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Understanding the Reaction Mechanism of Lithium–Sulfur Batteries by In Situ/Operando X-ray Absorption Spectroscopy

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Abstract

Because of the high theoretical energy density of 2600 Wh kg^{-1} , lithium–sulfur (Li–S) batteries are regarded as one of the most promising energy storage technologies to meet the increasing requirement from personal devices to automobiles. However, the practical application of Li–S batteries is still challenging due to technical obstacles, such as low sulfur utilization and poor lifetime. Therefore, understanding the electrode reaction mechanism is of critical importance to further improve the battery performance and lifetime. Here, we review recent progress in the application of in situ and operando X-ray absorption spectroscopy in characterizing Li–S batteries. We discuss in detail how this advanced technique helps researchers understand the redox process of the electrode materials as well as the influence of polymer binder and electrolyte additive on the polysulfide shuttle effect, which provide valuable information for designing better Li–S batteries. A general conclusion and critical further research directions are also provided at the end.

1 Introduction

Developing electrical energy storage systems with high energy density and low cost is vitally important for powering our future society. Lithium-ion batteries (LIBs) are one of the dominant energy storage devices at the moment, which have been widely applied in various areas, e.g., portable electronic devices and electric vehicles [1–7]. However, the specific capacities of the electrode materials for LIBs are approaching their theoretical limits, which hinders the widespread application in a variety of emerging mobile transport applications. As a consequence, new battery technologies with high energy density and low cost that go beyond conventional LIBs are highly required.

Lithium–sulfur (Li–S) batteries (Fig. 1) have attracted extensive attention in recent years due to their high theoretical capacity and specific energy compared to the existing

LIBs [8–20]. For a typical Li–S battery, it consists of a lithium metal anode, an organic electrolyte and an elemental sulfur-based composite cathode. During the discharge process, the elemental sulfur is reduced first to long-chain polysulfides Li_2S_x ($4 < x \leq 8$) and then to short-chain polysulfides Li_2S_x ($2 < x \leq 4$). For devices utilizing an ether-based organic solvent, there are usually two discharge plateaus at 2.3 and 2.1 V, corresponding to the transformations of S_8 to Li_2S_4 and Li_2S_4 to Li_2S , respectively (Fig. 2). During the subsequent charge process, Li_2S is oxidized to S_8 via the formation of lithium polysulfides. Assuming a complete conversion reaction of elemental S ($16\text{Li} + \text{S}_8 \rightarrow 8\text{Li}_2\text{S}$), Li–S batteries could deliver a high specific capacity of 1675 mAh g^{-1} and specific energy of 2600 Wh kg^{-1} (Fig. 2), which are much higher than those of LIBs. Moreover, sulfur is naturally abundant and inexpensive. Therefore, Li–S batteries are considered as one of the most promising candidates for next-generation electrical energy storage systems for electric vehicles and large-area grids [8–11].

Although Li–S batteries are promising, there are still many challenges facing the Li–S technology [9,10]. For one thing, both S_8 and Li_2S are insulators with a high resistance, resulting in a low rate capability and low sulfur loading. For another thing, a volume expansion as large as 80% is expected when

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Fig. 1 Schematic diagram of a typical Li-S battery. Reproduced with permission from Ref. [10]

S₈ is fully converted to Li₂S, which leads to the pulverization of the active materials and thus rapid capacity fading. In addition, the intermediate lithium polysulfides have a high solubility in the organic electrolyte. They can diffuse toward the lithium anode to be reduced chemically and then diffuse back to the sulfur cathode to be re-oxidized, resulting in the notorious polysulfide shuttle effect.

To overcome these challenges, extensive efforts have been devoted to comprehensively understand the electrochemical reaction mechanism of Li-S batteries during the discharge-charge process to further improve the cycling performance. Among them, many studies have been focused on the complex reaction mechanism of electrode materials using advanced in situ/operando characterization techniques, such as X-ray diffraction (XRD), small-angle X-ray scattering (SAXS), Raman, neutron diffraction (ND), transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR) [18,21–42]. For example, in situ/operando TEM has been applied to investigate the lithiation and volume expansion of sulfur electrodes across multiple length scales [40,41]. In addition, several groups have investigated the phase change of sulfur during cycling process using in situ/operando X-ray diffraction (XRD) [35,36]. The results indicate that the phase of sulfur obtained after charge process

is different from the initial phase. Moreover, the formation of crystalline Li₂S₂ was clarified recently [43]. However, the amorphous nature of the intermediate lithium polysulfides formed during the cycling process makes it impossible to identify them with XRD.

