Responsible (Name, Organisation) Massimo Ceraolo – Università Pisa	**DELIVERABLE REPORT**		Page 1(20)
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Deliverable 3200.6

Preliminary model definition for SC

Summary

This deliverable presents and discusses the details of the mathematical model developed for the project's supercapacitors (SC), based on experimental results, which was planned as part of WP3200 "Basic storage system testing and modelling", in Task 3230 "Modelling", with the scope to develop and validate, with experimental test work, dedicated mathematical models for Li and SC cells. The developed model can be also useful for a control strategy.
The structure of the model and all the numerical values of the parameters are found from experimental results obtained at Pisa's laboratories, with experimental contributions from DimacRed, and discussed thoroughly in this technical report.

In this report, an SC cell model, with its numerical parameters and detailed equations, has been chosen from the initial survey, adapted to the specific SC technology, experimentally verified. Then this model has been used as the basis of a model-based State-of-Charge estimator, whose details and related algorithm are described in Deliverable D3200.8 [1].

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Nomenclature

1. Acronyms

MST Multiple-Step test
OCV Open-Circuit Voltage
SC Supercapacitor
SOC State-of-Charge
SOC_Q charge-based State-of-Charge
SOC_E energy-based State-of-Charge

2. Other quantities

C_n nominal supercapacitor capacitance (e.g. in F)
E *energy content of supercapacitor (in Wh)*
I_t Main-branch supercapacitor current
R_0 Algebraic supercapacitor internal resistance
R_i (*i= 1, 2, ….*) i-block battery internal resistance
C_i (*i= 1, 2, …..*) i-block battery internal capacitance
θ inner supercapacitor temperature
θ_a ambient temperature
V_n rated capacitor voltage (=maximum under normal operation)
V_{oc} Open-circuit voltage *(same as OCV)*

Introduction

In Deliverable D3100.5 [2], discussion of mathematical models available for supercapacitors was presented. A general model was defined in collaboration with DimacRed. Figure 1 shows the general structure, with slight modification of symbols with respect to the version used in D3100.5. This is a family of models that allowed different degrees of precision, depending on the number of *R-C* blocks: the higher this value, the higher the model's precision, but also the model's complexity.

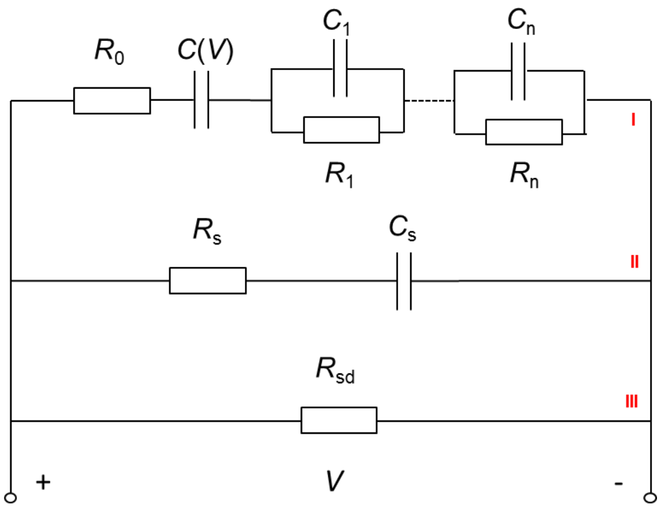

Figure 1. Generic structure of electric model of supercapacitor (1st form).

This model can be used as a graphical-mathematical model of the SC's behaviour. Its usage is not limited to off-line studies of the SC's behaviour, but it can be also very important in facilitating the determination SC's SOC (State-of-Charge), using Luenberger-style techniques, as described in deliverable D3200.8.

Therefore detailed experimental evaluations of the considered supercapacitor must be made, the parameters of the chosen model have to be determined, and verification of the model quality evaluated.

The full definition of this project's supercapacitor behaviour needs to be performed according to the following steps:

1. Verification of the applicability of the general model whose circuital description is shown in Figure 1, to the supercapacitor chosen for HCV demonstrators.
2. Detailed definition of the SC's mathematical model. It relates to the need of choosing a unique structure from the family of circuits shown in Figure 1, i.e. to neglect some features or to determine the number *n* of R-C blocks.
2. Detailed definition of model's numerical parameters (values of E, R's, C's at different values of SOC.

The next section of the deliverable in principle follows this order.

Technical progress

Measures of supercapacitors state in terms of charge and energy

Supercapacitor voltage variation during charge and discharge is much higher than the corresponding voltage of lithium batteries.

This high voltage variability must be taken into account when considering the energy entering or exiting the device.

The maximum safe, repetitive voltage that can be stored in a supercapacitor cell is normally called rated capacitor voltage V_n, and this term was used in deliverable D3100.5.
Therefore the maximum energy that can be stored in practice in a supercapacitor is:

$$E_{\max} = \frac{1}{2} C_n V_n^2$$

Correspondingly the maximum charge that can be stored in the device is:

$$Q_{\max} = C_n V_n$$

If we want to represent the *energy* stored in a supercapacitor as a ratio of the corresponding maximum, the following quantity may be used:

$$SOC_E = E / E_{\max} = \frac{(1/2) C_n V}{(1/2) C_n V_n^2} = \frac{V^2}{V_n^2}$$

If, however, we want to represent the *charge* stored in a supercapacitor as a ratio of the corresponding maximum, the following quantity may be used:

$$SOC_Q = Q / Q_{\max} = \frac{V}{V_n}$$

In deliverable D3100.5 SOC_E was introduced; however, to ease comparison with the battery, in this document SOC_Q is used. Supercapacitors are normally used between $V_n/2$ and V_n. As a consequence, SOC_Q varies between 0.5 and 1.

