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Modification of Al Current Collector/Active Material Interface for Power Improvement of Electrochemical Capacitor Electrodes

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This paper presents results about carbon nanofibers (CNFs) synthesis and their use as surface treatments for Al current collector for carbon electrochemical capacitors in organic electrolyte. CNFs have been successfully synthesized on a pretreated Al substrate; the pretreatment of Al consists of an etching followed by a carbonaceous sol-gel deposit. Performances of cells assembled with pretreated Al and pretreated Al coated by CNFs have been compared by using galvanostatic cycling measurements. Internal resistances as low as $0.4 \Omega \text{ cm}^2$ are obtained for cells using CNF-treated Al. The increase of the surface contact and interface conductivity between the Al and the active material are responsible for this internal resistance decrease. The capacitance obtained for the two cells is the same (95 F g^{-1} of activated carbon). Performances [both equivalent series resistance (ESR) and capacitance] are stable over 10 000 cycles, proving the great efficiency of surface treatments.

Carbon/carbon electrochemical capacitors are energy storage devices where the charges are stored in a purely electrostatic form at the electrolyte / active material interface. Various carbonaceous material can be used as active material such as activated carbon, carbon fibers, carbon aerogels, and carbon nanotubes.

Activated carbon powders are widely used because of their low cost, good electronic conductivity, and high specific surface area (between 1500 and 2500 m^2/g) that lead to high capacitance values.¹⁻⁴ Carbon fibers and carbon fiber fabrics can also be used even if their specific surface area are lower as compared to activated carbon.^{5,6}

Carbon nanotubes (CNTs) exhibit good properties (high electronic conductivity, high electrochemical stability, high degree of crystallization), which make them suitable to be used as electrode material. They have been widely studied in electrochemical capacitor applications, but their high cost and low specific surface area (generally lower than 1000 m^2/g) limit their interest in such applications.^{7,8} Recently, carbon aerogels have been prepared for electrochemical capacitor applications because of the existence of an interconnected three-dimensional mesoporous network that can be used for charge storage, but the low specific surface area developed by these materials leads to low capacitance values.^{9,10}

Carbon nanofibers (CNFs) with diameters ranging from 50 up to 500 nm have also been synthesized for electrochemical capacitor applications, mainly by using CNT-derived synthesis processes. But, the specific capacitances obtained with as-prepared CNFs are still low as compared to activated carbon (about 50–80 F/g).¹¹⁻¹⁴

For this reason, CNFs have not been used here as active material but as a surface treatment of the Al current collectors to improve the interface between the current collector and the active material film. Cells assembled with electrodes consisting of a pretreated aluminum current collector covered by CNFs and an active material film based on activated carbon have been investigated by galvanostatic cycling measurements and electrochemical impedance spectroscopy.

Experimental

Preparation of the pretreated aluminum current collectors.— The objective is to obtain a CNF growing directly onto the Al-foil current collector surface. But, aluminum substrates require a pretreatment before CNF synthesis, because Arcos et al. reported that as-received aluminum is not a suitable substrate for CNT growth.¹⁵ CNFs have been then synthesized using a catalytic chemical vapor deposition (CCVD) process by thermal decomposition of a $\text{C}_2\text{H}_4/\text{H}_2$

mixture on a pretreated aluminum foil. This pretreatment is a two-step process. In the first step, a surface roughness is created on the foil surface by a chemical etching treatment. This etching treatment consists of a soaking in a NaOH (1 M) solution in order to degrease the foil, followed by an immersion in a HCl solution (1 M) at 80°C . Figure 1 represents the field-emission gun-scanning electron microscope (FEG-SEM) picture of the Al surface after etching; a formation of channels can be observed on the surface, with a depth of about 10 μm . After etching, carbonaceous particles are deposited on the rough surface via a sol-gel process consisting of a suspension of small carbonaceous particles in a polymeric matrix. A thermal treatment is used in order to remove the polymeric matrix. This entire experimental process of the aluminum current collector surface treatment has been described elsewhere.¹⁶ Figure 2 represents the FEG-SEM picture of the etched Al surface covered by the carbonaceous sol-gel deposit; the carbonaceous particles cover the whole surface and are dispersed into the channels, creating a thin conductive film.

