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New insights into the limiting parameters of the Li/S rechargeable cell

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ABSTRACT

The lithium/sulfur (Li/S) battery is a promising electrochemical system that has high theoretical capacity of 1675 mAh g^{-1}. However, the system suffers from several drawbacks: poor active material conductivity, active material dissolution, and use of the highly reactive lithium metal electrode. This study was aimed at understanding the most important limiting parameters of a Li/S cell. Different sulfur material pre-treatments were experimented to increase the practical capacity, and various morphologies were obtained. But none of these treatments led to improvements in electrochemical performance. Electrolyte additives were also used to increase cell discharge capacity, but again without success. Finally, it was concluded that the cell capacity limitation may be linked to dissolution of sulfur material and to passivation of the positive electrode. As the final discharge products are insulating and poorly soluble, they precipitate and induce passivation of the positive electrode surface, leading to incomplete active material utilization. EIS measurements confirmed this passivation problem.

1. Introduction

The development of rechargeable batteries is of considerable importance because of the increasing energy consumption of portable devices. Lithium-ion batteries have been under intense research over the past 20 years due to their advantages, such as high energy density, high operating voltage and low self-discharge [1]. Lithium transition-metal oxides, especially $LiCoO_2$ and its counterparts, are currently dominating the commercial lithium-ion battery market. However, the gravimetric energy density is known to be limited to 200–250 Wh kg^{-1}, which is not sufficient to meet electric vehicle battery requirements for extended ranges. Moreover, cobalt is toxic and expensive, and layered oxides usually have safety issues [2].

Elemental sulfur is a promising positive electrode material for lithium batteries due to its high theoretical specific capacity of about 1675 mAh g^{-1}, much greater than the 100–250 mAh g^{-1} attainable with the conventional lithium-ion positive electrode materials [3]. The average discharge potential is around 2.1 V (*vs.* Li^+/Li) and the complete Li/S system should allow a gravimetric energy density close to 500 Wh kg^{-1} to be reached. In addition, elemental sulfur is readily available and non-toxic, advantages that should enable cheap and safe high-energy batteries to be produced [4]. All the above-mentioned key parameters help explain the increasing number of publications on this topic.

Sulfur reduction is a multistep electrochemical process that can involve different intermediate species [5,6]. Lithium metal reacts with elemental sulfur (S_8) to produce lithium polysulfides with a general formula Li_2S_n. The first polysulfides that are produced, such as Li_2S_8 and Li_2S_6, have a long chain length. During discharge, the polysulfide chain length is shortened as the sulfur is further reduced. At the end of discharge, the final product is lithium sulfide (Li_2S) and the overall reaction equation is [7]:

$$16Li + S_8 \rightarrow 8Li_2S$$

This technology has attracted the attention of the electrochemistry community for many years [4,8]. However, it still suffers from several drawbacks. Indeed, sulfur and lithium sulfide are highly insulating materials [9,10] and the positive electrode must contain a significant and well-dispersed amount of electronic conductor, such as carbon or metal. Sulfur and lithium polysulfides are also soluble in common organic liquid electrolytes [11]. They can spontaneously diffuse through the liquid electrolyte, thus leading to lithium metal corrosion and self-discharge, in parallel with an increase in the electrolyte viscosity [12,13]. Once dissolved in the electrolyte, they can also react at the negative electrode, leading to a shuttle mechanism that delays the end of charge and drastically decreases coulombic efficiency [12,13]. On the other hand, the fully reduced compound, Li_2S, is insoluble, insulating, and may passivate the surface of both positive and negative electrodes [14–16].

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For these reasons, sulfur utilization and cycle life are usually very low. Finally, the use of a lithium metal negative electrode is known to be a problem in large-scale utilization, since it may lead to short-circuits induced by dendrite formation and explosions.

The literature reports different strategies that have been considered to improve Li/S cell electrochemical performance. On the cathode side, carbon/sulfur composites can be designed so as to trap sulfur and lithium polysulfides [17,18]. The use of mesoporous or nanostructured carbon materials helps to decrease the shuttle mechanism as well as self-discharge by preventing sulfur material diffusion through the electrolyte. The authors report a high discharge capacity along with an improved cycle life. However, they finally agree that lithium polysulfides may diffuse at some moment [17,18], whatever is done to the positive electrode morphology and/or composition. Another strategy involves optimizing the liquid electrolyte composition and many studies have been carried out on this subject. The discharge capacity can be increased thanks to the use of an ether-based optimized electrolyte composition [19–21]. Some additives can also improve battery performance [22]. For example, it was recently found that lithium nitrate can be a successful additive, leading to coulombic efficiency of close to 100%. It is assumed that this chemical product decomposes on the lithium metal anode, leading to good lithium metal passivation and avoiding further reaction with lithium polysulfides [8,23]. Another promising strategy is to use polymer electrolytes such as polyethylene oxide-based ones. These polymer electrolytes delay diffusion of the lithium polysulfides and sulfur dissolution, leading to decreasing self-discharge [24,25]. Various studies have also been carried out on protection of the metallic lithium negative electrode [26,27]. This strategy is aimed at preventing contact between the dissolved lithium polysulfides and the highly reactive lithium electrode by using interlayers of polymer or ceramic materials.

