

Possible improvements in making carbon electrodes for organic supercapacitors

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Abstract

Properties of an Electrical Double Layer Capacitor depend both on the technique used to prepare the electrode and on the current collector structure. Capacitors can be built in a similar way to prismatic cells, with several electrodes connected in parallel for each polarity. Our Electrical Double Layer Capacitors included several carbon/carbon electrodes and all the components (electrodes and separators) were wetted with an organic liquid solvent containing a quaternary ammonium salt as electrolyte. In the present work, electrodes were prepared by two different ways: the first one consisted in spraying a liquid suspension of the electrode materials on a nickel foil, and the second one which consisted in filtering and pressing the electrode materials on to nickel collectors. The first technique allowed us to build seven capacitors of 600 F–2.5 V, with time constants of 12 s. Two banks with series connected supercapacitor cells, one as a 12 V–100 F bank and the other one as a 15 V–85 F were tested on cycling. In our experiments to test these banks of supercapacitors, we also coupled the 100 F–12 V bank to a 12 V–7 Ah secondary lead–acid battery in order to demonstrate the contribution of the supercapacitors during power peaks. Comparing the two techniques used to make the electrodes in terms of performances obtained on the supercapacitors prepared, we obtained the best results by using the second method of electrode preparation. Moreover, two kinds of nickel collectors were studied: expanded nickel grids—and various grades of nickel foams, nickel foams giving the best results. The Equivalent Series Resistance of the electrodes prepared with nickel foams depends on nickel foam grade; it is observed to be 1.75 Ω for a capacitance of 1.37 F in our experimental set up, leading to a time constant of 2.4 s. The mechanical properties of the electrodes were improved as well. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organic supercapacitor; Carbon electrode; Battery

1. Introduction

The main problems the Electric Vehicle potential manufacturers are facing are the size definition for the energy storage system and its management; this latter point is not completely satisfactory when using rechargeable batteries [1]. In order to meet the power requirements without reducing the battery capability, the use of supercapacitors associated with a battery should allow to deal with power peaks and available energy separately: the supercapacitors to supply power and the battery to supply energy. The power requirements for Electric Vehicles are in the range of 10 kW or more, with current magnitudes of several hundreds of amperes; this power could be obtained with about 10 kg or less of supercapacitors, instead of about

100 kg of batteries. Unlike batteries, present day supercapacitors have low energy densities (less than 5 Wh/kg so far) but this type of component is able to supply very high power densities from several hundred W/kg to a few kW/kg; they will give the necessary power, well suited to acceleration and for regenerative braking in electric or hybrid vehicles [2]. Our main goal was to prepare supercapacitors with low cost materials to verify the performances obtained.

2. Experimental

The unit cell capacitor was previously described [3]; these carbon/carbon electrodes were stacked with a separator in between, and all the components were wetted by an organic liquid electrolyte [4] (solvent and quaternary ammonium salt). To achieve good behaviour, the electrode

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Table 1
Components for making the electrodes

	Spray method	Filtration method
Carbon fibers RVC 4002	1 g	0.75 g
Norit Sx Ultra	1 g	0.75 g
Methylcellulose (15 g/l)	4 ml	20 ml
Ethanol	5 ml	20 ml

must have at the same time good mechanical stability as well as good electronic and ionic conductivity between the grains of the material. The current collector used was a nickel collector, chemically and electrochemically inactive within its electroactivity window. Since carbons having a high specific area are less conductive (Norit), they must be mixed with an electronic conductor such as carbon fibers (Carbone Lorraine). The cohesion of grains is achieved by an insoluble and stable binder which is methylcellulose (Merck); this type of binder is less expensive than fluorinated binders. The electrolyte used was acetonitrile with a quaternary ammonium (TEAMS—tetra ethyl ammonium methyl sulfonate) at a concentration of 1.7 M (Merck). The electroactivity window is large, with an oxidation at 2.4 V/Ag · AgCl and reduction at -2.1 V/Ag · AgCl on bulk platinum electrodes. In our electrolyte, activated carbon delivered a capacitance between 80 and 100 F/g.

We examined two preparation methods for making the electrodes:

- the first one consisted in spraying the electrode materials on a nickel foil,
- the second one consisted in filtering and pressing the laminate on the collector.

2.1. Electrodes preparation by the spray method [5]

The electrode collectors used were nickel foils of 1 dm². These collectors were cleaned with ethanol (Merck). The components of this spray method are presented in Table 1. A good spraying method depends on several key factors: spraying distance, spraying angle, gas pressure used to spray, powder granulometry, and solution viscosity. Once these parameters were determined, the suspension prepared was sprayed on the nickel foil and the electrodes dried at 60°C under a 10 kg/dm² pressure.

