**Aalborg Universitet**

# Experimental Study on Calendaristic Degradation and Self-Discharge of 3.4 Ah Lithium-Sulfur Pouch Cells

Knap, Vaclav; Stroe, Daniel-Ioan

# Experimental Study on Calendaristic Degradation and Self-Discharge of 3.4 Ah Lithium-Sulfur Pouch Cells

V. Knap[a] and D.-I. Stroe[a]

[a] Department of Energy Technology, Aalborg University, Aalborg, 9000, Denmark

Lithium-Sulfur (Li-S) batteries represent one of the possible development pathways of Lithium based batteries, as they are expected to provide benefits of high volumetric energy density, various safety features, and low production cost. In order to use them efficiently in practical applications, it is necessary to fill the wide knowledge gap about Li-S performance, especially at the size of commercial cells. The current study analyzes the long-term shelf storage behavior of pouch cells at various conditions of temperature and state-of-charge, by periodically monitoring the battery cell's performance parameters. Based on the obtained results, we have observed that especially the cells' resistance exhibited a complex behavior, when according to the applied storage conditions it has increased, decreased or remained constant over the storage period.

## Introduction

Lithium-Sulfur (Li-S) batteries represent one of the possible development pathways of Lithium based batteries, as they are expected to provide benefits of high volumetric energy density, various safety features, and low production cost (1). Already nowadays, one can find demonstrated applications, which heavily depend on the unique attributes of Li-S batteries, e.g. high-altitude long-endurance unmanned aerial vehicles capable to survive  extended periods of time in the air (currently proofed for 14 day without landing) (2). However, wide commercialization of Li-S batteries is still hindered mainly by their limited performance and short lifetime (3).

Both cycling and storage operation influence the Li-S battery lifetime. The degradation of the Li-S batteries is often assigned to the irreversible relocation of polysulfides, which results into the corrosion of the lithium metal anode, degradation of the sulfur cathode and surface passivation of both electrodes (4). These degradation aspects were studied and discussed in literature to a certain degree; however, as pointed out in Ref. (3), some observations are possible to be done only for commercial-size cells, and not for coin-size cells, which determines the further focus of this work on a larger format cell, specifically pouch cells. The Li-S pouch cells were previously studied for the effect of cycling degradation on sulfur cathodes (5) and lithium metal anodes (6). The current study analyzes based on an extended experimental investigation the battery capacity fade and self-discharge during calendar aging at various conditions of state-of-charge and temperature. The methodology presented in Ref. (7) is used for evaluation of the battery performance during the degradation in terms of capacity, resistance, power capability and shuttle current.

## Experimental

The study was performed on 3.4 Ah Li-S long-life type pouch cells provided by OXIS Energy. A Digatron BTS 600 battery test station was used for measurements. The overall procedure of calendaristic aging was composed of two steps: a reference performance test (RPT) and shelf storage, which are continuously repeated until the battery cells are removed from the test.

The used RPT procedure is in detail described in Ref. (7) and illustrated in terms of measured voltage and current in Fig. 1. This procedure was used to characterize the cell at the beginning of life and during the periodical monthly performance check-ups. It consists of a discharge step to obtain the remaining cell capacity after storage. Afterward, a pre-condition cycle is used to reset 'a cumulative history' of the cell and another cycle is used to measure actual maximum discharge capacity. The resistance of the cell is measured by a set of pulses (0.1, 0.2 and 0.5 C charging pulses and 0.2, 0.5 and 1 C discharging pulses). After that, the shuttle current is measured and at the end of the procedure, the cell is discharged to the target SOC level. Apart from the current pulses for the resistance measurement and the shuttle current measurement, the charging current is always 0.34 A (= 0.1 C) and the discharging current is 0.68 A (= 0.2 C). The charging cut-off limits are 2.45 V or 11 hours and the discharging cut-off limit is 1.5 V. Two cells were used for every test case. In order to expand the analysis, the shuttle current measurement was replaced by an electrochemical impedance spectroscopy (EIS) measurement for one of each two cells. Due to time demands, the full RPT was performed only for every even check-up. Odd check-ups were reduced by removing the shuttle current or EIS measurement, respectively.
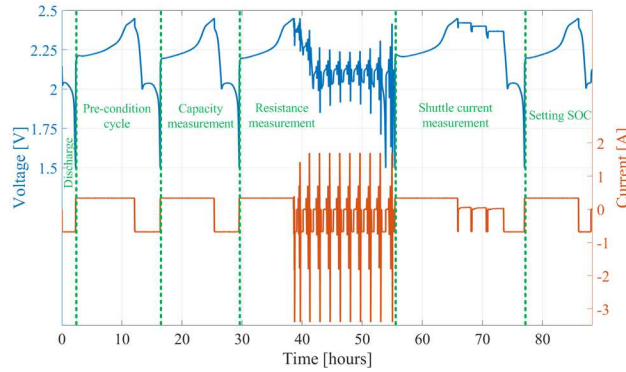


Figure 1. Illustration of the RPT procedure in terms of measured voltage and current.

