

Non-faradic carbon nanotube-based supercapacitors: state of the art

Analysis of all the main scientific contributions from 1997 to our days

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Received: 19 June 2012 / Accepted: 21 September 2012
Published online: 31 October 2012 – © EDP Sciences 2012

Abstract. This contribution deals with the state of the art of studies concerning the fabrication of electric double-layer capacitors (EDLCs) also called super- or ultracapacitors and obtained using carbon nanotubes (CNTs) without exploiting Faradic reactions. From the first work published in 1997, EDLCs fabricated using carbon nanotubes as constitutive material for electrodes showed very interesting characteristics. It appeared that they could potentially outperform traditional technologies based on activated carbon. Different methods to fabricate the CNT-based electrodes have been proposed in order to improve the performances (mainly energy densities and power densities), for example filtration, direct growth on metal collector or deposition using an air-brush technique. In this contribution we will introduce the main works in the field. Finally, we will point out an emerging interest for supercapacitors fabricated on flexible substrates, exploiting the outstanding mechanical performances of CNTs, for new kinds of applications such as portable electronics.

1 Introduction

This review presents the studies starting from 1997 and concerning the fabrication of electric double-layer capacitors (EDLCs), also called super- or ultracapacitors, using carbon nanotubes (i.e., CNTs). Supercapacitors are devices composed of two electrodes through which a potential is applied across a cell. An ion-permeable separator is usually placed between these electrodes, in order to avoid direct electrical contact between them. Compared to common capacitors, EDLCs store electrical charge at the interface between the surface of a conductor and an electrolytic solution. Therefore, the charges accumulated form an electric double layer where the distance, between the charged layers, is around some angstroms [1–3]. In this contribution, we will not deal with the assembly and packaging issues and we will focus our interest on the materials for electrode/collector fabrication without taking into account devices exploiting Faradic reactions (using nanocomposites of CNTs and metal oxides or polymers). In fact, these kinds of reactions do not strictly depend on the CNTs but on the material added to CNTs. In this paper our interest is exclusively concentrated on the role

of the CNTs. Moreover, considering the complexity of the matter, we will not deal with graphene/graphite-based devices because this would need another entire contribution in order to give a correct analysis of the multiple recent works on this domain. The study of the electrical charge storage using EDLCs began in 1957, when a patent was filed by Becker of General Electric for an electrolytic capacitor using porous carbon electrodes [4]. The device patented by Becker was highly impractical and both electrodes needed to be immersed in a container of electrolyte. For this reason this device was never commercialized. The merit of the EDLC device concept as perceived at present can be attributed to Rightmare and Boss of standard oil company of Ohio (SOHIO) thanks to two patents (one the follow-on of the other) filed in 1962 [5] and 1966 [6]. In 1978, NEC went on to produce the first commercially successful double-layer capacitors under the name “supercapacitor” [7]. These low voltage devices had a high internal resistance and were thus primarily designed for memory backup applications, finding their way into various consumer appliances. In the same applications field we can mention the so-called “Gold capacitor” commercialized since 1978 by Matsushita electric industrial company (Panasonic) [7]. By the 1980s a

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number of companies were producing EDLCs. The first high-power double-layer capacitors were developed by Pinnacle Research Institute (PRI) in the US. The “PRI Ultracapacitor”, developed from 1982, incorporated metal-oxide electrodes and was designed for military applications such as laser weaponry and missile guidance systems [8]. As mentioned, these devices were essentially used for applications such as smoothing circuits of power supplies, backup power sources of microcomputers or to block direct current flow. The range of applications was narrow because the delivered power was strongly limited by the high internal resistance of the device. With the improved performances recently achieved, other applications, which need high peak power for short duration, can be targeted. EDLCs are now tested in hybrid vehicles for regenerative braking, acceleration, stop/start operations in vehicles traction and electric steering since these functions all exhibit power requirements fitting with this profile. Nissan [9], Honda [9] and Toyota [10] have all experimented EDLCs to complement the battery in hybrid vehicles. The use of EDLCs to provide satisfactory transient behavior of experimental fuel cell vehicles has been described [11, 12]. We also point out the recent utilization of EDLCs in emergency doors of the Airbus 380 super jumbo jet [13]. Although this is a niche application, it demonstrates that these devices can respond to stringent specifications in terms of reliability and safety. The most interesting aspect of EDLCs is their ability to bridge the power/energy gap between traditional dielectric capacitors (characterized by high-power densities) and batteries (characterized by high energy densities). Just like regular capacitors, EDLCs store electric charges on the surface of the electrodes, which is different from batteries where charge storage is based on redox reactions occurring at the anode and cathode, often followed by diffusion processes in the bulk of the electrodes. Because charge storage/delivery in batteries relies on chemical reactions (and often solid-state diffusion), they take more time to charge/discharge than ultracapacitors. Batteries are currently the most common form of electrical energy storage, because they can store higher energy density than supercapacitors. Also, the voltage delivered by batteries tends to be constant and not influenced by the state of discharge. However, as told previously, batteries cannot reach the values of delivered power of the common dielectric capacitors. Moreover, due to their short life cycle and low power densities (i.e., <1 kW/kg) [12] batteries are not suitable for many lightweight power source applications. Analyzing the commercially available devices, non-rechargeable, dry batteries have an energy density spanning from 90 W h/kg to around 350 W h/kg [11]. Rechargeable Ni-Cd batteries can attain 1000 cycles in a lifetime, with an energy density of approximately 225 W h/kg [2, 13]. Concerning conventional electrochemical capacitors, they usually exhibit much higher power densities than batteries, reaching up to 30 kW/kg [13] and they have extended life cycles (i.e. $>500\,000$ [14, 15]). This value is lower than the value reachable with conventional capacitor but the energy density is dramatically larger: they can attain an energy density of

nearly 10 W h/kg [15, 16] (around two orders of magnitude higher than conventional capacitors). This has strongly contributed to increase the interest in the research of new materials (e.g., carbon nanotubes) to improve EDLC performances, in order to supply higher power (approaching conventional capacitors' performances) and energy density (bridging the gap with batteries).

2 Interest for carbon nanotube-based supercapacitors and the effect of pore size on capacitance value

As quoted previously, the EDLC (i.e., ultra-supercapacitors) exploits the double layer of charges formed when a voltage is applied to an electrode immersed in an electrolyte. To enhance this effect, in most traditional EDLCs, the electrodes are usually composed of porous carbon exhibiting a very large specific surface area (i.e., activated carbon, AC [17–21]). Briefly, AC is obtained using a thermal activation process that allows one to obtain highly porous carbon which is attached to the charge collector using a bonding agent. The very small charge separation in the double layer and the large surface area of the electrode results in a maximum specific capacitance of around 160 F/g [22]. The breakdown field strength of the EDLCs, calculated in V/cm, is extremely high compared to typical performances for conventional capacitors. However, the working voltage is limited by the stability of the electrolyte and by the potential contamination caused by the bonding agent. Therefore, a high surface area, a small charge separation distance and a high field strength are the three main factors that give rise to the very high energy density that is achievable with traditional EDLCs fabricated using AC as electrode material [23–33]. Considering that AC is extremely cheap and readily available from abundant sources, the replacement of this material with CNTs is principally driven by the potential of strong improvements of the final performances [34]. Indeed, the principal drawback related to AC is that it contains a wide distribution of pore sizes. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, there are three classes of pore sizes: (i) micropores of diameter <2 nm, (ii) mesopores of diameter ranging between 2 and 50 nm and (iii) macropores of diameters >50 nm. Ions in the electrolyte exist in a hydrated form in an aqueous solution. Since the sizes of hydrated ions are usually larger than 10 Å, the minimum effective pore size should be larger than ~ 15 Å [35, 36]. For this reason it appeared that pore sizes in the range of 2–50 nm were required to maximize the capacitance in the electrical double-layer capacitor [37, 38]. Moreover, macropores (>50 nm) seem to produce only a small enhancement of the electrode surface and so their contribution is considered minor. Knowing that the specific surface areas measured using gas adsorption on solid surface (the so-called Brunauer, Emmett and Teller, i.e., BET method) for activated carbon were in the range of 1000–3000 m²/g, scientists concluded that the main issue

