Demystifying the catalysis in lithium–sulfur batteries: Characterization methods and techniques

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Abstract
Lithium–sulfur (Li-S) batteries are promising next-generation energy storage systems with ultrahigh energy density. However, the intrinsic sluggish “solid–liquid–solid” reaction between S8 and Li2S causes unavoidable shuttling of polysulfides, severely limiting the practical energy density and cycling performance. Recently, the catalysis process has been introduced for the sulfur redox reaction to accelerate the conversion of polysulfides, providing a positive remedy for the polysulfides shuttling. Nevertheless, in-depth understanding of the catalyst evaluation criteria and catalytic mechanism still lies in the “black box”, and precise characterization technique is the key to unlock this puzzle. In this review, we provide a comprehensive overview of characterization techniques on the catalyst in Li-S batteries from two aspects of catalytic performance and catalytic mechanism, highlighting their significance and calling for more efforts to develop precise and fast techniques for Li-S catalysis. Moreover, we envision the future development of characterization for better understanding the catalysis toward practical Li-S battery.

KEYWORDS
Catalysis, catalyst characterization, lithium–sulfur batteries, polysulfides shuttling

1 INTRODUCTION
Rechargeable batteries are of great significance to address the energy crisis in modern society. Lithium-ion batteries (LIBs) have dominated the battery market for decades. However, the commercial LIBs have nearly reached their theoretical energy density (~400 Wh/kg), which can hardly meet the increasing energy demands of electric
vehicles and smart grids. Thus, next-generation batteries with higher energy density are urgently required. Lithium–sulfur batteries (LSBs) with high theoretical energy density (2600 Wh/kg), low cost, and environmentally friendliness have shown great potential for the next-generation alternatives to LIBs. With the joint efforts of scientific and industrial community, the industrialization of LSBs is constantly advancing.1–3

Different from the intercalation mechanism of LIBs, LSBs follow the multielectron sulfur electrochemical reaction, creating a series of soluble intermediate lithium polysulfides (LiPSs). The dissolution of LiPSs causes the severe shuttling between cathode and anode, resulting in low utilization of the active sulfur, poor coulombic efficiency, and short cycle life, which eventually slow down its practical use. Restricting LiPSs on the cathode through physical barrier or chemical adsorption have been demonstrated as effective ways to alleviate this shuttling problem, but the LiPSs are only blocked in the cathode side and the slow conversion of LiPSs cannot be accelerated. When the adsorption sites are saturated, shuttling will happen again. Thus, accelerating the sluggish conversion of LiPSs for further reducing their dissolution is probably the ultimate solution. Recent studies have found that introducing catalytic materials into LSBs is an effective strategy to solve this problem.4–6 A variety of catalysts have been proposed to accelerate the conversion and suppress the shuttling of LiPSs. However, unlike the traditional thermal catalysis, the redox of sulfur species is much more complicated, and the catalysis mechanism is still unclear. Most of the current research on complex catalytic processes of sulfur including adsorption, conversion, and desorption has focused on using electrochemical behavior to reflect the effect of catalysis on the performance of LSBs, such as cyclic voltammetry (CV),7–9 electrochemical impedance spectroscopy (EIS),10–14 cycling performance, and rate capability.15–18 The catalytic process especially how catalysts work during cycling cannot be accurately characterized by these “black box technologies,” whose results cannot reflect the catalytic process directly. Therefore, advanced characterization method is urgently needed to explore the catalytic mechanism, which is of great significance for understanding the sulfur redox chemistry in LSBs. Some key parameters in thermal catalysis and electrocatalysis such as activation energy, electron transfer number, Faradaic efficiency, and energy efficiency can also be used to evaluate the catalysis process in LSBs. Therefore, the comprehensive investigation on the above parameters in LSBs will pave the way of understanding the catalysis in LSBs. Many characterization and analysis methods in traditional thermal catalysis and electrocatalysis can provide inspirations to study the above-mentioned parameters of the catalysis in LSBs, such as the electrochemical techniques, electron microscopy techniques and optical spectroscopy techniques, etc. Electrochemical techniques20–23 can provide many parameters directly related to the catalytic ability and mechanism by the variation of current or voltage signals. Electron microscopy techniques24–26 can accurately characterize the structure and morphology evolution of the catalyst and the interaction of catalyst and sulfur. Optical spectroscopy techniques27–29 can precisely measure the surface chemistry of the catalytic material and the concentration of LiPSs in liquid phase.

