

Polypyrrole–MnO₂-Coated Textile-Based Flexible-Stretchable Supercapacitor with High Electrochemical and Mechanical Reliability

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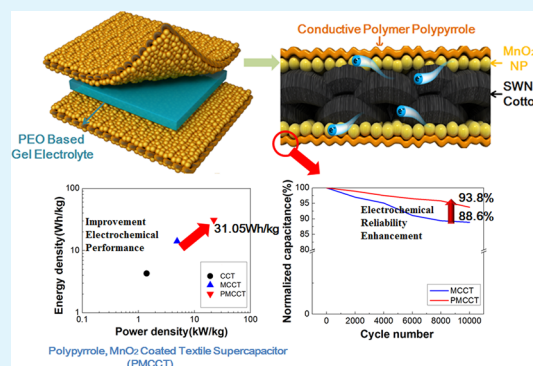
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S Supporting Information

ABSTRACT: Carbon-nanotube (CNT)-based textile supercapacitors with MnO₂ nanoparticles have excellent power and energy densities, but MnO₂ nanoparticles can be delaminated during charge–discharge cycles, which results in significant degradation in capacitance. In this study, polypyrrole conductive polymer was coated on top of MnO₂ nanoparticles that are deposited on CNT textile supercapacitor to prevent delamination of MnO₂ nanoparticles. An increase of 38% in electrochemical energy capacity to 461 F/g was observed, while cyclic reliability also improved, as 93.8% of energy capacity was retained over 10 000 cycles. Energy density and power density were measured to be 31.1 Wh/kg and 22.1 kW/kg, respectively. An in situ electrochemical–mechanical study revealed that polypyrrole–MnO₂-coated CNT textile supercapacitor can retain 98.5% of its initial energy capacity upon application of 21% tensile strain and showed no observable energy storage capacity change upon application of 13% bending strain. After imposing cyclic bending of 750 000 cycles, the capacitance was retained to 96.3%. Therefore, the results from this study confirmed for the first time that the polypyrrole–MnO₂-coated CNT textile can reliably operate with high energy and power densities with in situ application of both tensile and bending strains.

KEYWORDS: flexible-stretchable supercapacitor, textile, polypyrrole, gel-type electrolyte, electrochemical reliability



INTRODUCTION

Recently, flexible and wearable electronic devices and their associated technologies have significantly increased in demand, thereby attracting much interest in development of flexible and wearable energy storage systems. However, flexible and stretchable energy storage system must address design issues such as the selection of suitable flexible, stretchable active material, as well as supporting substrate and current collector. So far, many flexible substrate candidates, such as thin metal foils,¹ polymer substrates,² textiles,³ and papers,⁴ have been proposed, and the respective electrochemical performance and feasibility as energy storage systems have been reported.^{5,6} Among them, textile based substrates exhibit several benefits such as large surface area due to the porous structure of the textile fibers, as well as the mechanical flexibility, stretchability,^{7–10} and easiness of carbon-based material coating through simply absorbing the solution containing active materials. The carbon-coated textile has sufficient conductivity that can also eliminate the need for an alternative current collector.¹¹ Such textile-based supercapacitors have the ability to maintain electrochemical performance under mechanical strain^{12–14} and have high power density due to fast charge–discharge rates, which are characteristic of electrostatic double-layer capacitance.

One disadvantage of supercapacitors, however, is their low energy density^{15,16} compared to other energy storage systems

such as the Li-ion battery. To compensate for the low energy density, many researchers have deposited nanostructured pseudocapacitor materials such as metal oxides MnO₂ and RuO₂, as well as conductive polymers that can enhance the capacity by 200–300%.^{16,17} However, the metal oxide nanostructures result in large volume changes during charge–discharge cycles that cause delamination of the active materials and hence a decrease in electrochemical reliability. Another disadvantage of incorporating metal oxide nanostructures is the reduction in total electrical conductance due to the inherently low conductivity that contributes to lowering the power density.

To prevent the delamination of nanostructured pseudocapacitor materials, Yu et al.¹⁸ reported use of a thin layer of conductive polymer PEDOT:PSS coated on top of the graphene/MnO₂ pseudocapacitor nanostructures to demonstrate an improvement in the electrochemical reliability as well as the energy capacity. PEDOT:PSS serves as a conductive and adhesive layer, yet the materials capacity is quite low (200 F/g).¹⁹ Our aim is to use an alternative material for polymer coating that can serve as a conductive and adhesive layer while also enhancing capacitance.

