Working Interfaces



Sulfur Redox Reactions at Working Interfaces in Lithium–Sulfur Batteries: A Perspective

Hong Yuan, Hong-Jie Peng, Jia-Qi Huang, and Qiang Zhang*

Lithium-sulfur (Li-S) batteries have been strongly considered as one of the most promising future energy storage systems because of ultrahigh theoretical energy density of 2600 Wh kg⁻¹. The natural abundance, affordable cost, and environmental benignity of elemental sulfur constitute additional advantages. However, complicated reaction behaviors at working electrode/ electrolyte interfaces that involve multiphase conversion and multistep ion/electron diffusion during sulfur redox reactions have impeded the thorough understanding of Li-S chemistry and its practical applications. This perspective article highlights the influence of the ion/electron transport and reaction regulation through electrocatalysis or redox mediation at electrode/electrolyte interfaces on various interfacial sulfur redox reactions (liquid-liquid-solid interconversion between soluble lithium polysulfide with different chain lengths and insoluble lithium sulfides in liquid-electrolyte Li-S batteries and direct solid-solid conversion between sulfur and Li₂S in all-solid-state Li-S batteries). The current status, existing challenges, and future directions are discussed and prospected, aiming at shedding fresh light on fundamental understanding of interfacial sulfur redox reactions and guiding the rational design of electrode/electrolyte interfaces for next-generation Li-S batteries with high energy density and long cycle life.

1. Introduction

The upgrade and evolution of electrical and electronic industry is driven by increasing social requirement, appealing for highenergy density energy storage system that is the key component of electronic products and electric vehicles.^[1] Lithium–sulfur (Li–S) batteries have been regarded as one of the most promising next-generation battery technologies because of ultrahigh theoretical energy density of 2600 Wh kg^{-1,[2]} Unfortunately, the practical application of Li–S battery is hindered by a series

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DOI: 10.1002/admi.201802046

of obstacles: a) the huge volume fluctuation of sulfur cathode during lithiation/ delithiation leads to the cracking and pulverization of electrodes; b) the insulating nature of sulfur and its discharged products (Li₂S₂/Li₂S) induces a high redox overpotential and sluggish reaction kinetics; and c) lithium polysulfides (LPSs), soluble intermediates in liquid electrolytes, dissolve, diffuse, and decompose in electrolytes and/or at interfaces, leading to loss of active materials and interface destabilization. All above obstacles come together to render current Li-S batteries with low Coulombic efficiency, insufficient sulfur utilization, poor cycling stability, and severe anode corrosion.^[3,4]

In general, a typical Li–S battery is composed of a sulfur cathode, a lithium metal anode, and a suitable electrolyte either in liquid or solid state.^[5] The electrochemical redox reactions of sulfur in aprotic liquid electrolytes (or gel polymer electrolytes containing a fraction of liquid solvents) include complicated multiphase evolution and multistep charge-transfer/nontransfer

processes (S₈ (s) \leftrightarrow Li₂S_m (l) \leftrightarrow Li₂S_n (l) \leftrightarrow Li₂S₂/Li₂S (s), 4 \leq *n* < *m* \leq 8 while s and l refer to solid and liquid, respectively).^[6] Although the chemical equilibria of soluble LPSs in electrolytes has a positive effect on improving sulfur conversion rates to Li₂S product,^[7] the formation of LPSs and their dissolution and migration in liquid electrolytes between cathodes and anodes, that is so-called shuttle effect, is clearly one of the greatest threats to cycle life and stability of Li–S batteries.^[8–10]

Considerable efforts have been paid to mitigate the shuttle of soluble LPSs via spatial confinement by porous hosts and chemical adsorption by polar materials.^[11] However, the accumulation of soluble LPSs in catholyte always occurs and hence the shuttle driven by the concentration gradient can hardly be fully avoided. Therefore, enhancing conversion kinetics of soluble LPSs to alleviate the shuttle effect has attracted more attentions.^[12-14] On one hand, promoting the transformation (liquid to liquid) from higher-order and highly soluble LPSs (Li₂S₈ and Li₂S₆) to lowerorder and relatively poorly soluble LPSs (Li2S4) can reduce the overall dissolution of LPSs in liquid electrolytes.^[9] On the other hand, facilitating the conversion (liquid to solid) of LPSs to solid Li₂S₂/Li₂S can reduce the bulk concentration of active species and, more importantly, shorten their retention time in electrolytes. To realize rapid redox kinetics of LPSs, electrocatalysis at the working solid (electrode)/liquid (electrolyte) interface plays a pivotal role.



To completely address the shuttle issue of LPSs, another promising approach is all-solid-state Li-S batteries that avoid the use of organic liquid electrolytes in a working cell.^[15] Different from liquid electrolytes, sulfur is directly converted to Li₂S in a solidstate battery without going with LPS dissolution. Consequently, the shuttle is prevented at root. In comparison to organic electrolytes, solid electrolytes pose paramount advantages in battery safety as their rigidity restrains the formation of lithium dendrites to some extent and the nonflammability reduces the risk of battery firing. Furthermore, the adoption of solid electrolyte may have potential to achieve higher energy/power densities as long as with reduced thickness. However, all-solid-state batteries always suffer from the great challenge of charge transport at solid (electrically conductive scaffold)/solid (active materials)/ solid (ionically conductive electrolyte) triple interfaces.^[16] Any degradation in the contact between solid phases results in unsurmountable internal résistance.

Since the electrode/electrolyte interfaces have much profound influence on sulfur electrochemistry in a working battery whatever it uses, a liquid or solid electrolyte, we will briefly summarize recent advances in understanding of sulfur redox reactions at working interfaces and design strategies for these interfaces. Liquid- and solid-electrolyte Li–S batteries are both considered and compared. We will especially focus on the ion/electron transport and reaction regulation through electrocatalysis or redox mediation at the interfaces and attempt to make a perspective on existing challenges and future directions at the end.

2. Sulfur Electrochemistry in Liquid-Electrolyte Li–S Batteries

Sulfur electrochemistry in most organic electrolytes is a typical heterogeneous process and their conversion strongly depends on the physicochemical properties of heterogeneous interfaces where electrochemical reaction occurs.^[17] Therefore, it is very important to understand the interfacial behaviors of sulfur redox reactions in a working cell. In fact, oxygen and sulfur are in the same main group VI in the periodic table. Thus, they share some common features such as multi-electron transfer and multiphase transitions in terms of their interfacial redox behaviors. The oxygen electrochemistry, including oxygen reduction and oxygen evolution, has been strongly investigated as probe reactions in current material science to evaluate the performance of nanostructured electrocatalysts.^[18] If the energy chemistry concepts developed for oxygen electrochemistry can be implanted into sulfur electrochemistry, many innovative strategies can be proposed to reduce the overpotential and enhance the reaction kinetics in a working Li-S battery. This understanding can afford efficient guidance for the rational design and improvement of electrode/electrolyte interfaces and thus promote the practical applications of Li-S batteries.

