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Rauhala, Taina; Davodi, Fatemeh; Sainio, Jani; Sorsa, Olli; Kallio, Tanja

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# On the stability of polyaniline/carbon nanotube composites as binder-free positive electrodes for electrochemical energy storage

 Taina Rauhala<sup>a</sup>, Fatemeh Davodi<sup>a</sup>, Jani Sainio<sup>b</sup>, Olli Sorsa<sup>a</sup>, Tanja Kallio<sup>a,\*</sup>
<sup>a</sup> Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland
<sup>b</sup> Department of Applied Physics, School of Science, Aalto University, P.O. Box 15100, FI-00076

Aalto, Finland

## Abstract

Poor stability restricts the use of polyaniline as a transition-metal-free, high-capacity electrode material for electrochemical energy storage. To improve the durability, methods such as adding a carbonaceous support and thermal treatments have been suggested. Here, we combine both of these approaches and study their effects on the degradation of a composite of polyaniline and acid-treated multi-walled carbon nanotubes (PANI/a-MWNT) when used as a positive electrode in a lithium-ion cell. The composite is prepared through facile ultrasonic-assisted mixing of aqueous colloids, processed into binder-free electrodes and heat treated under vacuum (120–180 °C). PANI without the carbon support presents a poor cycling stability due to a decreasing conductivity and changes in the particle morphology. The a-MWNTs are shown to inhibit these changes and to enhance the electrochemical accessibility of PANI in the composite. The heat treatment, in turn, improves the stability of the composite during open circuit conditions, which is ascribed to cross-linking of the polymer. However, with prolonged cycling, the stabilizing effect is lost. Analysis of the electrodes after the cycling reveals that both the pristine and the heat-treated composite undergo dedoping and side reactions with the electrolyte. The extent of the changes is larger for the pristine composite.

**Keywords:** Polyaniline; Conducting polymer; Thermal treatment; Degradation analysis; Lithiumion battery

\* Corresponding author

*E-mail address:* tanja.kallio@aalto.fi

## 1. Introduction

The growing demand for electrochemical energy storage has triggered a quest to find sustainable alternatives to the traditional electrode materials that are often based on critical raw material resources. Conducting polymers, polyaniline (PANI) in particular, have been studied for energy storage applications since the 1980s due to their environmental friendliness, high specific capacity and good conductivity. In spite of the numerous research efforts, polyaniline electrodes have still not found commercial success mainly due to stability issues. The poor cycling stability arises from volume changes due to the doping and dedoping of PANI during electrochemical reactions as well as the poor reversibility at high potentials [1,2].

PANI stores charge through redox reactions of the polymer backbone. It has three distinguishable oxidation states: fully reduced leucoemeraldine, half-oxidized emeraldine and fully oxidized pernigraniline, with a continuum of average oxidation states existing in between (Fig. 1) [3–6]. The imine nitrogen atoms and part of the amine nitrogens of PANI base forms can be protonated in the presence of a suitable protonic acid to yield the corresponding salt forms of PANI [4]. This process, known as doping, also converts the emeraldine base form from a semiconductor to the highly conducting emeraldine salt form [7].



Figure 1. The oxidation and protonation states of PANI. A<sup>-</sup> denotes a counter anion. The aprotic reaction pathway expected in organic electrolytes is shown in blue.

Most of the research on PANI as an electrode material is concentrated on utilizing aqueous electrolytes. However, the use of an aqueous electrolyte limits the operating voltage window of the devices (max. ~1 V) and results in a low specific energy. Utilizing an organic electrolyte enables significantly higher cell voltages (up to ~4 V) and is therefore preferred in most applications. Especially, the utilization of PANI in organic electrolytes with lithium salts is an interesting approach, which has recently been studied e.g. by the groups of Lutkenhaus, Shao-Horn and Hammond [2,5,8–12]. In these studies, the primary application of the PANI-containing electrodes is in thin-film batteries, and thus the electrode loadings reported are rather low, generally less than 1 mg cm<sup>-2</sup>. If used in conventional supercapacitors, lithium-ion capacitors or lithium-ion batteries, the electrode loadings have to be significantly higher to produce cells with reasonable gravimetric and volumetric energy. However, Shao *et al.* [2] have shown that electrolyte penetration into PANI-based electrodes and diffusion limitations in thick polymer films have a significant impact on the charge storage capacity.

Several methods to improve the cycling stability of PANI in organic electrolytes have been studied in the past. In the early works, the upper potential limit of PANI-based electrodes was often restricted to roughly 3.5–4.0 V vs. Li<sup>+</sup>/Li to circumvent degradation [13,14]. At higher potentials, the redox reaction from emeraldine to pernigraniline takes place. The pernigraniline salt form is unstable, transforming readily to pernigraniline base, and due to the lack of protons in the organic electrolyte, this reaction is irreversible [2]. Unfortunately, restricting the potential range decreases the amount of charge that can be stored in the electrode, as not all of the redox states of PANI can be accessed. Another way to avoid the stability problems has recently been proposed; studies by Jeon et al. [5,11] suggested that forming a complex of PANI with a polyacid could stabilize the pernigraniline salt form through specific interactions with the polyacid. However, the polyanion in the complex is not conductive or electrochemically active, which decreases the energy and power density of the system. On the other hand, adding a carbonaceous material to act as a support for PANI is also expected to improve the stability without sacrificing the conductivity [12]. A carbonaceous support can improve the mechanical properties and increase the conductivity of the system when PANI is in its insulating oxidation states. To combine both of the latter approaches (immobilized anion sites and a carbon support), a composite of PANI with acid-treated multiwalled carbon nanotubes (a-MWNTs) was prepared in this study.

Finally, thermal treatments have also been proposed to improve the electrochemical durability of PANI. It is generally accepted that PANI undergoes several extrinsic and intrinsic structural

changes during exposure to temperatures above approximately 150 °C. These modifications include doping, dedoping, oxidation, chain scission, cross-linking and changes of the crystal structure [15]. It has been shown that the type and the extent of the changes depend on the dopant and the doping level of PANI [16,17] as well as on the heat-treatment environment [18]. Many of the changes are undesirable, such as the dedoping and the chain scission, because they decrease the conductivity of the polymer. However, the cross-linking of PANI could be beneficial for the mechanical stability of the material [15,19]. Thermal cross-linking of the polymer would also be easy to incorporate into the manufacturing process of PANI-based cells, as heating under vacuum (drying) is generally a part of the production process of a battery or a supercapacitor. The group of Liu et al. have studied the stabilization of both PANI [20] as well as composites of PANI and carbon nanotubes [21] through thermally-induced cross-linking. Their study suggested that a heat treatment in air at 160 °C was able to improve the cycling stability of PANI in acidic aqueous electrolyte [20]. Hyder et al. [8,9] have also performed heat treatments at 180 °C on composite electrodes of PANI nanofibers and carboxylic acid functionalized MWNTs, but they did not study the impacts of the thermal treatment further. Accordingly, the effects of thermal treatments on the degradation of PANI-based electrodes during cycling or storage in organic electrolytes have not been studied extensively before. Moreover, the degradation mechanisms of PANI-based composites in organic electrolytes in general are still not thoroughly understood.