The cell model that is obtained is independent on SOC choice between these two definitions, and therefore the results are not influenced by this choice.

The supercapacitor

While D3100.5 dealt with cell modelling in general, this document aims at adapting the model to the SC chosen for the HCV project. The basic characteristics of this SC cell, as reported by the manufacturer, are summarized in Table 1.

Table 1. Basic characteristics of the SC cells.

Manufacturer	Maxwell
Model	BCAP3000
Capacitance (F)	3000
Nominal voltage (V)	2,7
Max voltage (V)	2,85
Max continuous current ΔT 15°C (A)	130
Max continuous current ΔT 40°C (A)	210
Max peak current (A)	2200
Mass (kg)	0,510
Energy (Wh)	3,04
Specific energy (Wh/kg)	6,0
Usable specific power (W/kg)	5900
Impedance match specific power (W/kg)	12000
Cycle life	10^6

These are nominal values, referred to defined operating measuring conditions.

As for the LFP battery cell, it must be stressed that the highest efforts should be given to determine a good SOC estimation technique. Therefore the following procedure has been adopted. The procedure will involve:
- Detailed definition of the SC's mathematical model.
- Detailed definition of the procedure to determine the model's numerical parameters.
- Detailed definition of the algorithm to estimate the SC's SOC.
- Verification of model and SOC estimation algorithm quality.

Definition of the detailed model architecture

In the Deliverable D3100.5 a survey of literature about supercapacitor mathematical models was performed, that has shown a general uniformity of the models that all can be with minor differences reproduced using the equivalent circuit shown in Figure 1. As visible it consists of three branches:

- The first branch consists of the series connection of a resistance R_0, a capacitance $C(V)$, and a series of "n" parallel *RC* blocks. This branch takes into account the frequency response of the device in the frequencies ranging from 10^{-2} to 10^3 Hz (high frequencies). In particular, R_0 is the resistance of the device at high frequencies (several hundred Hz). Furthermore, $C(V)=C_0+K\cdot V$ 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).

The second and third branch take into account the slow dynamics, and they are represented by an R_s-C_s branch and an R_{sd} 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.
- The third branch is characterized by the leakage resistance R_{sd}; it accounts the self-discharge phenomenon of the device which effect becomes clear for frequencies below 10^{-6} Hz.

In case of no interest in considering the slow dynamic of the device, the second and the third branches of the model can be neglected, that means considering only the first branch. The model without the second and the third branch, and with a generic number of blocks *n*, is reported in Figure 2. It must be observed that this representation is equivalent to the lithium cell model reported in deliverable D3200.5.

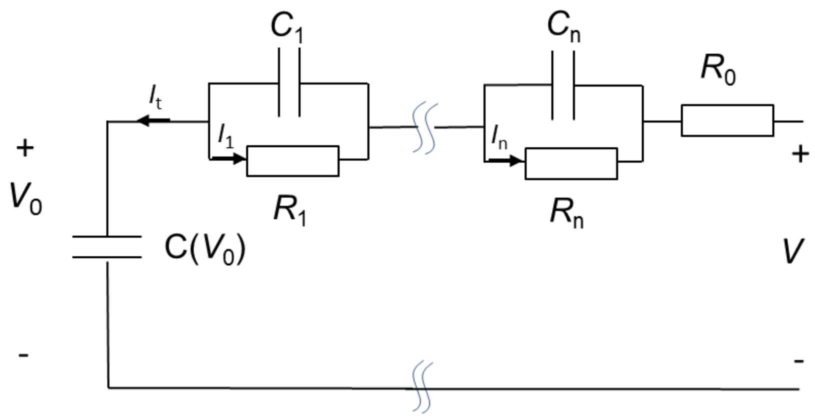

Figure 2. Model of Figure 1 without the second and the third branch.

The transients simulated by the *R*-*C* blocks have time constants R_kC_k around one second or tens of seconds respectively. Therefore they can be neglected whenever only the very first parts of capacitor dynamic response is of interest.
When slow transients (except the main charge/discharge process) can be disregarded, the first branch can be simplified with the electric circuit of Figure 3.

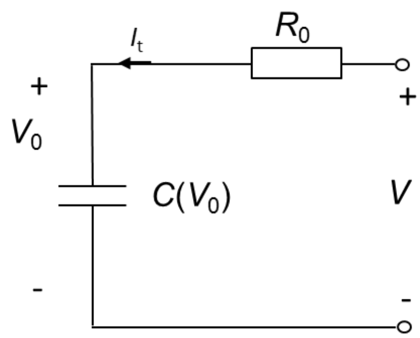

Figure 3. First branch model adequate when slow transients (except the main charge/discharge process) can be disregarded.

Differently from the case of lithium batteries, the two models do not include any hysteresis, because this, to the author's knowledge has been never documented in literature; all the University of Pisa's experimental results, part of which will be presented later in this deliverable, confirm this non-hysteretic behaviour.

