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Effects of three-dimensional current collectors on supercapacitors' characteristics

Noëlle Tassin [a,*], Guy Bronoel [a], Jean-François Fauvarque [b], Isabelle Bispo-Fonseca [b]

[a] *SORAPEC, 192 rue Carnot, 94124 Fontenay-sous-bois, Cedex, France*

[b] *CNAM, Laboratoire d'Electrochimie Industrielle, 2 rue Conté, 75003 Paris, France*

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Abstract

Supercapacitors made of high-area electrode materials are complementary to batteries as far as electrical energy storage is concerned. Indeed, supercapacitors show low energy-density but high power-density. To achieve this, the time constant *RC* must be as low as possible, so the internal resistance *R* must be low. Apart from the effect of electrolyte resistivity and electrode thickness on the internal resistance, we show that the structure of the current collector acts on this parameter; the use of a three-dimensional current collector, such as metallic foam, results in an important decrease of the internal resistance of the cell.

Keywords: Supercapacitors

1. Introduction

Electrochemical capacitors utilise both electrical double-layer and interfacial redox processes to store energy at an electrode/electrolyte interface. The electrical double-layer capacitance of a clean metal surface is in the range of 20 to 40 μF cm^{-2}. In order to enhance the energy stored, one must use high specific surface area materials. Activated carbon with surface area higher than 1000 m^2 g^{-1} is used for this purpose, leading to theoretical capacitances ranging from 200 to 400 F g^{-1}.

Due to their high power density, such energy storage devices, when coupled to batteries, are useful both for internal combustion vehicles as well as electric ones.

2. Experimental

The beneficial effect of using metallic foams as electrode collectors has been checked with three different methods of electrode preparation as well as two electrode compositions.

In all cases, the capacitors are made of two identical carbon electrodes with a porous polypropylene sheet as separator in between (CELGARD 5511). The electrolyte used is a 1.7 M solution of TEAMS (tetraethylammonium methane sulfonate) in acetonitrile. A high surface area activated carbon (NORIT SX ULTRA) is used in all cases, mixed with an electronic conductor (carbon fibres or graphite) and a binder (methyl cellulose). In such conditions, activated carbon delivers a practical capacitance in the range of 80 to 100 F g^{-1}.

2.1. Electrode preparation by filtration

Electrodes were prepared (1 dm^2) on expanded nickel grids or nickel foams (NITECH) with different numbers of pores per inch (ppi 125 and 45). The mass of active material was 1.5 g dm^{-2}. Twenty-five millilitres of a solution having the following components were prepared:

- carbon fibres RVC 4002: 1.5 g
- Norit SX Ultra: 1.5 g
- methyl cellulose (30 g l^{-1}): 20 ml
- ethanol: 20 ml

After obtaining a homogeneous suspension of carbon fibres in ethanol, the colloidal solution was added. The suspension was then filtered over JOSEPH paper used as a separator. This coating was pasted over the nickel foam or grid and the electrode dried at 60°C for 12 h under a 10 kg dm^{-2} pressure. After drying, the electrode was pressed under 26 tonnes dm^{-2} in order to obtain a thickness of 0.7 mm.

Samples of 4 cm^2 were cut out of the electrode prepared for testing.

* Corresponding author.

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Table 1
Results from supercapacitors made by different methods

Type of electrode	Resistance (ohm)	Capacitance (F)	Time constant (s)	Thickness (mm)
Expanded nickel grids 1.45 (filtering)	9.8	1.4	13.72	0.9
Nickel foam ppi 45 (filtering)	10.75	1.2	12.9	2.6
Nickel foam ppi 45 (filtering and pressing)	2.4	1.37	3.29	0.7

Table 2
The effect of foam pore diameter

	Resistance (Ω)	Capacitance (F)	Time constant (s)
ppi 45 electrodes	2.40	1.37	3.29
ppi 125 electrodes	1.75	1.37	2.40

Table 3
Effect of the structure of the electrode collector on capacitance and internal resistance

	Foil	Foam
Cycle 1		
C (Farad)	15	17
R (ohm)	0.32	0.20
Cycle 250		
C (Farad)	16	20
R (ohm)	0.28	0.16
Cycle 500		
C (Farad)	16	20
R (ohm)	0.21	0.16
Cycle 650		
C (Farad)	17	20
R (ohm)	0.25	0.14
Cycle 900		
C (Farad)	17	20
R (ohm)	0.19	0.15

2.2. Electrode preparation by spraying

The electrode collectors used were nickel foil or nickel foam (NITECH) with an average pore diameter of 0.30 mm (foam ppi 125 — international ppi appellation).

