Aalborg Universitet

Study on Self-discharge Behavior of Lithium-Sulfur Batteries

V. Knap[a], D-I. Stroe[a], M. Swierczynski[a], R. Teodorescu[a] and E. Schaltz[a]

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

Lithium-Sulfur (Li-S) batteries are a promising energy storage technology, which draws interest due to their high theoretical limits in terms of specific capacity, specific energy and energy density. However as a drawback, they suffer from a high self-discharge rate, which is mainly caused by ongoing polysulfide shuttle. In this paper, the self-discharge behavior of Li-S batteries is experimentally investigated, considering various conditions as depth-of-discharge, temperature and idling time. The self-discharge rate under different conditions is identified and quantified. Moreover, a methodology for estimating the capacity of the high voltage plateau based on a self-discharge constant was analyzed; however, the method needs further improvements in order to estimate this capacity accurately for all conditions.

Introduction

Lithium-Sulfur (Li-S) batteries have drawn a great interest in the chase for low-cost batteries with high power and energy density. Their theoretical performance, namely specific capacity of 1672 Ah/kg, 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 the cost and makes Li-S batteries more considerate towards 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 assess appropriate energy management and to determine 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 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. In 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). 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 (7).

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.) (8), (9), (10). In a similar manner, a study on a variety of sulfur electrode materials was conduct in (11), where the reversible and irreversible capacity loss of the materials were identified. 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), (5). Ryu et al., in (4), describe 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. present improvements of a Li-S cell with 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.

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 depth-of-discharge (DOD) and temperature are required. Moreover, a tool for self-discharge discharge estimation is needed. Therefore, an extensive systematic study of the self-discharge behavior of Li-S pouch cells is performed in this paper. The study considers the influence of idling time, (DOD) and temperatures on the self-discharge characteristics of the studied 3.4 Ah battery cells. The investigation uses open circuit voltage (OCV) measurements and discharge voltage curves for determining the self-discharged characteristic of the considered Li-S battery cells. Based on the experimental results, estimation of the remaining battery cell capacity has been done.

Experimental

The cells, which were used to perform this analysis, are 3.4 Ah Li-S pouch cells supplied by OXIS Energy. 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 3.4 Ah 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 hour; 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
- Step 2 – capacity check (charging: current of 0.1 C-rate (0.34 A), cut-off voltage 2.45 V or 11 hour; discharging: 0.2 C-rate (0.68 A), cut-off voltage 1.5 V) in order to measure actual discharge capacity of the cell
- Step 3 – self-discharge measurement; the cell was fully charged and later on discharged 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.

Step 1 and Step 3 were repeated for several DOD values and idling times. After several repetitions, Step 2 was inserted and the reference capacity value was updated, in order to reduce the error in the DOD level due to capacity fades.
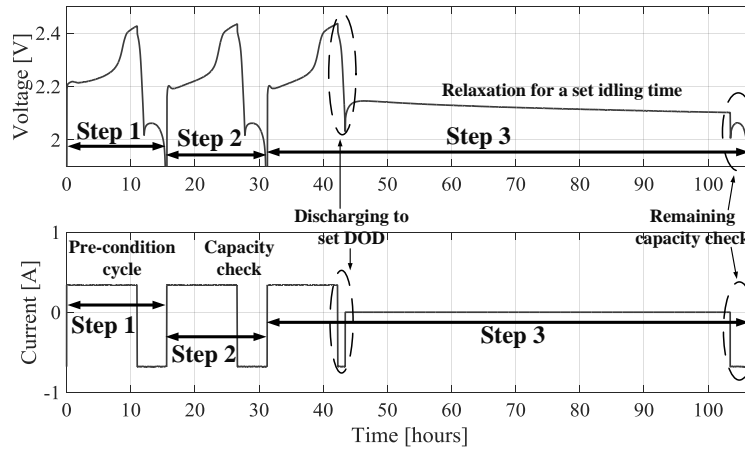

Figure 1. Standard test protocol for systematic self-discharge measurement.

Quantification of Self-Discharge Behavior

The self-discharge rate, expressed in percentage, was computed according to (4) as follows:

$$\text{Self-discharge rate (\%)} = ((C_{ini}-C_{dod})-C_{rem})/(C_{ini}-C_{dod})*100 \qquad [1]$$

Where 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.

