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Poly(3,4-ethylenedioxythiophene) nanotubes as electrode materials for a high-powered supercapacitor

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Abstract

We report the fast charging/discharging capability of poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes during the redox process and their potential application to a high-powered supercapacitor. PEDOT nanotubes were electrochemically synthesized in a porous alumina membrane, and their structures were characterized using electron microscopes. Cyclic voltammetry was used to characterize the specific capacitance of the PEDOT nanotubes at various scan rates. A type I supercapacitor (two symmetric electrodes) based on PEDOT nanotube electrodes was fabricated, and its energy density and power density were evaluated by galvanostatic charge/discharge cycles at various current densities. We show that the PEDOT-nanotube-based supercapacitor can achieve a high power density of 25 kW kg$^{-1}$ while maintaining 80% energy density (5.6 Wh kg$^{-1}$). This high power capability is attributed to the fast charge/discharging efficiency of nanotubular structures: hollow nanotubes allow counter-ions to readily penetrate into the polymer and access their internal surfaces, while the thin wall provides a short diffusion distance to facilitate the ion transport. Impedance spectroscopy shows that nanotubes have much lower diffusional resistance to charging ions than solid nanowires shielded by an alumina template, providing supporting information for the high charging/discharging efficiency of nanotubular structures.

1. Introduction

Recently, supercapacitors have received growing interest, with the increasing need for high-powered energy storage devices for electrical vehicles and mobile electronic devices [1–3]. The supercapacitors work in conjunction with batteries to provide necessarily high peak power and enhance the life expectancy of the batteries. Based on the charge storage mechanism, the supercapacitors are classified into two types: (i) an electrochemical double-layer capacitor (EDLC) [4] that stores the energy non-faradaically by charging an electrochemical double layer at the interface between the porous electrode and the electrolyte, and (ii) a redox supercapacitor [5] that stores energy faradaically using the pseudocapacitance behaviour of a redox-active material. In recent times, studies have been focused on investigating the redox supercapacitors because they feature high energy densities (or specific capacitances).

Conductive polymers [6–8] and transition metal oxides [9, 10] are promising materials for a redox supercapacitor because they can be readily converted between oxidized (doped) and reduced (dedoped) states by switching the applied potentials. This conversion process involves the diffusion of counter-ions into/out of conductive polymer or metal oxide films to keep their electroneutrality, which is a fundamental characteristic of a redox capacitor. Conductive polymers have been intensively investigated as electrode materials for supercapacitors because of their excellent electrochemical reversibilities, fast switching between redox states, high conductivity in a doped state, mechanical flexibility, low toxicity, and low cost [11, 12]. In particular, poly(3,4-ethylenedioxythiophene) (PEDOT) is a good candidate for a supercapacitor [13–16] because of its high stability among other conductive polymers [17]. To date, most of the studies on PEDOT-based supercapacitors have been focused on enhancing their specific capacitances. For example, Lota et al.
achieved a high specific capacitance of about 150 F g\(^{-1}\) by using PEDOT/carbon nanotube composites [15]. Li et al. enhanced the specific capacitance of PEDOT from 72 to 100 F g\(^{-1}\) using sponge-like PEDOT structures synthesized under ultrasonic irradiation [16]. Jang et al. reported that a high specific capacitance (155–170 F g\(^{-1}\)) of PEDOT was achieved by selective fabrication of PEDOT nanocapsules and mesocellular foams [18]. Besides achieving high specific capacitance (high energy density), how to obtain high power from PEDOT as an electrode material for a supercapacitor also needs immediate attention because more and more modern electronic devices require not only high energy but also high power.