Herein, we propose the characterization schemes probing the catalytic process in LSBs from the perspectives of catalytic performance and catalytic mechanism, combining with the application of electrochemical techniques, electron microscopy techniques, and optical spectroscopy techniques. The characterization of catalysis can be carried out from two perspectives: characterization of the catalytic performance and characterization of the catalytic mechanism (Figure 1). Specifically, we systematically summarize the parameters for characterizing catalytic performance in LSBs, including activity, selectivity, and stability. Furthermore, we review the characterization of the catalytic mechanism from the direction of accurate characterization of morphology, intermediates, and multistep reactions. Finally, the future directions of characterization catalysis in LSBs are proposed.

2 CHARACTERIZATIONS FOR CATALYTIC PERFORMANCE

In traditional catalysis research, activity, selectivity, and stability are the three most important factors that reflect the performance of a catalyst.20–23 These three parameters are also important for the catalysis in LSBs. The activity
corresponds to the ability of the catalyst to promote LiPSs conversion; the selectivity corresponds to the choice of multistep side reactions; the stability corresponds to the active period of the catalysts during cycling. The characterization of these three parameters can directly reflect the performance of the catalyst. Herein, the characterization for catalytic performance would be explained clearly from these three aspects.

2.1 Activity

The activity of a catalyst in LSBs is usually described by the electrochemical performance of batteries. However, the electrochemical performance of LSBs is affected by various factors such as the conductivity, porosity, and sulfur loading of the cathode materials. Therefore, it is not rigorous to describe the activity of the catalyst only through electrochemical performance.

Activation energy is one of the most important parameters to describe the catalytic activity in traditional catalysis process. The essence of the catalytic reaction is to reduce the activation energy of the target reaction. For thermal catalysis, the apparent activation energy is calculated by the Arrhenius equation, and the reaction rate is an important parameter, in which the concentration of the intermediates is important to calculate the reaction rate. In the LSBs, the concentration of various polysulfides is difficult to measure by a chemical method due to the complex reaction process, so it is almost impossible to calculate the reaction rate accurately.

Optical spectroscopic analysis provides a theoretical possibility for solving the problem of concentration measurement. Ultraviolet–visible (UV–vis) radiation has the advantages of rapid sample analysis, suitability for a wide variety of analytes, which has been widely adopted for the qualitative and quantitative analysis of LiPSs in LSBs. Molecules containing p-electrons or nonbonding electrons (n-electrons) can absorb energy in the UV and visible light region to excite these electrons to higher anti-bonding molecular orbitals. Thus, UV–vis spectroscopy has been proven to be a powerful characterization tool to analyze solution-based electrochemical reactions. LiPSs dissolved in electrolyte can absorb electromagnetic waves in the wavelength range of 300–700 nm. Therefore, UV–vis spectroscopy technique is often used to detect LiPSs.

Besides, in situ UV–vis technique could detect the concentration variation of LiPSs in real time. Patel et al. adopted in situ UV–vis spectroscopy for the qualitative and quantitative detection of polysulfides for the first time in 2013. The typical discharge/charge profiles with corresponding intermediates marked at different stages are shown in Figure 2. The in situ UV–vis spectra clearly indicated the evolution of polysulfides from long chain to
the short chain during the discharging, and the reverse conversion during charging. Recently, tremendous efforts have been devoted to detection of the concentration of polysulfide in real time by in situ UV–vis. However, the concentration–time relationship provided by in situ UV–vis rarely used to calculate the reaction rate. The LiPSs concentration change rate can be obtained by in situ UV–vis, and then the reaction rate can be calculated. This will help use the Arrhenius equation to calculate the activation energy of the LiPSs conversion reaction, and then (semi-)qualitatively characterize the catalytic activity.

