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Cell characterization of Lithium-ion capacitor with FreedomCAR and EIS method

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Abstract

Lithium ion capacitor is a new electric storage device which combines high power density of a EDLC and high energy density of a battery. It has four time higher energy density than conventional supercapacitor and four time higher power density than a lithium battery. The characteristics of an electric storage device are usually determined by testing *only one* cell or the *whole* pack (without looking at the individual cells), with a *low*, *constant* current and by considering *only one* internal resistor[1]. This is the easy way and gives good performance results, but this is not the reality where the batteries or capacitors are submitted to. In this research *individual* cell parameters (two internal resistors and two internal capacitors) of Li capacitor are determined at cell level and at module level with FreedomCAR model and Electrochemical Impedance Spectroscopy method. An *extreme* current profile is loaded to represent the reality. The model matches the measurements with an accuracy of 99%(+/-0.9%). The evolution of the parameters and the imbalance between the cells are studied as a function of SOC, frequency, current.

Keywords: lithium battery, cell characters, internal resistance, FreedomCar method, EIS

ABBREVIATIONS

OCV	Open Circuit Voltage: Ideal battery voltage [V]
C	Capacitance [F]
Cap	Capacity [Ah]
C_{eq}	Equivalent capacitance in the LiC model
CC	Continuous Current
EDLC	Electric Dual Layer Capacitor, supercapacitor
EIS	Electrochemical Impedance Spectroscopy method
$I_{dch,max}$	Maximum discharge current [A]
I_{ch}	Charge current [A]
I_L	Battery load current [A]
I_P	Current through polarization resistance [A]
LiC	Lithium ion capacitor
M	Mass [g]
OCV’	Variation of OCV per exchanged capacity [V/As]
$(\Delta)R_i$	General internal resistance (imbalance between cells) [Ω]
R_o	Battery internal "ohmic" resistance [Ω]
R_p	Battery internal "polarization" resistance [Ω]
SC	Supercapacitor
SOC	State of Charge [As]
T	Temperature [°C]
$(\Delta)V$	Voltage (imbalance between cells)[V]
V_{cc}	Closed circuit voltage [V]
V_L	Battery terminal voltage [V]
V_{oc}	Open circuit voltage [V]
τ	Polarization constant $=R_p * C$ [s]

1 Lithium-ion capacitor

The energy and power density and the elementary structure of LiC is resp. shown on Fig. 1 and Fig. 2 [2].

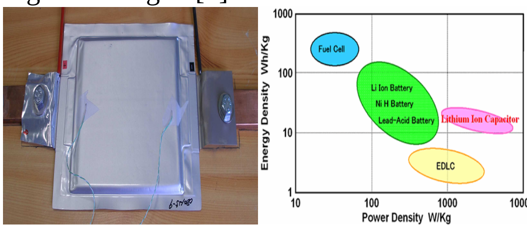

Fig. 1: Left: Lithium ion capacitor; Right: Energy and power density of LiC [2]

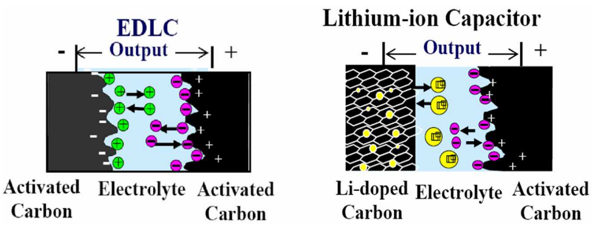

Fig. 2: Elementary structure of EDLC and Li-ion capacitor [2]

P	0,75kW		R_i	1,4±0,2mΩ(DC)
E	2,9Wh			1,2±0,2mΩ(ESR)
V	2,2…3,8V		Cycles	>100 000(90%Cap)
$I_{dch,max}$	250A		m	208g
Cap	1Ah (10A)		V	124ml (9-136-138mm)
	0,6Ah (200A)		E/m	14Wh/kg
C	2200 ±200 F		E/V	25Wh/L
$I_{ch,max}$	10A to 3.6V		Self discharge	<20mA (0,5h)
				1%V(init) (24h)
				5%V(init) (3m)

Table 1: datasheet

Table 1 shows the cell characteristics according to the producer.

