ITU Journal of Metallurgy and Materials Engineering

ITU/MMEJ

Lithium-Sulfur Batteries: Cell Reaction Mechanisms, Limitations and Solutions

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Abstract: Lithium-sulfur (Li-S) batteries are known for their high theoretical capacity (1675 mAh/g), high theoretical specific energy (2600 Wh/kg), non-toxicity, natural abundance and low cost of sulfur as the cathode active material. Especially thanks to their high specific energy, Li-S batteries are considered one of the most promising candidates as an alternative to lithium-ion batteries (LIBs) in the future. However, Li-S batteries are still not commercially available due to the rapid capacity fading stemming from intrinsic material-related issues — such as the use of lithium metal as the anode, the insulating nature of sulfur as the cathode and the discharge product (Li_2S), substantial volume expansion at the end of discharge. In this short review, Li-S batteries, their reaction mechanisms, limitations preventing the successful long-term operation and approaches suggested as solution in the literature will be introduced and mentioned.

Keywords: Energy storage, lithium-sulfur batteries, lithium metal anode, sulfur.

Lityum-Sülfür Bataryalar: Hücre Reaksiyon Mekanizmaları, Kısıtlamalar ve Çözümler

Özet**:** Lityum-sülfür (Li-S) bataryalar, sahip oldukları yüksek teorik kapasite (1675 mAh/g), yüksek özgül enerji (2600 Wh/kg), kullanılan malzemelerin toksik olmaması, katot aktif malzemesi olarak kullanılan sülfürün doğada bolca bulunması ve ucuz olması gibi nedenlerle öne çıkmaktadır. Özellikle sahip oldukları yüksek özgül enerji sayesinde Li-S bataryaların gelecekte lityum-iyon bataryalara (LİB'ler) alternatif olabilecek en uygun sistemlerden biri olduğu düşünülmektedir. Ancak, sistemde kullanılan metalik Li anot ve yalıtkan sülfür katotun hücrenin çalışması sırasında yol açtığı problemlerden kaynaklı hızlı kapasite kaybına uğraması nedeniyle Li-S bataryalar henüz ticarileşememiştir. Bu kısa derleme makalesinde Li-S bataryalar, ilgili reaksiyon mekanizmaları, sistemin uzun çevrimler boyunca başarılı bir şekilde çalışmasını engelleyen problemler ve bunlara dair literatürde önerilen çözüm yöntemleri tanımlanacak ve detaylandırılacaktır.

Anahtar Kelimeler: Enerji depolama, lityum-sülfür bataryalar, lityum metal anot, sülfür.

Short Review

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Reference: Cengiz, E.C. (2025). Lithium-Sulfur Batteries: Cell Reaction Mechanisms, Limitations and Solutions, *ITU Journal of Metallurgy and Materials Engineering*, 2(2), 18-21.

Submission Date: 07 July 2025
Online Acceptance: 11 July 2025
Online Publishing: 30 July 2025

1.Introduction

Energy is a subject affecting not only our daily lives but also global politics. Until recently, the main source of energy was fossil fuels; however, for over a decade, there has been a shift towards renewable energy sources mostly driven by governmental incentives due to the detrimental effects of using fossil fuels to the environment. Nevertheless, renewable energy sources are intermittent and cannot provide a continuous supply, as they can only generate energy when the source is available — for example, solar cells produce electricity when the sun is shining. Therefore, it is important to store the excessive energy generated from the renewable energy sources and batteries are among the most viable solutions for this purpose. Batteries can store electrical energy in the chemical energy form and release this energy as electrical energy form when needed. Compared to the other energy storage technologies, batteries can offer one of the highest efficiencies. Batteries have become an important energy source after the commercialization of Lithium-ion batteries (LIBs) in 1991, and it revolutionized the mobile devices. Since then, LIBs have attracted significant attention from the scientific community, and the performance of LIBs has increased year by year. In the last decade, due to the harmful environmental impact of internal combustion engines (ICEs), the use of electric vehicles (EVs) has been incentivized and 60 millions of EVs are on the road as of 2024 (Virta, 2025). The current EVs are made up of LIBs and because of the range anxiety, there is a huge demand for increasing the performance of the batteries by using alternative chemistries that offer higher energy density. Lithium-sulfur (Li-S) batteries are among the promising candidates for EV applications due to their high theoretical capacity. Sulfur has lower molecular weight (32.066 g/mol) than the conventional LIB cathode materials. Therefore, the theoretical capacity (1675 mAh/g) and specific energy (2600 Wh/kg) of Li-S batteries are significantly higher than those of LIBs, which makes Li-S batteries more attractive to use in EVs. In addition, natural abundance, low-cost and non-toxicity of sulfur make the system more attractive by offering a safer and more sustainable alternative compared to some heavy metal-containing LIB components.

