

Electrode optimisation for carbon power supercapacitors

L. Bonnefoi^a, P. Simon^{a,*}, J.F. Fauvarque^a, C. Sarrazin^b, A. Dugast^b

^a CNAM-Laboratoire d'Electrochimie Industrielle 2, rue conté 75003 Paris, France

^b EXIDE-CEAC, Departement Recherche 5-7, allée des Pierres Mayettes 92636 Gennevilliers cedex, France

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Abstract

The purpose of this work was to economically prepare large electrodes (32 cm²) in order to assemble mono-cell supercapacitors (100 cm³) of 250 F and to reach powers in the range of 120–130 W (2 V/cell) with the structure selected. We have reached more than 20 F/cm³ of electrode, with a time constant of a few seconds (close to 2 s) and reached powers compatible with starting applications. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Supercapacitors have been the center of interest for more than 20 years. Actually, these products were invented in order to answer to specific applications, intermediate between rechargeable batteries and capacitors [1–4]. Rechargeable batteries are generally characterized by an important autonomy (energy) associated with a rather low specific power. Usually, capacitors can supply high specific powers, but in return, the amount of energy stored in them is very low. It can be seen here that an important domain of applications, requiring high specific powers associated with consequent autonomy, cannot easily be realized using rechargeable batteries or capacitors. Supercapacitors have then been studied and developed for these applications [5,6]. One type of supercapacitor, called DLC (double layer capacitor), functions on the basis of the double layer capacity: adsorption of ions on electrodes containing material with an important specific area (≥ 1000 m²/g) [7]. The aim of this work is to realize a supercapacitor (DLC-type) for an automotive application, using an economical active material such as carbon. Capacitance of the single cell (100 cm³) will have to be close to 300 F, delivering a power of 150 W (2 V/cell). Calculations have

shown that a possibility was to use large electrodes (32 cm²) of 600 μ m thickness, with a volumetric capacitance close to 25 F/cm³. The time constant target for the cells was of less than 3 s.

2. Experimental

2.1. Electrodes

Norit SX Ultra activated carbon (1200 m²/g, 80 F/g) was used as the active material. An electronic conductor was added to the carbon in order to ensure a good electronic conductivity. A mixture containing the active material and the electronic conductor was added into a solution of carboxymethylcellulose (CMC) in water, or into a solution of poly-vinylidene fluoride (PVDF) in 1-methyl 2-pyrrolidinone. The mixture was then spread out on different current collectors: carbon cloth (500 μ m thickness), nickel foil (500 μ m), nickel foam (2 mm); After thermal treatment in vacuum first and then in air, electrodes were assembled face-to-face, with a separator in between, and introduced in a polyethylene bag. Bags were filled with electrolyte and then heat-sealed to ensure airtightness.

2.2. Electrolyte

Electrolyte used was a solution of acetonitrile (ACN) containing 1.7 M of NEt₄MeSO₃. This electrolyte has a

* Corresponding author. Tel.: +33-1-40-27-26-78; Fax: +33-1-40-27-24-20; E-mail: simon@cnam.fr

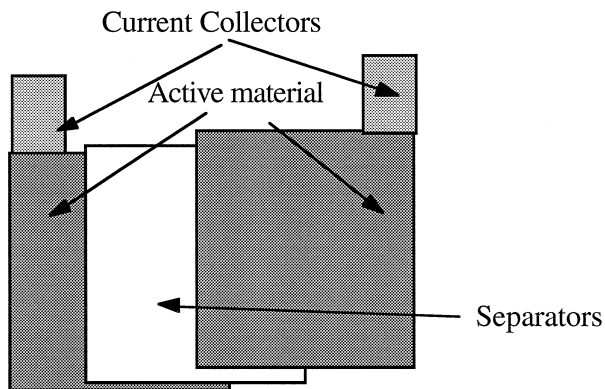


Fig. 1. Prismatic assembly of the 4 cm² 2-electrode cells.

good conductivity (25 mS/cm), and does not contain fluorine compounds.

2.3. Capacitance and resistance measurements

Laboratory cells were assembled in a prismatic way as shown in Fig. 1, with a cellulosic separator in between. Supercapacitors were cycled under galvanostatic conditions between 0 and 2 V, under a current density of 10 mA/cm². Capacity was calculated using the slope of the $V(t)$ plot. Resistance measurements were made using a HP 4338B milliohmmeter or an impedancemeter Solartron Schlumberger 1255, at 1000 Hz.