In contrast to XRD, synchrotron-based X-ray absorption spectroscopy (XAS) is an element-specific technique and able to detect species that are amorphous, disordered or crystalline [19,44–46]. As a consequence, XAS is suitable for studying electronic and structural changes in electrode and electrolyte materials during the electrochemical processes. For soft X-ray (100–2000 eV)-based XAS, it can detect the 1s to 2p excitations of low Z elements, such as C, N and O, and the 2p to 3d transitions of 3d transition metals, such as Mn, Fe, Co and Ni (Fig. 3a) [47]. During the XAS process, the core-level electron is excited to an unoccupied state above the Fermi level through dipole transition (Fig. 4a). The probability of such a transition is directly related to the X-ray absorption cross section.

The most straightforward measurement of the absorption process is to measure the attenuation of incident X-rays, which is the common method for hard X-ray. However, due to the short penetration depth of soft X-ray, the XAS usually collects the intensity of the decay products of core holes, i.e., auger electrons or fluorescence photons (Fig. 3b). The intensity of these secondary electrons or the photons is proportional to the X-ray absorption cross section. Because of the short mean free path of electrons, the total-electron-yield (TEY) method is very surface sensitive (typically several nm). In contrast, if the outgoing photons (total fluorescence yield, TFY) are detected, the XAS becomes bulk sensitive (several hundred nm to μm, depending on the X-ray energy) due to the comparatively larger attenuation length. It should be noticed that both TEY and TFY modes are based on secondary X-ray excitation and relaxation processes. The TEY mode is usually measured by the sample drain current and therefore is limited to conductive materials, while TFY mode may be distorted by the saturation effect resulting from the

Fig. 2 **a** Energy density of Li-S batteries compared with other batteries. **b** A typical discharge/charge voltage profile of Li-S batteries in ether-based electrolytes. Reproduced with permission from Refs. [8] and [10]

Fig. 3 **a** Elements and corresponding excitations that are accessible by soft XAS. Reproduced with permission from Ref. [44]. **b** The geometry of XAS detection

self-absorption effect. For example, by measuring C and O K-edge XAS (Fig. 3b, c), we have investigated the chemical interaction between sulfur and graphene oxide (GO). The results clearly indicate that the moderate chemical interaction between GO and sulfur can not only preserve the intrinsic electronic structure of GO but also confine the sulfur on GO sheets, which can greatly improve the cycling performance of Li–S batteries [48,49]. In addition, XAS is a powerful tool in resolving electronic structures and distinguishing different electronic states, such as the different oxidation states and spin states of different Ni species shown in Fig. 3d [50]. For S K-edge XAS spectra, different sulfur species, e.g., elemental sulfur, Li_2S and lithium polysulfides, can be clearly distinguished [22–24,51].

While most of the reported reviews have summarized the recent progress on structural design of different components (e.g., sulfur electrodes, separators, electrolytes and anodes) and performance improvement of Li–S batteries [8–10,12,13,52–54], only a few reviews focus on the fundamental understanding of the reaction mechanism [19,55]. Synchrotron-based characterization techniques (especially XAS) have been widely used to investigate the reaction mech-

anism of Li–S batteries. Specially, significant progress has been achieved by using in situ/operando XAS to understand the redox process of electrode materials for Li–S batteries. In this contribution, we review recent progress in advanced characterization of Li–S batteries using in situ and operando XAS through four aspects: (1) the redox mechanism of S electrode; (2) the redox mechanism of Li_2S electrode; (3) the influence of polymer binder on the polysulfide shuttle effect; and (4) the influence of electrolyte additive on the polysulfide shuttle effect. In addition, we also provide perspectives on how the in situ and operando XAS can contribute to the further development of high-performance Li–S batteries.

