TITLE: Standard operation procedure (SOP) on Self Discharge Current Measurement (SDM) for Li-ion batteries

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DOCUMENT PURPOSE: The document intends to provide a generic and instrument-unspecific guideline to help in the process of acquiring reliable and reproducible data with Self-discharge Current Measurement (SDM) for Li-ion batteries. It is formalized within the project NanoBat to ensure correctness and validation, as well as a guideline to repeat measurements externally (e.g. with Stakeholders). This will allow us to get input and feedback for further improvements. The areas covered are battery under test (BUT) and instrument handling, data storage, and general data analysis.

This SOP will be part of D6.7 of the NanoBat project.

ABBREVIATIONS / TERMINOLOGY:

SDM – Self-Discharge Current Measurement
CUT – Cell Under Test
ESD – Electrostatic Discharge
SOC – State of Charge
AC – Alternating Current
EEC – Electrical Equivalent Circuits

Contents

1. Introduction

This document attempts to provide a generic and instrument unspecific guideline for use of Self-Discharge Current Measurement (SDM) for batteries. The intention is to provide basic information needed to perform reliable, repeatable, and safe measurements.

Li-ion batteries gradually discharge even if they are dis-connected (i.e., at an open circuit state). This self-discharge leads to a loss of the stored energy and a reduction of the cell capacity [1]. When cells are assembled into modules and battery packs, differing rates of self-discharge led to voltage imbalances within a battery pack, leading to a shorter pack lifetime. Several factors contribute to varying self-discharge within cells this includes internal current leakage paths, external current leakage paths, particulate contaminants and dendrite growth producing internal “micro-shorts”, electrolyte degradation, electrode passivation by decomposition and/or film growth on electrodes, temperature, and internal pressure build-up [2]–[4].

An equivalent electric circuit (EEC) model of self-discharge of LIBs is shown in Figure 1. In this electric circuit, the voltage of a cell with an effective capacitance C_{eff} drops due to the self-discharge current I_{SD} flowing through the parallel self-discharge resistor R_{SD}, which is typically in the range of kΩ to MΩ. In the potentiostatic SDM described here (Figure 1, left part) the initial step is to precisely measure the cell voltage V_{cell}, and to adjust the internal voltage source of the SDM setup for a close match with the LIB within few micro-volts. The internal source is constructed for the lowest possible drift and can be considered as ultra-stable (< 10 µV drift over 24 hours).

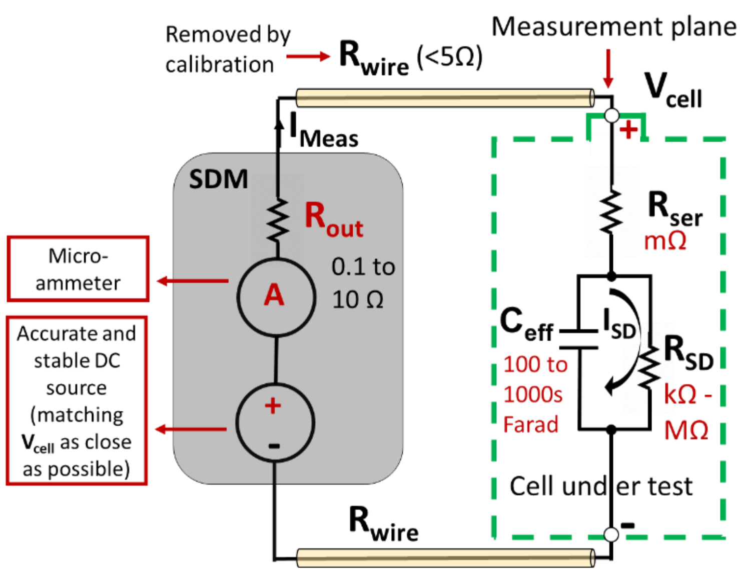

Figure 1. Self-discharge current measurement (SDM) and cell contact model

To start the actual SDM, the voltage source gets connected to the LIB through an adjustable output resistance R_{out}, usually in the range from 0.1 to 10 Ω. The current I_{Meas} is measured by a micro-ammeter with an accuracy < 1 µA. During the LIB self-discharge, the voltage source of the