Synthesis of CNFs.— Pretreated Al-foils substrates were impregnated by dip coating in a 0.1 M solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in absolute ethanol. The substrates were then dried overnight at 150°C in air. The samples were heated at 630°C for 1 h (heating and cooling ramps at $5^\circ/\text{min}$) in a mixture of ethylene and hydrogen gases containing 20 mol. % C_2H_4 , with a total flow rate of 250 sccm. The FEG-SEM pictures in Fig. 3a and b represent the surface of the pretreated Al foil covered by CNFs.

For comparison, the CCVD treatment has been also achieved on an untreated aluminum; it was shown that the catalyst impregnation was nonhomogeneous on the substrate and CNFs did not adhere on the surface. These results indicate that a previous treatment is necessary in order to synthesize CNFs directly onto the substrate.

Electrochemical characterization.— *Cell assembly.*— Two-electrode 4 cm^2 electrochemical capacitor cells were assembled in a glove box (with water and oxygen lower than 1 ppm). Electrodes were constituted with CNF-covered Al current collectors (as described in the preparation section) and an active material based on activated carbon with an active material weight density of 15 mg/cm^2 (i.e., 60 mg). The active material was constituted of 95 wt % of Picactif BP10 (Pica Co.), 3 wt % of CMC, and 2 wt % of poly(tetrafluoroethylene) (PTFE).³ Two 25 μm thick polymeric separators are used to isolate the two symmetrical electrodes. PTFE plates and stainless steel clamps were used to maintain the stack under pressure. Electrochemical characterizations were performed in 1.5 M NEt_4BF_4 + acetonitrile (extra dry) organic electrolyte.

Electrochemical tests.— Galvanostatic cycling measurements were performed with an Arbin cyler between 0 and 2.3 V at various

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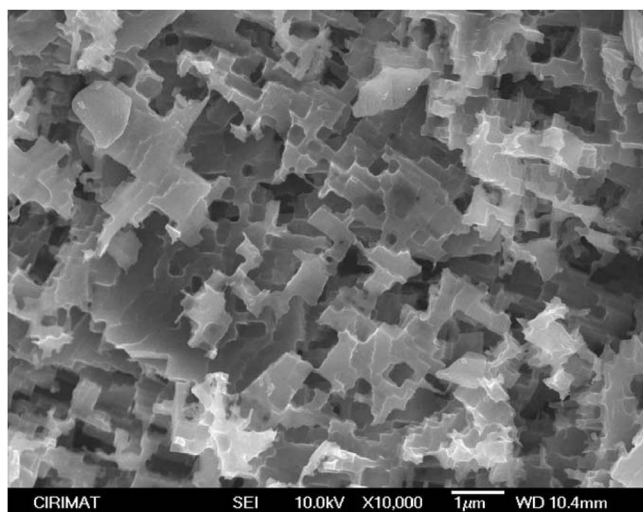


Figure 1. FEG-SEM picture of the etched aluminum.

current densities depending on the active material nature. A 5 s potentiostatic maintain was performed at 0 and 2.3 V during each cycle. The equivalent series resistance (ESR) was measured during a 1 ms current pulse: the voltage drop was recorded and the ESR was calculated. Cell capacitances are deduced from the slope of the discharge curve

$$C = \frac{I}{\left(\frac{dV}{dt}\right)} \quad [1]$$

where C is the capacitance of the cell in farads, I the discharge current in amperes (A), and dV/dt the slope in volts per second ($V s^{-1}$).

In a symmetrical system where the active material weight is the same for the two electrodes, the specific capacitance $C_{m_{AC}}$ in farads per gram of activated carbon ($F g^{-1}$) is related to the capacitance of the cell C by

$$C_{m_{AC}} = \frac{2C}{m_{AC}} \quad [2]$$

where m_{AC} is the weight (g) per electrode of CNFs or activated carbon.

