Highly flexible pseudocapacitor based on freestanding heterogeneous MnO₂/conductive polymer nanowire arrays†

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Flexible electronics such as wearable electronic clothing, paper-like electronic devices, and flexible biomedical diagnostic devices are expected to be commercialized in the near future. Flexible energy storage will be needed to power these devices. Supercapacitor devices based on freestanding nanowire arrays are promising high power sources for these flexible electronics. Electrodes for these supercapacitor devices consisting of heterogeneous coaxial nanowires of poly (3,4-ethylenedioxythiophene) (PEDOT)-shell and MnO₂-core materials have been shown in a half cell system to have improved capacitance and rate capabilities when compared to their pure nanomaterials; however, their performance in a full cell system has not been fully investigated. Herein, these coaxial nanowires are tested in both a symmetric and an asymmetric (utilizing a PEDOT nanowire anode) full cell configuration in the aspect of charge storage, charge rate, and flexibility without using any carbon additives and polymer binders. It is found that the asymmetric cell outperforms the symmetric cell in terms of energy density, rate capability, and cycle ability. The asymmetric device’s electrode materials display an energy density of 9.8 Wh/kg even at a high power density of 850 W kg⁻¹. This device is highly flexible and shows fast charging and discharging while still maintaining 86% of its energy density even under a highly flexed state. The total device is shown to have a total capacitance of 0.26 F at a maximum voltage of 1.7 V, which is capable of providing enough energy to power small portable devices.

Introduction

Currently, there is a growing interest in flexible electronics. The paradigm of electronics being encased in hard shells is slowly eroding. New technology is focused on flexible applications of electronics such as wearable electronics, paper-like electronics, and flexible biomedical devices. These novel electronic devices will require flexible energy sources to power them. Currently, energy sources based on electrochemical energy contain electrodes consisting of brittle energy dense metal oxides mixed with conductive carbon and polymer binders pressed into pellet form. The conductive carbon is needed to electrically connect, while the polymer binder is used to physically connect, all of the metal oxide material to the current collector. These electrodes must be encased in a rigid metal shell in order to prevent the cracking, breaking, and delamination of the electrode material from the current collector thus severely limiting their flexibility.

On the other hand, vertically aligned freestanding nanowire array electrodes have the ability to be highly flexible. These arrays are directly grown on the current collector providing good electrical connectivity, as well as excellent physical connectivity, of all of the energy dense material. This eliminates the need for additional carbon additives and polymeric binders. Their flexibility can be attributed to each nanowire’s independent movement during flexing.

As the flexible electronic devices will no doubt become multifunctional, they will need a high power energy source to help augment the low rate capability battery as a hybrid system. One energy storage device known for its high power is the capacitor. Electrostatic capacitors have been used extensively as high power load levelers in household devices such as radios and in air conditioners. To use capacitors in flexible electronic devices, they would need to deliver high power over even longer times for such things as Wi-Fi and GPS enabled wearable fabrics. However, these electrostatic capacitors have a very low energy density which would require them to be quite bulky, thus making them unacceptable for use in flexible device applications.

On the other hand, electrochemical capacitors, also known as supercapacitors, have shown large enough energy densities to allow them to be used in mobile electronics as high power load levelers. These devices could be used in conjunction with the battery in order to provide high power when running applications.
such as GPS, games, and videos on flexible paper-like electronics. These supercapacitor devices could then be recharged by the battery at lower current rates during standby times.

Electrochemical double layer capacitors (EDLCs) based on carbon materials have shown good performance metrics such as high power and high energy. However, supercapacitors based on pseudocapacitance have the capability to have larger specific capacitances (> 1000 F/g theoretical) in general. These pseudocapacitive materials involve a faradic transfer of charge across the electrolyte-electrode interface. These materials include conductive polymers such as polyaniline, polypyrrole, and polythiophene and their derivatives in addition to metal oxides such as RuO$_2$, MnO$_2$, V$_2$O$_5$, Fe$_3$O$_4$, Ni(OH)$_2$. Among these materials, poly (3,4-ethylenedioxythiophene) (PEDOT) and MnO$_2$ have a strong potential to be used in commercial supercapacitor applications.

PEDOT, a derivative of polythiophene, has received considerable attention as a supercapacitor material due to its large electroactive potential window and high chemical stability among conductive polymers. MnO$_2$ is considered a leading candidate for commercialization due to its large electroactive potential window, low cost, environmental friendliness, high theoretical capacitance, and abundance.