2 Capacity

Two new cells are placed in series. 24 capacity tests are done at 10, 25, 50 and 100A: 6 capacity measurements for each current value. For each current the mean capacity of 6 tests is calculated (Fig. 3). The voltage range in the tests (2,28-3,75V) was smaller than the allowed 2,2-3,8V in order to be safe at the voltage limits. That is why the capacity is lower than the value on the datasheet.

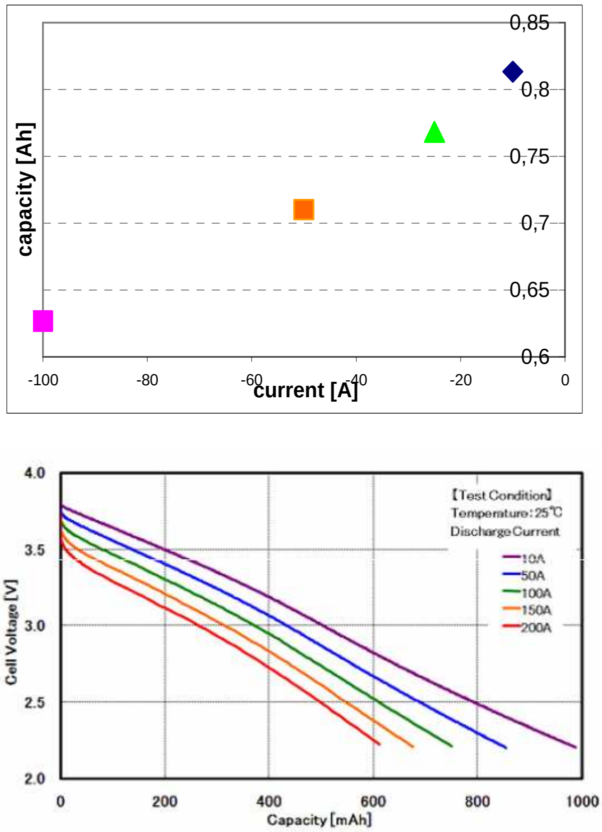

Fig. 3: Capacity tests of VUB (above) and the producer[2] (beneath) at 25°C

For currents from 10 to 100A the capacity varies between 0,82Ah to 0,63Ah.

3 FreedomCar model

The terminal voltage V_L and current I_L in the FreedomCAR model (Fig. 4) are declared by:

$$V_L = OCV - OCV'[\int I_L dt] - R_O[I_L] - R_P[I_P] \quad (1)$$

$$\frac{dI_p}{dt} = \frac{I_L - I_p}{\tau} \text{ or } \frac{dI_p}{I_L - I_p} = \frac{dt}{\tau} \quad (2)$$

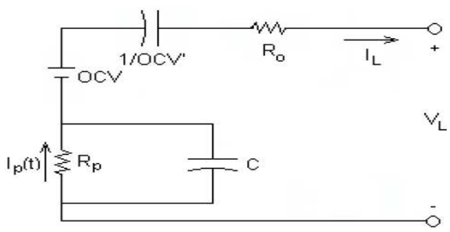

Fig. 4. FreedomCAR model

The differential equation (2) is solved with the starting condition ($I_{p,o}$=0):

$$I_{p,i} = \left\{1 - \left[\frac{1 - e^{\frac{-\Delta t}{\tau}}}{\frac{\Delta t}{\tau}}\right]\right\} \cdot I_{L,i} + \left\{\left[\frac{1 - e^{\frac{-\Delta t}{\tau}}}{\frac{\Delta t}{\tau}}\right] - e^{\frac{-\Delta t}{\tau}}\right\} \cdot I_{L,i-1} - \left\{e^{\frac{-\Delta t}{\tau}}\right\} \cdot I_{p,i-1} \quad \textbf{(3)}$$

In (1) OCV, OCV', R_o and Rp are calculated by linear regression method, I_p comes from (3), τ (=0,5) is chosen so that the fitting between the model and the measurements (Fig. 5) would be optimal[3][4][5][6][7].