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

$$C_H = C_{H\_ini}*e^\wedge-(k_S/t_S) \qquad [2]$$

Where C_{H_ini} is the initial high plateau discharge capacity, 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 $t_{S.}$.
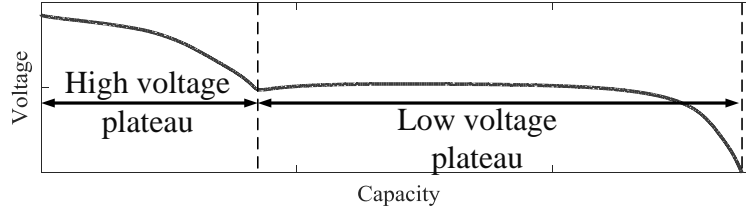

Figure 2. Typical voltage discharging profile of a Li-S battery with marked high and low voltage plateaus.

Results and Discussion

<u>Self-Discharge Dependence on DOD Level</u>

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. 3. The voltage of the Li-S battery cell went at first through recovery phase after a 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 (after 60 hours of relaxation) corresponds only until a DOD level of 25 % DOD, which reffers to the end of discharge in the high voltage plateau and the relaxation voltages are shown in Fig. 3 (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 and the relaxation voltages are shown in Fig. 3 (b).
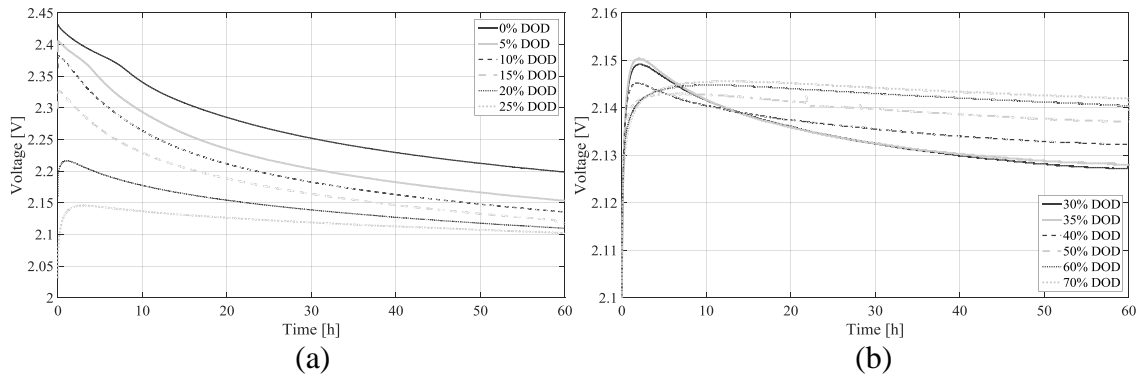

Figure 3. Voltage evolution during 60 hours of relaxation at 35 °C.

The dependence of the self-discharge rate on the DOD level is shown in Fig. 4. The self-discharge rate is decreasing with increasing the DOD level and from 30 % DOD the computed value becomes negative. The negative value of the self-discharge rate is an indicator that the total discharged capacity from the cell, after 60 hours of relaxation, is higher than the discharge capacity obtained during the capacity test by continuous discharge. Thus, a higher charge in the battery cell is available to be discharged by introducing relaxation periods before discharging at the low voltage plateau. However, this behavior was observed only for DODs between 30 and 50 %. From 60 % DOD, the cell presented again self-discharge behavior.
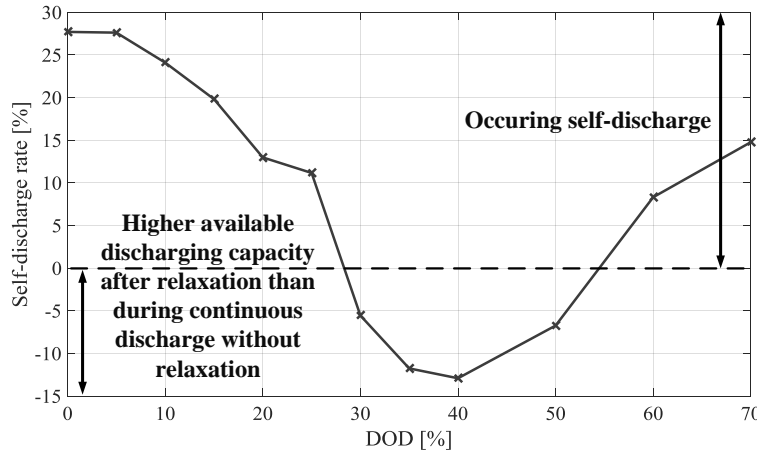

Figure 4. Self-discharge rate at 35 °C, computed after 60 hours of relaxation.

