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Published in: Journal of Power Sources

DOI: 10.1016/j.jpowsour.2022.231691

Published: 01/09/2022

Document Version Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

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Please cite the original version:

Panasenko, I. V., Bulavskiy, M. O., lurchenkova, A. A., Aguilar-Martinez, Y., Fedorov, F. S., Fedorovskaya, E. O., Mikladal, B., Kallio, T., & Nasibulin, A. G. (2022). Flexible supercapacitors based on free-standing polyaniline/single-walled carbon nanotube films. *Journal of Power Sources*, *541*, Article 231691. https://doi.org/10.1016/j.jpowsour.2022.231691

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Flexible supercapacitors based on free-standing polyaniline/single-walled carbon nanotube films

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Abstract

Advances in supercapacitor performance are boosted both by material design helping to improve specific capacitance and by tailoring of device architecture, often addressing flexibility to enable rolling-up packaging to reach high nominal values. This keeps attention to flexible lightweight materials, such as single-walled carbon nanotubes (SWCNTs), and conducting polymers, such as polyaniline (PANI). In this work, we design and study unique "dead-weight" free supercapacitors based on PANI electrochemically deposited on free-standing SWCNT films. Depending on the carbon nanotube film characteristics, we adjusted polymer inclusion into the nanotube films and evaluated its structure by TEM, SEM, XPS and Raman spectroscopy. Electrochemical methods were used to investigate the relationship between the morphology of initial SWCNT films, deposited PANI, and the electrochemical properties of the composite materials, including specific gravimetric capacitance and self-discharge processes. We show that thin free-standing films of SWCNTs with deposited PANI are less prone to self-discharge due to higher resistance arising from the lower density of the nanotubes in the film. Yet, such films enable better and more uniform deposition allowing to reach the maximum gravimetric capacitance value of 541 F g⁻¹. This synergistic performance allows the creation of an electrode material for flexible ultra-light and powerful supercapacitors.

Keywords: single-walled carbon nanotubes; polyaniline; composite; electrodeposition; cyclic voltammetry; supercapacitor

Highlights

- "Dead-weight" free supercapacitor based on free-standing SWCNT and PANI composite is designed.
- Thin SWCNT films favor deposition of ordered two-dimensional layered PANI structure.
- SWCNTs provide high capacitance retention and conductivity for PANI/SWCNT composite.
- The highest achieved specific gravimetric capacitance is 541 F g⁻¹.

Graphical abstract



1. Introduction

Miniaturization of power sources is foreseen to drive the development of electronic and electrical engineering industries in the design of new wearable devices and electric vehicles which require flexible and lightweight systems for storing and converting the energy [1–4]. On the one hand, there is a demand for materials capable to accumulate a large amount of charge, i.e. lightweight high energy density systems, to reach high gravimetric and volumetric specific characteristics. On the other hand, the employment of flexible materials might improve the performance due to rational packaging such as rolling-up architectures to reach appropriate nominal values and good compatibility with wearable devices [3–11]. Surely, the overall performance relies on many characteristics or parameters, such as cell geometry, charge storage mechanism, voltage loss, and current collector architecture. They also include the cycling stability of the electrody material and electrolyte durability under the applied current and the operating temperatures of the electrolyte.

Supercapacitors (SCs), first proposed by Becker [12] further studied by Trasatti [13] and Conway et al. [14-18], occupy an intermediate niche between "conventional capacitors" and "batteries" in the Ragone plot, constantly expanding the scope of their applications [2,19–21]. These devices possess a high power density close to or even superior to conventional capacitors, while their energy density approaches one of the batteries [22,23]. Formally, two major groups of SCs are differentiated depending on a charge storage mechanism: electrochemical double layer (EDL) capacitors and the ones based on electrochemical reactions, i.e. pseudocapacitance [20,24– 27]. The EDL based SCs involve the redistribution of charges at the electrode-electrolyte interface for energy storage requiring materials with a high specific area (distinct porosity) and excellent conductivity, such as carbon-based ones [23,28–30] with charge storage of ca. 0.18 e⁻ per surface atom. Whereas pseudocapacitive properties are attributed to different processes such as adsorption/underpotential deposition or fast reversible redox reactions (faradaic processes) with up to 1-2 e⁻ stored per atom [21,31]. Typical materials with pronounced pseudocapacitive properties are transition metal oxides [32–35], conducting polymers (CPs) [36–40], and carbon nanostructures decorated with electroactive functional groups [41]. Obviously, the rational combining of EDL and pseudocapacitive materials is expected to enhance the specific capacitance of SCs due to anticipated synergetic effects.

Carbon nanotubes (CNTs) are known materials for EDL-based SCs. The CNTs are proposed to be a feasible substitute for a metallic current collector such as aluminum due to their high conductivity and ability to operate at high current density without degradation [42]. CNT films are flexible and lightweight [43], allowing the reduction of the physical size of SCs, their weight, and cost [6,44]. Uniquely, films made of single-walled carbon nanotubes (SWCNTs) might be realized 4 in a free-standing configuration under a dry-transfer protocol enabling high access to the surface and great flexibility [45,46]. However, the high conductivity and chemical stability of these materials coexist with the low specific capacitance of ~ 150 F g⁻¹, which reduces the number of applications for SCs based on the SWCNTs [23,47]. Complementary, soft mater like CPs, with pseudocapacitive properties, ensures higher capacity, energy density, and good flexibility [46]. The CPs are usually characterized by a well-organized three-dimensional structure, high specific surface area, and good diffusion characteristics [47]. Polyaniline (PANI) is one of the most popular CPs due to its high electrochemical activity and simple synthesis protocols [38,50,51]. The specific capacitance of PANI strongly depends on the method of synthesis and protonation state reaching values up to 1000 F g⁻¹ [52]. Such a high capacitance value is theoretically proven to be associated with PANI molecules' structure favoring a proton-diffusion-based mechanism of conductivity, while many other CPs have lower conductivity and accumulate less energy [50]. The conductivity of a PANI film depends on the protonation state and form of a polymer chain leading to a change in conductivity during charging-discharging. PANI has the best performance in protonic media like an acid solution, whereas in other electrolytes charge accumulation is less efficient [53,54].

CNT/PANI composites are shown to possess both high specific capacitance and power values on top of good cyclic stability [26,55,56]. There are various methods to synthesize such composites: interphase [57] and single-phase [26,58] chemical synthesis, plasma-induced vapor deposition [37], and electrodeposition [31,55]. However, SCs prepared by interphase and single-phase chemical synthesis still need to employ a binder for electrode fabrication that results in a lower power density of SC [59,60] and often poor mechanical properties [61]. Recent studies indicate the development of flexible SWCNT/PANI composite materials [31,61]. This type of composite material promises good capacitance (around 500 F g⁻¹ [62]) when studied in 1 M H₂SO4 aqueous electrolyte. Also, this material demonstrates good specific capacitance up to 236 F g⁻¹ in the non-aqueous electrolyte, 1 M LiCIO₄ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethylene carbonate (DMC) solution [61].