To conclude, poor cycling stability is generally considered a main obstacle preventing the commercial use of conducting polymers in electrochemical energy storage applications. Thus, the objective of this work is to study the effectiveness of two stability-enhancing methods, the addition of a carbon support (a-MWNTs) and heat treatment, to mitigate the stability issues of PANI in organic electrolyte. In this work, PANI/a-MWNT composites are prepared using a straightforward, cost-effective and scalable method [22,23] and processed into binder-free positive electrodes with loadings in excess of 1 mg cm<sup>-2</sup>. Heat treatments are then performed (under vacuum at 120–180 °C) on the composites to induce cross-linking of the PANI phase. The electrochemical performance and stability of the electrodes in lithium-ion cells are studied, and the effects of the a-MWNT support and the heat treatments are discussed. Analysis of the electrochemically cycled electrodes is performed to determine the origin of the cycling-induced performance degradation as well as to elaborate the reaction mechanism of the composite.

## 2. Experimental

#### 2.1 Materials

Polyaniline emeraldine salt powder (product number 428329, average molecular weight >15 000 g mol<sup>-1</sup>, particle size 3–100  $\mu$ m) was purchased from Sigma-Aldrich, and the MWNTs (NC3100, carbon content >95 weight-%, average diameter 9.5 nm, average length 1.5  $\mu$ m) were obtained from Nanocyl. The PANI is doped with an organic sulfonic acid by the manufacturer and was used as received for the preparation of the PANI/a-MWNT composite.

A detailed description of the composite synthesis is presented in a recent publication [22]. In short, 250 mg of MWNTs were treated in a vigorously stirred 3:1 mixture of concentrated sulfuric and nitric acid for 3 h, then washed until neutral pH, and dried at 100 °C for 7 hours. This sample is referred to as acid-treated multiwalled nanotubes (a-MWNT). The purpose of the acid treatment is to aid in the synthesis of the composite by improving the interaction between the PANI and the a-MWNTs through the electrostatic interaction between the positively charged polymer backbone and the negatively charged carboxylic acid groups introduced by the acid treatment. To prepare the composite, 100 mg of the a-MWNTs were dispersed in 250 mL of aqueous HCl solution (0.0025 M, pH 2.6) and sonicated for 30 min, forming a stable black aqueous colloid (0.4 mg mL<sup>-1</sup>). Separately, 150 mg of emeraldine salt (ES) was dispersed in 150 mL of 0.0025 M HCl solution and sonicated for 30 min, as well, forming a stable deep green colloid (1.0 mg mL<sup>-1</sup>). Because the size of commercially prepared ES is on the nanoscale, a stable colloid can be formed through electrostatic repulsion of the ES backbone by dispersion in an acidic aqueous solution. In our experiments, to eliminate the influence of changing the pH value, the pH of both the a-MWNT and ES aqueous colloids were similar (~ 2.6). Then, the mixture of ES and a-MWNT (3:2) was prepared and immediately shaken to ensure sufficient mixing. Subsequently, the mixture was sonicated in an ultrasonic bath (FinnSonic M3, 40 Hz, 80 W) for 30 min. After centrifugation (ThermoFisher Scientific, Heraeus Megafuge), the sample was dried in a vacuum oven at 40 °C. The product was denoted as PANI/a-MWNT.

For reference measurements, the PANI/a-MWNT composite was compared with PANI (ES). The PANI powder was treated similarly to the first steps of the composite synthesis: the powder was dispersed in 0.0025 M HCl solution (1 mg mL<sup>-1</sup>), sonicated for 1 h, and then separated by centrifugation and dried in a vacuum oven at 40 °C overnight.

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#### 2.2 Electrode preparation and heat treatment

To prepare the electrodes, the active materials (PANI/a-MWNT, PANI or a-MWNTs) were dispersed in isopropanol (20 mg mL<sup>-1</sup> for PANI/a-MWNT and PANI, 10 mg mL<sup>-1</sup> for a-MWNTs) and mixed overnight with a magnetic stirrer followed by 2 h in an ultrasonic bath. No additional binders or conductive agents were added to the mixture. The homogeneous inks were then spray-painted with an airbrush (Badger 100-3 GF) on graphite foil (Graftech eGraf 1205, thickness 0.127 mm, operating temperature range from -40 to 400 °C). The loadings of the PANI/a-MWNT and PANI electrodes were 1.4–1.7 mg cm<sup>-2</sup> whereas a loading of 0.6 mg cm<sup>-2</sup> was used in the a-MWNT electrodes to match the a-MWNT amount in the composites. These loadings corresponded to electrode thicknesses of ~30–35 µm for PANI/a-MWNT and ~20–25 µm for pure PANI, demonstrating that the density of the composite electrodes was lower compared to PANI. After drying in air, the samples were weighed and cut to circular electrodes with 18 mm diameter. The electrodes and all test cell parts were dried under vacuum (~1·10<sup>-4</sup> bar) at 40 °C for at least 20 h and transferred into a glove box (Jacomex, oxygen and water vapor levels <1 ppm) for storing/cell assembling.

The heat treatments were performed in a Büchi B-585 glass oven under vacuum. Dried electrodes from the glove box were used for the heat treatment, which started by keeping the samples at 100 °C under vacuum for 30 min to remove possible residual moisture from the electrodes and from the glass parts of the oven. Then, the temperature was raised to 120/150/165/180 °C and the samples were kept at the temperature for 12 h. After cooling back to room temperature, the samples were transferred back into the glove box.