Our group has extensively studied the supercapacitor properties of PEDOT and MnO$_2$ in different morphological combinations, including PEDOT nanotubes, PEDOT/MnO$_2$ coaxial nanowires, and PEDOT nanowires embedded with MnO$_2$ nanocrystals. For example, it has been demonstrated that the supercapacitor performance of arrays of coaxial MnO$_2$-core PEDOT-shell nanowires is far superior when compared to their single component materials. The MnO$_2$ provides high energy density, while the PEDOT provides a conductive coating to induce fast electron transport and high ion permeability for ion transport to the MnO$_2$ core. The PEDOT also provides flexibility which can help buffer the stresses involved during the charging and discharging of MnO$_2$ in addition to allowing freestanding nanowires to be grown at high aspect ratios without breaking.

Previously, it was shown that the mechanism of synthesis for these coaxial nanowires was due to the annular shaped gold nanoelectrodes at the bottom of the AAO pores which promotes the growth of the PEDOT shell. These nanowires display a specific capacitance of 270 F/g even at a 9 A g$^{-1}$ current density in an aqueous electrolyte. Due to these properties, this material was chosen to be incorporated into a flexible supercapacitor device.

However, when designing a supercapacitor, maximizing the energy of the device is paramount. As the equation for the energy of a supercapacitor, $E = \frac{1}{2} CV^2$, demonstrates, one can not only improve the energy of the device by increasing the capacitance, $C$, of the electrode materials, but can also increase the energy of the device by increasing the voltage window, $V$. This increase in the voltage window can occur by using organic instead of aqueous electrolytes and also by using an asymmetric system where the anode and cathode utilize different materials. The asymmetric design has been utilized many times in the literature to offset MnO$_2$’s mediocre 1 volt potential window. This has included using activated carbon, carbon nanotubes, and graphene among other materials as the anode in this design.

Accordingly, for the coaxial MnO$_2$-PEDOT material, the maximum voltage window that can be used for the symmetric device is 1 V. This is due to MnO$_2$’s electrochemical reversibility window. However, if PEDOT, whose reversibility window extends beyond MnO$_2$’s, is utilized as an anode in an asymmetric system; the voltage window for the entire device can be enhanced up to 1.7 V. This increase in voltage has the capability of the asymmetric device having an almost 3 (1.7$^3$) times increase in energy.

Herein, a flexible asymmetric pseudocapacitor based on coaxial MnO$_2$-PEDOT and PEDOT nanowire arrays has been synthesized. This asymmetric device consists of a coaxial nanowire array as the cathode and a PEDOT nanowire array as the anode and is shown here to have a larger energy and power density along with better cycle ability than a symmetric device which incorporates the coaxial nanowire array as both the cathode and anode. The improvement in energy density is attributed to the asymmetric device’s larger (1.7 V vs. 1.0 V) voltage window, while the improvement in power density and cycle life is attributed to the PEDOT nanowire array’s improved stability as an anode material when compared to the coaxial nanowire array anode used for the symmetric device.

Evaluated as a full cell, the asymmetric device has a total mass, including all of the packaging materials, of 0.47 g with a total capacitance of 0.26 F and a maximum voltage of 1.7 V, which is capable of providing enough energy to power small portable electronics. This device’s electrode materials display an energy density of 9.8 Wh/kg even at a high power density of 850 W kg$^{-1}$. Finally, this device maintains 86% of its energy density even under a highly flexed state.

**Experimental**

**Chemicals and materials**

Poly(methyl methacrylate) (PMMA), 3,4-ethylenedioxythiophene (EDOT), manganese acetate, propylene carbonate (PC), and lithium perchlorate (LiClO$_4$) were purchased from Sigma Aldrich (Milwaukee, WI). Sodium dodecyl sulfate (SDS) and acetonitrile (ACN), was obtained from Fisher Scientific (Fair Lawn, NJ). Plastic paraffin paper (Parafilm™ M) was purchased from Pechiney Plastic Packaging Company (Chicago, IL). Pressure sensitive polypropylene tape (Scotch™ 3710), and copper electrical tape can be obtained from 3M Corporation (Maplewood, MN). Gold targets for sputtering were purchased from Denton Vacuum LLC (Moorestown, NJ). De-ionized water ($18$ MΩ cm resistivity) was made by a Milli-Q water purification system (Millipore; Dubuque, IA). Anodized alumina (AAO) membranes of 200 nm pore diameter and 60 μm thickness are commercially available from Whatman (Clifton, NJ). All electrochemical tests were done on a Bistat bipotentiostat from BioLogic (Clair, France).

