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Measuring Reversible and Irreversible Capacity Losses on Lithium-ion Batteries

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Abstract — In this paper we present an innovative and precise way to calculate the available capacity in a battery. This quantity is essential to assess the ageing process during real use or ageing tests. The most common way to measure the battery capacity consists on a constant current discharge. It is quite simple to implement but very dependent of impedance and relaxation state of the battery. Consequently, this method is not suitable to quantify reversible and irreversible capacity losses occurring on batteries. We propose an indirect measure of available capacity that reduces the distortion caused by battery relaxation and impedance changes.

Keywords — Lithium-ion batteries, capacity losses, capacity fade, self-discharge.

NOMENCLATURE

CC	Constant Current
CE	Coulombic Efficiency
CP	Constant Power
CV	Constant Voltage
EoC	End of Charge
EoD	End of Discharge
RPT	Reference Performance Test
SoC	State of Charge

I. INTRODUCTION

Battery is probably the most sensitive element in the Battery Electric Vehicle powertrain system because of their cost and lifespan. To study its lifespan, accelerated ageing tests are necessary in order to understand the ageing mechanisms in batteries and the performance evolution within this Energy Storage System.

Battery performances change due to parasitic reactions even during rest periods: internal impedance will grow and capacity decay. Capacity losses can be reversible or irreversible. Reversible capacity loss is known as self-discharge whereas irreversible losses are known as capacity fade.

The aim of this paper is to provide an accurate way to measure capacity losses to be able to distinguish self-discharge and capacity fade of batteries.

When a battery is stored at a determined SoC, after a period of time, this value of SoC decreases for two reasons: self-discharge and capacity fade. The issue is to separate the

contribution of each phenomenon. When the reversible and irreversible losses are coupled, data collected in ageing tests could be largely inaccurate.

A direct way to measure self-discharge of batteries consists on a full discharge to know the current quantity of charge in the battery. The problem lies on the definition of full discharge. Several standards [1–4] defined full discharge as a CC or CP discharge to the lower voltage limit of the cell (U_{min}). When using U_{min} as the stop criteria of a discharge, the quantity of charge taken off the battery will depend of impedance: if a battery is fresh a CC discharge will be deeper compared to an aged cell. This measure is also dependent of the relaxation state of the battery.

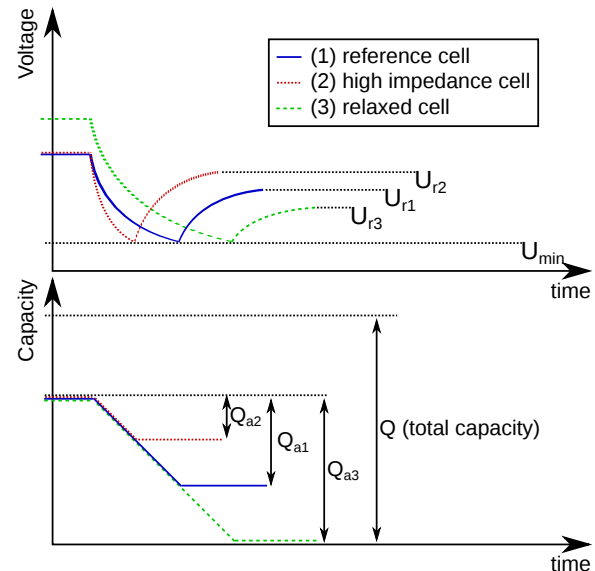


Figure 1: Influence of impedance and relaxation on available capacity measurement: (1) reference cell, (2) high impedance cell and (3) relaxed cell.

Figure 1 shows the influence of impedance and relaxation on available capacity measurement. In this example, three cells at the same initial SoC are discharged according to a CC with U_{min} stop criteria. Cell (2) has a higher impedance than cell (1). Cell (3) is more relaxed than cell (1), for example cell (1) was used then discharged and cell (3) was used then disconnected one day and then discharged. The

discharge is deeper for cell (3) than cell (1) and than cell (2): $Q_{a3} > Q_{a1} > Q_{a2}$. This effect is visible when looking at the voltage after a rest period: $U_{r3} < U_{r1} < U_{r2}$. From this simple example it could be seen that the measure of the actual capacity of a battery depends on impedance of the cell and on duration of eventual relaxation phase.