Bearing in mind all these strategies, our work was aimed at understanding some of the important limiting parameters of this Li/S system. We set out to determine the most relevant parameters that should be considered in order to improve the electrochemical performance of the Li/S cell. More precisely, we focused on the positive electrode side, trying to obtain different sulfur materials and cathode morphologies thanks to various pre-treatments, in order to extend both capacity and cycle life.

2. Experimental

Sulfur pre-treatments – Refined sulfur (−100 mesh, Aldrich) was used as the reference active material source. Sieved sulfur (−325 mesh, 99.5%) was also purchased from Alfa Aesar. Different sulfur pre-treatments were performed on the reference active material in order to obtain different sulfur morphologies. Sulfur was first ball-milled (dry or in hexane, planetary ball-mill, Retsch PM200, 50 mL stainless-steel jar, and three Ø20 mm diameter stainless steel balls) so as to decrease the particle size. Sulfur material was also ball-milled under the same conditions (dry ball-milling) with carbon black (Super P®, Timcal, S/C ratio of 10/90 wt%). A thermal treatment was finally performed on the sulfur material, the idea being to change the particle morphology.

Positive electrode preparation – Bare or pre-treated sulfur materials were then mixed with poly(vinylidene fluoride) (PVdF 1015, dissolved in N-methyl-2-pyrrolidinone (12 wt%), Solvay), carbon black (Super P®, Timcal) and mixed in N-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Aldrich). The S/C/binder mixing ratio was generally 80/10/10 wt%. But we also investigated the impact of carbon content, ranging from 10 to 45 wt%, decreasing the sulfur content while keeping 10 wt% of binder. After homogenization, the slurry was coated onto a 20 μm thick aluminum current collector by doctor blade technique. The resulting cathodes were dried at 55 °C for 24 h, then cut into Ø14 mm disks and finally dried for 24 h under vacuum at room temperature. The coating thickness was about 100 μm so as to obtain a 20 μm thick cathode after drying. The positive electrode area was 1.539 cm^2. The cathode compositions are summarized in Table 1.

2-Electrode cell assembly – The positive electrodes, described in Table 1, were assembled in an argon-filled glovebox in 2032 coin cells. Lithium metal foil was used as a negative electrode and Celgard 2400® as a separator. A non-woven Viledon® separator (polypropylene-based membrane) foil was also added between the cathode foil and the Celgard® to store a large amount of electrolyte on the cathode side. A liquid electrolyte was prepared by mixing tetraethylene glycol dimethyl ether (TEGDME, 99%, Aldrich) and 1,3-dioxolane (DIOX, anhydrous, 99.8%, Aldrich) with a volume ratio of 50/50. Lithium bis(trifluoromethane sulfone)imide (LiTFSI, 99.95%, Aldrich) was used as a lithium salt and was dissolved at 1 mol L^{-1} in the mixed solvents. About 150 μL of electrolyte were then added to the coin cell to fully wet both electrodes and separators.

3-Electrode cell assembly – The positive electrode was also assembled in an argon-filled glovebox in 3-electrode 2032 coin cells. The cells were assembled as previously described except that a second lithium metal electrode was inserted between the Viledon® and the Celgard® separators. This third electrode was wrapped in Kapton® beforehand. A schematic diagram of a 3-electrode coin cell is presented in Fig. 1.

Characterization techniques – The structure and morphology of pre-treated sulfur samples were analyzed by X-ray Diffraction (XRD, Brüker D8000 diffractometer, Cu Kα radiation) and Scanning Electron Microscopy (SEM, Philips XL30). Particle size analyses (Malvern MasterSizerS) and specific surface area analyses (BET method, Micromeritics, Tristar II 3020) were also performed. Electrochemical tests were monitored on 2-electrode cells with an Arbin battery cycler between 1.5 and 3.0 V (*vs.* Li^+/Li) at room temperature and a cycling rate of C/10. Electrochemical Impedance Spectroscopy (EIS) measurements were carried out on the 3-electrode cells with a VMP2 potentiostat (Bio-logic, Claix) within the 200,000–0.001 Hz range and with a 5 mV amplitude.

Table 1
Summary of cathode compositions.

Name	Sulfur source	Pre-treatment	Final S/C/PVDF ratio/wt%	Theoretical capacity/mAh cm^{-2}
Ref	Refined	None	80/10/10	3.3
C1	−325 mesh	None	80/10/10	2.7
C2	Refined	Dry ball-milling	80/10/10	3.3
C3	Refined	Ball-milling in hexane	80/10/10	3
C4	Refined	Thermal treatment	80/10/10	2.5
C5	Refined	Ball-milling with carbon	70/20/10	1.5
C6	Refined	None	70/20/10	1.7
C7	Refined	None	60/30/10	1.4
C8	Refined	None	45/45/10	0.7