



## Review

## Advances in lithium–sulfur batteries

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## ABSTRACT

This review is focused on the state-of-the-art of lithium-sulfur batteries. The great advantage of these energy storage devices in view of their theoretical specific capacity ( $2500 \text{ Wh kg}^{-1}$ ,  $2800 \text{ Wh L}^{-1}$ , assuming complete reaction to  $\text{Li}_2\text{S}$ ) has been the motivation for a huge amount of works. However, these batteries suffer of disadvantages that have restricted their applications such as high electrical resistance, capacity fading, self-discharge, mainly due to the so-called shuttle effect. Strategies have been developed with the recent modifications that have been proposed as a remedy to the shuttle effect, and the insulating nature of the polysulfides. All the elements of the battery are concerned and the solution, as we present herewith, is a combination of modification of the cathode, of the separator, of the electrolyte, including the choice of binder, even though few binder-free architectures have now been proposed.

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**1. Introduction**

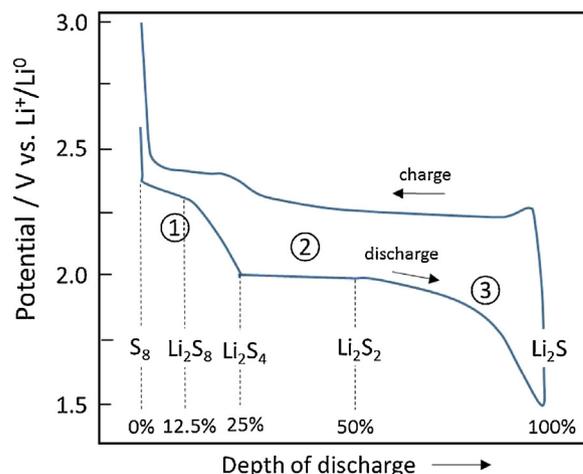
Due to the rapid development in our societies, energy storage has become critical. In this context, lithium-ion batteries (LIBs) have enabled the commercialization of electric and plug-in hybrid cars. They are also used for current regulation and leveling, solving the intermittence problems of sustainable energy supply (wind-mills, photovoltaic plants) and integration on smart grids [1]. The huge advantage of the Li-S battery in view of its theoretical capacity (2500 Wh kg<sup>-1</sup>, 2800 Wh L<sup>-1</sup>, assuming complete reaction to Li<sub>2</sub>S) [2] has been the motivation for a huge amount of works since its discovery. In addition, sulfur is very cheap. The concept of the Li-S battery dates from 1962 [3]. The first promising results were obtained in the late sixties with the use of organic electrolyte [4]. Unfortunately, this battery also suffers of disadvantages that have restricted its applications: high electrical resistance [5], capacity fading, self-discharge, mainly due to the so-called shuttle effect. All the reviews on Li–S batteries through the years have repeatedly reported these difficulties with which the community of researchers in electrochemistry struggle [6–10]. In addition, the problem of high resistance of the sulfur and the polysulfides has been solved by adding conductive elements, like carbon under different forms [11] in the cathode, at the expense of the amount of active material available for the electrochemical process [12]. Actually, if we add 40% of conductive carbon to the product, a figure that was still commonly met few years ago, the advantage with the lithium-ion batteries (LIBs) is small in terms of energy density and the volume density is even in favor of the LIBs [13]. Although these problems have never been completely solved, constant progress has been made, in particular in the recent years, giving hope today that these challenges will be met in the near future. It is the purpose of this work to review the results that have been obtained, mostly in the two last years, which justify this reasonable optimism. To limit the length of the review, attention is focused on the structural aspects and the electrochemical properties, but not on the synthesis aspects, which are detailed in the publications we have cited. In addition, we recommend the reading of a pertinent review on the atomic layer deposition applied to Li-S batteries that has been recently published [14].

In most cases, the capacities reported in the papers are reported by gram of sulfur (g<sub>sulfur</sub>). However, this is not a value for a battery, not even for an electrode, but just for one component of an electrode. Such values are absolutely useless for a comparison between different composite concepts. Any useful comparison needs to refer to the energy density on cell level, and this information is rarely available. When available, we report it in this review; otherwise we do not mention the capacities in the original works since they are useless for a comparison between different composite concepts, and we put the focus on the collection of the different approaches. Exceptions are results on which we wish to attract attention for their outstanding performance. Even though it does not permit any comparison with the performance at the cell

level, the information available per gram of sulfur gives some insight on the ability of the composite to use all or a part of the sulfur in the cycling process.

The electrochemical reaction during the discharge proceeds approximately in three steps [15,16] illustrated in Fig. 1: (I) a reversible conversion of sulfur through stepwise reduction up to the formation of S<sup>0</sup> → S<sub>4</sub><sup>2-</sup>. These polysulfides are soluble, so that the reaction kinetics are fast. (II) a conversion of S<sub>4</sub><sup>2-</sup>-polysulfides to solid Li<sub>2</sub>S<sub>2</sub>. This S<sup>0.5-</sup> → S<sup>-</sup> reduction is more difficult, because of the energy needed to nucleate the solid phase. (III) a conversion of solid Li<sub>2</sub>S<sub>2</sub> to solid Li<sub>2</sub>S. This is the most difficult step because of the sluggish diffusion of lithium in this solid environment [15,17]. This decomposition in three steps is an approximation. In particular, electrochemical impedance spectroscopy [18] and in situ X-ray diffraction spectra [19] revealed that Li<sub>2</sub>S appear immediately at the beginning of the lower plateau.

On the other hand, the charge process is such that all the polysulfides transform via charge transfer following the most facile oxidation state S<sub>8</sub><sup>2-</sup>. Upon cycling, the S<sub>n</sub><sup>2-</sup> formed on oxidation of Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S (or on reduction of S<sub>8</sub>) react with them to form S<sub>n-x</sub><sup>2-</sup> polysulfides at the anode side. They diffuse on the cathode side and are re-oxidized into S<sub>n</sub><sup>2-</sup> species. This parasitic cyclic process decreases the active mass available in the discharge process and is responsible for an important decrease of the coulombic efficiency in the charge process [20]. A model of this internal shuttle effect has reproduced quantitatively the self-discharge, coulombic efficiency, thermal effects observed experimentally [21,22], giving evidence that this internal shuttle effect is responsible for these problems. More recently, a complete modeling of the batteries with S/C composite cathode could be made [23], while the self-



**Fig. 1.** Discharge–charge profiles of a Li–S cell, illustrating regions (I) conversion of solid sulfur to soluble polysulfides; (II) conversion of polysulfides to solid Li<sub>2</sub>S<sub>2</sub>; (III) conversion of solid Li<sub>2</sub>S<sub>2</sub> to solid Li<sub>2</sub>S.

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