2 Redox Mechanism of S Electrode

For a typical Li–S battery, elemental sulfur S_8 -based composite materials are usually used as the cathode materials. During the past few years, the redox mechanism of S_8 has been extensively investigated for Li–S batteries under the working conditions by using in situ/operando XAS. For example, Cuisinier et al. investigated the sulfur speciation during

Fig. 4 **a** Schematic illustration of the X-ray absorption and emission processes. **b** Representative pattern of GO immobilizing S and C K-edge XAS spectra of GO and GO-S. **c** O K-edge XAS spectra of GO and GO-S. **d** The Ni L-edge XAS spectra of different Ni-related species. Reproduced with permission from Refs. [45–47]

redox behavior and the mechanisms that control the dissolution and deposition of the redox products (S₈ and Li₂S) using in situ/operando XAS with a focus on S K-edge with low dielectric solvents 1,3-dioxolane-1,2-dimethoxyethane (DOL–DME), as shown in Fig. 5 [33]. To avoid the potential distortion of the XAS spectra by bulk particles, they used extremely uniform porous carbon nanospheres (PCNS, with a controlled size of 220 nm)/S composites as the cathode

electrode. This unique composition can not only confine the active electrode materials within the cathode side and therefore improve the cycling performance, but also facilitate the in situ/operando investigation. By using a linear combination of the operando XAS spectra, it is revealed that owing to the supersaturation of S^{2–} the precipitation of Li₂S is delayed during discharge, while the surface oxidation of Li₂S proceeds straightforwardly with the formation of intermediate

Fig. 5 a–c SEM images and EDX line of synthesized porous carbon nanospheres for S cathode. **d** Pore size distribution of porous carbon nanospheres with and without sulfur. **e** The discharge–charge voltages

for the first, 50th and 100th cycles. **f** Evolution of sulfur K-edge XAS spectra upon electrochemical cycling based on linear combination analysis. Reproduced with permission from Ref. [33]

lithium polysulfides, i.e., Li_2S_4 and Li_2S_6 . The XAS results also indicate that the discharge capacity is not limited by the precipitation of Li_2S but restricted by the unreacted sulfur [33].

By changing the solvents from low dielectric DOL–DME to high dielectric dimethylacetamide (DMA), the Li–S batteries undergo a series of electrochemical and chemical reactions with the intermediate reaction products of S_8^{2-} , S_6^{2-} , S_4^{2-} and $\text{S}_3^{\bullet-}$, among which $\text{S}_3^{\bullet-}$ is the most stable and dominant intermediate species [56]. In addition, Vijayakumar et al. stated that $\text{S}_3^{\bullet-}$ is the only free radical anion shown in the dimethyl sulfoxide (DMSO) solvent [57]. Actually, $\text{S}_3^{\bullet-}$ is also the only radical anion for a sulfur electrode discharged in tetraethylene glycol dimethyl ether (TEGDME) [58]. Moreover, Wujcik et al. found that significant quantities of polysulfide radical species (LiS_3 , LiS_4 , and LiS_5) are present after initial discharge to 2.0 V for Li–S batteries using ether-based solvents, while increased concentrations of shorter polysulfide dianions are observed after further discharge to 1.8 V [51]. By using a specifically designed electrochemical cell, Gorlin et al. investigated the influence of the solvent (DOL–DME vs. DMA) on the conversion of polysulfides to Li_2S by using in situ/operando XAS [24]. The results clearly demonstrate the formation of Li_2S after ~ 25–30% discharge in both types of solvents. However, the subsequent conversion from polysulfides to Li_2S is more rapid in DOL–DME. At the end of charge, the presence of Li_2S and lithium polysulfides is observed for DMC cells, while a mixture of Li_2S and $\text{S}_2^{2-}/\text{Li}_2\text{S}_2$ like intermediate is observed for cells using DOL–DME. All these results clearly indicate that the intermediate polysulfide species are highly related to the choice of the solvent. Overall,

the in situ/operando XAS has provided invaluable insights toward a clear understanding of the redox mechanism of sulfur electrodes in Li–S batteries under real operation conditions, which is essential for further optimizing and improving the cycling performances.