The shelf storage of cells consists of their placement into a temperature controlled environment (an oven, an incubator, or a fridge) at no load conditions. Five test calendar cases (CCs) were considered for various temperatures and SOCs as illustrated in Table I. Storing cells

**Table I. Storing conditions for investigated calendar cases**

| Temperature [°C] | SOC level [%] | | |
| --- | --- | --- | --- |
| | 10 | 50 | 100 |
| 8 | - | CC1 | - |
| 30 | CC5 | CC2 | CC7 |
| 50 | - | CC3 | - |

## Results & discussion

Capacity Fade

    The obtained cumulative capacity fade for the CCs is shown in Fig. 2. As expected, the storage of the cells at a high temperature of 50 °C (CC3) led to an increased degradation. However, also the cells aged under CC1 conditions, stored at a low temperature at 8 °C, showed a higher degradation than the cells aged under CC2 conditions, stored at 30 °C. This is due to the sudden capacity drop of nearly 13% occurring between the first RPT (at beginning of life) and the second RPT (after one-month storage). Neither, the influence of SOC on the battery capacity fade is straightforward. The capacity fade is faster for the cells stored at the low SOC (10%). The cells stored in a fully charged state exhibit reduced capacity fade during the first six months, but then they exceed the capacity fade of the cells in CC2 (50% SOC); furthermore, according to their trend they are expected, in future months, to result to a higher capacity fade than the cells aged under CC5 conditions.
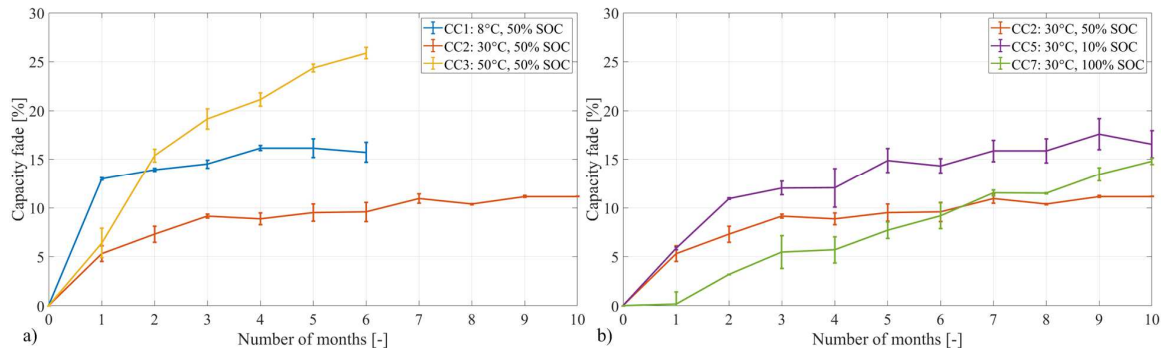


Figure 2.  Cumulative capacity fade for various a) temperatures, b) SOCs.

    Another option on how to look at the capacity fade is to consider its increment between the periodic check-ups. A common feature for all the CCs is that the incremental capacity fade is very high after the first and possibly the second RPT and then it decreases to a lower, but scattered values. By taking an average of the incremental capacity fade values for a specific CC, it is possible to compute the capacity fade per day. For the investigated CCs, the capacity fade per day varies between 0.035 and 0.138%. By putting these results into a context of literature reported values, summarized by S.-H. Chung and A. Manthiram (8) and presented in Fig. 3, one can see that the cells investigated in this work belong to the state-of-the-art with very low calendar degradation. They are outperformed only by Li-S batteries using a quasi-solid state electrolyte (9), Nafion coated separator to suppress the polysulfide anions' diffusion to the anode, while its surface was passivated through an use of $LiNO_3$ (10), or separators with triple-layer coated polyethylene glycol and carbon nanofiber structure (4); however, these results for laboratory coin cells and not for commercial pouch cells.
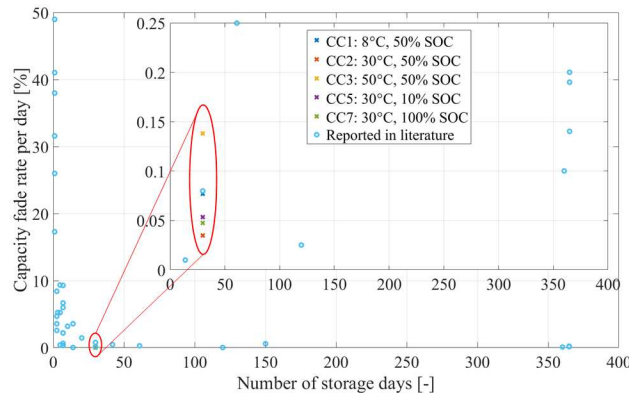
Figure 3. Capacity fade per day against a storage period. The obtained experimental data are placed in a perspective of reported results in the literature, summarized by S.-H. Chung and A. Manthiram (8).

