



Targeting the role of lithium sulphide formation for the rapid capacity fading in lithium-sulphur batteries



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HIGHLIGHTS

- Li_2S is one of the main reasons for the capacity fading in Li–S batteries.
- Cell polarization is linked with the formation of non-soluble S reduction species.
- The cut-off voltages can simply alter cycling retention and cell resistance.
- V_2O_5 and LiI additives help in assisting the re-oxidation of Li_2S .

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ABSTRACT

This work aims to study the reasons for the rapid capacity fading in the field of lithium-sulphur batteries. It is found that the formation of non-soluble and insulating lithium sulphide, Li_2S , upon sulphur reduction is one of the main reasons to account for the capacity fade due to its relatively low electrochemical activity and blocking of the carbon framework.

A variety of analytical techniques are used to assess the formation of Li_2S and visualize the resulting morphological changes in a mesoporous carbon/sulphur composite (MCS) during battery operation. It is shown that simply changing the cut-off voltages can alter retention and resistance of the cells during cycling. Since the electrochemical activity of lithium polysulphides decreases with the order, elimination of low order of polysulphides is considered critical. Thus, in order to oxidize the least sulphur reduction specie, Li_2S , two different additives are suggested; namely an electrolyte additive, LiI, or an electrode additive, V_2O_5 . Incorporation of the one of these components into the MCS composite enables the delivery of higher capacities (i.e. as compared to a bare C/S composite). The increased capacity is linked not only to the co-cathode materials, which contribute to the total capacity, but also to the oxidizing agent and internal redox mediator role of the additives.

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1. Introduction

The goal of replacing combustion engines with electrical vehicles still represents a challenge since current lithium-ion technologies provide a limited gravimetric energy density (140 Wh/kg for a full system) and driving range (160–200 km) [1]. In the context of increasing capacity, sulphur, an element found abundantly on earth, is considered one of the options for next generation cathode materials since it offers a five-fold increase in energy density

compared with the present Li-ion batteries. Despite the considerable advantages of the Li–S battery, there are several major issues that have prevented its practical realization and commercialisation. These issues typically originate from the need for separate cell compartments with the result of having a short cycle life, safety issues, low charging efficiency and a high self-discharge rate. One major problem is the insulating nature of sulphur which necessitates a close contact with conductive additives. Another known issue is the formation of polysulphides (Li_2S_x) which are generated during the battery operation. They are highly soluble in aprotic solvents resulting in redox shuttle parasitic reactions between the Li anode and sulphur cathode. Moreover, the lithium metal anode causes safety problems even though dendrite formation is not as vigorous as other Li metal cells since the soluble polysulphides

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might further react with those dendrites to form a solid–electrolyte interface (SEI)-type of layer. Last but not least, tackling the irreversible deposition of non-soluble and highly insulating Li_2S both at cathode and Li anode is highly challenging which will be the target of this paper.

Although Li–S batteries have been studied since the 1960s [2], they have recently received somewhat of a renaissance and extensive research interest [3]. Over the past few years, researchers have mainly focused on solving the challenges associated with the sulphur cathode, with a common solution being the confinement of the sulphur within conductive porous carbon skeletons [4–9]. In parallel, all-liquid systems that rely on the high solubility of polysulphide species (catholyte) as the active material have also been explored, [10–12] and in some cases demonstrated superior performance to the conventional Li–S cell configuration. Moreover, we found that these performances can be even further enhanced when the active sulphur material was directly deposited on the Li negative electrode due to a SEI on the lithium surface [11].

Currently, research in the field of Li–S batteries is migrating from those systems based on sulphur confinement strategies (i.e. entrapment of polysulphides) to the usage of chemically synthesised dissolved polysulphides [12]. Alternatively, dissolved polysulphides have even been used as electrolyte additives for improved cycling performance [13,14]. Having observed that solubility is not the primary limiting factor for the proper functioning of Li–S batteries, it was decided to further investigate the impact of the non-soluble species (Li_2S) on capacity fading.

Herein, the formation of solid and insulating Li_2S in a porous carbon/sulphur composite was initially examined using by detailed analytical techniques such as in-situ XRD, post-mortem analysis of TEM and SEM. Thereafter, in order to avoid polysulphide formation, the use of either LiI as electrolyte additive or the addition of an electrochemically active metal oxide (i.e. V_2O_5) is suggested which acts to chemically react with Li_2S , converting it to soluble polysulphide species.

