The formation of crystalline lithium sulfide on electrocatalytic surfaces in lithium–sulfur batteries

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Abstract

Lithium–sulfur (Li–S) battery is highly regarded as a promising next-generation energy storage device but suffers from sluggish sulfur redox kinetics. Probing the behavior and mechanism of the sulfur species on electrocatalytic surface is the first step to rationally introduce polysulfide electrocatalysts for kinetic promotion in a working battery. Herein, crystalline lithium sulfide (Li$_2$S) is exclusively observed on electrocatalytic surface with uniform spherical morphology while Li$_2$S on non-electrocatalytic surface is amorphous and irregular. Further characterization indicates the crystalline Li$_2$S preferentially participates in the discharge/charge process to render reduced interfacial resistance, high sulfur utilization, and kinetic advantages to rationalize the superior performances of Li–S batteries. The evolution of solid Li$_2$S on electrocatalytic surface not only addresses the polysulfide electrocatalysis strategy, but also demonstrates unsatisfactory performances with poor rate capability, rapid capacity fading, and limited cycling lifespan.

1. Introduction

Lithium–sulfur (Li–S) battery is highly considered as a promising next-generation energy storage system due to its ultrahigh theoretical energy density of 2600 Wh kg$^{-1}$ with additional cathode advantages including low cost, natural abundance, and environmental friendliness [1–4]. Except the issues of sulfur insulation and volume expansion well addressed by introducing conductive porous carbon hosts [5–8], sluggish kinetics of the sulfur redox reactions has become the current limitation to retard Li–S application [9–11]. Slow kinetics between dissolved lithium polysulfides (LiPSs) and solid lithium sulfide (Li$_2$S) aggravates the diffusion-induced LiPS shuttling with low Coulombic efficiency (CE) [12,13], and the electronic/ion insulated Li$_2$S goes through uneven deposition/dissolution under high polarization conditions to render surface passivation, dramatic phase migration, and consequent loss of active materials [14,15]. Therefore, practical Li–S batteries demonstrate unsatisfactory performances with poor rate capability, rapid capacity fading, and limited cycling lifespan [16,17].

Introducing electrocatalysts to facilitate the sulfur redox kinetics constitutes a rational strategy for battery performance promotion [18–21]. A pioneer work in 2015 by Arava and co-workers [22] demonstrated platinum with polysulfide electrocatalytic activity. Since then, the polysulfide electrocatalysis strategy has attracted growing attention that CoS$_2$ [23], Co$_3$N [24], MoS$_2$ [25,26], TiO$_2$–TiN heterostructures [27], defective Ni$_x$Fe$_{1-x}$N [28], Ni–Fe hydroxysulfide [29], and cobalt single atoms [30–32] were found to electrocatalytically improve the Li–S kinetics. Meanwhile, comprehensive electrochemical methods were proposed to identify polysulfide electrocatalysis from chemisorption [33–35]. Nevertheless, investigations into the behavior and mechanism of the sulfur species on electrocatalytic surfaces remain insufficient, hindering in-depth understanding of polysulfide electrocatalysis and further rational design of high-performance polysulfide electrocatalysts.

The deposition/dissolution of solid Li$_2$S is generally recognized as the rate determining step manifested by the obvious nucleation overpotential [36], high charge voltage [37] and large activation energy [38]. Therefore, to investigate Li$_2$S evolution during discharging/charging is of great significance to understanding polysulfide electrocatalysis and Li–S chemistry [39,40]. Nazar and co-workers pioneeringly addressed the speciation of Li$_2$S by operando...
X-ray absorption spectroscopy [41], and their following work identified the premature of Li$_2$S on polar surface [42]. In addition, morphology evaluation on conductive surface was performed by several research groups [43], where the current density [44], temperature [45], solvent [46] and salt [47,48] are observed to influence Li$_2$S nucleation and growth. However, structure and morphology evolution of Li$_2$S on electrocatalytic surfaces has been few touched yet. Insights are highly required to reveal the behavior and mechanism of Li$_2$S evolution on electrocatalytic surface for not only understanding the Li–S chemistry, but also promoting the Li–S battery performances.

In this contribution, we systematically investigate Li$_2$S evolution on electrocatalytic surface regarding its structure and morphology. Crystalline and spherical Li$_2$S is observed on electrocatalytic surface while routine conductive surface produces amorphous and irregular Li$_2$S particles. Time-dependent transmission electron microscopy (TEM) characterization reveals that the crystalline Li$_2$S preferentially participates in the sulfur redox reactions to render reduced interfacial resistance, high sulfur utilization, and activated sulfur redox reactions. Consequently, Li–S batteries with electrocatalysts demonstrate improved rate performances, higher capacity, and prolonged lifespan that unambiguously validates the significance of the polysulfide electrocatalysis strategy toward high-performance Li–S batteries.