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 % with 5 % resolution step) and t_S was set at four hours. Four measurement temperatures were considered, i.e., 15, 25, 35 and 45 °C. The self-discharge rate was computed according to [1] and its dependence on DOD and temperature is presented in Fig. 5. As expected, for the case of a 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 rate was observed; nevertheless, by further increasing the temperature to 45 °C, a decrease in the self-discharge rate 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. 6. The length of the high voltage plateau 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 around 30 %. In the case of 45 °C, the high voltage plateau reaches corresponds only to a 18 % DOD, which might be caused by the strong presence of polysulfide shuttle, which prevents the cell be fully charged and causing extremely high self-discharge in this region.
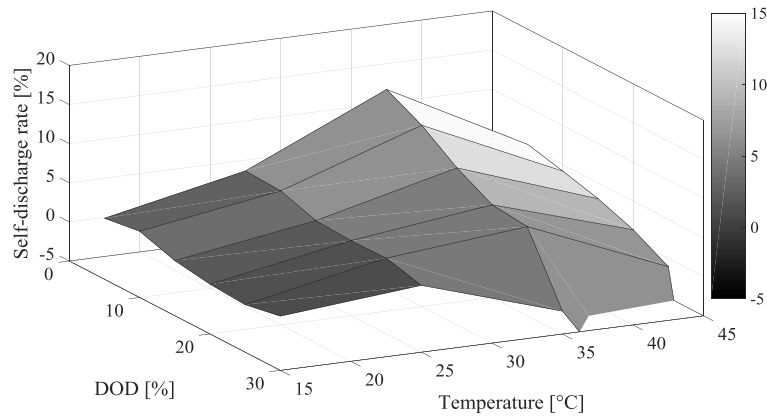
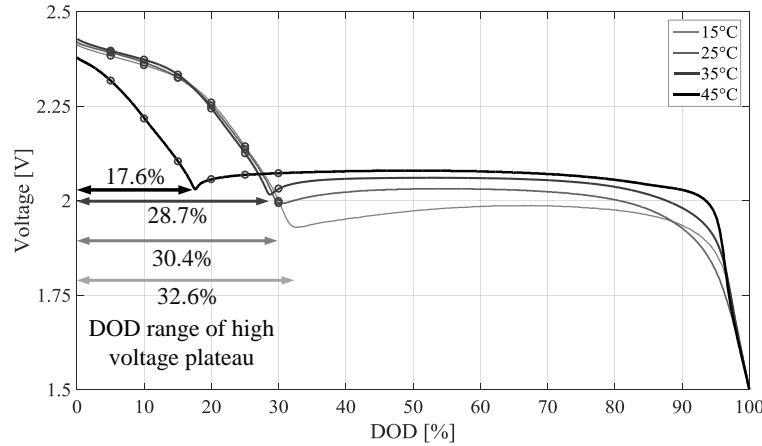Figure 5. The self-discharge dependence on the DOD level and temperature for an idling time of 4 hours.

Figure 6. Positions of the measured points for self-discharge at voltage curve during continuous discharge with relation to DOD levels.