Considering free-standing CNT films for flexible composites, the electrochemical deposition method allows control over the polymer layer thickness preserving the original 3D structure [36,63]. Because the charge transfer reactions take place at the CNT/electrolyte interface, the nucleation of PANI should occur onto the CNT surface, suggesting uniform layer deposition. Such architecture offers a synthesis of ready-made flexible electrodes without any "dead" weight of a substrate, on which CNTs are usually deposited [31,55,64]. Nevertheless, despite recent progress, the effect of the structure of the SWCNT framework, morphology, and properties of PANI electrodeposited on the SWCNT film, on the capacitive performance of SWCNT/PANI composites have not been well evaluated yet.

In this study, we have fabricated and examined SCs based on free-standing transparent SWCNT films with PANI deposited on the films by an electrochemical polymerization technique. Utilization of thick free-standing SWCNT films results in deposition of PANI on the film surface, with comparably lower deposition amount inside the film volume. The deposited PANI is amorphous and disordered even at a small number of employed deposition cycles. On the contrary, for thin films, we observe a high degree of polymer inclusion in the nanotube film volume where PANI is present in the form of crystallites. The specific gravimetric capacitance is established to increase with a decrease of the SWCNT film thickness, reaching the value of 541 F g⁻¹. We found that thin free-standing films of carbon nanotubes with deposited PANI retain capacitance better when connected via SWCNT contact which is determined by the thickness-dependent conductivity of the SWCNT films. The capacitance retention decreases with an increase in the thickness of the deposited polymer in the configuration when discharge occurs through the polymer layer. Composites made of thin SWCNT films with a small amount of deposited PANI are the most efficient for energy storage owing to a good 3D architecture and fast diffusion processes.

2. Experimental section

2.1. Synthesis of SWCNTs and fabrication of free-standing films

SWCNTs were produced by the aerosol chemical vapor deposition (CVD) method and collected on a filter [65]. This process is described in more detail elsewhere [45,66]. By varying the collection time, we made films of different thicknesses, which is associated with light transmittance, $T_h = 239 \times A_{550}$, where T_h is the film thickness (nm), and A is the absorbance at the wavelength of 550 nm [67–69]. We employed the films with the transmittance of 80%, 90%, and 95% further denoted as SWCNT80, SWCNT90, and SWCNT95, those thicknesses are around 20, 10, and 4 nm, respectively. Optical absorption of unpolarized light was measured using a UV-Vis-NIR spectrophotometer, Perkin Elmer Lambda 1050 (PerkinElmer, USA).

To calculate the masses of SWCNT films, the densities of the films were multiplied by the area of the films. The densities were calculated according to equation (1):

$$\rho_T = \rho_{0.5} * \frac{\log_{10} T}{\log_{10} 0.5},\tag{1}$$

where T is a transmittance of SWCNTs film at 550 nm, $\rho_{0.5} = 5.5 \ \mu g \ cm^{-2}$ is the density of the film with the transmittance of 50%, and ρ_T is a density of the film with the transmittance T [46].

Free-standing SWCNT films were prepared by a simple dry-transfer technique (Fig. 1a). The films were transferred from the filters to the 3 mm thick poly(methylmethacrylate) (PMMA)

frames with square openings of 1x1 cm². Free-standing SWCNT films on the PMMA frames were utilized as working electrodes for electrochemical deposition of PANI.

2.2. Electrochemical PANI deposition and measurements

We performed potentiodynamic deposition of PANI on SWCNT films using a threeelectrode cell configuration. SWCNT films, a platinum foil, and Ag|AgCl_(sat) electrode (ESr-10102, «Izmeritelnaya tekhnika», Russia; 202 mV *versus* standard hydrogen electrode) were used as working, counter, and reference electrodes, respectively. All electrochemical tests were performed with a potentiostat VMP3 Biologic SAS (Bio-Logic SAS, France). Electrochemical polymerization of C₆H₅NH₂ was carried out using cyclic voltammetry (CV) technique within the potential range [- 200; 800] mV vs. Ag|AgCl_(sat) electrode at the 20 mV s⁻¹ scan rate, using 0.5 M aqueous solution of C₆H₅NH₂·HCl in 1 M H₂SO₄ as the electrolyte and monomer source. We monitored the charge over the cycle number to control the thickness of the deposited PANI. Asdeposited films of SWCNT/PANI composites were washed with deionized water and dried in air for 24 h. We synthesized sample series with 40, 50, 60, and 70 PANI deposition cycles for each SWCNT film.

We evaluated the performance of SWCNT/PANI composites in 1 M H₂SO₄ exploiting both three- and symmetric two-electrode cell configurations. For three-electrode cell measurements, SWCNT/PANI composites were used in an as-prepared form, in a configuration similar to the one reported in 2.3. The potential range was [0; 1000] mV for CV and [0; 800] vs. Ag|AgCl_(sat) electrode for galvanostatic charge-discharge. Electrical contact was realized via the SWCNT film not covered by PANI. In the case of the three-electrode cell, CV studies were carried out using 20, 50, 100, 250 mV s⁻¹ scan rates, while galvanostatic charge-discharge tests were performed at 4.3 A g⁻¹ current density. Also, we measured capacitance retention by monitoring open circuit potential [21] for 10 min after charging to 800 mV vs. Ag|AgCl_(sat) electrode to evaluate self-discharge of prepared composites, which possibly stems from current leakage.

The specific capacitance of the SWCNT/PANI composites was calculated from CV data using equation (2):

$$C_{Sp} = \frac{\oint i dE}{2\Delta E \cdot v_S \cdot m},\tag{2}$$

where C_{Sp} is a specific gravimetric capacitance of the material, *i* is current, ΔE is the potential range, v_s is the potential scan rate, *m* is the material mass.

To realize the two-electrode configuration, two SWCNT/PANI composite films with a separator Whatman® GF/A, 0.26 mm were carefully transferred to an ECC-Std cell (Ell-Cell, Germany) imitating a coin cell type supercapacitor. In such a configuration, the entire film surface of the SWCNT/PANI composite films was in contact with cell current collectors (stainless steel) via the PANI layer. CV studies were performed at the 20 mV s⁻¹ scan rate and voltage range [0; 800] mV. Galvanostatic charge-discharge measurements were carried out at a current density of 4.3 A g⁻¹. Similarly, we tested capacitance retention by assessing the open circuit voltage for 10 min after charging to 800 mV.

The specific capacitance values of the composite materials were calculated by processing galvanostatic charge-discharge data using equation (3):

$$C_{Sp} = \frac{I \cdot t}{E \cdot m},\tag{3}$$

where C_{Sp} is a specific gravimetric capacitance of material, *I* is current, *E* is a potential range, *t* is a discharge time, *m* is a material mass.