Self-Discharge

The self-discharge was quantified according to the approach presented in Ref. (11), which allows separating the self-discharge (reversible capacity loss) from the degradation (irreversible capacity loss), and the results are presented in Fig. 4. The self-discharge rate for cells aged under CC7 conditions, at 100% SOC, was around 30% after the first month. This was an expected value, because this SOC range corresponds to the end of the high voltage plateau, where a strong influence of the polysulfide shuttle is visible, as reported earlier (11),(12). However, for the following months, the self-discharge rate increased to 50 – 60%, which vastly exceeds the SOC range of the high voltage plateau. Since the capacity fade (Fig. 2) and the resistance evolution (Fig. 6) do not show any abnormal change or trend, the only indication for the cause of such a high self-discharge might be found in an increase of the shuttle in the cells, as illustrated in Fig. 5. The other CCs exhibit a negative self-discharge rate (except the last measurement of CC3), which is a sign of a capacity recovery, reported in Ref. (13), and attributed according to Ref. (14) to the diffusion of trapped polysulfides in a separator back into the cathode after the end of the discharge.
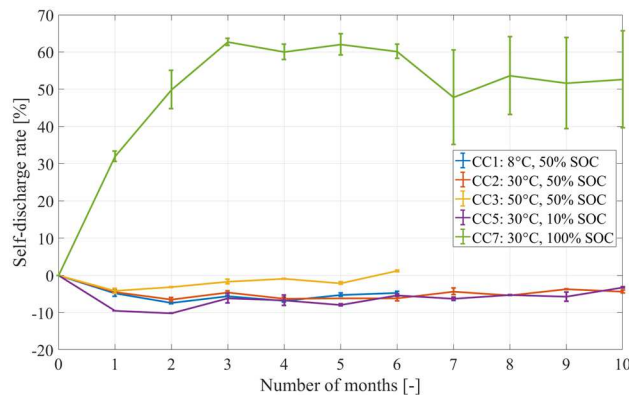


Figure 4. Self-discharge rate.

Shuttle current evolution

The evolution of the shuttle current is presented in Fig. 5. The ongoing shuttle is not significantly changed unless the cells are stored at high SOC (CC7) or high temperature (CC3). CC7 experienced a rapid increase every month, while CC3 shows a rather constant trend after an initial rise.
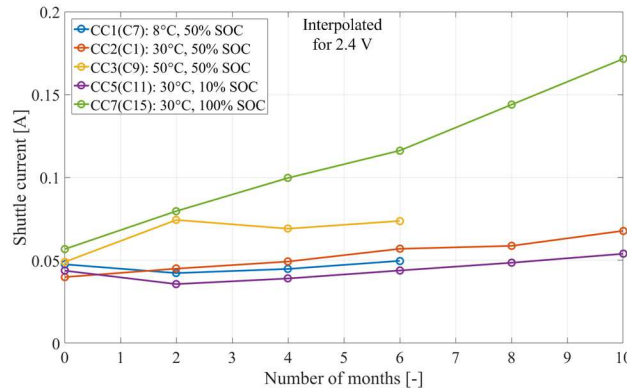


Figure 5.  Shuttle current value interpolated for 2.4 V.