2. Results and discussion

The model electrocatalyst (named as G@POF) was constructed by hybridizing framework porphyrin (POF) on the surface of conductive graphene (G). POF was proved with high electrocatalytic activity to particularly facilitate Li$_2$S nucleation through polysulfide electrocatalysis [49]. G, on the other hand, served as the conductive skeleton for POF hybridization and the control sample without electrocatalytic activity [50]. Scanning electron microscope (SEM) and TEM images demonstrate similar morphologies of G and G@POF (Figs. S1 and S2). Further nitrogen isothermal sorption measurements indicate comparable specific surface area and pore volume (Fig. S3). Similar morphology, surface area, and pore structure eliminate their interference between G@POF and G in the following electrochemical evaluation or mechanistic investigation.

The hybridization of POF on the surface of G was identified by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis. G@POF shows an additional diffraction peak at 13° assigned as the characteristic POF signal (Fig. S4) [51,52]. The XPS survey spectra exhibit a distinct increase in nitrogen content from 0.7 at.% for G to 5.5 at.% for G@POF, suggesting the hybridization of nitrogen-containing POF on nitrogen-free G (Fig. S5). Furthermore, high-resolution nitrogen 1 s XPS spectrum manifests pyrrole N as the dominant nitrogen species in consistence with the POF structure (Fig. S6) [53,54]. Conclusively, POF was successfully hybridized on the surface of G to provide a high-electrocatalytic surface.

The electrochemical performance of the G@POF electrocatalyst was evaluated in Li–S cells to validate the polysulfide electrocatalysis strategy. Sulfur cathodes with high sulfur contents of 90 wt.% were employed to amplify the electrocatalytic effect on the battery performances (Fig. S7), where G and G@POF served as the interlayer [55,56]. As exhibited in (a), G@POF contributes to a much improved rate performance with the capacity of 1127, 1060, 1017, and 811 mAh g$^{-1}$ at 0.2 C, 0.5 C, 1.0 C, and 2.0 C, respectively (1 C = 1672 mA g$^{-1}$). In contrast, the capacity degrades at higher rates with the G interlayer. Galvanostatic discharge–charge profiles in (b) demonstrate typical two discharge plateaus with G@POF while the second discharge plateau diminishes at 1.0 C with G. Stunted second discharge plateau indicates kinetic difficulty in Li$_2$S nucleation and growth on non-electrocatalytic surface. In addition, the cyclic voltammograms of Li–S cells also indicate enhanced kinetics of the sulfur conversion reactions with the G@POF electrocatalyst (Fig. S8).

The cycling performance was firstly evaluated using cathodes with conventional sulfur loading (1.3 mg cm$^{-2}$) at 0.5 C. The Li–S cells with the G@POF interlayer exhibit an initial capacity of 1115 mAh g$^{-1}$ and preserve the capacity of 747 mAh g$^{-1}$ after 500 cycles (Fig. 1c) corresponding to a cyclic decay rate of 0.08%. In comparison, the Li–S cells with the G interlayer fade with limited lifespan. Additionally, the CE is stable around 99% for G@POF throughout the cycling but fluctuates for G to imply inhibited polysulfide shuffling by the G@POF interlayer. Moreover, a high-sulfur-loading Li–S cell (6.7 mg cm$^{-2}$) with the G@POF interlayer affords stable cycling of 300 cycles with a high initial areal capacity of 5.4 mAh cm$^{-2}$ and stable CE. The excellent battery performances of G@POF explicitly confirm the effectiveness of the polysulfide electrocatalysis strategy to construct high-performance Li–S batteries.

The redox between dissolved LiPSs and Li$_2$S contributes three quarters of the total capacity and therefore dominantly determines the battery performances [57]. Evaluation of the redox behavior of Li$_2$S on electrocatalytic G@POF is of great essential to rationalize the polysulfide electrocatalysis strategy. Fully-discharged Li–S cells were disassembled and examined by TEM. Interestingly, the discharged Li$_2$S on electrocatalytic POF is spherical and uniform (Fig. 2a) but irregular in morphology on routine conductive G (Fig. 2b). This phenomenon was confirmed to be universal in more areas (Figs. S9 and S10). Further selected area electron diffraction (SAED) analysis identifies the Li$_2$S on electrocatalytic POF is crystalline with a characteristic Li$_2$S signal (diffraction of 4000 marked with red semicircle in Fig. 2c, PDF#26-1188) but amorphous on non-electrocatalytic G (Fig. 2d). The structure and morphology of Li$_2$S is distinguished to be crystalline and spherical on electrocatalytic surface. The above argument remains valid at higher discharge current density to further indicate the electrocatalytic effect as the determining factor (Fig. S11).

