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Investigation of the Self-discharge Behavior of Lithium-Sulfur Batteries

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Lithium-Sulfur (Li-S) batteries represent a perspective energy storage technology, which reaches very high theoretical limits in terms of specific capacity, specific energy, and energy density. However, Li-S batteries are governed by the polysulfide shuttle mechanism, which causes fast capacity fade, low coulombic efficiency, and high self-discharge rate. The self-discharge is an important characteristic of Li-S batteries for both practical applications and laboratory testing, which is highly dependent on the operating conditions. Thus, to map and to understand the Li-S self-discharge behavior under various conditions, such as depth-of-discharge, temperature, and idling time, a set of experiments were performed in this work on 3.4 Ah Li-S pouch cells. The results are systematically presented in form of open-circuit voltages during idling and self-discharge separated into reversible and irreversible capacity loss. Furthermore, estimation of the actual high voltage plateau capacity based on a self-discharge constant was performed according to an earlier proposed methodology; however, the method needs further improvements in order to estimate this capacity accurately for all conditions.

Introduction

Lithium-Sulfur (Li-S) batteries have attracted a great interest in the chase for low-cost batteries with high energy density. Their theoretical performance, namely specific capacity of 1672 Ah/kg, the specific energy of around 2600 Wh/kg and energy density of 2199 Wh/l, greatly overpass the limits of today's Lithium-ion batteries. Moreover, the usage of environmentally friendly and abundantly available sulfur, instead of other metals, reduces their cost and makes Li-S batteries more considerate towards the environment. Nevertheless, mainly due to their characteristic polysulfide shuttle mechanism, Li-S batteries suffer of: fast capacity fade, low coulombic efficiency, and high self-discharge.[1]

Identifying the battery self-discharge characteristic is important for both practical applications (i.e., to accurately estimate the SOC, to assess the appropriate energy management strategy, and to investigate the application economic viability) and laboratory testing (i.e., to retrieve accurate and unbiased measurement results). In Li-S batteries, the self-discharge process is related to the polysulfide shuttle and to the corrosion of the current collectors.[2,3,4,5] The polysulfide shuttle is caused by the diffusion of high-order polysulfides (S_8^{2-}, S_6^{2-}, S_4^{2-}), which are soluble in the electrolyte, from the sulfur electrode to the lithium electrode; there, the high-order polysulfides are reduced to low-order polysulfides and the soluble ones diffuse back to the sulfur electrode.[2,6]

There is a high interest in improving the characteristics of Li-S batteries and one of these improvements targets their self-discharge behavior. Thus, several researchers have proposed different solutions for improving the Li-S batteries self-discharge characteristic. Reducing the self-discharge rate by using a gold-coated current collector instead of a bare stainless steel current collector was proposed in [3]. An alternative solution presented in [7] was the addition of an ionic liquid into the electrolyte in order to enhanced the solid electrolyte interface, which resulted in a decrease of the self-discharge. Other improvements of Li-S batteries by advancing and utilization of cathode compositions, porous polysulfide reservoirs, porous current collectors, binders, interlayers, separators, electrode passivation layers, and electrode configurations are summarized in [8].

Most of the recent studies regarding the self-discharge behavior of Li-S batteries are focused only on simple comparisons between well-established and newly developed coin cells at one or two conditions (e.g., temperature value, depth-of-discharge etc.). [9,10,11] In a similar manner, a study on a variety of sulfur electrode materials was conducted in [12], where the reversible and irreversible capacity loss of the materials were identified. The self-discharge characteristics of Li-S coin cells were extensively studied through open circuit voltage (OCV) measurement, electrochemical impedance spectroscopy (EIS) and discharge curve at 25 °C in [4] and [5]. Ryu et al., in [4], described the self-discharge behavior for different types of current collectors. Moreover, they found a self-discharge rate of 34 % for 80 days of idling time. However, this rate has increased only to 36 % after 360 days, for a Li/TEGDME/S battery with Al current collectors. In [5], Kazazi et al. presented improvements of a Li-S cell with a pure sulfur cathode, by using shuttle suppressing sulfur-polypyrrole cathode materials, which reduced the self-discharge rate from 57.9 % to 29 %. Furthermore, by the use of an electrolyte 0.4 M $LiNO_3$, which prevents both the corrosion and the shuttle, they reduced the self-discharge rate to 3.1 %. Mikhaylik and Akridge quantified the self-discharge process in relation to the polysulfide shuttle in [2]; they observed a high self-discharge rate at the high plateau, while, at the low plateau, the charge was kept stable for several weeks. In all of their experiments presented in [2], Mikhaylik and Akridge have used prismatic cells. Another study on the newer generation of Sion Power Li-S cells was carried out in [13]; the dependence of the self-discharge on the storage time (in the range of days and months), was examined only for two depth-of-discharge (DOD) levels, i.e., 0 % and 60 %, at 20 °C. In this study, the capacity loss during storage is separated into the irreversible and reversible capacity loss.