2.1. Liquid Sulfur Redox Reaction

Owing to the high solubility of high-order LPSs in liquid electrolytes, LPSs are easily dissolved in organic electrolyte once formed through initial electroreduction of sulfur or electro-oxidation of





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Li₂S. Therefore, the electrical contact mode with the conductive substrate changes from solid–solid to liquid–solid contact.^[19] Conventional opinion held was that liquid LPSs had better electrical contact than solid sulfur/Li₂S as LPSs can diffuse to unoccupied conductive surface while solids cannot. It was true when relatively low-surface-area conductive agents were employed in early studies.^[20] However, after the adoption of high-surface-area carbon nanomaterials in Li–S batteries since 2009,^[21] the total conductive surface area has never been a bottleneck while the issue comes from gradual loss of contact between carbon and LPSs that shuttle away. Therefore, only if an active LPS molecule is adsorbed on the electrode surface, the electron can be exchanged across the solid/liquid interface and electrochemical reactions can occur.^[22] In this regard, routine nonpolar conductive surface like a carbon surface is unfavorable in terms of LPS







Figure 1. Schematic illustration of the conversion process of sulfur species on a) nonpolar conductive carbon substrates and b) polar CoS_2 -decorated conductive carbon substrates. Reproduced with permission.^[13] Copyright 2016, American Chemical Society. c) Scheme of the LPSs adsorption and diffusion on the surface of various nonconductive substrates, indicating that the balance between strong adsorption and excellent diffusion favors for LPSs redox reaction. Reproduced with permission.^[25] Copyright 2016, Nature Research.

adsorption.^[22,23] The interface with high affinity to soluble LPSs is imperative for not only surface immobilization of LPSs but also subsequent interfacial charge transfer.

Much more efforts have been made to improve the properties of solid/liquid interface by modifying the solid surface with desirable LPS affinity such as doping heteroatoms into carbon lattices and decorating inorganic nanomaterials into conductive frameworks.^[24] The dopants or decorators not only enhance binding energies of LPSs on host materials but also possibly offer active centers for electrocatalytic conversion of soluble LPSs (Figure 1a).^[13] Notably, starting active species and reduced products are highly soluble during liquid-liquid transformation (the higher-order LPSs to lower-order LPSs during discharge while the lower-order LPSs to higher-order LPSs in the reverse process) in a working cell. The binding strength between soluble LPSs and solid substrates/interfaces should be moderate to satisfy both reactant adsorption and product desorption. Especially for electrical insulative materials, additional surface diffusion of LPS species on solid substrates is particularly important for their electrochemical conversion owing to the hindered electron transfer on insulating surface (Figure 1b).^[25] Accordingly, the balance between surface adsorption and desorption of LPSs at reactive interfaces should be strongly considered. Moreover, very strong binding strengths as revealed by previous first-principle calculations might not always be the actual case. In general, a very strong binding strength is resulted from substantial charge transfer between LPSs and the reactive interface. Such charge transfer induces either the oxidation of LPSs into sulfates/polythionates on oxidative substrates such as high-valence metal oxides^[26] or the reduction of LPSs into sulfides on reductive materials such as metals and low-valence metal compounds.^[27] Therefore, in this condition, the decomposition of LPSs completely changes the composition and properties of the interface, and then the binding strength should be re-evaluated at the reconstructed surfaces/interfaces.

2.2. Redox Reaction of Liquid Polysulfides to Solid Sulfides

The shuttle of LPSs is responsible for rapid capacity decay and low cycle life in a Li-S battery. Actually, there is strong competition between polysulfide accumulation and their redox transformation. The LPS diffusion is attributed to not only the thermodynamic driving force by concentration gradient but also the sluggish kinetics of their redox consumptions. If LPSs can be rapidly transformed to immobile solid products, their shuttle will be mitigated. Moreover, it is well known that the discharge capacity of low-voltage plateau, corresponding to nominal Li_2S_4 to solid Li_2S , is 1254 mAh g⁻¹, which is three quarters of theoretical capacity (1675 mAh g⁻¹).^[4] The liquid-solid conversion is thereby the key to achieve high utilization of sulfur. Likewise, the conversion kinetics of LPSs to solid Li₂S can also be improved by enhancing the electrocatalytic capability of active surface by heteroatom doping or interfacial decoration (Figure 2).^[14,28-31] However, the diffusion of LPSs can lead to the redistribution of active species on electrode surface; therefore, inducing the nonuniform deposition of solid $Li_2S_2/$ Li₂S and causing the passivation of electrode/electrolyte active interface.^[32] Furthermore, the reaction kinetics of LPS conversion usually becomes worse with prolonged cycling owing to increased internal resistance as a result of the formation of insulative Li₂S and their uneven precipitation.^[33] Therefore, the regulation of soluble LPSs and their controllable deposition are of great importance for high-performance Li-S batteries.

The deposition morphology of Li₂S strongly depends on the initial nucleation and subsequent growth, both of which are controlled by surface properties of electrode following heterogeneous crystal nucleation/growth theory.^[34,35] The intimate affinity between liquid sulfur species and active conductive surfaces is favorable for controllable nucleation as high affinity reduces the difference in surface energy between electrode surface and Li₂S nucleus, thus resulting in higher nucleation







Figure 2. a) Schematic illustration of the cooperative interfaces of LDH@NG with "sulfiphilic" and "lithiophilic" sites to promote the conversion of LPSs to Li_2S . Reproduced with permission.^[29] Copyright 2016, Wiley-VCH. b) Role of various substrates in surface reaction and nucleation, indicative of polar conductor favoring both LPSs adsorption and charge transfer compared with nonpolar conductor and polar insulator/semiconductor, and c) potentiostatic discharge indicative of the necessity of appropriate binding energy and charge transfer for high-efficient LPSs electrochemical conversion. Reproduced with permission.^[30] Copyright 2016, Wiley-VCH.

density and smaller nuclei size (**Figure 3**).^[31] The small precipitation size further favors ion/electron transport across the liquid (electrolyte)/solid (Li₂S)/solid electrode interface through shortened diffusion length. At the same time, high electrocatalytic capability of electrode/electrolyte interface improves the local concentration of LPSs as reactants for solid precipitation and/or reduces the reduction barrier from LPSs to Li₂S, promoting further growth of Li₂S on initial nucleus.

Besides the solid side of the interfaces, the liquid electrolytes are regulated for controllable nucleation of Li₂S. For instance,

an electrolyte with a high donor number can render high solvation of Li⁺ and thus enhanced solubility of LPSs. This leads to high nucleation barrier of Li_2S and finally its 3D growth on conductive hosts. Vice versa, low-donor number solvent renders the 2D film growth of Li_2S . Hence, the moderate donor number of electrolyte solvent is of great significance for the balance between the nucleation and growth of the sulfur species.^[35] Recently, the high dielectric constant of solvent can contribute to the success in high solvation and solubility of short-chain polysulfides, which therefore realize the stable formation of active



Figure 3. a) Schematic illustration of the controllable Li_2S nucleation and uniform growth on a collaborative triple-phase interface with strong adsorption, high electrical conductivity, high reactivity and uniform distributed nucleation sites, and b) the mechanism of LPSs redox reaction and Li_2S nucleation. Reproduced with permission.^[31] Copyright 2019, Wiley-VCH.

 S_3 ⁻ radicals in electrolyte. Whereafter, the disproportionation of S_3 ⁻ radicals to S^{2-} cations can promote efficient conversion of active sulfur species into thicker and denser Li₂S precipitates.^[36] Alertly, the high reactivity of high dielectric solvent toward Li metal should be taken into considerable account.^[37] In fact, the solvation of lithium polysulfides is largely related to the interaction between alkali metal cation and paired polysulfide anion. The larger and higher electropositive cations render stronger cation–anion electrostatic interactions.^[38] Although it can induce higher stability and lower solvation of short-chain LPSs and thus promote the reduction of high-order LPSs to short-chain LPSs, the oxidation of short-chain LPSs to long-chain LPS becomes turning into a serious headache in the reverse charge process.

