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Task 3140 – Modelling test procedure definition

Deliverable 3100.5

Modeling Test Matrices for Li batteries and SC

Summary

This deliverable contains discussion of mathematical models available for batteries and supercapacitors (SC), having the main purpose of evaluating the battery State Of Charge (SOC) and State Of Health (SOH).

Different models, drawn from literature and from direct partners' experience, are presented and discussed. Finally, a reference model is chosen both for the battery and the supercapacitor, with specific attention devoted to the models complying with the specifications for both storage systems that will be found out by task 3110 (and reported in deliverable 3100.1).

In the final part of the deliverable, the test matrices needed to obtain the parameters of the chosen models are detailed.

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Nomenclature

1. Acronyms

DC Direct current; design capacity
FCC full charge capacity
LFP lithium-iron phosphate (a cell chemistry)
MST Multiple-Step test
NCA lithium cobalt aluminium (a cell chemistry)
NMC nickel manganese cobalt (a cell chemistry)
OCV Open-Circuit Voltage
SC Super-Capacitor
SOC State-of-Charge
SOH State-of-health

2. Other quantities

C electric capacitance (of the battery or supercap cell equivalent circuit)
C_{n} rated battery capacity (e.g. in Ah)
E_m Main-branch electromotive force
I_m Main-branch battery current
I_p Parasitic battery current
K K-factor for capacitance voltage variation in supercapacitors
K_n rated value of K-factor
Q_e extracted charge
R_0 Algebraic battery internal resistance
R_{i} (i>0) i-block battery internal resistance
C_{i} (i>0) i-block battery internal capacitance
C_n Nominal capacity (batteries), nominal capacitance (supercapacitors)
θ inner cell temperature
θ_{a} ambient temperature
V_{oc} Open-circuit voltage *(similar to OCV)*
Z_{m} Main-branch battery internal impedance
Z_{p} Parasitic-branch battery internal impedance

Introduction

This deliverable is prepared in the framework of task 3140 of WP 3100, with inputs from the other tasks of WP 3100.

The DOW programme for this task was as follows:
Arsenal, ENEA, Volvo and UPisa will collect and analyze models for determining SOC (state-of-charge) and SOH (state-of-health) of Li batteries and SC. In addition, mathematical models will be also looked as optimal control strategies for improving cycle life and safety of the storage systems. The results of this task will be the definition of a complete set of tests (test matrices) on cells and/or modules aimed at developing and validating storage system models and advanced control strategies.

This document follows the pattern indicated by this programme, and first concentrates on modelling, then on the test matrices required to validate the adopted models, and to find actual numerical values for the model parameters. It has been decided to use the simplest versions of the available models, just because in practice it was seen that the higher complexity implied large management burden while bringing just negligible or little increase in precision. Indeed when a lot of tests are used to estimate battery parameters, typically at the end of them the battery has changed its behaviour from the one it had at beginning, and therefore no increase in precision is obtained.
Inputs from other tasks will be as follows:
from task 3110: detailed specifications of batteries and SCs that are going to be used
from task 3130: input on tests required for SC. Cooperation between task 3130 and 3140 will be close.

Technical progress

Modelling Li batteries

General

To understand well how to size and manage vehicle lithium batteries, suitable mathematical models of their behaviour must be available, as well as and techniques to experimentally evaluate the numerical parameters to be inserted in those models to obtain realistic reproduction of the battery's behaviour.

General models, normally are mathematical systems that, when subjected to the actual battery current and environmental temperature, are able to give as output realistic profiles of the battery's voltage, and when subject to the battery voltage (as well as the temperature again) give as output realistic profiles of the battery's current.

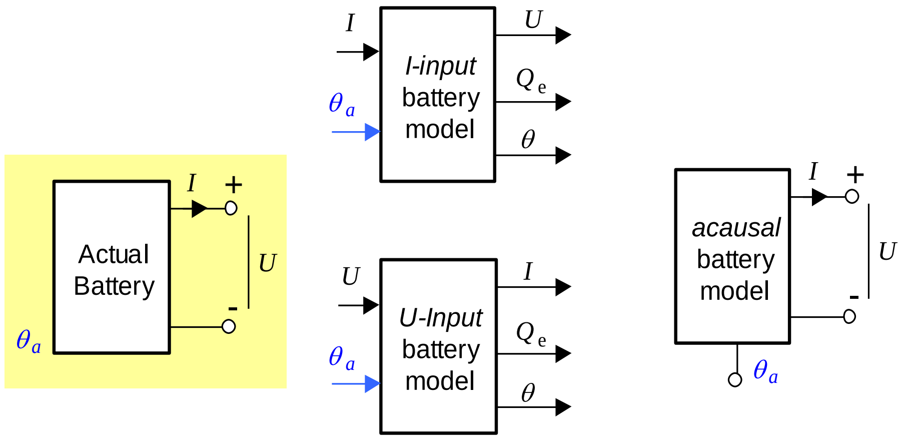

Figure 1. Different kinds of models of the battery's electric behaviour.
(left: battery as black-box; centre: causal models, right: acausal model).

As happens to every system modelling battery modelling can be approached basically in two ways (fig. 1): causal modelling, that requires to define ahead which is the input and which is the output and *acausal* modelling, that defines a set of equations that just describe the interaction of the battery with the external world [1, 2]. Acausal battery models are usually expressed in terms of equivalent electrical networks, and have the advantage that, in simulations as well as at run time, no beforehand choice must be made to what should be the input and what the output.

The difference in meaning of the arrows reported in the sections of causal and acausal models (such as reported in fig. 1) is rather obvious, but very important: in causal models, such as those reported at the centre of figure 1, arrows indicate actual the flows of different signals; in acausal ones, the arrow reported next to the current indicates just a references to evaluate the numerical value of the current (that is a positive number when in concordance with the arrow), just as the polarities give a reference for the evaluation of the actual sign of the voltage.

This section contains a discussion of the mathematical models available for SOC and SOH evaluation of lithium batteries, with indication of techniques to evaluate the numerical parameters to be determined.
Both models that can be found in literature and that are specific know-how of the project partners will be dealt with.

While, as said earlier, these general- purpose mathematical models can be used to evaluate the battery performance in on-line and off-line simulators, more specific models, because of their importance, are needed to estimate the battery's state Of Charge (SOC) and State Of Health (SOH).

It often, but not always, happens that SOC estimators are derived for general-purpose mathematical models, while normally different knowledge is needed to evaluate the battery SOH, since it implies estimation of modifications of battery behaviour during its life, while causal and acausal battery models of their electrical behaviour are normally time-invariant.

For either general purpose, and SOC-specific and SOH specific battery models, it is mandatory to have at disposal a procedure to determine the model numerical values so that the model is not just a generic representation of battery's behaviour, but models the actual battery considered.
The process can be discussed with reference to fig. 2, that refers, for simplicity just to the case models of the generic battery electric behaviour (not SOC or SOH specific models).

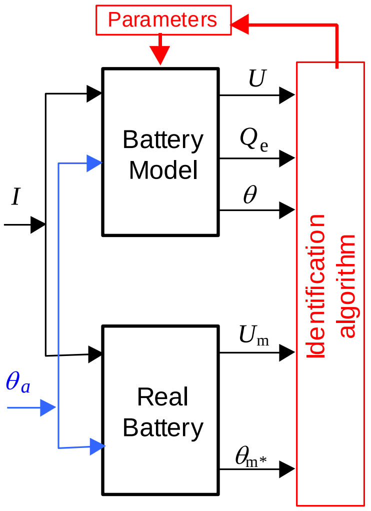

Figure 2. Parameters identification for a model of battery electric behaviour.

Electric behaviour models

A list of recent papers relating to battery electrical modelling is reported in the Reference chapter. Although this list concentrates to different kinds of lithium-based batteries, some papers related of other types of batteries (more often the lead-acid ones) are enclosed, whenever the models present general structures that might be easily enough be adapted to lithium- batteries (of different kinds).

A lot of the models found in literature are bases to equivalent electrical networks, whose general structure is of the kind shown in fig. 3.

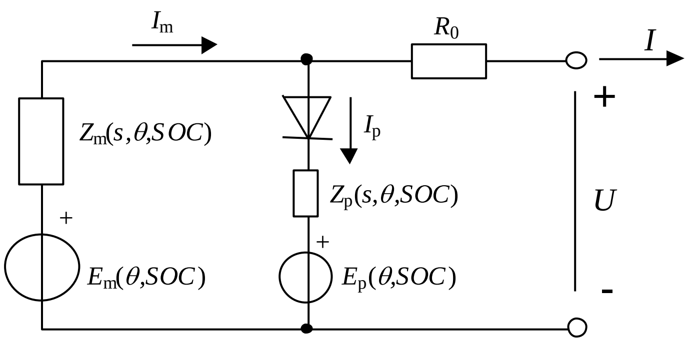

Figure 3. A generic electrical network often used to model electrical behaviour of different kinds of batteries.