To estimate specific capacitance at different charge-discharge rates and bent angles of freestanding electrodes we fabricated a device with the two-electrode free-standing configuration. First, 90 % SWCNT film of 1.3x1.8 cm² was transferred on Kapton substrate with an area available for the electrolyte of 1x1.5 cm². Then it was immersed in the 0.5 M aqueous solution of C₆H₅NH₂·HCl in 1 M H₂SO₄ to expose 1x1 cm² of free-standing SWCNT film for PANI electrodeposition employing 40 cycles. After composite material was obtained, a free-standing film 1*1.5 cm² (composite part is 1*1 cm², another part is uncovered SWCNT acted as a current collector) was transferred onto polydimethylsiloxane (PDMS) film. Two electrodes were then oriented so that composite films were overlapping, while current collector areas were directed to opposite sides (Fig. S1). Cu tape was utilized to connect assembled device to potentiostat clamps. For electrodes' separation, the Whatman glass microfiber filter (grade GF/A) was used. 1 M H₂SO₄ water solution was used as an electrolyte to wet the glass separator.

Usually, in a three-electrode cell, only the processes at a working electrode are analyzed, while in two-electrode cell processes at both electrodes are observed, especially when both positive and negative electrodes include active material. For instance, the two-electrode cell voltage accounts for the potentials of both electrodes and the potential drop between them [70], which might lead to the specific capacitance difference measured in two- and three-electrode cell configurations.

2.3. Instrumental methods

SWCNT films' sheet resistance was measured with a Jandel RM3000 Test Unit using a four-probe method in a linear geometry. Recorded sheet resistance values for each sample were averaged over the three directions with a displacement of 45°. For the gravimetric capacitance calculations, SWCNT/PANI composite films were weighted using scales of the simultaneous thermal analysis device NETZSCH STA 449 F3 Jupiter® (Netzsch, Germany), enabling estimation of mass with high precision (gravimetric resolution is 0.1 µg). For these tests, we transferred the material to alumina crucibles and weighted it in a closed device. The morphology and structure of prepared SWCNT/PANI composites were examined by scanning (SEM) and transmission electron (TEM) microscopy techniques. SEM micrographs were obtained using a JEOL JIB-4700F microscope (JEOL; Japan) at an accelerating voltage of 5 kV and using Thermoscientific Quattro (Thermo Fisher Scientific (FEI), USA), 10 kV accelerating voltage. TEM images were acquired using a 100 kV accelerating voltage JEOL JEM-2800 microscope (JEOL; Japan) and a 100 kV accelerating voltage FEI Tecnai G2 F20. Qualitative evaluation of the functional composition of the samples was carried out by Raman spectroscopy with Ar laser excitation (wavelength of 532 nm and excitation power of 0.5 mW) using DXRi Raman Imaging Microscope Thermoscientific (The Thermo Scientific[™], USA). For Raman spectroscopy studies, we utilized composites with 70 PANI deposition cycles. We collected at least 5 spectra per sample in the range from 80 to 2900 cm⁻¹ and averaged them to obtain more reliable results. All spectra were normalized to the G-mode to estimate the relative intensity of peaks. X-ray photoelectron spectroscopy (XPS) was used to analyze the qualitative and quantitative surface composition of the material. The overall and highresolution spectra of the material were recorded with a pass energy of electrons 117.4 and 23.5 eV using PHI 5000 VersaProbe II (Physical Electronics Inc., ULVAC-PHI Inc., Japan) equipped with Al K_{α} (1486.6 eV) source. The next parameters of the beam were used: the size of spot 200 μ m, power 50 W, and accelerating voltage 15 kV. The overall spectrum was registered in binding energies (BE) range from 0 to 1350 eV with a speed of 50 ms per step and resolution of 0.5 eV/step during 4 full sweeps. The high-resolution C1s, O1s, N1s, and S2p lines were measured in BE ranges (with a number of sweeps) 157.0 - 177.0 (7 sweeps), 275.0 - 295.0 (6 sweeps), 388.0 -410.0 (10 sweeps) and 520.0 - 542.0 eV (8 sweeps). The deconvolution of spectra as well as quantification of at. % concentration of different elements and their species was done using CasaXPS 2.3.17 software (Casa Software Ltd., Devon, UK). The BE scale was internally calibrated to the energy 284.4 eV of the C1s peak. The high-resolution spectra were deconvoluted using Gaussian/Lorentzian and Doniach-Sunjic functions after subtraction of the non-linear background by Shirley's method. The atomic concentrations of elements were calculated using peak areas considering photoionization cross-sections of the elements at given photon energy.

3. Results and discussion

3.1. Synthesis of SWCNT/PANI composite materials

Fabrication of free-standing SWCNT/PANI structures includes a transfer of a SWCNT film onto a PMMA frame followed by electrochemical synthesis of PANI and subsequent drying as schematically depicted in Fig. 1a along with the images of corresponding samples. During the synthesis, we identified the strong influence of SWCNT film sheet resistance on PANI deposition and evaluated the PANI growth versus the total charge consumed per cycle. Sheet resistance values measured for SWCNT80, SWCNT90, and SWCNT95 films are 106 ± 3 , 183 ± 3 , and 478 ± 16 Ohm sq⁻¹, respectively. Fig. 1b shows the exemplary CV curves recorded during 70 cycles of PANI deposition on a SWCNT95 film where at least two peaks can be identified. The first peak, denoted as al, is located at 212 mV on the anodic sweep. It corresponds to the oxidation of the leucoemeraldine non-conducting PANI form to the emeraldine (see Fig. S2, S3, Supplementary Note 1,2). The second peak, *c1*, located at 103 mV on the cathodic sweep of the curve corresponds to the transition of PANI from the emeraldine to pernigraniline state [52,71]. These redox processes are accompanied by the addition or elimination of protons, which also hints that PANI accumulates energy most efficiently in acidic media [52]. Notably, the maximal conductivity of PANI is achieved at a doping degree of 50%, which is attributed to PANI in the form of emeraldine salt, to be up to 10³ S cm⁻¹ while it is about 10⁻² S cm⁻¹ for emeraldine base [72] (Fig. S4, Supplementary Note 1,2).

The *a1* and *c1* peaks are weakly manifested on the CV curves at the beginning of the cycling. Starting from the 6th and up to the 30th cycle, we have observed the moderate growth of peaks' current favored by autocatalytic type of reactions, i.e. accelerated by the appearance of nucleates [73]. After 20 deposition cycles, the position of the *a1* peak shifts from 305 mV to 420 mV with a corresponded noticeable increase in the current. Following the 35th cycle, the growth is expected to be rather uniform with a linear dependence of consumed charge *versus* cycle number. This should be associated with the growth of polymer chains [74]. Peak potentials continue shifting with a cycle number, reaching 540 mV and 10 mV at the 70th cycle for *a1* and *c1* peaks, respectively. We observed similar trends for the electrodeposition of PANI on SWCNT90 and SWCNT80 films (Fig. S5). Peak shift could be associated with both increasing thicknesses of the growing PANI layer and elongation of the PANI chains [61]. The corresponding video (see Supplementary Videos) depicts the synthesis of PANI over a free-standing SWCNT film. It shows

both changes in color due to electrochromic transition under cycling and in intensity related to PANI growth.



