Impact of the ageing of supercapacitors in power cycling on the behaviour of hybrid electric vehicles applications

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***Abstract*- Supercapacitors are commonly based on porous activated carbon electrodes and on electrostatic charge storage mechanism. The carbon electrodes are supposed to be chemically and electrochemically inert and the electrostatic nature of the charge storage mechanism is highly reversible. These properties should ensure to supercapacitors an infinite shelf life. But in practice, supercapacitor cells exhibit a performances fading when they are used during months. The purpose of this paper is to study the influence of the performances fading of supercapacitors on the operation of a hybrid electric vehicle system composed of supercapacitors and battery. Therefore, results of supercapacitors ageing are presented in order to highlight the performances fading. Then an analytical impedance model is presented and used for the system simulation in Matlab/Simulink. The influence of the supercapacitor parameters changes with ageing will be studied and their impact on the complete system operation will be discussed.**

I. INTRODUCTION

Thanks to their high specific power and their long cycle life [1], supercapacitors (SC) are very interesting devices for on-board energy applications such as hybrid-electric vehicles (HEV). Due to their constitution and to the electrostatic principle of energy storage, supercapacitors are able to supply the discontinuous power demand [2]. In new on-board DC networks, batteries are used as energy sources for supplying the average power demand while supercapacitors are used as power sources for starting, accelerating and regenerative braking phases [1].

In the first part of this paper, a supercapacitor linear model is obtained by using the porous electrode theory. In order to reduce its complexity and to be used in time domain, this model is approximated. Then, a non linear model was deduced from porous electrode distributed models at different ageing states and was implemented in a HEV system. Then, the impact of SC state-of-health on the system behaviour is simulated in Matlab/Simulink environment.

II. SUPERCAPACITOR LINEAR MODEL

The supercapacitor constitution is based on two identical porous electrodes with a separator between them. All is impregnated with organic or aqueous electrolyte. Electrodes are composed of three layers: a carbon powder layer (conductive carbon layer) compressed on the current collector layer and an activated carbon layer added to the conductive carbon. These electrodes are characterized by a high conductivity and a high specific surface area due to the high porosity of activated carbon.. The energy storage, based on electrostatic process associated to the high electrode porosity, leads to different dynamics behaviour from those observed in electrolytic capacitors with planar electrodes that store energy by electrochemical process [2] [3].

Among existing behavioural models, RC equivalent circuits, (where R and C can depend on both voltage and temperature) are not well-suitable to describe accurately the supercapacitor voltage response, especially for discontinuous current profiles [2].

In the literature, supercapacitor useful models are obtained by using the porous electrode theory [3]. Because of its representation by distributed electrical time constants, most of them use the analogy with a transmission line. However, these models are based on the hypothesis that all the pores have an identical geometry and size. This hypothesis induces a vertical line in the Nyquist plan for the impedance in the low frequency range that is not observed in practice. Indeed, the penetration depth of the AC signals and the heterogeneity of pores induce, in the Nyquist plan, a slope of the impedance plot in the low frequency range. Such a system cannot be modeled by a finite number of pore geometry and pore size, but it can be approximated accurately on a given frequency range [4]. This frequency behaviour is representative of a Constant Phase Element (CPE) that is defined by the expression (1)

$$Z_{CPE} = \frac{1}{Q.s^{1-\gamma}} \quad (1)$$

where Q is the CPE magnitude and γ is a parameter linked to the pores size distribution. The value of the exponent varies from 0 (pure resistance) to 1 (ideal capacitor).

The CPE implementation within the impedance model of the equivalent transmission line, leads to the following expression:

$$Z_{SC} = R_S + \left(\frac{R_{el}}{Q.s^{1-\gamma}}\right)^{1/2} \coth\left[\left(R_{el}.Q.s^{1-\gamma}\right)^{1/2}\right] \quad (2)$$

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where R_s represents the resistance of the terminals, of the current collectors and of the separator, R_{el} is linked to the overall conductivity of the electrolyte through the whole porous structure [5].

This impedance model was validated on a wide frequency range. In spite of its good accuracy, this model remains complex for a time-domain simulation because of the *coth* function. If the model use is limited to the low frequency range, the Taylor series expansion of *coth* function can be investigated in order to simplify the model.