2.2. Electrodes preparation by the filtration method [6]

Electrodes were prepared (1 dm²) on expanded nickel grids or nickel foams with different numbers of pores per

Table 2
Supercapacitors design

Reference	Electrolyte	Number of electrodes and collectors	Material and method
Sc14, 15, 16, 17, 18, 19, 20	Sulfolan/Acetonitrile 50/50 TEAMS 1.7 M	Nickel foil 1 dm ² , Monoface, 14 electrodes, Thickness 0.6 mm	Spray method, MC 1.75 g, Norit SXultra 28 g, Carbon fibers 28 g, Separator: Cellgard 5501
ScX	Acetonitrile TEAMS 1.7 M	Nickel foam or expanded Ni grid, 0.04 dm ² , Monoface, 2 electrodes, Thickness 0.7 mm	Filtration method MC 0.07 g, Norit SXultra 0.12 g, Carbon fibers 0.12 g, separator: Joseph paper

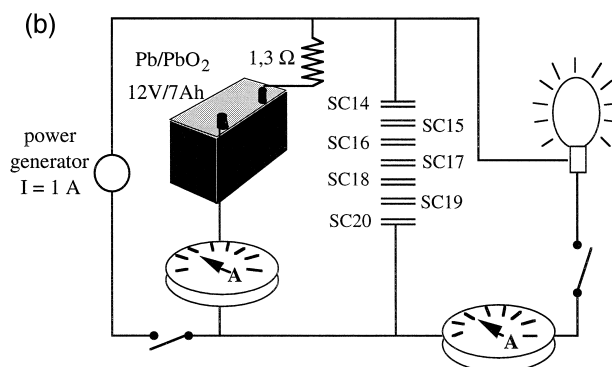
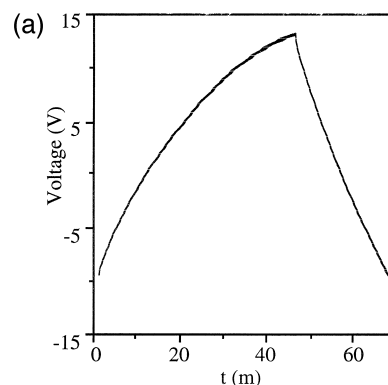


Fig. 1. a: Charge–discharge of series connected supercapacitors. b: Electric circuit.

inch (ppi; MN 90, MN 45 for foams with 90 ppi and 45 ppi). The mass of active material deposited on these collectors was 1.5 g/dm². Twenty five milliliters of a suspension had the composition presented in Table 1. After obtaining a homogeneous suspension of carbon fibers in ethanol, the colloidal solution was added. This suspension was filtered over JOSEPH paper used as separator. This coating was pasted over the nickel foam or grid, and the electrodes were dried at 60°C during 12 h under a 10 kg/dm² pressure. After drying, the electrodes were pressed under 26 tons/dm² in order to obtain a thickness of 0.7 mm. Samples of 4 cm², cut out of the large electrodes prepared, were then tested.

2.3. Supercapacitor preparation

Table 2 lists the different supercapacitors prepared and their characteristics. The electrodes were stacked on top of

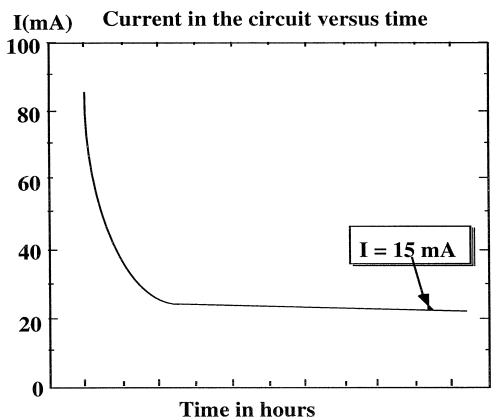


Fig. 2. Leakage current at a fixed voltage of 12 V.

each other with a separator between them [7]. The assembly was then placed in a container.

3. Results and discussion

3.1. Supercapacitors prepared by the spray method

Cycling results for supercapacitors prepared by the spray method and described in Table 1 are presented in Table 2. The capacities were calculated from the measurements of voltage vs. time curves slopes (linear part, between 0.5 to -0.5 V, where there are not faradic phenomena).

$$C = \frac{I(t_2 - t_1)}{U_2 - U_1}$$

The resistances were determined from the ratio of ohmic drop to current change in the circuit (to 0 V for the same reason as below).

$$R = \frac{\Delta U}{\Delta I}$$

The self discharge resistances R_f measured on supercapacitors (SC no. 14 to 20) appeared to be rather small with a

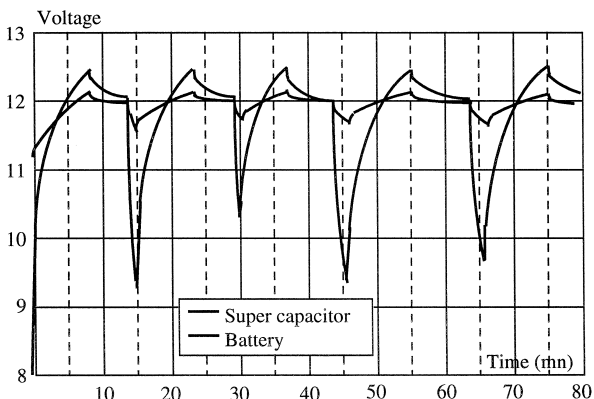


Fig. 3. Cycling of a supercapacitor and battery association.