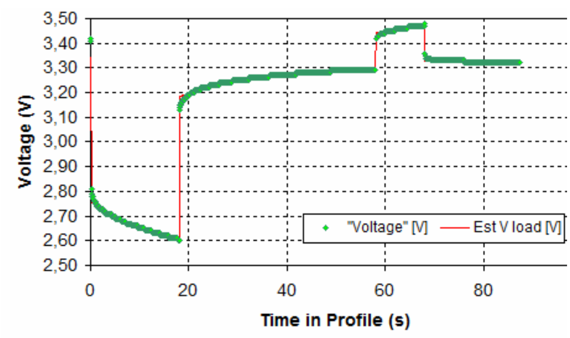

Fig. 5. Measured vs estimated voltage: curve fitting = 99% (+/-0.9%)

3.1 Internal resistance

The total internal resistance (=R_p+R_o) is calculated by pulsing currents of 100A (Fig. 6). There were 270 FreedomCar tests done on LiCs in order to calculate the internal resistance.

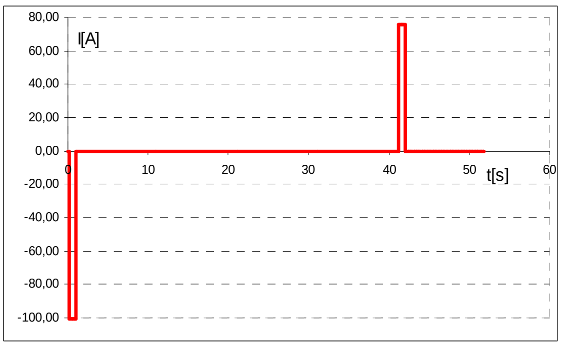

Fig. 6: Current in FreedomCar Test

Fig. 7 shows one of these tests. In this test 6 cycles are done. In every discharge cycle 9 FreedomCar tests are run. Only a few of this 54 FreedomCar tests is shown in the figures below. The matching accuracy between the simulation and the measurements was 99,46%: this is the average value of 54 matchings. The number of the test is on the horizontal axis e.g. t2.4 means 2nd discharge test and 4th FreedomCar test inside this 2nd discharge. There are 9 FreedomCar tests per discharge cycle so at the test t2.4 the SOC was nearly 50%.

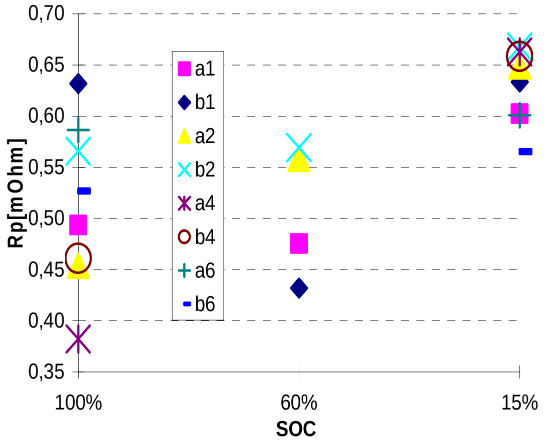

Fig. 7: Rp for cell a and b. The numbers indicate the tests

R_p (Fig. 7) is around 0,55mΩ if less energy has been exchanged. The ohmic resistance R_o (Fig. 8) is much higher and has a more static character than the polarization resistance R_p. The temperature is kept constant at 24°C by a fan.

