

Li₂S- or S-Based Lithium-Ion Batteries

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While members of the Li–S battery research community are becoming more conscious of the practical testing parameters, the widespread commercialization of S-based batteries is still far from realization. Particularly, the metallic Li used as the anode poses potential safety and cycle stability concerns. Alternatively, other S-battery configurations without a Li anode, i.e., lithium-ion, Li₂S, or S batteries, do not suffer from the same safety concerns and can possibly serve as better methods to bring room-temperature S-based battery technologies to industry. However, whether Li₂S or S will be used as the initiating cathode material remains unclear as each offers their own unique advantages and disadvantages. Here, both S and Li₂S as cathodes are briefly discussed and the key benefits of Li₂S are highlighted.

1. Introduction

Lithium–sulfur batteries (LSBs) have been a topic of much discussion in battery literature throughout the recent years. Initial promises of over 2500 Wh kg⁻¹ (based on only active materials) have been impeded by severe technical challenges such as the low electronic conductivity of S/Li₂S, volume changes during discharge/charge, and intermediate redox products (polysulfide (PS)) that are highly soluble in common organic electrolytes.^[1] Solvated polysulfides (PSs) tend to transfer out of the cathode, becoming inactive as it deposits onto electronically isolated parts of the cell. Many research papers have focused on mitigating the combined negative effects of solvated polysulfide (PS) and insulating S. Methods such as S encapsulation in porous carbon,^[2] porous hollow carbon,^[3] or sorption onto metal oxide^[4] along with the use of redox mediators^[5]

have dominated this research field. Over the years, valuable fundamental knowledge has been gained on LSBs. As the absolute amount of S is extremely critical to the practical energy density, some recent works have shifted toward increasing the areal and volumetric loading of S in the cathode in attempt to reach performance indices appropriate for practical application.^[6] Unfortunately, as the loading of S is increased, various problems of LSB are amplified along with the appearance of Li-anode symptoms. It is interesting that the highly researched LSB is actually a lithium-metal battery (LMB), and like all batteries based

on a pure Li anode, the problems of the anode becomes evident only when the areal capacity/current density are raised to a sufficiently high level. The same safety and durability problems for LSBs that stemmed from the dendritic Li formation and severe electrolyte decomposition had long been the seemingly unsolvable problems of LMBs. To this day, the LMB is still regarded as a technology far from commercialization and often considered the “holy grail” of electrochemical energy storage system,^[7] implying extreme difficulty.

Accordingly, LMBs have been commercially abandoned and replaced with lithium-ion batteries (LIB) after the invention of the carbon-based anodes by Sony in 1991. Carbonaceous anodes such as graphite and soft carbon were significantly more reliable in storing Li-ions than Li metal itself in terms of both cycle durability and safety. Following this logic, the LSB can also be converted into a LIB with a S-based (coupled with a prelithiated anode) or Li₂S-based (coupled with a non-Li-metal anode) cathode to avoid the problems of the Li-metal anode. However, like the shift from LMB to LIBs, S-LIB/Li₂S-LIB will inevitably have a lower energy density over LSB but superior stability. Therefore, the S-LIB/Li₂S-LIB will most likely be applied as a cost-effective, highly durable battery technology with acceptable energy densities. Here, we will provide a brief discussion on the emerging field of S-based LIBs. First, a quick distinction between LSBs, LMBs, LIBs, and the two types of S-based LIBs will be clearly made for the benefit of future references to these types of technologies. We will then discuss the advantages of Li₂S over S in more detail with respect to Li-ion sourcing, electrode packing, and potential polysulfide (PS) tunability.

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 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.201801190>.

DOI: 10.1002/adma.201801190

2. Definitions

The following acronyms will be used for the various technologies that will be discussed

LSBs: A battery configuration that incorporates with elemental S as starting active cathode material and elemental lithium as active anode material. Each cycle entails stripping and replating of Li.

LMBs: A battery configuration that incorporates pure Li-metal as active anode material. Each cycle entails stripping and replating of Li.

LIBs: A battery configuration that is manufactured/assembled with both cathode and anode as Li-ion hosts. Cycling does not include formation of pure elemental Li.