Li-S batteries were first developed in the 1960s, but significant progress began by following the groundbreaking work by Linda Nazar et al. in 2009 (Ji et al., 2009). Despite decades of research, Li-S batteries remain uncommercialized and have not succeeded in replacing LIBs so far, because of the challenging internal problems of Li-S batteries. Addressing these challenges in detail is essential for being able to move toward a solution. In this short review, cell reaction mechanisms of Li-S cells will be briefly introduced, the key limitations of the system will be given, and the potential solutions proposed in the literature will be discussed.

2. Cell Reaction Mechanism of Li-S Batteries

A typical Li-S battery is composed of a Li metal anode, a sulfur-based (S) cathode and an ethereal-based electrolyte (G. Li et al., 2015). Sulfur is usually in S8 form (orthorombic, α-S8). Because of the insulating nature of sulfur, it is commonly combined with porous carbon structures to enhance the conductivity of the cathode.

The cell reaction mechanism of Li-S batteries is based on conversion reaction. Figure 1 shows a typical discharge/charge profile of a Li-S battery, highlighting the regions associated with formation and conversion of various polysulfide species during cycling. In general, S8 reacts with Li metal to produce lithium polysulfides with Li2Sx formula. The plateau at approximately 2.4 V is attributed to the reduction of the cyclic structure of S_8 to Li_2S_8. In the voltage range between 2.4 V and 2.0 V, long-chain polysulfides (Li_2S_x, 8 > x > 4) are formed. The plateau observed around 2.0 V corresponds to the conversion of long-chain polysulfides into short-chain polysulfides (Li_2S_x, 4 > x > 2) (Fig. 1). Below 2.0 V, further reduction leads to the formation of Li_2S_2 and Li_2S. Up to 2.4 V, where the formation of Li_2S_4 occurs, approximately 25% of the total capacity (418 mAh/g) is obtained. In the voltage range between 2.4 V and 1.5 V, where the conversion from Li_2S_4 to Li_2S takes place, the remaining 75% of the total capacity (1252 mAh/g) is delivered (Park et al., 2018).

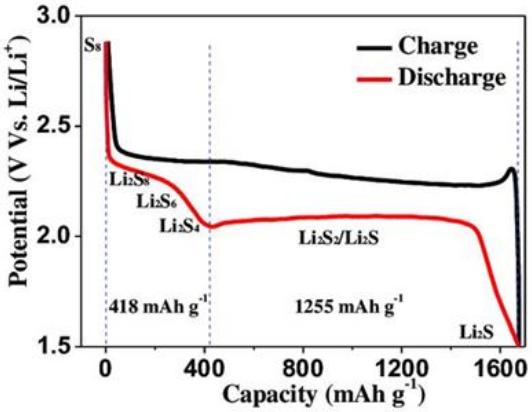

Figure 1. Typical charge-discharge voltage plateau of Li-S batteries. Reproduced from (Guo & Liu, 2019), under a Creative Commons Attribution 3.0 Unported Licence.
Şekil 1. Li-S pillerine ait tipik şarj–deşarj voltaj plato eğrisi. Guo ve Liu (2019)'dan, Creative Commons Attribution 3.0 Unported Lisansı kapsamında uyarlanmıştır.

3. Limitations and Solutions

Even though Li-S batteries are promising, their commercialization is hampered by the rapid capacity decay caused by the complicated cell reactions occurring in the cell. The limitations are listed and explained along with the respective solutions for each one, below.

3.1. The Insulating Nature of Sulfur

Sulfur has a highly insulating nature, with an electronic conductivity as low as $5x10^{-30}$ S/cm, which prevents it from being used as a standalone cathode material. To fully utilize the high capacity of sulfur, it needs to be combined with a conductive material, typically carbon. A common strategy involves impregnating sulfur into porous carbon structures (Arie et al., 2020; Ji et al., 2009; Zheng et al., 2011). But in recent years, this approach has become advanced by using multifunctional nanostructured frameworks (Baji et al., 2024; Kwon et al., 2021; Liu et al., 2019). Additionally, alternative conductive architectures- such as doped carbon materials (Y. Zhang et al., 2018), graphene-wrapped sulfur (Yu et al., 2015), core-shell structures (Miao et al., 2013) have also been used to increase the sulfur utilization by enhancing the conductivity of the cathode (Baji et al., 2024). Although using conductive additives is a viable strategy to fully utilize the capacity of sulfur, it is important to minimize their content to increase the specific energy, which is because the excessive use of inactive materials decreases the specific energy of system.