for AC was that a great part of its surface area (around 2/3) resided in unpercolated pores (smaller than 2 nm) not useful to support an electrical double layer [39–43]. At the same time, even if the surface area of CNTs (e.g., between 300 and 400 m²/g) was much smaller than for AC (>1000 m²/g [44]) or activated carbon fibers (1500–2000 m²/g [44]), the pore dimensions' distribution was more centered around the interval between 2 and 5 nm. This result drove, in the early times, the interest on the research of CNTs as electrode materials.

3 The first papers

This section goal is to present the main works from the end of 1990s. As told previously, we will not deal with EDLCs whose operation principle is based on redox reactions (more generally Faradic reactions). Indeed, the first work showing the great potentiality of CNTs to fabricate electrodes for supercapacitors was published in 1997 by Niu et al. of Hyperion Catalysis International Inc. [45]. This team used catalytically grown carbon nanotubes with diameters with an average value of 8 nm, mostly multi-walled carbon nanotubes – MWCNTs (see Fig. 1).

The nanotubes were nearly uncontaminated by other forms of carbon or other residues (except for small amounts of catalyst residue) after being submitted to a nitric acid treatment. The nanotubes after being functionalized using -COOH, -OH, and >C=O were dispersed in water and reassembled into an interconnected freestanding structure. After drying and thermally crosslinking, a rigid carbon nanotube electrode, with a thickness of around 25 μm, was formed without using binding materials which always bring impurities into the structure, reduce the breakdown voltage (i.e., the potential energy stored) and can degrade capacitor performance (the functionalized carbon nanotubes were self-adhesive on the current collector). One of the most interesting characteristics was that, unlike other types of AC-based electrodes, the pores in the nanotube electrode were uniformly spaced in the entangled nanotube network, thus they were all connected. A pore size distribution analysis of particles made by grinding up a thick mat revealed that the nanotube electrodes were essentially free of micropores. The total pore volume was 0.79 cc/g and the micropore (<20 Å) volume was a negligible 0.0016 cc/g. The average pore diameter was 9.2 nm (1.2 nm larger than the average diameter of their nanotubes). The BET-specific surface area of as-produced nanotubes was around 250 m²/g and it reached 430 m²/g after a nitric acid oxidation treatment to remove amorphous silicon and so freeing all the paths for ions. Since the measured micropore volume was negligible, the surface area of the nanotube-based electrodes resided in volumes and crevices greater than 2 nm in size. These were easily accessible to the electrolyte. A single-cell test device was fabricated with two carbon nanotube-based electrodes having diameters around 1.3 cm, thickness of 25 μm, separated by a 25-μm thick polymer membrane (Celgard) using 38 wt.% H₂SO₄ as the electrolyte. The resistivity of the electrode sheets measured using the van der Pauw method

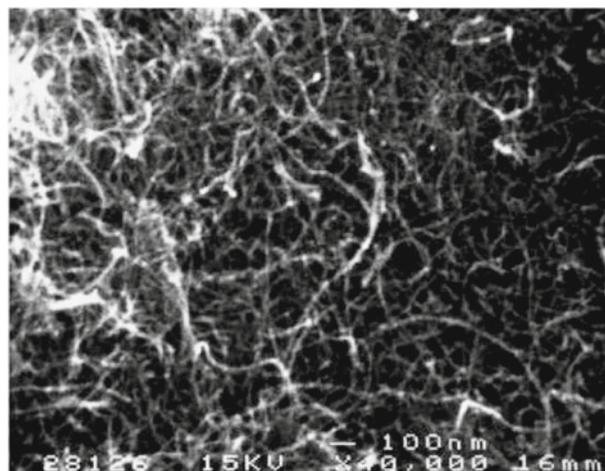


Fig. 1. SEM image of the entangled nanotubes film achieved by Niu et al. [45].

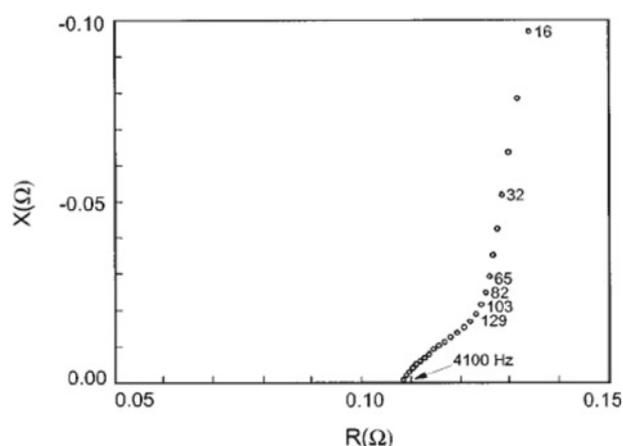


Fig. 2. Impedance spectroscopy performed by Li et al. [24].

was $1.63 \times 10^{-2} \Omega \text{ cm}$. The specific capacitance measured for this cell by a constant direct current charging method was 104 F/g. Figure 2 shows the results of the impedance spectroscopy of the capacitor, measured at a dc bias of 0 V with a 10 mV ac amplitude. The value of the “knee” frequency (i.e., the largest frequency value associated to a capacitor-type behavior [2]) in the plot was about 100 Hz, which suggests that around one half of its stored energy is accessible at frequencies up to this value.

All these results were very promising and justified the subsequent effort on CNTs, considering that, the highest reported “knee” frequency value for capacitors before 1997 was 6 Hz [46]. Concerning the other parameters, the average power density of the cell between 0.5 and 1 V was larger than 8 kW/kg and the energy density was around 0.6 W h/kg. We can notice that the authors do not comment on the evidence that below 100 Hz, the capacitance increases up to 104 F/g at 1 Hz. As they claim, micropores are rare and so the explanation might be that in some degree, a reorganization of ions species and solvent molecules takes place in the double layer in such a way that the ions distance from electrodes is reduced and

Table 1. Parameters measured for the different samples achieved by Frackowiak et al. [48]. Samples are labeled according to the substance used for carbon nanotubes growth (A = acetylene, P = propylene), the number corresponds to the growth temperature and the last part denotes the catalyst/substrate couple used for the growth. The capacitance-specific values have been measured at a low frequency of 1 mHz.