Even though the aforementioned studies are providing a close insight to the self-discharge behavior of coin and prismatic Li-S battery cells, the overall characterization of this behavior has not been analyzed in literature yet, to the best of authors' knowledge. For the practical cell operation, dependencies on DOD and temperature are required. Moreover, a tool for self-discharge estimation is needed. Therefore, an extensive systematic investigation of the self-discharge behavior of Li-S pouch cells is performed in this paper. The study considers the influence of the DOD, idling time, and temperature on the self-discharge characteristics of the studied 3.4 Ah Li-S pouch cells. The investigation uses open circuit voltage (OCV) measurements and discharge voltage curves for determining the self-discharge characteristic of the considered Li-S battery cells. Moreover, the reversible and irreversible capacity loss is distinguished in the study. Based on the experimental results, an estimation of the remaining battery cell capacity has been performed.

Experimental

The cells, which were used to perform this analysis, are 3.4 Ah Li-S pouch cells supplied by OXIS Energy, their electro-thermal characteristics are listed in Table I. All tests were performed using Digatron BTS 600 and MACCOR Series 4000 test stations. During all the tests, the cells were placed inside temperature chambers with controlled environment temperature at 15, 25, 35, and 45 °C.

Systematic Self-Discharge Measurement

The standard test protocol, which was used for the measurement of the self-discharge of the considered Li-S battery cells, is illustrated in Fig. 1. The test protocol was composed of three steps as follows:

- Step 1 – pre-condition cycle on a fully discharged cell (charging: current of 0.1 C-rate (0.34 A), cut-off voltage 2.45 V or 11 hours; discharging: 0.2 C-rate (0.68 A), cut-off voltage 1.5 V) in order to have the cell in a comparable state between the tests and to obtain the actual discharge cell capacity (C_{ini});
- Step 2 – the cell was fully charged and later discharged by the corresponding capacity (C_{dod}) to a pre-defined DOD value, where the cell was kept at open-circuit conditions for a certain idling time. Finally, after this idling time, the battery cell was discharged in order to measure the remaining cell capacity (C_{rem}).
- Step 3 – the cell was recharged in the similar way as in Step 1, in order to identify the new actual discharge capacity of the cell (C_{rch}), which allows to identify the irreversible capacity lost due to calendar and cycling ageing

This self-discharge test procedure was repeated for the considered DOD levels, temperature levels, and idling times.

Quantification of Self-Discharge Behavior

The self-discharge behavior was quantified based on the methodology presented in [13], which allows to separate the reversible and irreversible capacity loss, as illustrated in Fig. 2 and computed according to [1] - [4]:

$$C_t = (C_{ini}-C_{dod}-C_{rem})/C_{ini}*100 \qquad [1]$$

$$C_{sd} = (C_{rch} - C_{rem}-C_{dod}))/C_{ini}*100 \qquad [2]$$

$$C_{ir} = (C_{ini}-C_{rch})/C_{ini}*100 \qquad [3]$$

$$C_t = C_{sd} + C_{ir} \qquad [4]$$

Where C_t is the total capacity loss during the idling, C_{ini} is the initial discharge capacity, C_{dod} is the discharged capacity to the specific DOD point, and C_{rem} is the remaining capacity after the idling time, C_{sd} is reversible capacity loss, which is further referred as the self-discharge rate, C_{rch} is the new actual discharge capacity during recharge after the idling and C_{ir} is the irreversible capacity loss. The irreversible capacity loss was caused by cycling and idling (storage) degradation of the LiS cells;

According to Mikhaylik and Akridge[2], the actual capacity of the high voltage plateau (C_H), illustrated in Fig. 3, can be expressed as in [5].

$$C_H = C_{H\_ini}*e\hat{}-(k_S/t_S) \qquad [5]$$

Where C_{H_ini} is the initial discharge capacity corresponding to the high plateau, k_S is the self-discharge constant, and t_S is the idling time. The self-discharge constant k_S is possible to be determined experimentally, as the slope of the line describing the variation of $\ln(C_H/C_{H\_ini})$ with the idling time $t_{S.}$.

