Lithium Ion capacitor characterization and modelling

Hamid Gualous, G. Alcicek, Youssef Diab, A. Hammar, Pascal Venet, K. Adams, M. Akiyama, C. Marumo

ESSCAP'2008 – Lithium Ion capacitor characterization and modelling

H. Gualous(1), G. Alcicek(1), Y. Diab(3), A. Hammar(2), P. Venet(3), K. Adams(4), M. Akiyama(4), C. Marumo(5)

(1) FCLAB-SeT, UTBM-UFC, bat F, rue Thierry Mieg 90010 Belfort,
(2) PVI, Rue de maison rouge - Zone industrielle Gretz Armainvilliers France
(3) AMPERE UMR CNRS 5005, Université de Lyon, Université Lyon 1, 69622 Villeurbanne Cedex, France
(4) JSR Micro NV Leuven, Belgium
(5) JM Energy, Japan
hamid.gualous@univ-fcomte.fr

Abstract

To develop electrical busses for applications with a fast recharge system in stations, PVI has been testing some electrical energy components like supercapacitors and batteries with high power density. Neverthless, supercapacitors limit average autonomy between two recharge points, due to their poor energy density. On the other side cycle life of batteries are very dependent on current. To surmount these problems, PVI in collaboration with the FCLAB laboratory and the AMPERE laboratory, are studying Lithium-ion capacitor (LIC) for applications with fast recharge.

We take to assess how the storage system meets busses power and energy requirements in heavy electric vehicles. We note that the advantage of LIC technology compared to conventional supercapacitor lies in the fact that the energy density and the nominal voltage are higher. In this study, the Li-ion capacitor is characterized and modelled. The characterization and modelling methods are the same of supercapacitor with double layer activated carbon technology. The LIC efficiency will be discussed.

I. Introduction

Lithium Ion capacitor is a new storage device which combines high power density and high energy density compared to conventional supercapacitor of the market. It has four time higher energy density than conventional supercapacitor. The structure of the LIC is composed by two electrodes. The positive one is formed by activated carbon as in double layer capacitor. The negative electrode uses lithium ion doped carbon. This new electrode technology boosts the capacity of the negative electrode and increases the electrical potential difference. The electrolyte is based on the Li Ion.

Figure 1 shows the elementary structure of EDLC and Li-ion capacitor structure. It can be seen that the negative LIC electrode is formed by Li doped Carbone. The equivalent capacitance is formed by the positive electrode capacitance Cdl in series with the negative one Cli. The equivalent capacitor can be expressed as following:

$$\frac{1}{C_{eq}} = \frac{1}{Cdl} + \frac{1}{Cli} \quad (1)$$

where Cli >> Cdl ⇒

$$C_{eq} \approx C_{dl} \quad (2)$$

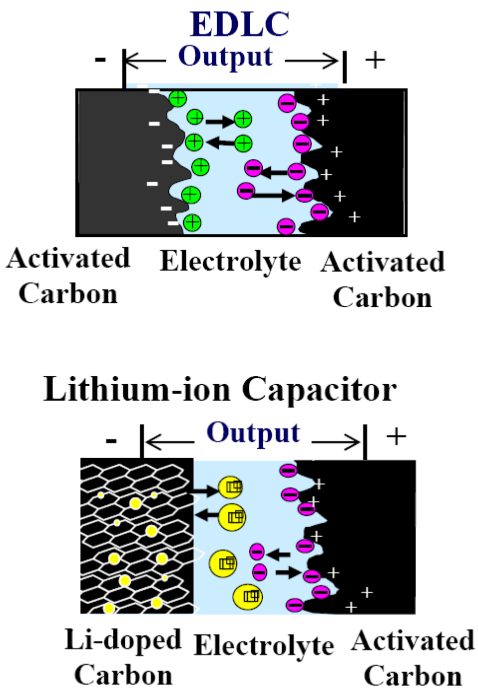

Fig. 1: Elementary structure of EDLC and Li-ion capacitor (JM Energy [1])

The Li Ion capacitor studied in this paper (figure 2) is fabricated by JM Energy. Their parameters are: nominal capacitance: 2000F; volume 124ml; weight: 208g, maximum operation voltage 3.8V and minimum voltage of 2.1V.

