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Deformable electrode architectures for energy storage applications

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2016년 2월

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Abstract

Deformable electrode architectures for energy storage applications

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Electronic devices have been surprisingly advanced as follows a Moore’s law. However, there is one electronics that hasn’t changed, energy storage systems, even though the increasing of a future needs for human integrated devices, transport and the storage of fluctuated energy sources. Especially, energy storage is of critical importance because it is a limiting factor in achieving complete and independent stretchable electronics for the next generation. Here, new type electrode architectures were developed to overcome the congested period of the energy storage systems.

First, new concepts are reported for the realization of transparent and flexible energy storage systems that are unavailable up to now, based on the interdigitated electrode design. Importantly, the technological basis for the transparent and ultra-bendable electrode without percolation is proposed and proves the excellent performances showing even at compressive and tensile deformation states.

Second, a concept of design with experimental proof was provided for an origami-type foldable electrode by a novel patterning approach. The proposed system is composed of periodically assembled isolated electrodes (IEs) and
sectionalized ion transferring paper (SITP), which are key factors for the densely packed series circuit analogues in the single system. The system shows a linear relationship between the potential window and the number of IEs, which does not have any limited asymptotic line. This system could increase energy and power simultaneously, which was conventionally not possible. Also, its folding characteristics accommodate highly stable stretching.

Third, I reported on a graphene–carbon-nanotube (CNT) layered structure for use as a stretchable electrode. In this system, graphene serves as a floating track and carbon nanotubes convert external stress into the stretching motion of the electrode. The structure provides omnidirectional deformation without inhomogeneous interface stress and slip stress between active sites and the stretching passive components. The suggested system offers significant improvement over existing methodologies for a fabricating stretchable electronics in terms of negligible passive volume, biaxial and twisted deformation, and durability. The physical characteristics of the system were revealed by first-principle calculations and three-dimensional finite-element methods.

Finally, I proposed two possibilities regarding energy storage wires. (1) I investigated the electrochemical performance of universal wire-type electrodes using an analytical derivation. From the derived equations, a difference existing between wire-type and conventional planar electrodes is verified and the fundamental limits of wire-type electrodes are identified. (2) To exclude the identified limits, I designed an electrode thread having completely different structure compared with previous wire-type electrodes. The electrode thread was designed as a dual plane-helix structure and does not show the analytical limits.

These strategies proposed here can be directly applied to energy storage systems. To show the application, simple examples were shown as a
capacitive energy storage system using an electrical double layer (EDL). Moreover, the electrode architectures can be easily extended to the other types of energy storages (e.g. lithium or Sodium ion batteries) by further studies. These concepts of new-type electrode architectures can provide noteworthy implications across a number of disciplines toward ultimate energy storage, power supply and stretchable devices for the next generation of electronics.

**Keywords:** Flexible energy storage device, transparent electrode, percolation, isolated electrode, sectionalized ion transferring paper, unlimited potential window, stretchable energy storage system, graphene-CNT layered electrode, dual planar-helix electrode.

**Student Number:** 2010-20988
Contents

Chapter 1. Introduction

1.1 Bendable and transparent electrode architectures ......................... 2
1.2 Foldable architecture for high voltage devices ............................ 3
1.3 Stretchable electrodes for various electronics ............................ 6
1.4 Dual planar helix wire-type electrodes ....................................... 9

Chapter 2. Transparent and ultra-bendable electrodes
without percolation problems

2.1 Experimental .................................................................................. 11
  2.1.1 Materials and methods .......................................................... 11
  2.1.2 Characterization .................................................................. 12
  2.1.3 Calculation of specific capacitance ...................................... 12
2.3 Results and discussion ................................................................. 13

Chapter 3. Origami-type foldable electrode chips with
integrated series circuit analogues

3.1 Experimental .................................................................................. 26
  3.1.1 Materials and methods ........................................................ 26
  3.1.2 Calculation of properties ..................................................... 27
3.2 Results and discussion ................................................................. 29
Chapter 4. Omnidirectionally stretchable, high performance electrodes based on a graphene-carbon-nanotube layered structure