Type of nanotube	A700Co/ Si	A900Co/ Si	A600Co/ NaY	P800/ Al
Mesopore volume (cm ³ /g STP)	435	381	269	643
BET surface (m ² /g)	411	396	128	311
Oxygen mass (%)	10.8	4.6	0.8	<0.3
Capacitance (F/g)	80	62	4	36

so the capacitance enhances at low frequencies. Another pioneer paper issued in the same period (1999) by Ma et al. at the Tsinghua University (P.R. China) [47] proposed the fabrication of “block-form” porous tablets of CNTs as electrodes in EDLC. The Chinese group achieved mixtures of CNTs and phenolic resin powders (wt.% ratio 15:85). The performances were quite limited concerning capacitance (15–25 F/g) and this was mainly related to the reduced specific surface (120 m²/g) compared with AC. However, this work confirmed that the fabrication of CNT-based electrodes was an extremely promising technology and pointed out that the chemical treatment of surfaces was a key factor to optimize the specific surface and so the capacitance. In 2000, Frackowiak et al. fabricated supercapacitors using MWCNTs [48]. The main novelty of their work was that it constituted the first effort to investigate systematically the effect of different growth catalysts and post-treatments of the MWCNTs on the microtexture and elemental composition of the materials, and so on the specific capacitances. These last mentioned factors were obtained by cyclic voltammetry measurements at different scan rates from 1 to 10 mV/s, galvanostatic discharge and impedance spectroscopy in the frequency range from 100 kHz to 1 mHz. The electrolyte used for these tests was a 6 M KOH solution (Tab. 1).

The presence of mesopores mainly due to the entanglement of the nanotubes networks in the mat, as previously explained, improves the accessibility of the ions to the electrode/electrolyte interface for charging the EDLC. Researchers observed that the values of specific capacitance varied from 4 to 80 F/g (at a frequency of 1 mHz), depending on the types of nanotubes or/and their post-treatments. These capacitance values confirmed that even if the specific surface area of MWCNTs electrodes was moderate (around 400 m²/g) compared to AC, MWCNT-based mats were potentially very attractive materials for supercapacitors, thanks to their pore distribution. In the following papers, the same team demonstrated that the capacitance value could be increased seven times after

chemical activation using KOH, thus developing the microporosity of the bare MWCNTs [48,49]. This appeared to be related to the creation of a multitude of defects on the surface of the carbon nanotubes, thus enhancing the micropore volume, while keeping the mesoporous volume percentage high. This very effective technique has also been used by other groups [50,51].

Liu and coworkers at University of Texas and University of California (UCLA) [52] issued a fundamental paper in 1999 where they performed for the first time, studies on thin film of SWCNTs deposited on Pt or Au electrode surfaces. In this pioneer work on these films the tested electrodes showed a good rectangular shape in cyclic voltammetry measurements. The capacitance value obtained was 283 F/g in 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) used as electrolyte. This value corresponded at around twofold the value for AC-based electrodes in nonaqueous solutions. The energy stored reached a value of around 15 W h/kg (calculated, see Tab. 2). These results were very promising, considering that this was one of the first supercapacitors achieved with SWCNTs simply dispersed on a metal collector. Concerning the cyclability of the samples, these ones showed stable values after a cycle of 30 min at 50 mV/s. Although now this cycle appears limited, we have to mention that these measurements were performed only 2 years after the first paper regarding CNT-based EDLCs and therefore they were considered as extremely promising.

Another point of view was adopted by Barisci and coworkers in 2000 [53]. They focused their work on the influence of the electrolyte on the CNT-based electrode performances, using single-walled carbon nanotube (i.e., SWCNT)-based buckypapers obtained by classical filtration method. In case of aqueous solutions, they tested as electrolytes, 1.0 M for NaCl, H₂SO₄ and KOH. They obtained for the different samples respectively a capacitance value of around 30 F/g, 80 F/g and 40 F/g (scan rate of 50 mV/s), and a maximum stored energy of ~1 W h/kg, ~4.5 W h/kg, ~3 W h/kg (calculated, see Tab. 2). However, the cyclic voltammetry graphs did not show an ideal rectangular shape (especially for H₂SO₄), pointing out the presence of redox reactions and demonstrating the presence of impurities linked to the production process or to the oxygen-containing functional groups (similar to those observed for other type of carbon [54] and CNTs [55]). These seemed to be generated by the purification step of the electrodes in nitric acid on the CNT surfaces or on the amorphous carbon present as impurity material [56]. The presence of impurities was also in part related to the filtration method. This is one of the reasons why in the previous paper of Liu et al. these redox reactions were not highlighted: they had directly deposited the solutions of SWCNTs on the metal current collector achieving a more pure electrode material strongly reducing the effect of these reactions. These results were also confirmed for nonaqueous electrolyte. Indeed, Barisci and coworkers tested also tetrabutylammonium tetrafluoroborate (i.e., TBTATFB) in acetonitrile and LiClO₄. Capacitance values obtained were, respectively, 40 F/g and 120 F/g and the maximum energy stored ~20 W h/kg and ~7 W h/kg

Table 2. Summary of all the mains parameters related to the devices described in the different papers cited in the contribution.

Materials	Highest specific power (kW/kg)	Highest specific energy (W h/kg)	Highest specific capacitance (F/g)	Frequency (Hz)	Highest specific surface (m ² /g)	Electrolyte	References
MWCNT-based mats	40	~1.2	104 49	1 100	250 and (450 after treatment)	38 wt.% H ₂ SO ₄ (a.s)	Niu et al. [45]
MWCNT-based block-form tablets using CNTs/phenolic resin mixtures	~0.002	~1	25	d.u.	120	38 wt.% H ₂ SO ₄ (a.s)	Ma et al. [47]
SWCNTs deposited directly on the current collector	d.u.	~15	283	d.u.	d.u.	0.1 M TBAPF ₆	Liu et al. [52]
MWCNT-based mats	~0.04	~4	80 (137, after treatment)	0.001	411 (475, after treatment)	6 M KOH (a.s)	Frackowiack et al. [48]
SWCNT-based mats mixed with PVDC (30 wt.%)	20	6.5–7	180	1000	357	7.5 N KOH (a.s)	An et al. [57]
VCNTs	d.u.	1.2	146	d.u.	d.u.	1 M H ₂ SO ₄ (a.s)	Chen et al. [62]
Highly pure SWCNT using HiPco method	d.u.	~10	40	d.u.	400	1 mol dm ⁻³ LiClO ₄ / propylene carbonate solution	Shiraishi et al. [87]
Highly pure SWCNTs	d.u.	~1 ~4.5 ~3 ~20 ~7	~30 ~80 ~40 ~120 ~40	d.u.	d.u.	1 M NaCl (a.s) 1 M H ₂ SO ₄ (a.s) 1 M KOH (a.s) 0.1 M LiClO ₄ (na.s) 0.1 M TBTAFB (na.s)	Barisci et al. [53]
VCNTs	d.u.	~7	39 (207, after treatment)	d.u.	10 (87, after treatment)	6 M KOH (a.s)	Yoon et al. [64]
Highly packed MWCNT mats	30	~0.04	20	d.u.	d.u.	6 M KOH (a.s)	Du and Pan [72]
MWCNT-based mats obtained using EPD technique	20	~0.03	21	7650	d.u.	6 M KOH (a.s)	Du and Pan [73,74]
MWCNT-based mats obtained by ESD technique	d.u.	~3	108	d.u.	400	1 M H ₂ SO ₄ (a.s)	Kim et al. [68]
SWCNT solid	43.3	69.4	80	d.u.	1000	Tetrafluoroborate (Et ₄ NBF ₄)/propylene carbonate	Futaba et al. [90]