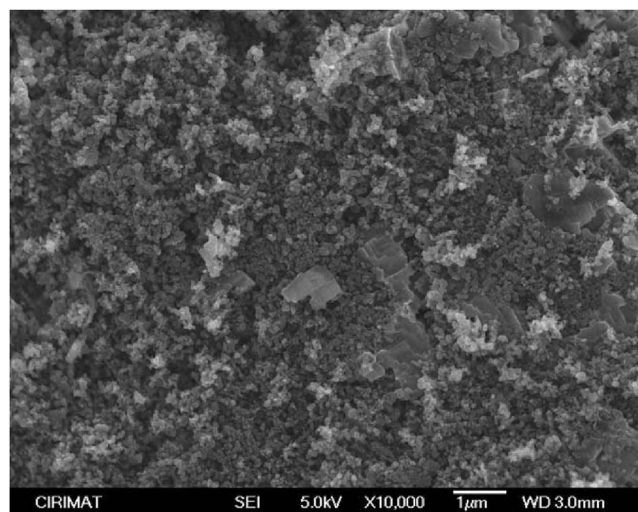
Electrochemical impedance spectroscopy was used to characterize the frequency behavior of cells; measurements are performed with an EGG 6310 between 10 mHz and 50 kHz, at a bias cell voltage of 2 V.

Result and Discussion

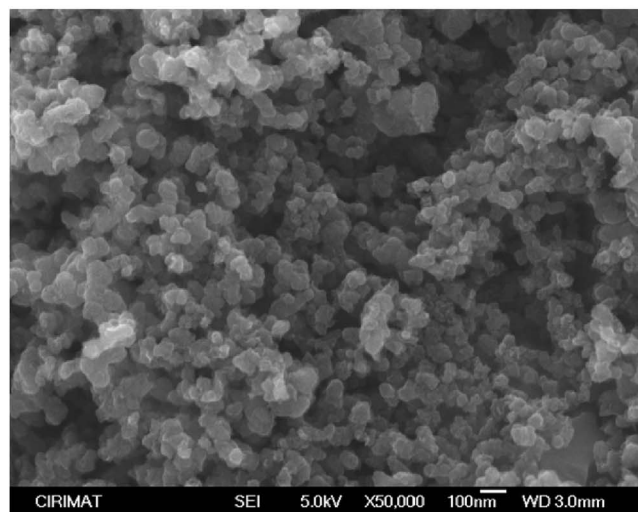
CNFs characterizations.—Figure 3 presents Raman spectra for the CNFs samples. Two characteristic bands appear. The D band, which appears at $1352 cm^{-1}$, corresponds to an sp^3 -like carbon and is generally proportional to a crystalline disorder. The G band at $1604 cm^{-1}$ corresponds to the graphitic structure (sp^2 carbon). The ratio between the intensity of the D band and the G band (baseline correction applied) $I_{D/G}$ is close to 70%, which corresponds to an important crystalline disorder.¹⁷

FEG-SEM pictures of the etched Al foil covered by the CNFs are presented in Fig. 4a and b. It can be seen that the CNFs cover the whole surface of the Al foil, forming a three-dimensional open network on the Al surface. Some interconnections between CNFs can be seen in Fig. 4b.

Figure 5 presents a transmission electron microscopy (TEM) picture of the CNFs. TEM image analysis give a diameter size between 8 and 15 nm. For TEM observation, the surface of the sample was



(a)



(b)

Figure 2. FEG-SEM picture of the etched aluminum covered by carbonaceous particles.

scratched with a razor blade and the material collected was sonicated in EtOH. A drop of the suspension was evaporated on a TEM grid (copper grid with a hollow carbon film). Samples were observed with a JEOL 2010 transmission electron microscope operated at 120 kV. TEM observations reveal that the filaments observed by FEG-SEM are poorly organized carbon nanofilaments (Fig. 5a). Images at high magnification (Fig. 5b-d) show that they consist of a stacking of graphitic fragments, randomly oriented with respect to the nanofilament growth direction. Only a minority of nanofilaments seems to have a hollow inner channel. Few nanofilaments contain metal particles inside, and some carbon-encapsulated metal particles can be observed (typical diameter around 10 nm). The CNF diameter is close to the one of Multiwalled carbon nanotubes. As compared to diameter values of CNFs given for electrochemical capacitor applications, this diameter is about 20 times lower.^{12,18}

Electrochemical characterizations.—*Galvanostatic cycling measurements.*—Galvanostatic cycling measurements were performed between 0 and 2.3 V at various current densities, ranging from 5 up to 100 mA/cm². Electrochemical capacitor cells of 4 cm² were assembled with treated Al current collectors covered by 60 mg

