



Electrolyte decomposition and gas evolution in a lithium-sulfur cell upon long-term cycling



Holger Schneider^{a,*}, Thomas Weiß^a, Chariclea Scordilis-Kelley^b, Jonathan Maeyer^b, Klaus Leitner^a, Hai-Jung Peng^a, Rüdiger Schmidt^a, Jan Tomforde^a

^a BASF SE, 67056 Ludwigshafen, Germany

^b Sion Power Corporation, Tucson, AZ, 85756, USA

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ABSTRACT

Experimental data elucidating the time-dependent composition of the electrolyte within a standard lithium-sulfur battery cell are presented. The electrolyte employed consisted of a solution of LiTFSI in a 1:1 mixture of dimethoxyethane and dioxolane, including nitrate salts. In order to track the decomposition reactions of the electrolyte components, the cells were run for a fixed number of cycles, after which they were opened and the remaining electrolyte was extracted with an excess amount of 1,4-dioxane. The amount of each of the components (namely LiTFSI, dimethoxyethane and dioxolane) within these mixtures was determined by means of gas chromatography and ¹⁹F-NMR. It was found that the amount of electrolyte accessible to extraction remains relatively constant during the first 25 cycles, but then continuously decreases within the subsequent 40 investigated cycles. The ratio of the organic constituents of the electrolyte does not change considerably, which means there is no preferred decomposition pathway for either of the two components dioxolane and dimethoxyethane, respectively. These results demonstrate that the capacity fading of a lithium-sulfur cell coincides with the loss of the electrolyte within the cell and there is a strong correlation between the failure of a lithium-sulfur cell and the decomposition reactions of its electrolyte. These findings are supported by a detailed analysis of the gaseous decomposition products after specified cycle numbers. Realistic pouch bag cells are used as test vehicles. Such cells do resemble industrially viable, commercial cells much closer as e.g. coin-type cells: Much lower electrolyte/active mass ratios can be used, thus allowing for a more realistic picture of the failure mechanisms involved.

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1. Introduction

The lithium-sulfur battery is one of the most promising candidates for next generation battery systems, as it offers high theoretical specific charges (1675 mAh/g with respect to sulfur) and high theoretical energy densities (~2500 Wh/kg with respect to the final reaction product Li₂S). However, their use is hampered by several challenges, such as pronounced volume changes upon cycling (in both the sulfur/carbon composite cathode and the metallic lithium anode), the polysulfide shuttle resulting from the diffusion and self-discharge of the intermediately formed polysulfide species and the decomposition of the electrolyte [1–8]. This means in practice the cells suffer from a fast fading of capacity and low efficiencies due to degradation processes taking place on both

electrodes. During the last years, many elegant strategies have been developed dealing with possible solutions to these problems, such as the encapsulation of the sulfur active material in porous carbon structures [9–11], the employment of polymer electrolytes [12,13], the use of additives, adsorbents (e.g. transition metals/oxides/nitrides) or doping (e.g. nitrogen doping of the carbon host matrix) for improved retention of the polysulfide intermediates within the cathode matrix [14–23] or the separation of anode and cathode by means of protective (solid state) membranes [24–28] or additives (improved SEI formation on the metallic lithium anode) [29,30], to mention a few among many others [31]. Encapsulation of Li₂S as an active material has been tried [32] as well as new concepts such as solid-state polymer lithium-sulfur batteries [33].

However, while many of these studies report an improved behavior of the batteries investigated, none of them has led to a real breakthrough in the lithium-sulfur technology so far and experimental evidence of the respective failure mechanisms and their improvements remains scarce. One major problem is the fact

* Corresponding author.

E-mail address: holger.schneider@basf.com (H. Schneider).

that while qualitatively known due to pioneering analytical investigations [34–53], the relative importance and contributions of these failure mechanisms are still not exactly known. Most importantly, there are no or few quantitative investigations from which the relative contributions could be derived – e.g. stating how much lithium sulfide is lost on both the anode and cathode during the aging of the battery or how fast the electrolyte decomposition is taking place on the anode. However, it is crucial to gain a more detailed insight into these phenomena in order to improve the design of the cell components and to tackle them in the right order. To the authors' opinion, especially the stability of the electrolyte deserves attention, as it is well known that the SEI formed on metallic lithium (which is widely used in standard lithium-sulfur cells) is not stable and fresh lithium surfaces are formed within the cell upon each charge process as dendritic structures start to grow on the surface of the metal, leading to a continuous loss of electrolyte during cycling.