Self-Discharge Dependence on the Idling Time

During this test, the cells were stored at three conditions: 10 % DOD and 25 °C, 10 % DOD and 35 °C, and 20 % DOD and 35 °C. The self-discharge rate dependence on the idling time t_S is shown in Fig. 7. As one can see, the self-discharge rate is increasing over time, but the steepness of growth is lowered as the cell is getting more discharged. The shift in the self-discharge rate due to the increase in the temperature is shown in Fig. 7 (a); at 35 °C the self-discharge rate of the Li-S battery cell is higher than at 25 °C however the same shape of the self-discharge dependence on idling time is obtained independent on the considered temperature. The comparison between the self-discharge rate increase as function of idling time measured at 10 % and 20 % DOD is shown in Fig. 7 (b). If for short idling times (i.e., up to two hours), a similar self-discharge rate has been obtained independent on the DOD level, once the idling time has increased a steeper decrease of the self-discharge rate was observed for the higher DOD level (i.e., 10 %).
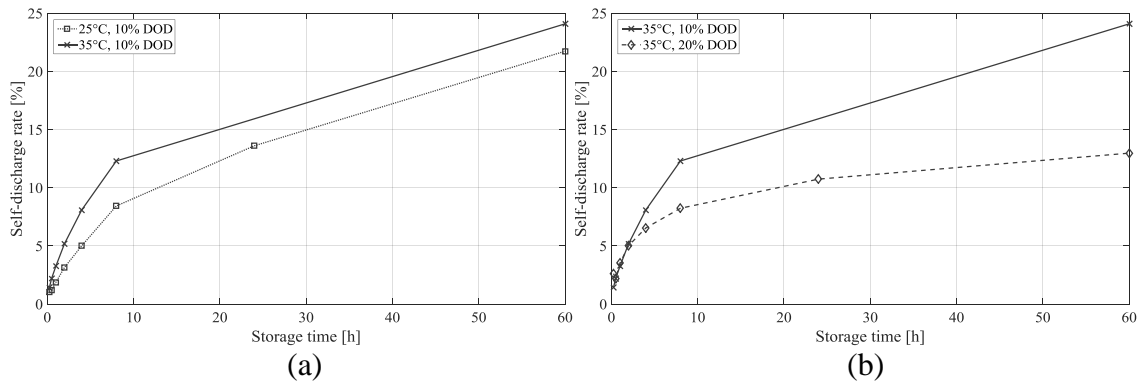
Figure 7. Self-discharge rate as a function of an idling time (a) at 10 % DOD for two temperature levels and (b) at 35 °C for two DOD levels.

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. 8. For this purpose, there were considered measurement data from self-discharge tests carried out for and 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. 8.
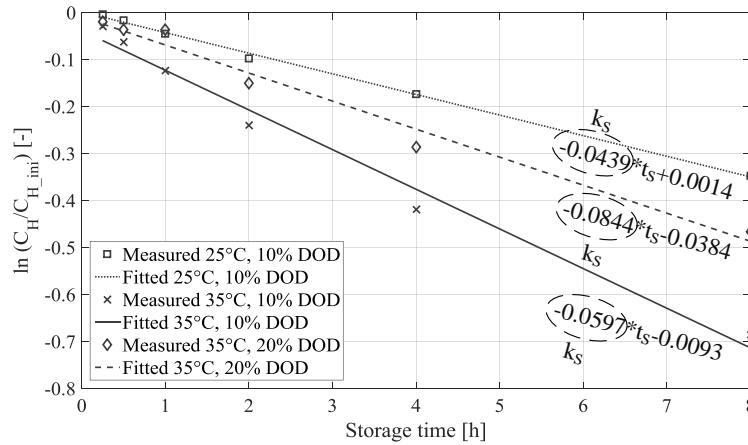

Figure 8. Logarithmic expression of remaining and initial high voltage plateau capacities from experimental results as a function of time and a fitted linear curve.