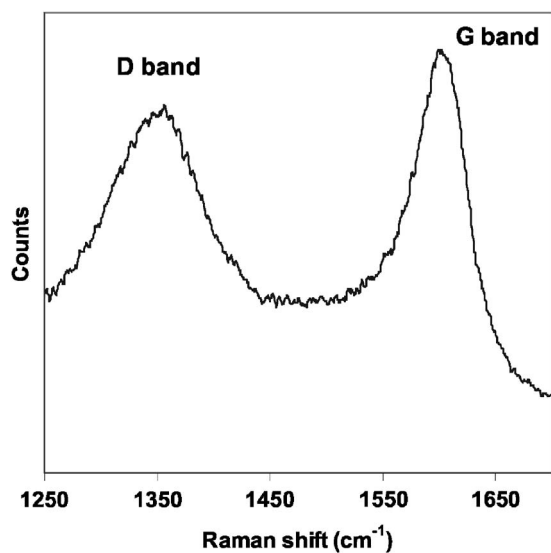
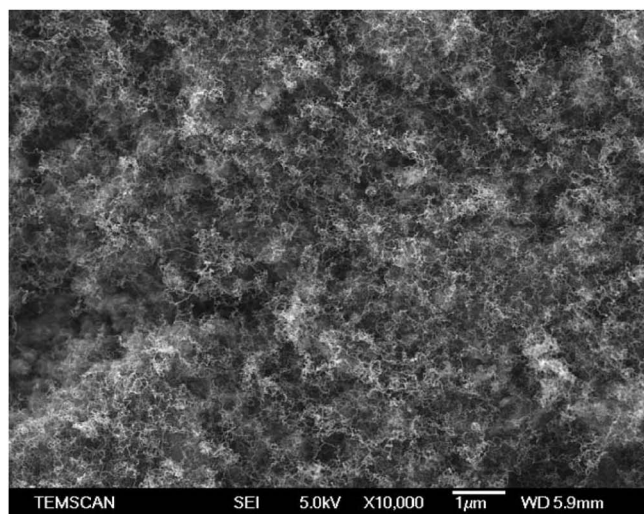
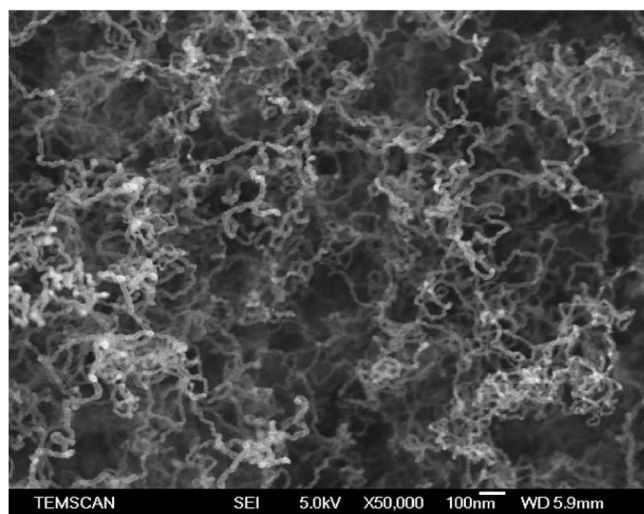


Figure 3. Raman spectra of CNF samples.



(a)



(b)

Figure 4. FEG-SEM picture of the prepared aluminum covered by carbon nanofibers.

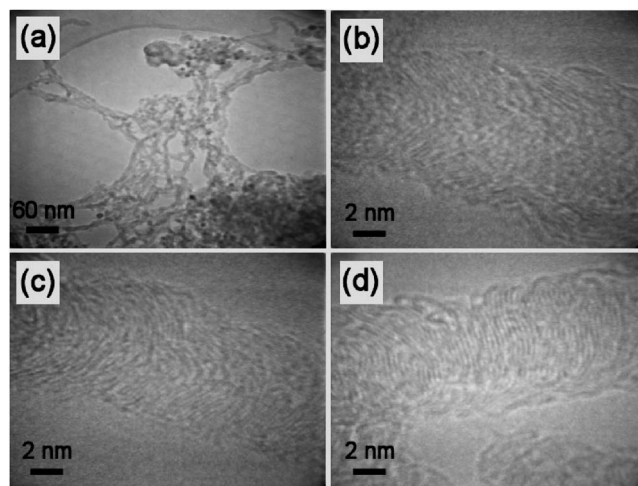


Figure 5. MET picture of CNFS samples (a) disorganized CNFs and encapsulated Co nanoparticles (b)–(d) High magnification of CNFs samples.

of active material (95% of Picactif activated carbon; see the Experimental section). Two different Al surface treatments were tested and compared.