Many other electrochemical parameters, such as the peak current density in the CV curve, the diffusion rate and the charge transfer resistance derived from the EIS, also reflect the reaction rate to a certain extent, showing a temperature-dependent Arrhenius-like behavior.\textsuperscript{38–41} The reaction activation energy calculated by the above relationship can also reflect catalytic ability. Peng et al. used EIS to calculate activation energy in LSBs.\textsuperscript{41} They performed EIS tests on LSBs at different temperatures, and fitted the relation of charge transfer resistance and temperature (Figure 3A and B). Using this method, they studied the activation energy at various voltages during charging and discharging, and confirmed the conclusion that the conversion of long-chain polysulfides is slower. This study provided a new viewpoint for the investigation of lithium–sulfur catalysis (Figure 3C). Shen et al. fitted the relation of CV peak currents and temperatures to the Arrhenius equation, and obtained the activation energy of the polysulfide conversion by calculating the slope (Figure 3D–F).\textsuperscript{39} The activation energy of Ni\textsubscript{2}Co\textsubscript{4}P\textsubscript{3} catalyst was calculated to be 3.97 kJ/mol, which was much smaller than carbon (36.35 kJ/mol). Based on these data, they evaluated the performance of Ni\textsubscript{2}Co\textsubscript{4}P\textsubscript{3} as a catalyst for LSBs.

The activation energy calculated by in situ spectroscopy or electrochemical methods could be used to compare the activity of the catalyst qualitatively. However, the apparent activation energy calculated by electrochemical means alone could not accurately describe the catalytic process. In the study of catalysis in LSBs, it is necessary to establish a catalytic reaction model suitable for the lithium–sulfur system to evaluate the catalytic activity.

2.2  Selectivity

In LSBs, the conversion of LiPSs contained many side reactions. The selectivity of the catalyst was reflected in the specific acceleration of the high-activity reaction. Although there was currently no research on the characterization...
of catalyst selectivity in LSBs, the discussion of the highly active intermediate $S_3^–$ radicals could also provide ideas for the characterization of selectivity, which was to characterize the specific intermediates produced by the target reaction.\textsuperscript{42} Cuisinier et al. carried out operando X-ray absorption spectroscopy (XAS) measurements at the sulfur K-edge on a LSB using a DMA-based electrolyte to detect $S_3^–$ radicals\textsuperscript{43} (Figure 4A and B). The low energy feature characterizing the $1s$–$3p(\pi^*)$ transition in the $S_3^–$ radical ion was observed at 2468.5 eV, its intensity reached a maximum around 340 mAh/g, and persists up to 850 mAh/g. As shown in Figure 4C, a linear combination fit (LCF) of the experimental spectra revealed that sulfur redox in the DMA-based electrolyte passed through the formation of $S_3^–$ free radicals to a large extent (up to 25%). Zhang et al. also used UV–vis and Raman spectroscopy to detect $S_3^–$ free radicals (Figure 4D and E, 625 nm for UV–vis and 535 cm$^{-1}$ for Raman), which revealed the stabilizing effect of tetramethylurea on $S_3^–$.\textsuperscript{44} For lithium–sulfur reactions involving catalysts, the use of XAS, UV–vis, Raman, and other technologies to detect target reaction products (such as $S_3^–$) was a reliable way to characterize the selectivity of the catalyst.

2.3 | Stability

The stability of the catalyst is an important parameter that was neglected in the study of catalysis in LSBs. At present, researchers only focus on the cycle stability of the battery after adding the catalyst, and do not consider the state of the catalyst after hundreds of cycles. Therefore, in terms of catalysis in LSBs, it is necessary to characterize the stability of the catalyst, including the chemical stability of the catalyst and electrolyte, the potential range for the catalyst to maintain electrochemical stability, and the failure mechanism of the catalyst that is now under investigation in our group.