Sulfur-Based Lithium-Ion Batteries (S-LIBs): A battery configuration where elemental S is used as initial active cathode material whereas a lithiated Li-ion host is used for the anode. Cycling does not include the formation of pure elemental Li.

Lithium-Sulfide-Based Lithium-Ion Batteries (Li₂S-LIBs): A battery configuration where lithium sulfide is used as initial active cathode material and a nonlithiated Li-ion host is used for the anode. Cycling does not include formation of pure elemental Li.

3. Sulfur or Li₂S

Historically, the LMBs have been highly sought after due to its high energy density but commercialization attempts in the 1980s have resulted in battery fires which have crippled the technology's reputation.^[8] Since LSB is essentially an LMB, its performance and safety will most likely be bottlenecked by the lithium anode. While one can argue that the dissolved polysulfide (PS) in the electrolyte can serve as an intrinsic safety mechanism to quickly eliminate initiating dendrites, this is not a complete solution as this will be at the cost of active S materials, i.e., cycle life. One method to eliminate the LMB problems of LSBs is to replace the Li with another anode such as Si or graphite, effectively transforming the LSB into a S-LIB/Li₂S-LIB.

Compared to the large volume of LSB literature, research articles featuring S-LIB or Li₂S-LIBs are surprisingly rare. To the best of our knowledge, there are only 16 published works that pairs a S-based cathode with a non-Li metal anode.^[9–12] Of these works, $\approx 1/3$ can be classified as S-LIBs (S-based, Li-free cathode) that relied on various prelithiation methods to employ the Li-ion into the system. Prelithiation can be a delicate process and greatly depends on the prelithiation cell setup. If the coin cell configuration is chosen, the researcher must decrimp the coin cell to retrieve the lithiated anode, which could damage the electrode, producing inconsistencies between cells. Other methods such as using a Swagelok cell or direct pressure contact with Li foil in electrolyte might be more suitable due to ease of electrode retrieval, but the lithiation process is hardly scalable. Additionally, any retrieval procedure of the lithiated anode must be performed in an inert environment to prevent reaction with air. Above all, commercial prelithiation of anodes such as Si or graphite will most likely be even more logistically problematic. A widely considered alternative could be the use of stabilized lithium metal powder (SLMP), but this type of powder can be quite dangerous. Designs of Si anodes would often include some form of nanosized morphology to mitigate its volumetric expansion/contraction challenges,^[13] which typically possess



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large surfaces areas. The higher surface area of the anode would promote a quick and possibly dangerous lithiation reaction with SLMP. In fact, the most common application of SLMP in LIB literature is to provide a capacity compensation against the slight capacity loss from solid electrolyte interphase (SEI) formation.^[14] Therefore, the quantities of SLMP often used are much lower than the required amount envisioned in lithiating the entire anode. Furthermore, since the absolute capacities of S-LIB are required to be significantly higher than that of commercial LIB (S-LIB has a lower operating voltage), it is likely that an uncontrolled lithiation of a high capacity anode with SLMP (technically a short circuit reaction) can lead to severe thermal runaways especially when brought to the commercial scale. Even under an inert atmosphere, a metal fire can still occur if the heat transfer is not properly managed. Alternatively, a more promising and scalable method is to introduce lithium into the cathode. Borrowing the idea from commercial lithium metal oxides, the use of Li₂S as starting cathode material not

only allows for circumventing the anode prelithiation problems but also offers a few unique advantages over the S electrode.

It is well known that S experiences a $\approx 80\%$ volume expansion upon being lithiated to Li_2S . This could be detrimental in maintaining a mechanically robust electrode throughout the cycles. Intriguingly, this problem of volume expansion is often overshadowed by the much emphasized polysulfide (PS) shuttle effect. A common practice in LSB research is the lack of calendaring, which allows for large electrode pore volumes. This conveniently helps to alleviate the problems associated with S volume expansion. Accordingly, work by Lv et al. have shown the negative effects on performance after calendaring to a certain thickness, especially for high areal loading cells.^[15] The lack of calendaring severely penalizes volumetric energy density estimates of the already intrinsically bulky S material (density $\approx 2 \text{ g cm}^{-3}$ ^[16]). Similar to the hidden symptoms of LSB's Li-anode, it could be expected that the problems associated with volume expansion of S to Li_2S will most likely reveal itself as research into S-based cathodes reach closer to commercial targets. A common strategy in LSB literature is to first coat S nanoparticles with protective shell (for instance, TiO_2) followed by a partial dissolution of S with a slightly solvating solvent (toluene), creating a "yolk-shell" structure.^[17] If Li_2S (Li_2S -LIB) is used instead of S (S-LIB), concerns with volume expansion can be effectively mitigated. A key advantage of Li_2S is that any typical encapsulation methods when used on Li_2S will inherently have volume accommodation properties built-in to its design.^[18]