3.2. Dissolution of Polysulfides in Aprotic Electrolytes and Shuttle Effect

As mentioned before, long chain polysulfides (Li_2S_x, 8 > x > 4) are formed as discharge proceeds, at around 2.4 V. These long chain polysulfides are highly soluble in aprotic electrolytes and

lead to irreversible active material loss by reacting with the lithium metal anode and being deposited on the Li surface. In addition, this problem decreases the ionic conductivity of electrolyte by increasing the electrolyte viscosity (Kolosnitsyn & Karaseva, 2008) which may in turn lower the power density of the cell.

Another detrimental issue associated with polysulfide dissolution is the “shuttle effect”. During discharge process, long-chain polysulfides dissolve into the electrolyte and diffuse throughout the cell, including towards the lithium anode, where they are continuously reduced to shorter chain polysulfides or lithium sulfide (Li_2S) species. These reduced species can then migrate back to the cathode side and undergo reoxidation to long-chain polysulfides. This repeated back-and-forth redox process is known as the "shuttle effect", which leads to active material loss and a significant decrease in coulombic efficiency. The shuttle effect becomes more severe at low C-rates, as polysulfides have more time to migrate through the cell during the extended time. As a result, the incomplete charging reaction caused by shuttle effect negatively affects the continuity of the electrochemical process. Consequently, cycle life is shortened, and eventually cell failure occurs.

There are some solutions to overcome the problems associated with dissolution of polysulfides and the shuttle effect. These include, but are not limited to, using additives in the electrolyte to protect Li by creating a stable SEI against polysulfide attacks (Aurbach et al., 2009; Shimoda et al., 2023), using interlayers between cathode and separator to keep polysulfides on cathode side (Celik et al., 2018; Cengiz, Ansari Hamedani, et al., 2019; Cengiz, Ozturk, et al., 2019; Cengiz, Salihoglu, et al., 2019; Cengiz & Demir-Cakan, 2020).

3.3. Using Li Metal as Anode

Li metal is used as an anode in Li-S batteries instead of graphite, which increases the theoretical capacity and specific energy. However, using lithium metal as the anode comes at a cost, primarily due to the formation of dendrites. Dendrite formation occurs during the charge process, when Li^+ ions return to Li anode. If the solid electrolyte interphase (SEI) is unstable or the anode surface is uneven, Li^+ ions tend to deposit unevenly, leading to dendrite growth. In some cases, these dendrites can pierce the separator, causing short circuits, which may result in cell failure and sometimes even explosions. There is no permanent solution to overcome Li dendrite issue. However, there are some approaches to alleviate it, such as the utilization of additives in the electrolyte to keep Li anode protected (Aurbach et al., 2009; Ovc-Okene et al., 2025), 3D-Li anode (Wei et al., 2021), alternative designs of current collectors (Pei et al., 2019), and protective coatings on Li (Baji et al., 2024; J. Zhang et al., 2020).

3.4. End-of-discharge Product Li_2S

Another challenge associated with the utilization of sulfur cathode is related to the end-of-discharge product, Li_2S. The issues with Li_2S include, but are not limited to, its insulating nature and significant volumetric expansion (80%). The electronic pathways collapse because of the volumetric expansion, which results in rapid capacity fading and cell failure. On the other hand, Li_2S is highly insulating, which makes it difficult to convert back into sulfur during the charging process (Demir-Cakan, 2015). This sometimes leads to the accumulation of Li_2S on the electrode surface during charging, resulting in an increase in cell resistance. Furthermore, the inability to fully reconvert Li_2S during charging causes a loss of active material and, consequently, rapid capacity fading.

There are some solutions to overcome problems associated with volumetric change resulting from formation of Li_2S, such as using Li_2S as active material (Celik et al., 2018). Using Li_2S as the cathode not only provides overcoming the volume expansion problem but also eliminates the necessity of using Li metal as an anode, which alleviates the safety concerns, since Li_2S is already in a lithiated state. However, like sulfur, Li_2S is also an electronically insulating material, which necessitates the use of conductive structures. Also, application of an activation charging cycle to upper voltages in the first cycle (Celik et al., 2018), decreasing size of Li_2S particles (Celik et al., 2018), using catalysts (He et al., 2022; Z. Li et al., 2022) and redox mediators (Demir-Cakan, 2015; Fan et al., 2023) also increase the utilization of Li_2S active material and provide longer cycle life.

4.Conclusion

Li-S batteries are still regarded as promising battery technology along with the other next-generation battery technologies like solid-state batteries. However, their commercialization is hampered by several problems associated with utilization of sulfur and Li metal, which are, in fact, the main reasons for the high theoretical capacity of Li-S batteries. To overcome these detrimental problems, there are plenty of approaches implemented by the academia and industry. However, none of them provide a permanent solution. Even if commercial production becomes possible, it will likely be limited to niche markets with high added value in the initial stages.

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