Fig. 1. Fabrication and characterization of the free-standing SWCNT/PANI composites. (a) Schematic illustration of the SWCNT/PANI composite preparation, images of the substrates, free-standing SWCNT95, and SWCNT80, and composites SWCNT95/PANI50 and SWCNT80/PANI50; (b) CV curves of electrochemical PANI polymerization on a free-standing SWCNT95 film recorded over 70 cycles at 20 mV s⁻¹ scan rate; (c) Normalized charge consumed per cycle for PANI electrodeposition on the SWCNT films with transmittance 80, 90 and 95%; (d)

dependence of the mass of the composite material on the number of PANI electrodeposition cycles;(e) dependence of the mass of the composite material on the SWCNT film transmittance. Lines are a guide for an eye.

The normalized charge consumed per PANI synthesis cycle *versus* the cycle number is plotted in Fig. 1c to evaluate the influence of the SWCNT sheet resistance on the PANI growth. Generation of aniline radical-cation in the near-surface layer of the electrode occurs during the first 10-15 cycles. Then dimeric, trimeric, and oligomeric anilines and products of their oxidation are being formed up to about the 40th cycle producing small quantities of PANI on the SWCNT surface. Moreover, electrochemical characteristics of the composite materials prepared with 20-35 deposition cycles should be rather similar to characteristics of the pristine SWCNT films and do not demonstrate redox reactions characteristic for PANI due to the small amount of the polymer on the SWCNT surface. Especially it is observed for SWCNT80. These films are characterized by a higher normalized charge over the first 30 cycles due to the higher specific surface area of the film. (Fig. S6)

The amount of the polymer deposited during 40-70 cycles was found to suit the most to assess the pseudocapacitive properties of PANI. Besides, controlling the quantity of the deposited polymer in this range is straightforward due to the linear dependence of charge *versus* cycle number. In that range, the behavior of all the samples is similar.

After 70 cycles, we observe a deceleration of the PANI growth indicating a change of polymerization mechanism to the termination stage due to a decrease in the concentration of monomer in the solution, impairment of diffusion with increasing thickness and density of the electrode, side electrochemical reactions [75]. However, even after 100 cycles, polymer growth continues. For evaluation of capacitive properties, we have selected composites synthesized using 40, 50, 60, and 70 deposition cycles, further denoted as PANI40, PANI50, PANI60, and PANI70 because this range has linear charge growth and enables deposition of sufficient but not excessive amounts of PANI. The dependence of the mass of the composite material on the applied number of cycles is presented in Fig. 1d. The increase in the mass of the composite materials corroborates well with an increase in the cycle number assessed in a linear range of 40-70 cycles.

3.2. Structure of the SWCNT/PANI composite materials

A pristine SWCNT film obtained by the aerosol CVD method is represented by randomly oriented distributed tubes, as it is shown for an exemplary SWCNT80 film in Fig. 2a. A dense PANI layer with no visible gradient of thickness appears at the surface of SWCNT80 already after

40 deposition cycles (Fig. 2b, Fig. S7). After the 70th deposition cycle, PANI occupies the entire visible surface of the SWCNT80/PANI70 composite and the tubes are noticed at the film cross-section only (Fig. 2c, Fig. S7). On contrary, we observe polymer deposition mainly in the cavities between SWCNTs in the case of SWCNT95/PANI40 (Fig. 2e, Fig. S7). A loose structure of the SWCNT95/PANI40 material depicted at a cut becomes denser with an increase in the number of PANI deposition cycles. In particular, PANI replicates the SWCNT95 film surface when the number of deposition cycles equals 70 (Fig. 2f, Fig. S7). As noted earlier, thick SWCNT films demonstrate greater conductivity, which leads to a generation of higher concentration of radical-cations in the vicinity of the SWCNT film surface, thus a dense layer of polymer is primarily formed on the surface of the material [74].



Fig. 2. Morphology and structure characterization of the SWCNT/PANI composites. (a) SEM image of the pristine SWCNT80 film; (b) SEM image of SWCNT80/PANI40; (c) SEM image of SWCNT80/PANI70; (d) TEM image of the SWCNT95/PANI40 composite; (e) SEM image of SWCNT95/PANI40; (f) SEM image of SWCNT95/PANI70 composites; (g) SAED image of SWCNT90/PANI40 composite film; (h) TEM images of SWCNT90/PANI40 composite films

TEM analysis is conducted to study the dispersion and morphology of SWCNT in a PANI matrix for a sample made of SWCNT with a transmittance of 90 % and 95 % and with 40 cycles of PANI deposition (SWCNT/PANI 90/40 and SWCNT/PANI 95/40) as shown in Fig. 2d,h and Fig. S7, Fig. S8. The images confirm the uniform distribution of SWCNT in the PANI matrix. According to TEM observations, the deposited PANI has the inclusion of ordered regions of 10 - 20 nm (Fig. 2d, Fig. S7, Fig. S8). Close to the SWCNT surface, PANI has a more ordered layered structure (approaching about 15 atomic layers calculated from TEM images). However, it is characterized by an amorphous three-dimensional structure in a polymer bulk which is related to specific interactions between PANI and SWCNTs. When a small amount of PANI is deposited, the polymer layers are oriented along the surface of the SWCNT due to van der Waals interactions between the conjugated SWCNT system and aromatic fragments of the polymer [75]. With an increase in the number of layers, van der Waals forces weaken and the polymer is no longer associated with the conjugated SWCNT system; it continues to grow chaotically with the formation of an entangled three-dimensional structure [74]. The main part of the SWCNT/PANI 90/40 material consists of amorphous PANI agglomerates surrounding SWCNT bundles. In some photos (Fig. 2d,h, Fig. S8), a well-pronounced PANI/SWCNT crystal structure is observed near the SWCNT surface, while PANI is represented predominantly as an amorphous polymer at a distance from the SWCNT. 90% SWCNT net is denser in the PANI matrix and has larger bundles when compared to 95% SWCNT film which is related to the larger number of CNT in in pristine films. To refine the crystal structure, selected area electron diffraction (SAED) patterns were acquired. Fig. 2g shows the presence of three halos, which are associated with the carbon nanotubes and correspond to CNT reflections (002), (100), and (004) [76]. The halos are significantly blurred since the polymer surrounding SWCNT does not have a clear crystalline structure when it is far from the SWCNT surface.

Raman spectroscopy was employed for the identification of the functional composition and structure of the samples (Fig. 3). All recorded spectra were normalized to the G-mode as noted in the Experimental section. A spectrum of pristine SWCNT95 exhibits several typical peaks those Raman shift values are shown in Table S1. An intensive peak at about 1600 cm⁻¹ corresponds to the in-plane tangential stretching of the carbon-carbon bonds [77] and is referred to as G-mode in literature [78]. Its appearance is associated with optical vibrations of two adjacent carbon atoms in the nanotube structure [79]. When two or more adjacent carbon atoms deviate from their ideal position (for example, when they are covalently bonded with functional groups) or are removed from the structure, defects arise, and the intensity of G-mode decreases. When it occurs, a peak located at ~ 1350 cm⁻¹ (D-mode) appears in Raman spectra [78]. This peak has a low intensity in spectra of pristine SWCNTs and the obtained composite films. The defectiveness of the pristine films and composites is usually estimated by the G-mode to D-mode intensity ratio (I_G/I_D) [80]. For the SWCNT95 sample, this ratio is more than 100, which corresponds to a low defectiveness, i.e. high quality of SWCNTs. The peak observed in the range of 2600 - 2700 cm⁻¹ is the overtone of the G-peak called 2D-mode [79]. This mode is responsible for the joined vibrations of carbon atoms in carbon hexagons [81]. Moreover, its shift and broadening correspond to the doping of SWCNTs [81]. The peak of the 2D-mode is located near 2672 cm⁻¹ in the spectrum of the pristine SWCNT95 and has a relative intensity of 0.11. Shift and broadening of that peak occur after deposition of PANI on the SWCNT films, the center of 2D-mode is shifted to ~ 2677 cm⁻¹ and is characterized by maximal intensity value 0.10 - 0.11. A different trend is observed for the SWCNT90/PANI70 composite spectrum. The center of the 2D-mode is located near ~ 2682 cm⁻¹ and with a maximum intensity of 0.11.