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Other conductive polymer candidates that offer higher capacities include polyaniline (750 F/g), polypyrrole (620 F/g), and polyindole (300 F/g).^{19–24} Although polypyrrole has a lower capacity (620 F/g) compared to that of polyaniline (750 F/g), polypyrrole is favorable due to its high chemical stability, electrical conductivity (50–100 S/cm), and thermal stability. The high conductivity of polypyrrole can result in enhanced power density when coated on top of MnO₂ loaded CNT textile, and high power and energy densities can be expected. In addition, polypyrrole can prevent delamination of active materials during charge–discharge cycles.

To demonstrate the possibility of flexible-stretchable supercapacitor under flexible and stretchable environments, many researchers performed mechanical bending and tensile tests with gel-type electrolyte. For example, an active carbon-based supercapacitor with enhanced electrochemical reliability under maximum tensile strain of 4% was demonstrated using a boron cross-linked graphene oxide/poly(vinyl alcohol) nanocomposite gel-type electrolyte.²⁵ A polypyrrole based paper supercapacitor using PVA/H₃PO₄ gel-type electrolyte was reported to maintain its electrochemical properties for 100 cycles under maximum mechanical bending of 90°.²⁶

In this study, the polypyrrole-coated CNT textile supercapacitor with MnO₂ pseudocapacitor nanoparticles was studied for electrochemical performance and cyclic reliability. In addition, polypyrrole–MnO₂-coated CNT textile supercapacitor was evaluated under both tensile and bending strains using an in situ measurement for coupled electrochemical-mechanical properties analysis. The in situ setup required the use of a gel-type electrolyte for stability under application of mechanical strain, and PEO/Na₂SO₄-based gel-type electrolyte was used for our study.

EXPERIMENTAL SECTION

Chemicals and Materials. Commercial cotton textiles were purchased from 4Science, and single-walled nanotubes (SWNTs) were purchased from Carbon Ins. Sodium dodecylbenzenesulfonate (SDBS), manganese nitrate (Mn(NO₃)₂), sodium nitrate (NaNO₃), potassium chloride (KCl), poly(ethylene oxide) (PEO), TiO₂ powder, and pyrrole monomer were purchased from Sigma-Aldrich. Pt wire (Fisher Scientific) as the counter electrode and Ag/AgCl (Fisher Scientific) as the reference electrode were purchased from Fisher Scientific.

Dip Coating of Single-Walled Nanotubes. Cotton textile was dipped in single-walled nanotube ink, which is a well-dispersed solution of 0.032 g of SWNTs (Carbon Ins.) and 0.4 g of SDBS surfactant (Sigma-Aldrich) solute in deionized (DI) water solvent. The prepared SWNT ink was sonicated with a tip sonicator for 10 min and further sonicated in a bath sonicator for 1 h to achieve uniform dispersion. Then, 0.065 mg/cm² of SWNT ink was deposited into cotton textile through a dip coating process. Consistent deposition of SWNT ink was achieved through control of ink concentration and immersion time. After the dip coating process, the sample was dried at 120 °C for 10 min in a box furnace to evaporate the remaining solvents. Average sheet resistance of CNT-coated cotton textile was 850 Ω/sq.

Electroplating of MnO₂ Nanoparticles and Conductive Polymer Polypyrrole Thin Layer. MnO₂ nanoparticles and polypyrrole thin layer were deposited on CNT-coated textile fibers by using a three-electrode electroplating system. A three-electrode electroplating system consists of the CNT coated textile electrode as the working electrode, Pt wire (Fisher Scientific) as the counter electrode, and Ag/AgCl (Fisher Scientific) as the reference electrode. To deposit MnO₂ nanoparticles, a constant current of 0.5 mA/cm² was applied to the CNT-coated textile electrode for 2 h. CNT-coated textile electrode was dipped in a Mn(NO₃)₂ (Sigma-Aldrich) and 0.1 M NaNO₃ (Sigma-Aldrich) mixed electrolyte solution. Average diameter of MnO₂ nanoparticles was determined to be 750 nm. To uniformly deposit polypyrrole thin layer, pulse-type voltage was applied to MnO₂

nanoparticles coated on CNT–textile electrode. Pulse-type voltage induces the electropolymerization of pyrrole monomer (Sigma-Aldrich) in KCl (Sigma-Aldrich) mixed solution. MnO₂ nanoparticles coated on CNT–textile electrode was dipped in 0.5 M pyrrole monomer and 1 M KCl mixed electrolyte solution. Polypyrrole thin layer was deposited for 360 s to achieve a thickness of approximately 70 nm (see Supporting Information for details).