## 2.3 Electrochemical characterization

All electrochemical tests were performed in commercial Ø 18 mm test cells (EL-CELL), which were assembled inside the glove box. Two-electrode setup was used for initial testing of the electrochemical characteristics with cyclic voltammetry (CV), whereas the rate capabilities, electrochemical impedance spectroscopy (EIS) and cycle stabilities were measured in a three-electrode setup. Both of the cell types utilized lithium metal (Sigma-Aldrich) as the counter electrode, and the reference electrodes in the three-electrode setup were also metallic lithium. A glass fiber separator of thickness 1.0 mm (EL-CELL) was used for the three-electrode measurements and 0.26 mm (Whatman, GF/A) for the two-electrode setup. The electrolyte solution

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consisted of 1 M LiClO<sub>4</sub> (Sigma-Aldrich, battery grade, dry, 99.99% trace metals basis) dissolved in propylene carbonate (Sigma-Aldrich, anhydrous).

Shao *et al.* [2] have shown that electrolyte penetration into PANI/V<sub>2</sub>O<sub>5</sub> electrodes has a significant impact on the measured capacity. Therefore, all the electrodes in this study were soaked in the electrolyte for 72 h before assembling the cells to ensure proper wetting. Without the soaking, the peak separation of the main peaks during the initial CV measurements was roughly 0.4 V larger and the charge-transfer resistance of the half-cell approximately 20  $\Omega$  higher compared to the electrolyte-soaked sample. Soaking for more than 72 h, on the other hand, was not observed to bring further benefits.

All of the electrochemical tests were carried out at room temperature. Cyclic voltammograms and EIS were recorded using a Metrohm Autolab potentiostat (PGSTAT302N) equipped with a FI20 filter integrator module. The CVs were recorded in a voltage window of 2.5–4.3 V (See Supplementary Materials for more information on the choice of the voltage window). The EIS spectra were measured at 3.1 V vs. Li<sup>+</sup>/Li in the three-electrode setup. This value corresponded to the middle of the lower voltage pair of peaks in the CVs, which is attributed to the leucoemeraldine/emeraldine redox process. A potential perturbation of 5 mV and a frequency range from 200 kHz to 10 mHz were used. Galvanostatic charging and discharging was conducted using a Neware battery testing station in a potential range of 2.5–4.3 V vs. Li<sup>+</sup>/Li. A 60 s rest period at open circuit was applied after each half cycle. Rate capability tests were performed using currents ranging from 0.1 A g<sup>-1</sup> to 2 A g<sup>-1</sup> and the cyclic stability of the samples was recorded during 200 cycles at 1 A g<sup>-1</sup>.

#### 2.4 Preparation of cycled electrode samples

After the electrochemical cycling, the electrode potentials (half-cell voltages) were set to 3.1 V vs. Li<sup>+</sup>/Li (3.1 V) and the cells were transferred into the glove box for disassembling. The electrodes recovered from the cells were carefully detached from the separator and washed three times in dimethyl carbonate to remove electrolyte residues. The electrodes were then left to dry in the argon atmosphere of the glove box and analyzed with scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). For the XPS measurements, the samples were transferred to the instrument inside an airtight

container (packed inside the glove box) in order to avoid contact with air. For the other analyses, the samples were exposed to air before the measurements.

#### 2.5 Materials characterization

SEM images of the electrodes were taken using a Tescan Mira3 microscope equipped with an EDX detector (Thermo Scientific). The samples were stored under argon until exposing them to air approximately 15 min before the imaging to minimize the effects of air exposure on the samples. The acceleration voltage used for imaging was 2–5 kV, and 10 kV was used for EDX analysis.

Raman spectra were recorded with a JY LabRam 300 microscope using a 633 nm laser. XPS was performed using a Kratos Axis Ultra spectrometer with monochromated Al K $\alpha$  radiation, using a pass energy of 40 eV and an X-ray power of 150 W. The analysis area was roughly 700  $\mu$ m × 300  $\mu$ m for all the samples. The binding energy scale was referenced to the graphitic C 1s peak at 284.4 eV. The peak fitting of the N 1s region was done using Gaussian–Lorentzian peaks (70% Gaussian) with positions fixed to within ±0.2 eV of given values and the full width at half-maximum (FWHM) restricted to be equal. The N-oxide peak position was restricted to between 404 and 408 eV with the FWHM restricted to below 4 eV.

#### 3. Results and discussion

#### 3.1 Morphology

The particle morphology and the electrode structure have a significant impact on the electrochemical response and the stability of PANI-based electrodes [11,24]. Thus, SEM images of the electrodes prepared from pristine PANI as well as pristine and heat-treated PANI/a-MWNT composites are presented in Fig. 2. It can be seen that the morphology of the PANI particles is mostly preserved during the preparation of the PANI/a-MWNT composite as well as during the manufacturing of the electrodes. The PANI particles (Fig. 2a and d) have a rough surface, and they are formed from primary particles of less than 1  $\mu$ m in diameter, which form secondary particles with a diameter in the range of 10  $\mu$ m. In the SEM images of the PANI/a-MWNT composite (Fig. 2b–c and e–f), in turn, the a-MWNTs can be seen on the surface of the PANI particles as well as embedded into the PANI matrix. Moreover, the a-MWNTs in the composite act as a binder

attaching some of the PANI particles together, thus forming somewhat larger secondary particles compared to pure PANI. However, the size of the primary particles is similar in all the samples. In contrast to some previous works [20,25,26], no differences can be seen in the morphologies of the PANI phases of the pristine and the heat-treated composite. It should be noted, however, that it is difficult to evaluate the roughness of the PANI particles of the composite from the SEM images due to the a-MWNTs on the surface.



Figure 2. SEM images of electrodes prepared from (a, d) pristine PANI, (b, e) pristine PANI/a-MWNT and (c, f) PANI/a-MWNT heat treated at 165 °C.

#### 3.2 Electrochemical characterization

#### **3.2.1 Cyclic voltammetry**

Cyclic voltammetry was conducted to study the electrochemical characteristics and the preliminary stability of the materials. CVs recorded at  $1 \text{ mV s}^{-1}$  in a two-electrode setup with metallic lithium as the counter electrode for pristine PANI, pristine PANI/a-MWNT and PANI/a-MWNT heat treated at 165 °C are shown in Fig. 3. The contributions from the different components to the

electrochemical response of the composite are shown in Fig. S1, and CVs measured with different scan rates from 1 to 10 mV s<sup>-1</sup> are shown in Fig. S2 in the Supplementary Materials. Two pairs of peaks arising from the redox reactions of PANI are seen in the CVs of all the materials in Fig. 3. The first pair of peaks, observed between 2.6 and 3.6 V, is attributed to the transition from leucoemeraldine base to the emeraldine salt form in the anodic scan, and vice versa in the cathodic direction [3–5]. The second pair of peaks at 3.6–4.3 V is assigned to the oxidation of emeraldine salt to the pernigraniline form of PANI in the anodic direction and the opposite reduction in the cathodic scan [3–5]. The plateau region between the two pairs of peaks, in turn, has been previously attributed to continuous faradaic charge transfer due to a higher formal potential of the electrochemical reaction at a higher oxidation state of PANI [27]. However, the exact origin of the plateau is still under debate in the scientific community [28].