3 | CHARACTERIZATION OF CATALYTIC MECHANISM

To confirm the catalysis process in LSBs, we have to firstly confirm the catalysis performance by different characterization techniques. Thereafter, the investigation of the catalysis mechanism is crucial for further promoting the performance of LSBs, which is still very vague. This is a key
problem to be solved to realize the goal of using catalysis to guide the industrialization of LSBs. With the development of advanced characterization technology, the mechanism of the catalysis process in LSBs are being clarified step by step.

3.1 Morphological characterization

Morphological characterization is effective to explore the catalytic mechanism by directly observing the morphological and structural evolution of the catalyst and the reactants. In order to ensure a tight contact with the active material and high activity, the catalyst usually has a fine nanoscale structure. Thus, high-resolution electron microscopy techniques are required to characterize the microscopic changes in catalysts and reactants. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the two most commonly used characterization methods in the study of catalysis in LSBs. Electron microscopy combined with X-ray energy dispersive spectroscopy (XEDS) can intuitively observe the basic morphology and element distribution of the material. High-resolution transmission electron microscopy (HR-TEM) combined with selected area electron diffraction (SAED) or electron energy loss spectroscopy (EELS) can obtain various intrinsic information of materials including crystal structure. Zhou et al. used HR-TEM to characterize the TiO$_2$-TiN heterostructure in the sulfur cathode. When the molar ratio of TiO$_2$ and TiN was controlled at an optimized value (e.g., 1:8), TiN and TiO$_2$ are twinborn in one large particle, and an interface between them can be clearly observed by the TEM observation in Figure 5A. Such an interface acts as the highly active sites showing high adsorption ability for LiPSs and providing a fast electron transfer path for their conversion.

At present, in the study of catalysis in LSBs, the main problem faced by using electron microscopy for morphological characterization is that the current electron microscopy characterization is mostly limited to the observation of the sulfide deposition state, but the catalytic process was basically not considered. Another important
issue was that the irreversible changes occurred during the water and oxygen sensitive samples preparation and transfer. The characterization results usually can no longer reflect the true information. In the traditional sense, it is the most intuitive way to study the catalytic mechanism that observing the various changes in the catalytic process through morphological characterization, but it is difficult to realize this idea limited by the accuracy and resolution of ordinary electron microscopes. The development of in situ and cryogenic electron microscopy techniques has provided the possibility of probing the mechanism of catalytic process in LSBs.

### 3.1.1 In situ electron microscopy

In situ TEM could provide more detailed dynamic processes of electrochemical reactions, with high spatial and temporal resolution of sulfur cathode. For example, a phase transformation of sulfur into nanocrystalline Li2S was observed in a solid-state setup of a Li-S nanobattery using TEM.52,53 The volume expansion rate of the sulfur/carbon structure could be calculated through the real-time TEM observations.54 Xu et al. conducted an in situ TEM study by applying an external voltage of −2 V to the porous carbon nanofibers/sulfur/black phosphorus quantum dots (PCNF/S/BPQD) working electrode versus Li/Li2O counter electrode to explore the catalytic behavior of black phosphorus quantum dots.55 A large volume expansion and overflowing of reaction products during the lithiation of PCNF/S/BPQD fibers was observed (Figure 5B and D), and SAED proves that this change is caused by the conversion of sulfur into lithium sulfide (Figure 5E and F). However, there was neither diffusion of yellow LiPS in a transparent battery nor an increase in battery impedance for the PCNF/S/BPQD electrodes in EIS measurements, thus demonstrating the effectiveness of the BPQD in immobilizing LiPSs.