A homogeneous suspension was prepared with activated carbon (NORIT SX Ultra), graphite (LONZA KS44), methyl cellulose and ethanol. This mixture was then sprayed on the collector. Electrodes were dried at 80°C overnight and pressed under 2.5 tonnes dm^{-2}.

2.3. Electrode preparation by pasting

Pasted electrodes were prepared on nickel foam collectors (NITECH, ppi 125). The viscosity of the mixture prepared for spraying was adapted to the pasting process (limited quantity of ethanol). Electrodes were dried at 80°C overnight and pressed under a 30 tonnes dm^{-2} pressure.

2.4. Testing of electrodes

Two identical electrodes were impregnated with the electrolyte and placed with a separator between them in a cell containing a large excess of electrolyte. The stack was maintained under a 10 kg dm^{-2} pressure. Cycling was done between 0 and ± 2 V at a 0.33 A dm^{-2} current density.

Some electrodes were also tested in sealed cells with a limited quantity of electrolyte.

3. Results

3.1. Results obtained from electrodes prepared by filtering

At first we studied the effect of electrode thickness on the resistance and the capacitance. The thickness was adjusted by compacting electrodes which leads to a better contact between Norit grains and carbon fibres. The resistance depends strongly on electrode thickness as shown in Table 1 and the time constant decreases from 12.9 to 3.29 s.

Furthermore, the study shows the influence of the pore diameter on the resistance and the capacitance. We prepared electrodes with nickel foam collectors having two different numbers of pores per inch: ppi 45 and 125, while the electrodes were prepared by filtering and pressing. The best results were obtained with the ppi 125 nickel foam (Table 2).

Indeed, the ppi 125 nickel foam allowed us to reduce the resistance by a 1.5 coefficient without changing the capacitance.

3.2. Results obtained with electrodes prepared by spraying

The behaviour of electrodes ($S = 0.6$ dm^2; carbon loading = 0.75 g dm^{-2}; thickness = 0.35 mm) made of nickel foil and nickel foam was compared in terms of capacitance (C) and internal resistance (R). Results reported in Table 3 show that a better capacitance as well as a lower internal resistance is obtained with the foam collector. This indicates that the

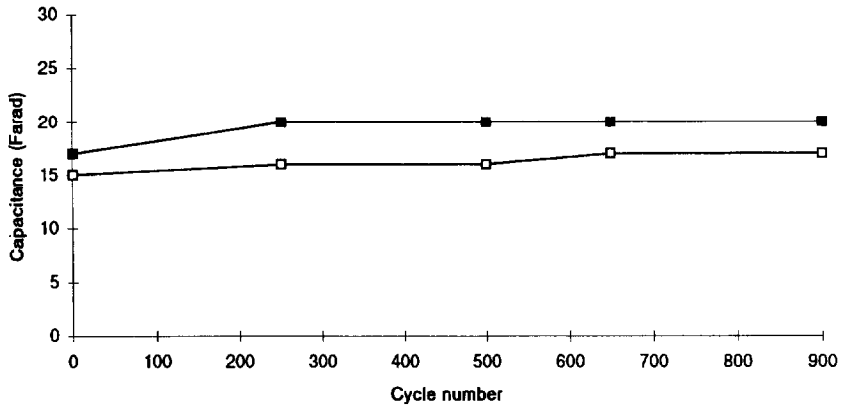

Fig. 1. Electrodes prepared by spraying. Activated carbon loading = 0.75 g dm^{-2}; $S = 0.6$ dm^2; thickness = 0.35 mm. ■, Foam collector; □, foil collector.

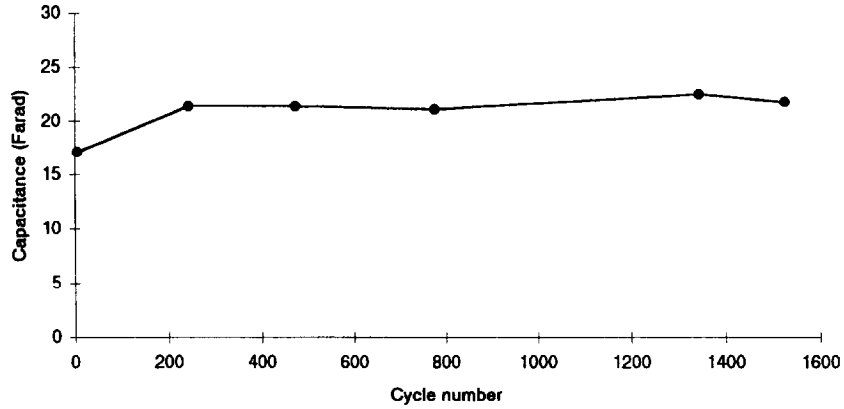

Fig. 2. Electrodes prepared by pasting a foam collector. Activated carbon loading: 1 g dm^{-2}; $S = 0.6$ dm^2; thickness = 0.55 mm.