3. Results and discussion

3.1. Active material

The composition of the active material was determined in relationship with the above objectives, by measuring the resistivity of mixtures containing activated carbon powder and graphite powder. Fig. 2 represents the resistivity of the mixed powders vs. graphite content. The resistivity sharply

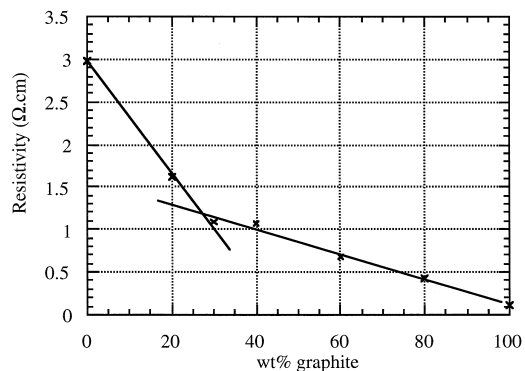


Fig. 2. Resistivity vs. graphite content plot for activated carbon/graphite powder mixtures.

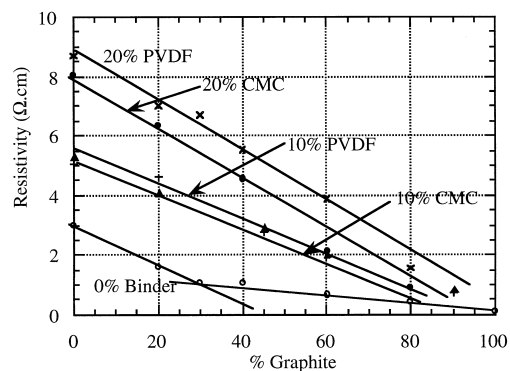


Fig. 3. Resistivity vs. graphite content plot; for activated carbon/graphite powder containing organic binder (CMC and PVDF).

decreases when the graphite content varies from 0 to 30 wt.%, and then levels off. From this figure, it is clear that a graphite content of 30 wt.% ensures a rather good electronic conductivity, associated with a good value of the capacitance (70 wt.% of activated carbon).

Fig. 3 shows the resistivity vs. graphite content for activated carbon/graphite powder mixtures with different binder contents. Two kinds of binder were studied: CMC and PVDF, at different rates (10 and 20 wt.%). From these plots, it can be seen that the difference between CMC and PVDF for the same content is not very large, but when the binder content decreases, so does the resistivity. Meanwhile, the lower cost of CMC has led us to select this compound, and the composition of the active material was fixed as follows: 60% activated carbon, 30% graphite, 10% CMC.

3.2. Current collectors

Electrodes (4 cm²) were prepared as described above, and 2-electrode cells were assembled using different current collectors: carbon cloth, nickel foil and nickel foam. Table 1 summarizes the capacitance and the serial resistance of these cells (cycled under constant current, $i = 10$ mA/cm²) at the 100th cycle. The amount of active material pasted on the electrode depended on the nature of the current collector: 100 mg (i.e., 60 mg of activated carbon) for the 2-dimensional current collector nickel foils and carbon cloth, and 180 mg (i.e., 110 mg of activated

Table 1
Characteristics of 4 cm² electrode cells assembled with different current collectors (100th cycle)

Current collector	Electrode thickness (mm)	C (F/cm ² electrode)	R (Ω cm ²)
Carbon cloth	0.5	1.3	27
Ni foil	0.5	1.1	15
Ni foam	0.8	2.3	5.5

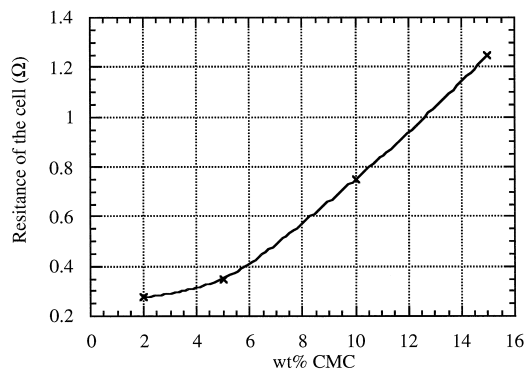


Fig. 4. Evolution of the serial resistance of 4 cm² cells vs. the binder content in the electrodes.

carbon), for the nickel foam 3-dimensional current collectors. The best results were obtained with the latter, in terms of capacitance and resistance: 2.3 F/cm² and 5.5 Ω cm². Meanwhile, the use of nickel foam as current collector limits the cell voltage at 2.3 V, due to the corrosion of the positive electrode collector. Considering the objectives of this work, nickel foam seems to be the most interesting current collector to use.