Especially in the CV of the pristine PANI/a-MWNT composite, the peaks are split to two, which is likely related to the exchange of the dopant ion in PANI. Initially, PANI is doped by the organic sulfonic acid. However, the organic sulfonate ions (RSO<sub>3</sub><sup>-</sup>) are exchanged with the perchlorate ions  $(ClO_4^-)$  in the electrolyte with cycling. As the  $ClO_4^-$  ions are smaller than the bulky  $RSO_3^-$  ions, they impose less diffusion limitations to the redox reaction. Consequently, the ClO<sub>4</sub><sup>-</sup>-doped part of the PANI induces the formation of the shoulder peaks with a smaller peak separation compared to the main peaks. As the cycling progresses, the pair of peaks with the larger peak separation diminishes. At cycle 40, only the pair of peaks with a smaller peak separation is observed, indicating that the PANI/a-MWNT composite is mainly doped with ClO<sub>4</sub><sup>-</sup>. Thus, using a different initial dopant than the anion in the electrolyte solution has enabled the study of the reaction mechanism of the composite electrodes. It also facilitated the investigation of whether the immobile carboxylic acid groups on the sidewalls of the a-MWNTs are able to switch the charge compensation mechanism from anion doping to cation doping. Moreover, the result is in contrast to previous studies, which have suggested that the large size or poor solubility of organic sulfonates would cause the electrolyte cation to be the charge-compensating ion in sulfonic acid-doped PANI [29,30]. The ion exchange was confirmed with EDX analysis, which will be discussed further in Section 3.3.1.



Figure 3. The cycling stabilities of the electrodes prepared from PANI and PANI/a-MWNT composite. The cyclic voltammograms measured in the voltage range of 2.5–4.3 V at a scan rate of  $1 \text{ mV s}^{-1}$  for (a) pristine PANI/a-MWNT composite; (b) pristine PANI; and (c) PANI/a-MWNT composite electrodes heat treated at 165 °C. The discharge capacities integrated from the cathodic current in the CVs are shown in (d) for pristine PANI and PANI/a-MWNT as well as PANI/a-MWNT heat treated at 150–180 °C.

In the CVs of Fig. 3 and Fig. S2, the peaks corresponding to the redox reactions of PANI are sharper for the pristine PANI/a-MWNT composite compared to pure PANI, which suggests that the kinetics of the electrochemical reactions of PANI are enhanced in the composite. Furthermore, the presence of the conductive a-MWNTs improves the electrochemical response of the electrodes at low voltages below 2.8 V and at high voltages around 4.3 V. Below 2.8 V, the current is higher for the PANI/a-MWNT composites compared to pure PANI in both anodic and cathodic scans. Around 4.3 V, in contrast to the composite, the anodic peak of pure PANI is not fully formed before the vertex potential. In the low voltage region, PANI is in the leucoemeraldine form, whereas at high voltages PANI is in the pernigraniline form. Both forms have low electric conductivities [4,31], and

therefore the effect of the conductive a-MWNTs in the composite is seen most clearly in these regions.

The CV of the heat-treated PANI/a-MWNT (Fig. 3c) shows a widening of the peaks and an increase of the peak separation compared to the pristine composite. Similarly to the non-heat-treated material, the peak separation decreases with cycling, suggesting a gradual improvement in the kinetics of the electrochemical reaction. The poorer initial response of the heat-treated electrodes likely results from structural changes in the PANI phase during thermal treatment. Dedoping, cross-linking or decrease of crystallinity reported earlier for heat-treated PANI [15] could all hinder the kinetics of the redox reaction and retard the diffusion of the counter ions in the material. XPS analysis of the heat-treated electrodes (discussed in Section 3.3.3), however, revealed that the PANI in the composites was fully protonated even after the heat treatment, and thus dedoping as a cause of the poorer kinetics can be ruled out. Accordingly, the most likely cause of the larger peak separation are increased diffusion limitations in the polymer due to cross-linking or changes in the crystalline structure. The effects of the changes are then diminished during cycling due to the exchange of the dopant ion from the bulky  $RSO_3^-$  ions to the smaller  $ClO_4^-$  ions, which improves the rate of mass transfer.

The specific discharge capacities determined by integrating the cathodic current in the CVs of the pristine PANI/a-MWNT composite, PANI/a-MWNT heat-treated at 150–180 °C as well as pristine PANI are shown in Fig. 3d. Heat treatments were performed at 120 °C, as well, but they did not change the performance of the composite considerably. Moreover, pure PANI electrodes did not show a significant improvement in stability even after heat treatment at 180 °C, and thus thermal treatments of PANI were not tested further. The above-mentioned tests are omitted from Fig. 3d to improve the readability.

All of the specific capacity values in Fig. 3d are calculated based on the total mass of the composite or pure PANI in the electrodes and include the masses of the PANI, the sulfonic acid dopant and the a-MWNTs (if present). The specific capacity is roughly 125 mAh  $g^{-1}$  for the pristine composite and the composite heat treated at 150 °C. In contrast, the PANI/a-MWNT composites heat treated at 165 °C and 180 °C show a somewhat lower initial capacity of approximately 100 mAh  $g^{-1}$ . Generally, the initial specific capacity decreases with an increase in the heat-treatment temperature. Surprisingly, the capacity of the pure PANI electrodes (120 mAh  $g^{-1}$ ) is similar to the pristine composite, even though the composite contains 40 weight-% of a-MWNTs, which demonstrate a

capacity that is lower than that of PANI (circa 45 mAh  $g^{-1}$ , Fig. S1). If the capacity calculated for the a-MWNTs in the pristine PANI/a-MWNT composite is subtracted from the total capacity of the material, the amount of charge stored in PANI can be estimated to correspond to approximately 180 mAh  $g^{-1}$ , which is significantly higher than the value for pure PANI. The a-MWNTs thus clearly enhance the electrochemical accessibility of PANI in the composites, which shows that complicated template polymerization methods or layer-by-layer assembly are not needed to attain the beneficial effect of the a-MWNTs on the composite performance. The composite electrodes also exhibit a lower density compared to pure PANI (Section 2.2), which likely makes the porous structure of the electrodes more accessible to the electrolyte.