The in situ TEM studies reported so far are based on a solid-state battery prototype that includes a sulfur-based working electrode and Li2O/Li-based counter electrode. The lithium ions react with sulfur through the Li2O solid-electrolyte that has been naturally generated at the surface of the Li counter electrode. While these solid-state-based setups could provide useful information on the lithium–sulfur reactions, it is infeasible to study the formation of lithium sulfides from liquid polysulfide solution as in real batteries. Xu et al. reported the observation of the nucleation and growth of lithium sulfides on designed hosts by utilizing a liquid in situ TEM technique for the first time.56 Polar TiO2-TiN binary composites were loaded on inner walls of the nonpolar hollow carbon sphere, and sulfur was encapsulated in it as the cathode. In situ TEM was used to study the nucleation and growth of lithium sulfide on the sphere inner walls immersed in liquid electrolyte. They used an electron beam instead of a voltage as the driving force for lithiation due to the lack of a suitable counter electrode. TEM images and SAED patterns show that Li2S nanoparticles appear uniformly inside the hollow sphere (Figure 6A and C). To further understand the growth behavior of Li2S, EELS analysis combined with TEM results proved that the crystalline structure of the lithium sulfides involves a phase change from crystalline to amorphous (Figure 6D and E). With the help of in situ TEM, the entire catalytic reaction process in TiO2-TiN interface was visually displayed. For the catalysis in LSBs, in situ TEM characterization techniques can provide real-time structure evolution of the catalytic active center in each step and shows great potential in probing the mechanism of the catalytic reaction. However, the limitation of this advanced characterization method is the critical test environment and their repeatability is not good enough. Therefore, how to observe the process of electrochemical reaction under an electron microscope would be the main technical problem to be overcome in the future.

### 3.1.2 Cryogenic electron microscopy

Cryogenic electron microscopy (cryo-EM), as a well-established characterization technique for investigating the structure of biological materials, has been widely used in the research of lithium metal, solid electrolyte interphase (SEI), cathode electrolyte interphase (CEI), and other air-sensitive energy materials in recent years. Xing et al. found that the sulfurized polyacrylonitrile (SPAN) cathode in Li-S battery could form CEI on the surface in a high-concentration ether-based electrolyte with LiTFSI.57 They first observed crystalline CEI of cathode with LiF and LiNO2 by cryo-TEM (Figure 7A). This CEI could avoid the formation of LiPSs in direct contact between the SPAN cathode and the electrolyte. This also provided evidences for the high cycle stability of SPAN cathodes. For sulfur cathode, the vapor pressure of elemental sulfur is very low, and sulfur sublimation easily occurs in the high vacuum environment in the sample chamber of the electron microscope, causing inaccurate characterization results.58-60 Additionally, the sublimation of S in the vacuum chamber will pollute the electron microscope.61 In contrast, cryo-EM can characterize the distribution of S in the composites by suppressing the sublimation of S and further avoid the potential damages of electron microscopy. Zhang et al. observed the distribution of S in various types of carbon/S composites through cryo-STEM and demonstrated that uniform S infiltration and dispersion through the melt infusion method was easier in activated porous carbon
**Figure 6** In situ liquid TEM observation of C/TiO$_2$-TiN/S. (A) Schematic illustration of in situ observation of a graphene liquid cell; (B) in situ TEM images of the lithiation of a C/TiO$_2$-TiN/S particle; (C) SAED patterns before and after lithiation. (D) EELS curves of the sulfur L edges and (E) lithium K edges of pristine and lithiated sulfur within a C/TiO$_2$-TiN/S particle. Copyright 2019, RSC Publishing.

**Figure 7** (A) The cryo-TEM image and corresponding SAED image of CEI layer on SPAN cathode. Copyright 2019, Elsevier Ltd. (B) Cryo-STEM images showing the elemental distribution between porous carbon with S. Copyright 2019, RSC Publishing.
hosts than in nonactivated porous carbon, hollow carbon spheres, and carbon nanotubes (Figure 7B).62

Particularly, polysulfides, lithium sulfide, and various catalytic intermediates are all electron beam-sensitive materials, and they will be directly exposed to high-energy electron beams during electron microscopy characterization. Cryo-EM can reduce the reactivity of these sensitive materials and has great potential for the high-resolution characterization of catalytic intermediates. It might be a simple and efficient means to characterize the catalytic process by cryogenic photographing the TEM grid loaded with catalytic materials, which removed from a Li-S coin cell that has undergone an electrochemical reaction.