In a redox supercapacitor, the high power can be achieved by enhancing the charge/discharge rate for the redox reaction. However, the conversion between redox states is governed by the mass transfer of counter-ions [19]. The difficulty in keeping pace with a fast charging/discharge process at high power demand will lead to inefficient utilization of the electrode material, i.e. a loss of usable energy. A similar problem exists in lithium ion batteries: the slow diffusion of the lithium ion in the solid phase of the electrode materials limits its rate capability [20–24]. Using arrays of one-dimensional hollow nanotubular structures has recently emerged as a solution achieving a fast charge/discharge rate because of their intrinsic structural characteristics [20–24]. The thin nature of the nanotube wall enables the rapid redox processes of electroactive materials such as conductive polymeric and metal oxides by providing a short diffusion distance to the counter-ions. Furthermore, long nanotubes can provide high surface area and enough mass loading for electrode materials to store sufficient energy. Martin’s group, one of the pioneers in achieving a fast charge/discharge rate of battery materials, has reported enhanced charge transport rates in template-synthesized one-dimensional nanomaterials [25–27]. For example, they showed that higher lithium ion insertion rates could be achieved using nanofibres of vanadium pentoxide [28, 29], tin oxide [30, 31], and LiFePO\(_4\)/carbon composite [32] and nanotubes of LiMn\(_2\)O\(_4\) [33] and TiS\(_2\) [34]. Fast switching between coloured and decoloured states of PEDOT can be found in our recent development of a nanotube-based devices [21, 22], that are also related to the fast charge/discharge rate. However, the application of PEDOT nanotubes as supercapacitor electrode materials has not been studied before.

In this study, we investigated the supercapacitive properties of PEDOT nanotube arrays electrochemically synthesized in the cylindrical pores of an alumina template membrane. The micron-long, thin-walled nanotubular structures enable us to develop a supercapacitor exhibiting both a high power density and high energy density (or specific capacitance). An alumina membrane is used as the template to direct the growth of PEDOT nanotubes owing to advantages in tailoring the diameter and length of desirable nanomaterials. The PEDOT nanostructures were synthesized by an electrochemical method rather than a chemical one to provide higher conductivity [17, 27]. Cyclic voltammetry was used to characterize the specific capacitance and rate capability of the PEDOT-nanotube-based electrodes. The energy densities and power densities were evaluated by galvanostatic charge/discharge cycling for the supercapacitor with two symmetric PEDOT-nanotube-based electrodes. All the electrochemical tests on the nanotube array were performed without removing the template, which offers the following advantages: first, the alumina template can directly serve as a substrate to support the electrode materials; second, the alumina template can be used as a separator between the electrodes, and the porous channels can store the electrolyte; third, the electrode materials are well protected inside the alumina pores to prevent nanostructure aggregation and electrode surface damage. Finally, impedance spectroscopy was used to investigate the diffusion resistance of the PEDOT nanotubes.

2. Experimental details

2.1. Chemicals and materials

3,4-ethylenedioxythiophene (EDOT), lithium perchlorate and anhydrous propylene carbonate were purchased from Sigma Aldrich (Milwaukee, WI). Tetraethylammonium tetrafluoroborate (Et\(_4\)NBF\(_4\)) (electrochemical grade) was obtained from Fluka (Switzerland). Acetonitrile was obtained from Fisher Scientific (Fair Lawn, NJ). Gold plating solution (Orotemp 24) was from Technic (Cranston, RI). De-ionized water (about 18 M\(\Omega\) cm\(^{-1}\) in resistivity) was made by a Milli-Q water purification system (Millipore; Dubuque, IA). Alumina membranes of 200 nm in pore diameter and 60 \(\mu\)m in thickness are commercially available from Whatman (Clifton, NJ).

2.2. Synthesis

PEDOT nanotubes were synthesized potentiostatically at 1.6 V in an acetonitrile solution of 20 mM EDOT, while PEDOT nanowires were made at 1.4 V in 100 mM EDOT. All electrode potentials were measured relative to an Ag/AgCl reference electrode using a Pt foil as a counter-electrode, if not specified otherwise. The preparation of a working electrode is as follows. A thin layer of gold (about 500 nm) was sputtered onto the branched side of an alumina membrane by using a sputtering system (Denton Vacuum Desktop III). The Au-coated membrane was connected to an electrical circuit using a copper tape from 3M (St Paul, MN). An electroactive window (0.32 cm\(^2\) in nominal area) was defined using Parafilm. Considered the porosity of a membrane (60%), the corrected surface area of the electroactive window was 0.2 cm\(^2\). For the synthesis of PEDOT nanowires, flat-top electrodes at the bottom of the pores were prepared by further electrodepositing gold galvanostatically at 1.0 mA cm\(^{-2}\) for 15 min in gold plating solution. The mass of the resulting PEDOT nanostructures was controlled by fixing the total charges passed during the electropolymerization.