Figure 6 represents the typical charge/discharge plot of cells assembled with etched Al current collector first covered by carbonaceous particles and then by CNFs. No faradaic reactions are observed because the voltage dependence versus time is linear: the Al current collector surface treatment does not affect the electrochemical behavior of the cell.

The first cell was assembled using a pretreated Al current collector as shown in Fig. 2: etched Al foil only covered by a sol-gel deposit of small carbonaceous particles (no CNFs). The second cell uses a fully treated Al current collector, i.e., covered with CNFs as presented in Fig. 4.

Figure 7 represents the change of the equivalent series resistance of the two cells versus the cycle number. The ESR value obtained with cells assembled with Al without CNFs is about 0.5 Ω cm². This is already a low ESR value measured in organic electrolyte showing the efficiency of such surface treatment: the contact at the Al current

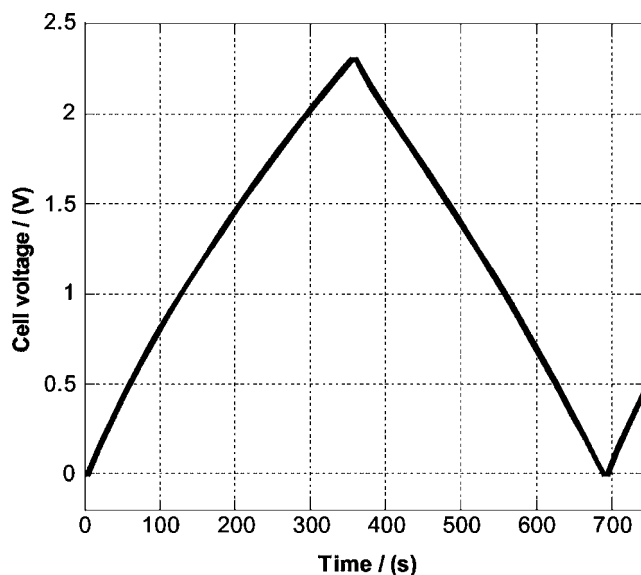


Figure 6. Charge-discharge curve of a cell assembled with etched Al covered by carbonaceous particles and CNFs between 0 and 2.3 V at a current density of 5 mA/cm².

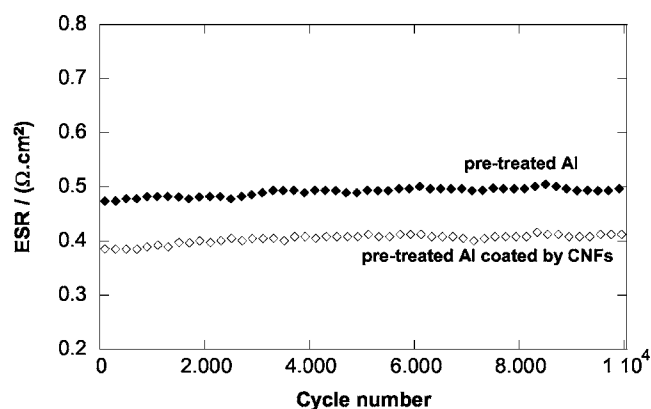


Figure 7. Variation of the ESR of cells constituted of a pretreated Al current collector and cells constituted of a pretreated current collector coated by CNFs and active material weight of 60 mg measured at 100 mA/cm² between 0 and 2.3 V.

collector/active material interface has been improved. The ESR obtained for cell using treated Al coated by CNFs is 0.4 Ω cm², i.e., a 25% decrease as compared to the previous one.

The ESR of the electrochemical capacitor is the sum of different ionic and electronic contributions; the major contributions are mainly the active material resistance, the ionic resistance of the electrolyte (into the porous structure of the electrode and the separator), and the Al/AM interface resistance. Zheng recently demonstrated that the current collector/AM interface plays a major role because it represents around 30% of the global internal resistance of electrochemical capacitors.¹⁹ Consequently, this interface contribution has to be minimized: this is the role of the surface treatments proposed here.