Table 3
Supercapacitors characteristics

Cap no.	Capacitance (F)		Resistance (Ω)		Time Constant (s)	
	1st cycle	200th cycle	1st cycle	200th cycle	1st cycle	200th cycle
Sc 14	600	610	0.02	0.02	12.00	12.20
Sc 15	608	618	0.02	0.02	12.16	12.36
Sc 16	573	580	0.02	0.02	11.46	11.60
Sc 17	612	620	0.02	0.02	12.24	12.40
Sc 18	582	590	0.02	0.02	11.64	11.80
Sc 19	573	580	0.02	0.02	11.46	11.60
Sc 20	600	610	0.02	0.02	12.00	12.20

value of $R_f = 3630 \Omega$ per cell (measured after charge, and stabilisation of the voltage evolution on self discharge—after about 5 h). The small variations between values allowed us to validate the spray method.

The seven supercapacitors were series connected in a 12 V–100 F assembly. Fig. 1a represents the charge discharge curve after 50 cycles at a current of 1 A. The resistance was found to be 0.1Ω (for seven supercapacitors). A system was then constituted with the parallel association of the supercapacitor bank with a 12 V–7 Ah secondary lead–acid battery (Pb/PbO₂) [8], similar to the schematic shown in Fig. 1b. This association reached a stable voltage of 12.2 V after connection, and the electrical current into the supercapacitor bank decreased progressively down to 15.5 mA (Fig. 2; leakage resistance of 800Ω for 7 cells under a voltage of 12.2 V). The voltage of each supercapacitor unit cell was checked and did not change (1.75 V).

To complete our experiments, we connected a light bulb (60 W/12 V) to a new association constituted of the supercapacitor series assembly (Fig. 1b) and a 1.3Ω resistance to limit the battery contribution in the power delivery. A generator was used to charge this system (1 A). First, we connected the bulb to the system and then, in a second step, the generator was connected to the

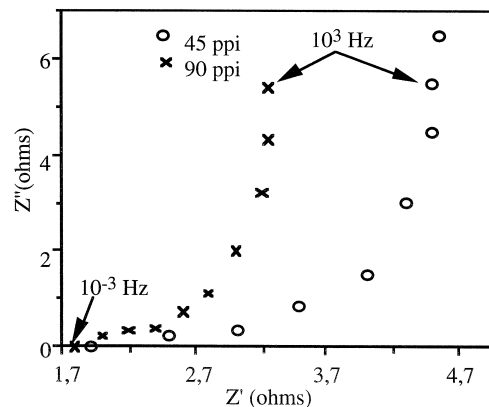


Fig. 4. Effect of the collector porosity, impedance plot of the two supercapacitors electrodes from 10^{-3} to 10^3 Hz.

Table 4
Pressure effect

Type of electrode	ESR (Ω)	Capacitance (F)	Time constant (s)	Thickness (mm)
expanded nickel grids 1.45 (Filtering)	9.8	1.4	13.72	0.9
MN 45 (Filtering)	10.75	1.2	12.9	2.6
MN 45 (Filtering and pressing)	2.4	1.37	3.88	0.7

battery. To demonstrate the capability of the supercapacitor bank, successively the bulb was connected to the system, and then the circuit was opened and the supercapacitors and battery were connected to the generator for recharge. Fig. 3 shows that the major part of the current was delivered by the supercapacitor bank.

In order to improve our supercapacitors' characteristics, we decided to evaluate other electrode preparation techniques, mainly in view of reducing time constants.

3.2. Results obtained on supercapacitors prepared by the filtering method

The best results were obtained with this second method which consists in filtering and pressing the mixture of the components on a nickel foam (Table 3).

At first we studied the pressure effect on the equivalent serial resistance and the capacitance as reported in Table 4. The resistance depends on pressure and the time constant decreases from 12.9 s to 3.88 s. The pressure applied allowed to decrease the resistance, by improving the contact between Norit grains and carbon fibers reducing the electrode thickness.

Furthermore, the study showed the influence of the porosity on the equivalent serial resistance and the capacitance. We prepared electrodes with nickel foam collectors of two different grades in terms of pores per inch: MN 45 and MN 90 and the electrodes were prepared by filtering and pressing. The best results were obtained with the MN 90 nickel foam (Table 5). Indeed, the MN 90 nickel foam allowed us to reduce the equivalent serial resistance by a factor of 1.5 without changing the capacitance. As shown

Table 5
Foam collectors

	ESR (Ω)	Capacitance (F)	Time constant (s)
MN 45 electrodes	2.40	1.37	3.88
MN 90 electrodes	1.75	1.37	2.40

in Fig. 4, the impedance response of the electrodes prepared with MN 90 and MN 45 electrodes confirmed the influence of the nickel foam porosity on the equivalent serial resistance.

4. Conclusion

We have built seven supercapacitors with the same characteristics (600 F and 12,2 s time constant) by the spray method. The supercapacitor serial arrangement, coupled to the battery shows the supercapacitor contribution when the power turned on and off. The method change of electrodes realization and the new collector utilization allow to decrease the equivalent serial resistance and the time constant.

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