The next step was to estimate, for each considered condition (DOD and temperature), the capacity of the high voltage plateau C_H according to [2], using the previously obtained self-discharge constant k_S, and compare it with the experimental measurements. The obtained capacities corresponding to the high voltage plateau are shown in Fig. 9. The estimated and measured capacities are following the same trend; however, their values are slightly different. The relative errors corresponding to the estimation of the high voltage plateau capacity are presented in Fig. 10. By analyzing these results, one can conclude that a prediction of the self-discharge based on [2] and experimentally found self-discharge constants k_S is considered not sufficiently accurate and another approach is needed to be used.
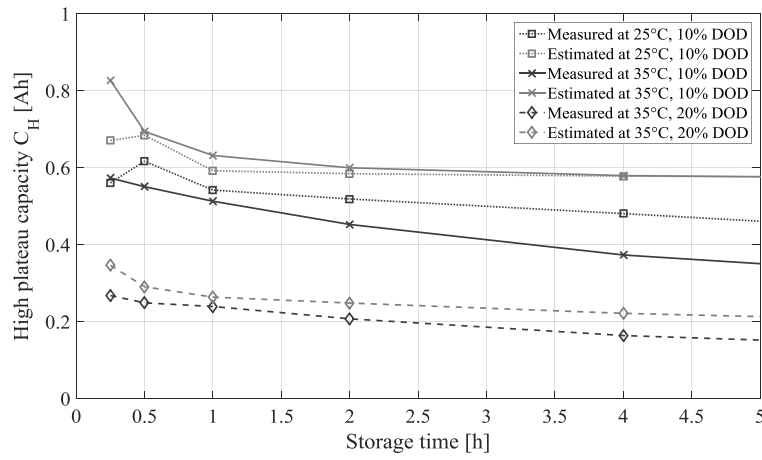
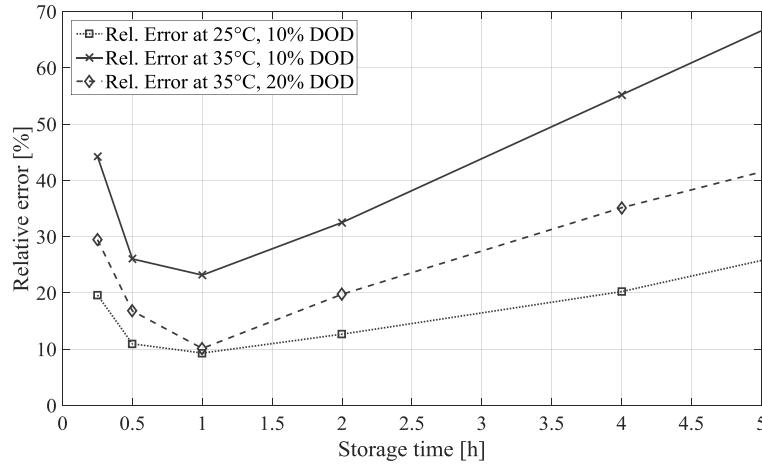Figure 9. Estimated and measured capacities of the high voltage plateau for varying idling conditions.

Figure 10. Relative error of the estimated C_H computed according to [2].

Conclusions

The self-discharge behavior of a 3.4 Ah Li-S battery cell was experimentally investigated in this paper. The self-discharge process is mainly caused by polysulfide shuttle and it appears especially at the high voltage plateau, where with increased DOD levels the self-discharge rate is reduced. At the low voltage plateau between 30 and 50 % DOD, for the considered idling time of up to 60 hours, the self-discharge 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.

Furthermore, the self-discharge rate was found to increase with increasing temperature, until 35 °C. At 45 °C, the self-discharge behavior is changing the trend due to a highly reduced high voltage plateau. Furthermore, an estimation of the remaining capacity 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

References

1. D. Bresser, S. Passerini, and B. Scrosati, *Chem. Commun.*, **49**, 10545–10562 (2013).
2. Y. V. Mikhaylik and J. R. Akridge, *J. Electrochem. Soc.*, **151**, A1969 (2004).
3. H. Ryu et al., *J. Power Sources*, **140**, 365–369 (2005).
4. H. S. Ryu et al., *Electrochim. Acta*, **52**, 1563–1566 (2006).
5. M. Kazazi, M. R. Vaezi, and a. Kazemzadeh, *Ionics (Kiel).*, 1–10 (2014).
6. D. Moy, a. Manivannan, and S. R. Narayanan, *J. Electrochem. Soc.*, **162**, A1–A7 (2014).
7. A. Manthiram, S.-H. Chung, and C. Zu, *Adv. Mater.*, **27**, 1980–2006 (2015).
8. N. Azimi et al., *J. Electrochem. Soc.*, **162**, 64–68 (2015).
9. M. L. Gordin et al., *ACS Appl. Mater. Interfaces*, **6**, 8006–8010 (2014).
10. J.-Q. Huang et al., *ACS Nano*, **9**, 3002–3011 (2015).
11. C. J. Hart et al., *Chem. Commun.*, **51**, 2308–2311 (2015).