In principle, the numerical values of the parameters are assumed to be function of SOC and temperature, even though the results presented in this document refer to room temperature only.

The mathematical model of Figure 2 has a generic number of *R-C* blocks, and the best value for *n* had to be chosen. To avoid excessive complexity of the model, and therefore of the procedure to evaluate the numerical values of parameters, the basic decision of considering two options was chosen: *n*=1 and *n*=2.

On the other hand, the model reported in Figure 3 is representative of the situation without any *R-C* block, in which *n* is equal to zero. Naturally, with *n*=0 the precision is expected to be low, but also the procedure to draw parameters from experimental tests is simplified.

The procedure to evaluate all values of R_k's and C_k's can be applied to the result of the Multiple-Step-Test, at different values of SOC, and thus values of R_k's and C_k's at different values of SOC are determined. Similarly to what was explained for LFP cells, the Multiple Step Test (MST) defined in deliverable D3100.5 came in two flavours charge-based and discharge-based. These two test types can be used to determine all the parameters of the SC's equivalent circuit. To understand the process, some results are discussed here.

Figure 4 shows a comparison between experimental and simulated voltage at the end of a discharge pulse, at SOC=76%. The voltage response to the same current of the considered battery model depends on the number *n* of *R-C* blocks, and the numerical values of all R_k's, C_k's and V_{oc}.
A procedure to identify all these values is used that minimises the error between actual and simulated voltage profile. The error function chosen is:

$$\varepsilon = \min\left\{\sum_{k=1}^{K}\sqrt{\left(v_{\mathrm{k,actual}} - v_{\mathrm{k,model}}\right)^2}\right\} \qquad (1)$$

Where *k*=1, 2, …*K* are the individual values at equidistant times t_1, t_2, t_K.

The numerical values obtained after this process has been carried out are reported in Table 2.

Table 2. Numerical values of model parameters as identified for SOC=76%.

n	V_{oc} (V)	R_0 (mΩ)	R_1 (mΩ)	R_1C_1 (s)	R_2 (mΩ)	R_2C_2 (s)
0	2.042	0.22	---	--	--	--
1	2.042	0.50	0.10	11	--	---
2	2.042	0.49	0.09	9	0.007	0.7

Figure 4 shows the actual and simulated voltages, considering all the analysed cases.

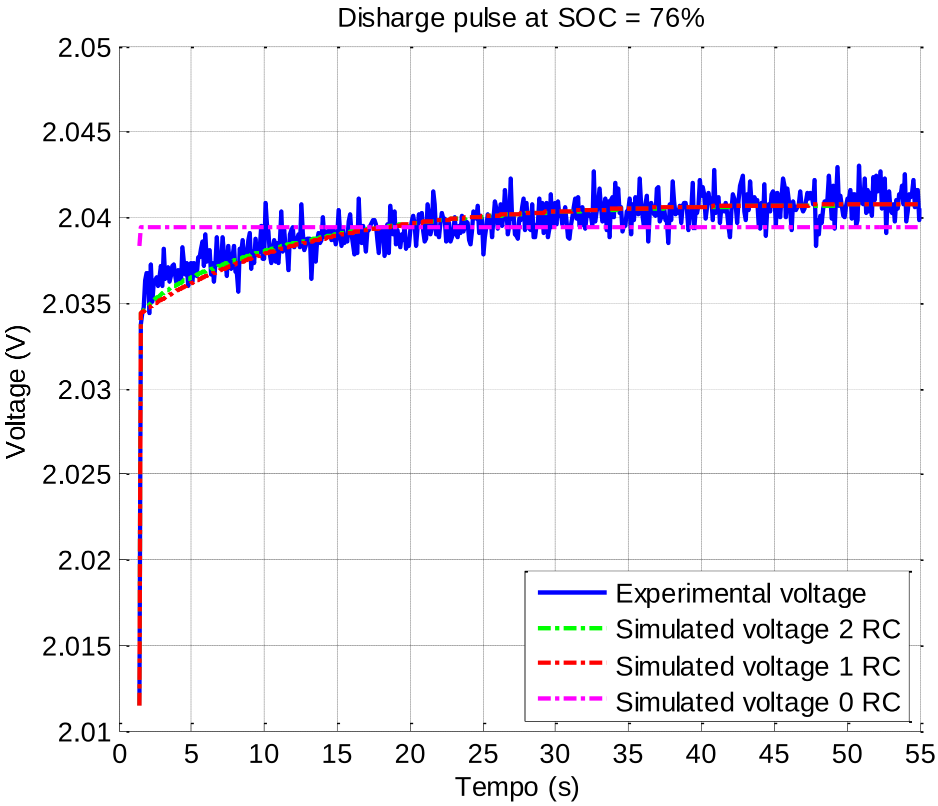

Figure 4. Voltage behaviour immediately after the end of a discharge process, while SOC=76%.
Comparison between experiment and model for 0 RC, 1 RC and 2 RC blocks
(R's, C's, V_{oc} determined by error minimisation).

The comparison demonstrates that the configurations with one RC block or two RC blocks show rather acceptable results, while the zero block type has a distinct disadvantage.

Moreover, results with n=1 and n=2 are nearly equivalent. It was therefore concluded that the complication due to the use of two R-C blocks can be avoided. Therefore the following has been adopted:

Decision. The adopted model was decided to have one *R-C* block.

If instead we consider the charge-based MST, the result when SOC=90% is that shown in Figure 5.