Table 4
Electrode characteristics of cell types A to E

	Carbon loading (g dm^{-2})	Electrode thickness (mm)
Cell A	1	0.65
Cell B	1	0.55
Cell C	1	0.50
Cell D	1.4	0.50
Cell E	0.62	0.52

current collection in the active mass is more efficient when a three-dimensional current collector is used. In addition, stabilisation of R and C values is faster when foam is used.

Under such conditions, time constants (RC) of approximately 3 to 5 s are obtained. Performances are stable upon cycling as shown on Fig. 1.

3.3. Results obtained with pasted electrodes

Pasted electrodes prepared on nickel foam ($S = 0.6$ dm^2; carbon loading = 1 g dm^{-2}; thickness = 0.55 mm) were tested under similar conditions. Results obtained so far show an interesting performance for this type of electrode, giving a 22 Farad capacitance and a time constant equal to 5 s. A good stability of performance was observed over 1500 cycles as can be seen in Fig. 2.

3.4. Results obtained from testing sealed cells

Pasted electrodes ($S = 0.81$ dm^2) made with a foam collector were pressed between two thick metallic plates with an insulating sealing frame so as to obtain a sealed cell. The quantity of electrolyte is limited to the volume contained in electrodes and separator porosity.

Evolution of cell capacitance as a function of carbon loading and electrode thickness was evaluated. The five cells described in Table 4 were cycled in similar conditions.

Fig. 3 shows the results obtained in terms of capacitance over a large number of cycles. For a constant carbon loading, the lower the electrode thickness, the higher is the cell capacitance. The internal resistance of the five cells is approximately the same, leading to a time constant that varies according to their respective capacitance value, i.e. time constant for cells A, B and C equals 2 s, $RC = 3$ s for cell D and a lower value ($RC = 1.4$ s) for cell E. The stability of performance is quite good as shown by the curves in Fig. 3.

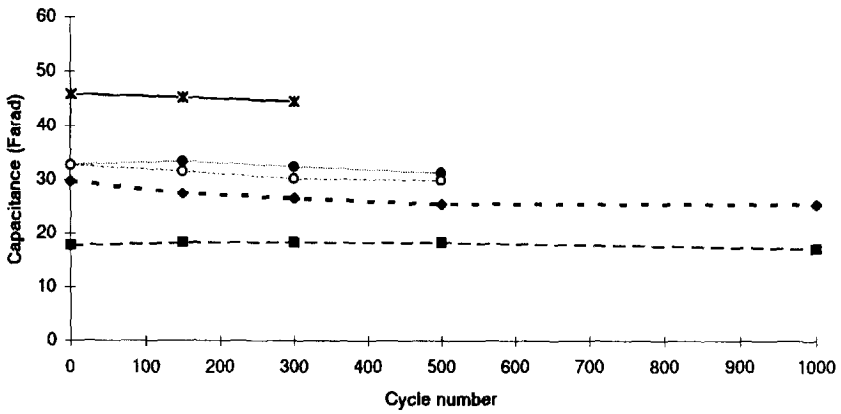

Fig. 3. Sealed capacitors made of pasted foam-based electrodes. ◆ Cell A: carbon loading = 1 g dm^{-2}; thickness = 0.65 mm. ● Cell B: carbon loading = 1 g dm^{-2}; thickness = 0.55 mm. ○ Cell C: carbon loading = 1 g dm^{-2}; thickness = 0.50 mm. * Cell D: carbon loading = 1.4 g dm^{-2}; thickness = 0.50 mm. ■ Cell E: carbon loading = 0.62 g dm^{-2}; thickness = 0.52 mm.

4. Conclusions

Results obtained so far show the beneficial effect of using metallic foam as current collectors for supercapacitors made of high surface-area activated carbon. The resistance is reduced considerably whatever the method of electrode preparation. The use of a metallic foam decreases the electrode resistance by improving the electronic contact between the activated carbon and the charge collector.

Under such conditions, the electrode resistance does not depend on the activated carbon loading, so supercapacitors' time constants can be adjusted to the desired value by choosing the right carbon loading.

In addition, cells with a 2 s time constant have been built and cycled over 1000 cycles without any degradation of performance.

Further work is in progress with metallic foams. As nickel foams are actually the only material available at an acceptable cost, the goal of the present work is to select an electrolyte able to decrease the nickel corrosion rate.