In fig. 3 there are:

- the variable s is the Laplace variable, indicating the dependence of the reported impedance on frequency.
- the branch, containing the battery electromotive force E_m, that represents the main, reversible reaction of the battery: the charge stored in the battery during the charge process is the time integral of the current I_m entering that branch. This branch is modelled as an electromotive-force, function of the battery state-of-charge SOC and the electrolyte temperature supposed uniform) T., in series with an impedance, again function of SOC and temperature;
- the branch, containing the battery electromotive force E_p, that represents the other, parasitic reactions inside the battery, that are not associated to the charge accumulation inside the battery. For instance, for lead-acid batteries, the parasitic reaction is constituted by the water electrolysis that occurs at the end of the charge process. This branch also contains an electromotive force in series with an impedance, in general both function of frequency, SOC, temperature; the diode indicates that that branch always dissipates power (since E_p is always positive in value).

In large regions of the battery operating states the parasitic reaction effects can be neglected. For instance, in the case of lithium batteries it can be neglected during the discharge process and during the first part of the charge one (for instance, all the models surveyed in [19] neglect parasitic reaction effects).
For this reason, a simplified model of the kind shown in fig. 4 can be used.

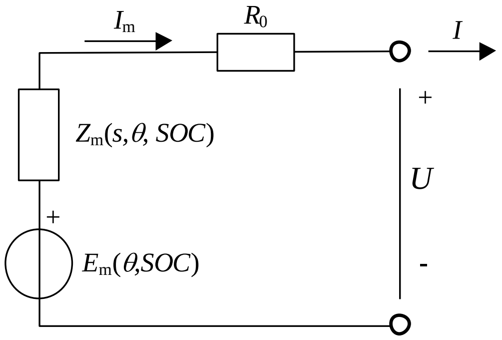

Figure 4. Simplified battery electric equivalent (neglecting the parasitic reactions).

The model shown in fig. 4**Error! Bookmark not defined.** can be used for batteries that show a very high coulombic efficiency: that means that the parasitic reactions have little influence on the battery behaviour.
If the battery, for a given state-of-charge and temperature, has a linear behaviour, the branch impedance is a function of the Laplace variable s only. In several battery types, the lithium battery included, however, more complex modelling is necessary, as will be detailed in the following.
In case of modelling of the Z_m as a function of Laplace variable s very often the dependence $Z_m(s)$ is rendered explicit using networks of parameters depending only on state-of-charge SOC and temperature T; just to give an example, in [9] the main branch of a Lead-acid battery model is expressed in terms of resistors and capacitors, as shown in fig. 5.

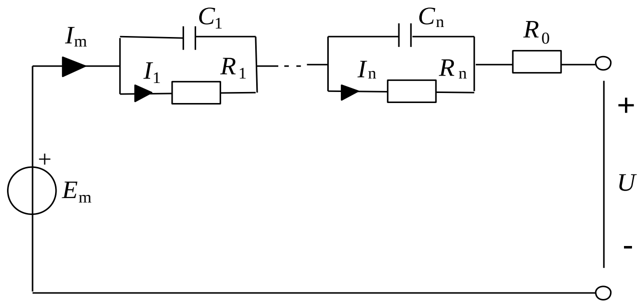

Figure 5. Electric network applicable when parasitic reactions are absent (parameters depend in general on SOC and inner battery temperature).

It must be however said that a large number or R_k-C_k blocks makes it very difficult to evaluate with experiments the numerical parameters of resistances and capacitances, according to the scheme of fig. 2. A reasonable compromise between quality of model and ease of usage is to use *n*=1, i.e. to adopt for evaluation of the battery electrical behaviour the electric network shown in fig. 6. The functional dependence of electrical parameters on temperature and SOC will depend on the particular lithium battery considered and will be inferred as part of the research, based on experimental evaluation of the considered cells.

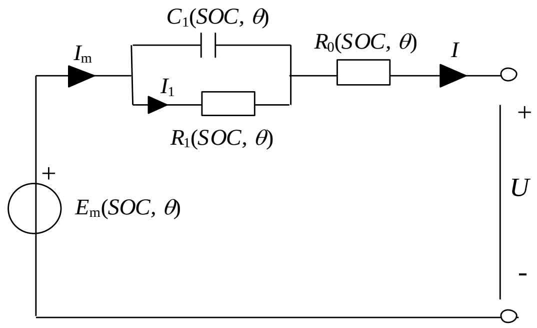

Figure 6. Electric network chosen for HCV lithium battery modelling (dependence on SOC, T and numerical parameters to be determined based on lab tests).

SOC models and evaluation

The State Of Charge of a battery can be estimated based on electrical models, as those discussed in the previous section, or with ad-hoc techniques.
In principle, the use of a well-tuned equivalent electrical network for a battery gives gratis an SOC evaluation: is the well-tuned battery model is subject to the current measured on the actual battery, it reproduces the inner battery behaviour, and the SOC can be simple read in the model. However this process has a lots of difficulties linked to the very non-linear and complex behaviour of the battery.

Another very important problem to be tackled is the issuing of a clear definition of “State-of-charge”.

Everyone agrees that SOC is an indicator that should be 1 (one) when the battery is full, and 0 (zero) when empty. However, the complexity of battery behaviour renders things more difficult.

A typical behaviour depicting this difficulties is as follows if a battery:

1. is first discharged at a high rate current (e.g. a current factor I/Cn 1 A/Ah)
2. is then put at rest for a rather long time (e.q. one hour)
3. it is discharged again

in phase 3 it will be able to still deliver non-negligible amounts of energy.

So when a battery is really fully discharged must be defined by convention.

This issue might be treated considering the capacity of a battery, i.e. the charge it can deliver under given conditions, to be a function of ambient temperature and discharge current time profile.
To keep things reasonable easy, a lot of studies consider the battery capacity under constant ambient temperature and discharge current, and consider the capacity itself to be a function of both:

$$C = C(\theta, I)$$

It is important to note that the battery capacity, i.e. the charge the battery can deliver under given conditions, is an *always decreasing* function of the discharge current: the lower the discharge current, the higher the delivered charge.

As a consequence of all this a SOC definition should be made according to the conditions in which a battery is supposed to be discharged.

All the SOC definitions can start from the charge a battery is able to deliver under given conditions, starting from battery fully charged) (cfr. [9, 22]):

$$SOC(t) = 1 - Q_e(t)/C \quad \text{where } Q_e(t) = \int_0^t I(\tau)\, d\tau \qquad (1)$$

(the battery is supposed to be full at *t*=0)

It is observed that for lithium batteries the integral of the battery terminals current I can be reasonable used instead of the main reaction current I_m because the coulombic efficiency of these batteries is very high and therefore the I_p can be, for simplicity sake, be neglected.

HCV partners are considering the following two definitions, among which they will choose one to be used onboard the Power Management Module of the future Vehicle prototypes:

<u>definition 1</u>: $SOC_1 = 1 - Q_e / C(0, \theta)$ (2.1)

With definition 1 reference is taken to the maximum charge the battery can deliver at the given ambient temperature,

<u>definition 2</u>: $SOC_2 = 1 - Q_e / C(I_{av}, \theta)$ (2.2)

With definition 2 reference is taken to the charge the battery can deliver at the given ambient temperature, under given average discharge current.

It is explicitly noted that definition 2 includes the one used by some authors (e.g. [22]):

$$SOC = SOC_0 + \frac{1}{C_n}\int_{t0}^{t} -(I - I_p)d\tau$$ (SOC_0 is $SOC(t_0)$, C_n is the rated battery capacity)

and is compatible, when coulombic efficiency is set to unity to that from [25]:

$$SOC = SOC_0 - \frac{1}{C_n}\int_{t0}^{t} \eta I d\tau$$ (η is the coulombic efficiency)

Usage of integral of the current.

The definition itself of SOC (by means of definitions (1) and (2.x)) gives an immediate hint on how SOC can be on-line estimated onboard hybrid vehicles:

Simply the battery current $I(\tau)$ is measured continuously of time τ, its integral numerically computed so that Q_e is determined using (1) and correspondingly SOC_1 or SOC_2 can be computed from (2).

The problem with the usage of the integral of battery current is that this evaluation is subject to several causes of errors that accumulate with time (well resumed in [7]):

- noise and errors on the current measurement (including sensor precision, resolution, Digital-to Analog conversion, rounding errors)
- errors due to numerical integration
- errors due to the non-unity coulombic battery efficiency (i-w the non –zero I_p current in the above-discussed equivalent battery electrical networks).

Therefore some means must be provided for error correction. Since the SOC is based on an integral quantity, and errors accumulate with time, error correction can be made also at discrete times, since between these times it can be assumed that all the causes of errors have had a negligible effect on the SOC.

Error correction based on a Luenberger state estimator

The availability of a suitable battery model allows a Luenberger state estimator to estimate the inner battery SOC.

The technique is still to evaluate the extracted charge by integration of the battery current and correcting the resulting value somehow.
The Luenberger state estimator allows to perform this correction continuously, as the actual and predicted battery voltages are compared to each other and the resulting error activates a feedback on the charge computed. Details on this technique can be found in [20].

The principle logic of this SOC evaluation is shown in fig. 7 drawn, with simple graphic modifications, from [20].