(continued on next page)

Table 2. (Continued)

Materials	Highest specific power (kW/kg)	Highest specific energy (W h/kg)	Highest specific capacitance (F/g)	Frequency (Hz)	Highest specific surface (m ² /g)	Electrolyte	References
VACNTs in cellulose matrix	1.5 d.u.	13 ~20	22 36	d.u.	150	RTIL 6 M KOH	Pushparaj et al. [98]
Purified SWCNTs sprayed on PET	23	6	36	d.u.	d.u.	Polyvinyl alcohol (PVA) powder with water (1 g PVA/10 mL H ₂ O) LiPF ₆	Kaempgen et al. [97]
SWCNTs and xerox paper	20	~10	200	d.u.	d.u.	Sulfuric acid	Hu et al. [100]
Electrodes with parallel high purity SWCNTs	210	94	160	d.u.	1300	1 MEt ₄ NBF ₄ /propylene carbonate	Izadi-Najafabadi and Futaba [95]
VACNTs with open tips	987	53	160	50	2240	[EMIm][NTf ₂]	Kim et al. [67]

d.u. = data unavailable, ~ = data calculated from parameters provided in the paper.

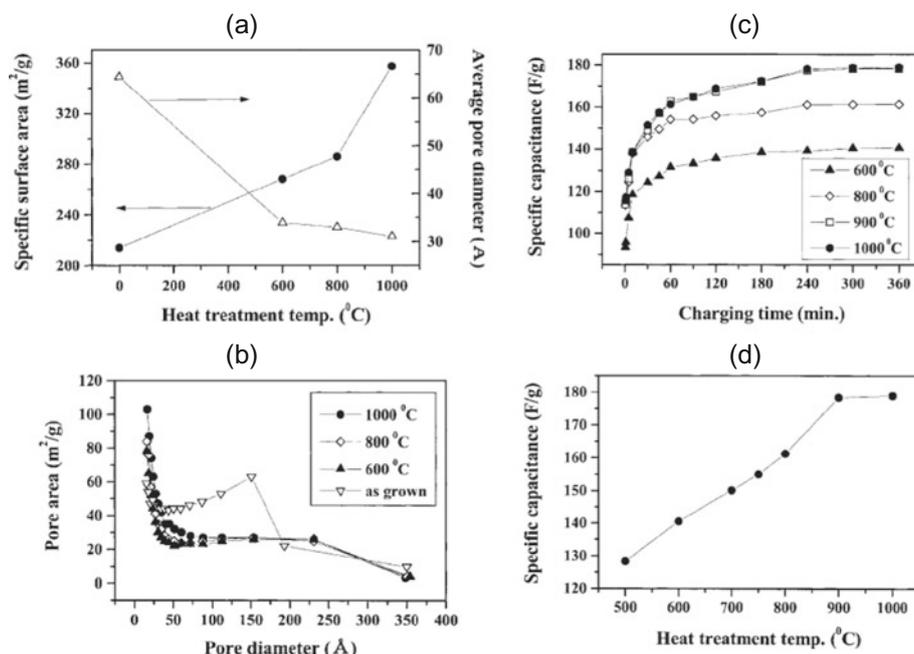


Fig. 3. Main characteristics of the samples as a function of the different parameters [26].

(calculated, see Tab. 2). These results were very interesting even if the redox reactions were quite strong, especially for LiClO₄ and so the cyclability of the capacitance limited.

An et al. [57] in 2001 showed more deeply the influence of the pore dimension on the specific capacitance after specific treatment. In this case, the CNTs were SWCNTs, obtained by an arc discharge technique, crosslinked and randomly entangled. The South Korean team measured the pore area of SWCNTs mixed with 30 wt.% of poly-

vinylidene chloride (PVDC), used as binder, as a function of the heat treatment. In this way, they pointed out that the binder function was not only to strengthen the electrodes, but also to facilitate the formation of pores with a specific size distribution. Indeed, the raw sample showed a peak at 15 nm and had a narrow distribution at smaller pore diameters around 2 nm (see Fig. 3).

The increase of the heat-treatment temperature corresponded to an enlargement of the diameter of smaller pores, reaching a maximum for a treatment temperature

value of 900 °C during 30 min. At this temperature, the authors claimed that the number of pores with diameters ranging from 5 to 25 nm decreased. Their conclusion was that the highest temperatures stimulated the formation of pores of dimensions around 3–5 nm, enhancing the accessible surface of the electrodes, see Figure 3a, and so the capacitance. The higher value obtained was 180 F/g (for a heat treatment at 1000 °C). We stress that, in this case, the specific surface area was around 350 m²/g (after heat treatment at 1000 °C) which is much smaller than 1000–3000 m²/g usually reported for AC. In this paper, the authors also tried to reduce the resistance between the current collector and the SWCNTs using a polished Ni foil, a plain Ni foil and a hybrid form of SWCNT-Ni-foam. The best results were obtained using the foam-based hybrid electrode which resulted in a dramatic reduction of the equivalent series resistance (ESR). In this way the power density was strongly improved obtaining a power density of 20 kW/kg and an energy density of 6.5–7 W h/kg. These results put in evidence the importance of the contact resistance on the final supercapacitor performances.

In 2002, Shiraishi et al. [58] decided to work with pure SWCNTs produced by the HiPco method. This choice was motivated by the fact that, in their opinion, the lack of consistency between the results obtained previously by the different teams using CNTs was mainly due to low purity of the nanomaterials. Shiraishi and coworkers fabricated electrodes composed of two SWCNT buckypapers. The specific surface was equal to 500 m²/g (obtained using the α_s -SPE technique which allows to diversify the micropore rate [59]) and the final capacitance of 45 F/g. The highest energy amount stored attained a quite high value equal to 20 W h/kg (calculated, see Tab. 2). The more interesting point of this work was that it seemed to demonstrate that using pure materials without binder or polymers, we could be able to raise the tension (in the paper it varied between 2 V and 4 V) and so to raise the potential stocked energy. However, this paper did not supply data necessary to calculate the delivered power, which constitutes a major lack.

4 Approaches to improve the power delivered and the frequency response

The first results shown in the previous paragraph highlight the key factors limiting the supercapacitor power density and frequency response: the internal resistance of the electrode itself, the contact resistance between the electrode and the current collector, and the resistance of the electrolyte within the porous structure of the electrode [60]. One option is to provide the direct growth of vertical CNTs (i.e., VCNTs) on the collectors to improve the conductivity. One of the first papers proposing this configuration was issued by Emmenegger et al. at the Fribourg University (Switzerland) in 2000 [61]. Indeed, the device fabricated by this scientific team constitutes the first example of EDLC cell achieved using aligned forests of vertically grown CNTs (i.e., VACNTs). More precisely,

they obtained well-aligned carbon nanotubes films on an aluminum substrate using Fe(NO₃)₃ as catalysts for CNTs growth. In fact, this paper mainly deals with growth mechanism and only some data are provided at the end concerning the measurements of capacitance, energy and power volumetric density, respectively, 120 F cm⁻³, 26 W h l⁻¹ and 700 kW l⁻¹. Unfortunately, these data cannot be accurately compared with the previous ones considering that we have no information about the weight (and density) of the EDLC cell.

