release agent (BNRA) on LATP to construct a composite protective layer. The chemical interaction between BN and Li forms Li—N bonds, reduces the interfacial resistance, and thereby promotes Li^+ migration and interfacial compatibility. Compared with oxide-based and polymer-based electrolytes, sulfide-based electrolytes show higher room-temperature ionic conductivity (even over 10^{-2} S·cm^{-1})[44-46]. However, it suffers from narrowed voltage range, interface issue and poor air stability[47-49]. In particular, sulfide-based electrolytes have poor electrochemical stability and compatibility with high-voltage cathodes (Figure 5f). Furthermore, sulfide-based electrolytes are not resistant to the air, which react with H_2O in the air and release toxic H_2S gas. Compared with inorganic solid electrolyte, quasi-solid electrolyte or gel electrolyte exhibit better processing performance, flexibility and more importantly the acceptably high ionic conductivity at room temperature, which can guarantee sufficient ion conduction, form a stable contact between the electrode and effectively avoid battery failure caused by volume change. Therefore, quasi solid or gel electrolytes are expected to achieve large-scale production earlier to meet the demands of high energy density batteries.

6 Summary and Perspective

Guided by the principle of multi-electron reaction materials, characterizations of multi-electron transfer, light weight electrode and multi-ion effect have boosted the significant development of energy density. For cathodes, the synergistic contribution from both cationic and anionic multi-electron reactions opens up new avenues for energy density enhancement. For anodes, alloyed materials with high specif-