2.3. Redox Reaction of Solid Sulfides to Liquid Polysulfides

An integrated charge/discharge cycle involves not only the reduction of elemental sulfur and precipitation of Li_2S but also the oxidation of Li_2S . In the reverse reaction process, the insulate Li_2S induces the high oxidation overpotential and thus, resulting in the sluggish kinetics of Li_2S dissolution.^[39] The low conversion efficiency of Li_2S causes the large irreversible capacity loss and poor active sulfur utilization.^[40] Therefore, the decomposition and oxidation of Li_2S in Li–S batteries should be strongly considered, which is of crucial importance in realizing high reversible capacity, high Coulombic efficiency, and long cycling stability for a practical working Li–S battery.

Similar to LPSs to Li₂S, the interfacial behavior at liquid (electrolyte)/solid (Li₂S)/solid (electrode) triple-phase boundary plays a critical role in Li₂S oxidation and electrocatalysis plays a predominant role (**Figure 4**).^[41] Different from the liquid–liquid



and liquid–solid conversions, the dissolution of Li₂S first suffers from the electron transfer across the solid/solid interface between conductive substrates and solid Li₂S particles. The intimate contact is one of the main factors to render rapid electron transfer. Moreover, the intrinsically insulative nature is also harmful for favoring electrons transfer. Consequently, there is a high active energy barrier during extraction of lithium ions in Li₂S.^[42] Especially, when elemental sulfur is replaced by Li₂S as starting active materials, the delithiation of Li₂S is more difficult during the first charging.^[39,40] Therefore, substrate surface with high electrocatalytic sites is necessary to reduce the reaction energy barriers and promote the reaction kinetics of Li₂S oxidation. Consequently, the energy efficiency is enhanced.

Obviously, the oxidative dissolution of Li₂S is not an individual process that is independent of Li₂S precipitation and LPS interconversion in a working Li–S battery. Unlike serving as the starting material, the morphology of Li₂S after discharging from sulfur is governed by last precipitation process. The nonuniform Li₂S deposition and their detachments from conductive frameworks induce a high electron transfer resistance as well as a large irreversible loss of Li₂S in the following dissolution of Li₂S in repeated cycling.^[31] Besides, there is always liquid LPS residue after discharge. These LPSs are served directly as redox mediators to promote the oxidation of Li₂S.

The Li₂S oxidation on an electrocatalyst in electrochemical cycles beyond the first charging of pristine Li₂S is still a black box. The catalytic substrate can either directly promote the decomposition of Li₂S or indirectly facilitate the regeneration of actual homogeneous redox mediators, LPSs, or both. An indepth fundamental understanding of the interrelation between the previous discharge process and the next charge process deserves more efforts to elucidate the effect of Li₂S morphology



Figure 4. Schematic illustration of the sulfur electrochemical reduction process and the Li_2S oxidation on the surface of a) conventional conductive polar substrate and b) catalytic substrate that favors the oxidization of Li_2S . c) Electrochemical decomposition mechanism and pathway of Li_2S on the various electrocatalytic surface and graphene. Reproduced with permission.^[41] Copyright 2017, National Academy of Sciences.

and residue LPSs on Li_2S oxidation and guide the interface design for the sulfur conversion chemistry.

3. Sulfur Electrochemistry in Solid-Electrolyte Li–S Batteries

In an all-solid-state lithium batteries, the solid electrolyte manifested in lithium-ion, sodium-ion, and especially in Li-S batteries has been considered as the primary advantage of practical battery systems toward achieving high safety, high energy density, and high power density.^[43] The electrochemical performance of solid-state batteries has been dominated by lithium ion transport in solid electrolyte.^[44] With the continuous development of solid electrolyte, a galaxy of solid electrolytes with high lithium ion conductivity in the order of 10^{-4} S cm⁻¹ at room temperature have exhibited great potential in all-solid-state lithium batteries, including oxide-type electrolytes and sulfide-type electrolytes.^[45] Especially for several state-of-the-art sulfide electrolyte materials, such as Li₁₀GeP₂S₁₂ (LGPS),^[46] Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3},^[47] $Li_3PS_{4,}^{[48]}$ and $Li_7P_3S_{11,}^{[49]}$ their ionic conductivity has reached the magnitude of 10^{-3} S cm⁻¹ and even exceeded 10^{-2} S cm⁻¹, which is comparable with or even surpasses that of routine liquid electrolytes. In spite of significant progress in all-solid-state Li-S batteries, a critical issue underlying solid/solid interfaces has hindered the exploration of all-solid-state Li-S batteries.^[50,51]

Unlike in routine liquid-electrolyte batteries where solid electrode can be infiltrated and wetted by liquid electrolytes to enable smooth lithium ion transport to the surface of solid electrode, there is a grand challenge in both ion/electron transports in composite all-solid-state cathode. The poor point-to-point contacts among solid electrolyte particles, solid active sulfur, and solid conductive agents impede the reliable



ion transport.^[52] A sulfur particle must be simultaneously connected by a solid electrolyte particle and a solid conductive agent particle. The solid electrolyte and conductive agent particles are interconnected to be continuous ion or electron transport frameworks, respectively. If any of the above insulation occurs during repeated cycling, this sulfur particle cannot be electrochemically utilized. Moreover, the ion and electron transport is more critical in all-solid-state Li–S batteries compared with other solid-state lithium batteries because of the intrinsic electronic and ionic insulation of solid sulfur and solid lithium sulfide.^[53] Therefore, the key for the high-efficiency operation of a working all-solid-state Li–S battery is to rationally design bicontinuous ion/electron frameworks that are mechanically steady, chemically stable, and structurally intimate with sulfur.

The most common strategy is to minimize the particle size of sulfur and solid electrolyte by a high-energy mechanical ball milling process.^[54] This method not only promotes the dispersion of active material in the cathode but also consolidates the interfacial contacts between active sulfur and conductive carbon as well as solid electrolyte. Considering the ultimate particle size at the range of micrometer obtained through strong ball-milling, the mixed-conductive networks in cathode composites can be further strengthened by constructing the intimate nanosized triple-phase contact. Recently, Xu and co-workers described a unique nanosized cathode with high electronic/ionic conduction by the deposition of sulfur nanoparticles on conductive reduced graphene oxide and then uniformly mixing with LGPS electrolyte and conductive carbon.[55] Wang and co-workers demonstrated a novel bottom-up approach to obtain a mixed ion/electron conductive Li2S nanocomposite, in which the active Li₂S and solid electrolyte with several nanometer size were in situ embedded on the conductive carbon matrix (Figure 5a).^[56] In comparison to the large and agglomerated particles, highly



Figure 5. a) Schematic illustration of the bottom-up synthesis of a mixed ion/electron conductive Li_2S cathode nanocomposite, in which nanosized Li_2S and solid electrolyte in situ embedded on the conductive carbon matrix. Reproduced with permission.^[56] Copyright 2016, American Chemical Society. b) Schematic of the 3D bilayer garnet solid electrolyte framework and ion/electron transfer pathways in this bilayer framework. Reproduced with permission.^[64] Copyright 2017, Royal Society of Chemistry.



dispersed nanoscale active materials and solid electrolyte and their close contact on carbon matrix rendered the reinforced ion/electron conductive capacity in solid/solid contact interfaces.