Another very interesting paper dealing with VACNTs was published by Chen et al. in 2002 [62] at the Ren's group (one of the pioneer groups working on emission field emitters achieved with VCNTs [63]) at Boston College. They obtained a capacitance as high as 115.7 and 146.6 F/g respectively for a scan rate of 100 and 25 mV/s using 1.0 M H₂SO₄ as electrolyte. The most interesting point of this contribution was the possibility to directly grow CNTs on a bare graphitic foil used as collector, fabricating a whole carbon-based electrode.

Yoon et al. [64] in 2004 fabricated EDLC capacitors using CNTs based electrodes where CNTs had been grown directly on an Ni current collector, without using any kind of catalyst. This method did not require the utilization of binders, simplifying the fabrication procedure of the electrodes. Using this kind of integrated electrode, Yoon et al. wanted to reduce the part of ESR related to the resistance between the electrode materials and the current collector. The so-called "Coin-type EDLC" cells were fabricated with a 6 M KOH solution as electrolyte and polypropylene membrane as separator. Each cell was fabricated using a stainless steel (SUS) can, two CNT-based electrodes, a polymeric separator and a SUS cap (see Fig. 4).

The authors compared the performances of two different types of CNT-based electrodes. In the first case (cell A), nanotubes were directly grown on electrodes. In the second case (cell B), they used binder-type electrodes, prepared by coating the Ni current collector with a CNT slurry consisting of 80 wt.% of MWCNTs and 20 wt.% of polyvinylidene fluoride. Figures 4b–4d report the cyclic voltammetry (CV) of both types of cells. The shape of the loop of an EDLC should be rectangular, provided that there are no internal, interfacial and contact resistances. Large resistance distorted the loop, resulting in a narrower loop with an oblique angle. The CVs of both cells were nearly rectangular at a scan rate of 100 mV/s (Fig. 4b). However, cell B showed almost resistance at a higher scan rate of 500 mV/s (Fig. 4c) while the CV loop remained somehow rectangular for cell A, even at 1000 mV/s (Fig. 4d). These results indicated that cell B was not appropriate for an application with a high discharge rate. On the other hand, cell A took advantage of the high conductivity of the CNTs and the direct conducting paths between CNTs and the current collector. Therefore, a higher discharge efficiency and good electrodynamic property could be obtained. Improvement of specific capacitance was obtained by the surface treatment of the CNTs with an NH₃ plasma. The specific capacitance of the cell increased from 38.7 to 207.3 F/g

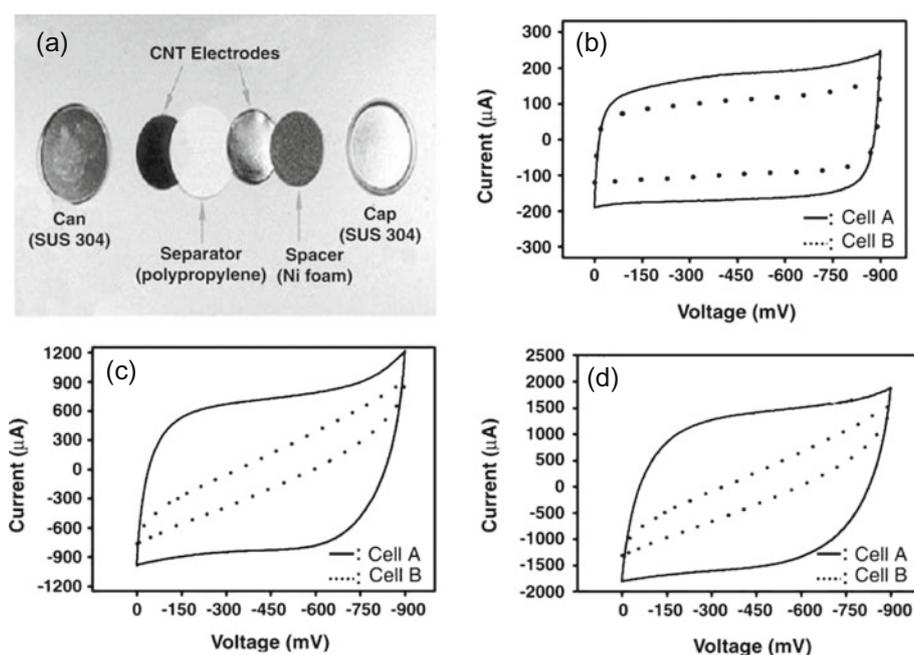


Fig. 4. (a) Construction of the coin cell. (b)–(d) Cyclic voltammograms of the EDLC cells at scan rates of (b) 100, (c) 500 and (d) 1000 mV/s. Cell A (solid line): the integrated CNT electrodes which are fabricated by mixed plasma of CH_4 and H_2 for 10 min after 5 min NH_3 plasma etching to the substrate; cell B (dotted line): the binder-type electrodes [64].

because of the enhancement of available surface: NH_3 plasma treatment resulted in a tenfold increase of the surface area. The values of the specific capacitance achieved by Yoon et al. were the largest obtained compared to the previous works. Actually, we were not able to find any information concerning the other fundamental parameters such as specific power. We also point out that the CNT array reached a thickness of only 20 nm, which is insufficient for viable energy storage purposes.

Considering the vertically grown forest of CNTs another possibility to develop the surface of the supercapacitors was proposed by Huang et al. in 2006 [65]. It consisted in opening the end-cap of carbon nanotubes. In this paper, it is suggested that the accessible surface for the EDLC can be largely enhanced, exploiting the internal surface area of CNTs. However in this contribution, no specific measurements related to the electrochemical properties of the materials were performed. This possibility has also been mentioned by Frackowiak and Béguin in 2002 [66] but in the case of entangled CNT networks for hydrogen storage applications. An impressive paper finally demonstrating the potential of exploiting the internal surface of VACNTs with opened tips has been recently issued by Kim et al. at the Korea University (Seoul) in 2012 [67]. In detail, they achieved excellent power and energy storage performance using VACNTs as an active electrode material for supercapacitors, respectively, ~ 987 kW/kg and ~ 53 W h/kg. High rate capability was attained thanks to the aligned and patterned CNT structures and the high energy density by increasing the CNTs available surface via electrochemical tip opening (increasing the specific capacitance from 75 F/g to 160 F/g) and by operating the

supercapacitors in nonaqueous solutions with wide operational voltage range.

As quoted at the beginning of this section, another way to increase the EDLC breakdown voltage (and hence energy and power densities) is to fabricate binder-free electrodes, as done by Yoon and coworkers. This can be achieved by direct growth on collectors, as seen in the previous paragraphs, but also by developing new deposition techniques. In this context, Kim et al. 2006 [68] reported on the preparation of an electrode based on a CNT film using a novel fabrication method involving electrostatic spray deposition (ESD). The ESD technique has been used for preparing thin films of metal oxides, such as lithium manganese oxide and lithium cobalt oxide, which are cathode materials for lithium-ion batteries [69–71]. Here, the solution was electrostatically sprayed downwards onto the substrate. Kim et al. tested a fabricated CNT film of around 20 μm of thickness on a surface of 1 cm^2 with a weight of around 1.3 mg. The specific capacitance maximum observed was 108 F/g at a potential scan rate of 10 mV/s, and it decreased slightly to 103 F/g at a potential scan rate of 100 mV/s. With a further increase in the potential scan rate to 500 mV/s, the specific capacitance decreased to 92 F/g (85% of the specific capacitance at 10 mV/s). Although these values were not the largest published in the literature, they were extremely interesting, considering that they were obtained with CNTs not being chemically or thermally treated, without any kind of binder. Moreover, this technique seems to be easier to deploy in practice, considering that it is not necessary to grow directly the CNTs on the current collector allowing a dramatic reduction of cost fabrication.