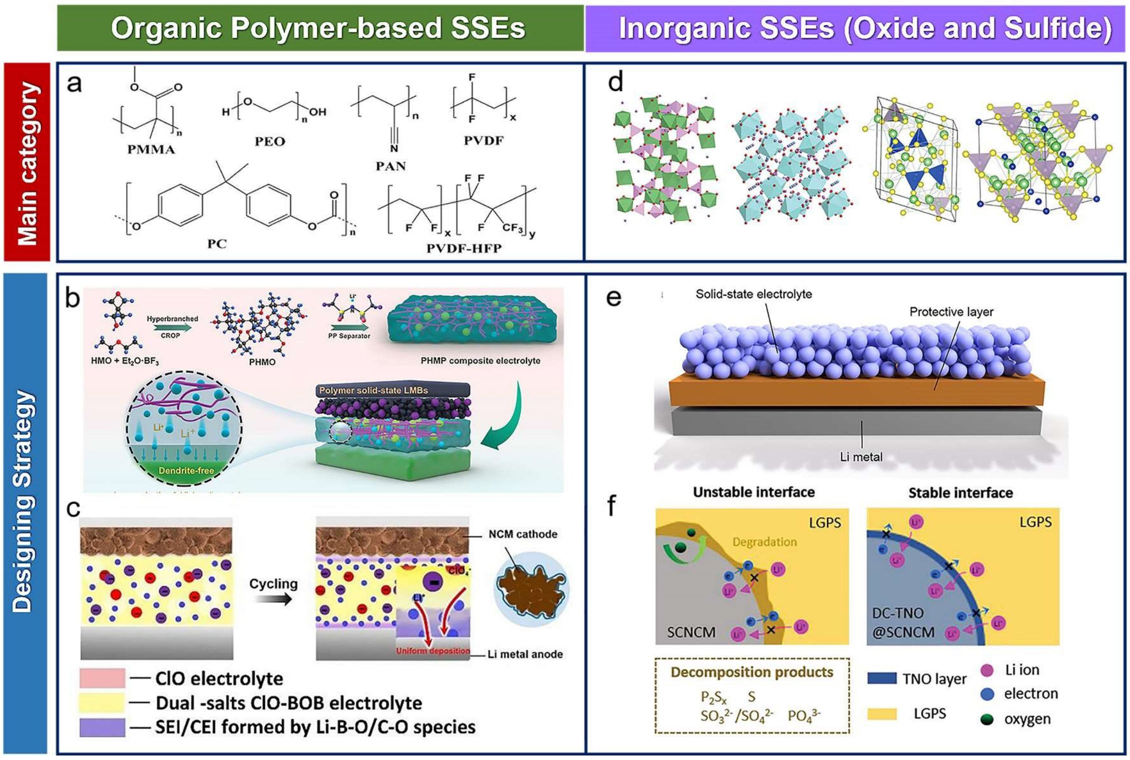

Figure 5 Overview diagram of the main three technology routes in solid-state batteries. (a) Common polymer based solid electrolyte systems; (b) Synthetic scheme of PHMP composite solid electrolyte. Reproduced with permission of Ref. 37, copyright 2022, Wiley. (c) Schematic illustration of the dual-salt achieving excellent high voltage cycling performance. Reproduced with permission of Ref. 39, copyright 2021, Elsevier. (d) Schematic diagram of typical oxide and sulfide electrolytes crystal structure. Reproduced with permission of Ref. 40, copyright 2018, Wiley. Reproduced with permission of Ref. 45, copyright 2022, Royal Society of Chemistry. (e) Schematic illustration of the role of protective layers on suppressing Li dendrite formation in SSEs. Reproduced with permission of Ref. 41, copyright 2022, Elsevier. (f) Schematic diagram of interface instability between sulfide electrolyte and high voltage cathode. Reproduced with permission of Ref. 48, copyright 2022, Wiley. (color on line)

ic capacity, low average delithiation potential, and multi-electron reaction characteristics are becoming the main trend of development. From the perspective of the long-term development of batteries, it is a recognized trend in the industry to continuously reduce the electrolyte content to develop solid-state batteries. The development of high-performance electrolyte materials and high-stability, low-impedance solid-solid interface preparation technology is expected to realize the application and popularization of high-voltage cathodes and metal-based composite anodes. Molecular design of polymer electrolyte has provided the possibility to apply polymer electrolyte, rather than inorganics or organic-inorganic hybrid systems. However, the room temperature ionic conductivity and the safety performance of the electrolyte itself still need more efforts to optimize. In terms of oxides or sulfides, the interface compatibility constitutes the major obstacle that generally requires additional interface protection or coating in practical. When paring with a Li anode, it is proved that even inorganic grain electrolyte cannot avoid the dendrite growth due to the relatively high electrical conductivity and structure defects. Therefore, it still faces a long way to go for oxides and sulfides to solve their interface issues, and optimize more reliable structure and system.

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多电子反应材料推动高能量密度电池发展：材料与体系创新

郭瑞琪[1,2],吴 锋[1,2],王欣然[1,2*],白 莹[1*],吴 川[1,2*]

(1. 北京理工大学材料学院,环境科学工程北京市重点实验室,北京 100081;
2. 北京理工大学长三角研究院(嘉兴),浙江 嘉兴 314019)

摘要: 全球能源结构转型推动了电化学储能系统的飞速发展，提高能量密度是发展新型二次电池的重要方向和研究热点。然而,受限于传统的嵌入式反应,锂离子电池在能量密度上已经逐渐达到极限。要发展更高能量密度的新型二次电池,需要在新理论、新材料和新体系上进行突破。基于此,本文总结了 20 年来多电子反应材料概念的形成、理论的发展、材料创制的历程。在“轻元素多电子反应”和“多离子效应”核心设计准则的指导下,具有上述特征的电极材料与电池结构不断发展迭代，引领了高能量密度电池的发展方向。从阳离子氧化还原到阴阳离子协同氧化还原,从嵌入式反应到合金化反应,从传统有机液态体系到电池固态化,本文梳理了典型的多电子反应正负极材料的结构特性、体系创新和工程化前景,剖析了多电子反应电极材料的瓶颈问题,并分析了电池固态化发展所面临的挑战。最后,对高能量密度电池的未来发展趋势和难点进行了归纳与展望。

关键词: 多电子反应；高能量密度；锂离子电池；电池固态化；电极材料体系