In order to obtain a rational model, the *coth* approximation was done using the Pade approximation method and that leads to the following expression of the impedance:

$$\tilde{Z}_{SC}(s) = R + R_1 + \frac{1}{Q_1.(s)^{1-\gamma}} + \frac{R_2}{R_2.Q_2.(s)^{1-\gamma} + 1} \quad (3)$$

where (R_1,R_2) and (Q_1,Q_2) are respectively proportional to R_{el} and Q. The four remaining parameters can be deduced from the following relations:

$$R_1 = \frac{R_{el}}{10}\ ,\ R_2 = 0{,}233.R_{el}\ ,\ Q_1 = Q\ ,\ Q_2 = 1{,}2.Q \quad (4)$$

As illustrated in Fig 1, this model is composed of a CPE in order to represent the pore size dispersion and also of a CPE in parallel with a pure resistance to take into account the pore penetrability in the medium frequency range.

Impedance spectroscopy measurements were used to validate the model behaviour in the frequency domain for two SC samples of different technologies (A and B). Fig. 2 shows a good agreement between the measured and the simulated impedance on the wide investigated frequency range and illustrates the frequency regions used for the model parameters identification.

III. SUPERCAPACITOR NON LINEAR MODEL

The proposed SC impedance model was validated in the frequency domain for small voltage variations around a given DC operating voltage. Consequently, this model is not able to accurately simulate large voltage variations in the time-domain because non-linear phenomena governing its behaviour are not taken into account.

Due to the pore size dispersion and accessibility, the charges mobility decreases with the increasing state-of-

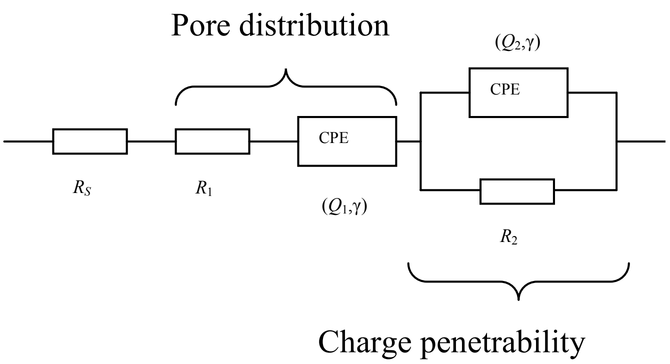

Fig. 1. Impedance model of the supercapacitor

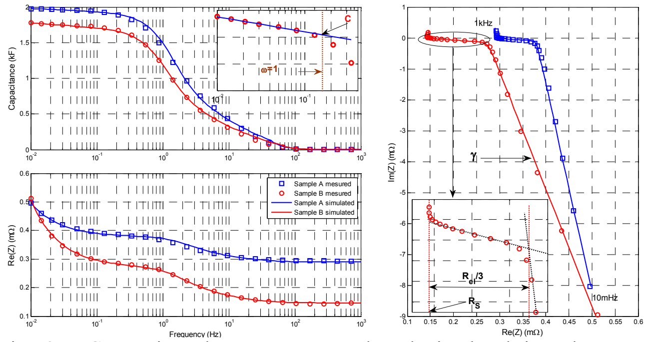

Fig. 2. Comparison between measured and simulated impedance and resulting capacitance for two SC samples

charge, that is the main reason of the non-linear voltage response to DC current.

Then, as the electro-diffusion process is not instantaneous, the charges transport to the electrode/electrolyte interface is slowing down. Each parameter of the SC model is influenced by these two phenomena. Hence, different operating voltages lead to differences in the measured impedance, especially in the low frequency range. However, only the capacitance variation has a predominant influence on the time response of the supercapacitor.

It has been demonstrated, that the first order Taylor approximation of a non-linear system allows to obtain local models. A method developed by Mouyon, has established the possibility to obtain a non-linear system by using several local models [6]. This method was applied to the SC case.