Fig. 3. Normalized Raman spectra of the samples SWCNT95, SWCNT95/PANI70, SWCNT90/PANI70, SWCNT80/PANI70 presented in Raman shift ranges: (a) from 80 to 250 cm⁻¹; (b) from 250 to 2000 cm⁻¹; (c) from 2450 to 2900 cm⁻¹.

A slight shift of these peaks after the PANI deposition to higher wavenumbers corresponds to the n-doping of SWCNTs by PANI. The discussed results are summarized in Table S1. In addition to the peaks described earlier, a group of low-intensity peaks is observed in the Raman shift range from 80 to 250 cm⁻¹. Those peaks are characteristic for only single- and double-walled CNTs and are known as radial breathing modes (RBM) [77,78].

All the peaks of PANI are located in the range from 80 to 1700 cm⁻¹. The peak at ~ 1590 cm⁻¹ overlaps with the G-mode of SWCNT and corresponds to the vibrational oscillation of C-C (v C-C) in benzene rings. The peak at 1490 cm⁻¹ corresponds to the vibration of v C-C bonds in quinoid rings and identifies the presence of doped PANI structures [84]. Peaks at 1322 and 1220 cm⁻¹ correspond to the v C-N⁺ and v C-N vibrations, respectively [84,85]. The peak at 1160 cm⁻¹ corresponds to the δ C-H oscillation in quinoid rings [86]. The peak at 874 cm⁻¹ is attributed to the deformational oscillation of C-N-C (δ C-N-C) and/or deformation of benzene rings in both polaron and bipolaron forms. The peak at 815 cm⁻¹ can be related to the deformations of benzene rings [87]. The two peaks at 714 and 647 cm⁻¹ are characteristic of highly ordered PANI and correspond to the δ C-C vibrations of rings [88]. The peak at 588 cm⁻¹ stems from the deformational vibrations of protonated amine groups. Peaks at 516 and 416 cm⁻¹ correspond to the δ C-NC out-of-plane vibration and indicate twister conformation of PANI [89]. Two peaks at 294 and 274 cm⁻¹ arise because of the δ C-H out-of-plane vibrations.



Fig. 4. High-resolution (a) C1s, (b) N1s, (c) S2p and (d) O1s XPS spectra of SWCNT95/PANI50 sample.

All the composite samples consist of similar PANI species regardless of the transmittance of films: benzene rings in aromatic and quinoid forms; nitrogen in neutral and positively charge states; polaron and bipolaron quasi-particles. However, in the spectrum of SWCNT90/PANI70, peaks have the highest intensity, which should correspond to rather thick PANI layers on the

SWCNT surface [64,90,91]. The presence of charged fragments and polaron/bipolaron quasiparticles in the Raman spectra of the composite materials indicates the deposition of PANI in emeraldine conducting form.

Evaluation of the functional composition and surface concentration of elements of the SWCNT95/PANI50 sample was done using the XPS method. The C1s, O1s, N1s, S2s, and S2p core-level photoemission lines were indicated in the survey spectrum of the SWCNT95/PANI50 sample (Fig. S9) as well as C KLL and O KLL edges. The at. % concentrations of C, O, N, and S elements are equal to 79.6, 9.0, 9.0, and 2.4 at.%, respectively. The high amount of O in the sample is related to both its functionalization by oxygen-containing functional groups (OCFG), resulting from the secondary reactions of oxidation of aniline monomer during the synthesis, and the presence of SO4²⁻ counter-ions. The C:O:N:S ratio in the sample is 1:0.11:0.11:0.03. The C1s spectrum is fitted by five peaks (Fig. 4a). The first one is located at BE 284.4 eV which is typical for sp²-hybrid carbon assigned to the C=C bonds in aromatic rings [92,93]. The second peak at BE 285.3 eV can be ascribed to both C-C and C-N bonds in aromatic PANI units [94] as well as C-C bonds in carbon nanotubes located mostly near edges or defects. The peak located at BE 286.2 eV is specific to hydroxyl OCFG connected with carbon atoms as well as polaronic groups in PANI (C-NH⁺) [95,96], while the peak located at BE 287.3 eV is related to the carbonyl OCFG [97] and neutral charge C=N fragments in quinoid PANI units [98]. The last peak at BE 289.0 eV is specific to carboxyl OCFG [99] and bipolaronic PANI units [100]. Thus, the C1s spectra of the sample demonstrate that PANI is functionalized by OCFG and can contain both charged and neutral units in aromatic and quinoid forms. The N1s spectrum of the sample proves the presence of PANI units in both charge states and forms (Fig. 4 b). The peak located at BE 398.3 eV is ascribed to the C=N bonds of quinoid PANI units in a neutral charged state, while the peak at BE 399.5 eV is related to the -NH- bonds of aromatic PANI units in a neutral charged state [101]. The peaks at BE 401.1 and 402.7 eV are assigned to the -NH⁺- bonds (polaronic structures) in aromatic PANI units and =NH⁺- bonds (bipolaronic structures) in guinoid ones [94,96,102]. The S2p spectrum of the material consists of one doublet with a distance between centers of peaks of 1.18 eV (Fig. 4c). The first and second peaks in doublet are located at BE 168.1 eV (S2p_{3/2}) and 169.2 eV (S2p_{3/2}), respectively. They can be assigned to the -SO₃ groups attached to the polymer units [103] and/or SO4²⁻ counter ions which are neutralizing charged N species [104]. The O1s high-resolution spectrum was fitted with four peaks (Fig. 4d). The peaks located at BE 531.1, 532.4, and 533.6 eV are specific to carbonyl, carboxyl, and hydroxyl OCFGs, respectively [95,97]. The peak at BE 532.4 eV can also relate to the -SO3 groups and/or SO42- counter-ions. The low amount of adsorbed water was additionally found in the O1s spectrum (peak at BE 535.2 eV) [97].