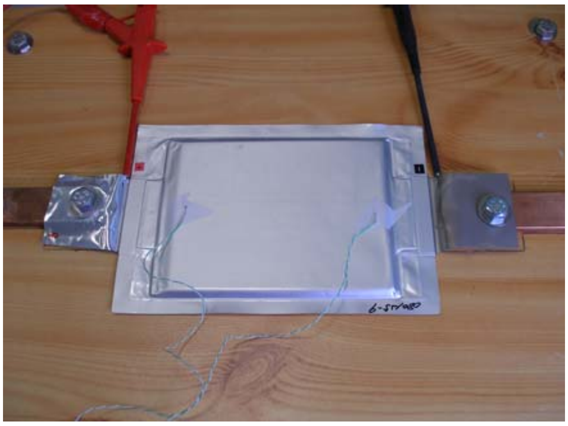

Fig. 2: Lithium Ion capacitor

II. LI ION CAPACITOR CHARACTERIZATION

A. DC characterization

Li-ion capacitor is charged and discharged under constant current constraints for several current values. Figure 3 represents the Li-ion capacitor voltage evolution as a function of time. The current of charge and discharge is fixed at 100A at ambient temperature; the device voltage varies between its nominal voltage 3.8V and 2.2V. Charge discharge result shows that voltage curves can be fitted with linear curve.

The DC ESR and C measuring methods are based on the Li-ion capacitor discharge at constant current. At the first approximation, Li-ion capacitor can be characterized by an equivalent series resistance and by an equivalent capacitance. The leakage current and the Li-ion capacitor inductive behavior can be neglected. The method used to determine ESR and C is presented in figure 4 and 5.

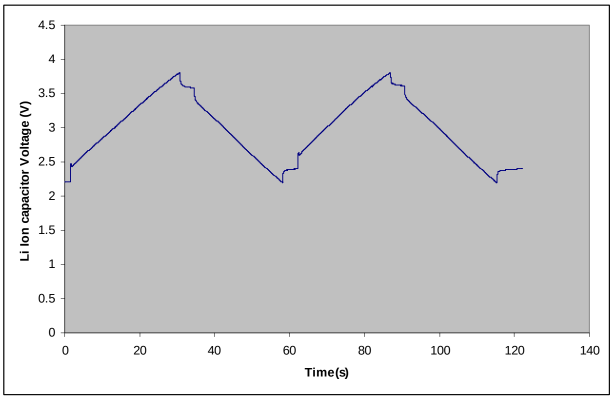

Fig. 3: Li-ion capacitor voltage evolution during charge and discharge, the current is regulated at 100A

The equivalent capacitance value is determined from the Li-ion capacitor discharge and charge at constant current between Vmax = 3.8V and Vmin = 2.2V (figure 4). The equivalent capacitance value is calculated using the following expression:

$$C = \frac{I\Delta t}{\Delta V} \tag{3}$$

where I is the current of discharge, Δt = t1 and ΔV=V2 - V1. Where V1 = Vmin + 40%*(Vmax - Vmin) and V2 = Vmin + 80%*(Vmax - Vmin).

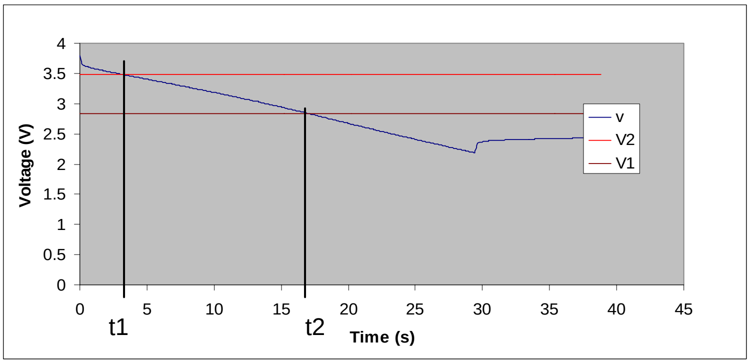

Fig. 4: Li-ion capacitor discharge at constant current

In the equation (3), I is the current, Δt can be the duration of charge or discharge and ΔV is the Li-ion capacitor voltage variation. Using this expression we have determined the equivalent capacitance of charge and discharge and for 50A, 100A, 150A and 200A. Table I gives the Li Ion capacitor of charge (Ceqch) and discharge (Ceqdis).

TABLE I. EQUIVALENT CAPACITANCE OF CHARGE AND DISCHARGE FOR SEVERAL CURRENT VALUES

Current (A)	Ceqch (F)	Ceqdis(F)	Ceqdis/Ceqch
50	2118	2100	99%
100	2083	2004	96%
150	2024	1955	96%

These results shows that Li-ion capacitor coulombic efficiency (Ceqdis/Ceqch) is very high (>96%) compared with battery.

For DC ESR measurement is based on the discharge at constant current (cf. discharge voltage figure 5). The time between the end of charge and the start discharge is fixed at 30 mn this duration can be reduced because of the very low Li-ion capacitor self discharge compared with double layer capacitor. The ESR is calculated by using the following expression:

$$ESR = \frac{\Delta U3}{I} \tag{4}$$

ΔU3 is the drop voltage obtained from the intersection of the auxiliary line extended from the straight part and the time base at time of discharge start, I is the constant current of Li-ion capacitor discharge.