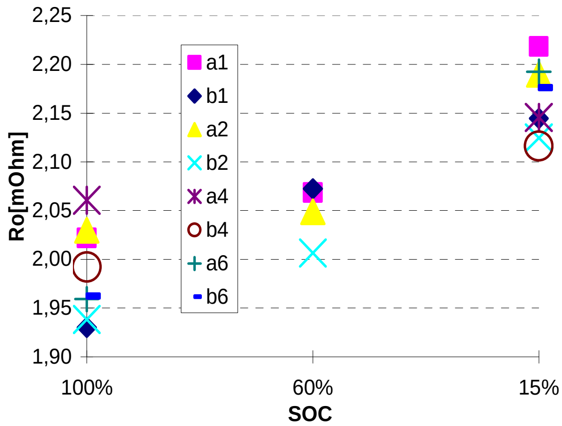

Fig. 8: R_o

The total internal resistance is the sum of R_p and R_o (Fig. 9).

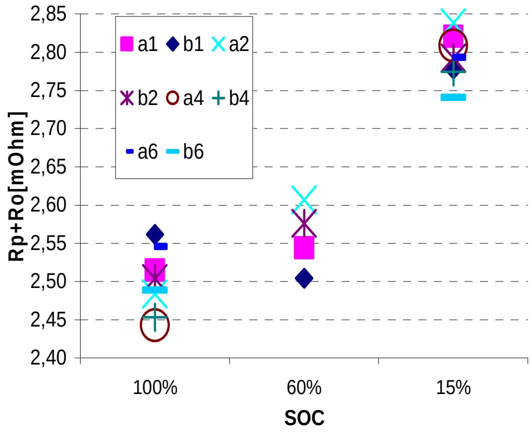

Fig. 9: Rp+Ro

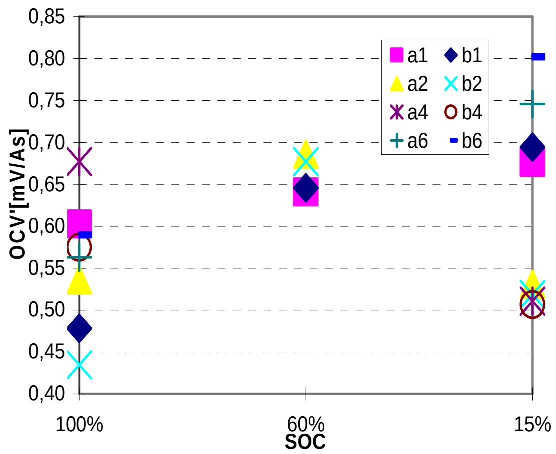

Fig. 10: OCV'

Table 2: Average value for Rp, Ro, Rp+Ro, ΔR_i, ΔV in case of 100%SOC, 5%SOC and after 45 FreedomCar tests are done (at full SOC). The reference for the percentages is the initial situation (100% SOC).

	Rp	Ro	Rp+Ro	ΔR	ΔV	OCV'
	[mOhm]				[mV]	[mV/As]
SOC 100%	0,54	1,98	2,52	0,05	28	0,51
SOC 5%	19%	10%	12%	-8%	-77%	18%
	0,64	2,17	2,81	0,04	6	0,6
after 45 FDC cycles	4%	-1%	0%	13%	-70%	12%
	0,56	1,96	2,52	0,05	8	0,6
10A	156%	52%	74%	483%	-78%	-16%
	1,37	3,02	4,39	0,27	6	0,4

Table 2 shows that the total internal resistance is between 2,52 mΩ and 2,8mΩ. It does not rise so much (12%) when the LiC becomes empty. It stays the same after many (45), heavy FreedomCar tests. The rise is especially due to the polarization resistance R_p. The average imbalance between the internal resistances of the two cells is very low (0,05mΩ) and decreases with 8% when the SOC decreases to 5% and increases with 13% after 45 FreedomCar cycles. But the imbalance between the cell voltages decreases with respectively 77 and 70% with decreasing SOC and increasing cycles.
If the FreedomCar test is done with a current of 10A instead of 100A, then the internal resistance increases with 70%.

