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A self-discharge model of Lithium-Sulfur batteries based on direct shuttle current measurement

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HIGHLIGHTS

- Concept of total capacity with respect to Li-S battery self-discharge is proposed.
- Shuttle current is identified for various temperatures and states-of-charge.
- Self-discharge model for Li-S batteries is proposed, parametrized and validated.
- Practical integration of the self-discharge model into other models is discussed.

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ABSTRACT

In the group of post Lithium-ion batteries, Lithium-Sulfur (Li-S) batteries attract a high interest due to their high theoretical limits of the specific capacity of 1672 Ah kg^{-1} and specific energy of around 2600 Wh kg^{-1}. However, they suffer from polysulfide shuttle, a specific phenomenon of this chemistry, which causes fast capacity fade, low coulombic efficiency, and high self-discharge. The high self-discharge of Li-S batteries is observed in the range of minutes to hours, especially at a high state of charge levels, and makes their use in practical applications and testing a challenging process. A simple but comprehensive mathematical model of the Li-S battery cell self-discharge based on the shuttle current was developed and is presented. The shuttle current values for the model parameterization were obtained from the direct shuttle current measurements. Furthermore, the battery cell depth-of-discharge values were recomputed in order to account for the influence of the self-discharge and provide a higher accuracy of the model. Finally, the derived model was successfully validated against laboratory experiments at various conditions.

1. Introduction

Lithium-Sulfur (Li-S) batteries represent a promising alternative to the Lithium-ion battery chemistry, due to their high theoretical limits in terms of specific capacity (i.e. 1672 Ah kg^{-1}) and specific energy (i.e. 2600 Wh kg^{-1}). Furthermore, they are expected to become a cheaper and more environmentally friendly solution, mainly due to the use of sulfur, which is an abundant and benign element. However, besides other chemistry related phenomena, Li-S batteries suffer from polysulfide shuttle, which results in several commonly known drawbacks: fast capacity fade, low coulombic efficiency, and high self-discharge [1,2].

For the practical use of the Li-S batteries, there is a need not only to characterize the self-discharge behavior as it was done in Ref. [3], but also to provide a proper simulation tool (a model), relevant for industrial applications and laboratory experiments as well; otherwise, biased results can be acquired (e.g. not corresponding depth-of-discharge (DOD) levels assigned). The main cause of self-discharge for Li-S cells was identified to be the polysulfide shuttle and afterwards the corrosion of the current collectors [4–7]. Because the polysulfide shuttle is present not only during the cell idling, but also during charging and discharging, the self-discharge appears as well during these conditions. A mechanistic model of

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the polysulfide shuttle causing the self-discharge of the Li-S battery cells was presented in Ref. [8]. However, the purpose of the model was to provide insights into the key battery mechanisms, rather than to be used from an end-application perspective. The mathematical model presented in Ref. [9] and a zero dimensional model for the Li-S batteries introduced in Ref. [10] are using the relations for the polysulfide shuttle derived from Ref. [4]. However, these relations are based on determining experimentally a shuttle constant k_S, which is a time-consuming procedure; moreover, it might not always provide sufficiently accurate results for the self-discharge estimation, as it was indicated in Ref. [3]. Another simple approach was used in Ref. [11], where the self-discharge current was related to the charge lost during idling at 100% state-of-charge (SOC). The self-discharge current was identified to be proportional to the square root of the idling time. However, the model characterization tests for the 100% SOC condition took more than nine days and it was assumed that self-discharge current is dependent on the used power profile. Furthermore, a methodology for direct shuttle current measurement was proposed in Ref. [12], where its results were analyzed and validated using the one-dimensional phenomenological model, which is based on Nernst and species concentrations equations. This methodology allows for a simple and time-effective measurement of the shuttle current at different SOC levels; it is based on the premise that the shuttle current can be observed as the steady-state current flows through the cell, while its voltage is kept constant during constant voltage operation to prevent the voltage decay.

In this paper, the direct shuttle current measurement method is used to identify the shuttle current of a 3.4 Ah Li-S pouch cell at different depth-of-discharge levels and temperatures. Furthermore, the obtained results are used to derive a simple and easy-to-use mathematical model of the self-discharge in the Li-S battery cell that is related to the polysulfide shuttle phenomenon. This model is validated against several self-discharge experiments at various conditions and it is suitable to predict the self-discharge during idling and operation of the battery.