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An extreme demonstration of this concept is to adopt atomically dispersed sulfur like sulfurized polyacrylonitrile (SPAN) as active materials.^[57] Originally, SPAN was synthesized to eliminate the dissolution and migration of LPSs in liquid electrolyte, because sulfur presented as the form of short $-S_{x}$ - chains/ units and sulfur atoms are covalently bonded onto the SPAN heterocyclic backbones at an atomic and/or molecular level.^[58] Although SPAN served as cathode active material has achieved significant success in inhibiting LPS shuttling and improving electrochemical performance in both liquid-electrolyte and solid-state Li-S batteries, there are controversies toward the actual state of sulfur in SPAN molecular structure and therefore still remains a large open room to full understanding of reaction mechanism of SPAN.^[59] Fortunately, compared to elemental sulfur, SPAN possesses higher intrinsic electrical/ionic conductivities,^[60] thus reducing the percolation threshold of both electrical conductive agents and solid electrolytes.

The intimate ionic contacts between active material and solid electrolyte can be improved by solid electrolyte solution impregnation into porous electrode and in situ deposition on active materials.^[61] The wetting strategy of liquid-containing electrolyte for all-solid-state cathode has also been applied to enhance the poor solid/solid contacts due to the easy impregnation of liquid solution into porous electrodes forming continuous ionic transport pathways.^[51,62] A 3D interconnected solid electrolyte interphase (SEI) can be achieved through the interfacial reaction for Li ion transportation if there are controllable reactions. The dense solid electrolyte layer working as a blocking layer can inhibit the shuttle of LPSs while the liquid-containing electrolyte can enhance the interfacial wettability of solid sulfur and promote rapid ion transport in hybrid electrolyte system (Figure 5b).^[63,64] However, the accumulation and decomposition of LPSs out of the electron/ion transport frameworks are an urgent issue. The current strategies proposed for liquid-electrolyte Li-S batteries are expected to be implantable in this hybrid configuration. In addition, the active materials suffer from huge volume expansion or shrink during the interconversion of sulfur and lithium sulfide, which can induce the loss of close contacts between active materials and ion or electron conductive skeletons. This interfacial instability will further lead to the rapid capacity degradation and finally battery failure.^[55,56] Therefore, there are main challenges in constructing 3D ionic and electronic transport framework to promote the reaction kinetics as well as maintaining the stability of solid/solid interface in all-solid-state Li-S batteries.

4. Perspective on Sulfur Redox Reactions at Working Interfaces

An ideal interface between electrode and electrolyte with high electron transfer capability, low ion transport resistance, and excellent stability is always expected to enhance the retention of active sulfur and improve their conversion kinetics in a working Li–S battery. Although many interfacial investigations have demonstrated the contribution in regulating sulfur conversion, an actual interface between electrode and electrolyte is dynamic and complex and, moreover, strongly depends on the interfacial reactions and their reaction paths. An in-depth fundamental understanding on the interfacial behaviors still remains a major challenge.^[65]

There are complex sulfur redox reactions in a working cell. The generation of soluble LPSs and their dissolution in electrolyte induce a severe shuttle issue and further causes very low efficiency, poor cyclability, and rapid capacity degradation. The electrocatalysis has been strongly considered in promoting the redox conversion of LPSs and inhibiting their shuttle in a working cell. Nevertheless, owing to the coexistence of multiple reactive species and the synchronization of multiple electrochemical conversions, it is difficult to distinguish the evolution of single reaction in a working cell and thus, resulting in inadequate understanding of the conversion behaviors of soluble LPSs on reactive interface. Currently, it still remains a critical controversy and grand challenge for probing and understanding LPS chemistry. In-depth mechanistic investigation of LPSs and their conversion chemistry are of paramount importance, which can afford targeted guidance for the rational design and construction of interface structure for different conversion process.^[66] Therefore, the development of advanced characterization techniques, such as in situ and operando methods, is critical to promote the understanding of the sulfur and polysulfide/sulfide electrochemistry. In addition, necessary combination with the first-principle theoretical calculation is also expected to obtain emerging knowledge with regard to polysulfide conversion mechanisms at the molecular and atomic scale and offers new horizons for interfacial design in Li-S batteries. However, we must notice that the theoretical simulation should be conducted in a more rational instead of handweaving way as the structure reconstruction in working condition, the selection of exposed solid surface, and the effect of solvents and ions should be taken into account in future studies.^[67] The model should be carefully selected to reflect the main scenario during the sulfur redox reaction and their transport phenomena should be quantitatively described. Simulation with vacuum and clean surfaces may lead to inappropriate conclusion and rationale. The actual surface with working electrolyte and potentials as well as the nonuniform distribution of feedstocks and ions/electrons should be further considered.

Active sulfur manifests as different chemical compounds at various states of charge. In other words, the working cathode is a dynamic electrochemical system. The electrochemical performance strongly depends on the active sulfur components in the cathode/catholyte system and the capability of electrode/ electrolyte interface to respond to sulfur conversion. In general, multitype electrochemical redox conversions, including liquid-liquid, liquid-solid, and solid-liquid transformations, always occur on the identical electrode/electrolyte interface. However, different transformations respond in various efficiencies. Considering the requirement of specific surface chemical property for specific redox reaction, only one or two reaction processes were considered in a full sulfur conversion reaction. The exploration of suitable surface chemistry of enhancing every transformation process, or compromisingly all ratelimiting steps, in sulfur electrochemistry by high throughput screening and deep data mining of the outcomes using artificial intelligence/machine learning are highly expected.



The ionic conductivities of most solid-state electrolytes have reached and even surpassed those of liquid electrolytes. The most important challenge is how to construct a favorable electron/ion conductive triple-phase interface between solid electrode, solid electrolyte, and solid conductive additive. In addition, the contact loss resulting from the volume changes of sulfur during extended cycling is a serious problem. Decreasing the particle size of sulfur and solid electrolyte in cathode composites or developing the solution impregnation method of solid electrolyte affords a convenient and effective approach to improve the solid/solid interface contact. There is a lack of clear understanding of solid/solid interface especially regarding the interface structure, interface behavior, and interface evolution in all-solid-state Li-S batteries. Therefore, in situ or ex situ characterization techniques as well as their cooperation are imperative for gaining fundamentally comprehensive and available information, which could further guide the effective regulation of complex interface.^[68] The challenge in interfacial characterization is the distinguishment and separation of solid/solid interfaces. Therefore, appropriate model system with exposed interface identical or similar to that is identified in an actual solid battery system should be rationally designed and built to improve interface characterization. Notably, the interfacial instability between the lithium anode and the solid electrolyte and the possibility of lithium dendrite across the solid electrolyte layer should deserve more attention.^[10,69] The former can render increased interfacial impedance for the lithium ion transport while the latter can cause battery short circuit and eventually result in severe safety problem.

Overall, despite the yielded fruitful achievements in Li–S batteries researches, there still remains a huge open space in fundamental understanding of interfacial behavior for sulfur redox reactions. With the persistently deepening research in interface science and characterization technology, it is expected that a bright future will be witnessed for practical applications of Li–S batteries.

