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9. RENAULT SAS (RENAULT)
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MAT4BAT

Advanced materials for batteries

FP7-2013-GC-Materials

Theme GC.NMP.2013-1 - Improved materials for innovative ageing resistant batteries

Collaborative project

Start date of the project: 01/09/2013
Duration: 42 months

Deliverable D1.2

Protocol to evaluate full Li-ion cell for charge/discharge modality and ageing test

WP	1	Battery ageing assessment – methods and tools
Task	1.2	Definition of accelerated testing protocols for battery ageing

Dissemination level[1]	PU	**Due delivery date**	31/12/2013
Nature[2]	R	**Actual delivery date**	17/01/2014

Lead beneficiary	**ZSW**
Contributing beneficiaries	CEA, VITO, CIDETEC, KIT, RENAULT, EIGSI, UNEW

[1] Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU)

[2] Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other

Deliverable abstract

Lithium-ion batteries are subject to ageing which leads to loss of capacity and increase of internal resistance. For a battery powered vehicle, this means that the driving range and the performance will be reduced during usage and time.

This report provides the test conditions for cell ageing to be done in the MAT4BAT project. The tests are divided into cycling ageing (corresponding to driving mode) and storage/calendar ageing tests (corresponding to parking mode). The cycling ageing tests include a Dynamic Stress Test (DST) procedure and the storage tests are done at Open Circuit Voltage (OCV). Different parameters such as temperature, charge C-rate and state-of-charge and state-of-charge window are varied in order to measure their influence on battery ageing.

Defined check-up procedures are described, which are used to quantify the degradation of the cells. The test protocols are compared with standard procedures in literature.

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1. Introduction

Lithium-ion batteries are subject to ageing which leads to loss of capacity and increase of internal resistance [1–6]. For a battery powered car, this means that the driving range and the performance will be reduced during usage and time [7]. In order to evaluate the ageing behaviour of Lithium-ion batteries, tests are usually divided in cycling ageing tests (corresponding to a driving car) and storage/calendar ageing tests (corresponding to a parking car) [1–6]. Since the speed of degradation and the underlying ageing mechanisms depends on the operation parameters, such as state-of-charge and temperature [1,2,6], different parameters have to be considered in ageing tests.

This report provides the test protocols for cell ageing under cycling and storage conditions, as well as defined check-up procedures to be done in the MAT4BAT project. Different parameters such as temperature, charge C-rate and state-of-charge / state-of-charge window are varied in order to measure their influence on battery ageing. Defined check-up procedures are described, which are used to quantify the degradation of the cells during ageing. These procedures and parameters used in this report are compared with standard procedures from literature.

2. Abbreviations

BEV	battery electric vehicle
CC	constant current
CCCV	constant current, constant voltage
CU	check-up
DOD	depth of discharge
DST	dynamic stress test
ECU	extended check-up
EIS	electrochemical impedance spectroscopy
EOL	end-of-life
OCV	open circuit voltage
PITT	potentiostatic intermittent titration technique
SCU	short check-up
SOC	state-of-charge
SOH	state-of-health

3. General test procedure

The tests will be performed at the facilities of the different partners in the MAT4BAT project and are divided into cycling and storage ageing tests. As shown in **Error! Reference source not found.**, the ageing procedure consists of ageing periods and check-ups (CU) in between. The ageing state of the cells is quantified by the state-of-health (SOH) from the CUs.

The SOH(t) at ageing time t will be calculated by dividing the real discharge capacity by the real discharge capacity of the cell before the ageing (t=0), according to the following relation [8,9]:

$$SOH(t) = \frac{\text{discharge capacity}(t)}{\text{discharge capacity}(t=0)} \times 100\% \qquad (1).$$

The discharge capacity t=0 is obtained in the initial CU. Although it is sometimes assumed that the rated capacity given by the cell manufacturer can be used [9], we want to point out that there are always small variations in the initial capacity. Thus, in the MAT4BAT project the individual initial capacity for all cells that are subject of an ageing procedure will be measured (see also section 4.1). An ageing procedure is stopped at SOH=80% or after t=2 years latest.