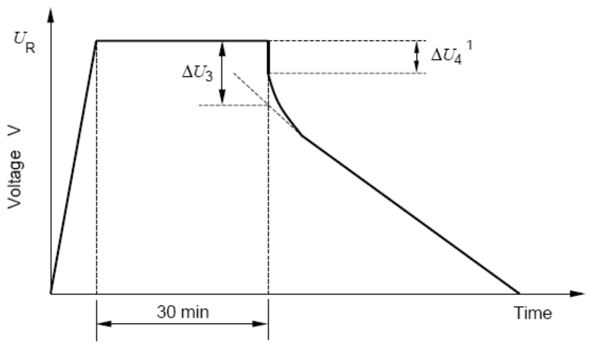

Fig. 5: Charge and discharge of Li Capacitor at constant current

TABLE II. ESR OF 2000F LI-ION CAPACITOR

Current (A)	ESR (mΩ)
50	1.84
100	1.70
150	1.78

ESR variations with current for these three values can be neglected.

B. *AC characterization*

The Li-ion capacitor AC characterization was realized using an Electrochemical Impedance Spectroscopy (EIS). To characterize the studied device, the sweep in frequency must be done for various voltage levels. EIS allows the study of the influence of frequency on the Li Ion capacitor. Figure 6 presents the variation of the negative imaginary part as a function of the real part for different voltage values. It can be seen that the Li-ion capacitor equivalent capacitance C is not linear with voltage.

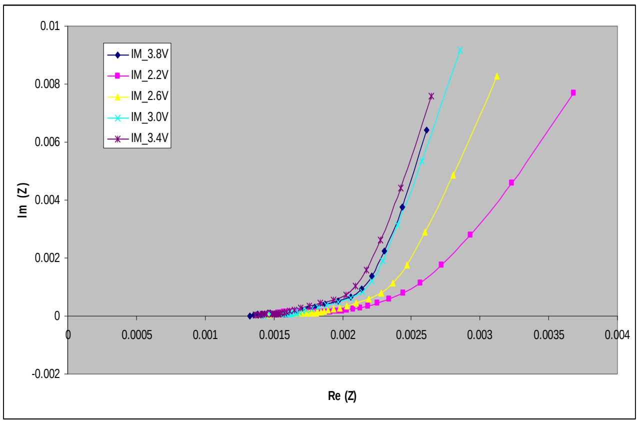

Fig. 6: Li Ion capacitor imaginary part as a function of real part for 2.2V, 2.6V, 3V; 3.4V and 3.8V

It assumed as a first approximation that Li-ion capacitor is modelled by a resistance in series with capacitance. Using the EIS results we deduced the C evolutions as a function of DC voltage. Figure 7 represents the experimental results. It can be seen that Li-ion capacitor equivalent capacitance decreases with voltage when V<3V and the capacitance increases.

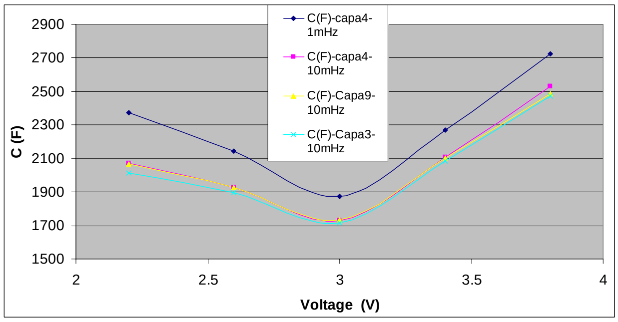

Fig. 7: C variations with Li-ion capacitor voltage

The dc voltage dependency of *ESR* is depicted in figure 8. No as the classical double layer capacitor, an increase in voltage leads to decrease the ESR. This means in high voltage, we can obtain best discharging power.

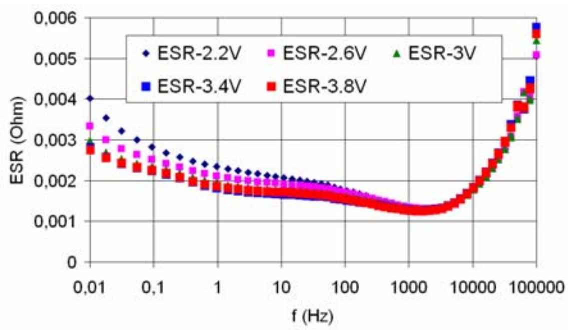

Fig. 8 : ESR v. frequency for different voltages

Figure 9 shows the variation of capacitance versus the frequency for different voltage from this figure, it(s clear that the Li-ion capacitor equivalent capacitance C is not linear with voltage.