Additionally, compared to Li_2S , S is highly volatile due to its low surface tension and will easily sublime at slightly elevated

temperatures or partial vacuums,^[19] limiting synthesis options and material stability during storage.^[20] Even the typical drying process of the electrode laminates can be detrimental to electrochemical performance if not carefully controlled.^[21] While Li_2S does succumb to reactions with ambient moisture, its thermal stability is far superior to S. As such, synthesis routes are more flexible when attempting to design uniquely structured Li_2S composites. For example, the Li_2S nanoparticles shown in **Figure 1a,b** are encapsulated in a graphene nanocapsule ($\text{Li}_2\text{S}@$ graphene) that was synthesized through a high temperature lithiothermic reduction of CS_2 vapors. Such a synthesis procedure for a S-based cathode is impossible.

On the other hand, Li_2S does present problems. The moisture sensitivity of Li_2S cannot be ignored, as it will most likely increase the cost of manufacturing. However, similar to Li_2S , elemental Li and lithiated anodes are also extremely reactive to moisture. Interestingly, the morphology of high air stability SLMP could be reproduced in Li_2S as most Li_2S active materials are typically in some form of core-shell configuration.

The most well-known and defining disadvantage of Li_2S is perhaps its electrochemical inactivity.^[11,12] In general, the 1st discharge of a S cathode (S-LIB) is relatively trivial compared to the 1st charge of a Li_2S electrode (Li_2S -LIB). An extremely high charging voltage ($>3.5 \text{ V}$) is often required to overcome both the thermodynamic and kinetic barriers to oxidize conventional Li_2S to S.^[22] This phenomenon has been attributed to the strong crystalline structure of bulk Li_2S that hinders proper charge transfer to its solid structure.^[12] Strategies to alleviate this problem revolves around polysulfide (PS) preinjections into the electrolyte to act as redox mediators, enhancing