Acknowledgements

This work was supported by the National Key Research and Development Program (Grant Nos. 2016YFA0202500, 2016YFA0200101, and 2015CB932500), the National Natural Science Foundation of China (Grant Nos. 21776019, 21825501, 21808124, and U1801257), and the China Postdoctoral Science Foundation (Grant No. 2017M620049).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

lithium-sulfur batteries, rechargeable batteries, shuttle of polysulfide intermediates, sulfur redox reaction, working interfaces

Received: December 18, 2018 Revised: January 7, 2019 Published online: January 30, 2019



- [1] a) P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, Nat. Mater. 2012, 11, 19; b) W. Li, J. Liu, D. Zhao, Nat. Rev. Mater. 2016, 1, 16023; c) S.-H. Chung, C.-H. Chang, A. Manthiram, Adv. Funct. Mater. 2018, 28, 1801188; d) H. Yuan, L. Kong, T. Li, Q. Zhang, Chin. Chem. Lett. 2017, 28, 2180; e) X.-Q. Zhang, X.-B. Cheng, Q. Zhang, Adv. Mater. Interfaces 2018, 5, 1701097; f) X. Zhang, X. Cheng, Q. Zhang, J. Energy Chem. 2016, 25, 967; g) J. Cui, T.-G. Zhan, K.-D. Zhang, D. Chen, Chin. Chem. Lett. 2017, 28, 2171; h) L. Wang, Z. Zhou, X. Yan, F. Hou, L. Wen, W. Luo, J. Liang, S. X. Dou, Energy Storage Mater. 2018, 14, 22; i) R. Zhang, X. Chen, X. Shen, X.-Q. Zhang, X.-R. Chen, X.-B. Cheng, C. Yan, C.-Z. Zhao, Q. Zhang, Joule 2018, 2, 764; j) X.-Q. Zhang, C.-Z. Zhao, J.-Q. Huang, Q. Zhang, Engineering 2018, 4, 831.
- [2] a) Q. Pang, X. Liang, C. Y. Kwok, L. F. Nazar, Nat. Energy 2016, 1, 16132; b) S. Xin, Z. Chang, X. Zhang, Y.-G. Guo, Natl. Sci. Rev. 2017, 4, 54; c) X.-B. Cheng, R. Zhang, C.-Z. Zhao, Q. Zhang, Chem. Rev. 2017, 117, 10403; d) X. Shen, H. Liu, X.-B. Cheng, C. Yan, J.-Q. Huang, Energy Storage Mater. 2018, 12, 161; e) Z. Cheng, H. Pan, H. Zhong, Z. Xiao, X. Li, R. Wang, Adv. Funct. Mater. 2018, 28, 1707597; f) W. Guo, Y. Fu, Energy Environ. Mater. 2018, 1, 20; g) Q. Pang, A. Shyamsunder, B. Narayanan, C. Y. Kwok, L. A. Curtiss, L. F. Nazar, Nat. Energy 2018, 3, 783; h) Z. Li, B. Y. Guan, J. Zhang, X. W. Lou, Joule 2017, 1, 576.
- [3] a) H.-J. Peng, J.-Q. Huang, Q. Zhang, Chem. Soc. Rev. 2017, 46, 5237; b) R. Fang, S. Zhao, Z. Sun, W. Wang, H.-M. Cheng, F. Li, Adv. Mater. 2017, 29, 1606823; c) X. Chen, T.-Z. Hou, B. Li, C. Yan, L. Zhu, C. Guan, X.-B. Cheng, H.-J. Peng, J.-Q. Huang, Q. Zhang, Energy Storage Mater. 2017, 8, 194; d) X. Li, X. Sun, Adv. Funct. Mater. 2018, 28, 1801323; e) G. Li, Z. Chen, J. Lu, Chem 2018, 4, 3.
- [4] H. Yuan, J.-Q. Huang, H.-J. Peng, M.-M. Titirici, R. Xiang, R. Chen, Q. Liu, Q. Zhang, Adv. Energy Mater. 2018, 8, 1802107.
- [5] a) B. Liu, R. Fang, D. Xie, W. Zhang, H. Huang, Y. Xia, X. Wang, X. Xia, J. Tu, *Energy Environ. Mater.* **2018**, *1*, 196; b) J. Balach, J. Linnemann, T. Jaumann, L. Giebeler, *J. Mater. Chem. A* **2018**, *6*, 23127; c) D. Zheng, G. Wang, D. Liu, J. Si, T. Ding, D. Qu, X. Yang, D. Qu, *Adv. Mater. Technol.* **2018**, *3*, 1700233; d) J. Park, S.-H. Yu, Y.-E. Sung, *Nano Today* **2018**, *18*, 35; e) Y. Zhu, S. Wang, Z. Miao, Y. Liu, S.-L. Chou, *Small* **2018**, *14*, 1801987.
- [6] a) H.-J. Peng, J.-Q. Huang, X.-B. Cheng, Q. Zhang, Adv. Energy Mater. 2017, 7, 1700260; b) G. Zhang, Z.-W. Zhang, H.-J. Peng, J.-Q. Huang, Q. Zhang, Small Methods 2017, 1, 1700134; c) M. R. Kaiser, S. Chou, H.-K. Liu, S.-X. Dou, C. Wang, J. Wang, Adv. Mater. 2017, 29, 1700449; d) L. Wang, Y. Ye, N. Chen, Y. Huang, L. Li, F. Wu, R. Chen, Adv. Funct. Mater. 2018, 28, 1800919.
- [7] Z.-W. Zhang, H.-J. Peng, M. Zhao, J.-Q. Huang, Adv. Funct. Mater. 2018, 28, 1707536.
- [8] a) G. Li, S. Wang, Y. Zhang, M. Li, Z. Chen, J. Lu, Adv. Mater. 2018, 30, 1705590; b) H.-J. Peng, J.-Q. Huang, X.-Y. Liu, X.-B. Cheng, W.-T. Xu, C.-Z. Zhao, F. Wei, Q. Zhang, J. Am. Chem. Soc. 2017, 139, 8458; c) L. Zhang, M. Ling, J. Feng, L. Mai, G. Liu, J. Guo, Energy Storage Mater. 2018, 11, 24; d) X.-B. Cheng, C. Yan, J.-Q. Huang, P. Li, L. Zhu, L. Zhao, Y. Zhang, W. Zhu, S.-T. Yang, Q. Zhang, Energy Storage Mater. 2017, 6, 18; e) Q. Li, H. Yang, A. Naveed, C. Guo, J. Yang, Y. Nuli, J. Wang, Energy Storage Mater. 2018, 14, 75; f) A. Shyamsunder, W. Beichel, P. Klose, Q. Pang, H. Scherer, A. Hoffmann, G. K. Murphy, I. Krossing, L. F. Nazar, Angew. Chem., Int. Ed. 2017, 56, 6192.
- [9] C.-Z. Zhao, X.-B. Cheng, R. Zhang, H.-J. Peng, J.-Q. Huang, R. Ran, Z.-H. Huang, F. Wei, Q. Zhang, *Energy Storage Mater.* **2016**, *3*, 77.
- [10] J.-Q. Huang, Q. Zhang, F. Wei, Energy Storage Mater. 2015, 1, 127.
- [11] a) H. Wang, W. Zhang, J. Xu, Z. Guo, Adv. Funct. Mater. 2018, 28, 1707520; b) Z. Li, H. B. Wu, X. W. Lou, Energy Environ. Sci. 2016, 9, 3061; c) H. Wang, B. D. Adams, H. Pan, L. Zhang, K. S. Han, L. Estevez, D. Lu, H. Jia, J. Feng, J. Guo, K. R. Zavadil, Y. Shao, J.-G. Zhang, Adv. Energy Mater. 2018, 8, 1800590; d) H.-J. Peng,