Electrochemical Properties Normalized by Mass Measurement. Electrochemical properties were measured with a symmetric electrode system consisting of the anode and the cathode, which are separated by an insulating polymer textile layer. A Na-based aqueous electrolyte with a concentration of 1 M Na₂SO₄ (Sigma-Aldrich) was used. Electrochemical performance was measured using both the charge–discharge and cycle voltammetry method at a fixed working voltage of 0–0.85 V. The specific capacitance in cyclic voltammetry method was calculated from the area under the curve in a current density and voltage graph at a scan rate of 100 mV/s.

$$C_s = \int_{E_2}^{E_1} i(E) dE / 2(E_2 - E_1)mv \quad (1)$$

where C_s is the specific capacitance of electrode, E_1 and E_2 are the working voltage in cyclic voltammetry, and $\int_{E_1}^{E_2} i(E) dE$ is the total voltammetric charge in cyclic voltammetry.

The charge–discharge measurement was performed in a voltage range of 0–0.85 V at current densities of 0.2, 1, 2, 4, and 8 A/g. Specific capacitance C_s was then calculated from the measured charge–discharge curve using the following equation for a symmetric measurement system.

$$C_s = 2I / (\Delta V / \Delta t) \quad (2)$$

where ΔV is the working voltage, Δt is change of time, and I is current density normalized by the weight of the active materials. C – V results were also obtained at voltage scan rates of 100 mV s^{−1} to examine the enhancement of specific capacitance across the samples.

Energy density and power density were evaluated with electrochemical impedance, working voltage, and charge–discharge time by using the following equations:

$$E = \frac{1}{2} C_T (\Delta V) \quad (3)$$

$$P = (\Delta V)^2 / 4m(\text{ESR}) \quad (4)$$

where ΔV is the working voltage, C_T is the total capacitance of the entire device, m is the total mass of both electrodes, and ESR is the total resistance. Total capacitance is expressed as

$$C_T = I / (\Delta V / \Delta t) \quad (5)$$

Fabrication of Stretchable-Flexible Supercapacitor System.

To confirm the feasibility for wearable application, we used PEO-based gel-type electrolyte for a full textile-based supercapacitor system. A high-viscosity gel-type electrolyte was used to serve as not only an electrolyte but also an adhesive between electrodes without separator. Homogeneous PEO electrolyte was synthesized from stirring the insoluble polymer solution consisting of PEO, TiO₂ nanopowder, and Na₂SO₄ (Sigma-Aldrich) solutes in an acetonitrile solvent for 2–3 days. TiO₂ nanopowder was mixed in gel-type electrolyte to enhance the ionic conductivity. Sodium gel-type electrolyte matrix exhibited no deterioration of electrochemical capacity even when exposed to ambient testing conditions during mechanical reliability test (over 1 week), thereby implying no evidence of crystallization even under prolonged exposure to the atmosphere. A 2 × 2 cm area of two textile electrodes was overlapped and glued together using the PEO-based gel-type electrolyte. The electrochemical energy is stored in the overlapped area, and the remaining textile electrode serves as the current collector (see Supporting Information for details). Mechanical bending strain was evaluated under the assumption that the neutral plane lies at half the thickness of the full supercapacitor system.

