Electrochemical Double Layer Capacitors (supercapacitors) ageing studies in the particular context of personal ground transports

Ronan German, *Laboratoire Ampère UMR CNRS 5005, Université Lyon1*
Pascal Venet, *Laboratoire Ampère UMR CNRS 5005, Université Lyon1*
Ali Sari, *Laboratoire Ampère UMR CNRS 5005, Université Lyon1*
Jean-Michel Vinassa, IMS UMR CNRS 5218,Université Bordeaux 1
Olivier Briat, IMS UMR CNRS 5218, Université Bordeaux 1

***Abstract*—This documents is a summary of the 2 first PHD years of Ronan German. Reserches are supervised by Pascal Venet and Ali Sari. The main goal of PHD is to integrate ageing constraints effects of personal ground transports on existing ageing laws concerning electrochemical double layer capacitors (EDLC). Firstly a quick introduction will present the PHD problematic. Secondly the different accomplished works will be introduced (test benches conception, EDLC impedance modeling, experimental ageing results interpretation). Finally conclusion and perspectives will present the envisaged future researches.**

***Résumé*—Ce document est un résumé des travaux de thèse effectués par Ronan German durant les deux premières années. Les recherches sont encadrées par Pascal Venet et Ali Sari. Le but principal du doctorat est d'intégrer aux lois de vieillissement préexistantes, l'effet des contraintes de vieillissement rencontrées par les supercondensateurs, dans l'environnement des transports routiers (vehicules mild hybrid ou full hybrid) . La problematique et l'objet d'étude (le vieillissement des supercondensateurs) seront tout d'abord présentés. Dans un second temps les travaux accomplis seront montrés (construction des bancs d'essais, modélisation d'impedance, interprétation des résultats de vieillissement). Enfin viendront conclusions et perspectives.**

I. INTRODUCTION

A. *EDLC ageing*

Supercapacitors (SC) also called electrochemical double layer capacitors (EDLC) are energy storage systems. EDLC storage principle is based on the double layer effect as shown on Fig. 1. Double layer effect is an ionic/ electronic electrostatic storage. It occurs when a potential difference (ΔV) appears between electrically supplied electrode and an electrolytic solution. As there is no faradic storage as in batteries, they are particularly interesting thanks to their high cyclability and their high power density. Nevertheless their mass energy is lower than batteries. They can be used in transports domain such as trolleybuses or in railway transports in applications where peak power is needed (braking energy recovery or stop and start systems). In transports area reliability and diagnostic of energy storage systems (ESS) are major issues. As a matter of fact as any ESS, EDLC are subject to ageing. Fig. 1 represents ageing causes and effects of EDLC. EDLC electrodes are porous to maximize contact surface between electrode and electrolyte. To get porous structure from carbon some chemical treatments are necessary. These treatments let parasitic surface groups on electrodes which react by redox reactions under voltage and temperature constraints of EDLC. The solid reaction products start to block electrode porosity causing capacitance loss. Produced off-gas makes electrode cracks. Binding agent ageing causes electrode grain drops implying an equivalent serial resistance (ESR) increase. Thus EDLC Ageing has an impact on EDLC impedance. That's why impedance will be used for EDLC state of health monitoring in our project.

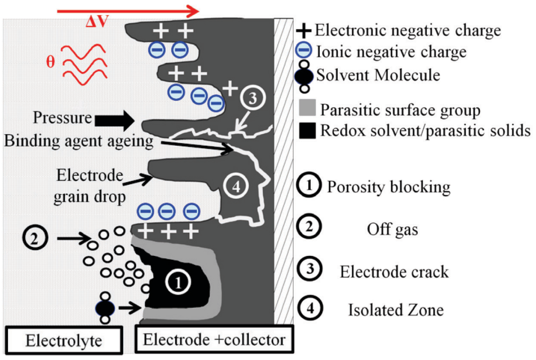

Figure 1. Ageing causes and effects of EDLC

B. Problematic

The major acceleration factors on EDLC ageing are temperature, voltage and current. Some studies have already been achieved on floating ageing (constant temperature and voltage constraints) and on cycling ageing (high current profiles). Nevertheless the environment of personal ground transports implies complex ageing constraints as shown on Fig. 2. As a matter of fact they are subject to parking phases which are equivalent to floating ageing and active driving phases which are equivalent to cycling ageing (high current). Moreover the presence of DC-DC converters on transports electrical network is a possible source of ageing. Finally the impact of day and night temperature changes has to be verified. The main goal of my PHD is to find ageing laws for EDLC taking into account all parameters of ground transports domain.