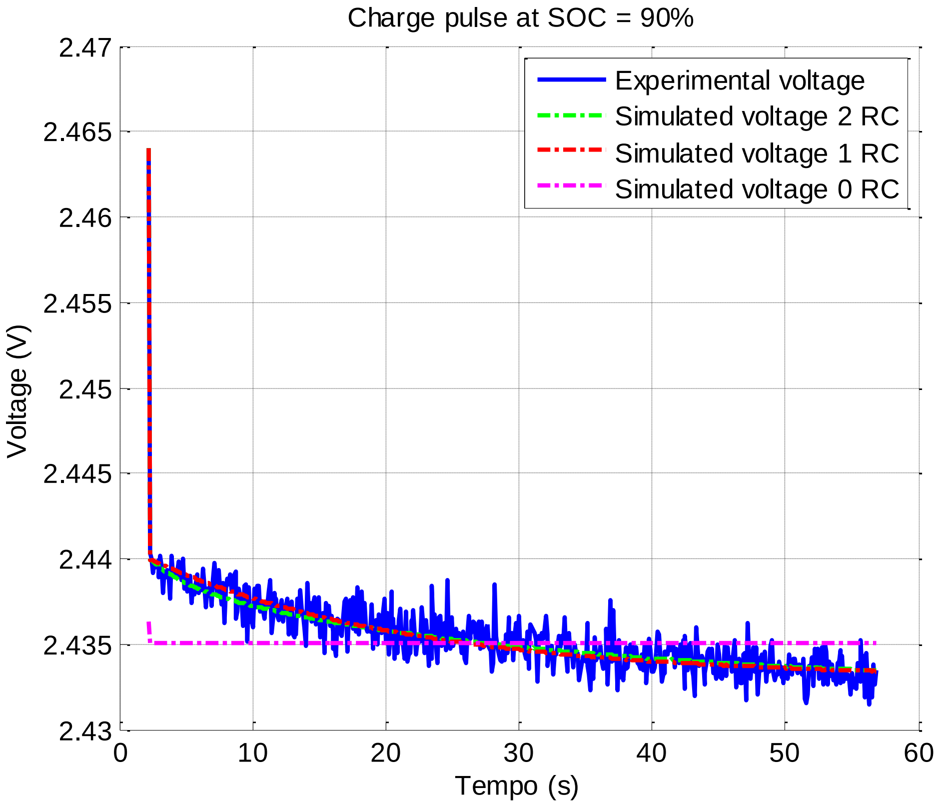

Figure 5. Voltage behaviour immediately after the end of a charge process, while SOC=90%. Comparison between experiment and model (R's, C's, and V_{oc} determined by error minimisation).

The corresponding numerical parameters are presented, at a predefined SOC, both for charge and discharge transients, in Table 3.

Table 3. Model numerical parameters at SOC=76%, after charge and discharge processes.

Transient	V_{oc} (V)	R_0 (mΩ)	R_1 (mΩ)	R_1C_1 (s)
After charge	2.042	0.53	0.07	9
After discharge	2.042	0.46	0.13	12

If the procedure to identify all parameters is taken literally, all parameters have values during charge and discharge.
This duality, however, is a potential source of big difficulties, arising when the supercapacitor is subject to continuously varying currents. Indeed, if the model parameters suddenly switch from charge to discharge values whenever the current at SC's terminals changes its sign, it is not difficult to foresee, large mismatches between simulation and actual values.

The basic idea, that is slightly different to what is presented for the lithium cell in deliverable D3200.5 [3], is therefore of adopting a unique value for V_{oc} both during charge and discharge due to the fact that hysteresis is absent, and using intermediate values for the other parameters:

Decision.
- The adopted model V_{oc}, *R*'s and *C*'s does not depend on history except for their dependence on temperature and SOC.

The choice of resistance and capacitance values for the model at different states of charge must somehow take into account what happens during charge and during discharge.

Figure 6 to Figure 8 shows the comparison of two techniques:

- Technique 1, in which the numerical values are the arithmetic mean between those obtainable during end-of-charge and end-of-discharge identification process. This technique is the simplest to implement.
- Technique 2, in which the numerical values are determined by minimising the error considering both end-of-charge and end-of-discharge transients.

