

Lithium–Sulfur Batteries: Problems and Solutions¹

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Received December 26, 2006

Abstract—This work considers the fundamental problems in the design of lithium–sulfur batteries (LSBs): low practical specific energy, rapid decrease in capacity during cycling, and high self-discharge rates. We demonstrate that these problems will be solved by the provision of an optimum combination of the rates of electrode and corrosion processes in lithium–sulfur batteries during cycling.

Key words: lithium–sulfur batteries, sulfur electrode, lithium electrode, lithium polysulfides, cycling

DOI: 10.1134/S1023193508050029

INTRODUCTION

An avalanche multiplication of autonomous electrical power consumers and more severe requirements for the volume and weight parameters of batteries demand for continuous progress in chemical batteries based on conventional electrochemical systems and development of batteries on the basis of fundamentally new systems.

A considerable progress in electrochemical power production was achieved in the 1990s, when Sony commercialized lithium-ion batteries; these batteries now have the highest energy density, which reaches 160–180 W h/kg. Inasmuch as the theoretical specific energy of electrochemical systems on which lithium-ion batteries are based (systems $\text{LiC}_6\text{–LiMeO}_2$, where Me stands for one or several 3-*d* transition elements) lies in the range 500–600 W h/kg, we can state that lithium-ion batteries have virtually reached the theoretical energy density limits. Their further improvement will be targeted at increasing the cycling time, safety, and other performances.

Electrochemical batteries having higher power parameters can only be created on the basis of electrochemical systems that have higher theoretical specific energy. One such system is lithium–sulfur. Some parameters of this system are listed in the table.

Proceeding from the theoretical specific energy values, we can suggest that the lithium–sulfur electrochemical system can serve as the basis to create batteries with specific energy of 450–650 W h/kg.

Other advantages of lithium–sulfur batteries (LSBs) are listed below:

- (i) low cost and availability of sulfur;
- (ii) intrinsic protection mechanism from overcharge, providing safety;
- (iii) wide temperature range of operation;
- (iv) possibility of long cycling.

It is not, therefore, surprising that this system keeps the attention of battery developers for more than two decades. It has not, however, been commercialized because the following problems remained unsolved:

- (i) relatively low practical specific energy (200–300 W h/kg) against expected values of 450–650 W h/kg;
- (ii) rapid decrease in capacity during cycling (0.1–0.4% per cycle);
- (iii) high self-discharge rates (8–15% per month).

A new type of battery with record-breaking power parameters will be created as soon as these problems are solved.

The parameters of lithium–sulfur batteries are dictated by the specifics of the lithium–sulfur electrochemical system. Although the positive electrode depolarizer in the fully oxidized state (elementary sulfur) and in the fully reduced state (lithium sulfide) is solid, lithium–sulfur batteries can be classified with chemical power sources with a liquid cathode: the electrochemi-

Comparative characteristics of lithium-ion and lithium–sulfur batteries

System	Characteristic		
	open circuit voltage, V	theoretical capacity, A h/kg	theoretical specific power, W h/kg
Lithium–ion	3.9	0.16	0.624
Lithium–sulfur	2.53	1.17	2.925

¹ Published on the basis of materials presented at the 9th International Conference “Fundamental Problems of Energy Conversion in Lithium Electrochemical Systems,” Ufa, 2006.

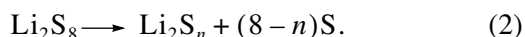
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cal processes occurring in these batteries during their charge and discharge result in lithium polysulfides, which are soluble in most aprotic electrolytes.

It is known that elementary sulfur can exist in various molecular species. The most stable species under the STP is octet S_8 . Elementary sulfur is soluble, although weakly, in aprotic electrolyte systems. In many cases, molecular sulfur species in solutions remain the same as in the solid phase.

The electrochemical reduction of sulfur during LSB discharge and the oxidation of the products of its reduction during battery charge occur in two stages [1–4]. This scenario is evidenced by the shape of discharge and charge curves (figure): each shows two plateaus.

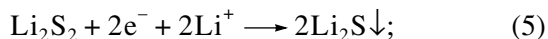
The first discharge stage of a sulfur electrode, which occurs in the potential range 2.5–2.0 V, involves the reduction of the elementary sulfur octet dissolved in the electrolyte to lithium octasulfide, which is soluble in electrolytes. Lithium octasulfides are unstable in many electrolyte systems and undergo disproportionation with the detachment of elementary sulfur, which again experiences electrochemical reduction. In a simplified form, the reduction of the elementary sulfur octet can be described by