We would also like to mention the work of Du and Pan at the University of California Davis [72–74]. Du and Pan have developed two different approaches to lower the ESR in fabricating CNT thin film electrodes. One approach is to prepare thin films with coherent structures using highly concentrated colloidal suspension of CNTs, achieving highly conductive network with drastically small electrode resistance. In this case, the CNTs adhered directly to the current collector since no binder was added, thus the contact between them was very good and contact resistance was reduced as well. The CV measurements highlighted a nearly ideal rectangular shape even for high scan rate of 1000 mV/s showing an extremely small ESR. Concerning the energy and power value, Pan and coworkers were able to obtain an excellent value for power 30 kW/kg but an extremely low energy level of around 0.03 W h/kg because the specific capacitance was too low compared to previous results (20 F/g). In our opinion this is simply related to the fact that apparently the too dense mats reduce the pore dimensions and so the accessible surface is very limited, rendering this technique suitable for small amount of energy stored. Similar results were obtained with the second approach which consisted in fabricating highly dense mats of MWCNTs on Ni foils using an electrophoretic deposition (EPD) process (for more details on this process, see Refs. [75–78]). $\text{Mg}(\text{NO}_3)_2$ was added to electrically charge the MWCNTs diluted in the solvent. The EPD films were heated at 500 °C for 30 min and then cut into small samples. For electrochemical measurement a test cell capacitor was fabricated using KOH as the electrolyte. The results showed a profile nearly rectangular for scan rate as high as 1000 mV/s. The capacitance calculated from CVs was 21 F/g with a power density reaching 20 kW/kg. However, the most important result concerning this work is related to the “knee” frequency attained that was 7560 Hz. This value is due to the very low overall resistance, which is the sum of the internal resistance of the thin electrode itself and the contact resistance between the electrode and the current collector (R_F) (around 800 m Ω). As proposed previously for other systems [79–81], the improved adhesion of the CNT film to the nickel foil in this study has likely resulted from the formation of magnesium hydroxide from magnesium ions at the surface of the EPD cathode, and these hydroxides could then hydrogen-bond to the surfaces of the acid-oxidized nanotubes. The adhesion strength was further enhanced by the post-deposition heat treatment in the hydrogen environment at 500 °C. Considering the strong adhesion and the high specific surface area of CNTs, efficient conducting paths between the CNTs and the current collector are ensured, leading to a very small contact resistance of the electrode. This method has also been developed by other teams [82–84]. Concerning the results achieved by Pan and coworkers, the energy stored was very low (around 0.03 W h/kg). As told previously by Shiraishi and coworkers, this is due to the ion sieving effect of the micropores that prevents an ion from going into the micropore section [85–87]. This consideration has also been advanced by Zhang et al. in 2008 [88] that compared

the performances (specific capacitance) of VACNT array (1 mm long) and entangled CNT electrodes mixed with 10% of polytetrafluoroethylene (i.e., PTFE). Moreover the same team demonstrated in 2008 [89] that using electrodeposition of manganese oxide on VACNTs (35 μm long), they were able to obtain hierarchical structures with high capacitance and power density. Indeed, the growth of sort of “nanoflowers” (dandelion-like nanostructure) promoted by the nucleation of the manganese oxide on the junctions of two or more vertical carbon nanotubes, then growing radially from them, leads to obtain a structure composed by macropores between VACNTs (avoiding a too strong packing of the CNTs and a too low capacitance value) and by micropores of manganese oxide. In this way, they achieved a hierarchical porous structure and so enhanced the available surface of electrodes. Researchers measured a capacitance of 200 F/g which was higher than the value measured by the same group with bare VACNTs (27 F/g). The energy and power-specific densities calculated were respectively ~ 14 W h/kg and ~ 20 kW/kg (see Tab. 2).

Regarding a new approach, we have to evoke the extremely innovative work by Futaba et al. in 2006 [90]. Their strategy was to fabricate a new bulk form of SWCNTs (defined “SWCNT solid”) where the SWCNTs were densely packed exploiting liquid-induced effect, while maintaining their intrinsic properties. Their density was around 8×10^{-12} tubes/cm². The main difference of this material compared to previous work with MWCNTs [91–94] is that the length of the “SCWNT solid” can attain the millimeter scale (in this study their length to fabricate supercapacitors was 500 μm maximum). “SWCNT solid” showed an extremely higher specific surface compared to CNTs mats (1000 m²/g). In order to compare their performances as electrodes in supercapacitors, Futaba and coworkers fabricated an EDLC cell built using “SWCNT solid” (with a length of 100 μm) using tetraethylammonium tetrafluoroborate (Et_4NBF_4)/propylene carbonate as electrolyte. They used two Pt-based collectors to build the test cells. They obtained a capacitance of around 80 F/g for a potential of 2.5 V. This corresponded to an energy density of around 69 W h/kg which was higher compared to all the previous works (see Tab. 2). In order to evaluate the performances for different electrode thicknesses, they tested “SWCNT solid” with two thicknesses 100 μm and 500 μm . Indeed, they wanted to verify that the power delivered did not change so drastically as for AC-based electrodes. Therefore, they tested two EDLC cells composed of “SWCNT solid”-based electrodes and of AC. The results clearly demonstrated that despite the use of thicker electrode material, the power densities delivered by “SWCNT solid” supercapacitors were higher than that for AC-based electrodes: respectively for 100 μm and 500 μm , 43.3 kW/kg and 31.2 kW/kg for the “SWCNT solid” electrodes and 24 kW/kg and 12 kW/kg for the AC-based electrodes. These results for energy and power densities were the best obtained for CNT-based electrodes for supercapacitors.

The same team at AIST in Tsukuba proposed some years later in 2010 (Izadi-Najafabadi and Futaba [95]) an

original technique to enhance capacitance, power and energy densities. They achieved SWCNT forests by water-assisted chemical vapor deposition to form dense SWCNT sheets. The SWCNT forests were placed between glass slide, sheared and wetted by the electrolyte. Thus, they achieved highly dense SWCNT sheet almost solely composed of SWCNTs with purity as high as 98.3 wt.% and they observed capacitances around 160 F/g. The high purity of the CNT-based electrodes (totally binder-free) allowed to withstand a very broad potential window (up to 4 V) in a regular organic electrolyte without showing distorted voltammogram. This is the highest operating voltage achievable so far for supercapacitors in conventional electrolytes and combined with a low internal resistance it leads to very high maximum power density (210 kW/kg) and energy density (94 W h/kg). These results seemed to confirm again the assertion of Shiraishi in 2002 concerning the extremely high influence of the purity of CNTs on the final device performances [87].