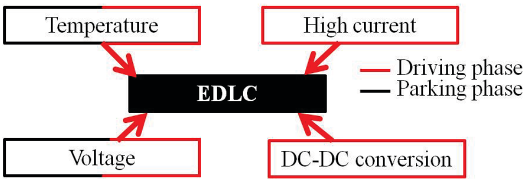

Figure 2. Ageing constraints on EDLC in personal ground transports

II. Works and Methods

A. Works accomplished

The works on my thesis are divided in four parts:

- Building experimental test bench for EDLC ageing and characterization
- Writing experimental protocols
- EDLC impedance model comparison
- Experimental EDLC ageing results

B. Building experimental test bench

Fig. 3 presents the experimental platform used for obtaining experimental results presented in this article.

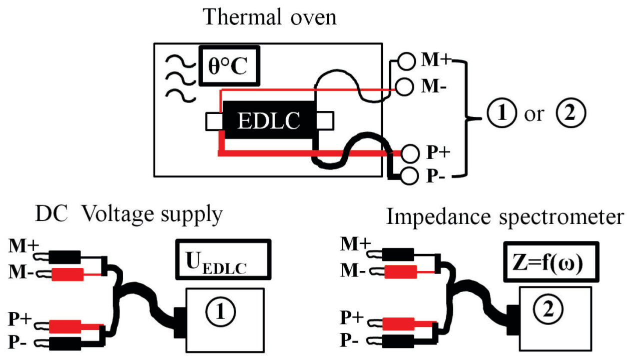

Figure 3. Presentation of experimental platform

It has been shown (Part. I.B) that ageing speed mainly depends on temperature and voltage constraints. EDLC is placed in a programmable precision incubator for applying the temperature constraint. As EDLC needs to be kept at the same voltage (we are currently studying floating ageing) a dispositive of electrical connection is plugged on EDLC. To not disturb EDLC temperature (as a matter of fact EDLC impedance is dependant of temperature) this connection dispositive is placed outside incubator thanks to a thermo isolated hole. As impedance of EDLC is the same order of magnitude than the electrical wires (0.1mΩ) a 4 point dispositive must be connected (M+ and M- are the pins used for voltage measurement and P+ and P- are the power pins where the charging /discharging current goes through). These pins are connected during ageing time to a DC voltage supply and regularly replaced by an impedance spectrometer for achieving characterizations.

C. EDLC impedance model comparison[1]

1) Single pore model

Single pore model has been developed for modeling frequency behavior of a porous structure of EDLC uniquely composed of perfectly identical cylindrical pores. In this working hypothesis, porous structure impedance can be modeled using simple equivalent components as shown in figure 4 .

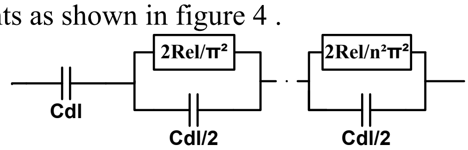

Figure 4 Equivalent electrical circuit of porous structure for single pore sized

C_{dl} represents the LF (low frequency) double layer capacitive effect; this parameter is called porous structure capacitance. R_{el} is called electrolytic resistance. Parallelized R_{el} and C_{dl} equivalent circuits model the increasing difficulty for charges to penetrate deep in the pore with increasing electrical signal frequency. Impedance of electrode can be defined by the following expression [2]:

$$Z_{PorousStructure} = \sqrt{\frac{R_{el}}{j\omega C_{dl}}} \times \coth(\sqrt{j\omega C_{dl} R_{el}}) \qquad (1)$$

Experimental results show that real EDLC porous impedance behavior appears to be far away from a single pore sized porous electrode model. It has been interpreted by Song and al [3] as the result of a pore size distribution on real porous electrode. This implies slow diffusion and sluggish surface reconstruction between the different pore sizes. Time constants of these phenomena can go from one second up to several hours. Thus influence of pore distribution on porous impedance occurs in the LF range (10 mHz to 100 mHz).