Results and Discussion

Self-Discharge Dependence on DOD Level

To identify the self-discharge dependence on the DOD level, the Li-S battery cell was kept at 35 °C for a period t_S of 60 hours. The battery cell voltage evolution during the 60 hours of relaxation is shown in Fig. 4. The voltage of the Li-S battery cell went at first through a recovery phase after the discharge, where the voltage was rising. The time of the recovery phase is increasing with higher DOD levels. After the recovery phase, the voltage was decaying for all DOD levels and as one can observe, 60 hours is not enough to reach steady-state. Moreover, a relationship between a higher DOD level and a lower voltage value (at the end of the 60 hours of relaxation) corresponds only until a DOD level of 25 %, which refers to the end of discharge in the high voltage plateau, as illustrated by the relaxation voltages in Fig. 4 a). From 30 % DOD, this trend is reversed and higher voltage values are achieved for higher considered DOD levels, which corresponds to the end of discharge in the low voltage plateau, as illustrated by the relaxation voltages in Fig. 4 b).

The dependence of the self-discharge on the DOD level is shown in Fig. 5. The self-discharge rate and total capacity loss is decreasing with increasing the DOD level until 30 % DOD. As this behavior occurs at the high voltage plateau, it might be related to the strong effect of the polysulfide shuttle. From 30 to 60 % and for 90 to 100 % DOD the computed self-discharge rate value becomes negative. The negative value of the self-discharge rate is an indicator that the actual discharged capacity from the cell, after 60 hours of relaxation, is higher than the expected discharge capacity, estimated based on the capacity test by continuous discharge without any idling. Thus, a higher charge in the battery cell is available to be discharged at these conditions by introducing relaxation periods before discharging. However, from 60 to 80 % DOD, the cell presented again a positive self-discharge rate. The specific reason and proof for such a non-consistent behavior, at the low voltage plateau, has not been identified. The irreversible capacity loss takes values between 0.77 and 4.24 % with an average of 2.29 % of the actual total capacity.

Self-Discharge Dependence on Temperature and DOD for 4 Hours Idling Time

In this test procedure, the Li-S battery cell was discharged to a specific DOD level (from 5 % to 30 % considering a 5 % resolution step) and the idling time t_S was set at four hours. Four measurement temperatures were considered, i.e., 15, 25, 35 and 45 °C.

The values of the capacity losses during storage were computed according to [1-4]. Their dependence on DOD is presented separately for each temperature in Fig. 7. Fig. 8 shows the dependence of the self-discharge rate on DOD and temperature. As expected, for the case of four hours idling time as well, the self-discharge rate is decreasing with increasing the DOD level. By increasing the temperature from 15 °C to 35 °C, an increase of the self-discharge was observed; nevertheless, by further increasing the temperature to 45 °C, a decrease in the self-discharge was obtained. This change of trend can be explained by examining the DOD measurement points and their position towards the high voltage plateau as illustrated in Fig. 8. As one can observe, the length of the high voltage plateau (expressed as function of DOD) is decreasing with increasing the temperature; nevertheless, for temperatures of 15, 25 and 35 °C, the high voltage plateau still corresponds to a DOD level of approximately 30 %. In the case of 45 °C, the high voltage plateau ends at approximately 18 % DOD, which might be caused by the strong presence of the polysulfide shuttle, which prevents the cell be fully charged and causing extremely high self-discharge in this region.