**Synthesis of electrode materials**

First, a thin layer of gold ($ca. 18$ MΩ cm resistivity) was made by a Milli-Q water purification system (Millipore; Dubuque, IA). Anodized alumina (AAO) membranes of 200 nm pore diameter and 60 μm thickness are commercially available from Whatman (Clifton, NJ). All electrochemical tests were done on a Bistat bipotentiostat from BioLogic (Clair, France).
(2.88 cm² in nominal area) is performed by sandwiching the template between two layers of silicone rubber with one layer having a 2.88 cm² hole punched out. Considering the porosity of the membrane (60%), the corrected surface area of the electroactive window is 1.8 cm². A separate gold-sputtered AAO membrane is then placed in the electrodeposition bath for the Coaxial and PEDOT nanowire as the working electrode.

Coelectrodeposition of the heterostructured MnO₂/PEDOT nanowire arrays is performed in an aqueous electrodeposition bath consisting of 80 mM EDOT monomer, 10 mM manganese acetate, 160 mM sodium dodecyl sulfate, and 100 mM lithium perchlorate. The gold sputtered AAO is the working electrode with platinum as the counter electrode and Ag/AgCl as the reference electrode. A voltage of 0.75 V vs. Ag/AgCl is applied until the charge reached 5C.

Electrodeposition of PEDOT nanowire arrays is performed in an acetonitrile solution of 100 mM EDOT monomer and 100 mM lithium perchlorate. The gold sputtered AAO is the working electrode with platinum as the counter electrode and Ag/AgCl as the reference electrode. A voltage of 1.2 V vs. Ag/AgCl is applied until the charge reached 8.55 C. The total mass of all electrode materials are calculated using the amount of charge passed and Faraday’s law.

\[ m = \frac{QM}{ZF} \]

Where \( Q \) is the charge passed in coulombs, \( M \) is the molar mass of the material in gram/mole (86.94 g mol⁻¹ for MnO₂ and 140.13 for PEDOT), \( z \) is the number of electrons transferred per unit material (1.7 for MnO₂ and 2.3 for PEDOT), and \( F \) is Faraday’s constant (96 485 coulombs per mole).

Assembly of the device

The gold sputtered side of each AAO with the energy material inside is attached to the adhesive side of a piece of polypropylene tape. Another piece of tape with a 2.8 cm² hole is attached to the adhesive side of the previously applied tape on top of the AAO support ring. This additional tape is used to define the electroactive window. Each electrode is then soaked in a 3 M NaOH solution for 12 min to dissolve the AAO, resulting in free-standing nanowires attached to a gold current collector. Each electrode is rinsed and soaked three times each in DI water followed by a rinsing and soaking in acetonitrile.

Next, the electrolyte is made by first mixing 4.2 mL of 1M lithium perchlorate in a 5:2 V:V ratio of acetonitrile: propylene carbonate with 0.8 g of PMMA. This mixture was then heated with vigorous stirring to 105 °C using a hotplate until the solution begins to gel. At this point, 100 µL of electrolyte solution is placed onto each electrode. For the symmetric device, the electrodes both consist of the coaxial nanowire array. The asymmetric device consists of the coaxial nanowire array as the cathode and the PEDOT nanowire array as the anode. The solution is allowed to set for 6 h to form a viscous gel. Finally, the electrodes are sealed together using more polypropylene adhesive tape.

Device testing

Cyclic voltammetry is done with 20, 50, and 100 mV s⁻¹ scan rates at potential windows of 1.0 and 1.7 V for the symmetric and asymmetric device respectively. Galvanostatic voltammetry is done from 0.25 A g⁻¹ to 10 A g⁻¹ based on the masses of 5.86 mg for the symmetric device and 8.29 mg for the asymmetric device in the same potential windows as the cyclic voltammetry. Using the GV curves, the specific capacitance (\( C_{sp} \)) for the device can be calculated using the following equation:

\[ C_{sp} = \frac{4C}{m} = \frac{4it_d}{V} \]

Where \( C \) is the capacitance of the device, \( m \) is the mass of the electrode materials, \( t_d \) is the time for discharge, \( i_d \) is the current density, and \( V \) is the voltage maximum.