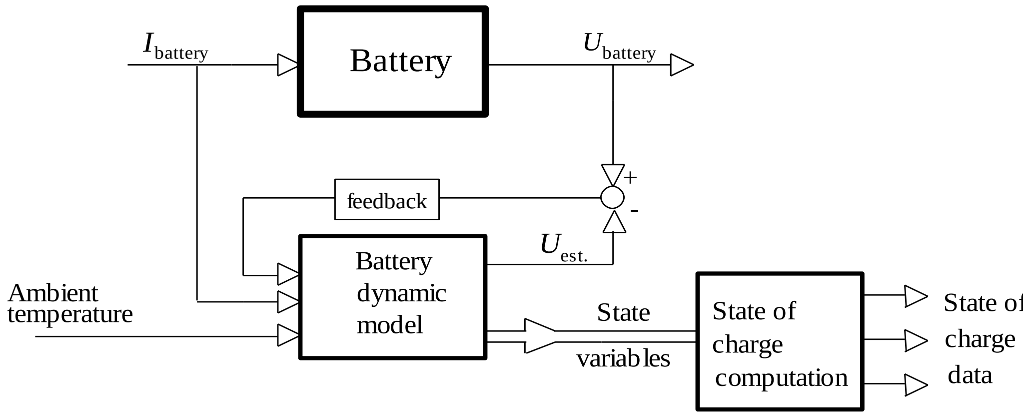

Figure 7. Principle scheme of a Luenberger battery state observer.

Basic comment: this method, that appeared to be very promising at the time of paper [20], is not very used and is not quoted in more recent papers.
Probably the reason resides on the difficulty in realising a battery model accurate enough for this method to give good results.

Error correction based on SOC-OCV relationships

Another way to perform this error compensation, that can be very effective with some lithium battery types, is the use of a correlation between SOC and Open Circuit Voltage (OCV).

A possible test to evaluate this correlation is shown in fig. 8 which reports actual experimental data. The battery is first charged (positive current), then subject to partial-discharge – rest phase cycles. At the end of each rest phase the voltage is independent on previous battery current, and is a good indication of battery state-of-charge.

The test shown in figure is able to give a lot of information on the battery, much more than only the OCV-Correlation curve. For its importance it is given in this document a name of its own: it will be called **Multiple-Step Test (MST)***. This test can be performed exactly how is reproduced in fig. 8, or starting from a fully–discharged battery and using charging current steps, instead of discharging current steps. Therefore the MST can be charge-based and discharge –based.*

From the knowledge of the current drawn from the battery at each step and the measure of the corresponding rest voltage, the correlation curve shown in fig. 8 can be derived.

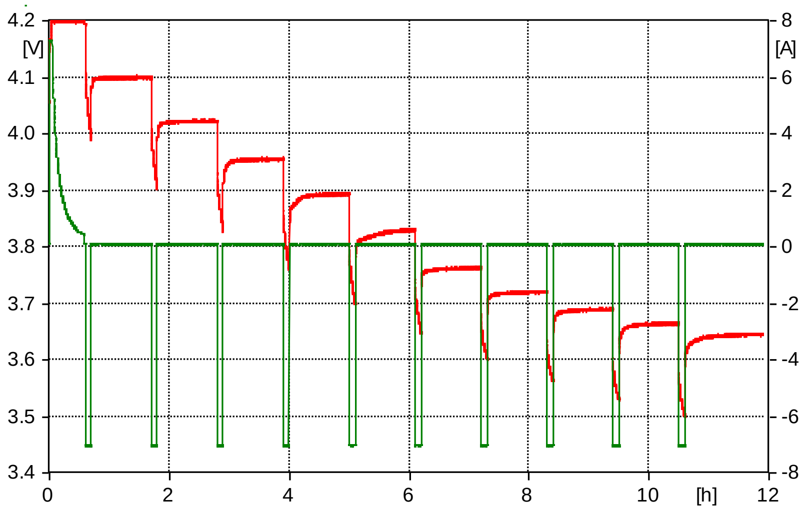

Figure 8. The discharge-based Multiple-Step Test.
Green: current; blue: voltage; horizontal scale :time (s).

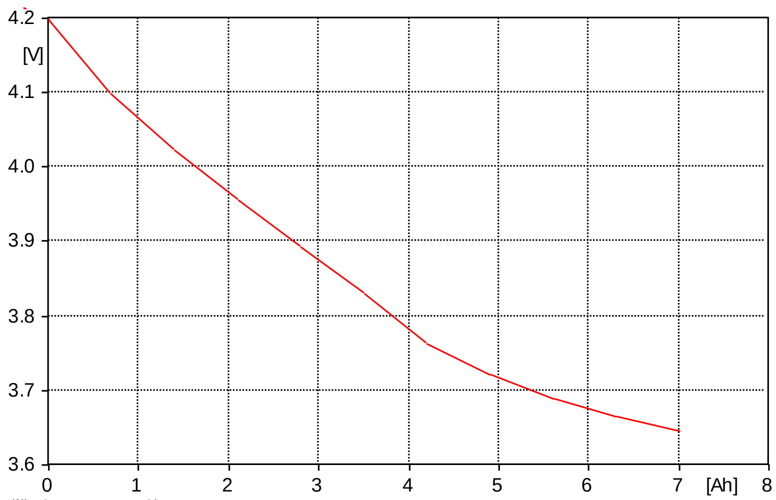

Figure 9. OCV-SOC correlation for a lithium battery, from results of fig.8 .

When the used battery shows an OCV-SOC correlation of the type shown in figure, monotonically decreasing this curve is a very effective and simple way to correct the SOC errors accumulated during current integration.

However, the following issues must be tacked:

- some lithium batteries (especially the $LiFePO_4$-based) might show significant hysteresis phenomena, so that the OCV_SOC correlation curve is significantly different if the test indicated in fig. 8 is made while charging the battery instead of discharging
- accurate evaluation must be made of the maximum time between two consecutive error correction actions based on OCV-SOC correlation: this time is typically in the

hours range, but depends on a lot of details of the actual system (sensor characteristics, ADC conversion, actual battery current profile, etc.)

Some batteries, however can hardly take advantage of this error-correction method, because of the shape of their OCV-SOC correlation curve.
A battery from Magna, for instance, a good candidate to be used onboard prototypes, has the OCV-SOC correlation shown in fig. 10. The following issues make it very difficult to use this curve for error correction:

- there is a very large zone in which the curve is very flat, showing no OCV variations over wide SOC ranges
- hysteresis is very marked

For instance, a OCV reading of 3,3 V can well correspond to a SOC of 30 to 65%.
Moreover, as Magna states, the battery should be maintained SOC in the range of 30%-60%, exactly the zone in which the OCV gives no usable information on SOC:

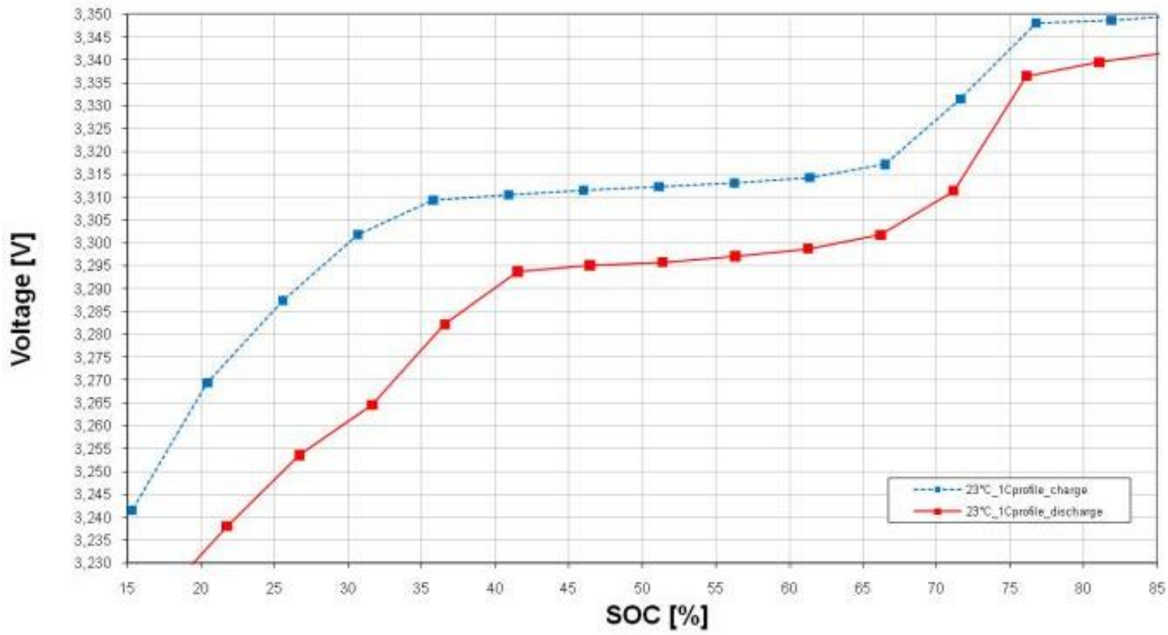

Figure 10. OCV-SOC correlation curves for some Magna Lithium batteries.