Self-Discharge Dependence on the Idling Time

During this test, the cells were stored at five different conditions in order to identify a self-discharge trend related to temperature and DOD for various idling time values. The considered test conditions were: 10 % DOD for 15, 25, and 35 °C and 35 °C for 0, 10, and 20 % DOD. The capacity loss dependence on the idling time t_S is shown in Fig. 9. As one can see, the self-discharge is increasing over time, but the steepness of its growth reduces with increasing the DOD level. The evolution of the self-discharge rate characteristic due to the increase in the temperature is shown in Fig. 10 a); the self-discharge rate of the Li-S battery cell is higher with increasing temperature within the first 24 hours. For 60 hours of idling time, the results are not conclusive. The comparison between the self-discharge rate increase as function of idling time measured at 0, 10 and 20 % DOD is shown in Fig. 10 b). If for short idling times (i.e., up to two hours), a similar self-discharge rate has been obtained for 10 and 20 % DOD, once the idling time has increased a steeper increase of the self-discharge was observed for the lower DOD level (i.e., 10 %). An overall visible trend from Fig. 10 b) is that the self-discharge rate is higher with a lower DOD level. Furthermore, by comparing the influence of the temperature and of the DOD influence on the self-discharge rate, one can conclude that the DOD has a higher impact than the temperature in the range 0 – 20 % DOD and 15 – 35 °C.

Self-Discharge Constant

To determine the self-discharge constant, the ratio between the measured initial and remaining capacities corresponding to the high voltage plateau was plotted against the idling time on a logarithmic scale and fitted by a linear curve as it is illustrated in Fig. 11. For this purpose, there were considered measurement data from self-discharge tests carried out for an idling time between 15 minutes and 8 hours. Based on [2], the self-discharge constants k_S were identified as the slopes of the fitting curves values, as shown in Fig. 11.

The next step was to estimate, for each considered condition (DOD and temperature), the capacity of the high voltage plateau C_H according to [5], using the previously obtained self-discharge constant k_S, and compare it with the experimental measurements. The obtained capacities in function of idling time, corresponding to the high voltage plateau, are shown in Fig. 12. The relative errors corresponding to the estimation of the high voltage plateau capacity, which were obtained according to the methodology proposed in [2], are presented in Fig. 13. By analyzing these results, one can conclude that a prediction of the self-discharge based on [5] and experimentally found self-discharge constants k_S is considered not sufficiently accurate and another approach is needed to be used.

Conclusions

The self-discharge behavior of a 3.4 Ah Li-S battery cell was experimentally investigated and quantified in this paper. The self-discharge process is mainly caused by the polysulfide shuttle and it appears especially at the high voltage plateau, where with increased DOD levels, the self-discharge is reduced. At the low voltage plateau, between 30 and 60 % DOD and between 90 and 100 % DOD, for the considered idling time of up to 60 hours and temperature of 35 °C, self-discharge of the Li-S battery cell was not observed; on the contrary, more charge was available to be discharged from the cell after idling than in the case of a continuous discharge of the Li-S battery cell. However, this trend is not consistent for the entire low voltage plateau at 35 °C, as self-discharge was measured for the interval 60 – 80 % DOD.

Furthermore, the self-discharge rate was found to increase with increasing temperature, until 35 °C for four hours idling period. At 45 °C, the self-discharge behavior is changing the trend due to a highly reduced high voltage plateau, which is caused by a not fully utilized charging. By comparing the temperature and DOD influence on the self-discharge rate, it was found out that the DOD has a higher influence than the temperature in the interval 0 – 20 % DOD and 15 – 35 °C.

By seperating the total capacity loss, occured for the investigated cases, into reversible and irreversible capacity loss, one can observe that the reversible capacity loss, referred as the self-discharge rate, which is caused by the self-discharge processes, plays a major role than the irreversible capacity loss, which comes from the degradation due to idling and cycling of the cell. The observed irreversible capacity loss appeared to be relatively constant during the experiments; in order to identify its dependence on the individual factors there is a need for further study.

Finally, an estimation of the remaining capacity corresponding to the high voltage plateau was performed by identifying the self-discharge constant k_S; however, the method needs to be further improved in order to provide more accurate results for various idling conditions.

Acknowledgments

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TABLE I. The electro-thermal characteristics of the Li-S cell.