Consequently, the self-discharge tests defined in [1–4] do not give an accurate measure of self-discharge. It is necessary to find a measurement protocol that is free of the influence of impedance or relaxation and suitable to separate self-discharge from capacity fade. The innovative method exposed in this work is a solution to such problem.

II. DESCRIPTION OF USUAL PROTOCOLS FOR CAPACITY MEASUREMENT

In fact, self-discharge tests cannot be performed separately from calendar ageing tests, because ageing and self-discharge phenomena act in the same timespan.

A. Accelerated ageing tests

In calendar ageing tests, mainly two factors -T (Temperature) and SoC- affect the degradation of battery performances (capacity fade and impedance increase). Usually these tests consist in a test matrix ($m \times n$) of m values of T and n values of SoC. Every cell is stored in open circuit conditions at a couple of values (T, SoC) during a relatively long period, usually several weeks to months.

Periodically, a RPT (Reference Performance Test) is performed to know the current value of capacity and impedance. RPT is normally carried out at the same temperature independently of ageing conditions, e.g.: 25 °C, to be able to compare the performance evolution between every cell in the test matrix.

Basically the RPT is composed of four steps:

- (i) Available capacity measurement Q_a .
- (ii) Capacity measurement Q .
- (iii) Impedance measurements at several SoC levels.
- (iv) Reset SoC for ageing.

Step (iii) is not in the scope of this paper and will not be considered thereafter.

Capacity (Q) will decay over time because of irreversible capacity loss. However available capacity (Q_a) evolution is influenced by both: irreversible and reversible capacity losses.

B. Definitions and base equations

For better understanding, in this section some useful definitions are included:

- Capacity (Q) is the quantity of electric charge that can be stored (and then delivered) in a battery cell. This characteristic is affected by irreversible loss.
- Coulombic Efficiency (CE) is the relation between Q_{cha} and Q_{dis} . Due to parasitic reactions, discharged capacity (Q_{dis}) is lower than charged capacity (Q_{cha}). For lithium-ion batteries $CE > 0.99$ after several initial cycles [5]. In this paper, we will consider $CE \simeq 1$ thus $Q = Q_{dis} = Q_{cha}$.

- Available capacity (Q_a) is the quantity of electric charge that is currently stored in a battery cell. This characteristic is affected by reversible and irreversible losses.

- Discharged capacity (Q_d) is the quantity of electric charge that has been delivered by a battery cell since the last full charge.

- Self-discharged capacity (Q_{sd}) is the reversible loss of electric charge.

- Capacity loss is the irreversible capacity loss. In this paper, we will use Q_l for the losses occurring between two successive RPTs and Q_L for the cumulative capacity loss from initial capacity (Q_0).

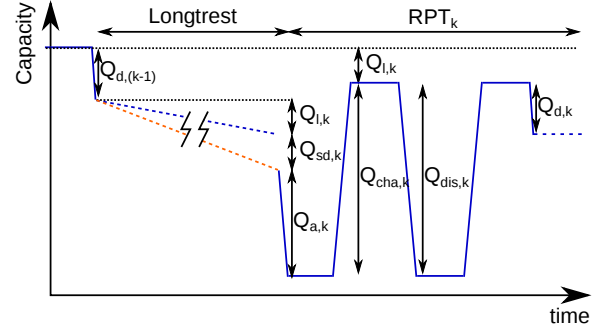


Figure 2: Capacity losses after long rest periods during the k^{th} RPT.