T.-Z. Hou, Q. Zhang, J.-Q. Huang, X.-B. Cheng, M.-Q. Guo, Z. Yuan, L.-Y. He, F. Wei, Adv. Mater. Interfaces 2014, 1, 1400227; e) S.-Y. Li, W.-P. Wang, H. Duan, Y.-G. Guo, J. Energy Chem. 2018, 27, 1555; f) H. Zhang, Z. Zhao, Y. Liu, J. Liang, Y. Hou, Z. Zhang, X. Wang, J. Qiu, J. Energy Chem. 2017, 26, 1282; g) R. Xu, Y. Sun, Y. Wang, J. Huang, Q. Zhang, Chin. Chem. Lett. 2017, 28, 2235; h) X. Shang, P. Guo, T. Qin, M. Liu, M. Lv, D. Liu, D. He, Adv. Mater. Interfaces 2018, 5, 1701602; i) Z. Zeng, X. Liu, Adv. Mater. Interfaces 2018, 5, 1701274; j) Y. Wang, X. Huang, S. Zhang, Y. Hou, Small Methods 2018, 2, 1700345; k) J.-L. Qin, H.-J. Peng, J.-Q. Huang, X.-Q. Zhang, L. Kong, J. Xie, M. Zhao, R. Liu, H. Zhao, Q. Zhang, Small Methods 2018, 2, 1800100; I) J. Zhang, H. Huang, J. Bae, S.-H. Chung, W. Zhang, A. Manthiram, G. Yu, Small Methods 2018, 2, 1700279; m) T. Wang, K. Kretschmer, S. Choi, H. Pang, H. Xue, G. Wang, Small Methods 2017, 1, 1700089; n) S. Zhao, R. Fang, Z. Sun, S. Wang, J.-P. Veder, M. Saunders, H.-M. Cheng, C. Liu, S. P. Jiang, F. Li, Small Methods 2018, 2, 1800067.

- [12] a) X. Liu, J.-Q. Huang, Q. Zhang, L. Mai, Adv. Mater. 2017, 29, 1601759; b) H. Yuan, W. Zhang, J.-G. Wang, G. Zhou, Z. Zhuang, J. Luo, H. Huang, Y. Gan, C. Liang, Y. Xia, J. Zhang, X. Tao, Energy Storage Mater. 2018, 10, 1.
- [13] Z. Yuan, H.-J. Peng, T.-Z. Hou, J.-Q. Huang, C.-M. Chen, D.-W. Wang, X.-B. Cheng, F. Wei, Q. Zhang, *Nano Lett.* **2016**, *16*, 519.
- [14] a) D. Liu, C. Zhang, G. Zhou, W. Lv, G. Ling, L. Zhi, Q.-H. Yang, *Adv. Sci.* 2018, 5, 1700270; b) S. Imtiaz, Z. A. Zafar, R. Razaq, D. Sun, Y. Xin, Q. Li, Z. Zhang, L. Zheng, Y. Huang, J. A. Anderson, *Adv. Mater. Interfaces* 2018, 5, 1800243.
- [15] a) L. Fan, S. Wei, S. Li, Q. Li, Y. Lu, Adv. Energy Mater. 2018, 8, 1702657; b) Y.-Z. Sun, J.-Q. Huang, C.-Z. Zhao, Q. Zhang, Sci. China: Chem. 2017, 60, 1508; c) X. Judez, H. Zhang, C. Li, G. G. Eshetu, J. A. Gonzalez-Marcos, M. Armand, L. M. Rodriguez-Martinez, J. Electrochem. Soc. 2018, 165, A6008.
- [16] L. Xu, S. Tang, Y. Cheng, K. Wang, J. Liang, C. Liu, Y.-C. Cao, F. Wei, L. Mai, *Joule* **2018**, *2*, 1991.
- [17] Q. Zhao, J. Zheng, L. Archer, ACS Energy Lett. 2018, 3, 2104.
- [18] a) C. Tang, M.-M. Titirici, Q. Zhang, J. Energy Chem. 2017, 26, 1077;
 b) C. Tang, H.-F. Wang, Q. Zhang, Acc. Chem. Res. 2018, 51, 881;
 c) C. Tang, Q. Zhang, Adv. Mater. 2017, 29, 1604103; d) H. Jin,
 C. Guo, X. Liu, J. Liu, A. Vasileff, Y. Jiao, Y. Zheng, S.-Z. Qiao,
 Chem. Rev. 2018, 118, 6337; e) D. Yang, L. Zhang, X. Yan, X. Yao,
 Small Methods 2017, 1, 1700209; f) Z. Yang, Z. Yao, G. Li, G. Fang,
 H. Nie, Z. Liu, X. Zhou, X. A. Chen, S. Huang, ACS Nano 2012, 6, 205.
- [19] N. Xu, T. Qian, X. Liu, J. Liu, Y. Chen, C. Yang, Nano Lett. 2017, 17, 538.
- [20] a) J. R. Akridge, Y. V. Mikhaylik, N. White, Solid State Ionics 2004, 175, 243; b) Y. V. Mikhaylik, J. R. Akridge, J. Electrochem. Soc. 2004, 151, A1969.
- [21] X. Ji, K. T. Lee, L. F. Nazar, Nat. Mater. 2009, 8, 500.
- [22] H.-J. Peng, Q. Zhang, Angew. Chem., Int. Ed. 2015, 54, 11018.
- [23] N. Wang, Z. Xu, X. Xu, T. Liao, B. Tang, Z. Bai, S. Dou, ACS Appl. Mater. Interfaces 2018, 10, 13573.
- [24] a) T.-Z. Hou, W.-T. Xu, X. Chen, H.-J. Peng, J.-Q. Huang, Q. Zhang, Angew. Chem., Int. Ed. 2017, 56, 8178; b) J. Sun, Y. Sun, M. Pasta, G. Zhou, Y. Li, W. Liu, F. Xiong, Y. Cui, Adv. Mater. 2016, 28, 9797; c) X. Chen, H.-J. Peng, R. Zhang, T.-Z. Hou, J.-Q. Huang, B. Li, Q. Zhang, ACS Energy Lett. 2017, 2, 795.
- [25] X. Tao, J. Wang, C. Liu, H. Wang, H. Yao, G. Zheng, Z. W. Seh, Q. Cai, W. Li, G. Zhou, C. Zu, Y. Cui, *Nat. Commun.* **2016**, *7*, 11203.
- [26] a) Q. F. Zhang, Y. P. Wang, Z. W. Seh, Z. H. Fu, R. F. Zhang, Y. Cui, Nano Lett. 2015, 15, 3780; b) X. Liang, C. Y. Kwok, F. Lodi-Marzano, Q. Pang, M. Cuisinier, H. Huang, C. J. Hart, D. Houtarde, K. Kaup, H. Sommer, T. Brezesinski, J. Janek, L. F. Nazar, Adv. Energy Mater. 2016, 6, 1501636.