“In situ” anode and cathode monitoring

Electrode materials for the symmetric and asymmetric devices were prepared by previous methods except the electroactive area of the AAO template and the amount of charge passed was reduced by one ninth. Each electrode is set up in a beaker cell containing 1 M LiClO₄ in a 5:2 V:V acetonitrile: propylene carbonate. The anode and cathode were cycled between absolute voltages of 0 to 1 V and 0 to 1.7 V for the symmetric and asymmetric device respectively. The anode and cathode’s relative voltages were monitored using a Ag/AgCl reference electrode.

Extended window voltage testing

Electrode materials for the asymmetric device are prepared by previous methods except the electroactive area of the AAO template and the amount of charge passed was reduced by one ninth. Each electrode is set up in a beaker cell containing 1 M LiClO₄ in a 5:2 V:V acetonitrile: propylene carbonate. The anode and cathode were cycled between −0.95 V and 0.20 V vs. Ag/AgCl for the PEDOT nanowire electrode and between 0.20 V and 1.45 V vs. Ag/AgCl for the coaxial nanowire electrode.

Results and discussion

Herein, a flexible supercapacitor device is tested that is capable of powering small electronics. This device consists of electrodes made of free-standing arrays consisting of poly (3,4-ethylene-dioxythiophene) (PEDOT) and coaxial PEDOT-shell MnO₂-Core nanowires. Both a symmetric Coaxial-Coaxial and asymmetric Coaxial-PEDOT device are tested and compared. The asymmetric device shows here a considerable improvement in energy density, power density, and cycle life when compared to the symmetric device.

A schematic for the devices can be seen in Scheme 1a and b. Each device consists of two electrodes with freestanding nanowires attached to a gold current collector. These electrodes are encased in polypropylene pressure sensitive tape acquired from the 3 M Corporation with the electrode material facing away from the adhesive. Each electrode is attached to copper tape in order to be connected to the electronic circuit. The electrolyte consists of 1 M LiClO₄ in a 5:2 V:V acetonitrile: propylene carbonate solvent that is mixed with poly(methyl methacrylate) (PMMA) as the gelling agent. The total device mass including packaging is 0.47 g, while the total active area is 2.8 cm².
Scheme 1  (a) Exploded schematic view of flexible supercapacitor device. (b) Side-view schematic of the asymmetric device where gray represents the Coaxial MnO2/PEDOT Nanowire Cathode and Blue represents the PEDOT Nanowire Anode (c) Top view and (d) side view image of demo device shown with a United States Nickel for scale.

The electrode nanomaterials are synthesized using a commercial anodized aluminum oxide (AAO) membrane by a template-electrodeposition method. Briefly, AAO membranes with a 2.8 cm² total area, 60-micron thickness, and 200-nm nominal cylindrical pore-size are used. A gold current collector is sputtered on one side of the AAO template. The template is then immersed in the electrodeposition bath with only the open pore side exposed to the solution. The electrode materials are then grown electrochemically at the surface of the gold current collector from the bottom of the pores. Finally, the AAO membrane is removed by NaOH wet etching, revealing freestanding nanowires attached to the gold current collector. These nanowire arrays are then combined with the electrolyte and sealed with polypropylene tape to make the completed device.

The PEDOT nanowire arrays for the asymmetric device anode are grown at 1.2 V vs. Ag/AgCl from an acetonitrile solution containing 3,4-ethylenedioxythiophene (EDOT) monomer and LiClO4 as the dopant. These wires are ~40 µm in length and have a 200 nm nominal diameter. The total mass of these nanowires is 5.36 mg. The SEM images in Fig. 1c and d, display the dense forest of freestanding PEDOT nanowires used for the electrode.

The coaxial MnO2/PEDOT nanowires for both the asymmetric and symmetric device are grown at 0.75 V vs. Ag/AgCl from an aqueous solution containing manganese acetate, EDOT monomer, LiClO4, and sodium dodecyl sulfate (SDS) as a surfactant for the dissolution of EDOT. Previously, it had been shown that by using a lower synthesis potential (0.70 V vs. Ag/AgCl) a thinner PEDOT-Shell could be grown resulting in a higher specific capacitance,29 however, since the coaxial nanowires grown here are more than 2.5 times longer it is believed that extra PEDOT-Shell can help support this elongated high aspect ratio structure. These 0.75 V synthesized nanowires are ~17 µm in length with a 200 nm nominal diameter. The total mass of these nanowires is 2.93 mg per electrode. Fig. 1a and b shows the SEM top view image of the freestanding coaxial nanowires attached to a gold current collector. The nanowires are seen to be agglomerated at their tips in the SEM images due to the surface tension of water during the drying process which is needed for the SEM imaging. However, in solution these nanowire tips will not be agglomerated.