A theoretical specific capacity value of 294 mAh  $g^{-1}$  is often reported for PANI-based electrodes, and it corresponds to the transfer of four electrons per repeating unit in the full transition from leucoemeraldine to pernigraniline. This value, however, does not include the mass of the doping anions and thereby corresponds to emeraldine base. Emeraldine base performs poorly in organic electrolytes, because lithium (pseudo)doping is often inhomogeneous and less effective than protonic acid doping in enhancing the electronic properties of PANI [32–34]. As the anions are essential in balancing the charges associated with the electrochemical reaction, the values taking into account the mass of the counter ions present a more realistic value to describe the performance in a battery cell. The theoretical value for emeraldine salt doped with the simplest sulfonic acid, methanesulfonic acid, is 193 mAh  $g^{-1}$ , which is close to the value obtained for PANI in the pristine PANI/a-MWNT composite. The specific capacities of the materials are discussed further in Section 3.2.2 together with the results of the galvanostatic cycling, which is the preferred method to determine the capacity of a material.

During the CV measurements, the cycling was stopped every 10 cycles to perform an EIS measurement at 3.1 V followed by a break of 12 h at open circuit. The duration of the break was approximately the same as the duration of the cycling sequence. Interestingly, it is seen in Fig. 3d that all of the samples, except the ones heat treated at 165 °C or 180 °C, present a drop in specific capacity during the 12 h break at open circuit. During the break, the open circuit voltage (OCV) of the cells also decreased by ~10 mV for the PANI/a-MWNT electrodes heat treated at 165 °C and by ~50 mV for the pristine PANI/a-MWNT. The drop in the OCV suggests that the capacity decrease is related to a self-discharge mechanism. High self-discharge rates of PANI-based electrodes have been reported by several groups [13,24,35–38], which have ascribed it to impurities, overoxidation of the polymer, an uneven oxidation state of the electrodes or a release of low-molecular weight

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polymer chains trapped within the polymer matrix. Moreover, redox reactions between the polymer and its degradation products, such as quinones, have been suggested to cause self-discharge [36]. Surprisingly, the capacity decrease of the pristine electrodes is higher during the break time than during the cycling. During cycling, the electrodes are constantly polarized, which could prevent dedoping, the release of oxidation products or the dissolution of loosely attached polymer chains into the electrolyte. Furthermore, the rate of the process could be affected by the oxidation state of the polymer.

The better open circuit stability of the heat-treated electrodes is likely related to cross-linking of the PANI phase. The heat treatment caused a noticeable decrease in the immersion potential of the electrodes, which suggests that reduction of the polymer occurs during the heat treatment. The OCV immediately after the cell assembling was 3.4 V for pristine PANI/a-MWNT and reduced to 3.0 V after heat treatment at 180 °C. Similar values were observed for pure PANI, as well. Reduction of emeraldine base to leucoemeraldine base during heat treatment has been reported before and it is associated with the cross-link formation [39,40]. The cross-linking proceeds at the imine nitrogen, which forms a chemical bond with the quinoid group of another polymer chain [16,39,40]. During the process, hydrogen atoms (H<sup>+</sup> + e<sup>-</sup>) are released and react with the neighboring quinoid groups, thereby reducing the polymer [39,40]. XPS analysis of the heat-treated electrode (Table S1 in the Supplementary Materials) also indicated a slightly higher benzoid/quinoid ratio after the thermal treatment, which is in line with the reduction of the polymer. Thus, it can be concluded that cross-linking of the polymer likely occurred during the heat treatments.

Cross-linking has been shown to reduce the solubility of PANI in organic solvents [39,41] and affect its mechanical properties [9,19,42]. Accordingly, it is suggested that the cross-linking of the PANI in the heat-treated composite as well as the interactions of the polymer with the a-MWNTs could prevent the release of the polymer and/or the (over)oxidation products of the polymer into the electrolyte. This is supported by the fact that dark blue discoloration of the separators of the cells with non-heat-treated samples was observed during the cell disassembling. The discoloration decreased with increasing heat-treatment temperature, and it could not be observed for samples heated above 150 °C. The deep blue color of the separators also suggests the presence of dedoped PANI either in the form of emeraldine base or pernigraniline base.

#### 3.2.2 Galvanostatic cycling

Galvanostatic cycling was performed to study the long-term effects of the heat treatment on the stability of the composites. A heat-treatment temperature of 165 °C was chosen for the study, because it was the lowest temperature that improved the stability significantly in the CV testing. As the heat treatment also causes hindrance to the reaction kinetics, choosing the temperature is a compromise between improved stability and initial electrochemical performance.

The rate capability and the cycle stability measured galvanostatically for PANI, PANI/a-MWNT and PANI/a-MWNT heat treated at 165 °C are presented in Fig. 4. Pristine PANI and PANI/a-MWNT show similar capacities of 130 mAh g<sup>-1</sup> at a low current density of 0.1 A g<sup>-1</sup> (roughly equivalent to a C-rate of 1C), whereas the heat-treated composite shows a slightly lower initial capacity of 120 mAh g<sup>-1</sup>. However, the performance of the heat-treated PANI/a-MWNT improves with cycling and eventually reaches the performance of the pristine composite, which is in line with the CV results in Section 3.2.1. The rate capabilities of the materials are good: they all give a capacity of around 90 mAh g<sup>-1</sup> at the rather high current density of 2 A g<sup>-1</sup> (roughly equivalent to a C-rate of 20C), which corresponds to ~70% of the value at the lower current density.



Figure 4. Galvanostatic cycling of pristine PANI, pristine PANI/a-MWNT and PANI/a-MWNT heat treated at 165 °C. (a) The rate capability performance; (b) the cycle stability measured galvanostatically at 1 A  $g^{-1}$ ; (c) the energy efficiency and the coulombic efficiency recorded during the stability test; and (d) charge-discharge curves recorded at 1 A  $g^{-1}$  in the beginning of the stability test.