2.3. Characterizations

The PEDOT nanostructures were investigated using a field-emission scanning electron microscope (SEM; Hitachi S-4700, operated at an acceleration voltage of 5 keV) and
a transmission electron microscope (TEM; Zeiss EM10CA, operated at 80 keV). The sampling methods for SEM and TEM analysis were described in detail previously [21, 22]. Briefly, the gold-coated side of a small piece of an alumina template was tightly attached onto an SEM specimen holder by using a carbon tape. The template was dissolved in 3 M NaOH to expose the nanomaterials. After rinsing them with de-ionized water repeatedly, the samples were dried in air before observation. For TEM sampling, the gold layer was removed by using an aqua regia solution after growing the desired nanostructures in a gold-coated alumina template. The alumina template was dissolved in 3 M NaOH. The released nanomaterials were repeatedly rinsed with de-ionized water and ethanol. Then, 6 µl of the nanomaterial solution was dropped and dried on a TEM grid.

Cyclic voltammetry was performed in a potential range between 0 and 1.2 V at various scan rates of 10–1000 mV s⁻¹ in 1 M LiClO₄ using the three-electrode system. A type I supercapacitor was built by assembling two PEDOT-nanotube-based electrodes with electrolyte (1 M Et₄NBF₄ in propylene carbonate) into an electrochemical cell. Galvanostatic charge/discharge curves for the type I supercapacitor were obtained by cycling the potential from 0 to 1.2 V. All the above electrochemical experiments were performed using a bi-potentiostat (BI-STAT; Princeton Applied Research). The impedance measurement was carried out using a potentiostat (CHI 660A) at 0 V (versus Ag/AgCl) with a perturbation amplitude of 5 mV over a frequency range 0.01–10⁴ Hz.

3. Results and discussion

3.1. Structure characterization and basic growth mechanism

Controlling the total charge during electropolymerization properly regulates the amount of PEDOT loaded in the pores of the template. By depositing PEDOT with a charge density of 500 mC cm⁻², we obtained a mass loading of around 0.3 mg cm⁻². PEDOT can be electrodeposited up to 3 C cm⁻² (PEDOT starts to grow out of the membrane around 3 C cm⁻²), which gives us 1.8 mg cm⁻² mass loading. By stacking the alumina membranes, higher mass loading can be achieved. The total charge dependence of PEDOT nanostructures is complicated because not only the length but also the wall thickness of nanotubes is affected by the total charge. The previous mechanism study showed that nanotubes grow at high overpotentials (>1.4 V) at low monomer concentrations (<50 mM).

The SEM images of PEDOT nanotubes (data not shown) have a similar appearance as before: highly collapsed and aggregated structures (data not shown) [23], which are caused by the intensive aggregation of nanostructures at their tops driven by the strong surface tension generated at the interface between the nanotubes and solvent during the solvent evaporation [35]. These structural defects can affect the charge/discharge performance of nanstructured electrode materials due to hindered diffusion of counter-ions. However, such structural defects of nanostructures can be avoided in this study since our electrochemical tests were performed under the support of a rigid template.

We investigated detailed nanostructures as a function of charge density to understand the capacitive properties. Figure 1 shows the TEM images of PEDOT nanotubes synthesized in 20 mM EDOT at 1.6 V for a total charge density of 200, 300 and 500 mC cm⁻², which correspond to 40 ± 5, 60 ± 5 and 110 ± 5 s of electropolymerization time, respectively. Nanotubes with thin, uniform, and smooth walls were grown along the template pore at the beginning (figure 1(a)). As the total charge was increased further, the nanotube length increased in proportion while the wall thickness and porosity changed in a complicated way. For example, we obtained nanotubes with gradually thinning walls along the nanotube axis rather than ones with uniform wall thickness at the total charge density of 300 mC cm⁻² (figure 1(b)). This can be attributed to the gradually decreasing monomer supply at the tips of the nanotubes during their growth, resulting from fast monomer depletion when the PEDOT is electropolymerized at lower monomer concentration and higher overpotential. Under the same conditions, we found that the upper part of the nanotubes became more porous with increased charge density (figure 1). This porous, loose structure at higher oxidative overpotentials was also observed in a film by Fröberg and co-workers [36]. The limited monomer supply also elucidated why the bottom of the nanotubes was porous (distinct from the solid nanowires) even though they were filled at the high charge density of 500 mC cm⁻² (figure 1(e)).