Equations 1 to 3 show the relations between these quantities. In these equations the index k refers to the values of the variables measured during the k^{th} RPT as illustrated in figure 2.

$$Q(k) = Q_a(k) + Q_d(k-1) + Q_{sd}(k) \quad (1)$$

$$Q_l(k) = Q(k-1) - Q(k) \quad (2)$$

$$Q_L(k) = Q_0 - Q(k) \quad (3)$$

C. Charging protocol

Full charge of lithium-ion cells is performed by a CCCV charge consisting in two phases (figure 3):

- (i) CC phase: Charge at a given current rate to the maximum voltage U_{max} .
- (ii) CV phase: Keep the cell on floating condition at U_{max} until the current drops to I_{end} (typically C/20). This phase ensures that the cell is completely charged regardless of impedance value of the cell.

D. Capacity measurement protocols

Generally the cell capacity (Q) is measured with a full discharge. Previously, the cell must be fully charged by using the charging protocol given above. Capacity can be measured by a CC or a CCCV discharge.

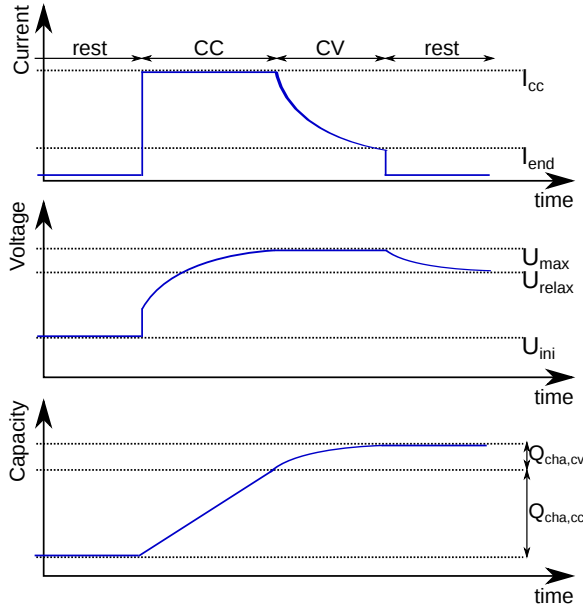


Figure 3: Charging protocol of a Lithium-ion battery.

1) *Constant Current (CC)*: The most common way is by a CC discharge with stop condition of U_{min} . The quantity of electric charge delivered by the battery in this manner (Q_{CC}) depends of the voltage drop due to the internal impedance of the battery. For example, Q_{CC} is higher in fresh cells or when discharged at low current rates or at high temperatures. Inversely, Q_{CC} is lower in aged cells or when discharged at high current rates or at low temperatures. Peukert law and other empiric laws [6] express capacity as a function of T and discharge rate (C). Other authors discussed about the influence of this dependence on SoC definition [7].

2) *Constant Current - Constant Voltage (CCCV)*: In the same way as for the charging protocol, a CCCV discharge consist in two phases:

- (i) CC phase: Discharge at a given current rate to the minimum voltage U_{min}
- (ii) CV phase: Keep the cell on floating condition at U_{min} until the current drops to I_{end} (typically $C/20$).

The quantity of charge in this way (Q_{CCCV}) is less impedance-dependent than preceding one (Q_{CC}).

III. INFLUENCE OF RELAXATION ON AVAILABLE CAPACITY MEASUREMENT

Available capacity measurement is the first step of a RPT. This measure can be performed by CC or CCCV discharge as indicated in the previous section. The direct way of measuring available capacity consists on simply integrate the current value over time during this initial discharge. An uncertainty of measure appears when CC discharge method is chosen because this measure depends on relaxation time and impedance.

To illustrate the relaxation effect, take for example one battery cell on which we perform three RPTs: RPT_0 , RPT_{1h} et RPT_{1d} (table I). The three RPTs have the same final Q_d .

Between RPT_0 et RPT_{1h} the cell must be disconnected (rest) during 1 hour. Between RPT_{1h} et RPT_{1d} the cell must be disconnected (rest) during 1 day.