SDM starts to supply a current which is exponentially converging towards an end value, which, once equilibrium is achieved, is equivalent to the measured self-discharge current. The corresponding time constant is $\tau = R_{ser} \times C_{eff}$, depending on the cell's effective capacity and on the series resistance. In SDM, a lower output resistor R_{out} leads to faster convergence and faster measurement of the self-discharge current. However, it also increases undesired artefacts and noise contributions because cell voltage fluctuations (e.g. due to temperature changes) are directly converted into current fluctuations with a gain proportional to $1/R_{out}$. The best trade-off between measurement speed of the self-discharge on the one hand, and the corresponding noise on the other hand depends on many factors and is not further examined in this document.

The following sections contain advice and procedures to ensure the stable and reliable operation of the SDM to obtain high-quality data.

2. Operator and equipment safety

Although low current values are typically involved, performing SDM measurements may expose the operator to the cells-under-test (CUT), and to the instruments and mechanical fixtures. Necessary precautions should be considered to avoid injury (e.g. from exposure to battery thermal runaway, sharp objects, or exposure to other harmful substances). Additionally, due to typical instrument specifications, in some cases high voltage safety measures ought to be considered.

SDM equipment is sensitive to static electricity, therefore special care should be taken to avoid damage from electrostatic discharge (ESD). Conducting wrist straps are advised to be used to prevent high voltages from accumulating on workers bodies, also anti-static mats or conductive flooring materials are desirable.

3. Setup and calibration

A typical measurement system using SDM method consists of the measurement hardware, the software to control the hardware and to calculate the voltage and current, a fixture to connect to the CUT, cables, and connectors (see Figure 2).

At first, a proper connection of the cables from the instruments to the fixture should be ensured. All connectors are to be checked for damages and residues. Ensure the cables are firmly connected and have a stable position, while taking into consideration their specific minimal bending radius. Furthermore, try to keep cables as short as possible, and make sure all cables are specified to work in the current and voltage range used in the experiments.

Before the CUT measurement, a calibration process is performed. The SDM supports precise control of the output resistance R_{out} value by calibrating the resistance of the wiring connections to the cells (see Figure 1). This can be done either with a fast *in situ* calibration with the CUT connected to the analyzer for a short compensation, or by replacing the cells with calibration shorts standards. However, it is recommended to ensure a rest period for the CUT after a calibration is performed (e.g. 15-30 min) in order that the cells are settled and to avoid any undesired effects to the SDM.