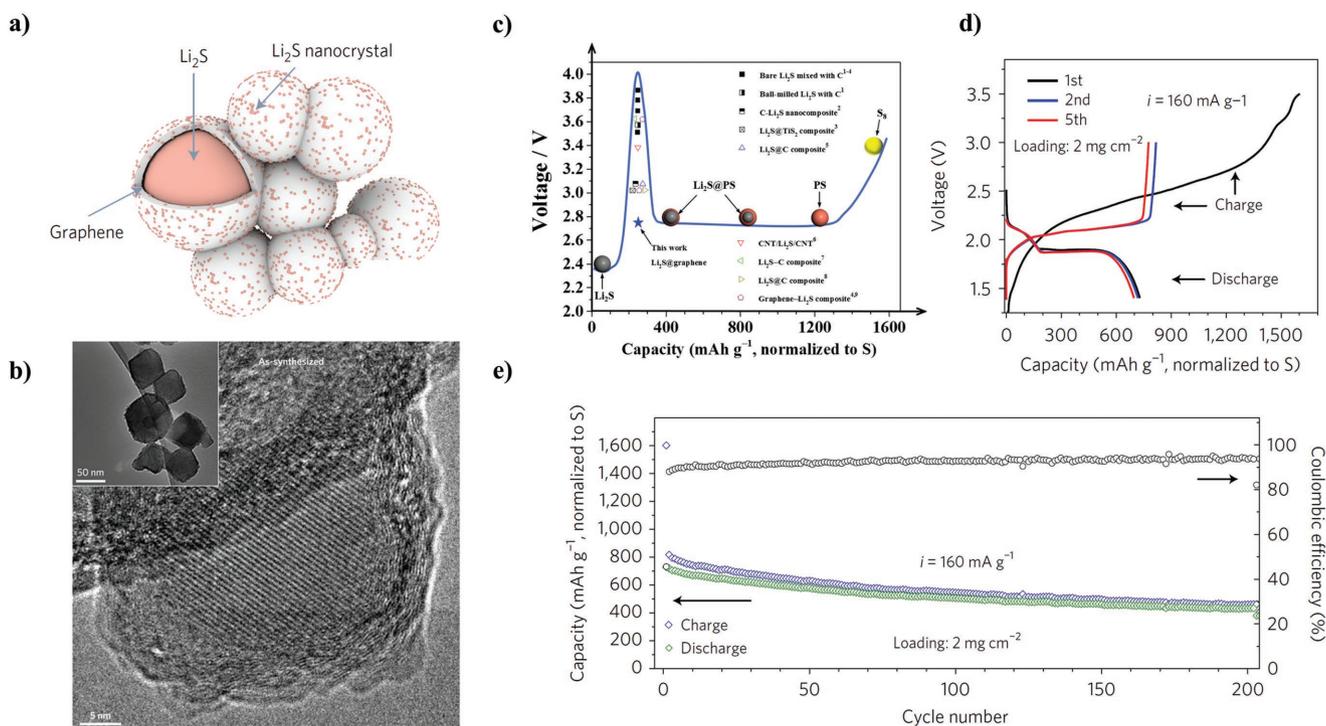


Figure 1. a) Schematic of Li_2S nanoparticles in a graphene nanocapsule, b) the corresponding HRTEM image, c) comparison of Li_2S activation voltage to the literature, d) charge and discharge voltage profile, and e) cycle stability of full cell with a graphite anode. Reproduced with permission.^[10] Copyright 2017 Springer Nature.

the oxidation kinetics of Li_2S .^[11,12,23] Reducing the crystallinity (i.e., amorphous Li_2S films) can also significantly reduce the charging overpotential.^[24] Alternatively, the graphene wrapped nanosized Li_2S have presented an extremely low 1st cycle charging overpotential of <2.8 V as shown in Figure 1c. This is most likely due to the nanosized nature of the material. When paired with a graphite anode in a full cell configuration (voltage profiles shown in Figure 1d), this material demonstrated good stability over 200 cycles (Figure 1e). There is still much room for improvement for Li_2S to reach higher capacities that are comparable to S cathodes (on the same $\text{mAh g}^{-1}\text{S}$ basis), but recent progress is encouraging. If the stability of Li_2S can be shown to be superior to S cathodes, a Li_2S -LIB could be a truly advantageous system where cost- and cycle durability are more desired over energy density. It should be noted that the anodic stability of the Al current collector and ether-based electrolyte at >4 V is an enormous concern for conventional Li_2S cathode. However, we believe that the recent research progress and direction to reduce the 1st charge overpotential will most likely be reflected in any foreseeable commercializable variations of a Li_2S cathode.

Taking note from commercial LIB technology, it is quite interesting that a large part of stability control for LIBs lies in restricting the amount of available capacity by controlling the upper charging voltage of the cathode's metal oxide. Much of recent LIB research efforts have been placed on reaching higher charging voltages and as such, state of charge, to achieve a higher degree of cathode Li-ion storage. A fully delithiated metal oxide cathode is difficult to achieve due to unstable cycling. A similar argument can be made for Li_2S and S. With a fully delithiated S cathode in a S-LIB or LSB, the most soluble and arguably most problematic polysulfide (PS) species, the long chained $\text{Li}_2\text{S}_{6-8}$ molecules, are unavoidably formed first. This allows easy loss of S material through the well-known polysulfide (PS) shuttle effect, resulting in very poor cycle stability. Using a S cathode could be analogous to using a fully delithiated metal oxides as the starting cathode. In contrast, by approaching the complicated polysulfide (PS) formation from the lower oxidation state/short chained PS, i.e., Li_2S , the cell can potentially tune/limit the highest forming polysulfide (PS) chain. Smaller polysulfide (PS) chains which are only slightly soluble in low dielectric aprotic organic solvents (1,3 dioxolane and 1,2 dimethoxyethane)^[25] can be formed first. As such, the final advantage that Li_2S offers over S is the ability to limit polysulfide (PS) dissolution. By starting with Li_2S instead of S, it might be possible to form only the low solubility Li_2S_4 and avoid the majority of the symptoms associated with the highly soluble polysulfide (PS) species. Even more encouraging is that the majority of the capacity of a S-based cathode resides in the second plateau where transformations between short order polysulfide (PS) (Li_2S_n , $n \leq 4$) and Li_2S salts occur. This suggests that if successful, circumventing the formation of long polysulfide (PS) chains will likely only compromise minimal capacity but have enormous implications on increasing cycle stability. Furthermore, incremental improvements can follow from a more realistic incremental increase in the "level of engineering difficult" with increasing charging voltage, analogous to current strategies in enhancing metal oxide cathode. With