The specific capacities are in line with the values reported previously for PANI-based materials. For example, Hyder *et al.* [9] reported a capacity of 147 mAh g<sup>-1</sup> for their PANI nanofiber/MWNT composites, whereas Jeon *et al.* [12] reported values as high as 461 mAh g<sup>-1</sup> for their composite of PANI nanofibers and electrochemically reduced graphene oxide. However, these values were obtained for thin film electrodes with significantly lower thicknesses compared to this work. The loadings in the study by Hyder *et al.* [9] were in the range 0.15–0.23 mg cm<sup>-2</sup> (30  $\mu$ m), whereas the electrode thicknesses reported by Jeon *et al.* [12] were 271–1520 nm. It is known that the thickness of the electrode has a major impact on the measured capacity values, and generally lowering the electrode thickness/loading increases the measured specific capacity by improving the utilization of the material. Nevertheless, high electrode loadings are needed for high-energy batteries and

supercapacitors. In a recent study, Jimenez *et al.* [43] were able to prepare lithium n-doped PANI, and reported an impressive stability with a 230 mAh  $g^{-1}$  specific capacity and a loading in the range of a few mg cm<sup>-2</sup>. However, the synthesis process of the lithium-doped PANI is rather complicated compared to the simple ultrasonic-assisted mixing used in this work and the rate capability performance reported for lithium-doped PANI [43] was not as good as in the present work.

Both the pristine and the heat-treated PANI/a-MWNT composite show a similar cycling performance in the galvanostatic test (Fig. 4b). The coulombic efficiency (Fig. 4c) is high for both materials, staying above 99% throughout the cycling. Moreover, the energy efficiencies of both composites remain above 90% during the cycling. The initial cycling stability is also good: the capacity retention after 100 cycles is 91.7% for the pristine electrode and slightly higher at 94.3% for the heat-treated one. However, after the 100 cycles, both of the materials again show a capacity drop during a 12 h break at an OCV of 3.1 V. As discussed in Section 3.2.1, the behavior is suggested to result from a lower release rate of polymer or its oxidation products to the electrolyte and a lower rate of dedoping when the electrode is polarized during cycling. This causes the capacity drop to be delayed to the rest period at OCV. Thus, the stabilizing effect of the heat treatment is lost during prolonged cycling. As the doping and dedoping of PANI as well as solvent uptake [44] during the cycling cause significant volume changes, the heat-treated composite seems to eventually lose its improved stability regardless of the cross-linking. Moreover, the capacity loss could be caused by reactions between the polymer and the electrolyte taking place during prolonged cycling, as has been suggested in previous studies conducted in aqueous electrolytes [36,45]. In fact, XPS analysis (discussed further in Section 3.3.3) suggested that side reactions with the electrolyte occur during the cycling for both pristine and heat-treated materials.

The PANI electrodes, in turn, show a poor stability throughout the cycling. The drop in specific capacity during the 12 h rest period at 3.1 V is not as well distinguished for PANI as it is for the composites, which is likely related to the higher capacity loss of PANI already during the cycling. The coulombic efficiency is above 99% throughout the cycling, whereas the energy efficiency decreases from 90% to 85% during the course of 200 charge-discharge cycles. Surprisingly, the energy efficiency of the PANI electrodes is lower compared to the PANI/a-MWNT composites (Fig. 4c and d), even though the electrodes show the smallest total impedance in the EIS spectra (Fig. S3). This suggests that the process limiting the galvanostatic response has a larger time constant than the time scale probed in the impedance measurement at frequencies from 200 kHz to 10 mHz or that it occurs at a higher current density. The PANI electrodes also showed a larger

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potential relaxation during the 60 s rest periods (at open circuit) between the half cycles in the galvanostatic testing: the potential drop was ~45 mV in the beginning of the cycling at 1 A g<sup>-1</sup> and increased to ~215 mV after 200 cycles. For the composite, the relaxation increased from only ~5 mV to ~70 mV. The relaxation at such time scales is expected to include contributions from activation overpotentials as well as mass transfer (the *iR*-drop is not included in the numbers). Thus, it suggests that diffusion limitations are a major contributor to the decrease of the charge-storage capacity of the pure PANI electrodes. To investigate the causes of the performance degradation, the cycled electrodes were analyzed with SEM, EDX, Raman spectroscopy and XPS.

#### 3.3 Analysis of the electrodes after electrochemical cycling

#### 3.3.1 Changes is bulk composition and morphology during cycling

The poor cycling stability of PANI-containing electrodes is often attributed to poor mechanical stability, as PANI is known to undergo significant volume changes during the electrochemical reactions. Indeed, the SEM images in Fig. 5a-c show a drastic change in the morphology of the pure PANI electrodes after the electrochemical testing. The morphology changes explain the increased mass-transfer limitations and the poor stability observed during the cycling of the pure PANI electrodes. Furthermore, the conductivity of the PANI electrode had decreased significantly during the cycling, which is seen as severe charging of the cycled sample during the SEM imaging. In contrast, both the pristine and the heat-treated PANI/a-MWNT composite retain their porous structure and good conductivity throughout the electrochemical testing. Thus, the interactions between the a-MWNTs and the PANI together with the rigid backbone provided by the conductive a-MWNTs are able to improve the mechanical stability of the electrodes and preserve the conductivity throughout the cycling. However, all of the materials show trench-like features, which have been caused by the fibers of the separator pressing against the soft electrode material during the electrochemical testing. Some fibers from the separator are also seen still attached to the electrode surfaces, the amount being largest for the pure PANI and the pristine PANI/a-MWNT electrodes. This is also evidenced in the EDX spectra of Fig. 5e, where the Na and Si signals are stronger for these samples.



Figure 5. SEM and EDX analysis of the electrodes after cycling in 1 M LiClO<sub>4</sub> in PC. SEM images of the cycled (a) PANI, (b) PANI/a-MWNT and (c) 165 °C-heat-treated PANI/a-MWNT electrodes. EDX spectra of the electrodes (d) before and (e) after cycling. The peak intensities are normalized to the carbon peak.