### 3.2 Detection of intermediates

The detection for LiPSs is a necessary step to clarify their conversion mechanism. Optical spectroscopy techniques, including Raman spectroscopy,63 Fourier transform-infrared spectroscopy,64 and UV–vis,65–67 have gained much attention in LSBs due to their ease of operation, nondestructive nature, high time and spatial resolutions, ample information, etc. Combining optical spectroscopy and in situ techniques could track changes of LiPSs during cycling.68

Huang et al. monitored the discharge-charge processes with in situ Raman spectroscopy by adopting the multifunctional iron phosphide (FeP) nanocrystals incorporated onto a 3D porous rGO-CNT scaffold as an efficient host material.69 As shown in Figure 8A, the left side shows a typical discharge–charge profile of the LSBs, and the right side shows the Raman signal collected of the corresponding voltage. Raman signals of LiPSs and sulfur appear alternately with discharge and charge. During the discharge process, the Raman peak of S₈ becomes very weak due to the conversion of S₈ to polysulfide (Li₂Sₓ,
After charging to 2.32 V, the Raman pattern of polysulfide species reappeared. After further charging to 2.8 V, the polysulfide is converted back to solid sulfur. These results confirmed that the FeP nanocrystals can promote the conversion of polysulfides and facilitate their redox reaction, thus suppressing the polysulfide shuttling effectively. The LSBs showed ultra-stable cycling and excellent rate performance.

Song et al. applied the in situ Raman method to investigate the enhanced polysulfide redox at a VN/VO₂ hybrid host. The hybrid host combines the merits of ultrafast anchoring (VO₂) with electronic conducting (VN) to accomplish the smooth immobilization–diffusion–conversion of polysulfides (Figure 8B). Figure 8C shows the Raman signals of the S@VO₂-VN/G cathode, showing a gradual disappearance of the Li₂S₈ (∼119, 279 and 396 cm⁻¹) and Li₂S₆ (∼178, 397 and 458 cm⁻¹) signals during the discharge process and signal regeneration upon the charge process. However, the Raman spectra of the bare graphene cathode showed that the pronounced polysulfide signals exited throughout the whole discharge–charge process (Figure 8D). This striking contrast clearly demonstrated that the introduction of the VO₂-VN heterostructure hosts enabled fast conversion of LiPSs and effective suppression of their shuttling. The LiPSs could be easily and clearly observed with the Raman and other optical spectroscopy techniques. However, the catalytic process is often involved in the formation of catalytic intermediates, which are different from LiPSs, and might be chemically stable compounds formed by lithium, sulfur, and catalysts. The detection of such compounds could also use spectroscopy techniques.

### 3.3 Multistep reaction mechanism

The electrode reaction of LSBs was a multielectron process, which means that exploring the mechanism of each step will enable the overall process to be more deeply understood. Rotating-ring disk electrodes (RRDE) are often used to calculate the number of electrons transferred in a catalytic reaction to explore the mechanism in electrocatalysis, and are also potential to use in the catalysis process of LSBs. Lu et al. exploited rotating RRDE voltammetry and the specifically designed lithium-sulfur catholyte cells to examine the sulfur charge/discharge behavior in low- versus high-dielectric solvents (i.e., DOL:DME vs. DMSO). They calculated the number of electron transferred at each step of the reaction and discussed the reaction process in detail (Figure 9). In sulfur electrode reactions with catalysts, RRDE might be used to detect changes in the number of electrons transfer during the catalytic process. However, the application of RRDE in the catalytic characterization of LSBs still needs to be systematically investigated, including the calculation of complex system parameters (electrolyte viscosity) and the preparation of electrolyte with specific concentrations of sulfides.

### 4 PERSPECTIVE

In summary, recent years have witnessed a burgeoning interest in introducing catalytic components to accelerate the conversion of polysulfides for development of high-energy and long-life LSBs. The existence of catalysis and its performance improvement in LSBs have been confirmed by common characterization technology, but the catalytic performance has not been systematically described and the catalytic mechanism has not been fully explained. This paper, based on traditional catalytic characterization and characteristics of lithium-sulfur system, has discussed the current problems in catalytic characterization, and summarized the existing and promising characterization techniques with their corresponding functions for probing the parameters of catalysis in Li-S battery (Table 1). Important conclusions drawn with several key challenges and prospects in this exciting field are as follows.