Basic comment: this method is very often quoted in literature and has been successfully adopted by University of Pisa. However, as already noted, in case the OCV-SOC correlation is characterised by big hysteresis and large parts of near zero slopes, such that the ones of fig. 10, this method cannot be applicable, except in cases in which the SOC indication has interest only in the extremes of its range, i.e. for SOCs near 0 or 1.

In general, $LiFePO_4$ batteries suffer the following drawbacks, which make task of modelling its SOC more challenging:
(1) a very flat OCV vs. SOC curve for most of the operating window; and
(2) a pronounced hysteresis phenomenon.

Paper [36] demonstrates use of a very simple battery model to emulate the SOC of a $LiFePO_4$ battery, even with the above-mentioned drawbacks. This model however operates at a constant temperature. This model could be used to estimate the SOH accurately.

Other error correction methods

Other methods have been proposed to evaluate the battery SOC, or a combination of SOC and SOH. these are surveyed in [22]. Mainly they are:

- *impedance spectroscopy*: the behaviour of the inner impedance has a good correlation with SOC; this method has been proposed with acceptable accuracies (errors within ±5%) for nickel/metal hydride cells. In principle it may be promising also for lithium cells. The main disadvantage is the impedance curves are strongly influenced by temperature effects. Therefore the best utilisation of this method is with batteries in temperature controlled environments.
- *internal resistance*. This method is related to impedance spectroscopy; the “resistance” *R* is conventionally defined as $R = \Delta U / \Delta I$, i.e the variation of voltage as consequence of a current step. This variation is evaluated after a given time after the step. In case this time is below 10 ms, it might be said that only ohmic part of the inner impedance is measured, and this differentiates this method from impedance spectroscopy. This method gives a combination of SOC and SOH, although it has been used and discussed mainly for lead-acid batteries.
- *Kalman filters*. Kalman filters can be seen here as algorithms to estimate the inner states of any dynamic system. Therefore the Kalman filter approach is similar to the Luenberger state estimator previously discussed. As for the Luenberger case, the Kalman filter approach requires the availability of a good model of the considered battery.

Some summarising remarks

The analysis performed in this section of the available methods for SOC determination have shown that:

- the measure of the charge exchanged by the battery is a parameter that must always be taken into consideration. It is very simple and cheap to use, and it is particularly suitable for batteries with very high coulombic efficiencies, such as lithium batteries. However, it cannot be used without some correction algorithm, since all the causes of errors accumulate during the battery current integration;
- correction of the Ah-based SOC evaluation can be successfully made with lithium batteries having modest hysteresis effects and reasonably high OCV–vs– SOC slopes; in other cases it might only signal big deviations from the central region of SOCs This method will be called Ah-OCV
- other algorithms, (e.g. internal resistance, impedance spectroscopy, Luenberger and Kalman state estimators, fuzzy logic or neural network based estimators) are much more complex to use, but might be necessary in the cases in which the OCV-SOC curve does not suit the requirements of SOC estimation. One definite drawback is that they have mainly been studied and experimented for lead-acid batteries, so more study is needed to use them in a commercial realisation based on lithium batteries.

For HCV the Ah-OCV method is provisionally chosen; in parallel kalman filtering techniques are taken into consideration. the final choice will depend on the actual lab results on the cells.

Estimation of error with the Ah-OCV

In case a OCV-SOC correlation of the type reported in fig. 9 is found, the Ah-based method would operate satisfactorily due to the sufficiently high slope of the OCV-SOC correlation and the high coulombic efficiency of lithium batteries.

For this method the main cause of error is due to the integration of current, while the reliability of SOC-OCV correction is considered to be total.

The Ah evaluation can be made using rather precise current sensors, since only two sensors are to be provided per vehicle, and therefore their usage will not cause large costs on the vehicle.

the considered A123 battery is expected to have a maximum current of 200 A; a sensor with a precision of 0,05% can today be accomplished for DC currents, provided that periodic offset reset is done. During vehicle operation sensor offset reset can be performed when the vehicle is stopped, e.g. every night.

Such sensors would therefore have a maximum error on the current measure of 0,1A; imagining to make the OCV-SOC error correction each 6 hours, the maximum expected SOC error immediately before the correction would be below 14%. It is not so good, but acceptable for a hybrid vehicle. After the correction the error should be negligible.

Estimation of the Kalman filter option

In case, however the actual OCV-SOC correlation curves are found to be more problematic such as that reported in fig 10, the Ah-OCV technique is totally unacceptable and kalman filtering based ones will be tried. Errors on SOC cannot be estimated by now.

Obviously enough, in case the Kalman filtering technique shows to be able to produce errors that are below the one estimated using the Ah-OCV technique, or in case the precision is comparable at lower costs, it could be used even in case of favourable OCV-SOC correlation.

SOH models and evaluation

Accurate prediction of the remaining battery capacity, as the battery ages with time is one of the most important requirements for the battery power management module in a HEV. It must provide an accurate indication to avoid causing irrevocable damage to the battery through battery overcharging, overheating etc, and to favour planning battery substitution on time.

However, this task is made difficult with the battery aging dependent upon a number of factors..

There are different types of cathode materials used for lithium ion batteries –$LiCoO_2$, $LiFePO_4$ (LFP) or mixed $LiNi_xCo_yAl_zO_2$ (NCA), $LiNi_xMn_yCo_zO_2$ (NMC) etc. Unfortunately, there is very few literature on State of Health (SOH) of lithium batteries, and lesser for olivine based lithium batteries, such as LFP, which is one of the batteries under consideration. These olivine based cathode materials for lithium batteries are more promising instead of cathodes based on rare-metals or other conventional cathodes in terms of power density, costs, thermal stability, environmental friendliness and life cycle. However, their energy density is lower than other Li batteries due to lower operating voltage (2.5 – 3.6V). Another unusual feature of LFP based electrodes is their constant Open Circuit Voltage, which is nearly independent of the SOC. In fact, the OCV changes less than 100mV in the range of 20-80% SOC [35].

Definition of SOH

First of all, it is necessary to clearly define the *State of Health (SOH) concept* for this document. Due to aging, the *full charge capacity (FCC)* may be significantly less than the *design capacity (DC)*, where DC denotes the FCC of a newly manufactured battery. Then, SOH is defined as the ratio of FCC of a aged battery to its DC.

There are, however, many factors which are important, when trying to predict SOH or evaluate it based only on the stress the battery has undergone, including the periods of charging / discharging, periods of rest, test cycles, ambient temperatures, SOC operation window etc.

Literature review

Though each Li-ion chemistry may behave differently, there are a few basic phenomena, which account for the general aging phenomena in Li ion batteries. These are summarised in Table 1. However, it is mentioned that there are some contradicting properties as well.

Table 1. Li-ion aging effects as reported in literature.

Cathode	Characteristic
$LiCoO_2$ based	Active lithium loss is the main decay mechanism [33] Strong increase in cell resistance [33] Temperature decrease accelerates fading rate [33]
NCA	Resistance increases dominate cell aging behaviour [45].
$LiFePo_4$ / natural graphite	Active lithium loss is the main decay mechanism; but there is a lack of impedance or low frequency resistance increase. However, there is a slight increase in high frequency resistance [43].

Paper [29] validates the relationship between capacity decline and change in impedance at various frequencies of a battery, and provides the possibility of using a low-cost battery impedance monitoring device to estimate capacity loss. The model proposed by Rong et al. [30] is accurate only for fixed average currents drawn by the battery, and hence cannot be applied for this project.

The majority of the considered papers describe the mechanisms associated with SOC and SOH variation; some of them, however, namely [26, 30, 39, 41] deal with techniques for on-line determination of these parameters and thus are more interesting for HCV purposes.

The underlying chemical changes which cause the process of aging have been explained in [32, 33, 35, 43]. However, these are rather abstract and cannot be formulated directly into models for SOH of lithium batteries.

Method for determining SOH

As discussed above (in *Other error correction methods* paragraph), there are two predominant approaches to estimate the SOH of an olivine based lithium battery:

a. Using battery impedance measurement: ambient temperature affects the battery impedance, especially at low frequencies. In environments of uncontrolled tempe-rature, the solution is to use high frequency impedance measurement (between 10 and 100 Hz) for determination of the ohmic resistance, or its reciprocal which is the conductance. In this frequency range, the influence of temperature is less than 10% of the absolute impedance/conductance value [42]. At frequencies above 10 Hz, the impedance parameter is close to the ohmic resistance of the battery cell.

b. using ohmic resistance of a battery: it may be defined as:

$$IR = \Delta V / \Delta I \qquad (T \le 10ms) \tag{3}$$

i.e. if ΔV is instantaneously measured $(T \le 10ms)$, only the ohmic effects are involved. Preliminary studies in using ohmic resistance to predict SOH have been successful [26].

The method that will be adopted in the HCV experience will be chosen after analysis of the experimental results on cells and batteries

Modelling Supercapacitors

General

Supercapacitors store energy in an electrostatic field and are characterized by higher power and lower energy density than traditional electrochemical batteries. Due to the absence of electrochemical reactions during the charging and discharging processes, supercapacitors are suitable for continuous charging and discharging cycles, also characterized by a high dynamic. A model able to properly represent Supercapacitors behaviour in each conditions, from dc up to dynamic of several hundreds Hz, is needed.