Nominal capacity (30 °C)	3.4 Ah
Nominal voltage	2.05 V
Charge cut-off voltage	2.45 V
Discharge cut-off voltage	1.5 V
Nominal charging current	0.34 A (0.1 C-rate)
Nominal discharging current	0.68 A (0.2 C-rate)
Ambient temperature operation range	5 – 80 °C

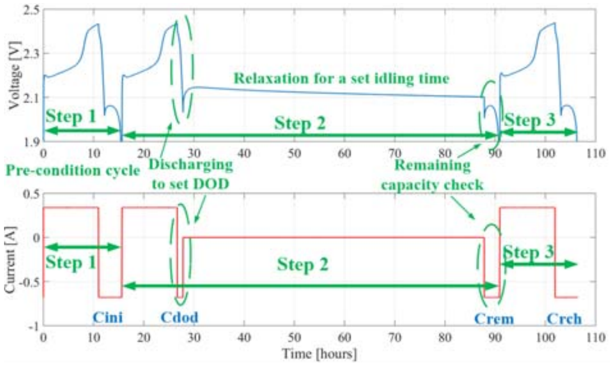


Figure 1. Standard test protocol for systematic self-discharge measurement.

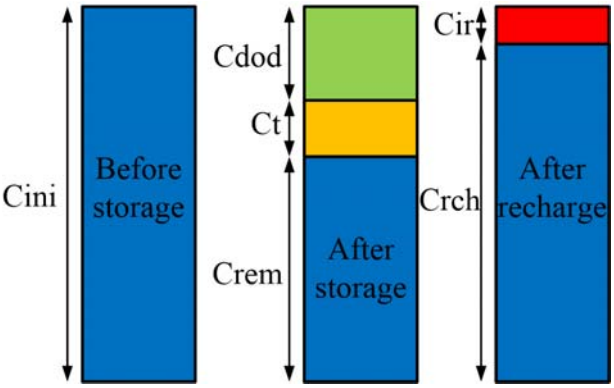


Figure 2. Illustration of self-discharge quantification and separation.

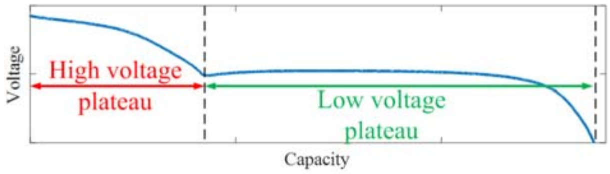


Figure 3. Typical voltage discharging profile of a Li-S battery with marked high and low voltage plateaus.

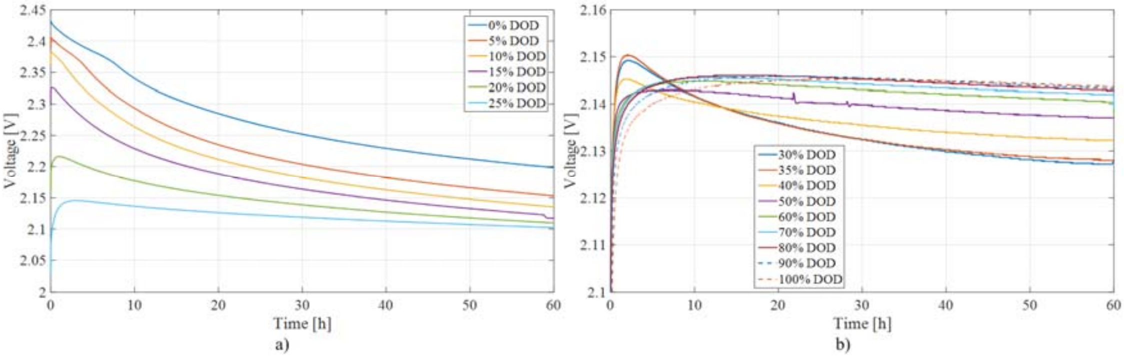


Figure 4. Voltage evolution during 60 hours of relaxation at 35 °C, a) for initial DOD between 0 and 25 %, b) for initial DOD between 30 and 100 %.

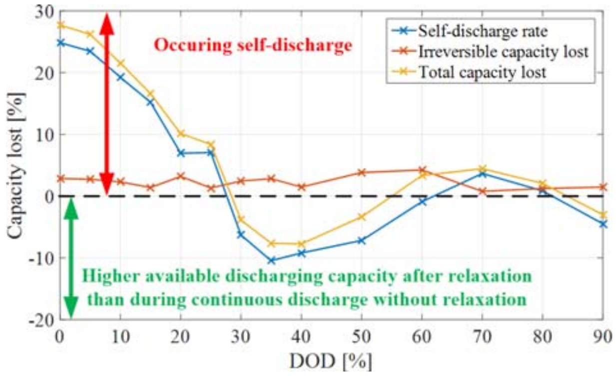


Figure 5. The self-discharge (capacity lost) at 35 °C computed after 60 hours of relaxation.