2. Methodology

The work flow followed in this paper is summarized and presented in Fig. 1. At first, the measurements were performed and they are described in Section 2.1 for direct shuttle current measurements and in Section 2.2 for the self-discharge model validation measurements. The current shuttle measurement results are presented in Section 3 and later on in Section 3.1 it is also shown how the mathematical expression for the self-discharge model dependent on DOD and temperature is derived. Later on, there were considered three fitting cases. Fitting Case 1 (Section 3.1.1) uses the pre-determined DOD points to develop the model, Fitting Case 2 (Section 3.1.2) recomputes and ‘corrects‘ the DOD points according consideration of the self-discharge ongoing during the measurements and Fitting Case 3 (Section 3.1.3) adds up simulation of the measurement to update the DOD points. Each of these fitting cases parameterize the self-discharge model and its accuracy is later validated in Section 3.2 by an use of the validation measurements (Section 2.2) and the SOC estimation model for the validation (Section 2.3) with the consideration of the total capacity concept (Section 2.4). The discussion about SOC reference frame and cell history effect, which are related to the self-discharge model integration and use, is hold in Section 4.1. Furthermore, the alternative version of the self-discharge model considering dependence on the open-circuit voltage rather than DOD is discussed in Section 4.2.

All the measurements were performed on a single 3.4 Ah long life chemistry Li-S pouch cell manufactured by OXIS Energy. A Digatron BTS 600 battery test station was used for the direct shuttle current measurement procedure. To avoid battery cell overcharging and in order to reduce the degradation of the cell at a high current shuttle region, for all the charging conditions, charging time limitations were applied as well (8.5 h for 15 °C, 9 h at 25 °C and 10.5 h for 35 °C). The values of 0.1 and 0.2 C-rate correspond to 0.34 and 0.68 A currents, respectively.

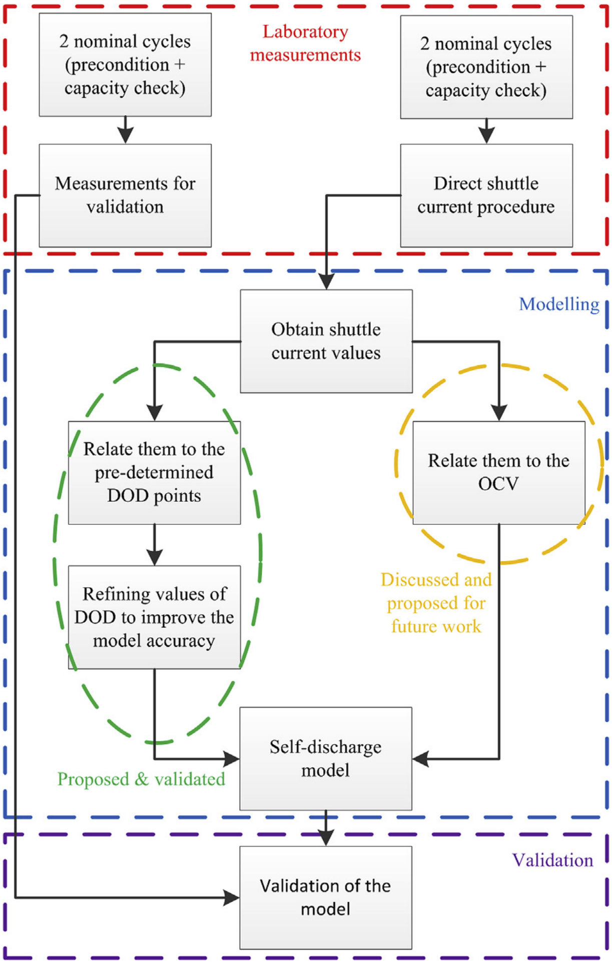

Fig. 1. Work flow scheme used for the self-discharge model derivation and validation.

2.1. Direct shuttle current measurement

The applied test procedure for the direct shuttle current measurement is based on the methodology presented in Ref. [12] and illustrated in Fig. 2. The procedure started with two nominal cycles: 0.1 C-rate constant current charging until 2.45 V and 0.2 C-rate discharging to 1.5 V. The first cycle served as a pre-condition cycle, which is needed in order to ‘reset’ the cell's history (as the Li-S is a soluble chemistry) and to bring the cell to the similar initial condition at the selected temperature. The second cycle was used for the cell's capacity check and its calculation for the further procedure steps. Afterwards, the cell was charged fully (by 0.1 C-rate to 2.45 V) and discharged (by 0.2 C-rate) to a set DOD point (i.e. 2%). Then, the cell was rested in open circuit condition in order to reach an open-circuit voltage (OCV) value. The OCV is considered as an equilibrium voltage point, which is the peak value between voltage rise during the recovery period and voltage fall during the predominant self-discharge. However, in practice, due to the noise in the voltage signal, the reliable value of the OCV was determined