Internal resistance increase

The resistance evaluated here was measured after one second of 0.2 C discharge pulse and the obtained results are presented in Fig. 6. Fig. 6 a) presents the resistance values over the whole SOC area at the beginning of life and after 6 months of calendar aging. The resistance-SOC curves have a typical shape for the Li-S batteries. A pronounced increase in the resistance is visible mainly for CC3 (in the 0 – 70% SOC range) and CC5 (in 0 – 30% SOC range). However, especially CC7 shows that after six months of storage, the resistance decreased in the SOC region of 30 – 100 % SOC. Thus, the resistance evolution is plotted for 90% SOC, representing the high SOC region, in Fig. 6 b), for 50% SOC, representing the medium SOC region, in Fig. 6 c), and for 10% SOC, representing the low SOC region, in Fig. 6 d). During calendar aging, the resistance at 90% SOC has decreased for all the cases, except CC5, for which it has increased during the first two months. At 50% SOC, the resistance increases for CC3 – high-temperature storage, and CC5 – low SOC storage, while it clearly decreases for CC7, high SOC storage. CC1 and CC2 show only a minor change in the resistance (less than 10%). The resistance of cells aged under CC3 and CC5 conditions and measured at 10% SOC has rapidly increased in the first two months and then it stabilizes at the higher value. The resistance of the cells aged under CC1 and CC2 conditions experienced an increase after the first month and then the resistance is converging back to its original value. For CC7, the resistance is constant during the whole storage period.
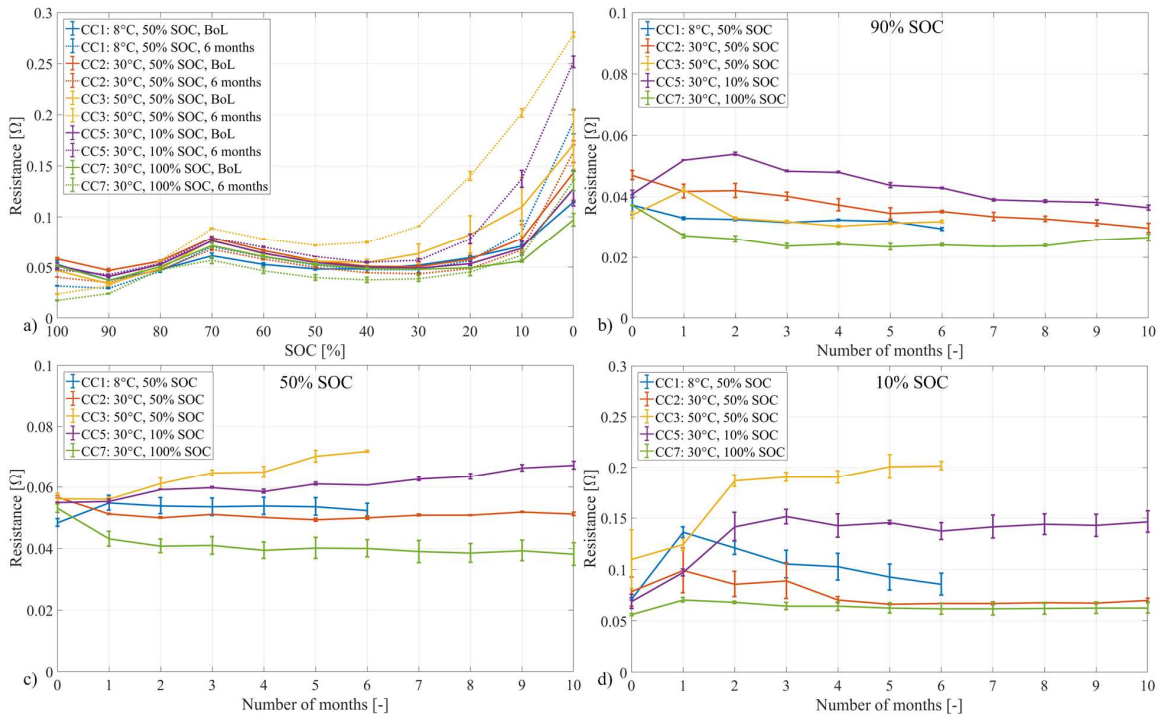
Figure 6. Resistance measured for a 1-second discharge with a 0.2 C current: a) comparison of resistance at beginning of life and after 6 months for the whole SOC range; resistance evolution at b) 90% SOC, c) 50% SOC and d) 10% SOC.

The evolution of the Li-S battery parameters was qualitatively evaluated according to their aging behavior and their first derivatives, and they are summarized in Table II. They are separated into two phases: initial phase, which is typically between the beginning of the storage until up to three months, and long-term, which covers the remaining period. Initially, there is a fast capacity fade for all CCs, which gets slower in the long-term. The self-discharge rate evolves during the initial phase, while it stays rather constant further on. The shuttle current varies according to the storage conditions, the most influencing factors for its growth seems to be high SOC and high temperature. The high temperature and low SOC are the factors which the most enhance the most the resistance growth, while high SOC has a rather opposite effect.