Figure 4 shows the voltage and capacity evolutions for RPT_{1h} and RPT_{1d} during the first steps of the RPT:

- (i) Available capacity measurement Q_a .
- (ii) Rest.
- (iii) Full CCCV charge (Q_{cha}).
- (iv) Rest.
- (v) Full CC discharge (Q_{dis}).
- (vi) Rest.

Table I: Chronogram.

RPT_0	1 hour rest	RPT_{1h}	1 day rest	RPT_{1d}
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Because of the short period of time between these three RPTs, we can assume that no capacity losses occurred ($Q_{sd} = Q_l = 0$). According to this hypothesis and from equations 1–3, available capacity (Q_a) and total capacity (Q) must remain the same in each RPT independently of the rest time (1 hour and 1 day).

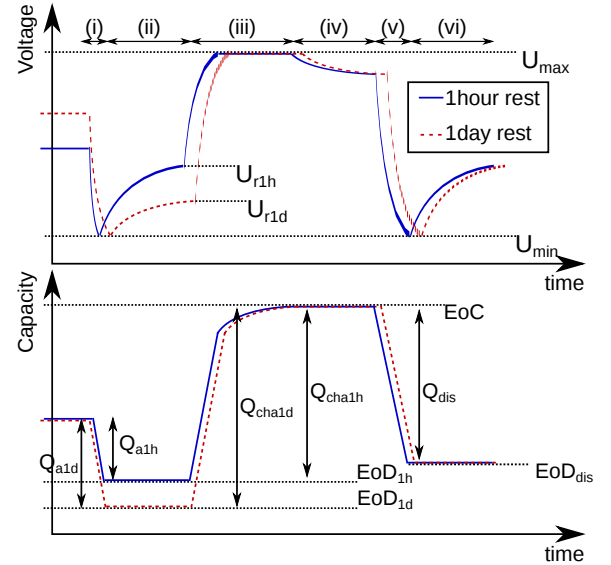


Figure 4: Relaxation effect on Q_a measurement.

However, cell is more relaxed in RPT_{1d} because of the difference in the rest time. Then, the initial voltage is higher (figure 4) and the stop criteria U_{min} arrives later than in RPT_{1h} . Hence, relaxation effect makes a greater Q_a in RPT_{1d} than in RPT_{1h} (step (i)). This is in contradiction with the preceding equations (1–3) and highlights the relaxation distortion in the CC discharge method. This distortion is quantifiable in figure 4 by taking a look on EoD (End-of-Discharge) states: $EoD_{1d} < EoD_{1h}$, i.e. discharge is deeper when relaxation is higher.

A full CCCV charge is performed after the initial discharge (step (iii)). The CCCV mode ensures that EoC (End-of-Charge) is independent of relaxation time. As the initial

discharge was deeper in RPT_{1d} than in RPT_{1h} , the charged capacity is greater in RPT_{1d} than RPT_{1h} :

$$\left. \begin{array}{l} EoD_{1d} < EoD_{1h} \\ EoC_{1d} = EoC_{1h} = EoC \end{array} \right\} \Rightarrow Q_{cha,1d} > Q_{cha,1h} \quad (4)$$

For the capacity measurement (full CC discharge, step (v)) the following relations are true:

$$\left. \begin{array}{l} EoC_{1d} = EoC_{1h} \\ EoD_{dis,1d} = EoD_{dis,1h} = EoD_{dis} \end{array} \right\} \Rightarrow Q_{dis,1d} = Q_{dis,1h} \quad (5)$$

The final part of the RPT is the SoC reset (full CCCV charge and partial CC discharge, Q_d) as in figure 2.

With a CC discharge method, it appears that the measurement of available capacity Q_a is dependent on the duration of relaxation phase. This makes difficult to use Q_a in any attempt to separate reversible and irreversible losses. On the contrary, the discharged capacity Q_{dis} is independent of any relaxation phase. Therefore, in this way, irreversible losses (Q_l) are measurable but reversible losses (Q_{sd}) are not.