## 4.1 More rigorous electrochemical techniques

Electrochemical technique is a kind of characterization technique that uses the specific response of tested system to various modes of current or voltage signals to characterize the electrochemical process, including CV, EIS, and polarographic analysis, etc. At present, electrochemical technique is widely used in the field of energy storage devices including LSBs to demonstrate the overall...
TABLE 1  Characterization techniques with their corresponding functions for probing the parameters of catalysis in Li-S battery

| Characterization techniques | Parameter |
|----------------------------|-----------|
| **Electrochemical techniques** |                      |
| CV,9 EIS8–14 | Reversibility of electrode reaction |
| Linear sweep voltammetry (LSV), galvanostatic intermittent titration (GITT)73 | Redox capacity of sulfur species |
| Variable temperature electrochemical test38–41 | Calculation of activation energy |
| Rotating-ring disk electrodes (RRDE)71 | Calculation of electron transfer number |
| **Electron microscopy techniques** |                      |
| Scanning electron microscopy (SEM)50 | Deposition state of Li2S |
| High-resolution transmission electron microscopy (HR-TEM)49,51 | Crystal structure of catalytic materials |
| In situ TEM56 | Real-time morphology of sulfide and catalyst |
| Cryogenic electron microscopy (cryo-EM)58–61 | Accurate characterization of sulfur |
| **Optical spectroscopy techniques** |                      |
| Ultraviolet-visible spectroscopy (UV–vis)33–35 | Liquid concentration of polysulfide |
| Fourier transform-infrared spectroscopy (FT-IR), Raman spectroscopy, X-ray absorption spectroscopy (XAS)43,64 | Qualitative or quantitative detection of polysulfide |
| In situ UV–vis, in situ Raman36,37,69,70 | Sulfur conversion process during charge and discharge |

Electrochemical performance. Upon introducing catalysts into the LSB system, electrochemical techniques are extensively used to confirm the catalysis process by comparing the overall electrochemical performance. For example, shift of the peak position in the CV curves as evidence of the existence of catalysis; comparing the Tafel slope fitted by CV curve to evaluate the catalytic ability of the material; description of the improvement effect of the catalyst on the utilization rate of the active material by calculating of the dissolution/deposition amount of lithium sulfide using potentiostatic electrolysis technique; shortening of the diameter of the semicircular area of the EIS curve to prove that the catalyst can accelerate the conversion of the LiPSs. Most of the current electrochemical characterization in lithium-sulfur catalysis is tested using a two-electrode battery, and the polarization current is generally not negligible (> 1 A g_sulfur⁻¹). Under such conditions, the polarization of the lithium electrode will affect the results of potential test, lowering the reliability of the potential measurement. Therefore, it is necessary to study the sulfur electrode with catalyst by using a three-electrode battery to eliminate the interference of other electrodes.

The three-electrode system is the most commonly used method in electrochemical analysis, which consists of working electrode, reference electrode, and counter electrode. Three-electrode system separate the measurement circuit that measures the potential from the polarization circuit that applies current to eliminate the polarization of other electrodes for accurately measuring the potential of the working electrode. A lot of work has used different types of three-electrode systems to solve the measurement error caused by the polarization of the lithium metal anode. Wang et al. built a three-electrode coin-cell by the insertion of a lithiumated Li4Ti5O12 electrode as the reference electrode, which is stable against the generation of LiPSs in the bulk electrolyte during cycling.72 This special coin-cell was used to monitor the real-time impedance evolution and to explain the effect of the dissolution of LiPSs on the viscosity and conductivity of the electrolyte. However, the additional potential consumption between the reference electrode and the working electrode due to the presence of the separator cannot be ignored for catalytic characterization. Therefore, the reference electrode of a three-electrode system should be built in free electrolyte to avoid the use of separators. Pang et al. constructed a three-electrode Swagelok cell for LSV testing to examine the redox kinetics of polysulfides on the surface of MgB2, MgO, and VC.73 The overpotential and the current response from the LSV experiment were used to construct the Tafel plot. The linear region of the semilogarithmic Tafel plot was manually fitted and extrapolated to obtain the exchange current density according to the Bulter–Volmer equation. At present, most three-electrode batteries in the lithium–sulfur system use lithium metal as the reference electrode, which is unfavorable for the accurate measurement of potential, due to its poor stability in LiPSs, and it is not an unpolarized electrode. Therefore, the electrode that maintains electrochemical stability in the LiPS-based electrolyte should be selected as a reference electrode, such as a platinum electrode. Manthiram et al.25 used a three-electrode system with Pt foil as a reference electrode to demonstrate the advantages of three-dimensional graphene/IT MoS2 heterostructures as an electrocatalyst towards LiPSs conversion.