3.3. Binder content

A study has been carried out in order to minimize the binder content in the electrodes. By improving the fabrication process of the electrodes, it has been possible to prepare electrodes containing less than 10 wt.% of binder (CMC). Laboratory cells containing two 4 cm² electrodes, each pasted with 180 mg of active material were then assembled and tested. The current collector was a nickel foam.

Fig. 4 shows the serial resistance of the cells vs. the binder content in the electrodes. The serial resistance *R*

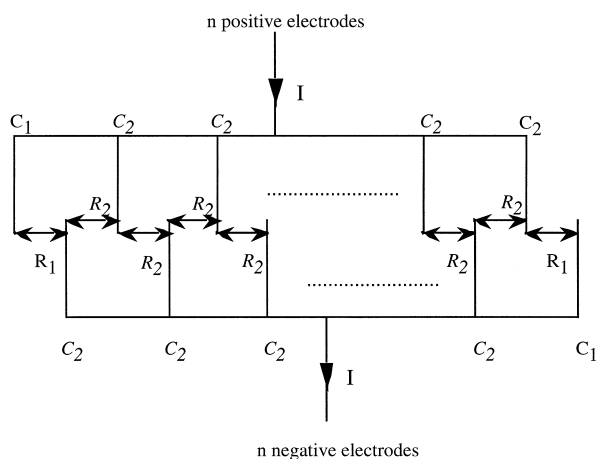


Fig. 5. Schematic diagram of the *n*-electrode cell (upper view), with *R*₁, the resistance associated with the outer electrodes, *R*₂ the resistance associated with the inner electrodes, *C*₁ the capacitance of the two outer electrodes, *C*₂ the capacitance of the inner electrodes.

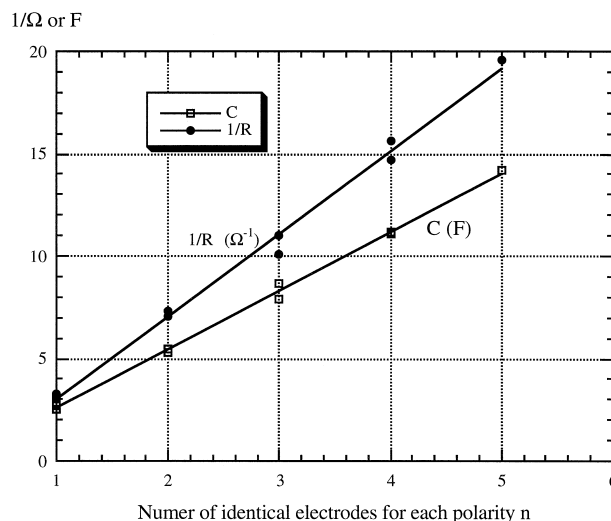


Fig. 6. Variation of the capacitance *C* and the conductance (*1/R*) of a cell vs. *n*, the number of identical electrode for each polarity.

decreases with decreasing binder content, but as the mechanical properties of the electrodes containing 2 wt.% CMC were not good enough, it has been decided to use the following composition of active material: 60% activated carbon, 35% graphite and 5% CMC.

3.4. Multi-electrode 4 cm² cells tests

Multi-electrode 4 cm² cells have been assembled, in order to characterize the evolution of the capacitance *C* of the cell when the number of identical electrodes (same thickness and same capacitance) varies from 2 to 10. Indeed, it is important to verify if the capacity of the cell increases in a linear way when the number of identical electrodes increases. In the same way, we have plotted the change of the reverse of the cell resistance (*1/R*) vs. the number of identical electrodes.