2. Experimental section

2.1. Preparation of the mesoporous carbon and corresponding sulphur composite

For the synthesis of mesoporous carbon, a sacrificial SBA-15 template was synthesised according to the method described by Stucky et al. [15]. After the synthesis, the pores of the SBA-15 template were completely filled with an aqueous solution of sucrose/ H_2SO_4 . The resulting wet sucrose/SBA-15 was calcined at 900 °C under an inert atmosphere. The silica was thereafter removed from the composites using a 4 M aqueous solution of ammonium hydrogen difluoride yielding carbon replicas. Then mesoporous carbon and sulphur (50/55 wt%) were mixed and placed in a crucible, the mixture was heated to 155 °C with a 0.2 °C min^{-1} heating ramp, and no additional washing procedure was applied afterward. The carbon/sulphur composite (MCS) after impregnation at 155 °C has 50 wt % sulphur, as proven by thermogravimetric analysis (TGA) (data not shown).

Prior to testing, the composite was hand-milled with 20 wt% Ketjen Black carbon. Final composite contains 40% S. The experiment was repeated with the same 50 wt % sulphur containing composite (MCS), the only difference being the amount of Ketjen black additive that was increased from 20 wt% to 43 wt% which kept the sulphur content at 28.5 wt% ($100 - 43 = 57\%$ of MCS, since MCS has 50% S, the final composite contains 28.5 wt% S) in the entire composite. This experiment was performed to enable comparison the role of V_2O_5 (see below) in which V_2O_5 added composite has 28.5 %S into the entire composite. For the

electrochemical test, 0.1 mL of 1 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) containing tetra methylene sulfone (TMS) was used as an electrolyte.

2.2. Preparation of mesoporous C/S composite + V_2O_5

50 wt % sulphur containing mesoporous carbon/sulphur (MSC) and 20 wt% Ketjen black added composite was ball milled with V_2O_5 (from Aldrich) for 15 min at 150 rpm. The sulphur and V_2O_5 weight ratio were kept at 1:1. Thus, final composite contains 28.5% S and 28.5% V_2O_5 , with the remainder representing 14.5 wt% Ketjen black and 28.5 wt% mesoporous carbon.

2.3. Chemically synthesized lithiated V_2O_5

4 mol V_2O_5 and 3 mol Li_2S were mixed in 10 mL electrolyte inside a glove-box at room temperature ($4\text{V}_2\text{O}_5 + 3\text{Li}_2\text{S} \rightarrow 4\text{LiV}_2\text{O}_5 + \text{Li}_2\text{S}_3$). During synthesis, an initially clear reaction solution colour transformed to greenish, which is characteristic colour of short range polysulphides as demonstrated in previously reported UV–vis spectroscopy studies [16].

2.4. Electrochemical measurements

Galvanostatic cycling measurements were performed with a classical two-electrode Swagelok-type™ cell using a 1 M LiTFSI containing TMS at a C/10 current density (which corresponds to the current required to completely charge/discharge an electrode in 10 h) voltage range between 1.0 and 3.0 V vs. Li at galvanostat/potentiostat VMP3 from Biologic.

For the experiment involving the addition of the LiI electrolyte, 0.1 M LiI was dissolved into the electrolyte (1 M LiTFSI containing TMS).

The quantity of the electrode was carefully tuned, thus, 7 mg composite were used for the electrochemical test resulting 2.8 mg of sulphur for the C/S composite and LiI electrolyte added ones. For the V_2O_5 electrode additive composite, 10 mg weight was used in order to have 2.8 mg sulphur content in the cell. In all experiments sulphur content and electrolyte ratio was fixed and 0.1 mL electrolyte was used for all the measurements.

2.5. Characterizations

Powder X-ray diffraction of the solids were recorded using a Bruker D8 Advance diffractometer (θ – 2θ mode, $\text{Co K}\alpha$ radiation $\lambda = 1.7903$ Å, and a linear position-sensitive detector).

Microstructural and chemical analyses were proceeded using a transmission electron microscope (TEM-FEI TECNAI F20 S-TWIN) fitted with a scanning mode and both a high-angle annular dark-field (HAADF) detector and EDAX EDS.

3. Results and discussions

A number of analytical techniques were used to assess the formation of Li_2S and visualise the resulting morphological changes in the mesoporous carbon/sulphur composite (MCS) during battery operation. *In-situ* X-ray diffraction studies performed on a Li/S cell (Fig. 1) show the appearance of a Bragg peak near $2\theta = 32^\circ$ corresponding to the formation of crystalline Li_2S through the end of discharge (Fig. 1 inset). This Li_2S does not fully convert back to crystalline sulphur upon oxidation since its corresponding Bragg peaks is still visible at the end of the first charge. To confirm further the deposition of Li_2S during cycling, cycled electrodes were investigated by SEM and TEM, and the micrographs were recorded (Fig. 2a, b, c) for a pristine C/S composite electrode and a similar

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