The at.% concentrations of different species are represented in Table S 2. The 21.5 at. % of carbon atoms is connected with OCFG and different nitrogen species, while the remaining 53.3 at.% and 25.3 at. % of carbon relates to the sp²-hybrid carbon and sp³-hybrid carbon (including C-C and C-N bonds). The concentrations of different OCFG were calculated from O1s high-resolution spectra. Thus, carbonyl OCFG is the main in PANI (39.5 at. %), while the concentration of carboxyl/SO4²⁻ and hydroxyl OCFG is equal to the 37.4 and 18.9 at. %. The low amount of water (4.2 at. %) adsorbed on the polymer surface was also obtained. The total concentration of neutral charged nitrogen species (=N- in quinoid PANI units and –NH- in aromatic PANI units) is equal to 78.5 at. %. It means that the main part of the polymer is in a neutral state. As the concentration of =N- (14.1 at. %) is much lower than those of –NH- (64.4 at. %), the polymeric chain predominantly consists of aromatic PANI units. The total concentration of charged nitrogen species is equal to 21.5 at. % and corresponds to the formation of polaronic and bipolaronic structures.

3.3. Electrochemical measurements

The representative CV curves recorded in the three-electrode cell for the composites prepared using 40 and 70 PANI deposition cycles are characterized by the appearance of three pairs of redox peaks (Fig. 5 a,b). These peaks correspond to redox reactions of PANI [39], i.e. the peak a1 at 350 mV and counter peak c1 at 180 mV corresponds to the leucoemeraldine-emeraldine transition. The peak a^2 at 550 mV and counter peak c^2 at about 400 mV may be associated with cross-linking reactions between polymer chains [52,105]. The peaks a3 at 850 mV and c3 at 700 mV can be related to the emeraldine-pernigraniline transition. A minor shift of the peaks is observed. It can be associated with the distinct architecture of the polymer chains and composite agglomerates. These peaks are better expressed on the CV curves of the thinnest SWCNT films with a small number of PANI deposition cycles (40 cycles). A thick polymer layer formed at a greater number of deposition cycles prevents the diffusion of the electrolyte that turns the redox peaks to be weakly manifested. Materials based on SWCNT90 have a better oriented 3D structure, which contributes to better conductivity and faster redox processes. Besides, a lot of polymerization by-products might affect the shape of the CV curves what also explains less pronounced peaks and a slightly different shape of curves observed in the case of thicker polymer layers [31]. CV curves for all the samples are presented in Supplementary Material, Fig. S10.

Galvanostatic charging-discharging is presented in Fig. 5c for the SWCNT95/PANI70 composite as an example. At a current density of 4.3 A g⁻¹, the discharge cycle can be described by two regions. A fast region corresponds to a range of potentials from the upper one to ca. 400

mV, while another region is characterized by a more moderate slope (400 mV – 0 mV). The charge-discharge curves show good stability over the presented 10 cycles with the same temporal characteristics for discharge (or charge) cycles. Afterward, once being charged, we monitored potential values in an open-circuit mode for 10 min (Fig. 5d). We observe that the thickness of the SWCNT film used for the PANI deposition influences the retained potential value, i.e. capacitance performance of the SC. The lowest self-discharge value is measured for the films with the highest transmittance (95%). The low self-discharge rate for the composite materials based on the more transparent films is most likely associated with the higher resistance of the SWCNT95 framework [106]. The charge leakage is blocked due to the lower density of the films giving a rise to a greater impact of barriers at contacts between the semiconductor, and metallic SWCNTs in the film.

To further evaluate the synergetic effect of the combination of SWCNTs and PANI in freestanding composites, we have assessed the contribution of the capacitive and pseudocapacitive, and Faradic processes in total capacitance based on different kinetics *versus* the scan rate (eq. (4)) [107].

$$Q = Q_{\nu=\infty} + a \cdot \nu^{-1/2} \text{ and } Q^{-1} = Q_{\nu=0}^{-1} + a \cdot \nu^{1/2},$$
(4)

where Q is a total charge (eq. (5)):

$$Q = C \cdot m \cdot \Delta U = S \cdot (2\nu)^{-1}, \tag{5}$$

S is a total area of CV, $Q_{\nu=\infty}$ is a charge of EDL, $Q_{\nu=0}$ is a maximal charge. Since the capacitance depends on the charge, the following expressions can be obtained by eq. (6):

$$C = C_{\nu=\infty} + \frac{a}{m \cdot \Delta U} \cdot \nu^{-1/2} \text{ and } C^{-1} = C_{\nu=0}^{-1} + m \cdot \Delta U \cdot a \cdot \nu^{-1/2}.$$
 (6)

The dependences of C on $v^{0.5}$ and C^1 on $v^{-0.5}$ are shown in Fig. S11-S13 and detailed in tables S3-S5. The experimental dependences of C on $v^{0.5}$ and C^1 on $v^{-0.5}$ show that there is a noticeable contribution of the mass transport through the PANI layers to SWCNTs for the materials based on SWCNTs with 80% transmittance only, and it decreases with an increase in the number of deposition cycles (Fig. 5e). This is due to the formation of amorphous PANI after 50 deposition cycles that (along with the increase of the PANI layer thickness) limits ions' diffusion.

A comparison of specific capacitance of the composite materials in the three-electrode cell at a scan rate of 20 mV s⁻¹ is given in Fig. 5f. The highest capacitance is observed for the SWCNT95 samples (up to 541 F g⁻¹), and it is \sim 3 times higher than the capacitance of original SWCNTs (178 F g⁻¹) [48]. The high capacitance of the SWCNT95/PANI## samples (when

compared with other composites, especially with the samples of 40-50 PANI deposition cycles) is explained by the porous structure of these samples, which facilitates the diffusion of the electrolyte into the composite film [61]. The SWCNT95 films have a low density, allowing PANI to be deposited inside the SWCNT network so that the polymer bounds directly with the tubes. The lower capacitance of composites based on the SWCNT80 and SWCNT90 films is associated with the preferential growth of PANI on the surface of the film and higher PANI surface density. Moreover, in the later composites, the accumulation of the ions proceeds through amorphous PANI, which does not bound with SWCNTs directly, leading to a decrease in the efficiency of the materials [61]. The composite materials based on SWCNT80 and SWCNT90 reach the maximum capacitance when 70 deposition cycles yield an amorphous PANI layer with a characteristic 3D structure. Notably, the retention of charge is much greater in the case of the SWCNT95/PANI composites, again, caused by the higher electrical resistance of the SWCNT film.

Thus, using an excessive number of deposition cycles and/or using SWCNT films with the low transmittance (i.e., greater thickness) as a template yields charge accumulation primarily attributed to amorphous PANI. Whereas films with high transmittance and a small PANI loading are characterized by a more ordered structure that causes the entire volume of the material to be included in the charge accumulation [74].

