Self-balancing feature of Lithium-Sulfur batteries

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HIGHLIGHTS

- The self-balancing feature of the Li-S batteries is identified.
- Quantification methodology to evaluate balancing of the cells is proposed.
- Li-S battery model to predict the self-balancing is proposed and validated.
- The self-balancing feature is evaluated for various charging limits and temperatures.

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ABSTRACT

The Li-S batteries are a prospective battery technology, which despite to its currently remaining drawbacks offers useable performance and interesting features. The polysulfide shuttle mechanism, a characteristic phenomenon for the Li-S batteries, causes a significant self-discharge at higher state-of-charge (SOC) levels, which leads to the energy dissipation of cells with higher charge. In an operation of series-connected Li-S cells, the shuttle mechanism results into a self-balancing effect which is studied here. A model for prediction of the self-balancing effect is proposed in this work and it is validated by experiments. Our results confirm the self-balancing feature of Li-S cells and illustrate their dependence on various conditions such as temperature, charging limits and idling time at high SOC.

1. Introduction

Lithium-Sulfur (Li-S) battery is a prospective battery chemistry for current and future applications. Nowadays, their specific energy has reached 160–350 Wh/kg, with a prospect to accomplish 500–600 Wh/kg, which gives them an advantage above the widely used Lithium-ion (Li-ion) batteries with specific energy of 140–240 Wh/kg. Moreover, in a long-range their cost is expected to be lower than that of Li-ion batteries due to the use of less expensive active materials. However, as they are not a mature battery technology, there are several drawbacks, which have to be addressed either from the cell assembly or battery application point of view; i.e. fast capacity fade, shuttle phenomenon leading to high and quick self-discharge, solubility of active species and complex charge and discharge characteristics. [1] [2].

From the battery balancing perspective, one can see that it is an essential part of battery operation, as it has high impact on safety, amount of available capacity and battery lifetime. A proper balancing scheme primarily helps to achieve most energy per use, but also prevent

states such as over-charging, over-discharging or thermal runaway, which may lead to dangerous situations. Furthermore, when cells with various state-of-charge (SOC) levels are present in a series connection, the battery pack operation is limited by the cell with the highest (charging) or the lowest (discharging) SOC, as illustrated in Fig. 1a). Moreover, ageing phenomena are often related to cell potential, SOC level or temperature, which might vary at unbalanced cells and consequently cause non-uninform degradation, which might result in cell premature failing. [3], [4] [5].

Balancing methods are typically classified into passive or active. The passive methods rely on dissipating the excess energy, which is usually done through a shunt resistor. This solution is simple and low cost, but may not be sufficient for applications with very strict energy use. Active methods rely on transferring energy between cells or controlling flowing current. They have usually higher efficiency and speed of balancing than the passive methods; however additional power electronic elements and controls are needed, which increase the complexity and cost of the solution. [3], [4] [5], [6] [7].
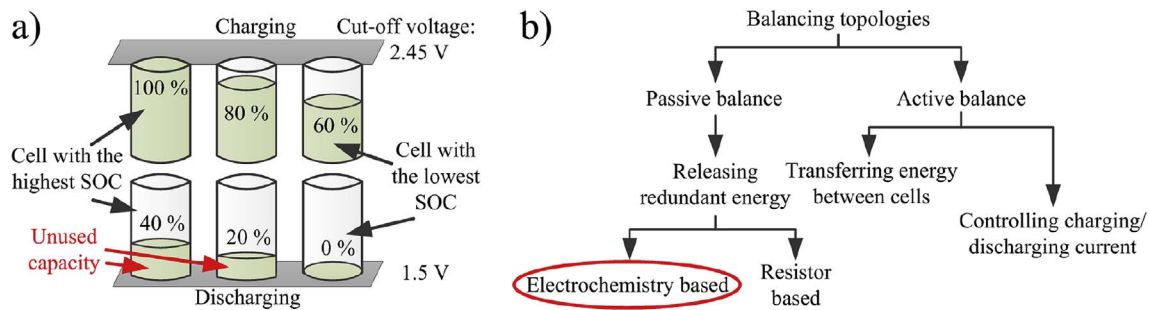

Fig. 1. a) Illustration of the cells with an unbalanced state-of-charge and consequently resulting an unused capacity. Voltage levels are typical for cycling of Li-S cells. b) Classification of typical balancing methods, together with the proposed electrochemistry based method.

Li-S, being a complex solution based chemistry, introduces a new type of passive dissipative balancing method, which is electrochemistry-based. A classification of balancing methods is shown in Fig. 1 b), together with this new concept. Polysulfide shuttle mechanism, which is present in Li-S batteries, and explained in detail in Refs. [8] and [9], introduces high self-discharge, especially at high SOC levels. This inherent self-discharge process can be utilized for dissipating the energy of the unbalanced cells with higher charge. Therefore, by the adequate operation, the Li-S cells can be fully or at least partially self-balanced without any additional switches.