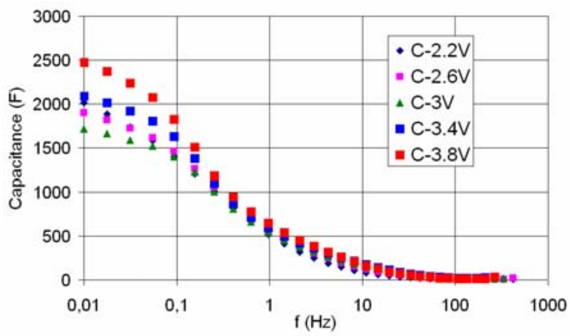

Fig. 9: Capacitance v. frequency for different voltages

III. LI-ON CAPACITOR MODELLING

To model the LIC components, we have chosen a “multipenetrability” [2] model presented on figure 10. It is composed of four elements, inductance L, series resistance and complex parallel pore impedances described by the equation below. In the presented model only Zp1 and Zp2 are considered. The model parameters are calculated using the experimental results of EIS. The comparison between simulated and measured Nyquit plot are presented on figure 11.

$$Z_{Pi} = \sqrt{\frac{R_{eli}}{j\omega.C_{dli}}} \times \coth \sqrt{j\omega.C_{dli}.R_{eli}} \quad (5)$$

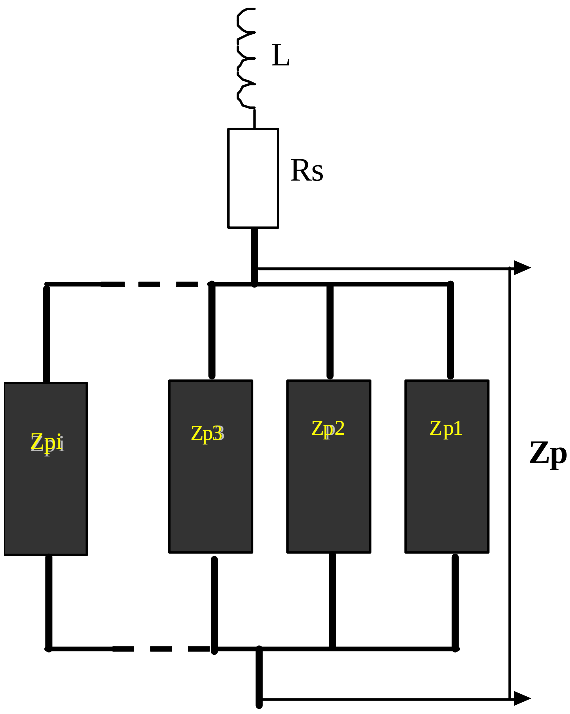

Fig. 10: Multipenatrability model

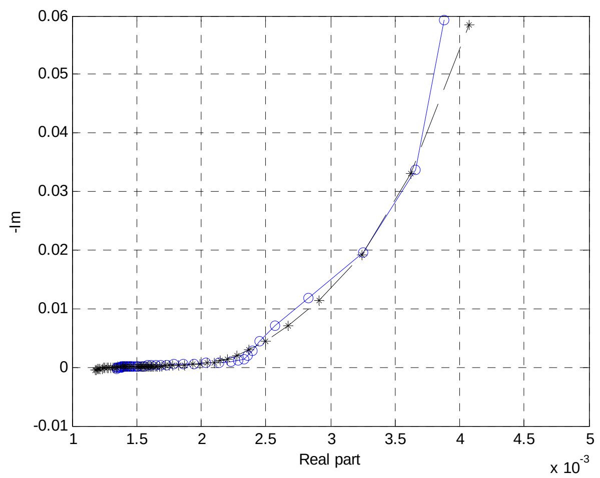

Figure 11: Comparison between simulated and measured impedance in Nyquist plot

IV. Conclusion :

We have described in this paper t Li-ion capacitor, its characterization and modelling. This new energy storage device presents a high energy density compared to conventional supercapacitor and a high power density compared to battery. It can be used for energy and power applications, in particular for electric heavy vehicles.

We have presented Li capacitor and its electrical parameters according to electrical model. It shows high capacitance density with relatively high resistance, it is due to the nature of electrolyte employed. This resistance limits efficiency of the component for high current values (>200A). Capacitance shows two linear behaviours, under and above 3V, it may be due to the lithium doping effect.

Electrical model and characterization methods applied to supercapacitors kept valid in the case of Li-capacitor. In our future papers, we try to study thermal behaviour and ageing of Li-ion capacitors.

References

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