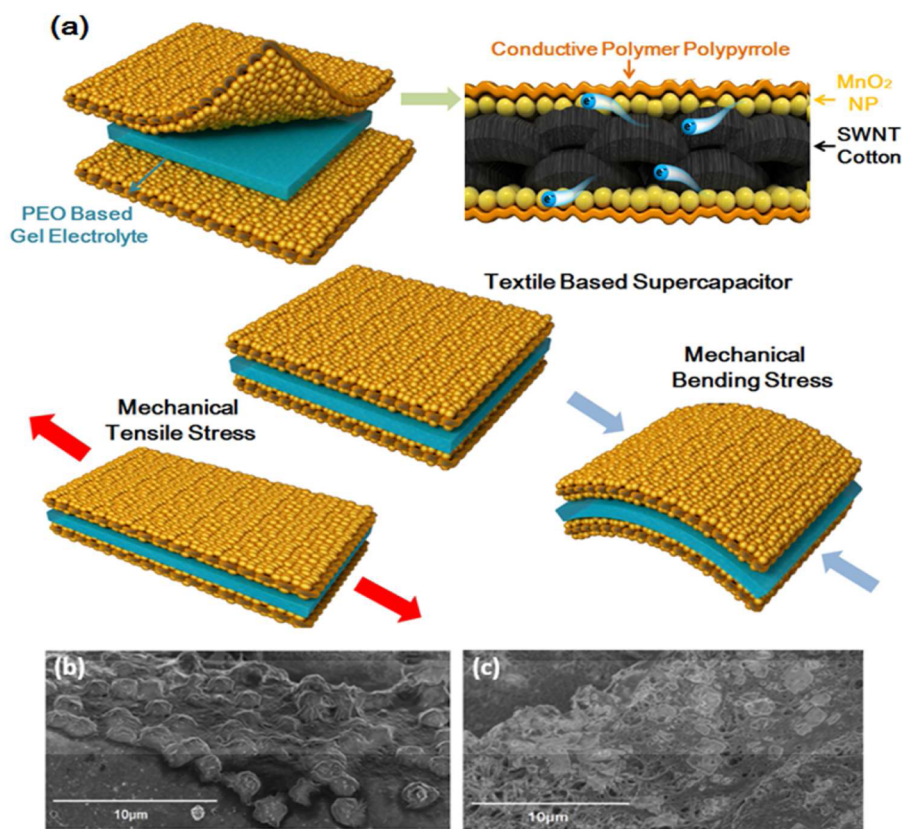


Figure 1. (a) Schematic illustration of the fabrication of polypyrrole–MnO₂-coated textile supercapacitor. SEM images of (b) MnO₂-nanoparticle-coated CNT textile and (c) polypyrrole-coated MnO₂-CNT textile.

$$s = \frac{B_0 t_0^2 + B_1 (t_1^2 + 2B_0 B_1)}{2(B_0 t_0 + B_1 t_1)} (t_1 = 0) \quad (6)$$

$$\epsilon_{\text{strain}} = \frac{y - t_0}{R} \quad (7)$$

where s is the neutral plane of the entire device, t_0 is the thickness of the entire device, B is the biaxial modulus, and R is the bending radius.

RESULTS AND DISCUSSION

The polypyrrole–MnO₂-coated CNT textile was fabricated by three-step process, as illustrated schematically in Figure 1. The first step involved coating the SWNTs on the textile fibers via dip coating. The second step involved coating MnO₂ nanoparticles on the CNT fiber by constant current electroplating of MnO₂ by using three-electrode electroplating. The third step involved coating a polypyrrole layer on top of MnO₂ nanoparticles using pulse voltage electroplating.

To evaluate the enhancement of electrochemical properties by using polypyrrole, we compared electrochemical properties of the different electrodes, CNT-cotton (CCT), MnO₂-coated CNT-cotton (MCCT) and polypyrrole–MnO₂-coated CNT-cotton (PMCCT) using charge–discharge and cyclic voltammetry tests. The charge–discharge test were performed in fixed voltage range of 0–0.85 V, and the cyclic voltammetry test compared the enclosed plot area in normalized current density versus voltage plot. Comparison of charge–discharge and cyclic voltammetry results for all electrodes are shown in Figure 2a,b. PMCCT was measured to have the longest discharge time and largest enclosed area. These results indicate that PMCCT electrode has the highest specific capacitance, as capacitance is inversely proportional to discharge time and proportional to

enclosed area. With the addition of pseudocapacitor materials, energy is stored during charge–discharge through faradic reaction, which is the electron transfer when oxidation/reduction reaction occurs between electrolyte and electrode surface. Capacity loss (difference in charge–discharge curves) is due to the faradic reaction occurring at a slower rate than charge–discharge rate of typical electrostatic double layer supercapacitor.²⁷ A 6.5% enclosed area loss was confirmed during cycling of the PMCCT electrode as shown in the CV graph, which presumably is naturally expected for the faradic reaction of polypyrrole, as reported elsewhere.^{28,29}