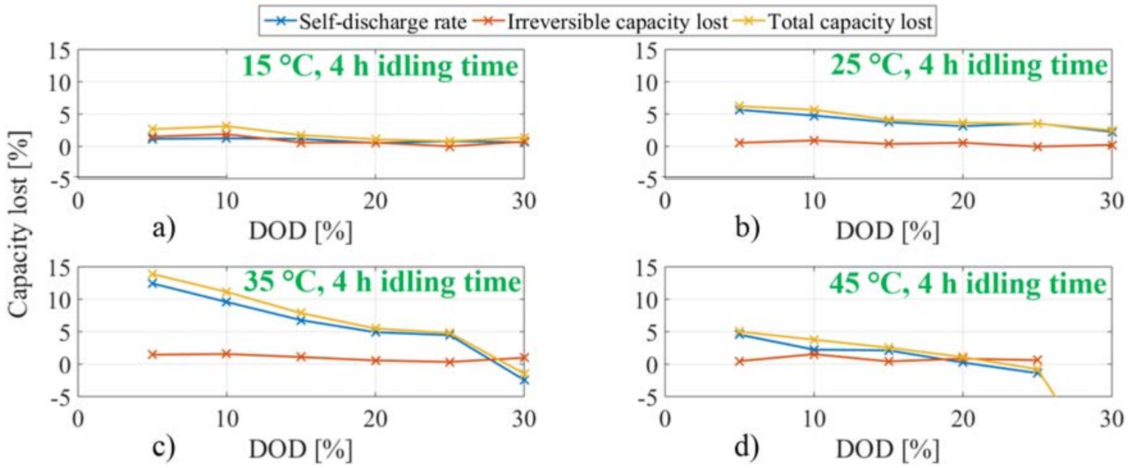


Figure 6. The self-discharge dependence break down to reversible (= self-discharge rate), irreversible and total capacity lost for 4 hours idling time at various temperatures and DOD levels.

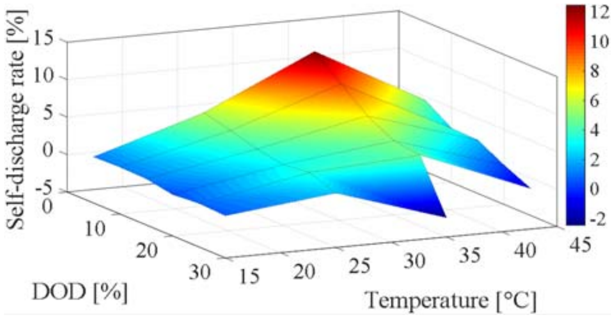


Figure 7. The self-discharge rate dependence on the DOD level and temperature for an idling time of 4 hours.

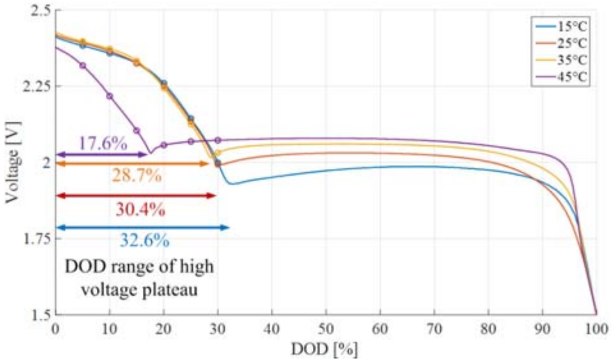


Figure 8. Positions of the measured points for self-discharge at voltage curve during continuous discharge with relation to DOD levels related separately to each temperature.