The EDX analysis also helped to verify the charge compensation mechanism during the redox reactions of PANI. In the EDX spectra recorded before the electrochemical cycling (Fig. 5d), all of the samples show a strong S signal arising from the sulfonic acid dopant. The S signal is the highest for pure PANI, and the addition of the a-MWNTs decreases the relative amount of S in the composite. The S signal is strong for the heat-treated PANI/a-MWNT sample, as well, which suggests that the thermal treatment is not able to remove the bulky organic sulfonic acid dopant. After the cycling (Fig. 5e), the S signal is reduced, and the Cl and O signals become stronger for all of the materials. This suggests that during the electrochemical cycling, the changes in the charge on the polymer backbone are mostly compensated by the doping and dedoping of the anions from the electrolyte. During the process, the RSO<sub>3</sub><sup>-</sup> dopant originally associated with the nitrogen moieties is replaced by the  $ClO_4^-$  of the electrolyte, as discussed in Section 3.2.1. It is also worth noticing that electrochemical cycling is required for the anion exchange to occur. As evidenced by the low Cl

content of the samples before the cycling, the ultrasonic-assisted dispersing of PANI in dilute HCl solution during the composite synthesis is not enough to induce anion exchange from  $RSO_3^-$  to Cl<sup>-</sup>.

Fig. 5e also shows that the amount of Cl and O present after cycling is significantly lower for the PANI electrode compared to both the composites. This suggests a lower degree of doping for pure PANI, as the S signal is also diminished. The lowered doping degree explains the increased resistivity, and it is likely caused by the irreversible formation of pernigraniline base, which has been reported to occur in PANI electrodes during cycling in organic aprotic electrolytes [5]. Together with the morphology changes, the irreversible formation of pernigraniline base also explains the capacity decrease of the PANI electrodes, as it would cause part of the PANI to become electrochemically inactive.

## 3.3.2 Raman analysis of cycled PANI/a-MWNT composite electrodes

As the SEM and EDX analyses did not show clear causes for the capacity decrease observed for the PANI/a-MWNT composites, the cycled electrodes were studied further using Raman spectroscopy and XPS. The Raman spectra for the pristine and heat-treated PANI/a-MWNT electrodes, before and after electrochemical cycling, are presented in Fig. 6. The spectra were recorded using red laser excitation (633 nm), which is known to enhance the bands related to the oxidized (quinoid) segments [6,16,46–50].



Figure 6. Raman spectra of the PANI/a-MWNT composites before and after cycling.

All of the samples display three major bands, which can be attributed to the a-MWNTs: the D band at ~1330 cm<sup>-1</sup>, the G band located at ~1580 cm<sup>-1</sup> and the overtone of the D band (2D) at ~2600– 2700 cm<sup>-1</sup> [51,52]. Most of the bands expected for PANI are masked by the high intensity of the a-MWNT-related bands. The thermal treatment of emeraldine salt at 150 °C in air has been reported to give rise to phenazine-like segments, which should be seen in resonance Raman (633 nm) as bands arising at ~575, ~1390 and ~1640 cm<sup>-1</sup> [16,53]. Unfortunately, the a-MWNT bands as well as features related to PANI mask the bands at ~1390 and ~1640 cm<sup>-1</sup> in this study. A very small band at 574 cm<sup>-1</sup> seems to appear for the heat-treated electrode, which is, however, difficult to ascertain due to the low intensity of the band.

In the Raman spectra of the cycled electrodes, new bands emerge at ~1100–1250 and ~1470–1480  $cm^{-1}$ , which have previously been ascribed to the C–H bending and the C=N stretching of quinoid units in (partially) oxidized base forms of PANI [6,16,46–48,50]. At least part of the quinoid groups could originate from emeraldine base or pernigraniline base formed in the electrodes during cycling. However, considering the oxidation state of the electrodes after the electrochemical testing (potential was set to 3.1 V vs. Li<sup>+</sup>/Li), some leucoemeraldine is likely present in the electrodes. It is known that leucoemeraldine base can be chemically oxidized to emeraldine base in the presence of oxygen [40,54]. Therefore, part of the quinoid segments could also have been formed as a result of the air exposure and laser heating during the Raman measurements. Therefore, XPS (no air exposure) was also conducted on the samples in order to be sure of the origin on the quinoid groups. The XPS results are reviewed more closely in the next section.

Both cycled electrodes also show a decrease in the intensity of the three main bands related to the a-MWNTs. This decrease can be explained by the limited probing depth of the laser and the volume changes of PANI during electrochemical reactions, which cause the a-MWNTs to be embedded deeper into the PANI matrix. Moreover, side reactions of the electrodes with the electrolyte, leading to the formation of a cathode electrolyte interface (CEI) layer, could contribute to the decreased intensity.

#### 3.3.3 XPS analysis of cycled PANI/a-MWNT composite electrodes

To study the chemical changes induced by the cycling more rigorously and to ascertain the origin of the quinoid groups detected with Raman, XPS was conducted on the composite electrodes. In the XPS analysis, the samples were not exposed to air, and it provided a further advantage of being able

to detect Li, which is difficult with most methods. XPS measurements were carried out for both heat-treated and pristine PANI/a-MWNT samples, before and after electrochemical cycling. Fig. 7 shows the C 1s, N 1s and Li 1s spectra. Survey spectra and atomic concentrations are found in the Supplementary Materials together with O 1s, Cl 2p and S 2p spectra (Fig. S4 and Table S1).



Figure 7. X-ray photoelectron spectra of PANI/a-MWNT samples: a) C 1s region, b) N 1s region and c) Li 1s region.

The XPS analysis shows an increased amount of N on the surface of the cycled electrodes. This is related to the volume changes of PANI during the electrochemical reactions, causing the PANI part to be more exposed after the cycling, which is in line with the Raman results. Moreover, a clear increase in the amounts of Cl and O in cycled samples is observed, as in EDX. The XPS analysis (Fig. S4) further reveals that the increase in the Cl and O signals arises from the presence of both perchlorate and oxidation products of the electrolyte. In contrast to EDX, the reduction of the S signal with cycling is not observed in XPS. This is most probably due to the different probing depths of the methods. Since XPS is much more surface sensitive than EDX, any changes in the relative amounts of PANI and a-MWNTs on the outer surface of the sample will have a large effect on the XPS signal levels.

Fig. 7a shows C 1s spectra of all the composite samples. In the pristine and heat-treated samples, a typical graphitic carbon peak for a-MWNTs is observed at about 284.4 eV. In addition, a small feature is observed at ~289 eV which can be assigned to O–C=O bonds [55] of carboxyl groups on the sidewalls of the a-MWNTs. After the electrochemical measurements, shoulder peaks are

observed at ~285 eV and ~286.5 eV, and the higher binding energy feature becomes broader and moves to higher binding energy ~289.5 eV. These changes are consistent with additional C–C, C–O and O–C(=O)–O bonds, which could all be related to propylene carbonate found in the electrolyte [56]. For example, Desilvestro *et al.* [44] have shown that the doping-dedoping of PANI during electrochemical reactions is accompanied by solvent intake and repulsion, which could cause propylene carbonate to be trapped in the polymer matrix. Moreover, side reactions of the electrolyte on the surface of the positive electrode are common in lithium-ion cells and can cause the deposition of oxidation products of propylene carbonate on the surface.