Therefore, this study focuses on the composition of the electrolyte within the cell upon extended cycling. It is found that the amount of extractable electrolyte decreases continuously from the 25th cycle onwards and is correlated to the decline in cell capacity. The capacity of an average lithium-sulfur cell decreases after 55 cycles, corresponding to a 50% loss of electrolyte. Based on these data, the life time of the test cells used can be extrapolated from the electrolyte's perspective to about 100 cycles.

2. Experimental

Pouch bag cells were used as a standard test system. A metallic lithium sheet of 50 μm thickness was used as anode. The cathode originally consists of 55% elemental sulfur (active material), 40% conductive carbon materials and 5% binder material. The sulfur loading within the cathode amounts to $\sim 2 \text{ mg/cm}^2$, the overall amount of sulfur/test cell to $\sim 65\text{--}71 \text{ mg}$. A picture of a typical standard pouch bag test cell is shown in Fig. 1. After formation (discharge with a 0.02C rate), all cells were charged with a 0.1C rate and discharged with a 0.15C rate (based on the theoretical charge capacity of the sulfur active material). The cells were cycled between 1.7V–2.5 V.

The electrolyte consists of a 1:1 mixture of 1,2-dimethoxyethane (DME, 44 wt.%) and 1,3-dioxolane (DOL, 44 wt.%). LiTFSI (8 wt.%) is used as the conductive salt within the electrolyte, lithium nitrate is used as an additive (4 wt.%). Minor amounts of other additives do not change any of the conclusions discussed in the following. It is well known from the literature that lithium

nitrate has beneficial properties with respect to the protection of the lithium anode from the internal polysulfide shuttle [54–57]. The overall amount of electrolyte used varied between $\sim 400\text{--}450 \mu\text{l/cell}$.

In order to conduct the extraction experiments, the test cells were stopped and analyzed after a certain number of cycles (25, 40, 50 and 65, respectively). Before opening, the cells were completely discharged. The cells were opened in a glove box under inert gas atmosphere with a pair of scissors and 2 ml of 1,4-dioxane were inserted into the cell by means of a syringe. Afterwards, the cells were carefully macerated for about 30 s with the extraction solvent 1,4-dioxane, the complete solution was then extracted from the cell again by a syringe (Fig. 2). The extract has a greyish color due to carbon components from the cathode matrix. The solution was then filtered through a syringe membrane filter (0.5 μm) to remove any of these solid/dispersed components stemming from the electrodes (Fig. 3).

The residual amounts of both the DME and the DOL could be determined quantitatively by means of gas chromatography (GC) and separate calibration experiments.

The extract (residual electrolyte and d8-1,4-Dioxane) was injected in the gas chromatograph (Agilent 7820A; Colum: CP-SIL 8; 50m; ID: 0.32 mm; film 5 micrometer). Both DME and DOL were identified quantitatively by flame ionization detection (FID) at a retention time of 8.05 and 8.75 min, respectively, and an accuracy of 0.1% after calibration.

The amount of LiTFSI could be followed quantitatively as well by employing ^{19}F -NMR. For this reason, 1,4-dioxane- d_8 was used as a solvent for the extraction experiments. The quantification of LiTFSI in the extract was carried out by adding a known amount of 2-Chloro-4-fluorotoluene (CFT; approx. 50 mg). According to the relative integral ratio of the ^{19}F -signals (TFSI anion: -79.7 ppm ; CFT internal standard: -115.3 ppm) the integral of the 6 F atoms in the TFSI anion was used to calculate the amount of LiTFSI. The signal position of the fluorine spectrum was referenced against the TMS-signal of the corresponding ^1H -spectrum. The measurement was carried out with a Bruker DPX-400, 400 MHz at 25 °C. By the combination of both methods both the composition of the electrolyte and the ratio of its constituents as well as the absolute



Fig. 1. Standard pouch bag test cells.



Fig. 2. Pouch bag cells are opened after a specified number of cycles (25, 40, 50 and 65, respectively) and 1,4-dioxane is inserted. The solution is then extracted from the cell by a syringe.

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