Fig. 5 presents the multi-electrode cell. If *n* (*n* > 0) is the number of identical electrode of each polarity, *C*₁ the capacitance of the two outer electrodes, *C*₂ the capacitance

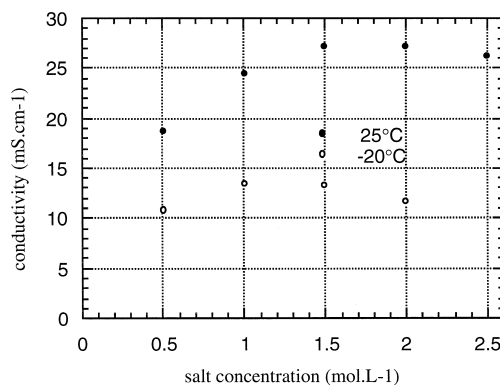


Fig. 7. Evolution of the electrolyte conductivity vs. the concentration in salt, at two temperatures (–20°C and +25°C). Salt: MeSO₃[–], NEt₄⁺.

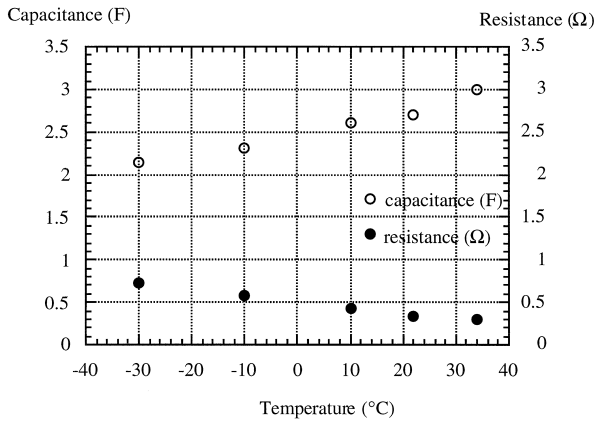


Fig. 8. Influence of the temperature on the resistance and the capacitance of a 2-electrode 4 cm² cell.

of the inner electrodes, then the capacitance of each polarity C' is (Eq. (1)):

$$C' = C_1 + (n - 1)C_2 \quad (1)$$

and the capacitance C of the cell is given by Eq. (2):

$$C = \left[\frac{C_1}{2} - \frac{C_2}{2} \right] + \left(\frac{C_2}{2} \right) n \quad (2)$$

If n is the number of identical electrodes of each polarity, there are $(2n - 1)$ intervals between the electrodes. If R_1 is the resistance associated with the outer electrodes and R_2 is the resistance associated with the inner electrodes, then the reverse of the cell resistance ($1/R$) is composed of two terms, Eqs. (3) and (4):

$$\left(\frac{1}{R_1} + \frac{1}{R_1} \right) \quad (3)$$

related to the resistances existing between the outer electrodes,

$$\left[\frac{(2n - 3)}{R_2} \right] \quad (4)$$

related to the resistances existing between the inner electrodes.

The reverse of the cell resistance is then (Eq. (5)):

$$\frac{1}{R} = \left[\frac{2}{R_1} - \frac{3}{R_2} \right] + \left(\frac{2}{R_2} \right) n \quad (5)$$

The variations of C and $1/R$ vs. the number n of identical electrodes of each polarity are shown in Fig. 6.

Table 2
Characteristics of the 2-electrode 32 cm² cells

P (kg/cm ²)	Thickness (μm/electrode)	C (F/g)	R cell (mΩ)	C cell (F)	C (F/cm ³ electrode)	P_{\max} (W)	E_{\max} (J)
0	600	77	80	23	24	12.5	47
100	610	75	100	23	22	10	40
200	740	65	100	24	22.4	10	48
250	1050	68	100	36	27.2	10	68

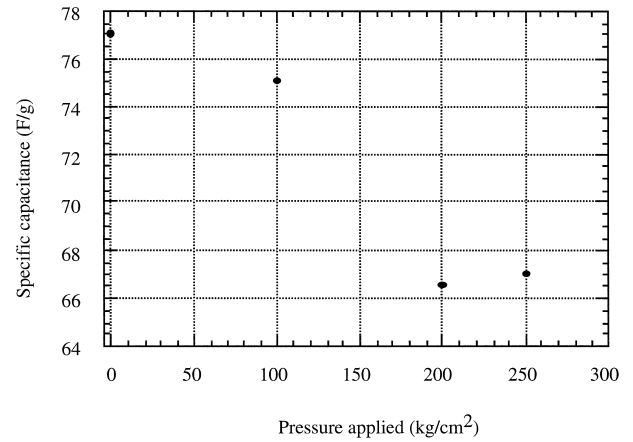


Fig. 9. Influence of the applied pressure (after electrode formation) on the specific capacitance of the activated carbon (2-electrode cells).