The local model defined in (3) can be rewritten as the pseudo state-space model described by (5).

$$\begin{cases} \dfrac{d^{1-\gamma}\delta z_1}{dt^{\gamma}} = \delta z_2 \\ \dfrac{d^{1-\gamma}\delta z_2}{dt^{\gamma}} = -\dfrac{1}{R_2 Q_2(V_0)}\delta z_2 + \dfrac{1}{R_2 Q_2(V_0) Q_1(V_0)}\delta I \end{cases} \quad (5)$$

$$\delta V = \delta z_1 + \left(Q_2(V_0)R_2 + Q_1(V_0)R_2\right)\delta z_2 + \left(R_S + R_1\right)\delta I$$

Pseudo-integration of (5) gives the following non-linear fractional model:

$$\begin{cases} \dfrac{d^{1-\gamma} z_1}{dt^{\gamma}} = z_2 \\ \dfrac{d^{1-\gamma} z_2}{dt^{\gamma}} = -\dfrac{1}{R_2 Q_2(V)} z_2 + \dfrac{1}{R_2 Q_2(V) Q_1(V)} I \end{cases} \quad (6)$$

$$V = z_1 + \left(Q_2(V)R_2 + Q_1(V)R_2\right)z_2 + \left(R_s + R_1\right)I$$

It can be verified that the Taylor approximation of (6) around the operating voltage V_0 leads to relations (5).

The fractional integrator is approximated by a transmittance based on recursive distribution of poles and zeros as described in [7]. To avoid long time simulation, it is important to optimize the number of poles and zeros with the frequency width. However, this method does not allow to

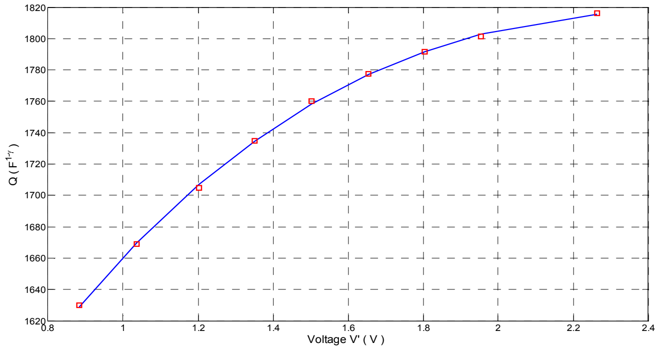

Fig. 3. Polynomial approximation of the Q vs. cell voltage dependency

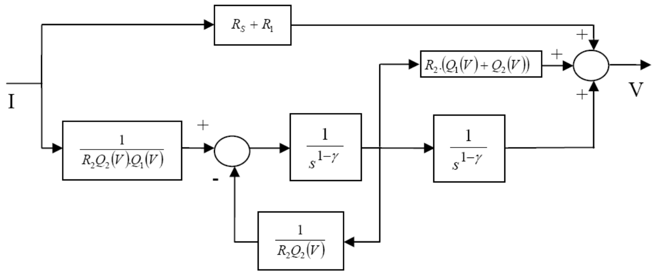

Fig. 4. Implementation of the non-linear model

obtain the best precision for the approximation of the non integer order that it can be possible to do.

As illustrated in Fig. 3, the voltage dependency of the capacitance is taken into account in the model by using a polynomial approximation of the stored charge Q vs. voltage.

The resulting non-linear model (6) can be implemented in Matlab/Simulink according to the bloc diagram of Fig. 4 [8].

The voltage dependency of Q is taken into account through $Q_1(V)$ and $Q_2(V)$.

Thanks to the reduced number of parameters, this model is well-suitable for a multiple identification procedure as required for taking ageing into account. In this aim, power cycling tests with periodic characterization measurements have been investigated in order to study the evolution of the model parameters with SC ageing.

IV. SUPERCAPACITOR POWER CYCLING

The power cycling of SC was done on the laboratory platform by using a specific current profile obtained thanks to a synthesis of the HEV power requirements but also from intrinsic properties of SC [9]. This profile is characterized by a typical period of one minute and is composed of a charge-rest-discharge sequence. The charge and discharge phases are made at 400A and the rest period at open-circuit is chosen in order to obtain, in our case, a RMS current value of 185A.