3.2. Electrochemical characterizations

The electrochemical performances were tested for the PEDOT nanotubes electropolymerized at the various total charge densities of 100, 200, 300, 400, and 500 mC cm⁻². The best electrochemical performances for fast switching between redox states were obtained from the nanotubes with lowest
total charge density (100 mC cm\(^{-2}\)) because of the facile electrochemistry caused by their thin wall structures. However, the mass loading at the lowest charge density was too limited to provide high mass loading, which is required to achieve high capacitance. Therefore, electrochemical experiments were performed at the charge density of 500 mC cm\(^{-2}\) if not specified otherwise. For notational convenience, we call nanotubes with total charge density of 500 mC cm\(^{-2}\) ‘NT 500’, and do likewise for other charge densities.

Cyclic voltammetry (CV) was used to characterize the capacitive properties of the PEDOT nanostructures. The pseudocapacitance behaviour of PEDOT is originated from diffusion of charged counter-ions (here, ClO\(_4^−\)) during the redox processes, as shown in scheme 1. All cyclic voltammetric scans were performed in a potential range from 0 to 1.2 V, within which high conductivity and good electrochemical reversibility of PEDOT can be maintained [37]. Figure 2(a) shows the cyclic voltammograms of NT 500 at different scan rates of 50, 100, 250, 500 and 1000 mV s\(^{-1}\). The shape of the CV plot of PEDOT nanotubes closely resembles a rectangle even at the high scan rate of 1000 mV s\(^{-1}\), showing its ideal capacitor behaviour. Furthermore, the resulting anodic current in nanotubes increases in proportion to the scan rate, as shown in figure 2(b). This helps to achieve a constant specific capacitance, which is independent of the scan rate, as expected by the following equation:

\[
C_{\text{spec}} = \frac{i}{m_e \Delta V/\Delta t},
\]  

where, \(C_{\text{spec}}\) is the specific capacitance in F g\(^{-1}\), \(i\) is the charge/discharge current in mA, \(m_e\) is the weight of one electrode material (PEDOT weight) in mg, and \(\Delta V/\Delta t\) is the scan rate in V s\(^{-1}\). The specific capacitance for NT 500 is approximately 140 F g\(^{-1}\), calculated using a current of about 0.8 mA from the CV plot in figure 2(b), \(m_e\) of 5.72 × 10\(^{-2}\) mg and scan rate of 100 mV s\(^{-1}\). This value is satisfactory and comparable to that in previous works mentioned earlier in this paper [15, 16, 18]. Compared to the theoretical maximum specific capacitance of PEDOT (about 200 F g\(^{-1}\)), which is determined by the molecular weight of polymer (142 g mol\(^{-1}\)) and the doping level of counter-ions (0.3) [38], the specific capacitance here is around its 70%.

Conductive polymer based supercapacitors can be classified into three types [6]. Type I is a symmetric system using a p-dopable conductive polymer as each electrode of the capacitor. Type II is an asymmetric system based on two different p-dopable conducting polymers. Type III is a symmetric system based on a conducting polymer which can be both p- and n-doped. Due to the difficulties of n-doping for PEDOT [39], in this study we attempted to build a type I supercapacitor using two identical electrodes with PEDOT nanotubes. Galvanostatic charge/discharge cycles were performed to evaluate the power density and energy density of PEDOT-nanotube-based supercapacitors. Here, only the weight of electroactive polymers is taken into account.