the benefits clear, it is interesting that the fundamental possibility for a state of charge control (SOCC) has been a largely unexplored area for Li_2S -LIB. Conversely, in other battery technologies, investigation into SOCC has shown great promise.

In addition to commercial LIB, the comparison between using S or Li_2S is conceptually very similar to the open and closed Li–O₂ systems. Many of the expected benefits of a closed Li–O₂ system are similar to that of a Li_2S -LIB. An open Li–O₂ battery system uses O₂ (analogous to S₈) as active cathode material, whereas a closed system utilizes a lithiated oxygen ($\text{Li}_2\text{O}/\text{Li}_2\text{O}_2$, analogous to Li_2S) as the starting cathode material.^[26] The recently reported anion-redox mechanism in LIBs can in fact be described as an implementation of SOCC on Li_2O cathode where oxygen gas evolution is prevented to achieve exceptional stability enhancements.^[27]

Finally, if the polysulfide (PS) generation can be successfully controlled, carbonate decomposition due to the nucleophilic polysulfide (PS) could be drastically reduced. In turn, the industrially problematic volatile nature of ether-based electrolytes can be avoided by replacing (partially or fully) with the commercially preferred higher boiling point carbonate electrolyte solvents. SOCC is just one methodology that can serve to limit polysulfide (PS) generation. Another method already explored is the infiltration of smaller sulfur allotropes into micropores.^[28] This effectively circumvents the formation of long chain polysulfides (PSs), as the starting sulfur material is already the short chain S₂₋₄. Resulting discharge voltage profiles shown in Figure 2, reveals a single sloped plateau instead of the common two plateau regions of long-chained polysulfide (PS) generating cathodes. Accordingly, stable cycling was shown even in traditional LIB carbonate electrolytes. Regardless of the method employed, if solvated polysulfides (PSs) generation can be largely avoided, the practical aspects of a sulfur-containing cathode will be drastically increased.

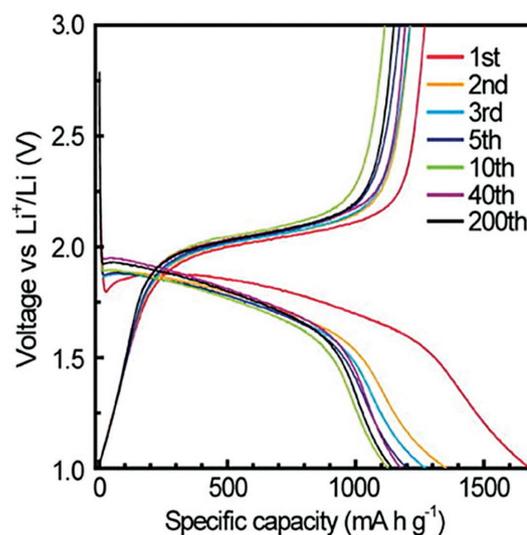


Figure 2. Charge and discharge voltage profiles of small allotropes S over 200 cycles. Reproduced with permission.^[28] Copyright 2012 American Chemical Society.