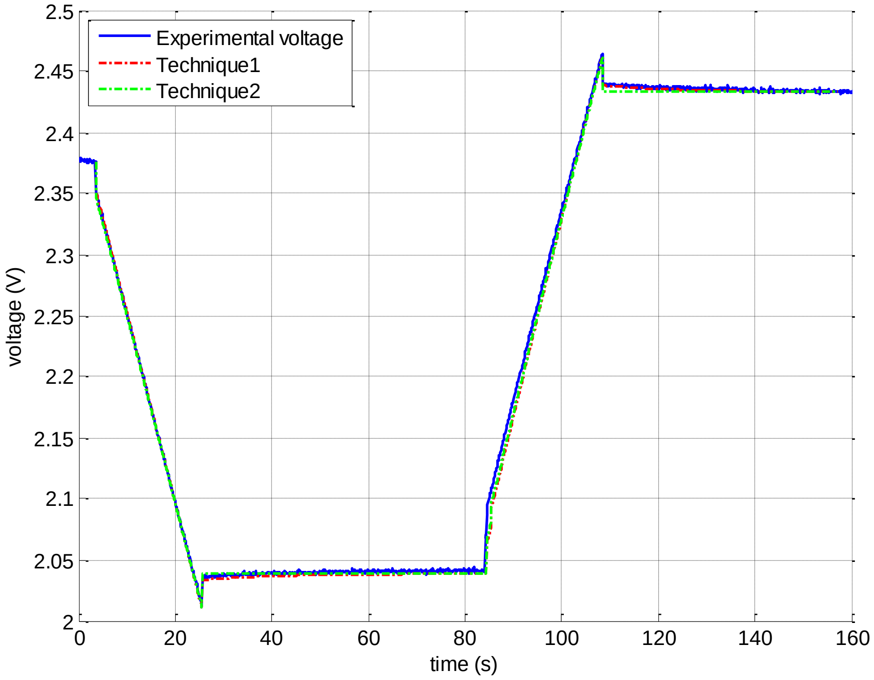

Figure 6. Comparison of voltage behaviour of models whose R-C parameters are evaluated with mean value charge/discharge (tech. 1) or global optimisation (tech. 2).

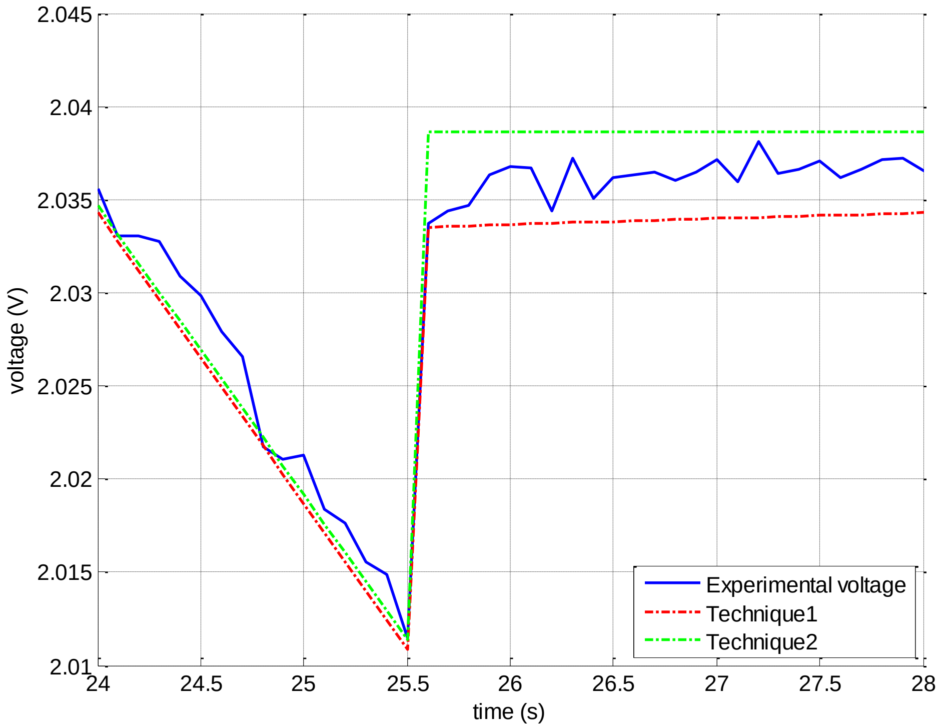

Figure 7. Expansion of left part of Figure 6.

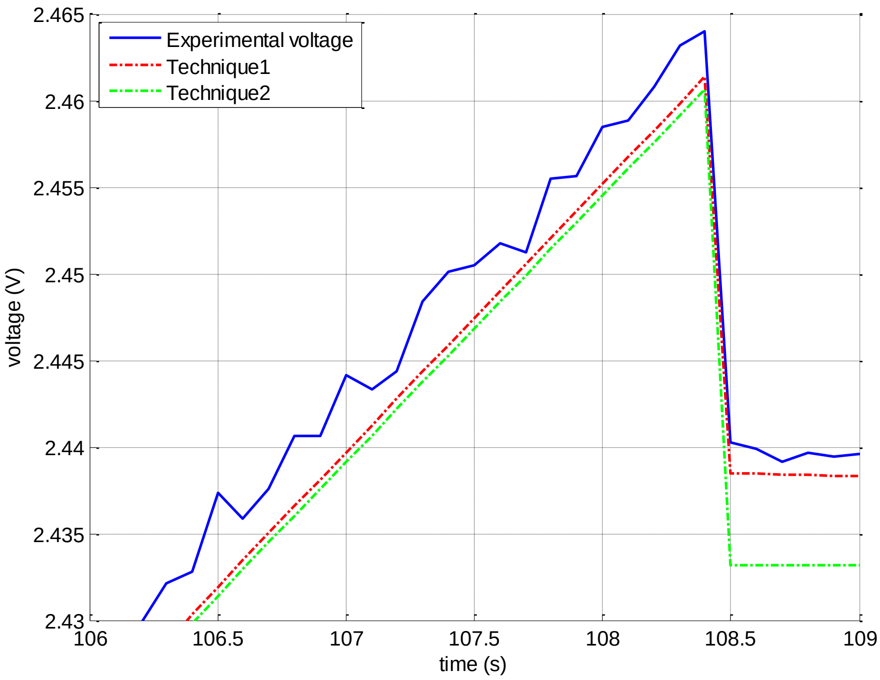

Figure 8. Expansion of right part of Figure 6.