Models in literature are based on an equivalent electric circuit able to represent the voltage/current profile when a current/voltage profile is imposed to its terminals. In modelling two general approaches are followed: one based on means of analysis in time domain [48]-[54], the other in frequency domain [55]-[57]. The attention has been focused on a model with the following characteristics:

- to represent the full dynamic of the device;
- a low number of independent parameters easy to determine with simple test or with the information contained in the manufacture's datasheet
- the possibility to easy adapt the model according to the dynamic to represent.

Due to the technology and in particular the very limited influence of the temperature on the electric parameters variation, the estimation of state of charge (SOC) of the device is mainly related to the voltage across its terminals.

Supercapacitors electric Behaviour models

In the SC Modelling literature survey (see References), the list of current scientific articles regarding supercapacitor models is reported.

The attention is focused on [55] representing a full frequency range model based on the Electrochemical Impedance Spectroscopy. As shown in Fig. 11 the frequency response of a supercapacitor cell at different polarization voltage is reported. It is clear how the internal resistance and capacitance of the device are dependent on both the polarization voltage and frequency.

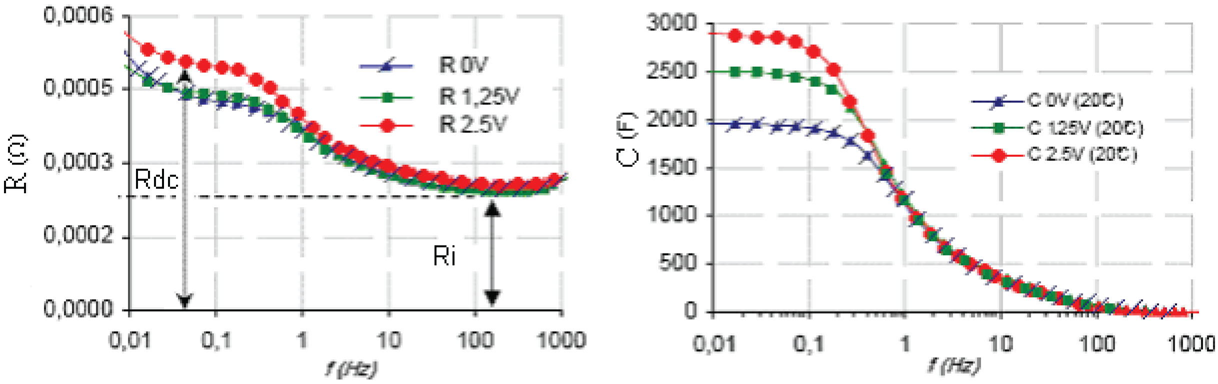

Figure 11. Frequency response of Maxwell BCAP0010 cell (2700F@2.7V).

Besides this, the effect of charge redistribution and self discharge has to be taken into account.
The model, able to represent all these effects, is represented in fig.12 [55].

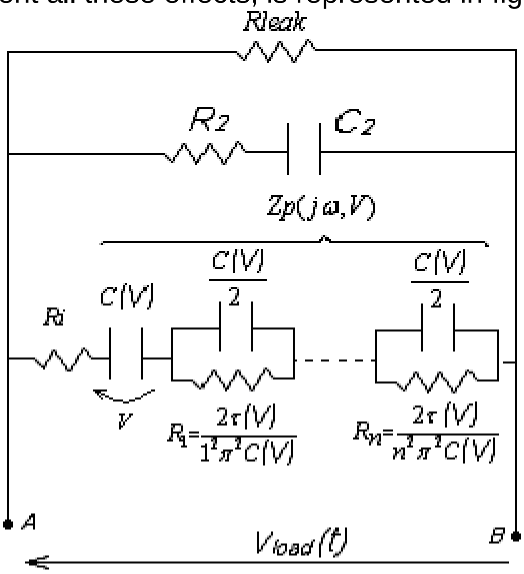

Figure 12. Complete electric model of Supercapacitors.

It consists of three branches: the first branch consists of the series connection of a resistance R_i, a capacitance C(V), and a series of "n" parallel RC branches representing the transfer function $Zp(j\omega,V)$ [57]. This branch takes into account the frequency response of the device in the frequencies ranging from 10^{-2} to 10^{3} Hz (high frequencies).
Despite of the number of elements, the number of independent parameters of the first branch is only 3 and in particular:

- Ri is the resistance of the device at high frequencies (several hundred Hz);
- $C(V)=C_0+K\cdot V$ is the capacitance of the device at low frequencies (0.01-0.1 Hz) as linear function of the polarization voltage (C_0 and K constant).
- $\tau(V)$ is a time constant equal to $3\cdot(R_{dc}-R_i)\cdot C(V)$, with R_{dc} the resistance of the device at low frequencies (0.01-0.1 Hz).

As shown in [55] and in *Supercapacitor test matrices* paragraph, all these parameters can be determined by a simple charging test and by the information contained in manufacturer's datasheet.

For frequencies tending to 10^{-2} Hz the first branch can be simplified with the electric circuit of Fig. 13 [55].

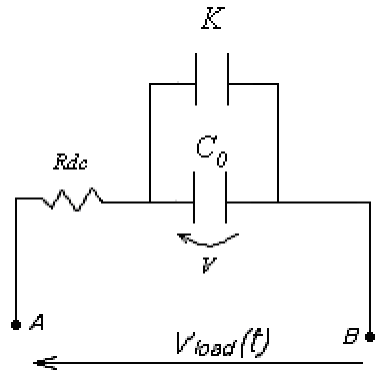

Figure 13. First branch model for frequencies tending to 10^{-2}Hz.

In particular the resistance R_{dc} is equal to the sum of all resistive elements of the first branch of the complete model of fig. 12. This simplification will be used to determine various parameters.

The second and third branches take into account the slow dynamics, and they are represented by a R_2-C_2 branch and an R_{leak} branch, both in parallel with the first one. The second branch takes into account the dynamics of the device for frequencies between 10^{-3} and 10^{-6} Hz that is the redistribution phenomenon, for which the charges of the electrolytic solution accommodate in the structure of porous carbon after fast charging/discharging.

Finally, the third branch is characterized by the leakage resistance R_{leak}; it accounts the self discharge phenomenon of the device which effect becomes clear for frequencies below 10^{-6} Hz.

These parameters are determined by measuring the voltage profile at the terminals of the device at open circuit after a fast charge starting from the device fully discharged.

In case of no interest in considering the slow dynamic of the device, the third or second+third branches of the model can be neglected, that means considering only the first+second or only the first branch.

SOC of supercapacitors

Based on the absence of electrochemical reaction, evaluation of the State of Charge of supercapacitor is simpler than an electrochemical battery. The state of charge is mainly related to the open circuit voltage of the device.

According to the required level of confidence in estimating the available energy stored in a supercapacitor, two expressions can be used. The first evaluates the stored energy considering the device characterized by an ideal capacitance of constant value; the second one, more accurate and in accordance with the reference model previously described, considers the variation of capacitance according to voltage. In the first case the available stored energy can be expressed as:

$$W_{stored}\_1 = \frac{1}{2} C \cdot V_{oc}{}^{2} \qquad (1)$$

where:

C: device capacitance;

V_{oc}: open circuit voltage of the device.

Considering $C=C_0+K\cdot V$, the expression of the stored energy becomes:

$$W_{stored}\_2=\frac{1}{2}C_o\cdot V_{oc}^{\ 2}+\frac{1}{3}K\cdot V_{oc}^{\ 3} \quad (2)$$

The relative error between the expression (1) and (2) is about 10 %.

Consequently the SOC, as ratio between the stored and the rated energy, can be expressed as:

$$SOC\_1=\frac{C\cdot V_{oc}^{\ 2}}{C_n\cdot V_n^2} \quad (3)$$

where:

C_n: rated capacitance

V_n: rated voltage

$$SOC\_2=\frac{C_0\cdot V_{oc}^{\ 2}}{C_{0n}\cdot V_n^2}+\frac{K\cdot V_{oc}^{\ 3}}{K_n\cdot V_n^3} \quad (4)$$

where:

C_{on}: rated coefficient C_0

K_n: rated coefficient K.

Last two expressions show how the SOC is function of the real capacitance of the device and the open circuit voltage. In particular the parameters C in (3) or C_0 and K in (4) have to be referred to a nominal value. This is due to a capacitance variation related not to the operative temperature variation but to ageing factors. As shown in next section and in manufacture's datasheets the range variation is within 20% between a new supercapacitor and one at the end of life.

Over sizing the storage system of a factor 1.2 it is possible neglecting the capacitance variation during the life of the system, because it's ensured the rated capacitance value at the end of life. Consequently it's possible defining the SOC as:

$$SOC\_1^{*}=\frac{V_{oc}^{\ 2}}{V_n^2} \quad (5)$$

$$SOC\_2=\frac{V_{oc}^{\ 2}}{V_n^2}+\frac{V_{oc}^{\ 3}}{V_n^3} \quad (6)$$

SOH of supercapacitors

First of all the definition of END OF LIFE is given:

SUPERCAPACITOR END OF LIFE: A supercapacitor module or cell is at the end of life when one or both two following conditions are verified:

- a capacitance lower than 80% of nominal value
- an internal resistance greater than 200% of nominal value. The state of health of supercapacitors is related to the operative conditions of use.