For comparing energy capacity of PMCCT with MCCT and CCT electrodes, the specific capacitances were calculated from charge–discharge results at varying current densities between 0.2 and 8 A/g, as shown in Figure 2c. Maximum specific capacitance was 461.0 F/g for PMCCT electrode at current density of 0.2 A/g. For all ranges in current densities, PMCCT electrode had the highest specific capacitance, followed by the MCCT electrode and then the CCT electrode. Deposition of polypyrrole thin layer is expected to hinder delamination of MnO₂ nanoparticles during charge–discharge cycles. To confirm the reduction in MnO₂ particle delaminations, we compared normalized capacitance up to 10 000 cycles, as shown in Figure 2d. MCCT electrode retained 88.6% normalized capacitance, and PMCCT electrode showed a 5.2% improvement in electrochemical reliability with 93.8% normalized capacitance after 10 000 cycles. Therefore, polypyrrole thin layer greatly enhances the electrochemical reliability by preventing delamination of the MnO₂ nanoparticles. The low modulus polypyrrole layer acts as a glue that holds the MnO₂ nanoparticles as they go through volume expansion/contraction during cycling.

To measure the increase in electrical conductivity after polypyrrole coating, electrochemical impedance spectroscopy

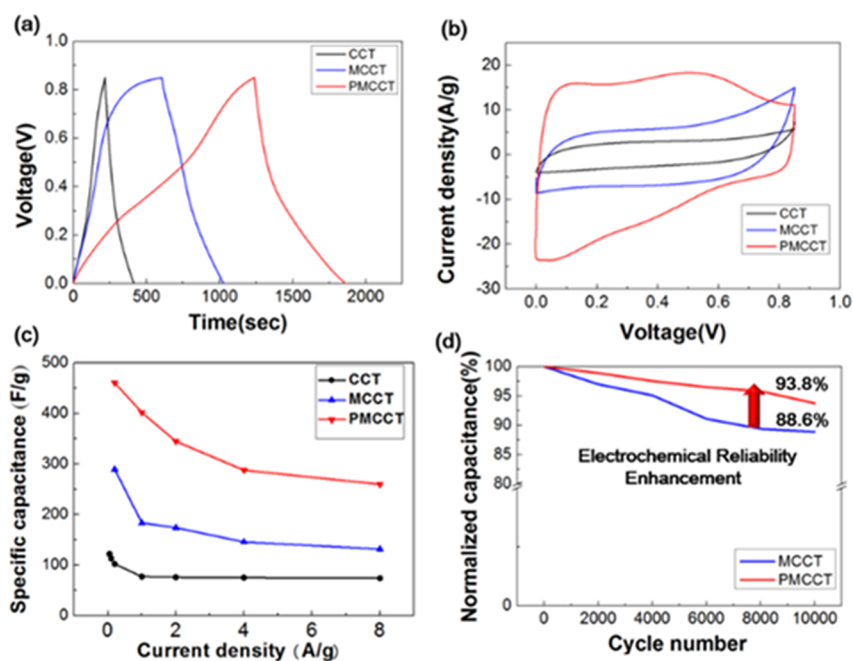


Figure 2. (a) Charge–discharge test, (b) cyclic voltammetry test, and (c) specific capacitance normalized by the mass for polypyrrole–MnO₂-coated CNT-textile (PMCCT), MnO₂-coated CNT-textile (MCCT) and CNT-cotton (CCT) electrodes. (d) Electrochemical reliability testing 10 000 cycles for polypyrrole–MnO₂-coated CNT-textile (PMCCT) and MnO₂-coated CNT-textile (MCCT).

measurements were carried out using a sinusoidal voltage input with a frequency in the range of 100 kHz to 100 mHz with a voltage amplitude of 10 mV. The equivalent series resistance (ESR) value is then determined by the real part of the Nyquist plot. In Figure 3a, the impedance of CCT, MCCT, and PMCCT are plotted together for comparison. The ESR value of MCCT was significantly increased to 76 Ω compare with the ESR value of CCT of 34 Ω , which means that electrical conductivity of overall electrode is reduced by the addition of metal oxide MnO₂ nanoparticles. However, ESR value of PMCCT was dramatically decreased to 19 Ω compared with ESR value of MCCT 76 Ω , and these results indicate that electrical conductivity was enhanced by deposition of a polypyrrole thin layer. Such an increase in the electrical conductivity of textile-based supercapacitor can improve electrochemical performance, which can play a key role in enhancing the power density.