5 Carbon nanotube-based supercapacitors on flexible substrates

A new tendency is highlighted by some extremely interesting works recently published and concerning the exploration of the potential of fabricating supercapacitors on light, cheap, flexible substrates, using low-cost fabrication methods, possibly compatible with large surfaces.

In this context, we can mention the technique developed at Oxford University by Zhao et al. [96] in 2009, based on a simple spray of functionalized CNTs. The CNT deposition technique relies on ambient pressure spray, which is relatively low cost and compatible with large surface area applications. The Oxford scientists deposited CNTs suspensions (fabricated using sodium dodecylbenzene sulfate – SDBS – as surfactant) during an interval varying from 5–60 min, obtaining CNT layers with thickness ranging from 150 nm to 5 μm in less time than more classical dip coating (some hours). They deposited films on polyethylene naphthalate (PEN) and Al foils demonstrating that this technique is compatible with flexible substrates. However, in this paper, the tests have been only performed on stainless steel-based substrates where a layer of polyetherimide-b (i.e., PEI-b) was preliminarily deposited to improve adhesion thanks to its strong hydrophilic character that binds with the hydrophilic head of SDBS. They tested different kinds of CNTs (SWCNTs and MWCNTs) functionalized using different materials (ester, carboxylic functional group) and compared the results obtained with steam-purified CNTs. As explained previously, for all the films, the specific capacitance logically decreased with the scan rate (lower efficiency of ion infiltration). The results are better for SWCNTs than for MWCNTs. Zhao et al. explained that this is due to the larger surface per mass unit of SWCNT mats compared to MWCNT. The results concerning different thickness (from 2 μm to 10 μm) showed that the dependence on capacitance was linear. The best result was a specific ca-

pacitance of 160 F/g (quite constant on the scan interval) for carboxylic-functionalized SWCNTs. The conclusion was that all the pores were accessible for the ions independently from the thickness. This points out the extremely good uniformity of the achieved CNT mats. These results are very important because the specific capacitance obtained was comparable with the best performances achieved using the other more complex and expensive technique (mentioned previously).

Indeed, the spray deposition appears to be highly scalable to fabricate CNT-based films for energy storage applications with a relatively low cost. Another original approach has been followed by Kaempgen et al. [97] at UCLA in 2009. They fabricated EDLCs using printable materials to make flexible devices on plastic. The active electrodes were made from sprayed networks of single-walled carbon nanotubes (SWCNTs) serving as both electrodes and current collectors (usually made up of metals). In this manner, they were able to dramatically reduce the weight of their ultracapacitors, enhancing the energy and power density. Using a printable aqueous gel electrolyte as well as an organic liquid electrolyte, the devices show very high energies and power densities (6 W h/kg for both electrolytes and 23 and 70 kW/kg for aqueous gel electrolyte and organic electrolyte, respectively) which are comparable to the performances in other SWCNT-based supercapacitor devices fabricated with different methods. These results underline the potential of printable thin film supercapacitors. The simplified architecture and the sole use of printable materials may lead to a new class of entirely printable charge storage devices allowing for full integration with the emerging field of printed electronics. Even if this work was extremely original, maybe the first paper in the field of CNT based flexible supercapacitors was issued by Pushparaj and coworkers in 2007 at the Rensselaer Polytechnic Institute [98]. Their technique was quite different from the method employed by Kaempgen et al. at UCLA. They grew VACNTs on a silicon substrate and using cellulose dissolved in 1-butyl-3-methylimidazolium chloride (i.e., a room temperature ionic liquid (RTIL)) embedded the VACNTs. After peeling them from the substrate, they used it as electrode for supercapacitor (Fig. 5).

The team from Rensselaer calculated the specific capacitance in case of use of these electrodes with aqueous (RTIL) and nonaqueous electrolytes (KOH) (see Tab. 2 for more details) and obtained respectively 36 and 22 F/g. These results were not the best ones obtained using CNT-based supercapacitors but in this case the main advantage, and the principal aim, was to achieve a flexible operational device with a relatively low-cost technique. The other fundamental point to underline is the potential to work in a large temperature interval between 195 and 423 K (see Fig. 6) using RTIL as electrolyte. Actually, the common supercapacitors are reported to work typically between around 230 and 360 K. In fact, temperature is an extremely limiting factor to push forward the supercapacitor on wider markets as avionics and spaceflight operations. Only a limited number of teams have focused their interest on this issue, mainly because it is an electrolyte-related

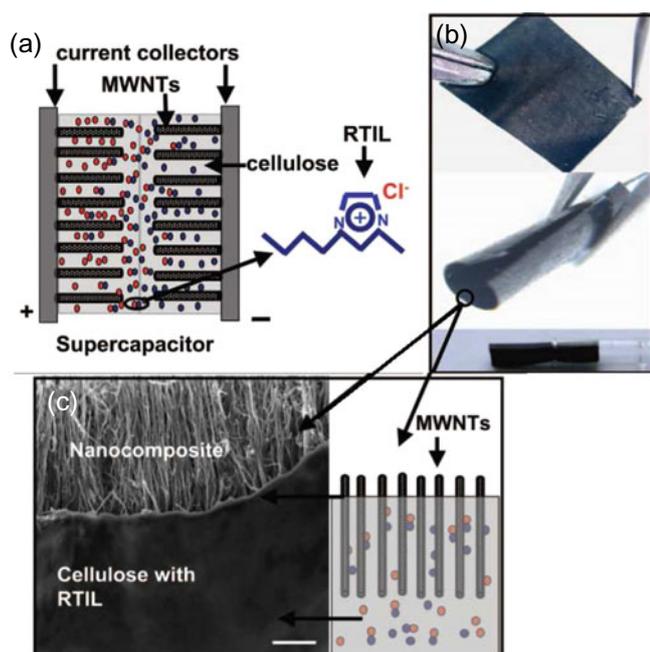


Fig. 5. (Color online) Fabrication of the nanocomposite paper units for supercapacitor and battery. (a) Schematic of the supercapacitor assembled by using nanocomposite film units, (b) photographs of the nanocomposite units demonstrating mechanical flexibility. Flat sheet (top), partially rolled (middle) and completely rolled up inside a capillary (bottom) are shown. (c) Cross-sectional SEM image of the nanocomposite paper showing MWNT protruding from the cellulose-RTIL thin films (scale bar, 2 μm). The schematic displays the partial exposure of MWNT [98].

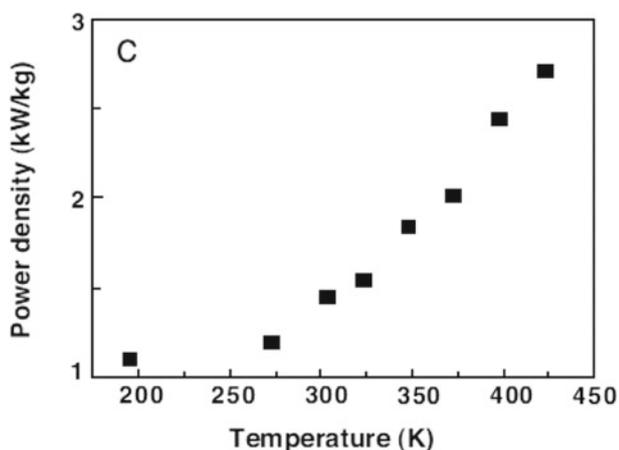


Fig. 6. Power density of the supercapacitor device (using the RTIL electrolyte) as a function of operating temperature. The supercapacitor operates over a record range of temperatures (195–450 K).

problem more than an electrode material one. Therefore, we can clearly state that finding a new kind of electrolyte working in a larger temperature windows will be one of the most important challenges to improve the EDLC performances of CNT-based supercapacitors and of supercapacitors in general.