The power cycling is periodically stopped in order to make a characterization test in the frequency domain by impedance spectroscopy at 2V operating voltage.

As illustrated in Fig. 5, the large variation of the frequency behaviour in the Nyquist plan, confirms the increase of the resistance, the increase of the γ parameter and the decrease of the capacitance.

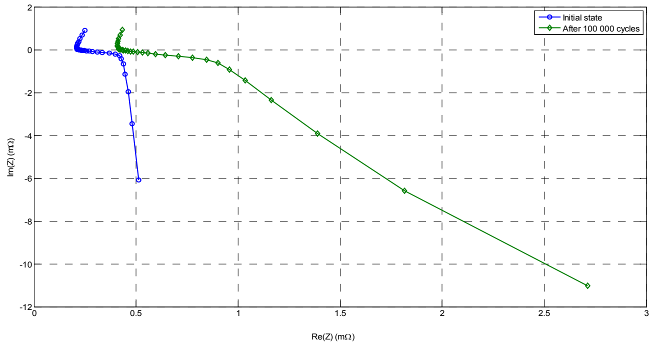

Fig. 5. Results of impedance spectroscopy for two states-of-health

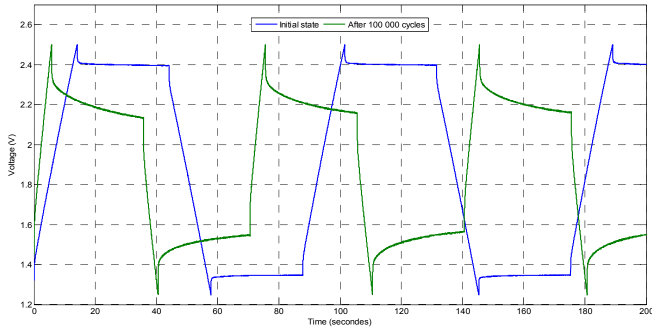

Fig. 6. 200A charge-discharge cycles in the [1.25, 2.5V] voltage range for two different states-of-health

The changes in the time-domain behaviour due to power cycling are quantified thanks to a charge-discharge test at 200A on a voltage range comprised between 1.25V and 2.5V as illustrated in Fig. 6.

The characterization with constant current shows a decrease of charge and discharge phase duration that is essentially due to the decrease of the capacitance. Also, we can notice the increase of the relaxation phenomenon after each charge-discharge phase. This is due to the increase of the γ parameter that is linked to the redistribution of species at the electrode/electrolyte interface.

The corresponding model parameters for these two ageing states are summarized in table I.

TABLE I

Parameter	R_S (μΩ)	R_{EL} (μΩ)	Q (F.s$^{-\gamma}$)	γ
Initial state	176	740	2540	8.5 10-3
100 000 cycles	354	1315	1060	105 10-3

V. HYBRID-ELECTRIC VEHICLE APPLICATION

The increase in the electrical requirements in terms of both power and energy for hybrid-electric vehicles implies the development of new on-board power network architectures [10]. Among typical architectures, one includes the classic network produced by the conventional 12V battery and a power network that consists in a machine-converter group coupled mechanically with the internal combustion engine (ICE) as illustrated in Fig. 7.

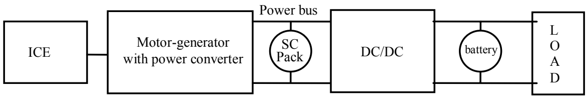

Fig. 7. One typical HEV architecture

The main functionalities of such architecture are the ICE start/stop, the boost that corresponds to an additional power in order to assist the ICE during accelerating phases, and the regenerative braking capability. In such HEV architecture, a supercapacitor pack is connected to the power bus and to a DC/DC converter that allows the adaptation of the voltage levels between this two networks.

This system has been modeled in Matlab/Simulink environment. The DC/DC block is based on a pseudo-continuous model which is able to reproduce the dynamic behaviour of the currents and of the voltages. A regulation loop is integrated for the battery voltage with a current limitation. This converter allows, on one hand, to have a regulated network less sensitive to the peak power demands than the conventional network and on the other hand to assure the battery charge under constant voltage.