Fig. 10 shows the decrease of the cell voltage in mV per retrieved As from the cell. It is 0,5mV/As. When the LiC is nearly empty, it increases a little bit (10%) and also increases with the number of cycles.

3.2 Effect of many cycles

Table 3 shows the cell parameters before and after 72 discharge cycles, which corresponds to 130 Ah exchanged capacity, including 270 FreedomCar tests at different currents.

Table 3: Cell parameters at test 5 and 72 discharge cycles after test 5 (=test 17)

	Rp	Ro	Rp+Ro	ΔR	ΔV	OCV'
	[mOhm]				[mV]	[mV/As]
t5	1,99	1,76	3,75	0,38	23	0,48
t17	-68%	9%	**-32%**	-91%	19%	13%
	0,64	1,92	2,56	0,04	28	0,5

The internal resistances was initially high (3,75mΩ) and decreases at the end of the tests with 32% to 2,56mΩ. This last value is 1mΩ more than on the datasheets. The matching between the measurements and the simulation was always 99%(+/-0,9%) except test 5 (97%).

The voltage difference only increases with 20%, which is low.

4 Electrochemical Impedance Spectroscopy

LiC is modelled by a resistance R_i in series with an equivalent capacitance C_{eq} (Fig. 15):

$$\frac{1}{C_{eq}} = \frac{1}{C_{dl}} + \frac{1}{C_{li}} \quad \text{where } C_{li} >> C_{dl} \Rightarrow C_{eq} \approx C_{dl} \qquad \textbf{(4)}$$

C_{dl} and C_{li} are the positive and the negative electrode capacitances.

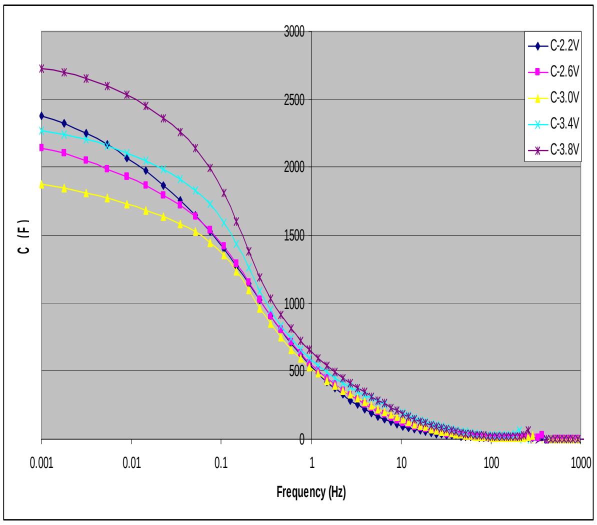

Fig. 11: C_{eq}(f) for different voltages

Using EIS method at various voltage and frequency levels, C_{eq} is determined (Fig. 11). C_{eq} is maximal at low frequency and is not linear with voltage.

Fig. 12 shows that C_{eq} decreases before U=3V and increases after U=3V. It is around 2200F as it is mentioned in the datasheet.