The electrochemical properties of the different electrodes are plotted for comparison as shown in the Lagone plot in Figure 3b. For the case of MCCT, the energy density was calculated as 14.2 Wh/kg, whereas the power density of the MCCT electrode was determined as 4.9 kW/kg. Our results indicate that the energy density is significantly enhanced by the addition of MnO₂, as expected, but the power density is decreased, which is also indicated by the increased ESR value. For the case of PMCCT, power and energy density were evaluated as 22.1 kW/kg and 31.1 Wh/kg, respectively. Therefore, electrochemical performance can be maximized by using a polypyrrole thin layer because it improves the electrode electrochemical energy capacity by use of inherently high-capacity material and enhanced power density due to the high conductivity of the polymer.

Electrochemical performance of our newly developed polypyrrole–MnO₂-coated CNT textile can be compared with other reported supercapacitors and pseudocapacitors energy storage systems. For example, nitrogen-doped carbon nanofiber electrode material derived from bacterial cellulose supercapacitor was

reported to have 6.03 Wh/kg energy density but less than power density of 0.2 kW/kg.³⁰ Other examples of mesoporous carbon-based electrodes supercapacitor that yielded low energy density, power density include 3D graphene and 1D silver nanowire.³¹ Polyester cellulose paper supercapacitor yielded high energy density, but low power density.³² In comparison, our polypyrrole–MnO₂-coated CNT textile supercapacitor has a well-balanced energy and power density values of 31.1 Wh/kg and 22.1 kW/kg.

Once the supercapacitors for wearable storage systems are developed, it is crucial to confirm the feasibility of the developed system to be suitable for flexible and stretchable environments. Mechanical testing while monitoring the electrochemical performance in situ is needed. For such in situ testing, the conventionally used liquid electrolyte must be replaced with a gel-type to eliminate the difficulties associated with short circuiting, electrolyte leakage, and evaporation during strain application. Therefore, textile-based supercapacitor are assembled using PEO-based gel-type electrolyte. PEO-based electrolyte can adhere to textile electrode due its high viscosity. Gel-type electrolyte was used not only as an electrolyte but also as an adhesive between electrodes without separator. A green LED was operated using our newly developed polypyrrole–MnO₂-coated CNT textile supercapacitor. To achieve a high voltage, we combined three textile-based supercapacitors in series to increase the working voltage from that of a single supercapacitor (0.85 V) to 2.4 V, as shown in Figure 3c. Charge–discharge time was measured to evaluate the electrochemical performance, which is shown in Figure 3c. Therefore, textile-based supercapacitor can be applied to controlled electrochemical performance of energy storage system by in series connection of textile-based supercapacitors.

The application of wearable energy storage system requires the system to sustain its electrochemical performance under heavy strain, such as that imposed near the joints of the human body during movement. Therefore, the study of electrochemical