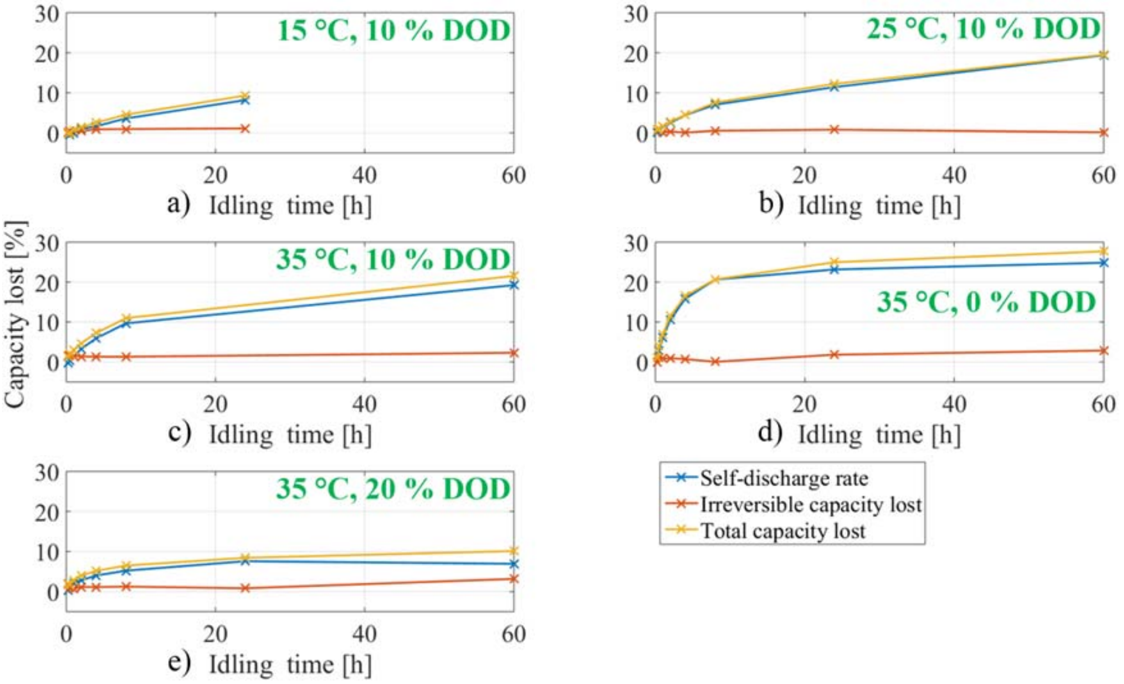


Figure 9. The self-discharge dependence break down to reversible (= self-discharge rate), irreversible and total capacity lost for various temperature, DOD and idling time.

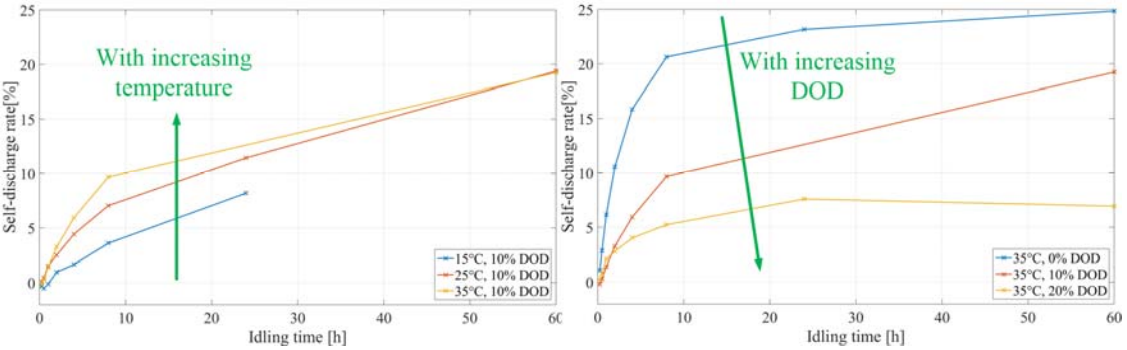
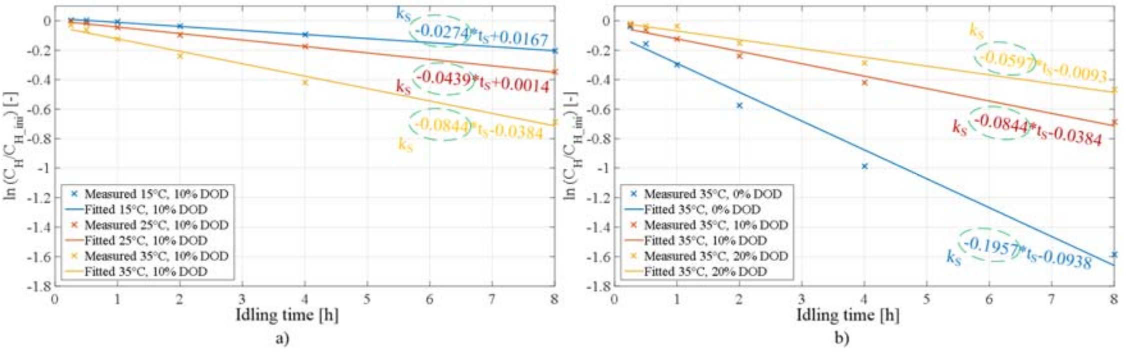
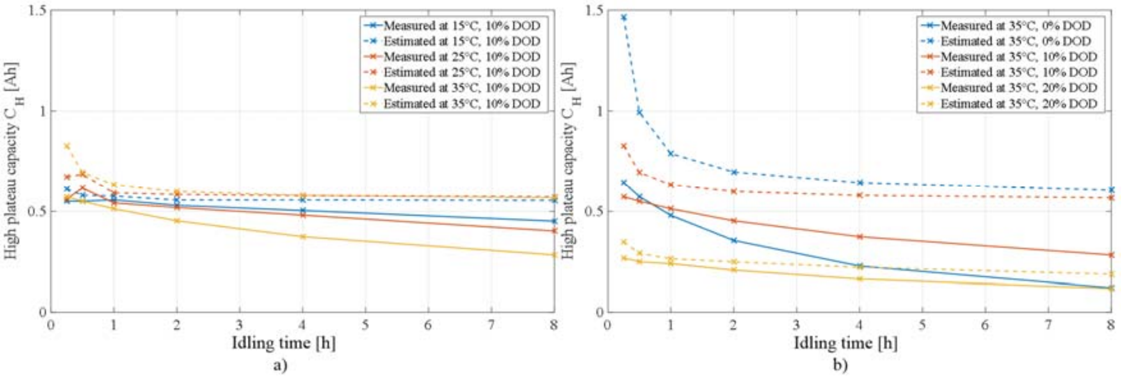