The coaxial nanowires are characterized using EDS line scans and mapping as can be seen in Fig. 1e–g. The Mn comes from the MnO2 material while the S comes from the thiophene ring of the PEDOT. The EDS shows that the PEDOT is located on the outside of the wires, while the MnO2 is found in the core. Fig. 1g indicates that the MnO2-core PEDOT-shell coaxial morphology continues along the axis of this nanowire up to the tip.

The total mass of the electrode materials is 8.29 mg for the asymmetric Coaxial-PEDOT device and 5.86 mg for the symmetric Coaxial-Coaxial device, calculated based on Faraday’s law. The PEDOT anode’s mass was made much larger than the coaxial cathode’s in the asymmetric device because of the higher specific capacitance of the coaxial nanomaterial compared to PEDOT nanowires (210 F/g and 115 F/g, respectively).28

Fig. 2a shows the CV curves of the asymmetric device at different scan rates between 0 and 1.7 V. The asymmetric device maintains its rectangular CV even at scan rates up to 100 mV s⁻¹, indicating good rate capabilities. Fig. 2b shows the cyclic voltammetry (CV) curves of the symmetric device at different scan rates between 0 and 1 V. The 20 mV s⁻¹ CV curve again shows a near ideal rectangular shape; however, at the higher scan rate of 100 mV s⁻¹, the curve shows a deviation from this shape indicating a low rate capability.

Fig. 2c shows the rate capability of both the symmetric and asymmetric devices calculated from galvanostatic voltammetry. As eluded to qualitatively in the CV curves, the asymmetric shows a much better rate capability than the symmetric device. Case in point, the symmetric device has a lower specific capacitance than the asymmetric device (163 F/g to 125 F/g, respectively) at a low current density (0.25 A g⁻¹), but at a high current density (8 A g⁻¹) the symmetric device has a lower specific capacitance (6 F/g to 24 F/g). This increased rate performance of the asymmetric device is highly encouraging for potential high power applications of flexible electronics such as GPS or Wi-Fi enabled wearable devices.

For the previous results, one must keep in mind that although specific capacitance is a great figure of merit to compare supercapacitor materials, voltage window is even better as \( E = 1/2 \ CV^2 \). Therefore, although the symmetric cell has a higher specific capacitance at low current densities, the asymmetric cell will still have a higher energy density as it
has a higher voltage window (1.7 to 1.0 V). This is examined further during the discussion of the Ragone Plot.

Fig. 2d shows the cycle ability for both the symmetric and asymmetric devices calculated from 1 A g\(^{-1}\) GV cycling. Here, the asymmetric device shows a better cycle ability and actually has a larger specific capacitance after 1250 cycles.

The improved cycle ability and rate capability of the asymmetric device over the symmetric device can be explained by a closer examination of the chemistry taking place at the cathode and anode in each device during use. In each device it is assumed that a fast faradaic reaction at the surface of the electrode nanomaterials is only reaction contributing to the charge. However, if one monitors the referenced cycle potential windows for the cathode and anode during cycling, the reactions contributing to the charge can be monitored. This is accomplished by using a bipotentiostat where the potential is controlled to be between 0 and 1 absolute voltage between the anode and cathode with each electrode’s relative potential monitored by a reference electrode. Fig. 3 shows the referenced potential window for the coaxial anode of the symmetric device during CV cycling. These qualitative experiments were done in beaker cells at a one ninth scale with the same electrolyte as the device sans PMMA.

As can be seen in Fig. 3, the referenced potential window changes with each cycle. In the first cycle, the coaxial anode’s potential is from \(-0.25\) to \(0.15\) V vs. Ag/AgCl. According to the literature, the ideal cycle stability window for MnO\(_2\) in aqueous solution is between 0 and 1 V vs. Ag/AgCl which means in a symmetric capacitor that the anode should be between 0 and 0.5 V vs. Ag/AgCl. Fig. 3 shows that even in
the first cycle the MnO₂-PEDOT coaxial anode is outside MnO₂’s reversibility window.