3 Redox Mechanism of Li_2S Electrode

Besides the sulfur electrode, the Li_2S electrode (theoretical capacity: 1166 mAh g^{-1}) also attracts extensive attention because it can be paired with not only lithium but also other much safer anodes (such as graphite, silicon and tin), which can obviate the safety issues of the lithium metal anode when using sulfur [59–67]. In addition, compared with the low melting point of sulfur (115°C), Li_2S has a much higher melting point (1372°C), which guarantees the application of high-temperature heat treatment of Li_2S to protect the electrode materials and prevent the dissolution of lithium polysulfides into the electrolyte. Moreover, the mechanical damage of the cathode during the cycling process can also be circumvented because Li_2S is in the maximal volume and the empty space generated during the charge process therefore can hold the volume expansion of sulfur during the discharge process.

The electrochemical performance of Li_2S has been investigated in detail previously. For example, Yang et al. found that a large overpotential barrier (~ 1V) exists for micrometer-sized Li_2S particles [65]. The initial potential barrier can be overcome by applying a high charging cut-off voltage. During the activation process, polysulfide phase can be formed, which greatly improves the kinetics of Li_2S .

The Li_2S particles with an average side of $10\text{ }\mu\text{m}$ can also be activated by using this method, and a high discharge capacity of 850 mAh/g is achieved [65]. The activation mechanism was also investigated by using in situ X-ray diffraction. The results indicate that the origin of the initial barrier is a result of phase nucleation, while the height of the barrier is mainly related to the poor charge transfer at the surface of Li_2S and limited diffusivity of lithium ions inside Li_2S . Cai et al. further improved the cycling performance of Li_2S electrode by using a cost-effective way preparing nanostructured Li_2S -carbon composite using high-energy dry ball milling of commercial Li_2S powder [61]. More recently, Nan et al. reported an easy synthesis strategy for the preparation of Li_2S spheres with controlled size and a chemical vapor deposition (CVD) method for coating Li_2S spheres with a carbon shell, which is porous enough to allow Li^+ diffusion in and out of the core-shell particles [60]. The unique core-shell particles deliver both high specific capacity and stable cycling performance.

For all the reported results, an activation process is always necessary to make full utilization of the Li_2S electrode materials [60]. To understand this abnormal behavior, the charging mechanism of Li_2S electrode has been extensively investigated [22,23,30,60,63,66,68]. For instance, by using spatially resolved XAS characterization, which can detect lithium polysulfides in the electrolytic solutions and amorphous/crystalline solids and differentiate between species formed in the electrode and the electrolytic solutions, Gorlin et al. investigated the intermediate products formed in the cathode and electrolytic solutions during the first and second charge processes to gain insight into the Li_2S redox mechanism in the DOL-DME solvent [22]. The results indicate that the first charge process leads to a complete conversion of Li_2S to S_8 with no significant concentration of intermediate polysulfides detected throughout the whole process. The oxidation of Li_2S particles also requires a chemical step, which is facilitated by the presence of a significant concentration of intermediate polysulfides.

However, the reason for the presence of the energy barrier was not explained in that report. To answer this question, we have investigated the electrochemical charging mechanism of nanosized Li_2S with a uniform size of $\sim 500\text{ nm}$ by in situ/operando XAS [23]. As shown in Fig. 6, the characteristic XAS features of different sulfur species can be well discerned in the XAS spectra. The in situ/operando XAS results indicate that in the first charge process, Li_2S is directly converted to S without the formation of lithium polysulfides, while the formation of lithium polysulfides is visible from the beginning of the second charge process (Fig. 6). As a consequence, a high charging voltage is always essential to fully extract Li^+ from Li_2S into electrolyte in the first charge process considering the fact that Li_2S is an ionic crystal. The presence of lithium polysulfides at the beginning of the

second charge process has multiple effects: (1) reducing the charge transfer resistance from Li_2S to electrolyte and leading to a lower overpotential in the charge voltage profile; (2) acting as the polysulfide facilitator for the electrochemical reaction of Li_2S ; and (3) reacting chemically with Li_2S to form low-order polysulfides. This investigation provides a new fundamental insight into the charge mechanism of the Li_2S electrode and highlights the double roles of the lithium polysulfides in both the electrochemical and chemical processes. It should be noted that Li_2S is most likely amorphous after the first cycle, as revealed by in situ/operando high-energy XRD [69].