IV. NEW METHOD TO SEPARATE REVERSIBLE AND IRREVERSIBLE LOSSES WITH NO INFLUENCE OF RELAXATION

This new method lies on an indirect way of measuring the real available capacity Q'_a . This quantity represents the measured available capacity if no relaxation effect had taken place. From figure 5 and with $CE = 1$:

$$Q_{cha}(k) - Q_{dis}(k) = Q_a(k) - Q'_a(k) \quad (6)$$

Then:

$$Q'_a(k) = Q_a(k) + Q_{dis}(k) - Q_{cha}(k) \quad (7)$$

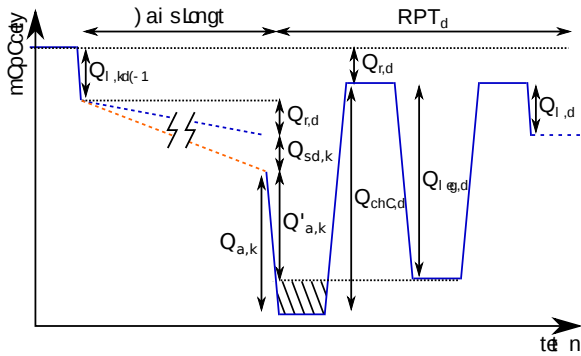


Figure 5: Indirect available capacity measure (Q'_a).

From 5 we also obtain the following identity:

$$Q_d(k) + Q_l(k) + Q_{sd}(k) + Q'_a(k) = Q_l(k) + Q_{dis}(k) \quad (8)$$

Then:

$$Q_{sd}(k) = Q_{dis}(k) - Q'_a(k) - Q_d(k) \quad (9)$$

Q'_a is an indirect measure of the available capacity which is independent of relaxation state of the cell and capacity losses (Q_l , Q_{sd}). Q'_a can be calculated with the equation 7

where $Q_a(k)$, $Q_{cha}(k)$ and $Q_{dis}(k)$ are directly measurable by current integration over time. In this way we can decouple the measure of available capacity from relaxation phenomena and separate reversible from irreversible capacity losses by using equations 9 and 2 respectively.

A. Experimental validation

In order to validate the new method to calculate the available capacity, some tests were carried out on three fresh cells KOKAM SLPB 283452H. The nominal capacity of this cells is 350 mAh and their chemical composition is NMC / graphite.

The tests consisted on:

- (i) Full CCCV charge
- (ii) Partial CC discharge to a target SoC (SoC_t)
- (iii) Rest for t_r
- (iv) Full CC discharge (Q_a)

Three values of t_r (5 minutes, 1 hour and 1 day) and three values of target SoC (10, 50 and 90%) have been tested. Discharged capacity measured in step (iv) would be different for each t_r according to the relaxation state. The full sequence of tests applied on three different cells is shown in table II. Capacity measurements at the beginning and at the end of the tests allow to check if any irreversible capacity losses occurred during the test.

Table II: Cell and target SoC (SoC_t) distribution on validation tests.

Test no.	Cell no.	SoC_t (%)	t_{r1}	t_{r2}	t_{r3}
1	1	10	5m	1h	1d
2	2	50	5m	1h	1d
3	3	90	5m	1h	1d
4	1	50	5m	1h	1d
5	2	90	5m	1h	1d
6	3	10	5m	1h	1d

Table III: Results of validation tests. Q_a and Q'_a are expressed in % of the nominal capacity.