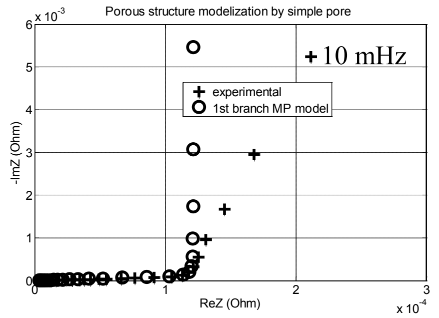

Figure 5 Comparison between EDLC electrode impedance and single pore model Nyquist diagrams

2) CPE Model

As the single pore model was precise to model HF diffusion phenomena Kötz and al. in [4] proposed to combine strength of single pore with CPE component including CPE element into the single pore equation (Eq.1). They replaced consequently the frequency dependant factor $j\omega C_{dl}$ by $(j\omega)^{1-\gamma} C_{dl}$ in Eq. 1 to model pore distribution influence in LF. This model is called the CPE model. Then mathematical expression of porous structure impedance becomes [4]:

$$Z_{PourousStructure} = \sqrt{\frac{R_{el}}{(j\omega)^{1-\gamma} C_{dl}}} \times \coth\left(\sqrt{(j\omega)^{1-\gamma} C_{dl} R_{el}}\right) \quad (4)$$

Equivalent electronic circuit is obtained by replacing the serial C_{dl} capacitance by a CPE element (C_{dl}, γ) in figure 4 to model LF impedance. As the HF diffusion phenomena were correctly modeled in single pore model the HF part of the circuit does not change.

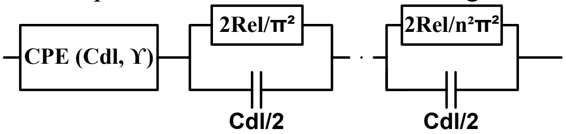

Figure 8. CPE model equivalent circuit [4]

The figure 9 presents the graphs of experimental porous structure impedance and the CPE model fitting.

LF distribution associated phenomena effects appear to be well represented by the CPE model. The gain in term of LF fitting precision is important compared to single pore model. Moreover the simple mathematical expression makes it easy to extract parameters with a simple fitting algorithm. Nevertheless, two major drawbacks appear. The first one is the fact that CPE element is a fractional derivative element. It cannot be represented by an equivalent LRC circuit. The second one concerns the health monitoring of EDLC. Indeed, evolution of global parameters such as (C_{dl}, γ, R_{el}) does not allow to know if there is some pore category which are more or less concerned by the ageing processes. Identification of separated pore impedance evolution could enable to monitor the effect of different chemical ageing reactions [7].

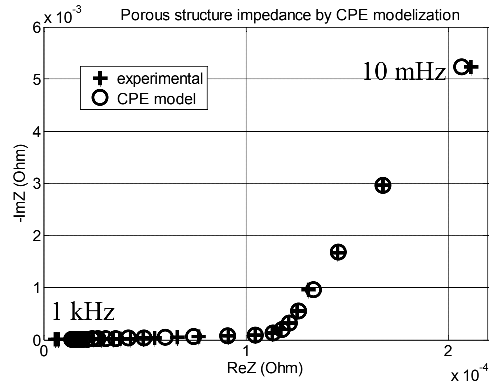

Figure 6 Porous structure impedance CPE model fitting

3) MP Model[5]

The MP model has been published in 2006. The idea of Hammar [5] was to group the n_i pores of the same individual impedance characteristics. The parameters Z_{pi}, R_{eli}, C_{dli} depend on the impedance of one pore and the number n_i of parallel pores in the group. Each group of pores can be modeled by a branch. The parallelization of each branch results in the impedance of the whole porous structure. The second interesting fact is that each pore of the branch owns the same (R_{eli}/n_i, n_iC_{dli}) characteristics. Then a single pore model with (R_{eli}, C_{dli}) parameters is sufficient for representing the behavior of each branch (Fig. 11). Thus impedance of porous structure can be expressed thanks to the parallelization of single pore impedance expression(2).

$$Z_{PorousStructure} = \sqrt{\frac{R_{el1}}{j\omega C_{dl1}}} \times \coth\left(\sqrt{j\omega C_{dl1} R_{el1}}\right) // \ldots \quad (2)$$
$$\ldots // \sqrt{\frac{R_{e1k}}{j\omega C_{d1k}}} \times \coth\left(\sqrt{j\omega C_{d1k} R_{e1k}}\right)$$

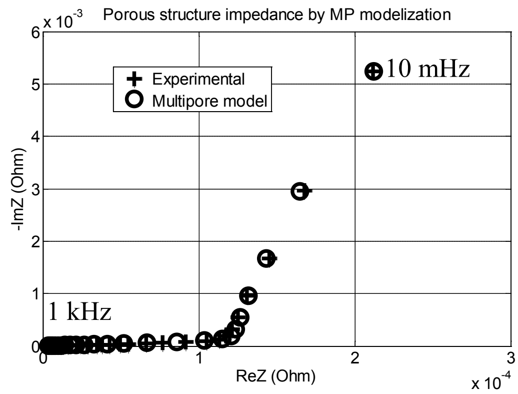

Figure 7 Porous structure impedance MP model fitting

The LF precision of MP model is much better than with single pore model (see Fig. 6) and equivalent at CPE model (see Fig. 8). The issue of equivalent circuit on CPE model (see Fig. 7) has been settled as the impedance models just uses R and C components. The major appearing drawback is the mathematical difficulties to extract parameters. As a matter of fact the model equation is far much complicated than with CPE models because of the branches parallelization.