To eliminate the interference from other electrodes, it is necessary to use a three-electrode system for
4.2 More systematic performance characterization

Catalytic studies in LSBs should use a more systematic evaluation system suitable for catalysts, instead of simply evaluating the pros and cons of the catalyst through electrochemical performance. A rational design of catalyst in LSB should pay attention to the three important parameters of activity, selectivity, and stability. Regarding activity, the most traditional and recognized way of describing it is to use the activation energy calculated by the Arrhenius equation. The reaction rate, as a necessary parameter of Arrhenius formula, could be expressed indirectly by some electrochemical techniques or advanced in situ spectroscopy techniques. Specifically, the diffusion rate, charge transfer resistance, and peak current density obtained by EIS or CV could be used to indirectly express the reaction rate; the real-time measurement of the concentration of different types of LiPS by in situ UV–vis spectroscopy could directly calculate the reaction rate. Regarding selectivity, unlike traditional catalytic studies, the selectivity of catalysts in LSBs is reflected in the promotion of reactions that can produce highly reactive intermediates. The qualitative and quantitative measurement of target reactions using UV–vis, Raman spectroscopy, and XAS are effective means of characterization. Regarding stability, the existence, and the failure problem of catalysts during cycle process have always been neglected issues. The stability of the catalyst can be explored by characterizing the electrodes after cycling.

4.3 More clear mechanism characterization

The mechanism of catalysis in LSBs is very complicated. Various characterization techniques could help to understand the catalytic process more deeply, even if the mechanism cannot be fully explored. For morphological characterization, electron microscopy is the most intuitive means of directly observing the interaction between catalyst and reactants, and is of great significance for in-depth understanding of lithium–sulfur catalysis. Especially, observing the deposition state of the discharge product lithium sulfide through electron microscope is considered to be an important basis for describing the catalytic process. Accurate electron microscope images will help understand and design catalysts from this perspective. However, the irreversible damage caused by the preparation and transfer of the sample seriously hindered the accurate shooting of the electron microscopy. In situ EM and cryo-EM techniques will help to avoid and solve this problem, and greatly improve the time and spatial resolution of electron microscopy, which will provide us with more convincing images. For detection of intermediates, in situ optical spectroscopy techniques have shown their great potential in analyzing the real reaction routes of Li-S systems. The future directions depend upon the well-designed electrochemical cells with high reproducibility and high-resolution detection of catalytic intermediate products. For exploring the multistep reaction mechanism, the reliable and mature electrocatalytic testing techniques (such as RRDE) would be rewarding with regard to the accurate monitoring of the electrochemical reaction mechanism of LSBs at a higher level. This could provide us with not only the information on the rate control steps in a multipart reaction, but also quantitative calculation of the electron transfer number and, therefore, deeper insight into lithium–sulfur catalysis.

Using catalysis to accelerate the conversion of LiPSs is a feasible method to solve the shuttling problem in LSBs from the source and realize the industrialization of LSBs. But the premise of using catalysis is to describe this process scientifically and rigorously. Therefore, a reasonable combination of electrochemical techniques, spectroscopy techniques and electron microscopy techniques, and other characterization techniques will provide more perspectives for the research of catalysis in LSBs, making reasonable catalyst design possible.

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