The main ageing factors are:

- operative voltage;
- operative temperature;
- cycles number.

Dimac Red, as project partner, can give the information regarding the expected lifetime using a Maxwell Technologies property spreadsheet. This information can be matched with the experimental data collected in the abuse tests.

Results and discussion

The lithium battery and supercapacitor matrices to be defined are needed for modelling purpose, and therefore they should be able to reveal all the main aspects of their behaviour.

All the previous paragraphs have shown that these components have non-linear behaviour, since the battery parameters depend on temperature and state-of-charge, and the supercap capacitance depend on voltage.

The more effective approach to evaluate the component's performance in a comprehensive and effective way, is to submit them to tests that show their linearised performance around significant points, e.g. at different SOC-temperature combinations, for batteries and different voltage levels for supercaps.

Since around each point the behaviour is supposed to be linear (i.e. the battery is linearised around each point), its evaluation can be made in time-domain or Laplace-variable domain: mathematical treatment of results obtained on any of these two approaches allows building the corresponding result in the other,

Taking for instance the batteries, good results can be obtained for each temperature from the test type shown in figure 8, that was called *Multiple-Step Test*: it is able to show for each state-of-charge the step response (voltage response to current steps).
From each voltage response a lot of parameters can be inferred (fig. 14).

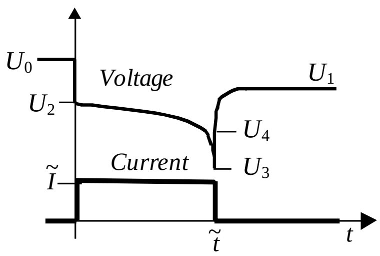

Figure 14. Evaluation of battery parameters from step response.

If, for instance, the battery model shown in fig. 6 is taken as reference:

- the resistance R_0 is easily determined at beginning and end of the shown partial discharge as $R_{0beg} = (U_0 - U_2)/\tilde{I}$, $R_{0end} = (U_4 - U_3)/\tilde{I}$
- the resistance R_0+R_1 is easily determined at the end of the shown partial discharge as $R_{0end} + R_{1end} = (U_1 - U_3)/\tilde{I}$ i.e. as the ratio of voltage variation to current variation
- the electromotive force at the end of the shown partial discharge is $E_{end} = U_1$

Therefore the lithium battery test matrices are defined according to this procedure, based on the response of fig. 8.
An additional comment must be made: if the test of the kind reported in fig. 8 is repeated starting from fully discharged battery and recharging it, the values of the circuit parameters are different. The differences can be very small (for instance in the case of Nickel-Cobalt-

Aluminium, or NCA-type lithium batteries) or rather large (for instance in the case of Iron-phosphate lithium batteries). This very fact jeopardises the idea behind these tests, that the battery can be effectively linearised around operating points; however, since this approach is still considered the only one able to give acceptable results with reasonable testing effort, it is maintained; however, test of fig. 8 will be performed, for each temperature using both starting from battery full, and using discharge steps, and starting from battery empty, using charging steps.

Li battery test matrices

The battery test matrices for modelling purposes are based on the Multiple-Step Test (MST), as discussed in par 6. Each MST will be performed, both in charge and discharge ad different temperature. Moreover, they will be basically performed on single cells, to evaluate actual cell performance, independently on the effects of the Battery Management System (BMS)

The test matrix is therefore that shown in Table 2.

Table 2. Test matrix at different temperatures for batteries.

temperature/°C test		-15	0	20	40
	charge-based MST	x	x	x	x
	discharge-based MST-	x	x	x	x

The tests reported in Table 2 will be performed in these cases:

- for 3 different new cells to evaluate not only the cell performance, but also its statistical spread
- for some (1-3) cells having given fault types inside, such as ion-loss or electrode active-material loss
- for 3 different old cells to evaluate cell performance and statistical spread for old batteries.

Normally MST's will be performed at a unique current, the best candidate being 4,4 A, i.e the one-hour discharge for the project cell.
However, since the chosen cell will be able to deliver and absorb up to 50 times that value, for the more common temperature, i.e. 20°C, an additional test at much larger current (e.g. 10 times the current used for the majority of tests) will be made.

Aging of the cells will be done according to the deliverable D.3100.2.

Supercapacitor test matrices

Model parameters identification

The test procedure for the parameters identification consists of two series of test. The first ones to determine the model parameters of the first branch (Fig. 12), while the second one to determine the parameters of the second and third branch.

First branch parameters identification

The test consists of a constant current charging test, starting from device fully discharged at initial voltage of 0V up to the rated value, during which the terminal voltage is measured.

To determine these parameters is necessary that slowest dynamics (redistribution and self discharge) can be neglected, that means a charging time lower than 20 s.
Whit this consideration the charging current can be set as:

$$I_{charge} = C_n \frac{\Delta V}{\Delta t} \quad (7)$$

where:
C_n: rated capacitance;
ΔV: voltage variation between 0V and nominal voltage
Δt: charging time, equal to 20s.
To identify the charging current in (7) the supercapacitor is considered with an ideal constant capacitance equal to the rated value (C_n).

By measuring the voltage profile it is possible to obtain the information collected in next figure:

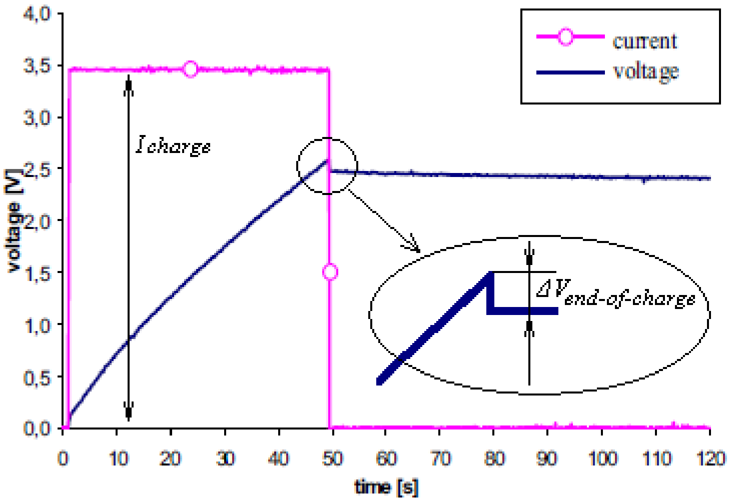

Figure 15. Supercapacitor terminal voltage charging at constant current.

Considering the equivalent simplified circuit of the first branch of fig. 13, the resistance R_{dc} can be calculated as:

$$R_{dc} = \frac{\Delta V_{end-of-charge}}{I_{charge}} \quad (8)$$

that means to consider the terminal voltage drop when the current isswitched off.
Always considering the simplified circuit in Fig. 13, the absorbed current can be written as:

$$i(t) = (C_0 + K \cdot V)\frac{dV}{dt} \quad (9)$$

The result of the integration, in case of a constant current charge (I_{charge}), is the following:

$$t = \frac{C_0}{I_{charge}} V + \frac{1}{2}\frac{K}{I_{charge}} V^2 \quad (10)$$

that is function of the two unknown parameters C_o and K. By fitting the measured voltage profile (net value without the internal resistive voltage drop on R_{dc}) with the expression in (10) it's possible to determine the two coefficients C_o and K.
Finally last parameter of the first branch of the complete model (Fig. 12), that is the high frequency resistance R_i can be determined in two way:

- measuring the supercapacitor impedance at high frequency (100-1000Hz)

- using the high frequency resistance value contained in manufacturer's datasheet.

At this point all the parameters of the first branch can be determinate:
- R_i from the information contained in manufacturer's datasheet
- $C(V)=C_0+K\cdot V$
- $\tau(V) = 3\cdot (R_{dc}-R_i)\cdot C(V)$.

Second branch parameters identification

After charging the supercapacitor with the constant current I_{charge} up to the nominal voltage V_n, the charging current is set to 0 and the terminal voltage is measured for a time depending on the time interval to be modeled.
First the time constant $\tau_2=R_2\cdot C_2$ must be chosen according to the time interval to be modeled. If the time constant is too small, a good accuracy in the medium term would be reached, but rough errors would be performed in the long period. Choosing instead a time constant too high, the exact contrary would happen. For this reason the value must be mediated opportunely. Assuming the redistribution process of the branch 2 is completed the total charge supplied to the supercapacitor during charging can be written as:

$$Q_{tot} = I_{charge} \cdot T_{charge} = C_2 \cdot V_{2f} + \left(C_0 + \frac{K}{2} V_{2f} \right) \cdot V_{2f} \qquad (11)$$

where V_{2f} is the final voltage after 3 times τ_2. In (11) all quantities are known except C_2 that can be easily determined.
The parameter R_2 can be determined as:

$$R_2 = \frac{\tau_2}{C_2} \qquad (12)$$

Third branch parameter identification

The third branch parameter, leakage resistance R_{leak}, can be determined by the information contained in manufacturer's datasheet. In particular this value is usually the leakage resistance estimation considering the voltage discharge within 72h.