The validation of the simulation results of the system depends on the models and the state-of-charge and state-of-health of the storage elements. For the supercapacitor pack, we use the proposed model associated with a parameters set for initial and aged state. For the battery, we use a Randle's model that is modified to take into account the state-of-charge dependency of the open-circuit voltage and of the serial resistance and also the floating current during charge phases.

One of the simulation purposes is to estimate the impact of the SC pack ageing on the system behaviour.

The originality of this work resides in taking into account not only of the state-of-charge of storage devices but also their state-of-health in order to elaborate strategies for optimal energy management with the reduction of fuel consumption as the main criterion.

In micro-hybrid applications, power levels are strictly linked to the vehicle usage and to their various equipments. The synthesis of power requirements allows defining a typical and representative profile for an urban usage, which corresponds to the current supplied by the machine-converter network. This profile includes a restart phase of the ICE (500A, 1s), a torque assistance phase (150A, 3s), a regenerative braking phase (150A, 3s) and finally a rest phase. To keep the SC pack state-of-charge in a given voltage range during a large number of cycles, the reference cycle was balanced by adjusting the current level during the alternator phase.

The simulation results illustrated in Fig. 8.a and Fig. 8.b correspond to two states of SC pack ageing and two consumption levels on the network battery.

In the case of a new pack, the excursion of the power network voltage stay in acceptable limits, both for the DC/DC converter and for the SC pack. On the other hand, in the case of an aged pack, for an equipment consumption of 50A, the voltage becomes too low during the restart to assure a good

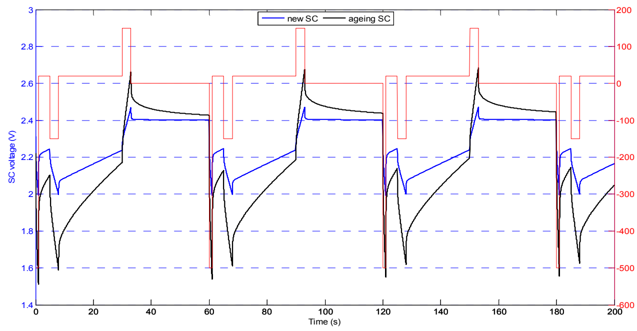

Fig. 8.a. HEV current profile without equipment consumption

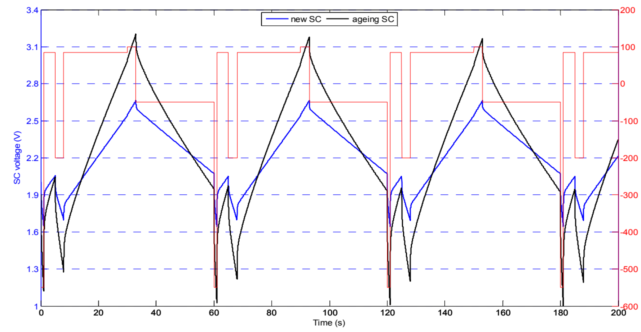

Fig. 8.b. HEV current profile with 50A equipment consumption

behaviour of the DC/DC and too high for the SC pack during the regenerative braking phase. In view of these results, one of the objectives is to define control strategies for the static converters which inhibit some functionalities of the hybrid vehicle.

VI. CONCLUSION

In the first part of this study, a supercapacitor model, based on an analogy with an equivalent transmission line, was presented. It allows taking into account the distribution of the pore size in the electrodes which has an influence on the impedance at low frequency.

The model parameters were identified from impedance spectroscopy measurements, and a non linear model of the supercapacitor, presented in the second part, has been deduced. Only the voltage dependency of the double layer capacitor is taking into account in this non linear model. The time responses take well into account the voltage dependency for the different test phase (charge, discharge, relaxation).

Power cycling tests have been done on several SC cells, with specific current profiles deduced from HEV power requirements. These measurements have been done to obtain parameters set which describes the supercapacitor behaviour in the initial state and at the end of 100000 cycles.

Finally, on the basis of the proposed model and of a micro hybrid EV architecture, the ageing impact on the supercapacitor behavior and the system process is studied.

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