4 Effect of Polymer Binder for Polysulfide Shuttle Effect

As mentioned above, the soluble nature of lithium polysulfides results in the shuttle effect for Li-S batteries, which is harmful for the electrochemical performance. Tremendous efforts have been taken to solve this problem, such as integrating sulfur with porous carbon, graphene and graphene oxide [48,49,70–74]. The physical trap of sulfur is effective for improving the electronic conductivity and suppressing the shuttle effect. An alternative route is to modify the functional polymer binders for Li-S batteries, which play a role of gluing the elemental sulfur and conductive additives together. Polyvinylidene fluoride (PVDF) is a conventional binder for Li-S batteries, but lacks chemical bonding with intermediate lithium polysulfides that are formed during the discharge and charge processes.

As a consequence, different functional polymer binders have been developed to improve the cycling performance of Li-S batteries [75–80]. For example, by applying a new amino-based functional binder with 3D network flexibility structure, the capacity is still retained at 91.3% over 600 cycles [76]. In addition, a high specific capacity of 987.6 mAh g^{-1} is achieved with a high sulfur loading density of 8.0 mg cm^{-2} . According to the in situ UV-Vis absorption spectra analysis, the origin responsible for the enhanced electrochemical performance is related to the abundant amino groups of the binder with high binding strength to lithium polysulfides, which could effectively reduce the polysulfide dissolution and therefore the shuttle effect [76]. This also spurred the investigation into natural polymers as multifunctional binders for Li-S batteries to suppress the shuttle effect. For example, gum Arabic, a bio-derived polymer with abundant functional groups, has been successfully applied to Li-S batteries, resulting in an outstanding performance and stability over 500 cycles [81]. Recently, we demonstrated that there exists a nucleophilic substitution reaction between lithium polysulfides and carrageenan polymer binder, which can fix the lithium polysulfides to the

Fig. 6 Reaction mechanism of Li_2S electrode by in situ and operando XAS. **a** Schematic illustration of the in situ coin cell for simultaneous electrochemical and X-ray spectroscopic measurement. **b** S K-edge XAS of different sulfur species. **c** Operando XAS spectra of Li_2S elec-

trode for the first charge process. **d** Operando XAS spectra of Li_2S electrode for the second charge process. **e** The proposed reaction mechanism of Li_2S electrode during the initial charge and discharge processes. Reproduced with permission from Ref. [23]

sulfur electrode via the newly formed C-S covalent bond [82]. These polymer binders can continuously react with the polysulfides when they break from the electrode during the cycling process. In addition, we showed that the

polyethylenimine (PEI) polymer can be applied as a polar binder for Li-S batteries to hinder the shuttle effect [83]. The sulfur electrode (8.6 mg cm^{-2}) with PEI binder can deliver a high initial areal capacity of 9.7 mAh cm^{-2} , and

Fig. 7 Effect of polymer binder for polysulfide shuttle effect. **a** Schematic illustration of the lithium polysulfide confinement through PEI polymer binder. **b** Cell configuration for operando XAS study. **c** Operando sulfur K-edge XAS mapping and representative XAS spectra of PEI-based cathode during first discharge. **d** Operando sulfur K-edge

XAS mapping and representative XAS spectra of PVDF-based cathode during first discharge. **e** Concentration of polysulfides in electrolyte for PEI- and PVDF-based cathodes as a function of specific capacity during first discharge. Reproduced with permission from Ref. [83]

the capacity is still maintained at 6.4 mAh cm^{-2} after 50 cycles, which is comparable to that of commercial LIBs. The in situ UV-Vis and in situ/operando XAS spectra clearly show the strong adsorption capability of PEI binder toward

lithium polysulfides because of the electrostatic interaction, which is responsible for the superior cycling performance (Fig. 7) [83].