The capacitance C of the cell was calculated from the galvanostatic cycling under 10 mA/cm², and the resistance R of the cell was measured at 1000 Hz. The capacitance of the cell varies in a linear way with the number of electrode n . This is an important result which shows that, in this system, the performances of the small surface area cells can easily be extrapolated to larger cells. It can then be possible to compare the characteristics of small surface area cells (4 or 32 cm²) to our objectives defined for larger cells.

From the fit of the plots shown in Fig. 6, the solutions of the Eqs. (2) and (3) are:

$$\begin{aligned} C_1 &= 5.4 \text{ F} & C_2 &= 5.7 \text{ F} \\ R_1 &= 0.393 \text{ } \Omega & R_2 &= 0.498 \text{ } \Omega \end{aligned}$$

The capacitance of the outer electrode C_1 is a little bit lower than the one of the inner ones C_2 . It can then be seen that even if the active material in the outer electrodes does not work in all the volume (or the thickness) of the electrode, the difference is not very large, in terms of capacity (95% efficiency for the outer electrodes). Then the prismatic-type assembling seems to be well adapted to our electrodes.

3.5. Influence of the temperature

Fig. 7 presents the evolution of the electrolyte conductivity vs. the concentration in salt, at two temperatures (-20°C and $+25^\circ\text{C}$). The conductivity goes through a

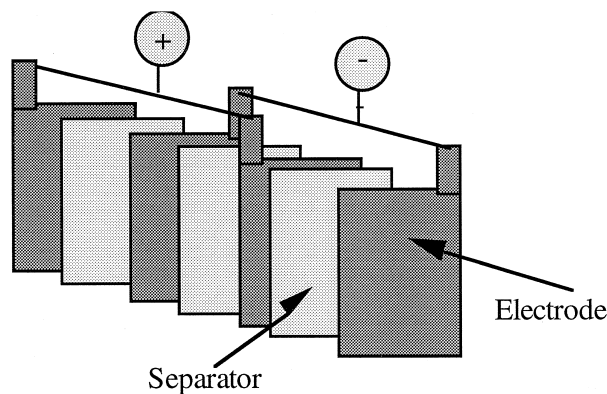


Fig. 10. Assembly of the 32 cm² 4-electrode cells.

maximum, corresponding to a concentration close to 1.7 M. The conductivity is approximately divided by a factor of 2 when the temperature decreases from 25°C to –20°C.

A 4 cm² cell with 2 electrodes was assembled and then cycled at different temperatures, between –30°C and +35°C. The evolution of the capacitance and the resistance of the cell (measured at the 50th cycle) vs. the temperature is presented in Fig. 8. At low temperature, the conductivity of the electrolyte decreases, leading to the increase of the cell resistance. At this temperature, it has also been observed a recrystallisation of the salt into the porosity of the electrodes. This can explain the slight decrease of the capacitance of the cell when the temperature decreases. A concentration of 1.7 M of salt in acetonitrile seems to offer a good compromise between resistance and capacitance in the range of temperatures explored: the resistance of the cell is multiplied by a factor of only two and the capacitance decrease is less than 20% when the temperature varies from 25°C to –30°C.

3.6. 32 cm² cells tests

Laboratory cells with 2 or 4 electrodes of 32 cm² were assembled and cycled under constant current. Table 2 summarizes the results obtained for the 2-electrode cells.

For the non-compressed electrodes ($P = 0$), the volumetric capacitance is 23–24 F/cm³ and the time constant is lower than 2 s. These values are close to the objectives defined above, which are a time constant lower than 3 s and a volumetric capacitance of 25 F/cm³ of electrode.

The influence of the pressure applied on the electrodes after formation has also been studied, and is presented in Fig. 9. During electrode processing, the nickel foam was

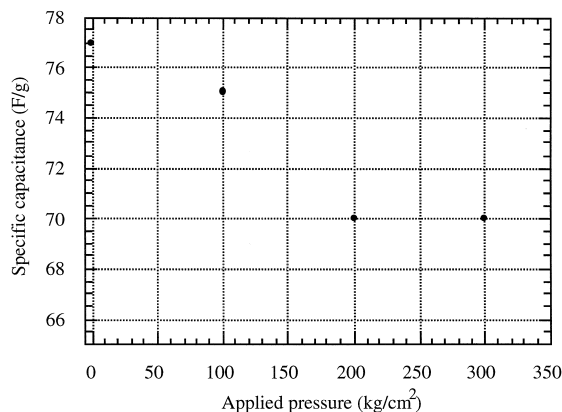


Fig. 11. Influence of the applied pressure (after electrode formation) on the specific capacitance of the activated carbon (4-electrode cells).