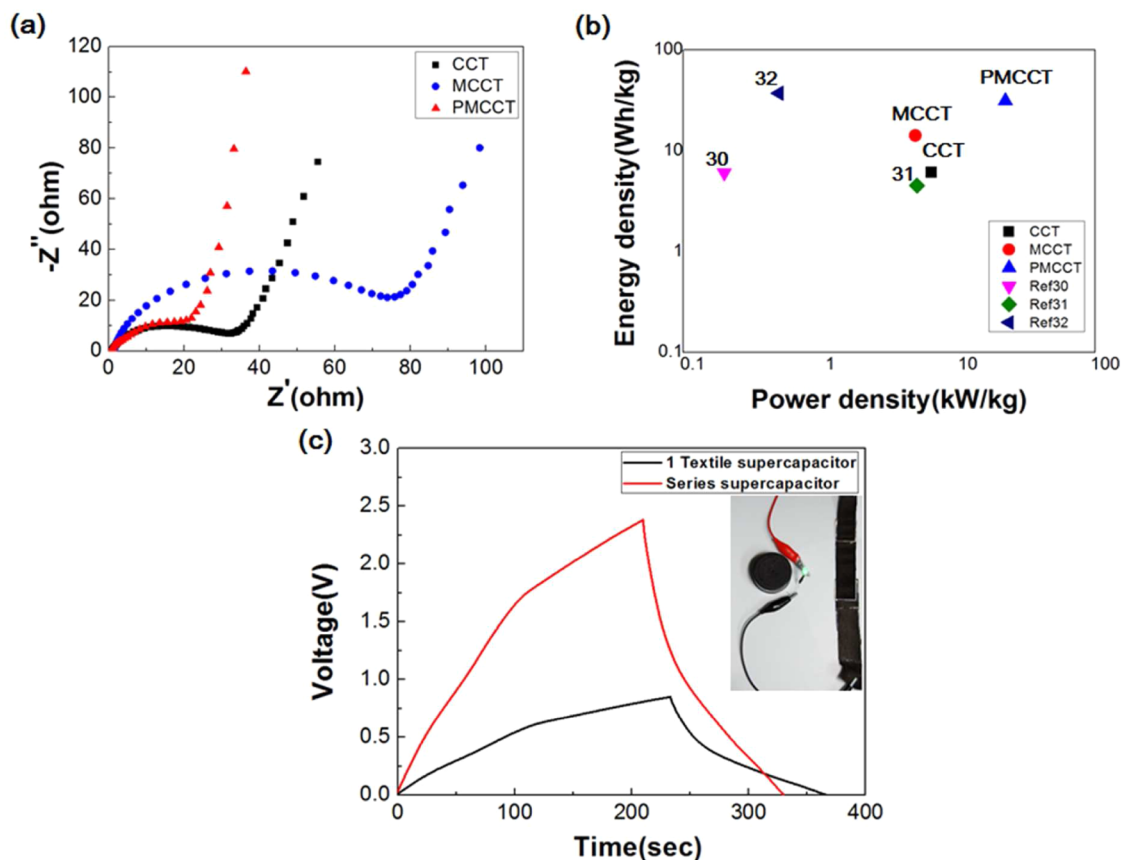


Figure 3. (a) Electrical impedance and (b) Ragone plot of polypyrrole– MnO_2 -coated CNT-textile (PMCCT), MnO_2 -coated CNT-textile (MCCT) and CNT-cotton (CCT) electrodes. (c) Charge–discharge test of single and series polypyrrole– MnO_2 -coated textile supercapacitor; (inset) to confirm energy storage, green LED was operated using series supercapacitor.

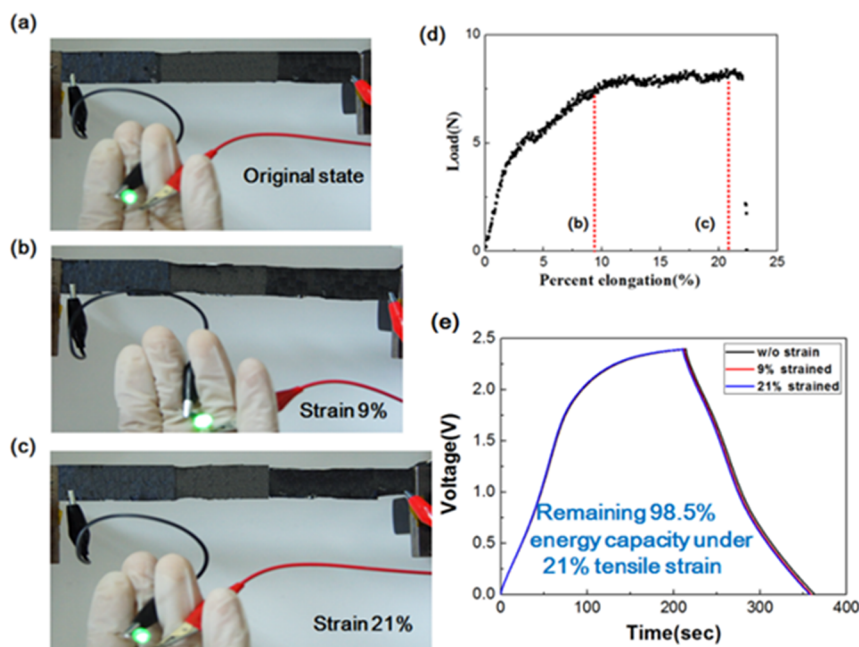


Figure 4. (a) Operation of a green LED using polypyrrole– MnO_2 -coated textile supercapacitor before application of any strain. After application of (b) 9% and (c) 10% tensile strain, and (d) the corresponding normalized load and percent elongation curve. (e) In situ changing charge–discharge time measurements under 0, 9, and 21% tensile strain.