D. EDLC Ageing [2]

Fig.8 represents the influence of 2.8V 60°C ageing on the EDLC 10 mHz capacitance and the resistance R_0 (defined as the real part of EDLC impedance when the imaginary part of EDLC impedance is null). This study has been launched on 2 manufacturers since the 12 December and is still running. Capacitance is calculated at a frequency of 10 mHz (3).

$$C(\omega) = \frac{-1}{Im(Z_{EDLC}(\omega)) \times \omega} \quad (3)$$

Where ω is the pulsation and $Im(Z_{EDLC}(\omega))$ is the imaginary part of EDLC impedance. As presented in Fig. 1 porosity blocking is accompanied by capacitance loss. The increase of R_0 is characteristic of connections defects evolution and binding agent ageing. Other models can be applied to get more ageing parameters (single pore, CPE, MP). A paper studying ageing interpretation by MP model has been submitted to the IPEC conference in Vietnam [6]. The acceptation date is the 15 September.

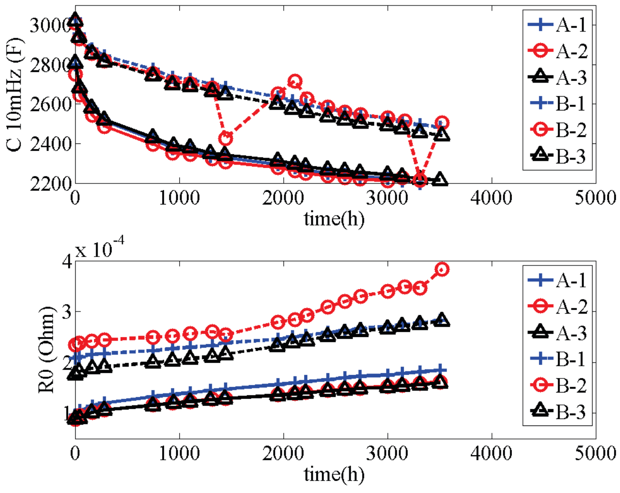

Figure 8 EDLC parameters evolution with ageing

III. CONCLUSIONS AND PERSPECTIVES

The first year of PHD has been dedicated to the conception and building of experimental test benches. Important investments have been made (28 tracks programmable CC/ DC/ CP supply, high power cycling bench and thermal oven acquisitions). Then the second year has been dedicated to publications. An article has been presented in conference REVET (Renewable Energy and VEhicular Technologies) 2012. It won the best paper award. The aim of this article was to present and compare EDLC impedance models in term of low frequency fitting precision and ageing monitoring quality. The multipore (MP) model has shown a lot of qualities in both domains. Thus it will be used for ageing results and interpretations. A review with more precisions is about to be submitted to IEEE IES [7]. The first experimental results on EDLC floating ageing (constant temperature and EDLC voltage) have been collected and interpreted. An article has been written and submitted to a conference with the first ageing interpretations by MP model. The next step is to include the particular ageing constraints encountered in the personal ground transports environment. Interpretation of difference between simple floating ageing and ageing caused by ground transports constraints (temperature changes, DC-DC conversion effects) will be done and constitutes the major point of interest of PHD.

PUBLICATION WORKS

[1] R. German, P. Venet, A. Sari, O. Briat, and J. Vinassa, “Comparison of EDLC impedance models used for ageing monitoring,” in *Renewable Energies and Vehicular Technology (REVET), 2012 First International Conference on*, march 2012, pp. 224 –229. **Published**

[6] R. German, P. Venet, A. Sari, O. Briat, and J. Vinassa, “Interpretation of electrochemical double layer capacitors (supercapacitors) floating ageing by multi-pore model,” in *The 10th International Power and Energy Conference IPEC 2012*, 12 - 14 December 2012. **Submitted**

[7] R. German, P. Venet, A. Sari, O. Briat, and J. Vinassa, “Review on electrochemical double layer capacitors ageing impacts and comparison on ageing monitoring impedance models,” *IES*, 2012. **Submission**

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