pressed to allow the active material to enter into the 3-dimensional structure. The thickness of the nickel foam (2 mm as received) is then close to 0.6 mm after processing. After that, different pressures were applied on the electrodes before assembling the cells, up to 300 kg/cm² to measure the influence of this parameter on the characteristics of the cells. From Fig. 9, it can be seen that when the pressure applied is higher than 100 kg/cm², the specific capacitance of the activated carbon decreases from 77 to 68 F/g. This means that a part of the activated carbon is not accessible to the electrolyte, due to the electrode porosity which is closed in a greater extend at such high pressures. It seems that there is no need to press our electrodes after formation.

The 4-electrode cells were realized by assembling 2 pairs of electrodes in parallel, as presented in Fig. 10. This system can be described by two capacities connected in parallel, with a total face-to-face surface of 96 cm². Table 3 presents the results obtained. The volumetric capacitance is 25 F/cm³ for the non-compressed electrodes, and the time constant is close to 1.7 s.

These measurements first show a good linearity between the results obtained with the 4 cm² electrodes, the two and four 32 cm² electrodes. The serial resistance is close to 35 mΩ, say 3.4 Ω cm².

In the same way as previously, the influence of the pressure applied on the electrodes (after formation) has been studied, and is presented in Fig. 11. When the pressure applied on the electrodes increases, the specific capacitance of the activated carbon decreases to 70 F/g, in the same way as above. Once again, when the applied pressure is higher than 100 kg/cm², the electrode porosity

Table 3
Characteristics of the 4-electrode 32 cm² cells

P (kg/cm ²)	Thickness (μm/electrode)	C (F/g)	R cell (mΩ)	C cell (F)	C (F/cm ³ electrode)	P_{\max} (W)	E_{\max} (J)
0	620	77	35	48	25	29	96
200	600	70	40	42	22	25	84
300	900	70	40	62	23	25	124

is closed in a greater extend, and the specific capacitance of the activated carbon decreases. These 4-electrode cells exhibited characteristics which are compatible with the objectives: a time constant of less than 2 s, a serial resistance of about $3.5 \Omega \text{ cm}^2$ and a volumetric capacitance between 22 and 25 F/cm^3 .

4. Conclusions

The aim of this study was to realize carbon-based electrodes for power supercapacitors. The study of the different components of the electrodes has led to the following conclusions.

(1) On the basis of electrical measurements carried out on activated carbon/graphite/binder mixtures, the active material composition has first been determined as 60% Norit, 30% Cg, 10% CMC.

(2) The study of 2-electrode 4 cm^2 cells has shown that interesting results were obtained when the nickel foam was used as current collectors. In this case, the internal resistance of the cells were close to $2\text{--}3 \Omega \text{ cm}^2$.

(3) The optimisation of the electrode processing has led to decrease the amount of organic binder (CMC) in the electrodes, up to 5 wt.%. The active material composition has now been settled as 60% Norit, 35% Cg, 5% CMC.

(4) The conductivity of the electrolyte is divided by a factor of 2 when the temperature decreases from 25°C to -30°C . The galvanostatic cycling of 2-electrode 4 cm^2 cell at different temperatures has shown that the resistance of the cell is multiplied by a factor of two in the same range of temperatures while the capacitance decrease is less than 20% (between 25°C and -30°C).

(5) The evolution of the capacitance of prismatic multi-electrode 4 cm^2 cells vs. the number of electrodes has shown that the outer electrodes work with 95% efficiency, which means that the prismatic assembling is well-adapted to our electrodes.

(6) A good linearity has been observed between the results obtained with the 4 cm^2 electrodes, the two and

four 32-cm^2 electrodes, in terms of capacitance and resistance of the cells. The 4-electrode cells exhibited the following characteristics: a time constant of less than 2 s, a serial resistance of about $3.5 \Omega \text{ cm}^2$ and a volumetric capacitance between 22 and 25 F/cm^3 . These values are close to our defined objectives.

Follow-up works will first consist the improvement of the active material amount in the electrode. Larger cells will then be assembled and tested.

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