Figure 2 shows the galvanostatic charge/discharge curves of PEDOT-nanotube-based supercapacitors at the current density of 5 mA cm\(^{-2}\). As expected, the galvanostatic measurements agreed well with the CV studies: the nanotubes produced linear and symmetrical curves, and the specific capacitances of PEDOT-nanotube-based supercapacitors from figure 3 are 132 F g\(^{-1}\). This high linearity and symmetry in the galvanostatic charge/discharge curve of a nanotube-based supercapacitor indicate high charge/discharge efficiency (η) of 99.5%, which is the ratio of discharge time \(t_d\) and charge time \(t_c\). The slower potential change rate, \(\Delta V/\Delta t\), indicates higher specific capacitance according to equation (1).

Figure 4 shows the summarized specific capacitances of supercapacitors made of nanotubes which were synthesized at the various electropolymerization charges (100, 200, 300, 400, 500, 1000, 2000 and 3000 mC cm\(^{-2}\)). The specific capacitance for nanotubes decreased less than 20% when...
Figure 3. Galvanostatic charge/discharge curves of supercapacitors made of NT 500. Potentials were cycled from 0 to 1.2 V at a current density of 5 mA cm\(^{-2}\) in an acetonitrile solution of 1 M LiClO\(_4\). Here \(t_c\) and \(t_d\) represent charge and discharge time respectively.

Figure 4. Specific capacitances of type I supercapacitor based on PEDOT nanotubes synthesized at various total charge densities (100, 200, 300, 400, 500, 1000, 2000 and 3000 mC cm\(^{-2}\)). The electropolymerization charge density was increased from 100 to 3000 mC cm\(^{-2}\). This small decrease in the specific capacitance at the high electropolymerization charge indicates that the conductive polymers are effectively charged and discharged independently of the nanotube lengths.

As in a conventional battery, the maximum power \(P_{\text{max}}\) that can be delivered by a supercapacitor is given by

\[
P_{\text{max}} = \frac{V^2}{4R}.
\]

where \(V\) is the potential range for the charge/discharge cycling in V and \(R\) is the equivalent series resistance (ESR) in ohms. In order to maximize the deliverable power, many efforts have been made to minimize the ESR \([40-42]\). Practically, however, high power requires a fast charge/discharge rate and is always accompanied by the loss of usable energy, especially in a redox supercapacitor because of the incomplete utilization of redox-active materials. Thus, the efficient use of the materials is an important issue in achieving the optimal high power density while maintaining a high energy density.

The energy density \((E_d\text{ in W h kg}^{-1})\) of a symmetric supercapacitor at a constant current is expressed as

\[
E_d = \frac{i \int V \, dt}{m_{\text{total}}},
\]

where \(m_{\text{total}}\) is the total mass of two electrode materials \((2m_e)\). When the voltage varies linearly from 0 to \(V_{\text{max}}\) over time, in a type I supercapacitor, equation (3) becomes

\[
E_d = \frac{1}{8} C_{\text{spec}} V_{\text{max}}^2.
\]

This is also used in calculating the energy density \([43]\).

The power density \((P_d\text{ in kW kg}^{-1})\) can be calculated as

\[
P_d = \frac{E_d}{t_d}.
\]

The experimental values for \(P_d\) and \(E_d\) were obtained by analysing the charge/discharge curve of PEDOT nanostructures at various current densities. Figure 5 shows the plot of \(E_d\) versus \(P_d\), known as a Ragone plot, for a type I supercapacitor made of NT 500. Nanotube-based supercapacitors can maintain at least 80% of their energy densities (5.6 W h kg\(^{-1}\)) and specific capacitance (120 F g\(^{-1}\)) even when the power density increases from 5 to 25 kW kg\(^{-1}\). The power density (specific power) obtained by this PEDOT-nanotube-based supercapacitor is higher than that of previously reported PEDOT and other conductive polymer film based supercapacitors \([44-56]\). Some of these reports demonstrated that energy densities decreases dramatically when the power density is boosted less than 10 kW kg\(^{-1}\) \([44-46]\). Therefore, a nanotubular structure is an excellent candidate to provide high power density with less loss of energy density as a supercapacitor. The energy density of the system is comparable to the one from the work.
that uses similar type I [47, 48] or even type III supercapacitors [44, 49, 50] design. However, based on equation (4), higher energy density can be obtained using different conductive polymers that have high specific capacitance [51, 52]. Also, designing a supercapacitor with higher voltage range can help to achieve higher energy density according to equation (4) [53–56]. One approach is to build a type III supercapacitor because additional voltage range can be obtained from the n-doping region [53, 54]. Another solution is to build a hybrid-type supercapacitor, i.e. find a suitable material such as activated carbon [55, 56] that can store electrochemical energy under negative potentials as the counter-electrode to the conductive polymer.