In order to demonstrate the self-balancing ability of a Li-S cell, the cell is modelled including the self-discharge behavior, which is caused by the polysulfide shuttle. The simulations are performed for three cells connected in series in order to evaluate the self-balancing capability at various conditions. Afterward, the model and the self-discharge capability are validated by experimental tests conducted on 3.4 Ah Li-S pouch cells and the usability of the self-balancing is discussed.

The paper is structured as follows: In the second section – Methodology, the laboratory experiment is described, together with the quantification methods for evaluating the cell balancing. The third section describes the modelling of the single Li-S cell and also the general simulation platform and the fourth section presents the simulation results for various conditions. The experimental results are shown and discussed in Section 5 and the discussion related to the self-balancing capability and its practical implementation is in Section 6.

2. Methodology

Three Li-S cells (labelled S1, S2, S3) connected in series are tested in order to evaluate the balancing. The cells are unbalanced by setting their initial SOC to 0, 10 and 20%, respectively. The cells are cycled five times at 0.34 A (0.1 C-rate) for charging with various cut-off limits and 0.68 A (0.2 C-rate) for discharging to the 1.5 V. These currents are considered as the nominal currents for the cell.

2.1. Laboratory experiment

The cells used for the laboratory experiment were 3.4 Ah Li-S long-life type cells from OXIS Energy. They consist of a carbon/sulfur composite cathode, a lithium foil anode, organic solvent and polymeric separator. The cells were individually characterized using a Digatron BTS 600 battery test station and they were cycled in series using a FuelCon Evaluator B Battery Test Station, illustrated in Fig. 2 a). Only the nominal currents were always applied to the cells, except during constant voltage charging mode, when the charging current was reduced. The typical 'nominal' cycle is composed from the charge and the discharge. The charge has 2.45 V or 11 h cut-off limits, whatever is reached first, and then the cell is considered fully charged. The discharge has 1.5 V cut-off limit, when the cell is considered fully discharged.

The individual characterization consisted of discharging the cell to

obtain the information about the remaining charge from the previous cycling, a pre-conditioning cycle [10], a cycle to obtain the actual capacity of the cell, the direct shuttle current measurement [10] and a cycle to discharge the cell to a pre-determined SOC level. For the experimental tests, the SOC was computed according to (1),

$$SOC = Q_{meas} / Q_{cap} \qquad (1)$$

Where Q_{cap} is the capacity obtained from the capacity check cycle and Q_{meas} is:

a) the measured discharged capacity obtained during the first discharge step, when the voltage reached the discharging cut-off limit of 1.5 V,
b) the discharged amount of ampere-hours to reach the target SOC during the cycle for setting the SOC (after the cell being fully charged), computed as $Q_{meas} = 0.9 \cdot Q_{cap}$ and $Q_{meas} = 0.8 \cdot Q_{cap}$ for the remaining 10% and 20% of SOC, respectively.

The specific composition of the characterization for each round is shown in Table 1. The voltage profile from the 5th round of the characterization tests is illustrated in Fig. 2 b) for cell S1.

During the cycling of the cells connected in series, the voltage of each cell was monitored, together with the current flowing through the cell string and temperature measured on the middle cell S2. The performed experiments together with their charging cut-off limit are illustrated in Fig. 3. The term 'balanced cells' means that all the cells were individually discharged to 0% SOC at the previous characterization test. The term 'unbalanced cells' means that the cells were discharged at the previous characterization test to 0, 10 and 20% SOC for cell S1, S2 and S3, respectively. A cycle for cycling the series-connected cells consisted of a charging and a discharging step. Each step (charge/discharge) was completed when the cut-off limits were reached by at least one of the cells. The discharging cut-off limit was always 1.5 V. The cells were subjected to five consecutive charging – discharging cycles.

2.2. Quantification and evaluation of balancing

In order to compare and evaluate specific balancing strategies, it is necessary to quantify their performance. For this purpose, we have selected the three following metrics. The maximum difference between the cells in SOC is represented by max ΔSOC. The performance of the series-connected cells in terms of 'useful' capacity is expressed by the throughput discharge capacity. Furthermore, an extent of the unified behavior of the cells is quantified as a dissimilarity of voltage discharging curves.

2.2.1. Maximum difference in SOC (max ΔSOC)

The max ΔSOC is computed as the difference between the cell with the highest SOC and the cell with the lowest SOC. In the beginning of the balancing test, the maximum difference in SOC between the cells is max ΔSOC = 20%. The ideally balanced cells in terms of SOC would