The three-electrode cell configuration is useful for analyzing redox reactions; however, real devices are operated as two-electrode cells. Cell capacitance in a two-electrode configuration is at least two times lower when compared with a three-electrode cell with the same mass of electrodes [70]. Moreover, a two-electrode cell, imitating coin cell architecture, offers a configuration where the PANI layer is in contact with the current collector mitigating the contribution of the SWCNT films in electron transport related to its sheet resistance. Fig. 6a demonstrates CV curves recorded for the composite materials based on the SWCNT films of different transmittance after 50 deposition cycles of PANI at 20 mV s⁻¹ in a symmetrical twoelectrode cell. We identify peaks at 350 - 550 mV during charging while the corresponding peaks are at 450 - 100 mV on the reverse scan. These peaks are related to the redox PANI reactions. The peaks are not well pronounced, rather wide, and overlap each other, which is associated with the lower sensitivity of the two-electrode cell [70]. Peaks on the CV curves of the materials based on the films with high transmittance (95% and 90%) appear earlier than peaks on the curves acquired for SWCNT80/PANI50 material. This indicates better diffusion availability of the SWCNT95 and SWCNT90 based composite materials for the electrolyte, which conforms to the conclusions made above. The calculated capacitance of the composites using recorded CVs equals 130 and 175 F g⁻

¹ for SWCNT80/PANI50 and SWCNT90/PANI50 respectively, while it is 106 F g⁻¹ for the SWCNT95/PANI50.



Fig. 5. Characterization of capacitive properties of the SWCNT/PANI composites using the threeelectrode cell configuration. (a) CV curves of the samples based on SWCNT95, 90, and 80 and PANI deposited during 40 polymerization cycles, recorded at the scan rate of 20 mV s⁻¹; (b) CV of the samples based on SWCNT95, 90, and 80 and PANI deposited during 70 polymerization cycles, recorded at the scan rate of 20 mV s⁻¹; (c) Charge-discharge curves of the SWCNT95/PANI40 composites; (d) Open circuit potential transient recorded during 10 min after

charging at 4.3 A g^{-1} for the SWCNT##/PANI70 composites; (e) EDL contribution for the composites based on SWCNT80; (f) Specific capacitance of the composites measured in the three-electrode cell at the scan rate of 20 mV s⁻¹.

We studied next the capacitive properties of the composites in galvanostatic chargedischarge cycles at 4.3 A g⁻¹ (Fig. 6b), followed by an assessment of self-discharge characteristics. The films of SWCNT95/PANI50 tend to show rather asymmetric performance with long charging and fast discharging, which can be related to the high contribution of the redox process. The composites show low retention of capacitance with ca. 780 mV fade of voltage. For SWCNT95/PANI50, the specific capacitance measured in the two-electrode cell reaches the value of 25 F g⁻¹. The highest capacitance, in this case, is for the thicker PANI films, i.e., the SWCNT90/PANI50 samples have a capacitance of about 98 F g⁻¹ while for SWCNT80/PANI50 it is around 118 F g⁻¹. Moreover, we can identify the trend for increasing the charge retention going from SWCNT95 to SWCNT80, which we can relate to a greater mass of PANI. Thus, in the case of the two-electrode cell configuration, the thinner composite films lose their charge faster when compared with the thicker films. The self-discharge related losses in a two-electrode cell could be associated with a contact of composite with the current collectors through PANI. In the threeelectrode cell, the current collector is in contact with the SWCNT film which is why the selfdischarge related losses increase with decreasing the transmittance (i.e., increasing resistance) as discussed above. An increase in the PANI thickness leads to the rise of the polymer layer resistance and, thus, higher charge retention. The high charge retention can be also supported by the higher contribution of Faradaic processes. Therefore, the most significant influence on the self-discharge related losses in the two-electrode configuration has the thickness of the polymer coating, but not the SWCNT film.

We evaluated the dependency of capacitance for the composites based on the SWCNT80 films *versus* the number of deposition cycles of PANI, as well as their self-discharge characteristics after galvanostatic charge-discharge cycles. The specific capacitance measured in the galvanostatic mode at a current density of 4.3 A g⁻¹ in the two-electrode cell configuration tends to increase with an increase in the number of polymer deposition cycles to be up to 132 F g⁻¹ (Fig. 6c,d). There is a minor hint on the improvement of charge retention during self-discharge with an increase in the number of polymer deposition during self-discharge with an increase in the number of charge retention during self-discharge with an increase in the number of polymer deposition during self-discharge with an increase in the number of charge retention during self-discharge with an increase in the number of polymer deposition cycles to be correlated with the measured capacitance.



Fig 6. Capacitive properties of the SWCNT/PANI composites in the two-electrode cell configuration. (a) CV of SWCNT95/PANI50, SWCNT90/PANI50, and SWCNT80/PANI50 measured in the two-electrode cell at 20 mV s⁻¹; (b) Remaining potential after self-discharge for the SWCNT films with 50 PANI deposition cycles and capacitance calculated using galvanostatic discharge semi cycle; (c) galvanostatic charge-discharge curves of SWCNT80/PANI##; (d) Remaining potential after self-discharge for SWCNT80/PANI and capacitance of

SWCNT80/PANI calculated using galvanostatic discharge semi cycle; (e) Capacitance retention and coulombic efficiency during long cycling; (f) photograph of bent two-electrode supercapacitor device (SWCNT90/PANI40 film). Green curved line – electrodes location in the cell, red lined – directions of electrode terminations; (g) Ragone plot of SWCNT/PANI composites described in this work in comparison with actual literature sources related to carbon nanostructures/PANI composites (Ref. I [108], Ref. II [109], Ref. III [110], Ref IV [111], Ref. V [112], Ref. VI [113]); (h) specific capacitance of the cell for different charge-discharge rates for every 5 consecutive cycles (SWCNT90/PANI40 film); (i) comparison of 3 consecutive charge-discharge cycles for flat (bright) and bent (pale) geometry of supercapacitor (SWCNT90/PANI40 film) recorded at 10 μ A current (ca. 0.14 A g⁻¹).

The power and energy densities [21,70] of the assembled SC symmetric devices based on CNT/PANI composites obtained in this work were compared with the ones recently reported for SC devices based on PANI and carbon nanostructures (Fig. 3i). The resultant SC devices show a high energy density of 4.3 - 7.2 W h kg⁻¹ at a power density of 1558 - 1794 W kg⁻¹, which is greater when compared to the symmetrical supercapacitors reported last years ([108–113]). While energy density remains similar or slightly lower than the ones depicted in other works, power density reaches higher values. The calculated energy and power values are typical for hybrid SCs based on carbon nanostructures and PANI. Thicker SWCNT layers (80% transmittance) demonstrate higher energy values when compared to the 90% and 95% because of the slower self-discharge processes demonstrated above.

The electrochemical stability of the SWCNT95/PANI50 material was also studied during long-term cycling in a two-electrode cell at a scan rate of 100 mV s⁻¹ and in a voltage range [0; 800] mV (Fig. 6e). The coulombic efficiency was calculated as the ratio of the cathodic charge, Q_c, and anodic capacitance, Q_a, while the capacitance retention was calculated as maximum capacitance divided by the capacitance of a given cycle. Tendency to an increase in capacitance during the first thousand cycles is observed, which is possibly associated with the saturation of the polymer with the electrolyte. This behavior is typical for all CPs [114]. After 1000 cycles, a decrease in the capacitance is observed and it reaches about 60% of the original capacitance after 5000 cycles. This indicates relatively high stability for pseudocapacitive materials, but it is lower than that achieved in other works [115,116]. The behavior of coulombic efficiency is different from that of capacitance. The factor has a maximum value close to unity for only a few first cycles, after which it dramatically decreases, reaching a plateau (about 0.7) by the 500th cycle. Such a difference between the charge and discharge is associated with the side reactions of this type of film described above and can also be a reason for the low cyclic stability of the material.