It is apparent that, the two techniques are rather equivalent. The actual implementation of evaluation of numerical parameters of the model can therefore be done in either way.
The choice could be made considering practical issues related to the automatic determination of the numerical values from experimental tests. In fact since it is expected that a periodical update of these values will become necessary to follow the supercapacitor aging during the vehicle usual life, it is advisable to produce techniques to identify the numerical values of the model parameters that is as easy automatable as possible.

Conclusions.
This section's analysis allows for the following conclusions to be drawn:
1) An equivalent circuit of the type shown in Figure 2 is adequate for simulation purposes, assuming n=1 (one R-C block).
2) The numerical values for the circuit parameters (C, R_0, R_1, C_1) can be obtained as the arithmetic mean of those achieved in charge and discharge phases.

Determination of model parameters as a function of SOC

In the previous section several alternatives for the supercapacitor model architecture have been analysed and compared to each-other.
Two main conclusions were drawn regarding the circuit architecture and the parameter evaluation procedure.

This section documents the results obtained by evaluation of the circuit's parameters at different values of supercapacitor State Of Charge.

To draw these parameters, a simplified MST (multiple-step-test) profile was carried out, which allows for the determination of three values of the SOC. The current profile shown in the upper part of Figure 9 was applied to the supercapacitor and the corresponding measured voltage is shown in the lower part of the same figure.

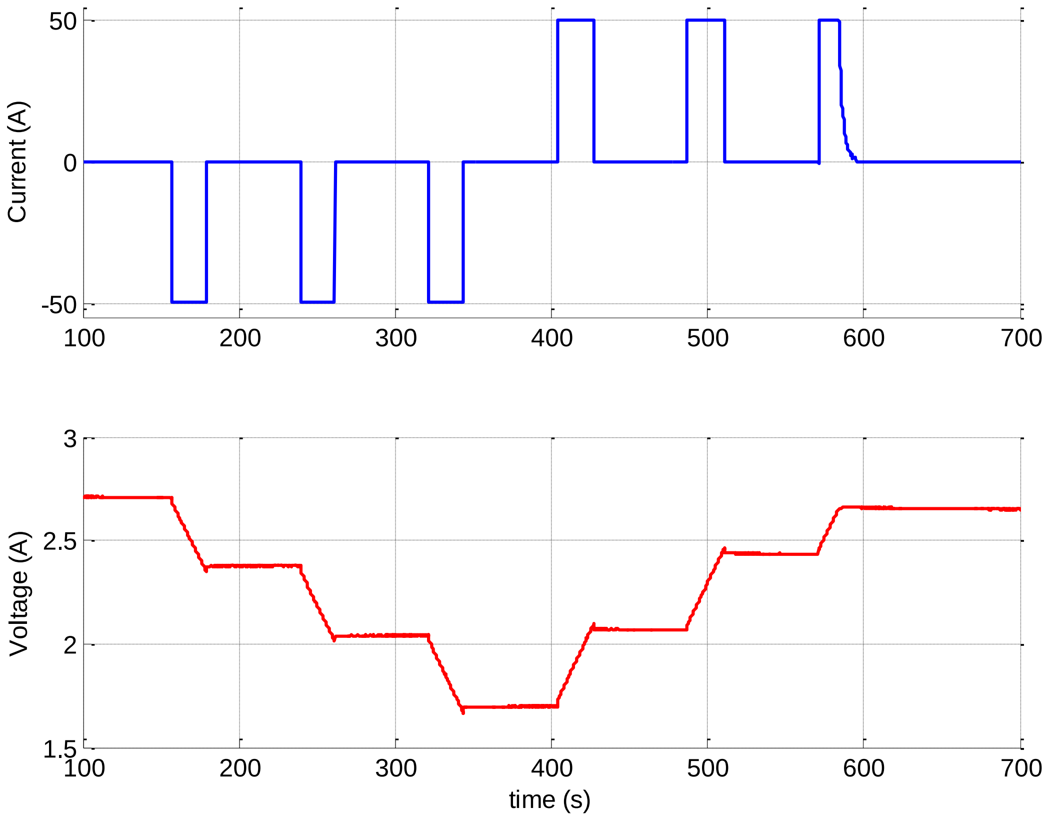

Figure 9. Current and voltage profiles as measured during MST.

Determination of the five parameters, R_0, R_1, C_1, R_2, C_2, has been performed in this way at various values of SOC, by using the error minimisation technique discussed in the previous section. The results obtained are displayed in Figure 10 to Figure 12.

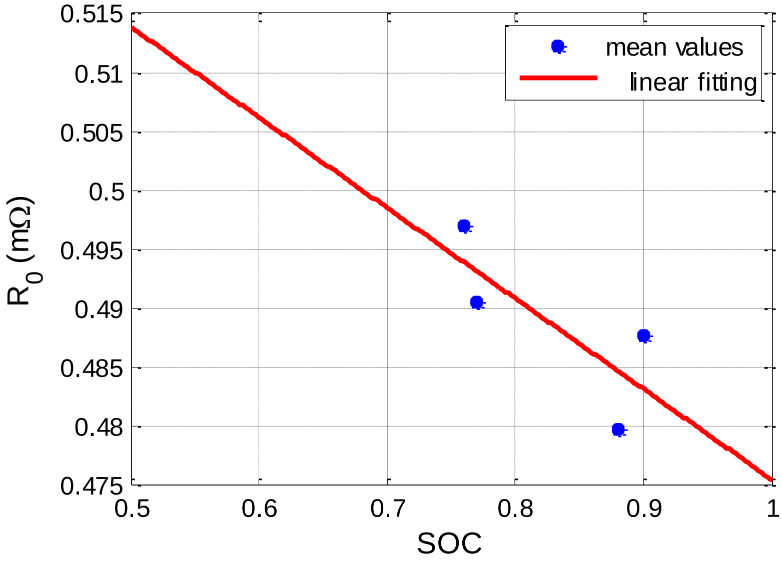

Figure 10. Experimental data on R_0 and linear interpolation.