Fig. 8 Effect of LiNO₃ additive for polysulfide shuttle effect. In situ/operando S K-edge XAS spectra of Li-S batteries with (a) and without (b) LiNO₃ additive collected for the first discharge. c S K-

edge XAS spectra of Li-S batteries at different states of charge. d The proposed reaction mechanism of the SEI layer. Reproduced with permission from Ref. [25]

5 Effect of Electrolyte Additive for Polysulfide Shuttle Effect

LiNO₃ has been widely applied as an electrolyte additive in Li-S batteries for suppressing the polysulfide shuttle effect [84–95]. It has been reported that LiNO₃ can participate in the

formation of solid electrolyte interphase (SEI) layer on the surface of lithium anode [86,88]. The passivation film formed with LiNO₃ can not only protect lithium anode from chemical reaction with the dissolved lithium polysulfides but also prevent lithium polysulfides from electrochemical reduction on the lithium anode surface [86]. The reaction product of

LiNO₃ as well as the influence on the formation of SEI layer has been investigated extensively. For example, Xiong et al. investigated the structure of SEI layer formed in the electrolytic solution with mixed lithium salts and additives (LiNO₃ and lithium polysulfides) using X-ray photoelectron spectroscopy and argon-ion sputtering technology [91]. It is found that the thin SEI layer is mainly composed of two sub-layers: The top layer is mainly composed of oxidized polysulfide products while the bottom layer is formed by the reduced polysulfide and LiNO₃ products [91]. The unique SEI film results in a smooth and compact layer, which can effectively hinder the continuous reaction with lithium anode. In addition, the LiNO₃ additive can also inhibit the gassing of Li–S batteries [96]. CH₄ and H₂ are found as the major gaseous decomposition products for the operating Li–S batteries, especially during the charge process when a fresh lithium surface is created. When adding LiNO₃ in the electrolyte, the formation of CH₄ is greatly suppressed and very little or no H₂ is generated during discharge process. This phenomenon is possibly related to the formation of a relatively stable SEI layer on lithium surface and the suppression of polysulfide shuttle effect. Moreover, it seems that the produced gases are also consumed during the cycling process and possibly buried in the SEI layer. In addition, the concentration of dissolved lithium polysulfides can also influence the performance of LiNO₃ additive. If it is too high, the formed SEI layer is not well maintained and the lithium metal is easily etched, resulting in the growth of lithium dendrites and lower cycling efficiency [97].

More recently, we have comprehensively investigated the influence of LiNO₃ additive on the formation mechanism of the SEI layer on lithium anode surface using in situ/operando XAS (Fig. 8) [25]. The results imply that the improved cycling performance of Li–S batteries using LiNO₃ additive is related to the synergetic effect of LiNO₃ and dissolved lithium polysulfides in the electrolytic solutions. The LiNO₃ additive oxidizes the lithium polysulfides while itself is reduced to LiNO₂. The oxidation products Li₂SO₃ and Li₂SO₄ form a compact and stable layer on lithium anode surface during the initial discharge stage. This passivation layer can inhibit the reaction between lithium polysulfides and lithium metal, leading to the decrease of the shuttle effect and improvement in the cycling performance. This study therefore provides a deeper insight into the role of LiNO₃ for ameliorating the shuttle effect, which is important for the further development of high-performance Li–S batteries.

6 Conclusions

To summarize, we have summarized recent progress on the application of in situ/operando XAS in the understanding of the redox mechanism of Li–S batteries, which is of great

significance for the development of high-performance Li–S batteries. The new insights that the in situ/operando XAS results have offered contribute to a real-time monitoring on the electronic structure evolution of both cathode and anode materials for Li–S batteries. With the aid of in situ/operando XAS, the reaction mechanism of sulfur and Li₂S electrodes has been clearly revealed. In addition, the confinement of intermediate lithium polysulfides formed during the discharge and charge processes by functional polymer binders has been visualized in detail by the same method. Moreover, the synergetic effect of LiNO₃ and lithium polysulfides on the formation process of the SEI layer on lithium anode and polysulfide shuttle effect are also well understood.

Although significant progress has been achieved by using in situ/operando XAS for Li–S batteries, there are still quite some questions to be answered. For example, how are the single sulfur and Li₂S particle discharged and charged during the cycling process? What is the reaction path of sulfur and Li₂S electrode during the fast discharge and charge process? Why the concentration of lithium polysulfides in the electrolyte can influence the passivation behavior of lithium anode? To answer these questions, time- and space-resolved in situ/operando XAS combined with other characterization techniques is highly required. With the recent development of diffraction-limited storage ring technique [98,99], the X-ray nanoprobe method with high beam flux and brilliance is highly promising, which can be greatly beneficial for better understanding of the reaction mechanism of Li–S batteries in the future.

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