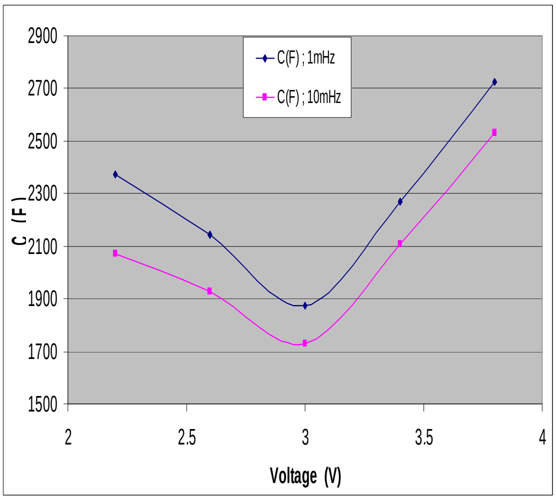

Fig. 12. C(V) at 1mHz and 10mHz

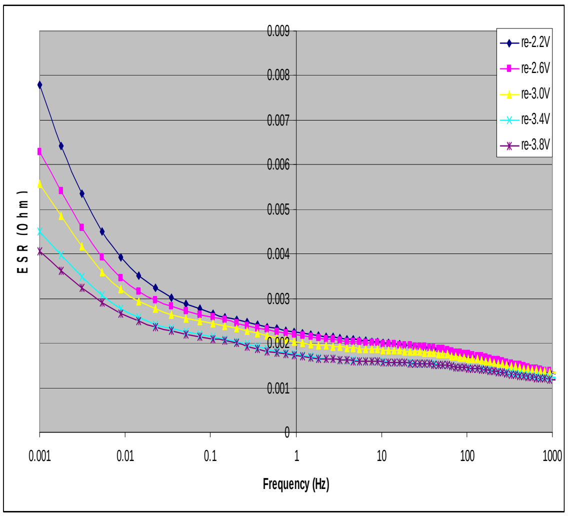

Fig. 13. ESR(f) for different voltages

ESR is shown on Fig. 12: it decreases with increasing frequency and voltage. At very low frequency the ESR is high because of the LIC parallel resistance.

Now the imaginary part (the capacitance) and the real part (ESR) of the impedance of the LiC is determined for different voltages and frequencies, they can be plotted in one figure: Fig. 14. Fig. 15 shows a zoom on the curve on Fig. 14.

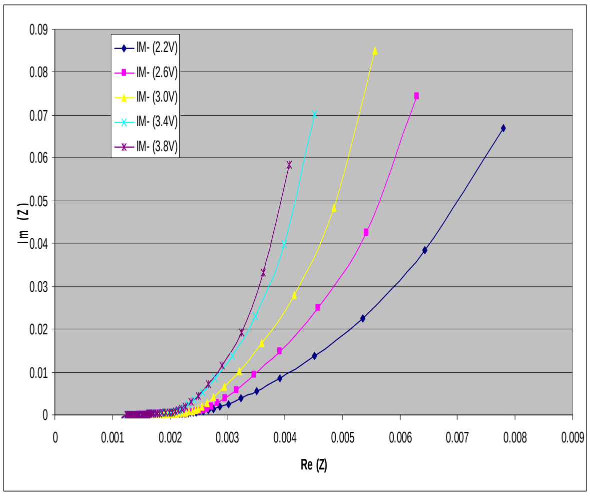

Fig. 14. Nyquist plot

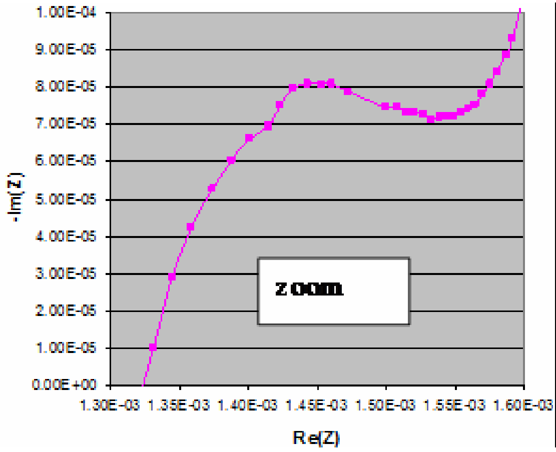

Fig. 15: Zoom in Nyquist plot

A constant power discharge (Fig. 16) gave 14Wh/kg as energy density value, which is much more than other capacitors. Given that LiC can deliver 250A, the power density of LiC is 3600W/kg, which is very high.