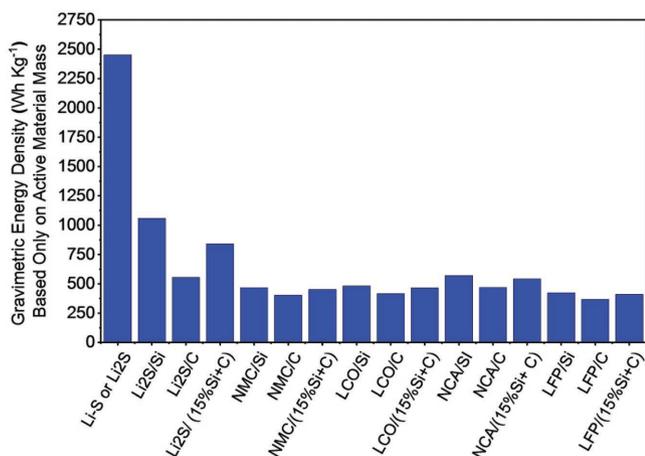


Figure 3. A comparison of the calculated theoretical gravimetric energy density of various Li₂S-LIBs at commercial LIB materials. Calculations were only based on active material mass. Data used for calculations can be found in Table S1 in the Supporting Information. Please note that NMC = LiNi_{0.33}Mn_{0.33}Co_{0.33}, NCA = LiNi_{0.8}Co_{0.15}Al_{0.05}, LFP = LiFePO₄, LCO = LiCoO₂, C = graphite.

4. Summary and Perspective

Lithium–sulfur batteries have been incredibly popular in the recent years, but only recently have the underlying lithium-metal battery symptoms been revealed. By increasing the areal loading and current density, the dendritic nature of the Li anode has once again been brought to the center of attention. However, by using a non-Li-metal anode and forming a S-based lithium-ion battery (S-LIB or Li₂S-LIB), this problem can be circumvented. While these LIB configurations still have technical challenges, it could be said that it is less ambitious than the LSB technology and potentially more industrially realistic. Specifically, the Li₂S-LIB configuration presents many hidden benefits that could be very impactful at the commercial scale. Among the obvious benefits of avoiding a prelithiation step and volume buffering, Li₂S offers very interesting capacity tuning characteristic analogous to the commercial metal oxide batteries. Furthering of future Li₂S-LIBs can follow the similar, “incremental voltage increase” strategy currently employed by LiNi_{0.33}Mn_{0.33}Co_{0.33} (NMC), LiCoO₂, and other commercial cathode technologies. More work must first be made to understand the mechanism of the 1st charge and validate the possibility for a Li₂S-LIB state of charge control scheme. Variations in charging mechanism in response to different electrode materials and electrolyte additives could be drastic. It should be noted that the lower forecasted capacity/energy density due to replacing the Li anode^[29] and partial charging could be an issue for applications where space or mass limitation is paramount (electric vehicles) but satisfactory for others (grid storage). Interestingly, based on our brief energy density calculations (Figure 3), a Li₂S-LIB is still theoretically superior to the commercial LIBs whether paired with a graphite, Si, or 15% Si + graphite blended electrode. However, the true practical energy density is still unclear as they heavily depend on testing conditions such as electrolyte volume, active material ratio in electrode.

Lastly, the benefits of Li₂S do not depend on the anode and if the problems of LMB are to be solved, Li₂S could still be paired with the more energy dense Li-metal where the majority of the Li

are sourced from the Li₂S. We hope this brief article has properly articulated some of the potential practical benefits of Li₂S over S.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

J.L. gratefully acknowledges support from the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy through the Advanced Battery Materials Research (BMR) Program (Battery500 Consortium). Argonne National Laboratory is operated for DOE Office of Science by UChicago Argonne, LLC, under contract No. DE-AC02-06CH11357. T.W. gratefully acknowledges support from the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, under Contract No. DE-AC02-06CH11357. Z.C. and M.L. would like to acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Waterloo Institute for Nanotechnology (WIN). As part of a special Advanced Materials (Wiley-VCH) issue dedicated to celebrate the 60th anniversary of the University of Science and Technology of China (USTC), T.W. (9819) and J.L. (9503) would like to wish their Alma Mater, USTC, a fruitful and innovative future.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

Li₂S cathodes, Li–S batteries, lithium-ion sulfur batteries, lithium-metal batteries, polysulfides (PSs)

Received: February 20, 2018

Revised: March 29, 2018

Published online:

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