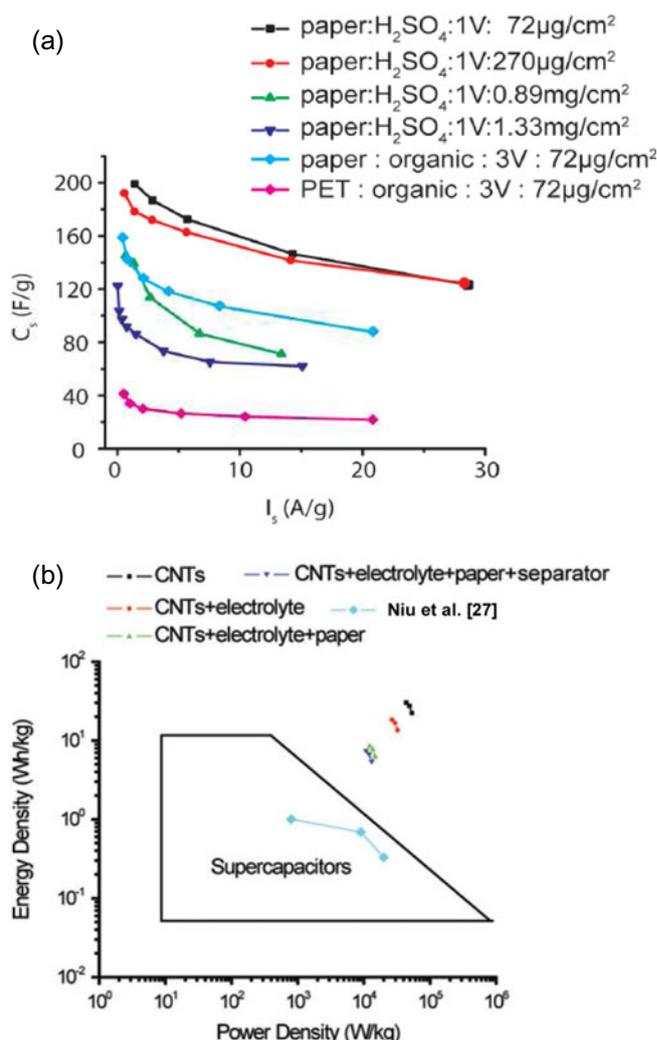


Fig. 7. (Color online) (a) Capacitance as a function of current for capacitors fabricated using organic and aqueous electrolytes [99,100]. The voltage value is the bias applied to the capacitance. The last parameter is the surface density (e.g., mass loading) of CNTs. (b) Ragone plot of EDLC from references [99,100] compared to the results obtained by Niu et al. in 1997 [45] (taking into account all the dead components). The trapezoid shows the performances of commercial existing devices based on activated carbon electrodes.

Another example of EDLC fabricated using flexible substrates has been proposed by Hu et al. at Stanford University in 2009 [99,100]. Their technique echoes to the previous one using cellulose as matrix for CNTs. In this case Hu and coworkers fabricated EDLCs using aqueous CNT-based inks with dodecylbenzene sulfonate (SDBS) as surfactant. The ink was simply applied onto a paper, acting as the separator in the EDLC configuration, so transforming its surfaces in highly conductive media, with very low sheet resistance (10 Ω/s). They demonstrated that this paper had impressive mechanical properties: it could be bent down to a 2 mm radius or folded without any measurable change in the electrical characteristics. This can be performed 100 times with a total increase of only 5% of the resistance. The Stanford team claimed that this

behavior could be explained by the strong binding of CNTs with the paper which permits stress relaxation. The performances of EDLCs fabricated with paper were tested using aqueous electrolytes. The results showed that the specific capacitance values measured were larger than those achieved in previous works: a capacitance of 200 F/g was obtained using sulfuric acid. Moreover, the fact that this device seemed to be able to afford high current density is highly worth noting. Stanford scientists stated that this is due to the very good ions accessibility from both sides of the CNT film and the intimate electrolyte-CNT wetting thanks to the naturally porous nature of paper. Considering cycle life, they reached 40 000 cycles with only 3% and 0.6% capacitance losses in sulfuric acid and organic electrolyte, respectively. In view of energy and power density, their values were larger (see Fig. 7) than the data reported in the literature and this considering the totality of the mass of the EDLC (dead components such as electrolyte, separator, paper plus the active materials, i.e., CNTs).

This paper points out the extremely important impact of replacing the current collector (usually made of metal) with a conductive paper (or other lighter current collectors such as plastic-based substrates).

6 Conclusions

In this review, we have dealt with the main papers concerning supercapacitors based on CNTs and published since 1997 (the year of the first paper by Niu et al. [45]). Recently, the research efforts of several scientific teams in this field have strongly increased thanks to the great interest in smart energy management and hybrid vehicles. Different approaches have been proposed to enhance energy and power delivered by CNT-based EDLCs. It has appeared clearly from the beginning that the potential performances of EDLC devices fabricated using CNTs could be largely superior compared to AC-based supercapacitors. Although the CNTs have a lower average BET surface area ($\sim 200\text{--}400\text{ m}^2/\text{g}$) compared to AC ($\sim 1000\text{--}3000\text{ m}^2/\text{g}$), the pore dimensions enable the CNT films to be more effective for rapid energy delivery and energy storage. However, we point out that the energy and power densities in mostly all the papers are defined without taking into account the weight of the “dead components” of the final device. Indeed, only the weight of CNTs is used to calculate these values. This is not completely suitable to fairly compare the different performances and potentialities of supercapacitors. Another fundamental issue is the final cost of the device. In our opinion, considering that activated carbon is a cheap material, only low-cost fabrication techniques can be employed to achieve industrially suitable CNT-based supercapacitors to hugely strike a large market. In this context, we have analyzed different techniques to fabricate carbon nanotube-based electrodes, such as vertical growth, filtration and spray. Recently, we have noticed a strong interest in spray deposition [68–71] of CNTs to fabricate electrodes. Indeed, this technique is very versatile (it could be adapted to

different substrates and surfaces) and compatible with highly flexible substrates. The total cost of the final device can be reduced considering that the fabrication is easier, from a technological point of view, compared to a fabrication technology based on directly grown CNTs. This point is extremely important to find a real alternative to activated carbon. Maybe more expensive techniques can find their way in specific applications which target high performances without cost or weight limitation (military or space applications). Finally the last point pointed out by the last analyzed papers is the fabrication of EDLCs without a metallic current collector. This is extremely important to increase the energy and power delivery compared to directly grown CNTs where the substrate (the current collector) is metallic and thus quite heavy. This is well demonstrated by the results obtained recently at Stanford [99–119] and UCLA [97] where carbon nanotube films directly act as electrodes and current collectors. These results open new horizons and potentialities for the applications of the EDLC devices, showing the interest for flexible substrates and for extremely low weight devices (and so very high energy and power densities).

DP would like to acknowledge funding from the WCU (World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-2008-10029).

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