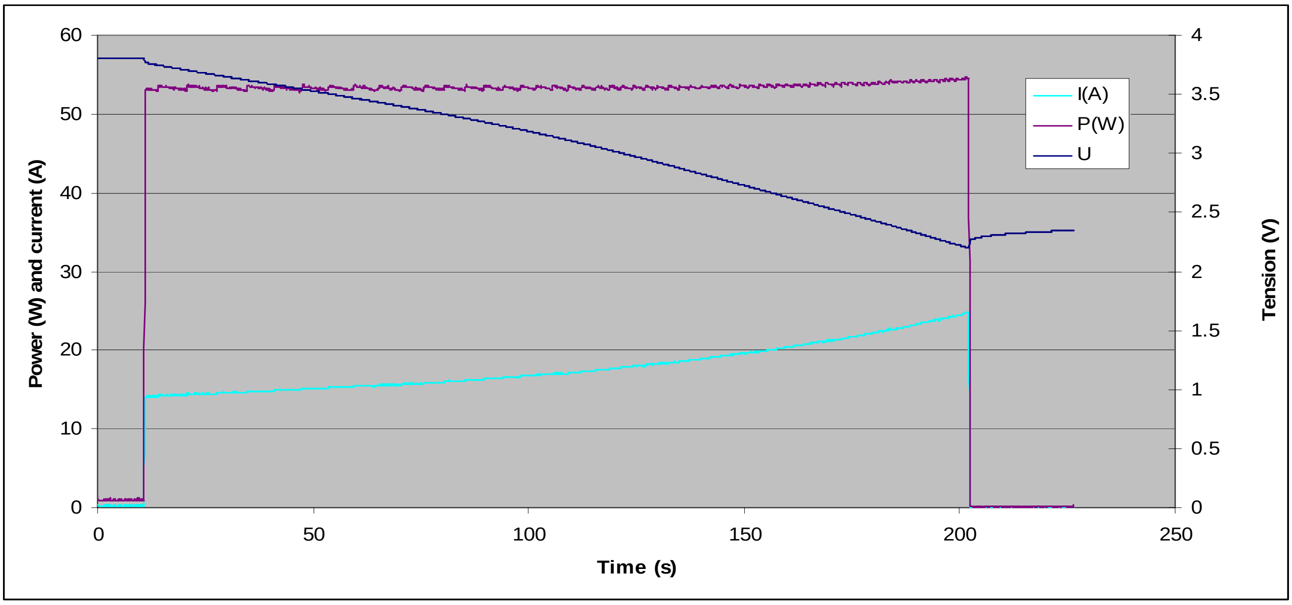

Fig. 16. Constant power discharge

5 Conclusion

The FreedomCar tests gave a value around 2,5mΩ for the internal resistance of LiC, which is very low.
The internal resistance is divided into two parts in FreedomCar model: a dynamic polarization resistance R_p (~0.5mΩ) and a more static ohmic resistance R_o (~2mΩ).

EIS method gave a value around 2mΩ. ESR is 5mΩ at 1mHz and decreases to 1mΩ at 1kHz.

When the SOC decreases, the internal resistance does only increase with 12%, which is very low.

After doing many cycles the internal resistance does not increase and the voltage difference only increases with 20%.

The capacitance is 1900F at 1mHz and at 3V. And it increases till 2700F at the limits of the voltage range. The average value is 2200F as it is mentioned in the datasheet.

The voltage imbalance decreases as a function of SOC and cycles. So there is less need for a voltage balancing system.

With its 3600W/kg, 100 000 cycles-lifetime, 14 Wh/kg, 2,2mΩ/cell, LiC is able to conquer the power storage area.

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Joeri van Mierlo received M.S. and PhD degree in electromechanical engineering from Vrije Universiteit Brussel in 1992 and 2000 with greatest distinction. From 2004 he has been appointed as a fulltime professor at the Vrije Universiteit Brussel. Prof. Van Mierlo is head of the MOBI- Mobility and automotive technology research group. Currently his research is devoted to the development of hybrid propulsion (converters, supercaps, energy management, etc.) systems as well as to the environmental comparison of vehicles with different kind of drive trains and fuels.