Furthermore, as the cycle number increases, the referenced cycle window moves to increasingly detrimental negative potentials. Also, the negative peak at the bottom right of the curve slowly increases during the first 50 cycles. This peak at negative potentials has been associated with the formation of Mn²⁺, which is not electroactive. This irreversible conversion reduces the amount of active material in the electrode. This reaction is also a slow bulk faradaic reaction which could explain the low rate capability for the symmetric device. Furthermore, from the 50th to the 500th cycle, this same peak decreases, probably due to the complete transformation of all the active manganese species to Mn²⁺. It may also be noted that the shape of the curve becomes increasingly rectangular, which is characteristic of a PEDOT-only electrode. Thus, it can be inferred that after 1000 cycles only the PEDOT in the coaxial structure remains electrochemically active.

Another trend is the increasing size of the potential window. Ideally the anode voltage window would be 0.5 V in width, since the absolute cycling voltage for this symmetric device is maintained between 0 and 1 V. In this ideal case, both electrodes would carry the same amount of charge and the same voltage window indicating that both would have the same capacitance. However, in the symmetric device, the anode’s window is only 0.4 V during the first cycle indicating that the anode has a larger capacitance than the cathode. This larger capacitance is deceiving because the charge is coming from an irreversible faradaic reaction. Furthermore, as the cycle number increases, the cycle window increases from 0.4 V to 0.7 V indicating a decreasing capacitance for the anode. Again, this can be explained by a decrease in the active manganese species, since this decrease reduces the amount of the high capacitance material, leaving only the moderately capacitive PEDOT material carrying the charge.

Therefore, the degredation in capacitance of the coaxial anode can mainly be attributed to the large PEDOT electrochemical stability window. This large potential window allows
the coaxial structure to choose an anode voltage that is in MnO$_2$’s electrochemical irreversibility window. Thus the coaxial PEDOT-MnO$_2$ structure can not be considered for use as an anode in a symmetric supercapacitor device system. Though this is not entirely discouraging information, since MnO$_2$ itself as an anode material for supercapacitors has been seen as an issue.$^{41}$ However, the coaxial cathode maintains its cycle window in MnO$_2$’s preferred electrochemical stability window, thus showcasing its ability as a great cathode for supercapacitors. Therefore an asymmetric device using the coaxial structure as the cathode is ideal as a possible high power energy storage device.

One of the advantages of PEDOT as an anode material is its very large voltage window. Therefore in the asymmetrical device, the voltage window can be expanded. A practical voltage up to 1.7 V is found to be possible for the asymmetric device. Fig. 4b shows the “in situ” cycle potential windows relative to a Ag/AgCl reference for the anode and cathode. Again, this is accomplished by using a bipotentiostat where the potential is controlled to be between 0 and 1.7 absolute volts between the anode and cathode, but each electrode’s relative potential is monitored versus a reference. These qualitative experiments were done in beaker cells at one ninth the electroactive area with the same electrolyte as the device.

If the voltage is increased above 1.7 V, detrimental effects appear for both the cathode and anode. As can be seen in Fig. 4b, an oxidation peak begins to appear above 1.2 V vs. Ag/AgCl for the cathode which has been attributed to the irreversible oxidation of MnO$_2$ to an electrochemically inactive higher oxidation state of manganese. As for the anode, PEDOT begins the dedoping process below $-0.5$ V vs. Ag/AgCl causing a loss of conductivity that reduces its capacitance. Therefore, 1.7 V is the maximum potential that can be established from this asymmetric device. In order to compare our devices to other current capacitors, their energy and power densities were calculated. The calculation for the energy density of a supercapacitor device is:

$$E_d = \frac{CV^2}{2m}$$

Where $E_d$ is the energy density, $C$ is the capacitance, $m$ is the mass of the electrode materials, and $V$ is the maximum voltage. This equation shows that any increase in the maximum voltage window for a supercapacitor results in an exponential increase in energy density. This voltage window is shown to be increased from $1.0$ V for the symmetric Coaxial-Coaxial device to $1.7$ V using the asymmetric Coaxial-PEDOT device. Therefore, the asymmetric device can have roughly a three times ($2.9\times$) improvement in energy density over the symmetric device if one assumes the same capacitance for each device.