To estimate specific capacitance at different charge-discharge rates and bent angle the device in a two-electrode free-standing configuration was employed (SWCNT90/PANI40 film). Using current density values during synthesis and mass to cycle number correlation of initial composite batch, obtained previously, the mass of resulting electrodes was estimated to be 73.6 μ g. Five charge-discharge curves for each of four currents, i.e. 20, 50, 100, 200 μ A, were recorded which corresponded to current densities of 0.27, 0.68, 1.36, and 2.72 A g⁻¹ respectively (Fig. S14).

The voltage drop decrease is observed with a decrease in charge-discharge rate. Also, the same behavior with 2 regions is taking place (the first region of rapid discharge down to 400 mV and then comparatively slower discharge from 400 mV down to 0). With low currents (20 μ A) cell does not reach 0.8 V even after 450 s, therefore, the capacitance was calculated for discharge semicycle employing the highest reached voltage in this case. Fig. 6h represents the dependence of specific capacitance of the cell depending on the charge-discharge rate for all 5 cycles of each rate. It was calculated according to the equation (3) with mass of active material to be equal to mass of two electrodes. We conclude that the higher the rate of supercapacitor cell charge, the lower is specific capacitance. It could be the result of two related effects: increase of voltage drop with the growth of current and higher contribution of Faradaic processes at lower charge-discharge rates. After 25 cycles measured at different current densities, 90% of the initial capacitance remains. A high drop in capacitance might be due to unperfect flat cell architecture and side process in the first cycles.

A similar two-electrode cell was prepared for bending tests. Charge-discharge curves were measured for the flat and then for the device bent at an angle of 125° and also with some additional twisting along the device length. (Fig. 5f,i and Fig. S15). For both flat and bent geometry 3 charge-discharge cycles were recorded at 10 μ A current (ca. 0.14 A g⁻¹). Fig. 5i shows the comparison of consecutive cycles for flat and bent devices. Starting from the second cycle, the device exhibits a representative pattern. We observe that device discharge capacitance per cycle decreases by 35 %. It is mainly represented by the smaller time consumed for each charge-discharge cycle. Besides, voltage drop increases for the bent sample that is manifested in some drop of the capacitance of the bent sample, although such effect might be corrected by optimizing cell configuration. On top of that, the coulombic efficiency of the bent sample is 94 % while for the flat it reaches 84 % only which can relate to worse electrolyte penetration and additional unwanted side reactions.

Capacitance retention of the prepared two-electrode free-standing device was assessed by cycling in a galvanostatic mode at 0.34 A g-1 (25 μ A) over 1000 cycles charging it to 0.8 V. Before testing, the assembled device was conditioned for 24 h just at room temperature and afterward, 10

training cycles were performed. The capacitance retention *versus* cycle number is given in Fig. S16. We observe a moderate decrease in capacitance up to 200 cycles. The device capacitance reaches the stable values after about 500 cycles, maintained up to 1000 cycles.

4. Conclusion

We examined composite materials based on free-standing transparent SWCNT films and PANI deposited by electrochemical polymerization. SWCNT films with the transmittance of 95%, 90%, and 80% at 550 nm wavelength were chosen as templates. The weight of the composite material increases linearly with decreasing the transmittance and increasing the number of deposition cycles in the transmittance range of 95% to 80% and in the range from 40 to 70 cycles of polymer deposition. Deposited polyaniline consists of the most conductive and effective for the supercapacitor application emeraldine salt. Layered PANI stricture is observed near SWCNT surface only while PANI between nanotube bundles is represented as an amorphous polymer.

The effect of the density of the SWCNT film, which is correlated with the transmittance, on the morphology of the deposited polymer has been studied. The thicker film, the more amorphous and disordered polymer is deposited, even with a small number of deposition cycles. It was found that PANI is deposited on the surface of thick films, with a comparably small amount of deposited polymer inside the network due to high nanotube density and film conductivity. Whereas for thinnest films, a high degree of polymer penetration into the nanotube film is observed. The specific gravimetric capacitance increases as the transmittance of SWCNT film ranges in a row of 80%, 90%, and 95%. The maximum gravimetric capacitance is 541 F g⁻¹, and it has been reached with 50 PANI deposition cycles for SWCNTs with a transmittance of 95% when a three-electrode cell was used. For denser films, the specific capacitance is greater for the samples made using 70 deposition cycles, due to the large amount of amorphous PANI, which is not directly bound to SWCNTs.

The films based on SWCNT80 and SWCNT90 show the highest specific capacitance measured in the two-electrode cell reaching values of 130 and 175 F g⁻¹, respectively. Maximum values of specific energy (7 Wh kg⁻¹) and specific power (1700 – 1800 W kg⁻¹) are reached for 80% transparency SWCNT template with no dependency on PANI deposition cycle number.

The most efficient for energy storage according to three-electrode measurements are more transparent films with a small number of PANI deposition cycles, which makes it possible to obtain a composite material with a good 3D architecture and fast diffusion processes. The self-discharge process was investigated in two- and three-electrode setups with different cell architectures. In a three-electrode cell, when contact with an electrode is made through SWCNT film, self-discharge is determined by the conductivity of the SWCNT films and decreases with the transmittance increase. In a two-electrode cell, with contact through the PANI layer, self-discharge is determined by the conductivity of the polymer and decreases with an increase of the deposited polymer layer

thickness. The difference in the self-discharge mechanism explains the difference in capacity for the different cell architectures applied in this work. Synthesized SWCNT composites were tested as free-standing flexible symmetric supercapacitors showing good stability during cycling and bending.

Author contribution

Panasenko I. V. – investigation, visualization, formal analysis, writing – original draft; Bulavskiy M. O. – investigation, writing – review and editing; Iurchenkova A. A. – writing – original draft, visualization; Aguilar-Martinez Y. – investigation; Fedorov F. S. – supervision, conceptualization, methodology, writing – review and editing; Mikladal B. – investigation; Fedorovskaya E. O. – investigation, resources, formal analysis, writing – original draft, supervising; Kallio T. – resources; writing – review and editing; Nasibulin A. G. – resources, supervision, writing – review and editing. All authors have given approval to the final version of the manuscript

Acknowledgment

We thank Dr. Timur Aslyamov (Skolkovo Institute of Science and Technology) and Prof. Leif Nyholm (Uppsala University) for fruitful discussions. This work was supported jointly by the Russian Foundation for Basic Research and the Royal Society of London for Improving Natural Knowledge (project 20-53-10004 KO_a). Aalto Nanomicroscopy Center is acknowledged for its support of SEM and TEM studies. Fedorov F. S. acknowledges the Russian Science Foundation (project No. 21-73-10288). Nasibulin A. G. thanks the Council on grants of the President of the Russian Federation grant number HIII-1330.2022.1.3.

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