3.3. Mechanism of fast charge/discharge behaviour in nanotubes

The charge/discharge process of a PEDOT-based supercapacitor is different from that of an EDLC: the PEDOT-based supercapacitor uses the redox reaction of PEDOT while the EDLC utilizes the electrostatic charges built on the electrode surface. PEDOT-based supercapacitors require the diffusion of counter-ions into/out of the polymer (doping and dedoping of conductive polymer) to balance the charges generated during the redox reaction. The criterion for a PEDOT-based supercapacitor to exhibit ideal capacitor behaviour is that the doping/dedoping rates should be fast enough to provide constant current during the redox reaction. This doping/ dedoping process involves not only charge (electrons or holes) transport but also ion transport. Here, the ion transport rate determines the charge/discharge rate of PEDOT because it is slow compared to charge transport. The ion transport rate, limited by the diffusion of counter-ions, is greatly influenced by the thickness of the polymer layer. A thinner film has a lower resistance to counter-ion diffusion due to its shortened diffusion distance. Therefore, thinner film can charge/discharge counter-ions more efficiently at a given current. In other words, the voltage change rate (ΔV/Δt) in a thin film is smaller than in a thick one to provide constant current. This leads to a higher specific capacitance in the thin film, as shown in equation (1).

Now, if we take a close look at one single nanotube out of the nanotube array, as illustrated in scheme 2, the hollow nature of the nanotube allows the electrolyte ions to penetrate into the polymer and access the internal polymer surface easily. Because the thickness of the nanotube wall can be approximated by the film thickness, it is natural that NT 100 and NT 200 can have the highest specific capacitance values (figure 4). It is also notable that the specific capacitance change as a function of charge density (up to 500 mC cm⁻²) is not significant in a nanotubular structure (figure 4). This can be well understood by taking into account the structure of NT 500, which still has thin walls at the top and porous structures at the bottom (figures 1(d) and (e) and scheme 2).

In order to prove the mechanism of fast charge/discharge of the nanotubes, we studied the electrochemical properties of solid nanowires protected by the alumina template. Solid nanowires were grown on the gold flat-top electrode at 1.4 V in 100 mM EDOT solution. The charge density of solid nanowires was controlled to be the same as in NT 500. Here we denote them as NW 500. Figure 6 shows that solid nanowires shielded by alumina template have much less capacitive current compared to the NT 500 at the same scan rate (figure 2). The specific capacitance estimated based on average current density is only 50 F g⁻¹. In addition, it has a significantly distorted rectangular shape that corresponds to the deviated potential-dependent capacitive behaviour (non-ideal capacitive behaviour). This can be explained as follows. First, nanowires have a denser and more rigid structure (higher diffusional resistance) than hollow nanotubes. Second, the side wall of the nanowires is completely shielded by a template, so the
diffusion of counter-ions is only allowed from the tops of the nanowires. Here, the diffusion length of counter-ions corresponds to the lengths of nanowires (equivalent to the thickness of dense bulk film). Thus, the counter-ion transport in the dense and long nanowires is very sluggish, and only some part of the nanowire is involved in the charge/discharge process at the high scan rate or current. After template removal, however, the capacitive current increased significantly, and is comparable to that of the nanotubes (figures 2 and 6). In addition, the rectangle-like shape also indicated better capacitive properties. This is because the cylindrical side of the nanowires can be accessed by the electrolyte after the template has been removed. However, after template removal, the exposed nanostructures are subject to be lost and damaged mechanically without the template protection [33]. The thin conductive substrate (sputtered metal) may easily crack after wetting and drying, which will affect the electrochemical performance. The above facts indicate that the nanotubes indeed take advantage of their internal surface to allow ion transport owing to their unique hollow nature.