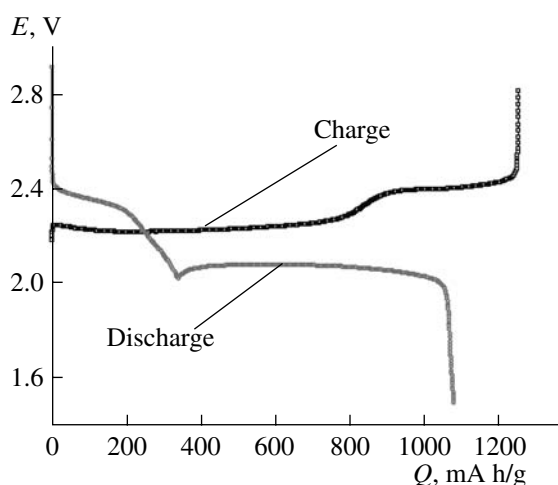
Actually, the reduction of elementary sulfur to lithium polysulfides is much more complex. Some aspects of sulfur reduction mechanisms in nonaqueous solutions are considered in [5–8].

The second stage of LSB discharge involves the reduction of sulfur in lithium polysulfides dissolved in the electrolyte. The mechanism of this process is yet unclear, but we can suggest the following major schemes:

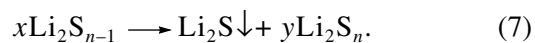
(i) the reduction of polysulfide sulfur with a systematic decrease in the polysulfide chain length and the retention of the overall lithium polysulfide concentration in the solution:



(ii) the reduction of polysulfide sulfur as a result of the rapid disproportionation of Li_2S_n , with the polysulfide chain length retained but with a systematic decrease in the overall lithium polysulfide concentration in the electrolyte solution:



Representative charge/discharge curves for an LSB.

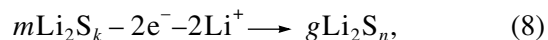


Because the negative charge on sulfur atoms will increase with decreasing lithium polysulfide chain length, the redox potential of sulfur atoms will change. Therefore, if the first scheme is implemented, either separate plateaus corresponding to lithium polysulfides with certain chain lengths are expected to appear on the discharge curve, or the arrest potential will decrease systematically.

In most experiments, a single arrest appears on the discharge curve due to lithium polysulfide reduction, with the potential remaining almost unchanged to the end of the arrest. This fact provides evidence in favor of the second scheme, according to which the reduction of soluble lithium polysulfides is accompanied by their disproportionation.

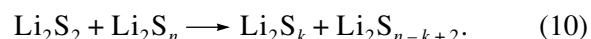
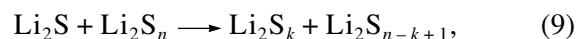
The actual mechanism of the electrochemical reduction of lithium polysulfides is more complex. Quite likely, the first or second mechanism can both be implemented depending on the composition of the electrolyte system.

The charge of lithium–sulfur batteries also occurs in two stages. First, medium-chain lithium polysulfides are reduced to long-chain ones. Roughly, the scheme of this process can be described by

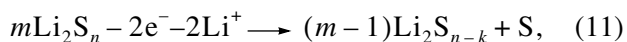


where $mk = gn$.

The resulting long-chain lithium polysulfides enter the reaction with sparingly soluble short-chain lithium polysulfides, producing medium-chain polysulfides (Eqs. (9) and (10)); the latter are again oxidized to long-chain lithium polysulfides (Eq. (8)):



This process continues until sparingly soluble lithium polysulfides localized in the reaction zone are fully consumed.² After this process is over, long-chain polysulfides are reduced to elementary sulfur in the potential range 2.4–2.6 V relative to the lithium electrode:



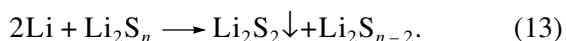
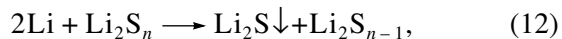
where $(mn) = (m-1)((n-k)+1)$.

The generation of lithium polysulfides Li_2S_n (which are soluble in electrolytes) during LSB cycling increases the electrical conductivity of electrolytes at low Li_2S_n concentrations and considerably increases it at high lithium polysulfide concentrations [9, 10]. The viscosity of electrolyte solutions also increases with increasing lithium polysulfide concentration.

Studies show that the decrease in the rate and depth of the electrochemical reduction of lithium polysulfides is the result of the decrease in the electrical conductivity and the increase in the viscosity of electrolyte solutions [10]. In addition, as the viscosity of electrolyte solutions enclosed in pores of the positive electrodes of LSBs increases, electrochemical reactions are displaced from the bulk of the electrode to its surface. The displacement of electrochemical reactions to the surface of the sulfur electrode makes thick porous electrodes unusable for LSBs. The optimal active layer thickness for sulfur electrodes is usually 15–40 μm , and the surface capacity is 2–4 mA h/cm².

Acceptable sulfur reduction depths can be provided by the use of high electrolyte : sulfur (wt/wt) ratios and thin positive electrodes. Engineering of LSBs with high specific energy fails because of the high contributions of the electrolyte, current collectors, separators, and other auxiliary components to the total battery weight.