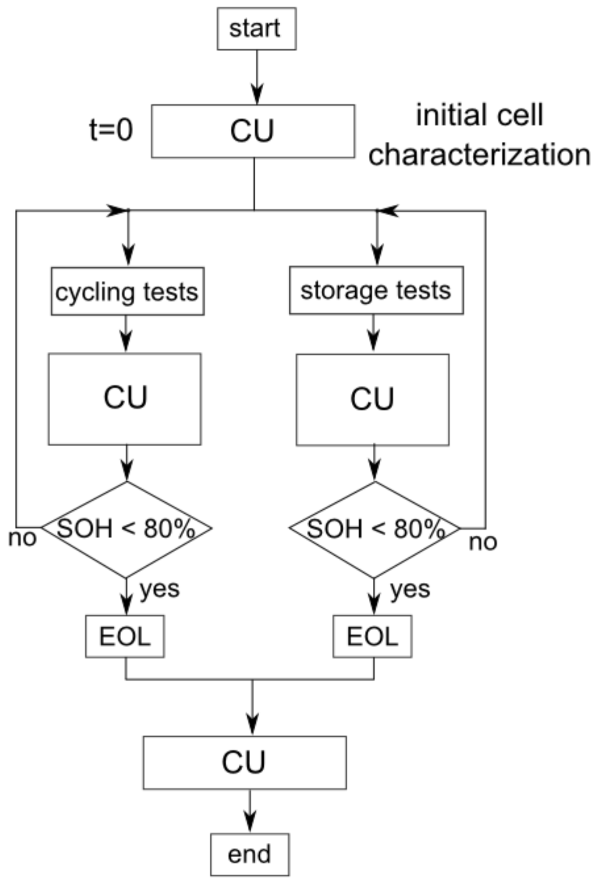

Figure 1. General principle of ageing tests in the MAT4BAT project

4. Check-up (CU) procedure

The conditions for the CUs are the same for all tests performed in the MAT4BAT project. Although it is often not mentioned in literature, the equilibration of the cell temperature is an important point, especially for large cells. In theMAT4BAT project the cells will be equilibrated for 8h.

Since the cell capacity depends strongly on the cell temperature [10], a clearly defined temperature during the CUs is also very important to get comparable results for the different ageing tests. Several authors/projects used temperatures for CUs near room temperature [8,11,12]. In the MAT4BAT project 25±2°C will be used as defined in ISO 12405-2.

Similar to tests in the Helios project [12], CUs in the MAT4BAT project are performed periodically between the ageing periods (see **Error! Reference source not found.**) and are divided into short check-ups (SCU) and extended check-ups (ECU) as shown in Figure 2. The SOH difference between two ECUs is at least 5%, in order to see clear differences between the tests. SCU and ECU are described in section 4.1 and 4.2, respectively.

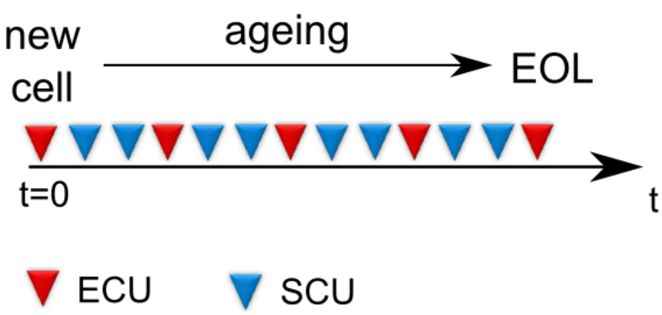

Figure 2. Sequence of CU procedures in the project

Since the speed of SOH decrease depends strongly on the ambient temperature during ageing [1,2,6], the periodicity of the CU intervals will be adapted to the temperature of the tests. As the CU interval also depends on the battery chemistry [4,5], an exact value cannot be given before the beginning of the tests.

4.1. Short check-up (SCU) procedure

In the SCU, first the OCV is measured at 25°C followed by the resistance (at 80% SOC) of the cells. The cells are then subject of a 100% DOD discharge capacity measurement at a rate of 1C. 100% DOD is obtained by using the upper and lower voltage limits (end-of-charge and end-of-discharge voltages). The capacity test procedure is explained in the following: The cells are discharged at 25°C using a CCCV protocol (abort critera: end-of-charge voltage, I<C/10) with a rate of 1C (DOD=100%). After a rest of 30 min, the cell is charged to the end-of-charge voltage by a CCCV protocol at a rate of 1C. Charging is stopped at I<C/10 in the CV phase. After 5 min, the cell is again discharged at 1C by a CCCV discharge (abort critera: end-of-charge voltage, I<C/10). The described charge/discharge procedure is conducted two times. The last discharge step provides the real discharge capacity with respect to 100% DOD at time t and is used in combination with the real discharge capacity of the same cell at t=0 to calculate SOH(t) according to equation (1) (see also section 3). The SCU procedure is summarized in Table 1. The capacity test at a rate of 1C is similar to that used in previous projects [1,2,11,12]. However, in the MAT4BAT project, we use a CCCV protocol (instead of a CC protocol) to determine the discharge capacity.