Table II. Summary of the storage cases and its effect on the Li-S battery parameters

| Case | Capacity fade | | Self-discharge | | Shuttle current | | High SOC resistance | | Medium SOC resistance | | Low SOC resistance | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Initial | Long-term | Initial | Long-term | Initial | Long-term | Initial | Long-term | Initial | Long-term | Initial | Long-term |
| CC1 | ↑↑↑ | ↑ | ↓ | ~ | ↓ | ↑ | ↓ | ↓ | ↑↑ | ↓ | ↑↑ | ↓ |
| CC2 | ↑↑ | ↑ | ↓ | ~ | ↑ | ↑ | ↓ | ↓ | ↓↓ | ~ | ↑↓ | ~ |
| CC3 | ↑↑↑ | ↑↑ | ↓ | ~ | ↑↑↑ | ~ | ↑↑↓↓ | ~ | ↑↑ | ↑↑ | ↑↑ | ↑ |
| CC5 | ↑↑ | ↑ | ↓↓ | ~ | ↓ | ↑ | ↑↑ | ↓ | ↑ | ↑ | ↑↑ | ~ |
| CC7 | ↑ ½ | ↑ ½ | ↑↑↑ | ~ | ↑↑↑ | ↑↑↑ | ↓↓ | ~ | ↓↓ | ↓ | ↑ | ~ |

## Conclusions

The degradation behavior of 3.4 Ah Li-S pouch cells was experimentally studied in terms of long-term storage under various conditions of temperature and SOC. The most stable cells performance was observed for medium conditions levels of 30 °C and 50%

SOC. In contrast, storing the cells at a high temperature of 50 °C resulted in the highest capacity fade, the highest resistance increase and also in an increase of the shuttle current. The cells stored at 100 % SOC exhibited a major self-discharge and steep increase of the shuttle current, while the cells resistance has decreased. It is worth to note that the achieved results were obtained by periodical check-ups and resetting the cells SOC, whereas uninterrupted idling might lead to different results, especially for the case with 100% SOC.

## Acknowledgments

## References

1. M. Wild, L. O'Neill, T. Zhang, R. Purkayastha, G. Minton, M. Marinescu, and G. J. Offer, *Energy Environ. Sci.*, **8**, 3477–3494 (2015).
2. http://defence.airbus.com/portfolio/uav/zephyr/, accessed on 20.11.2017.
3. T. Cleaver, P. Kovacik, M. Marinescu, T. Zhang, and G. Offer, *J. Electrochem. Soc.*, **165**, A6029–A6033 (2018).
4. S.-H. Chung and A. Manthiram, *ACS Energy Lett.*, 1056–1061 (2017).
5. S.-E. Cheon, S.-S. Choi, J.-S. Han, Y.-S. Choi, B.-H. Jung, and H. S. Lim, *J. Electrochem. Soc.*, **151**, A2067 (2004).
6. X. B. Cheng, C. Yan, J. Q. Huang, P. Li, L. Zhu, L. Zhao, Y. Zhang, W. Zhu, S. T. Yang, and Q. Zhang, *Energy Storage Mater.*, **6**, 18–25 (2017).
7. V. Knap, D. I. Stroe, R. Purkayastha, S. Walus, D. J. Auger, A. Fotouhi, and K. Propp, *ECS Trans.*, **77**, 479–490 (2017).
8. S.-H. Chung and A. Manthiram, *Supportive information: Lithium–Sulfur Batteries with the Lowest Self-Discharge and the Longest Shelf life*, p. 1-26, (2017).
9. H. Zhong, C. Wang, Z. Xu, F. Ding, and X. Liu, *Sci. Rep.*, **6**, 1–7 (2016).
10. W. T. Xu, H. J. Peng, J. Q. Huang, C. Z. Zhao, X. B. Cheng, and Q. Zhang, *ChemSusChem*, **8**, 2892–2901 (2015).
11. V. Knap, D.-I. Stroe, M. Swierczynski, R. Teodorescu, and E. Schaltz, *J. Electrochem. Soc.*, **163**, A911–A916 (2016).
12. V. Knap, D. I. Stroe, M. Swierczynski, R. Purkayastha, K. Propp, R. Teodorescu, and E. Schaltz, *J. Power Sources*, **336**, 325–331 (2016).
13. V. Knap, T. Zhang, D. I. Stroe, E. Schaltz, R. Teodorescu, and K. Propp, *ECS Trans.*, **74**, 95–100 (2016).
14. T. Zhang, M. Marinescu, S. Walus, and G. J. Offer, *Electrochim. Acta*, **219**, 502–508 (2016).