Test matrices

With the previous procedure, the parameters identification has to be conducted at different temperature according to Table 3.
The same procedure can be used both for cell and module.

Table 3. Test matrix at different temperatures for supercapacitors.

temperature/°C test	-40	-20	0	20	40	60
Cell parameters identification	x	x	x	x	x	x
Module parameters identification	x	x	x	x	x	x

The tests reported in Table 3 will be performed in these cases:
- for 3 different cells (BCAP3000P270 that is a 3000F cell at 2.7V) to evaluate not only the cell performance, but also its statistical spread
- for 1 module (BMOD0063 that is a 63F module at 125V)

Conclusions

The report allows to characterize the storage systems (lithium battery and supercapacitors) in terms of electrical characteristics, by using simplified models for each of the two storage systems: Li cells and supercapacitor cells. This preliminary approach will be further analysed and developed as part of the modelling activities for energy storage systems in the HCV project.
The sequence of tests described aims at identifying the electrical parameters of the two models.
The modelling has the aim of correctly simulating the electrical performances/dynamics of the two storage devices according to the application. In this way it is possible to integrate them in a more complex system where more different storage systems and/or different loads are connected and, consequently, to quantify the benefits in using them.
The models are finally a valid support in the choice of the storage size according to the wanted electrical vehicle mission.

References

In all sections the papers are ordered by increasing publication date.

General modelling

[1] Mattsson, S. E., M. Andersson, and K. J. Åström (1993): “Object-oriented modelling and simulation.” In Linkens, Ed., CAD for Control Systems, chapter 2, pp. 31–69. Marcel Dekker Inc, New York.

[2] Åström, K. J., H. Elmqvist, and S. E. Mattsson (1998): “Evolution of continuous-time modeling and simulation.” In Zobel and Moeller, Eds., Proceedings of the 12th European Simulation Multiconference, ESM’98, pp. 9–18. Society for Computer Simulation International, Manchester, UK.

Battery modelling

[3] Z. M. Salameh, M. A. Casacca, and W. A. Lynch, “A mathematical model for lead-acid batteries,” *IEEE Trans. on Energy Conversion*, vol.7, no.1, pp. 93–98, Mar. 1992.

[4] S. C. Hageman, “Simple pspice models let you simulate common battery types,”EDN,pp.17–132,Oct.1993.

[5] P. Baudry, M. Neri, M. Gueguen, and G. Lonchampt, “Electro-thermal modeling of polymer lithium batteries for starting period and pulse power,” J. Power Sources, vol.54, no.2, pp.393–396, Apr.1995.

[6] M. Valvo, F. E. Wicks, D. Robertson, and S. Rudin, “Development and application of an improved equivalent circuit model of a lead acid battery,” Proc. *Energy Conversion Eng. Conf*., vol.2, Aug. 1996, pp. 1159–1163.

[7] M. C. Glass, “Battery electrochemical non linear/dynamic SPICE model,” *Proc. Energy Conversion Engineering Conf*., vol.1, 1996, pp.292–297.

[8] S. Gold, “A pspice macro model for lithium-ion batteries,” Proc. 12th Annual Battery Conference Applications and Advances, 1997, pp. 215–222.

[9] M. Ceraolo, “New dynamical models of lead-acid batteries,” IEEE Trans. Power Syst., vol. 15, no.4, pp. 1184–1190, Nov. 2000

[10] L. Song and J. W. Evans, “Electrochemical-thermal model of lithium polymer batteries,” *J. of Electrochemical Society*, vol. 147, pp.2086-2095, 2000

[11] S. Barsali and M. Ceraolo, “Dynamical models of lead-acid batteries: Implementation issues,” *IEEE Trans. Energy Conversion*, vol.17, no.1, pp.16–23,Mar.2002.

[12] L. Gao, S. Liu, and R. A. Dougal, “Dynamic lithium-ion battery model for system simulation,” *IEEE Trans. Component Packaging Technol*., vol. 25, no.3, pp.495–505, Sep. 2002.

[13] P. M. Gomadam, J. W. Weidner, R. A. Dougal, and R.E. White, “Mathematical modeling of lithium-ion and nickel battery systems,” *J. of Power Sources*, vol.110, no.2,pp.267–24, Aug. 2002.

[14] D. W. Dennis, V. S. Battaglia, and A. Belanger, “Electrochemical modeling of lithium polymer batteries,” *J. of Power Sources*, vol.110, no.2, pp. 310–320, Aug.2002

[15] B. Schweighofer, K. M. Raab, and G. Brasseur,“ Modeling of high power automotive batteries by the use of an automated test system,” *IEEE Trans. Instrumentation and Measurement*, vol.52, no.4, pp.1087–1091, Aug. 2003.

[16] J. Newman, K. E. Thomas, H. Hafezi, and D. R. Wheeler, “Modeling of lithium-ion batteries,” *J. of Power Sources*, vol. 119–121, pp. 838–843, Jun. 2003.

[17] S. Abu-Sharkh and D. Doerffel, “Rapid test and non-linear model characterization of solid-state lithium-ion batteries,” J. Power Sources, vol.130, pp. 266–274, 2004.

[18] S. Buller, M. Thele, R. W. D. Doncker, and E. Karden, “Impedance-based simulation models of supercapacitors and Li-ion batteries for power electronic applications,” *IEEE Transact. on Industry Applications*, Vol 41, 2005, N. 3, pp 742-747.

[19] M. Chen, and G. A. Rincon-Mora, “Accurate electrical battery model capable of predicting Runtime and I_V Performance”, *IEEE Transact. on Energy Conversion*, Vo. 21, 2006, N. 2, pp504-511.

Battery SOC and SOH

[20] R. Giglioli, G. Zini, M. Conte; “Battery state of charge observer to improve energy management on electric storage plants”, *third International conference on Batteries for Utility Energy Storage*, 18-22 March 1991, Kobe, Japan.

[21] Alvin J. Salkind, Craig Fennie, Pritpal Singh et al: “Determination of state-of-charge and state-of-health of batteries by fuzzy logic methodology “Journal of Power Sources, Vol 80, 1999, pp. 293-300.

[22] S. Piller, M. Perrin, A. Jossen: “Methods for state-of-charge determination and their applications” *Journal of Power Sources*, 96(1), Jun 2001

[23] Bhangu, B.S.; Bentley, P.; Stone, D.A.; Bingham, C.M.: “Nonlinear observers for predicting state-of-charge and state-of-health of lead-acid batteries for hybrid-electric vehicles” *IEEE Transactions on Vehicular Technology*, Volume: 54 , Issue: 3, year 2005, Page(s): 783 - 794

[24] Asumadu, J.A.; Haque, M.; Vogel, H.; Willards, C.; “Precision Battery Management System” IEEE Instrumentation and Measurement Technology Conference, 2005. IMTC 2005. Volume: 2 2005 , Page(s): 1317 - 1320

[25] Haifeng Dai; Xuezhe Wei; Zechang Sun: “Online SOC Estimation of High-power Lithium-ion Batteries Used on HEVs”, *IEEE International Conference on Vehicular Electronics and Safety*, 2006. ICVES 2006. Page(s): 342 - 347

[26] Dai Haifeng, Wei Xuezhe, Sun Zechang: “A new SOH prediction concept for the power lithium-ion battery used on HEVs” *IEEE Vehicle Power and Propulsion Conference*, 2009. VPPC '09, pp 1649-1653.

[27] J. B. Gerschler, D. U. Sauer: “Investigation of Open-Circuit-Voltage Behaviour of Lithium-Ion Batteries with Various Cathode Materials under Special Consideration of Voltage Equalisation Phenomena”, International Electric Vehicle Symposium, EVS-24, Stavanger, Norway, May 13-16 2009.

[28] IL-Song Kim: “A Technique for Estimating the State of Health of Lithium Batteries Through a Dual-Sliding-Mode Observer”, *IEEE Transactions on Power Electronics*, Volume: 25, 2010, Issue: 4 Page(s): 1013 – 1022

[29] Martin Kiel, Dirk Uwe Sauer, Pierre Turpin, Mohammed Naveed, Eric Favre: “Extensive Validation Of A Nonintrusive Continuous Battery Monitoring Device” International Stationary Battery Conference, Marco Island, Florida, USA, May 5-7, 2008

[30] Peng Rong; Pedram, M.; , "An analytical model for predicting the remaining battery capacity of lithium-ion batteries," Very Large Scale Integration (VLSI) Systems, IEEE Transactions on , vol.14, no.5, pp. 441- 451, May 2006 doi: 10.1109/TVLSI.2006.876094 URL:http://ieeexplore.ieee.org/stamp/stamp.jsp?tp=&arnumber=1650223&isnumber=34605

[31] J. Vetter, P. Novak, M.R. Wagner, C. Veit, K.-C. Moller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, Ageing mechanisms in lithium-ion batteries, Journal of Power Sources, Volume 147, Issues 1-2, 9 September 2005, Pages 269-281, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2005.01.006. (http://www.sciencedirect.com/science/article/B6TH1-4FPN9VC-1/2/c4aefa68cd1a0396b0ebfc3e40a7de75)