To further reveal the evolution of the crystalline spherical Li$_2$S on electrocatalytic surface, time-dependent TEM characterization was performed by characterizing Li$_2$S at different states of discharge or charge. Concretely, Li–S cells were discharged or charged to a given state, disassembled, and characterized, where the states are marked in (a). At the initial state of Li$_2$S nucleation, several contrast is suggested to be Li$_2$S with neither defined morphology nor crystalline signal (Fig. 3b). At the half-discharged state, crystalline Li$_2$S can be identified according to the SAED patterns (Fig. 3c). Crystalline Li$_2$S is distinguished to be crystalline and spherical on electrocatalytic surface. The above argument remains valid at higher discharge current density to further indicate the electrocatalytic effect as the determining factor (Fig. 3c).

When the Li–S cell is charged half-way, the Li$_2$S crystalline signal vanishes while the Li$_2$S contrast can be distinctly observed (Fig. 3e), suggesting crystalline Li$_2$S possesses higher reactivity to be oxidized to dissolved LiPSs. As expected, nearly no Li$_2$S contrast can be identified at the fully discharged state (Fig. 3f) in agreement with high CE endowed by the G@POF interlayer. Based on the above Li$_2$S evaluation, it is concluded that crystalline Li$_2$S appears at the early stage of discharge and vanishes at the early stage of charge as well. Crystalline Li$_2$S participates preferentially in the sulfur redox reactions throughout the discharge/charge process.

In order to bridge the Li$_2$S behavior and the electrochemical performance on electrocatalytic surface, kinetic evaluation and impedance analysis were carried out. G@POF affords earlier and higher current responses for both Li$_2$S precipitation and dissolution than G, identifying the electrocatalytic effect of POF on facilitating the kinetics of the Li$_2$S-involved conversion reactions with reduced
Fig. 1. Battery performances of Li–S cells with G@POF electrocatalysts. (a) Rate performance, (b) corresponding discharge–charge profiles, and (c) cycling performance of Li–S cells with G or G@POF interlayers. (d) Cycling performance of high-sulfur-loading Li–S cells with G@POF interlayer.

Fig. 2. Structure and morphology evaluation of Li2S. (a, b) TEM images of G@POF and G interlayers after full discharge. (c, d) SEAD patterns corresponding to (a) and (b), respectively.
activation energies (Fig. S12). In addition, Fig. 3g demonstrates the origin Nyquist plot and the simulated resistance is exhibited in Fig. 3h. Despite similar electrolyte resistance ($R_\text{l}$), the charge transfer resistance ($R_\text{ct}$) of G@POF is significantly lower than G at both states. Correspondingly, bulk Li$_2$S can be observed on G after fully charged (Fig. S13). Considering crystalline Li$_2$S on electrocatalytic G@POF and amorphous Li$_2$S on G, crystalline Li$_2$S is suggested to be beneficial to improve the interfacial kinetics to realize enhanced battery performances.

Based on the above characterizations, we proposed a mechanism to explain the Li$_2$S behavior on electrocatalytic surface. It is assumed that crystalline Li$_2$S and amorphous Li$_2$S compete during the discharge and charge processes. Crystalline Li$_2$S possesses thermodynamic and kinetic advantages over amorphous Li$_2$S. On non-electrocatalytic surface (for instance, G herein), the energy barrier for Li$_2$S deposition and dissolution is so high that amorphous Li$_2$S dominates as the main participant at high polarization conditions (Fig. 4a). Amorphous Li$_2$S is sluggish in kinetics to render irregular morphology and low reversibility, performing inactive “dead Li$_2$S” with capacity loss during cycling. On the contrary, electrocatalytic surface significantly reduces the energy barrier for Li$_2$S nucleation and growth. Consequently, thermodynamically favorable crystalline Li$_2$S serves as the main product during discharge although partial amorphous Li$_2$S may possibly exist (Fig. 4b). The crystalline Li$_2$S is also favorable in kinetics to be preferentially oxidized during charge, where the LiPS facilitates the oxidation of the remained amorphous Li$_2$S through comproportionation. Electrocatalytic surface relieves the kinetic pressure with reduced polarization, and uniform spherical Li$_2$S with low surface energy, high CE, and high active material utilization are therefore achieved.

3. Conclusions

In conclusion, crystalline Li$_2$S is exclusively observed on electrocatalytic surface with uniform spherical morphology. Crystalline Li$_2$S preferentially participates in the discharge and charge processes to imply its thermodynamic and kinetic advantages. Electrocatalytic surface is identified to be highly responsible for the formation of crystalline Li$_2$S and the corresponding promoted
battery performances. This work addresses the importance of polysulfide electrocatalysis for Li–S chemistry and reveals the structural evolution of Li$_2$S on electrocatalytic surface. The proposed mechanism herein can inspire further comprehensive investigations into the chemistry of energy-related processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2021.05.023.

References


Fig. 4. Schematic of Li$_2$S evolution on (a) non-electrocatalytic surface and (b) electrocatalytic surface. Crystalline Li$_2$S is achieved on electrocatalytic surface with uniform spherical morphology and preferentially participates in the discharge/charge process with high sulfur utilization and promoted battery performances.