The Ragone plot in Fig. 5 shows how the symmetric and asymmetric device electrode materials compare to current electrochemical capacitors.$^5$ At relatively low power densities ($213$ W kg$^{-1}$), the symmetric device shows a larger energy density (7.7 Wh/kg) than current capacitors; however, at high rates this energy decreases rapidly. This low rate capability is explained above to be due to bulk faradaic reactions which contribute to the charge at low rates but are too slow to contribute to the charge at high rates. However, the asymmetric device shows a higher energy density for its electrode materials than current electrochemical capacitors at low and at high power rates ($E_d = 12.6$ Wh/kg at $210$ W kg$^{-1}$ and 1.3 Wh/kg at $8500$ W kg$^{-1}$), indicating that this device has tremendous potential to power current small electronics. The total asymmetric device including electrolyte and all of the packaging materials (mass = 0.47 g) has an energy density of 0.22 Wh/kg at a power density of 3.7 W kg$^{-1}$. Improvement and optimization of the current bulky packaging and rudimentary electrolyte is expected, which should decrease the weight significantly and improve the total energy and power densities dramatically.

In order to apply a supercapacitor device to mobile electronics which are projected to become flexible, this energy source needs to show its capabilities in both the normal and flexed state.

![Fig. 4](image1.png)

**Fig. 4** (a) “In situ” CV curves at a 50 mV s$^{-1}$ scan rate exhibiting the referenced potential window vs. Ag/AgCl for the coaxial nanowire cathode (blue) and PEDOT nanowire anode (red) when cycled between the absolute potential bias between cathode and anode of 0.0–1.7 V and (b) three-electrode cyclic voltammetry at 20 mV s$^{-1}$ of a PEDOT nanowire electrode (red) cycled between $-0.95–0.20$ V vs. Ag/AgCl and a coaxial nanowire electrode (blue) cycled between $0.20$ V and 1.45 V vs. Ag/AgCl.

![Fig. 5](image2.png)

**Fig. 5** Ragone plot of energy density versus power density, comparing the symmetric Coaxial-Coaxial (red) and asymmetric Coaxial-PEDOT (blue) device electrode materials to current electrochemical capacitors (teal area) found in ref. 5.
Fig. 6a and b shows the asymmetric device powering a laboratory timer in both the normal and highly flexed states, respectively. An additional supplementary video that showcases the high energy, flexibility, and fast charge rate of this device can be found in the supporting information.† In the video it is demonstrated that this device can power a laboratory timer including its high power drain speakers for 10 min with only a fast charge of 3 s.

Fig. 6c illustrates the difference in the CV curve between the normal and the bent state close to 90°. The curve becomes less rectangular in the bent state indicating a decrease in rate capability. From the galvanostatic discharge curves in Fig. 6d, the specific capacitance is shown to decrease from 114 F/g for the normal state and 98 F/g for the bent state at the 0.5 A g⁻¹ charge rate. This shows the device can deliver 86% of its energy even in the bent state. This demonstrates a great ability for this device to be used in future flexible electronics.

Conclusion

Flexible supercapacitor devices based on freestanding nanowires are shown here to produce enough energy and power to operate small electronic devices. An asymmetric device consisting of a PEDOT nanowire array anode and coaxial PEDOT/MnO₂ nanowire array cathode exhibited an improvement in energy density, power density, and cycle life when compared to a symmetric device consisting of a coaxial nanowire array as the cathode and anode. The improvement in energy density can be attributed to the increase in the electrochemically reversible voltage window; however, the increase in power and cycle ability can be attributed to the PEDOT anode, since the coaxial PEDOT/MnO₂ nanowire array is shown here to be unsuitable as an anode. This is due to the fact that the voltage window chosen by this heterogeneous anode is centered in MnO₂’s irreversible reduction window. This reduces the symmetric cell’s cycle ability due to MnO₂’s slow conversion to inactive Mn²⁺ and limits its power capability, since a slow faradaic process is contributing to the charge.

This superior asymmetric device is highly flexible and shows fast charging and discharging while still maintaining 86% of its energy in the bent state. The asymmetric device has a total mass including packaging of 0.47 g with a total capacitance of 0.26 F and a maximum voltage of 1.7 V, which is capable of providing enough energy to power small portable devices. This device’s electrode materials display an energy density of 9.8 Wh/kg even at a high power density of 850 W kg⁻¹. Furthermore, this device maintains 86% of its energy density even under a highly flexed state, demonstrating its ability to be used as a high-power energy source in future flexible electronic devices. In addition, we believe the energy and power density of the full cell including packaging and electrolyte can be improved further with the optimization of the packaging and electrolyte materials.
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