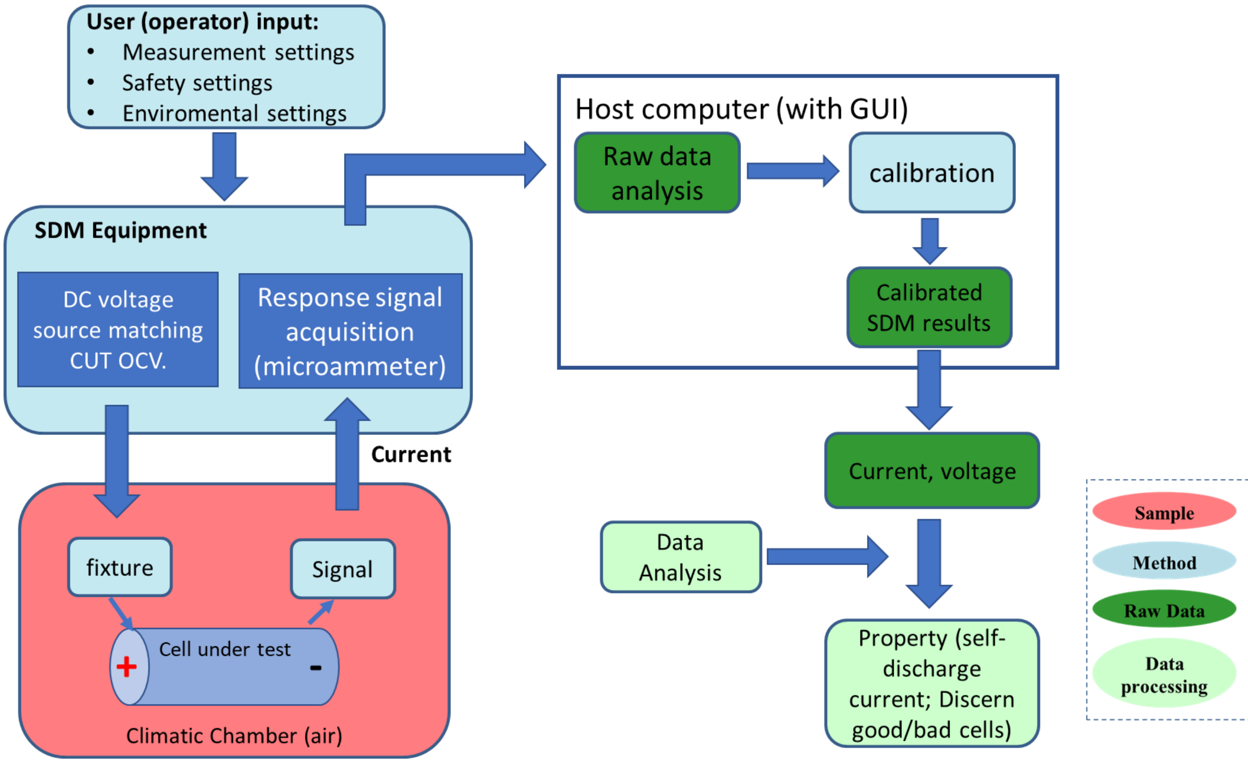

Figure 2*. Flow chart for SDM. The sketch is based on the EIS CHADA template (characterization data templated developed by EMCC, European Materials Characterization Council)*

4. Measurement

Pre-measurement points to consider:

1) Ensure proper connections are established and that all relevant devices are switched on while considering a sufficient instrument warm-up period.
2) Make sure the CUT is properly installed in the specific fixture and the cable connectors are firmly attached.
3) Allow the cell-under-test to rest. This lets the cell achieve a stable charge distribution state after any charge or discharge activity.
4) Establish a stable environment to assure uninfluenced and repeatable measurements, especially a stable and known environmental and CUT temperature.
5) Record all measurement metadata, such as the ambient temperature, CUT specifications, SoC, measurement date and time.

SDM measurement

1) If a climatic chamber is used, set a specific environment temperature and keep the CUT and fixture at this temperature long enough in order to adapt and settle to this temperature.
2) Set safety parameters (over current, over voltage, under voltage).
3) Choose a suitable SDM test duration (e.g. few seconds to several hours).
4) Choose a proper measurement interval (e.g. 10s).
5) Insert the value of the programmable SDM output resistor (50 mΩ to 10 Ω).
6) Set an initial cell current (e.g. at 0A or with an offset).
7) Record the SoC and temperature of the CUT.
8) Start the SDM measurement.

Example case of conducting an SDM with in-situ wire calibration:

a) Select the calibration current level in the SDM software (e.g. 1 mA).
b) Set the duration of the SDM measurement [minutes]. For your initial tests, it's generally better to run a long-duration test so that the cells have enough time to settle to their usable or final values
c) The long test improves the chances that you can see any issues that affect your measurement results, such as temperature stability, charge redistribution, initial current value. You can then take actions to mitigate and improve those issues. Fixing these issues is important to getting faster measurements that produce valid results.
d) Set the Measurement Interval [s] value in the range of 10-60 seconds, which is recommended as a good typical range for your initial measurements.
e) Start the measurement.

The self-discharge test typically takes a few hours, with the time depending on the cell size, capacity, chemistry, and configuration. Figure 3 shows a SDM result using in-situ calibration.