3.4. Electrochemical AC impedance spectroscopy

To support our explanation, we used AC impedance spectroscopy, which is an essential tool to study the ion transport occurring during doping/dedoping process. Figure 7 shows the impedance plots of PEDOT nanostuctures recorded using a perturbation amplitude of 5 mV in a frequency range from $10^4$ to 0.01 Hz at the applied voltage of 0 V versus Ag/AgCl. Our electrochemical system has finite nanostructured electrodes in template pores and can be described by using the ‘classical’ finite-length transmission line model developed by Macdonald [57]. The useful electrochemical information can be extracted from the impedance plot in figure 7 by considering the limiting behaviour at high and low frequencies. At the high-frequency region, it is hard to observe a well-defined semicircle. This indicates that the charge transfer resistance is small, and our electrochemical system is kinetically fast. Thus, charges (electrons) can be readily transferred into the highly conductive PEDOT solid phase. This favourable charge transfer between the PEDOT and electrode surface is natural because the PEDOT was grown electrochemically in good contact with the base electrode. The $x$-intercepts provide quantitative information on the effective internal resistances, $R_s$, mostly contributed by the uncompensated solution resistance. Since we used the same electrolyte solution, the $R_s$ values for NT 500 and NW 500 systems are very close (18 and 17 Ω, respectively).

At the low-frequency region, we can obtain information on the ion transport: the extrapolation for the low-frequency data gives another $x$-intercept equal to $R_s + \Omega$, where $\Omega$ represents one-third of ionic resistances [58] in the pores for the distributed $RC$ network of the nanoelectrode in the pore. The thus-obtained resistance values for nanotubes and nanowires are 6 and 170 Ω, respectively. Almost pure capacitive behaviour in nanotubes is manifested by this low internal resistance. The abnormally large ionic resistance in nanowires is related to the slow ion diffusion into the dense, rigid nanowires. The knee frequency for the nanowires, at which they start to behave like a capacitor, is about 0.1 Hz. This suggests that nanowires in the template are not suitable for a high power supercapacitor which requires fast charge/discharge response.

From the impedance curve (figure 7), the specific capacitances of the nanotubes and nanowires can be calculated by

$$C_{\text{spec}} = \frac{1}{2\pi f Z_{\text{Im}}},$$

where $f$ and $Z_{\text{Im}}$ are the frequency in Hz and the imaginary part of impedance in ohms, respectively. The calculated specific capacitances for NT 500 and NW 500 at low frequency (11.8 mHz) are 144 and 133 F g$^{-1}$, respectively. The $C_{\text{spec}}$ value for NT 500 is in good agreement with that from the galvanostatic study (132 F g$^{-1}$ in figure 3). On the other hand, the value of $C_{\text{spec}}$ for NW 500 is much higher than the value (50 F g$^{-1}$) in figure 6. This means that NW 500 can be operated with almost full use of its capacitance at low frequency. As the frequency is increased to 1 Hz, the calculated $C_{\text{spec}}$ of NT 500 remains as high as 126 F g$^{-1}$, while the $C_{\text{spec}}$ of NW 500 drops dramatically to 30 F g$^{-1}$. At the much higher frequency of 1000 Hz, both nanotubes and nanowires suffer from insufficient counter-ion diffusion, and the calculated $C_{\text{spec}}$ values for NT 500 and NW 500 drop significantly, to 26 and 6 F g$^{-1}$, respectively.

4. Conclusion

We have demonstrated that nanotubular structures could dramatically improve the electrochemical performance in a PEDOT-based supercapacitor. The thin-walled nanotubes provided short diffusion paths and low ionic resistance for the diffusion of counter-ions to make all PEDOT available during complete charge/discharge even at a fast scan rate.
This fast electrochemical reaction enables us to achieve high power density without much loss of energy density (specific capacitance), which is the basic requirement for a supercapacitor to meet the demand of modern instruments on high peak power. The electrochemical performance of nanotube-based supercapacitors can be further improved by optimizing the electrolytes, electrode materials, and cell design. This study will also provide the fundamental understanding for high performance in other nanotube-based organic electronic devices which require fast charge/discharge processes, such as batteries, electrochromic displays, sensors, and actuators.

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