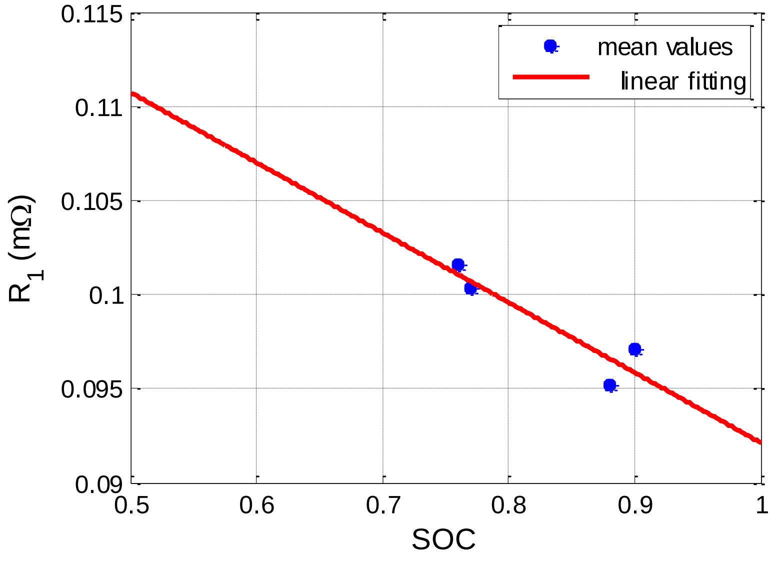

Figure 11. Experimental data on R_1 and linear interpolation.

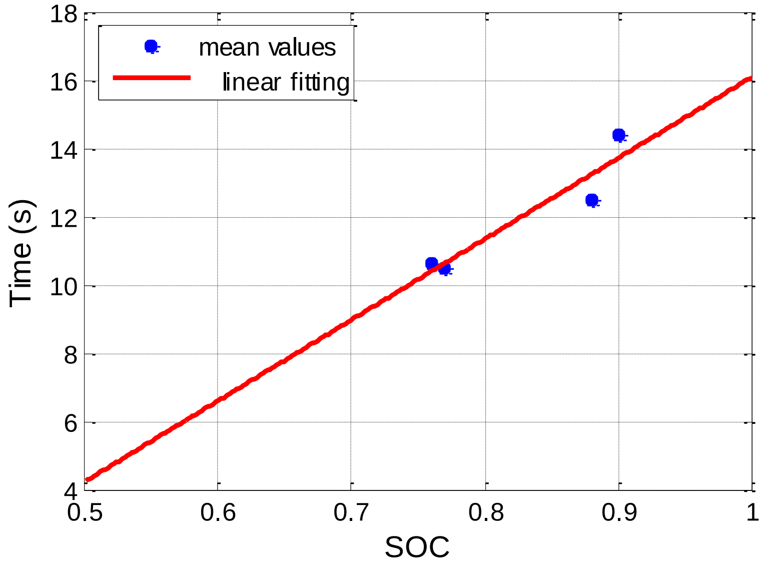

Figure 12. Experimental data on time constant R_1C_1 and linear interpolation.

Finally, Figure 13 shows the V_{oc} values. Since the absence of hysteresis, there is no difference between those obtained during the discharge-based MST, and the other obtained during the charge-based MST.

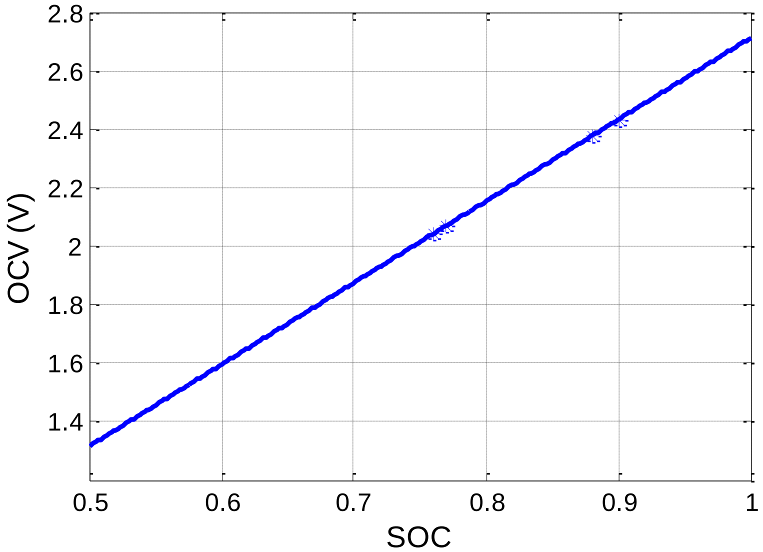

Figure 13. Experimental data on voltage V_{oc}, after discharge steps and after charge steps.