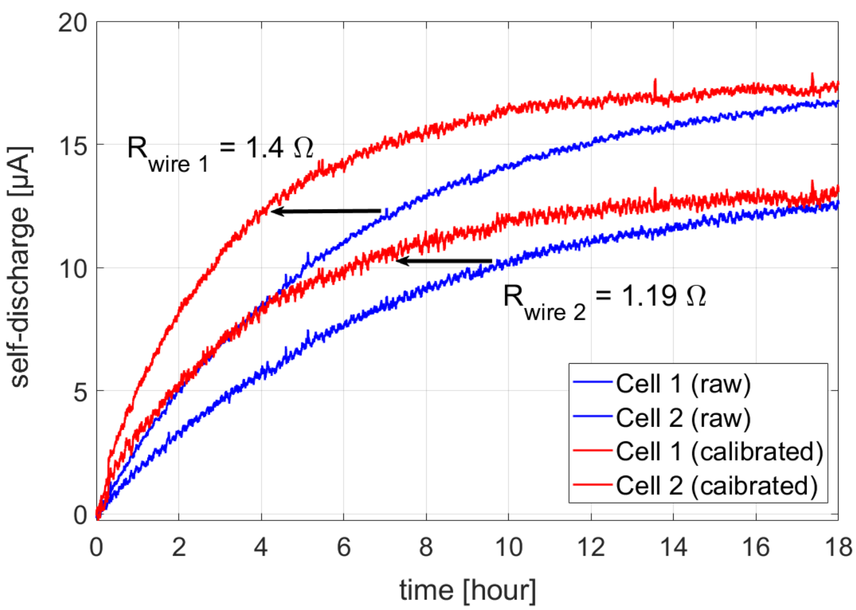

***Figure 3**. Self-discharge current of two cylindrical cells measured using SDM. The in-situ calibrated results are compared to the raw data.*

While the equipment is still turned on, the same calibration file will be used for any repeated SDM measurements. Once the power to the equipment is recycled, the calibration file should be loaded, or a new calibration can be done.

5. Data acquisition, fixtures

The time domain current and voltage are acquired, containing information of the self-discharge current, and temperature data from sensors attached to the surface of the CUT. The SoC of the CUT is computed, and the temperature is logged. For visualizing the SDM data, a time domain plot is done with current (see Figure 3); additionally, the cell voltage can be also plotted on the right axis. The logged temperature is plotted against time, to ensure that low temperature fluctuations were maintained.

The SDM fixture type depend on the CUT form. The fixture contains contact point to connect the positive and negative electrodes to the SDM. For user safety requirements, integrated fuses are implemented in the fixture for short circuit protection.

6. Feedback from collaborators

The described SDM method has been evaluated together with several industrial partners for LIB and NiCd batteries. SDM was also evaluated with the battery pilot lines TUBS and PLEIONE (with LIB pouch cells). The results from the pilot line pouch cells were compared to the standard OCV method and show good agreement. A conference proceeding was published showing SDM for commercial cylindrical cells (18650, LIB) and comparison to FEM modelling [1].

The SOP drafts were discussed with Metas (Bern, Switzerland) in 21.09.2021, and guidance was provided by Metas to Keysight for the SOP structure and content. Part of this work was done in the frame of the ongoing European Commission project NanoBat.

7. References

[1] N. A.-Z. R-Smith, G. Gramse, M. Moertelmaier, M. Kasper, and F. Kienberger, “Advanced Self-Discharge Measurements of Lithium-Ion Cells and Comparison to Modeling,” in *2020 IEEE International Instrumentation and Measurement Technology Conference (I2MTC)*, May 2020, pp. 1–5. doi: 10.1109/I2MTC43012.2020.9128757.

[2] T. Utsunomiya, O. Hatozaki, N. Yoshimoto, M. Egashira, and M. Morita, “Self-discharge behavior and its temperature dependence of carbon electrodes in lithium-ion batteries,” *J. Power Sources*, vol. 196, no. 20, pp. 8598–8603, Oct. 2011, doi: 10.1016/j.jpowsour.2011.05.066.

[3] J. P. Schmidt, A. Weber, and E. Ivers-Tiffée, “A novel and fast method of characterizing the self-discharge behavior of lithium-ion cells using a pulse-measurement technique,” *J. Power Sources*, vol. 274, pp. 1231–1238, Jan. 2015, doi: 10.1016/j.jpowsour.2014.10.163.

[4] M. Lewerenz *et al.*, “New method evaluating currents keeping the voltage constant for fast and highly resolved measurement of Arrhenius relation and capacity fade,” *J. Power Sources*, vol. 353, pp. 144–151, Jun. 2017, doi: 10.1016/j.jpowsour.2017.03.136.