Figure 10. Self-discharge rate as a function of the idling time: a) at 10 % DOD for 15, 25, and 35 °C temperature levels and b) at 35 °C for 0, 10, and 20 % DOD levels.



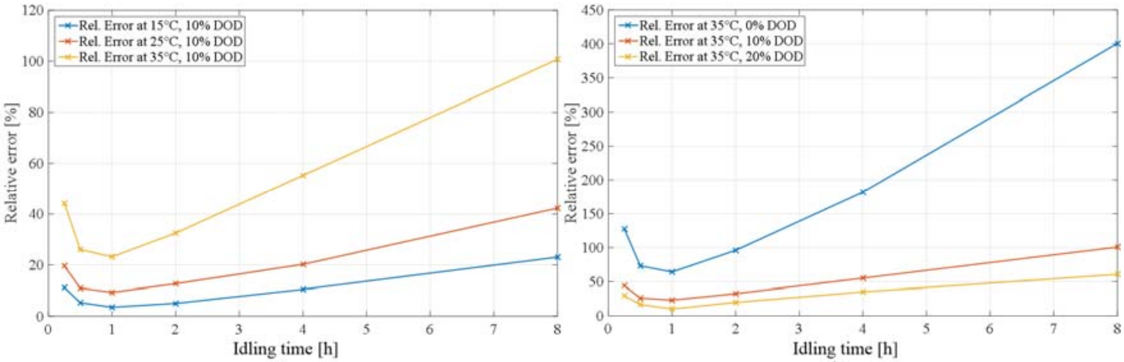
a) b)

Figure 11. Logarithmic expression of remaining and initial high voltage plateau capacities from experimental results as a function of time and a fitted linear curve: a) at 10 % DOD for 15, 25 and 35 °C temperature levels and b) at 35 °C for 0, 10 and 20 % DOD levels.



a) b)

Figure 12. Estimated and measured capacities of the high voltage plateau for various idling conditions: a) at 10 % DOD for 15, 25 and 35 °C temperature levels and b) at 35 °C for 0, 10 and 20 % DOD levels.



a) b)

Figure 13. The relative error of the estimated C_H computed according to [5], a) at 10 % DOD for 15, 25 and 35 °C temperature levels and b) at 35 °C for 0, 10 and 20 % DOD levels.