Table 1. Sequence of tests during SCU

#	action
1	Equilibration of cell to 25°C for 8 h
2	OCV measurement
3	Internal resistance measurement at 80% SOC
4	1C discharge capacity (CCCV) measurement
5	Recharge in case of storage test
6	Equilibration of cell to ageing temperature

4.2. Extended check-up (ECU) procedure

The ECU procedure consists of the SCU described above and additionally C-rate capability, power capability at different SOC (from OCV/resistance measurements), Potentiostatic Intermittent Titration Technique (PITT) and Electrochemical Impedance Spectroscopy (EIS). The ECU procedure used in the MAT4BAT project is summarized in Table 2.

Table 2. Sequence of tests during ECU

#	action
1	Equilibration of cell to 25°C for 8 h
2	OCV measurement
3	Internal resistance measurement at 80% SOC
4	C-rate capability test (C/5, C/2, 1C, 3C, 5C)
5	Power Capability
6	PITT measurement
7	EIS measurement
8	Recharge in case of storage test
9	Equilibration of cell to ageing temperature

In literature, all the techniques applied here are often applied alone but not in combination for the same ageing state [5,12]. In contrast, measurements by the complementary methods C-rate capability, power capability, PITT and EIS in the MAT4BAT project will provide deeper insights into battery ageing.

5. Ageing procedures

5.1. Storage ageing

The calendar ageing will be done by storage of the cells at Open Circuit Voltage (OCV). OCV storage ageing is a common technique used by several battery researchers [1,13] and has the advantage to get information on the decrease of the OCV voltage during ageing. Furthermore, compared to float storage ageing [3,14] (calendaric ageing at a constant voltage), OCV storage ageing requires less channels and thus saves resources.

The regarded operation parameters affecting the ageing will be temperature and state-of-charge (SOC) [1,2] as shown in Table 3. If necessary, the parameters will be adapted for specific cell chemistries. After a CU, the cells are provided by the same amount of charge (Ah) as they had before the CU and ageing is continued.

Table 3. Varied parameters in storage ageing tests in the project

Parameters	Tested values
Temperature	5°C, 25°C, 45°C, 60°C
SOC	50%, 90%, 100%

5.2. Cycling ageing

For cycling ageing, the varied conditions are temperature, SOC window and charge rate as summarized in Table 4. These are the main effects affecting battery ageing during cycling ageing [1,2,6]. If necessary, the parameters will be adapted for specific cell chemistries. The SOC windows are chosen, to vary the depth-of-discharge (DOD) in a range of 80% as well as 100%. The temperatures used in the ageing tests of the MAT4BAT project are typical in the range above 25°C [1,2,12]. Recently, a systematic study with cycled 1.5 Ah cells carried out by ZSW in a temperature range between -20°C and 70°C revealed a different ageing mechanism at low temperature [6] involving Lithium plating [6,15]. The tests at 5°C in the MAT4BAT project will show if this is also the case for large cells that have about 10 times higher capacity and if there are differences between cycling and storage ageing.

Table 4. Varied parameters in cyclic ageing tests in the project

Parameters	Tested values
Temperature	5°C, 25°C, 45°C
SOC window	0-80%, 10-90%, 20-100%, 0-100%
Charge C-rate	1C, 2C, 3C

In the cycling ageing tests, the cells will be discharged by a Dynamic Stress Test (DST) similar to Profile A of ISO 12405-2 and IEC 62660-1 including CCCV for charge and discharge. The maximum power in the DST will be adapted with respect to the maximum power/C-rate of the tested cells and to the application of a battery electric vehicle (BEV). Proposed is 4C since this covers battery electric vehicles quite well. The sequence of the DST procedure will be the same for all cycling tests of a certain battery type. If the lower DOD value of the SOC window is reached during the DST, the cells will be recharged with a current specified in Table 4. Charging will be done by a CCCV protocol until I<C/10 in the CV phase and DOD of the upper limit of the SOC window is reached.

6. Summary

The described protocols are appropriate to find influences of the typical operating conditions affecting ageing of Lithium ion batteries for automotive applications. In particular, the tests include the modalities to find optimum parameters for the charge C-rate, temperature and SOC/SOC-windows during cycling and storage ageing. Ageing is quantified by measurements of internal resistance, OCV, capacity, C-rate capability, power capability, PITT and EIS.

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