During charge of LSBs, lithium is deposited on the negative electrode both as a compact metal with good adhesion to the electrode surface and as dendrites.³ Only the insignificant part of dendritic lithium having electric contact with the electrode surface can participate in further electrochemical reactions. Compact metallic lithium and, especially, dendritic lithium actively react with lithium polysulfides dissolved in the electrolyte. The reactions on the lithium electrode in lithium polysulfide electrolyte solutions can be described by the equations below.



² The reaction zone means the space containing the products capable of entering electrochemical processes on the positive electrode under the specified parameters (current density and potential range).

³ Hereafter, dendritic lithium means finely disperse lithium deposits of any geometric shape, which have poor contact with the electrode surface.

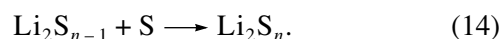
The resulting lithium sulfide and lithium disulfide are deposited on both the surface of compact metallic lithium and the surface of dendritic lithium particles, forming dense surface layers, which slow down or even fully inhibit further reactions between metallic lithium and the components of the electrolyte system. Therefore, dendritic lithium in sulfide systems has a low reactivity.

However, lithium sulfide and lithium disulfides can also react with long-chain lithium polysulfides (Eqs. (9) and (10)), yielding electrolyte-soluble medium-chain lithium polysulfides. The interplay of the formation and dissolution of soluble lithium sulfides dictates the surface layer thickness on metallic lithium.

Part of the sulfur is removed from the electrochemical processes that occur during the charge and discharge of LSBs, being piled up as lithium sulfide and lithium disulfide on the negative electrode and decreasing the battery capacity during cycling. The capacity fading is determined by the ratio of the rates of two processes: the formation of sparingly soluble lithium sulfides and their dissolution. The LSB capacity decrease rate during cycling is proportional to the relative formation rate of sparingly soluble lithium sulfides.

The lithium dispersion rate (dendrite formation rate) during LSB cycling strongly depends on the purity of the lithium electrode surface, i.e., on the existence of various types of contaminants on this surface. Such contaminants are compounds that physically obstruct the surface and inhibit electrochemical processes. Even small amounts of solid contaminants dramatically decrease the efficiency of the cathodic deposition of compact lithium. In this case, most lithium deposits as dendrites. Therefore, the piling up of sparingly soluble lithium sulfides on the lithium electrode enhances dendrite formation during cathodic deposition of lithium. In turn, the increasing dendrite formation intensity brings about a considerable rise in the lithium sulfide and lithium disulfide formation rates. The above-described phenomena, which occur during cycling of a lithium electrode in electrolytes containing lithium polysulfides, generate some type of positive feedback between the dendrite formation intensity and the piling-up rate of insoluble lithium sulfides on the negative electrode and, through this, the LSB capacity decrease rate during cycling.

A specific feature of LSBs is shuttle sulfur transfer between electrodes. Shuttle sulfur transfer is a result of the interaction of long-chain lithium polysulfide dissolved in the electrolyte with insoluble lithium sulfides (lithium sulfide and lithium disulfide) and with metallic lithium on the negative electrode (reactions (9), (10) and (12), (13)) and the interaction of medium-chain lithium polysulfides with elementary sulfur on the positive electrode (reaction (14))



The shuttle sulfur transfer rate is determined by the solubility of lithium polysulfides in electrolytes, the transport properties of electrolyte systems, and the dissolution rates on electrodes. The structure of the positive electrode also considerably affects the shuttle sulfur transfer rate.

Shuttle sulfur transport has a dual function. On one hand, it induces the self-discharge of LSBs; on the other, it protects LSBs from overcharging. Optimization of the properties of electrolyte systems and the structure of the positive electrode offers a means for efficient control of the shuttle sulfur transport rate and, through this, the self-discharge rate and the efficiency of protection of LSBs from overcharging.

Batteries with a lithium-based negative electrode cause anxiety because of the possibility of short circuits between electrodes as a result of dendrite formation. Lithium–sulfur batteries have far lower dendrite formation intensities than other types of batteries with metallic lithium electrodes. Moreover, dendritic lithium particles in electrolytes that contain soluble lithium polysulfides are soon coated with a film of sparingly soluble lithium sulfides, which have no electronic conductivity and which strongly decrease the possibility of short circuits between electrodes because of lithium dendrites.

In summary, having analyzed the results of the above study, we found that the key factors governing the operation parameters of lithium–sulfur batteries are the electrical conductivity, viscosity, lithium polysulfide dissolving power, and other physicochemical properties of electrolyte systems. The transport properties of separators and positive electrodes are of great signifi-

cance. The best characteristics of lithium–sulfur batteries (high capacity, long cycling, and low self-discharge rate) will be achieved by the provision of an optimum combination of the rates of electrode and corrosion processes.

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