The results shown from Figure 10 to Figure 13 indicate modest variation of parameters over SOC. Therefore two ways are possible:

- The SOC dependence is totally disregarded, and R, R_1, C_1 and C are all taken as constant over SOC.
- A linear dependence is supposed.

The electrical circuit of Figure 2 in the form of one RC-block has been modelled, and the parameters evaluated with technique 1 were introduced, considering or not the SOC dependence. Giving as input to the model the MST current profile, the voltage output was compared to the measured experimental voltage. Results are substantially equivalent, as it is possible to infer by the following two figures (Figure 14 and 15).

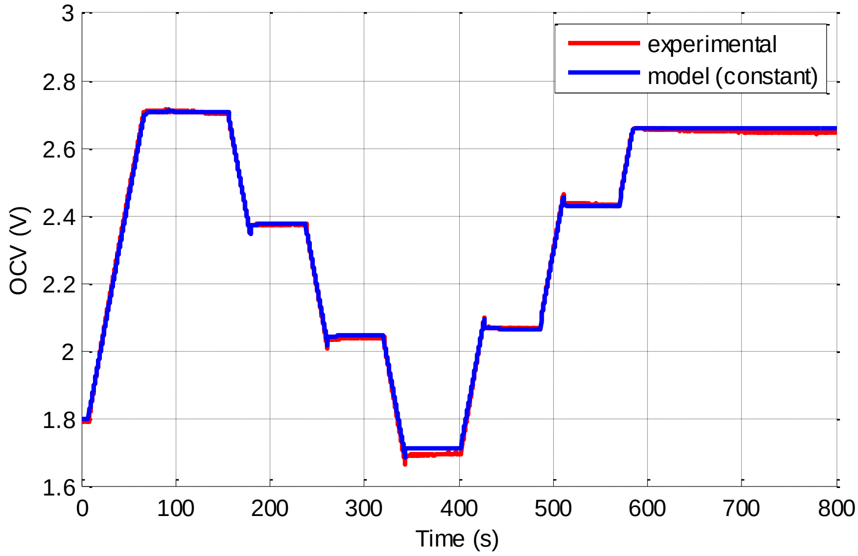

Figure 14. Experimental and simulated voltage during MST, constant parameters.

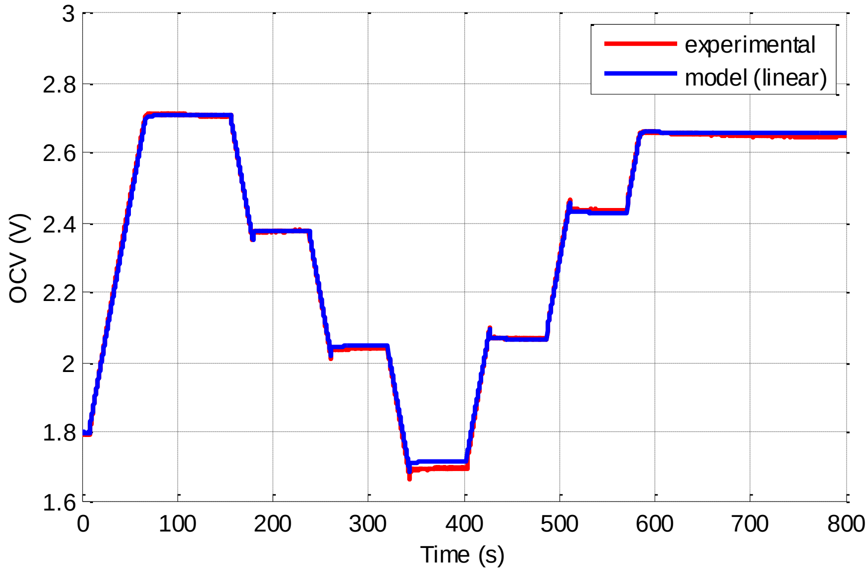

Figure 15. Experimental and simulated voltage during MST, linear dependence of parameters over SOC.

Conclusion.
Considering the modest variation of the parameters with simulation results, R, R_1, C_1 and C, can be taken as constant over SOC.

Discussion

The application of parameter identification procedure to the experimental results of the MST on the HCV SC cells has allowed a correct evaluation of numerical values for R_0, R_1, C_1, C_2, U_{oc} as a function of SOC.

Some of the parameters, especially R_1 and R_1C_1 showed a clear trend over SOC.
It is not necessary, however, to find an analytical formula to interpolate the plots of parameters R_0, R_1, C_1. To ease the ability of an easy automation of parameter extraction from experimental tests, it is simpler to make linear interpolation or spline interpolation between the values outputted by the error minimisation algorithm. This will be used in the SOC evaluation algorithm that will be discussed in deliverable D3200.8.

Conclusions

- This deliverable has dealt with all the practical issues encountered when implementing in practice for the HCV's supercapacitor a suitable mathematical model.
- The attention was concentrated towards the behaviour at room temperature (23°C).
- Test results were obtained at the University of Pisa's laboratories, analysed and discussed.
- Suitable numerical values for all the model's parameters have been determined.
- This model will be used as the basis for SOC estimation, detailed in deliverable D3200.8.

References

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