Test no.	1	6	2	4	3	5
Cell no.	1	3	2	1	3	2
SoC_t (%)	10	10	50	50	90	90
Q_a ($t_r = 5m$)	9.51	10.06	49.19	49.35	90.12	89.09
Q_a ($t_r = 1h$)	9.71	10.25	49.25	49.37	90.07	89.01
Q_a ($t_r = 1d$)	9.76	10.28	49.13	49.26	89.42	88.37
ΔQ_a	0.25	0.22	0.12	0.11	0.70	0.72
Q'_a ($t_r = 5m$)	9.25	9.84	48.68	49.21	89.92	88.54
Q'_a ($t_r = 1h$)	9.30	9.83	48.74	49.21	89.94	88.53
Q'_a ($t_r = 1d$)	9.30	9.88	48.71	49.16	89.82	88.37
$\Delta Q'_a$	0.05	0.04	0.06	0.05	0.11	0.17
P_g	4.9	4.9	2.0	2.1	6.3	4.3

Table III summarizes the results of the validation tests. For every test, Q_a as well as Q'_a are reported in this table. Q_a is computed by integrating the current value over time during step (iv). Q'_a is computed following the equation 7. The uncertainty of each measure ΔQ_a and $\Delta Q'_a$ are computed as the difference between the maximum and the minimum value

obtained in one single test ($t_r = 5m, 1h, 1d$). Finally, the precision gain (P_g) is the relation between ΔQ_a and $\Delta Q'_a$:

$$P_g = \Delta Q_a / \Delta Q'_a \quad (10)$$

Precision gain is around 2.1 for SoC 50%, 4.9 in SoC 10% and 4.3 to 6.3 in SoC 90% (table III). This validate the new method as a more precise way to measure the available capacity.

B. Case study: Calendar ageing tests

In this work reversible and irreversible losses of several cells of SIMCAL project have been calculated. In SIMCAL project [8], 6 different technologies of lithium-ion battery cells have been tested in calendar ageing at three temperatures (30, 45 and 60°C) and three SoC (30, 65 and 100%).

The cell technology considered in this paper is KOKAM SLPB 70205130P. The nominal capacity for this type of cell is 12 Ah and the chemical composition is NMC / graphite.

As an illustration of our method, we applied it to the measured results of one SIMCAL test (ageing at 60°C and SoC 65%) for which the loss of capacity was 20% after 500 days of test. Figure 6 shows the result of self-discharge calculated by the classic method (Q_a), and by the new method (Q'_a). When using Q_a , relaxation and impedance increase distort self-discharge calculation giving more spread out results. In particular, "negative" self-discharge (meaning "self-charge") could appear when using the classic method which has no physical signification.

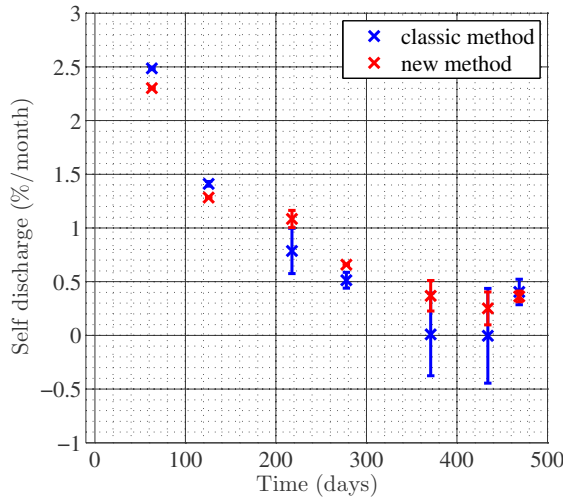


Figure 6: Reversible capacity losses in T60SoC65 KOKAM cells (self-discharge), using the direct way (blue) and the new method (red). The crosses represent the mean value between two cells and the error bars represent the max and min values.

V. CONCLUSION

The common way for measuring available capacity consists on counting the electric charge during a full CC discharge with a stop condition of U_{min} . The voltage limit strongly depends of the voltage drop caused by the cell's internal impedance and relaxation state. We propose in this work an indirect way to measure available capacity without changing the RPT protocol, by taking into account the full charge and full discharge following the first discharge.

The method has been validated by 6 tests on three different cells, three SoC levels and three relaxation times. From these experimental results, the new method is 2 to 6 times more precise than the classic way, especially at high and low SoC levels (90 and 10%). This precision improvement allows a better assessment of self-discharge as illustrated by an application of the method on results of ageing tests from the SIMCAL project.

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