The ESR decrease for cells assembled with treated Al current collector covered by CNFs is due to an Al/AM interface properties improvement. This can be explained first by an increase of the interface conductivity, because the CNFs have a high electronic conductivity²⁰ as compared to the carbonaceous particles, and also by the increase of the surface contact between the aluminum and the active material. Consequently the ESR decreases, leading then to an increase of the power performances of the cells.

This surface treatment can be compared with another one which consists of the use of Al current collector covered by a conductive paint.^{21,22} The use of such a treatment aims to improve the contact and the adherence between the painted current collector and the active material. An ESR value of 0.8 Ω cm² was found by using

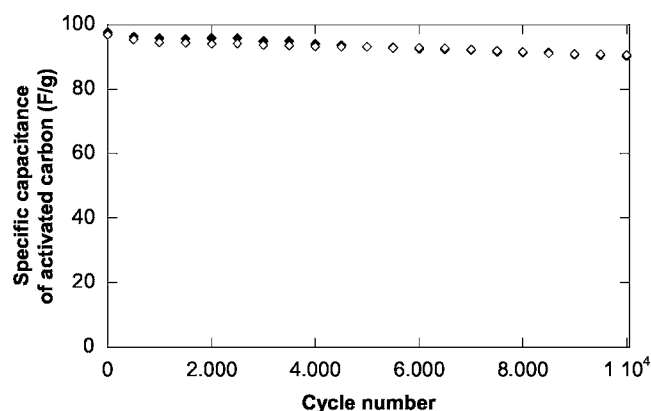


Figure 8. Variation of specific capacitance for cells assembled with pretreated Al and pretreated Al coated by CNFs; galvanostatic cycling between 0 and 2.3 V at 100 mA/cm².

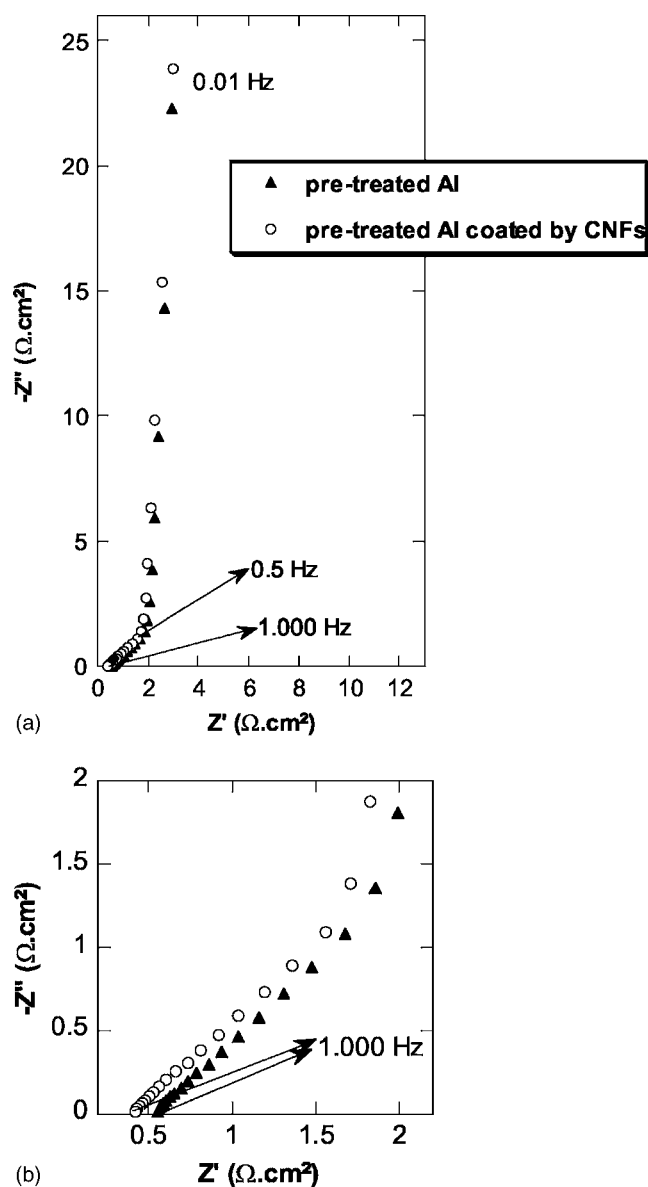


Figure 9. (a) Nyquist plot of cells assembled with electrodes constituted of a pretreated Al and pretreated Al coated by CNFs and active material based on activated carbon between 10 mHz and 50 kHz. (b) Zoom of the Warburg-type region.

painted Al and an activated carbon active material. The surface treatment proposed here is efficient to decrease the ESR, leading then to a marked improvement of the power performances. These results show the large influence of the Al/AM interface series resistance of a electrochemical capacitor cell in the same way as previously described by Zheng.¹⁹

From Fig. 7, the ESR remains stable over 10 000 cycles, demonstrating that the surface treatments do not modify the aging behavior.