reliability under application of in situ mechanical strain is crucial. In this study, in situ measurement of the electrochemical performance change under mechanical strain was performed. First,

in situ electrochemical performance was measured under tensile strain, and the result is shown in Figure 4d. Figure 4d shows the tensile load and percent elongation applied on the textile based

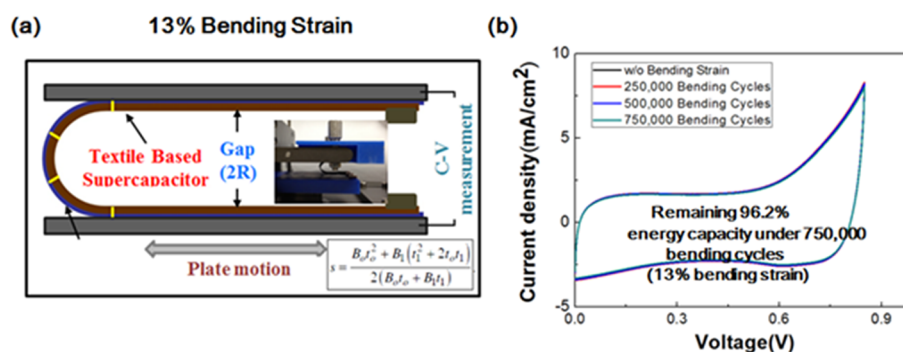


Figure 5. (a) Schematic for bending test was performed on polypyrrole–MnO₂-coated supercapacitor (b) cyclic voltammetry of supercapacitor under 13% bending strain.

supercapacitor and maximum load of 8N and 21% percent elongation was applied to the textile based supercapacitor. As shown in Figure 4e, the charge–discharge curves of textile based supercapacitor was measured to be 0, 9, and 21% percent elongation in working voltage range. At 21% percent elongation, 98.5% of the discharge time was retained compared to the original discharge time. This result indicates that the electrochemical performance of textile-based supercapacitor was stable even under mechanical tensile strain. Further evidence of stability under tensile strain can be observed by the operation of green LED at 9 and 21% elongation, shown in Figure 4a–c.

In addition to tensile testing, cyclic bending tests were also performed while the electrochemical performance was monitored in situ. Bending the fabricated textile-based supercapacitor with a thickness of 1.3 mm to maintain 1 cm gap distance results in calculated bending strain of 13%. Initial bending caused no observable change in capacitance but degradation in capacitance after cyclic bending was observed. Cyclic bending was imposed by lateral motion of the lower plate that induced center portion of the textile to be bent and straightened repeatedly. A total of 750 000 bending cycles were imposed, and intermittent CV curves were measured at 0, 250 000, 500 000, and 750 000 bending cycles, as shown in Figure 5b. The capacitance evaluated from the area under the CV curve indicated capacity retention of 98.9, 98.4, and 96.2% of initial value after 250 000, 500 000, and 750 000 bending cycles, respectively. Therefore, stable electrochemical performance with minimal change in capacitance was demonstrated for the case of polypyrrole–MnO₂-coated CNT textile under large tensile and bending strains, thereby showing its potential as a stretchable and flexible energy storage system.

CONCLUSION

A flexible and stretchable textile-based supercapacitor with high electrochemical performance and cyclic reliability using PEO-based gel-type electrolyte was fabricated and analyzed in ambient conditions. An enhanced electrochemical performance textile-based supercapacitor was achieved with an improvement of electrochemical reliability of the device by 5.2%—from 88.6% for an electrode without polypyrrole thin layer to 93.8% when coated with a polypyrrole thin layer. The polypyrrole thin layer prevents the delamination of active materials thereby enhancing electrical conductivity and energy storage capacity. The fabricated flexible and stretchable energy storage device is suitable for wearable environments as demonstrated by mechanical tensile test and bending test results, which showed 98.5% capacity retention at 21% tensile strain and 96.3% capacity retention at

13% bending strain. Therefore, due to the enhanced electrochemical performance and cyclic reliability, even under mechanical and bending strain, a textile-based supercapacitor energy storage system is an excellent candidate for application in wearable and flexible electronics.

ASSOCIATED CONTENT

Supporting Information

Description of fabrication process of the textile-based flexible-stretchable supercapacitor and measurement of areal capacitance of textile based flexible-stretchable supercapacitor. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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