[32] M. Broussely, S. Herreyre, P. Biensan, P. Kasztejna, K. Nechev, R. J. Staniewicz, Aging mechanism in Li ion cells and calendar life predictions, Journal of Power Sources, Volumes 97-98, July 2001, Pages 13-21, ISSN 0378-7753, DOI: 10.1016/S0378-7753(01)00722-4. (http://www.sciencedirect.com/science/article/B6TH1-43DM123-4/2/52dd07e9c83960c6ddf970a36fbd9284)

[33] M. Broussely, Ph. Biensan, F. Bonhomme, Ph. Blanchard, S. Herreyre, K. Nechev, R.J. Staniewicz, Main aging mechanisms in Li ion batteries, Journal of Power Sources, Volume 146, Issues 1-2, Selected papers presented at the 12th International Meeting on Lithium Batteries, 26 August 2005, Pages 90-96, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2005.03.172. (http://www.sciencedirect.com/science/article/B6TH1-4G94HKR-S/2/4c80d33799e675ea51a363f7e0608228)

[34] JM Tarascon, M Armand: “Issues and challenges facing rechargeable lithium batteries”, Nature, Vol. 414, Pages 359-367, Nov 2001

[35] Michael A. Roscher, Jens Vetter, Dirk Uwe Sauer, Characterisation of charge and discharge behaviour of lithium ion batteries with olivine based cathode active material, Journal of Power Sources, Volume 191, Issue 2, 15 June 2009, Pages 582-590, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2009.02.024.

(http://www.sciencedirect.com/science/article/B6TH1-4VNH3XX-D/2/7b7ecd95abd4d9b9056ee8de1bfbc0f6)

[36] Michael A. Roscher, Jens Vetter, Dirk Uwe Sauer, Cathode material influence on the power capability and utilizable capacity of next generation lithium-ion batteries, Journal of Power Sources, Volume 195, Issue 12, 15 June 2010, Pages 3922-3927, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2009.11.143. (http://www.sciencedirect.com/science/article/B6TH1-4XY9DJ4-2/2/a415c7ede3b00c765165de8d2b90500d)

[37] Scott B. Peterson, Jay Apt, J.F. Whitacre, Lithium-ion battery cell degradation resulting from realistic vehicle and vehicle-to-grid utilization, Journal of Power Sources, Volume 195, Issue 8, 15 April 2010, Pages 2385-2392, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2009.10.010. (http://www.sciencedirect.com/science/article/B6TH1-4XFY0GC-1/2/3cfba849ffb09d5f8a88a836be291d0d)

[38] Matthieu Dubarry, Vojtech Svoboda, Ruey Hwu, Bor Yann Liaw, Capacity loss in rechargeable lithium cells during cycle life testing: The importance of determining state-of-charge, Journal of Power Sources, Volume 174, Issue 2, 13th International Meeting on Lithium Batteries, 6 December 2007, Pages 1121-1125, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2007.06.185. (http://www.sciencedirect.com/science/article/B6TH1-4P37JH7-N/2/2f031d1cff8ef755fbc38b2f86bdef2d)

[39] Matthieu Dubarry, Bor Yann Liaw, Development of a universal modeling tool for rechargeable lithium batteries, Journal of Power Sources, Volume 174, Issue 2, 13th International Meeting on Lithium Batteries, 6 December 2007, Pages 856-860, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2007.06.157. (http://www.sciencedirect.com/science/article/B6TH1-4P2S92R-J/2/0de051252c81d21de7aa2382530a68d8)

[40] Jungst, RG ; Nagasubramanian,G ; Crafts,CC. ; Ingersoll,D; Doughty,DH: Analysis of Lithium-Ion Battery Degradation During Thermal Aging , 198th Meeting of the Electrochemical Society, Phoenix, AZ (US), 23-27 October 2000

[41] Michael A. Roscher, Dirk Uwe Sauer, Dynamic electric behavior and open-circuit-voltage modeling of LiFePO4 based lithium ion secondary batteries, Journal of Power Sources, In Press, Accepted Manuscript, Available online 7 July 2010, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2010.06.098. (http://www.sciencedirect.com/science/article/B6TH1-50GJ2M8-3/2/01dd707697eb2c1f5347b21add052cf6)

[42] F. Huet, A review of impedance measurements for determination of the state-of-charge or state-of-health of secondary batteries, Journal of Power Sources, Volume 70, Issue 1, 30 January 1998, Pages 59-69, ISSN 0378-7753, DOI: 10.1016/S0378-7753(97)02665-7. (http://www.sciencedirect.com/science/article/B6TH1-3SJNDT8-9Y/2/9b36d9414b009378018b298e47d6386f)

[43] P Liu, J Wang, J Hicks-Garner, E Sherman, S Soukiazian, M Verbrugge, H Tataria, J Musser & P Finamore, Aging Mechanisms of $LiFePO_4$ batteries deduced by electrochemical and structural analyses, Journal of Electrochemical Society, Volume 157, Issue 4, pp. A499-A507 (2010)

[44] K. Zaghib, K. Striebel, A. Guerfi, J. Shim, M. Armand, M Gauthier, LiFePO4/polymer/natural graphite: low cost Li-ion batteries, Electrochimica Acta, Volume 50, Issues 2-3, Polymer Batteries and Fuel Cells:Selection of Papers from First International Conference, 30 November 2004, Pages 263-270, ISSN 0013-4686, DOI:

10.1016/j.electacta.2004.02.073. (http://www.sciencedirect.com/science/article/B6TG0-4D1V5DT-V/2/4db8df2373fffbb138df072c19038539)

[45] Robert Kostecki, Jinglei Lei, Frank McLarnon, Joongpyo Shim, Kathryn Striebel, “Diagnostic Evaluation of Detrimental Phenomena in High-Power Lithium-Ion Batteries” J. Electrochem., Soc., 153, A669 (2006)

[46] Marine Cuisinier, Jean-Frederic Martin, Nicolas Dupre, Atsuo Yamada, Ryoji Kanno, Dominique Guyomard, Moisture driven aging mechanism of LiFePO4 subjected to air exposure, Electrochemistry Communications, Volume 12, Issue 2, February 2010, Pages 238-241, ISSN 1388-2481, DOI: 10.1016/j.elecom.2009.12.003. (http://www.sciencedirect.com/science/article/B6VP5-4XY9DR6-1/2/9da1ae289436067de3ae4efccf7fd208)

[47] Hui-Fen Jin, Zhen Liu, Yan-Mei Teng, Jun-kui Gao, Yong Zhao, A comparison study of capacity degradation mechanism of LiFePO4-based lithium ion cells, Journal of Power Sources, Volume 189, Issue 1, Selected Papers presented at the 14th INTERNATIONAL MEETING ON LITHIUM BATTERIES (IMLB-2008), 1 April 2009, Pages 445-448, ISSN 0378-7753, DOI: 10.1016/j.jpowsour.2008.12.124. (http://www.sciencedirect.com/science/article/B6TH1-4VCH6WM-T/2/78bffe1fe8c5ce233fa269aa2528b90b)

SC Modelling

[48] L. , R. Bonert: “Characterization of double layer capacitors for power electronics applications”, Industry Applications, IEEE Transactions on, Pages: 199 – 205, Vol.36 (2000)

[49] F. Belhachemi, S. Rael, B. Davat: “A physical based model of power electric double-layer supercapacitors ”, IEEE Industry Applications Conference, Pages: 3069 - 3076 vol.5 , (2000).

[50] H. Gualous, D. Bouquain, A. Berthon and J. M. Kauffmann, “Experimental study of supercapacitor serial resistance and capacitance variations with temperature”, Journal of Power Sources, Pages 86-93, Vol. 123, Issue 1, (2003).

[51] F. Rafik, H. Gualous, R. Gallay, M. Karmous, and A. Berthon: “Contribution to the sizing of supercapacitors and their applications,” First European symposium on supercapacitors and applications (ESSCAP), Belfort, France, (2004).

[52] P. Venet, Z. Ding, G. Rojat, H. Gualous: “Modelling of the supercapacitors during self discharge”, EPE Journal, Pages 6-10, Vol. 17, Issue1, (2007).

[53] Lingling Du: “Study on supercapacitor equivalent circuit model for power electronics applications”, Power Electronics and Intelligent Transportation System International Conference on (PEITS), Pages 51 – 54, Vol.2, (2009).

[54] Faranda,R.; Gallina,M.; Son,D.T.: *A new simplified modelof Double-Layer Capacitor*, Clean Electrical Power, 2007.ICCEP ’07. On pages: 706-710.

[55] E. Tironi, V. Musolino: “Supercapacitor characterization in power electronic applications: proposal of a new model”, International Conference on Clean Electrical Power, 2009, pp. 376 – 382

[56] R. De Levie: “Electrochemical response of porous and rough electrodes”. Advances in Electrochemistry and Electrochemical Engineering, vol. 6, Wiley, Interscience, (1967).

[57] S. Buller, E. Karden, D. Kok, R. W. De Doncker: " Modeling the dynamic behavior of supercapacitors using impedance spectroscopy", Industry Applications Conference, Vol. 4, 2001, pp. 2500 - 2504