- [27] M. Zhao, H.-J. Peng, Z.-W. Zhang, B.-Q. Li, X. Chen, J. Xie, X. Chen, J.-Y. Wei, Q. Zhang, J.-Q. Huang, *Angew. Chem., Int. Ed.* **2019**, *58*, 1812062.
- [28] a) H. Lin, S. Zhang, T. Zhang, H. Ye, Q. Yao, G. W. Zheng, J. Y. Lee, Adv. Energy Mater. 2018, 8, 1801868; b) H. Lin, L. Yang, X. Jiang, G. Li, T. Zhang, Q. Yao, G. W. Zheng, J. Y. Lee, Energy Environ. Sci. 2017, 10, 1476; c) J. Park, B.-C. Yu, J. S. Park, J. W. Choi, C. Kim, Y.-E. Sung, J. B. Goodenough, Adv. Energy Mater. 2017, 7, 1602567; d) J. Zhang, Y. Shi, Y. Ding, L. Peng, W. Zhang, G. Yu, Adv. Energy Mater. 2017, 7, 1602876; e) T. Zhang, M. Marinescu, S. Walus, P. Kovacik, G. J. Offer, J. Electrochem. Soc. 2018, 165, A6001; f) X. Zhang, Z. Zhang, Z. Zhou, J. Energy Chem. 2018, 27, 73; g) T. Zhou, W. Lv, J. Li, G. Zhou, Y. Zhao, S. Fan, B. Liu, B. Li, F. Kang, Q.-H. Yang, Energy Environ. Sci. 2017, 10, 1694; h) J.-L. Shi, C. Tang, J.-Q. Huang, W. Zhu, Q. Zhang, J. Energy Chem. 2018, 27, 167; i) M. Wang, G. Liu, H. Wang, H. Zhang, X. Li, H. Zhang, J. Mater. Chem. A 2018, 6, 7639.
- [29] H.-J. Peng, Z.-W. Zhang, J.-Q. Huang, G. Zhang, J. Xie, W.-T. Xu, J.-L. Shi, X. Chen, X.-B. Cheng, Q. Zhang, *Adv. Mater.* 2016, 28, 9551.
- [30] H.-J. Peng, G. Zhang, X. Chen, Z.-W. Zhang, W.-T. Xu, J.-Q. Huang, Q. Zhang, Angew. Chem., Int. Ed. 2016, 55, 12990.
- [31] H. Yuan, H.-J. Peng, B.-Q. Li, J. Xie, L. Kong, M. Zhao, X. Chen, J.-Q. Huang, Q. Zhang, Adv. Energy Mater. 2019, 9, 1802768.
- [32] L. C. H. Gerber, P. D. Frischmann, F. Y. Fan, S. E. Doris, X. Qu, A. M. Scheuermann, K. Persson, Y.-M. Chiang, B. A. Helms, *Nano Lett.* **2016**, *16*, 549.
- [33] a) H. Yao, G. Zheng, P.-C. Hsu, D. Kong, J. J. Cha, W. Li, Z. W. Seh, M. T. McDowell, K. Yan, Z. Liang, V. K. Narasimhan, Y. Cui, *Nat. Commun.* **2014**, *5*, 3943; b) J. Yan, X. Liu, B. Li, *Adv. Sci.* **2016**, *3*, 1600101.
- [34] F. Y. Fan, W. C. Carter, Y.-M. Chiang, Adv. Mater. 2015, 27, 5203.
- [35] H. Pan, J. Chen, R. Cao, V. Murugesan, N. N. Rajput, K. S. Han, K. Persson, L. Estevez, M. H. Engelhard, J.-G. Zhang, K. T. Mueller, Y. Cui, Y. Shao, J. Liu, *Nat. Energy* **2017**, *2*, 813.
- [36] G. Zhang, H.-J. Peng, C.-Z. Zhao, X. Chen, L.-D. Zhao, P. Li, J.-Q. Huang, Q. Zhang, Angew. Chem., Int. Ed. 2018, 57, 16732.
- [37] A. Gupta, A. Bhargav, A. Manthiram, Adv. Energy Mater. 2019, 9, 201803096.
- [38] Q. L. Zou, Z. J. Liang, G. Y. Du, C. Y. Liu, E. Y. Li, Y. C. Lu, J. Am. Chem. Soc. 2018, 140, 10740.
- [39] D. Su, D. Zhou, C. Wang, G. Wang, Adv. Funct. Mater. 2018, 28, 1800154.
- [40] Y. Yang, G. Zheng, S. Misra, J. Nelson, M. F. Toney, Y. Cui, J. Am. Chem. Soc. 2012, 134, 15387.
- [41] G. Zhou, H. Tian, Y. Jin, X. Tao, B. Liu, R. Zhang, Z. W. Seh, D. Zhuo, Y. Liu, J. Sun, J. Zhao, C. Zu, D. S. Wu, Q. Zhang, Y. Cui, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 840.
- [42] a) S. Meini, R. Elazari, A. Rosenman, A. Garsuch, D. Aurbach, J. Phys. Chem. Lett. 2014, 5, 915; b) S. S. Zhang, J. Power Sources 2013, 231, 153; c) H. Pan, K. S. Han, M. H. Engelhard, R. Cao, J. Chen, J.-G. Zhang, K. T. Mueller, Y. Shao, J. Liu, Adv. Funct. Mater. 2018, 28, 1707234.
- [43] a) A. Manthiram, X. Yu, S. Wang, Nat. Rev. Mater. 2017, 2, 16103;
 b) S. Chen, D. Xie, G. Liu, J. P. Mwizerwa, Q. Zhang, Y. Zhao, X. Xu, X. Yao, Energy Storage Mater. 2018, 14, 58; c) O. Sheng, C. Jin, J. Luo, H. Yuan, H. Huang, Y. Gan, J. Zhang, Y. Xia, C. Liang, W. Zhang, X. Tao, Nano Lett. 2018, 18, 3104.
- [44] a) Y. Wang, W. D. Richards, S. P. Ong, L. J. Miara, J. C. Kim, Y. Mo, G. Ceder, *Nat. Mater.* 2015, *14*, 1026; b) K. H. Park, Q. Bai, D. H. Kim, D. Y. Oh, Y. Zhu, Y. Mo, Y. S. Jung, *Adv. Energy Mater.* 2018, *8*, 1800035.
- [45] a) P. Bron, S. Johansson, K. Zick, J. S. auf der Guenne, S. Dehnen,
 B. Roling, J. Am. Chem. Soc. 2013, 135, 15694; b) X. Tao, Y. Liu,
 W. Liu, G. Zhou, J. Zhao, D. Lin, C. Zu, O. Sheng, W. Zhang,

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H.-W. Lee, Y. Cui, *Nano Lett.* **2017**, *17*, 2967; c) R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem., Int. Ed.* **2007**, *46*, 7778; d) V. Thangadurai, H. Kaack, W. J. F. Weppner, *J. Am. Ceram. Soc.* **2003**, *86*, 437; e) G. Liu, D. Xie, X. Wang, X. Yao, S. Chen, R. Xiao, H. Li, X. Xu, *Energy Storage Mater.* **2018**, https://doi.org/10.1016/j. ensm.2018.07.008.