Figure 8 represents the change of the specific capacitance measured at 100 mA/cm² for cells assembled with pretreated Al foil and pretreated Al coated by CNFs. The specific capacitance is similar for the two cells, around 95 F g⁻¹ of activated carbon. This result shows that the surface treatments do not affect the capacitive performances of the cells. Moreover, the specific capacitance remains stable over 10 000 cycles.

Galvanostatic cyclic measurements characterize power and energy performances of 4 cm² electrode cells using two types of current collectors, and can be calculated by Eq. 3 and 4,

$$P_{\max} = \frac{V^2}{4 \times (\text{ESR}) \times m_{\text{AM}}} \quad [3]$$

$$E_{\max} = \frac{1C \times V^2}{2m_{\text{AM}}} \quad [4]$$

where m_{AM} is the total active material weight on the two electrodes (30 mg cm⁻²).

CNFs synthesis on the etched Al coated by carbonaceous particles induces a great decrease of the ESR leading then to an increase of power performances ($P_{\max} = 110 \text{ kW kg}^{-1}$ of active material) and the energy value remains high ($E_{\max} = 17 \text{ Wh kg}^{-1}$ of active material) because the capacitive behavior is not affected.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy allows one to characterize the frequency behaviour of the cells. Figure 9a represents the Nyquist plot of cells assembled with electrodes constituted of a pretreated Al current collector and pretreated Al current collector coated by CNFs. The shape of the Nyquist plots is the one obtained for standard carbon-carbon electrochemical capacitors.^{23(a),23(b)} Three main parts are observed. At high frequencies, down to 1256 Hz, the resistive behavior can be seen; for $Z'' = 0$ (at a frequency of 1256 Hz) the ac internal resistance is obtained. For medium-range frequencies (between 1256 Hz down to 0.5 Hz), the ion migration into the porous structure of the electrode can be seen (Fig. 9b). For frequencies lower than 0.5 Hz, the capacitive behavior appears.

No high-frequency loop can be seen in these Nyquist plots. In a previous paper, we showed that cells assembled with untreated Al current collectors exhibit a high-frequency RC loop in the Nyquist plot. Because this loop disappeared for cells assembled with etched Al current collectors coated by carbonaceous particles, it was attributed to the Al collector / active material interface impedance,¹⁶ as others authors did.²⁴⁻²⁶ From the results presented here, it can be concluded that the CNFs surface treatment is efficient to improve the current collector / active material interface properties in terms of conductivity and contact surface; the capacitive behavior is not shifted by a RC loop to lower frequency and higher resistance (Z') values.

Conclusion

This paper describes the synthesis of carbon nanofibers (CNFs) prepared by a CCVD process on a pretreated aluminum current collector, and the influence of such a treatment on electrochemical performances of carbon/carbon electrochemical capacitor in organic electrolyte.

CNFs were synthesized through the decomposition of a C₂H₂/H₂ gas mixture at 630°C on a pretreated Al foil; the pretreated Al foil consists of an etching treatment followed by a carbonaceous

sol-gel deposit via the sol-gel route. This led to the synthesis of small diameter (in the range of 8–15 nm) CNFs with a poor graphitic structure.

This CNF synthesis was used as surface treatments for Al current collector in order to decrease the Al/active material interface impedance. Performances of cells assembled with CNF-treated Al current collector coated with an activated carbon film were investigated. Galvanostatic cycling measurements showed the great efficiency of this new surface treatment because these cells exhibit a very low internal resistance: 0.4 Ω cm². This ESR decrease led to an increase in power performances (110 kW/kg of active material). The specific capacitance measured for both cells was found to be the same, showing that the CNF coating does not affect the capacitive behavior. A constant behavior of internal resistance and specific capacitance is observed over 10 000 cycles. This result showed the great efficiency of such a surface treatment, confirmed by the electrochemical impedance spectroscopy measurements.

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