The N 1s spectra of the PANI/a-MWNT samples are shown in Fig. 7b. The spectra have been fitted by assuming the presence of five different nitrogen species: imine (=N–) at 398.5 eV, amine (–NH–) at 399.5 eV, protonated amine (–NH<sub>2</sub><sup>+</sup>–) at 401.1 eV, protonated imine (=NH<sup>+</sup>–) at 402.2 eV, and one broader peak representing different nitrogen oxides (N-oxide) at 404–408 eV [57]. The percentages of different nitrogen species derived from the peak fitting are shown in Table S1. For the pristine and heat-treated samples, no imine bonds were found as would be expected, indicating their full protonation.

After the electrochemical measurements, no protonated imine bonds are observed anymore – mainly amine bonds and protonated amine bonds are found. The higher amount of amine bonds after cycling is likely related to the slightly lower oxidation state of the electrodes after the electrochemical testing in comparison to the pristine composite. For the samples after electrochemical measurement, the peak fit quality is however poorer. In this case, it is possible that at least part of the protons are replaced with lithium, causing a shift in the binding energy. Some XPS data for lithium-doped polyaniline has been previously reported [43,58,59]. In these, lithium-coordinated nitrogen has been found at binding energies between 400.5 eV and 402 eV, in the same region as protonated nitrogen bonds, but with varying peak assignments. We believe that the  $-NH_2^+$ - component found in the samples after electrochemical measurement could be in part due to lithium-coordinated nitrogen. However, because of large uncertainty in the type and binding energy of lithium-nitrogen bonds, we have refrained from introducing any new components in the fitting.

Fig. 7c shows the Li 1s spectra. The Li 1s peak is found at 55.6 eV (the ~63 eV is a Na 2p peak related to remaining fibers of the separator). The Li 1s binding energy is not very sensitive to the chemical state, but possible forms include LiClO<sub>4</sub> from the electrolyte, lithium coordinated to nitrogen or different oxidized forms of lithium. [60] Comparison of the atomic concentrations of Li,

Cl and N in Table S1 reveals that several lithium chemical states should be simultaneously present to account for the amount of lithium. Oxidation products of the lithium salt are commonly found on the surface of lithium-ion battery electrodes cycled in carbonate solvents at potentials above ~4 V vs. Li<sup>+</sup>/Li [61,62]. Moreover, the presence of chloride species on the surface of the electrodes after cycling (Fig. S4b in the Supplementary Materials) suggests that side reactions with the electrolyte occur. Accordingly, it is postulated that the most likely sources of the detected lithium are the oxidation products of LiClO<sub>4</sub> from the electrolyte, LiClO<sub>4</sub> salt trapped in the polymer matrix, and lithium coordinated to nitrogen.

The presence of lithium-coordinated nitrogen would suggest that lithium takes part in the charge compensation mechanism during the electrochemical reactions. It is known from previous studies, however, that lithium (pseudo)doping is inhomogeneous and less effective than protonic acid doping in enhancing the electronic properties of PANI [32–34]. Accordingly, at least part of the capacity decrease during the electrochemical cycling probably arises from the formation of dedoped PANI segments, most likely pernigraniline base [2,5]. This is confirmed by the small amount of imine bonds that were detected after the cycling (Table S1) as well as the Raman spectroscopy results, which suggested the presence of quinoid units in the samples. Moreover, the oxidative side reactions of the electrolyte likely contribute to the capacity loss, as they could cause parts of the electrode to become electrochemically inaccessible.

## 4. Conclusions

In this work, PANI/a-MWNT composites were prepared using a straightforward, cost-effective and scalable method and their use as a binder-free positive electrode of a lithium-ion cell was studied. Moreover, the degradation of the composites during electrochemical cycling in organic electrolyte was investigated. The pristine PANI/a-MWNT composite presents a specific capacity of 130 mAh  $g^{-1}$  and a good rate capability performance. Moreover, the electrochemical accessibility of PANI as well as the cycling stability are clearly enhanced in the composite compared to pure PANI electrodes.

Thermal treatments of the composites were also performed in order to improve the durability further and to understand the causes of the stabilizing effect. It is shown that a heat treatment at a temperature  $\geq 165$  °C (under vacuum) improves the stability of the PANI/a-MWNT composites in

the initial stages of cycling. However, with prolonged cycling the stabilizing effect is lost. The improved durability is seen most clearly, when the materials are kept in open circuit conditions, and it is attributed to increased interactions between the a-MWNTs and the PANI as well as to the cross-linking of the polymer. Unfortunately, the heat treatment also causes hindrance to the kinetics of the electrochemical reactions likely due to increases in the mass-transfer limitations induced by the cross-linking. Therefore, selecting the heat-treatment temperature is a compromise between the stability and the initial performance of the material.

To investigate the causes of the performance decrease observed during the cycling, the electrodes were studied after the electrochemical testing. Analysis of the cycled PANI electrodes without the carbon support revealed that PANI suffers from decreasing conductivity and drastic changes in the particle morphology. In contrast, both pristine and heat-treated PANI/a-MWNT composites retain their morphology and conductivity throughout the cycling. However, closer analysis with Raman spectroscopy and XPS suggests that both composites undergo side reactions with the electrolyte as well as changes of the composite microstructure. Moreover, evidence of slight dedoping of the polymer is found, which could be related to irreversible formation of pernigraniline base [5]. The changes in both composites are similar, but their extent is larger for the pristine composite. Accordingly, the better initial stability of the heat-treated samples is attributed to a better mechanical stability and a smaller reactivity with the electrolyte, both induced by the cross-linking of the PANI phase. However, the beneficial effects of the thermally induced cross-linking are lost during prolonged cycling most likely due to the large volume changes in PANI with electrolyte.

This study also demonstrates that testing merely the cycle stability of a material does not necessarily give a realistic picture of its suitability in real-life applications, in which devices spend a large portion of time idle. Consequently, it is important to consider also the calendar aging stability when novel materials are developed.

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