- [46] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat. Mater.* **2011**, *10*, 682.
- [47] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, Nat. Energy 2016, 1, 16030.
- [48] F. Mizuno, A. Hayashi, K. Tadanaga, M. Tatsumisago, Adv. Mater. 2005, 17, 918.
- [49] Y. Seino, T. Ota, K. Takada, A. Hayashi, M. Tatsumisago, Energy Environ. Sci. 2014, 7, 627.
- [50] a) X. Yu, A. Manthiram, Acc. Chem. Res. 2017, 50, 2653; b) J. Dai, C. Yang, C. Wang, G. Pastel, L. Hu, Adv. Mater. 2018, 30, 1802068.
- [51] D. Lei, K. Shi, H. Ye, Z. Wan, Y. Wang, L. Shen, B. Li, Q.-H. Yang, F. Kang, Y.-B. He, Adv. Funct. Mater. 2018, 28, 1707570.
- [52] a) J. C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, *Chem. Rev.* **2016**, *116*, 140; b) J. Yue, M. Yan, Y.-X. Yin, Y.-G. Guo, *Adv. Funct. Mater.* **2018**, *28*, 1707533.
- [53] W. Chen, T. Lei, C. Wu, M. Deng, C. Gong, K. Hu, Y. Ma, L. Dai, W. Lv, W. He, X. Liu, J. Xiong, C. Yan, *Adv. Energy Mater.* **2018**, *8*, 1702348.
- [54] U. Ulissi, S. Ito, S. M. Hosseini, A. Varzi, Y. Aihara, S. Passerini, Adv. Energy Mater. 2018, 8, 1801462.
- [55] X. Yao, N. Huang, F. Han, Q. Zhang, H. Wan, J. P. Mwizerwa, C. Wang, X. Xu, Adv. Energy Mater. 2017, 7, 1602923.
- [56] F. Han, J. Yue, X. Fan, T. Gao, C. Luo, Z. Ma, L. Suo, C. Wang, Nano Lett. 2016, 16, 4521.
- [57] a) J. L. Wang, J. Yang, J. Y. Xie, N. X. Xu, Adv. Mater. 2002, 14, 963;
 b) J. L. Wang, J. Yang, C. R. Wan, K. Du, J. Y. Xie, N. X. Xu, Adv. Funct. Mater. 2003, 13, 487; c) J. E. Trevey, J. R. Gilsdorf, C. R. Stoldt, S.-H. Lee, P. Liu, J. Electrochem. Soc. 2012, 159, A1019; d) L. Yin, J. Wang, F. Lin, J. Yang, Y. Nuli, Energy Environ. Sci. 2012, 5, 6966.
- [58] Z.-Q. Jin, Y.-G. Liu, W.-K. Wang, A.-B. Wang, B.-W. Hu, M. Shen, T. Gao, P.-C. Zhao, Y.-S. Yang, *Energy Storage Mater.* **2018**, 14, 272.
- [59] a) W. Wang, Z. Cao, G. A. Elia, Y. Wu, W. Wahyudi, E. Abou-Hamad, A.-H. Emwas, L. Cavallo, L.-J. Li, J. Ming, ACS Energy Lett. 2018, 3, 2899; b) S. S. Zhang, Energies 2014, 7, 4588; c) S. Wei, L. Ma, K. E. Hendrickson, Z. Tu, L. A. Archer, J. Am. Chem. Soc. 2015, 137, 12143.

- [60] a) J. Wang, F. Lin, H. Jia, J. Yang, C. W. Monroe, Y. NuLi, Angew. Chem., Int. Ed. 2014, 53, 10099; b) Y.-Z. Zhang, Z.-Z. Wu, G.-L. Pan, S. Liu, X.-P. Gao, ACS Appl. Mater. Interfaces 2017, 9, 12436.
- [61] a) X. Y. Yao, D. Liu, C. S. Wang, P. Long, G. Peng, Y. S. Hu, H. Li, L. Q. Chen, X. X. Xu, *Nano Lett.* **2016**, *16*, 7148; b) D. H. Kim, D. Y. Oh, K. H. Park, Y. E. Choi, Y. J. Nam, H. A. Lee, S. M. Lee, Y. S. Jung, *Nano Lett.* **2017**, *17*, 3013.
- [62] a) M. M. U. Din, R. Murugan, *Electrochem. Commun.* 2018, 93, 109; b) S. Xu, D. W. McOwen, L. Zhang, G. T. Hitz, C. Wang, Z. Ma, C. Chen, W. Luo, J. Dai, Y. Kuang, E. M. Hitz, K. Fu, Y. Gong, E. D. Wachsman, L. Hu, *Energy Storage Mater.* 2018, 15, 458; c) Y. Lu, X. Huang, Z. Song, K. Rui, Q. Wang, S. Gu, J. Yang, T. Xiu, M. E. Badding, Z. Wen, *Energy Storage Mater.* 2018, 15, 282; d) N. Li, Z. Weng, Y. Wang, F. Li, H.-M. Cheng, H. Zhou, *Energy Environ. Sci.* 2014, 7, 3307; e) S. Gu, X. Huang, Q. Wang, J. Jin, Q. Wang, Z. Wen, R. Qian, *J. Mater. Chem. A* 2017, 5, 13971; f) Q. Wang, Z. Wen, J. Jin, J. Guo, X. Huang, J. Yang, C. Chen, *Chem. Commun.* 2016, *52*, 1637.
- [63] a) K. K. Fu, Y. Gong, S. Xu, Y. Zhu, Y. Li, J. Dai, C. Wang, B. Liu, G. Pastel, H. Xie, Y. Yao, Y. Mo, E. Wachsman, L. Hu, *Chem. Mater.* **2017**, *29*, 8037; b) Q. Wang, J. Jin, X. Wu, G. Ma, J. Yang, Z. Wen, *Phys. Chem. Chem. Phys.* **2014**, *16*, 21225.
- [64] K. Fu, Y. Gong, G. T. Hitz, D. W. McOwen, Y. Li, S. Xu, Y. Wen, L. Zhang, C. Wang, G. Pastel, J. Dai, B. Liu, H. Xie, Y. Yao, E. D. Wachsman, L. Hu, *Energy Environ. Sci.* **2017**, *10*, 1568.
- [65] a) E. Zhao, K. Nie, X. Yu, Y.-S. Hu, F. Wang, J. Xiao, H. Li, X. Huang, *Adv. Funct. Mater.* **2018**, *28*, 1707543; b) S.-H. Chung, A. Manthiram, *Joule* **2018**, *2*, 710.
- [66] a) S.-Y. Lang, Y. Shi, Y.-G. Guo, D. Wang, R. Wen, L.-J. Wan, Angew. Chem., Int. Ed. 2016, 55, 15835; b) S.-Y. Lang, Y. Shi, Y.-G. Guo, R. Wen, L.-J. Wan, Angew. Chem., Int. Ed. 2017, 56, 14433; c) M. Li, Z. Amirzadeh, R. De Marco, X. F. Tan, A. Whittaker, X. Huang, R. Wepf, R. Knibbe, Small Methods 2018, 2, 1800133.
- [67] P. Christopher, ACS Energy Lett. 2018, 3, 3015.
- [68] Z. Yang, Z. Zhu, J. Ma, D. Xiao, X. Kui, Y. Yao, R. Yu, X. Wei, L. Gu, Y.-S. Hu, H. Li, X. Zhang, *Adv. Energy Mater.* **2016**, *6*, 1600806.
- [69] a) S. Wenzel, S. Randau, T. Leichtweiss, D. A. Weber, J. Sann, W. G. Zeier, J. Janek, *Chem. Mater.* **2016**, *28*, 2400; b) F. Han, Y. Zhu, X. He, Y. Mo, C. Wang, *Adv. Energy Mater.* **2016**, *6*, 1501590; c) X. Xu, S. Wang, H. Wang, C. Hu, Y. Jin, J. Liu, H. Yan, *J. Energy Chem.* **2018**, *27*, 513; d) X.-B. Cheng, C. Yan, X. Chen, C. Guan, J.-Q. Huang, H.-J. Peng, R. Zhang, S.-T. Yang, Q. Zhang, *Chem* **2017**, *2*, 258.