4.1 Experimental .......................................................................................................................... 54
   4.1.1 First-principles calculations and 3D FEM modeling.................................................. 54
   4.1.2 Fabrication of graphene-CNT stretchable electrodes .............................................. 55
   4.1.3 Fabrication of electric surgery glove and contact lens .............................................. 55
   4.1.4 Fabrication of stretchable supercapacitor ................................................................. 56
   4.1.5 Morphology and electrochemical characterization ..................................................... 56
4.2 Results and discussion .......................................................................................................... 58

Chapter 5. Dual planar-helix type energy storage wires to circumvent universal energy lag effect

5.1 Experimental .......................................................................................................................... 82
   5.1.1 Fabrication of planar and cylindrical shape elongated electrodes ............................. 82
   5.1.2 Fabrication of dual planar helix supercapacitor wires ............................................. 83
   5.1.3 Weaving of energy storage textiles with warp and weft electrode ............................. 83
   5.1.4 Characterization and electrochemical measurement ................................................. 84
5.2 Results and discussion .......................................................................................................... 85

Chapter 6. Conclusions .............................................................................................................. 109

Chapter 7. Recommendation for Further Research ..... 111
Bibliography ......................................................................................................................112
요약 (국문초록)........................................................................................................ 122
List of publications ........................................................................................................124
List of Tables

Table 3-1. Total energy in eV for each molecular structure component and the thermodynamic decomposition voltage of poly(vinyl alcohol) (PVA) at half and full decomposition by density functional theory (DFT) calculation. ................................................................. 45

Table 4-1. The calculated total energy (eV U.C.\(^{-1}\)) of structure components. Structure components contain the CNT and graphene with various strains and graphene-CNT layered structure (AA and AB stacking). 72
List of Figures

Figure 2-1 Photographs of a transparent and flexible supercapacitor with interdigitated patterned electrodes based on vertically oriented hierarchical MnO$_2$ nanostructures; (a) flat and (b) bending state....19

Figure 2-2 (a) Process flow for fabricating a transparent and ultra-bendable supercapacitor without the same platform. (b) Schematic illustration of the transparent and ultra-bendable supercapacitor with interdigitated patterned electrodes.................................20

Figure 2-3 Pattern design and linear dimensions of an interdigitated electrode system on a transparent and flexible supercapacitor without per 1.5 cm × 1.5 cm. This area can be increased up to an area limit of the electrodeposition method (size of the counter electrode).........21

Figure 2-4 (a) Magnified optical image and (b–c) SEM images of the interdigitated patterned electrode based on vertically oriented hierarchical MnO$_2$ nanostructure in transparent and flexible supercapacitors; b) boundary of electrode and (c) inside of electrode. (d) Transmittance spectra of a PET substrate and a full cell of the transparent and flexible supercapacitor with interdigitated patterned electrode.................................................................22

Figure 2-5 (a–c) Typical shapes of CV curve were observed for the different bending states of transparent and ultra-bendable supercapacitor with interdigitated patterned electrode system; (a) flat, (b) compressive and (c) tensile bending state. Scan rate is 10mV s$^{-1}$ and bending radius is 1.5 mm (curvature is 6.7 cm$^{-1}$). (d) Cyclic voltammograms (CV, current density versus voltage) for a transparent and flexible supercapacitor with interdigitated patterned electrode based on a hierarchical MnO$_2$ structure for three different scan rates (10 mV s$^{-1}$, 30 mV s$^{-1}$, 50 mV s$^{-1}$). (e) Nyquist impedance plots for the
transient and flexible supercapacitor with interdigitated patterned electrode based on a hierarchical MnO$_2$ structure for three various bending states (flat, compressive and tensile bending state). (f) Capacitance versus cycle for the transparent and ultra-bendable supercapacitor with interdigitated electrode in before, during (compressive and tensile deformed) and after (released) deformation.

Figure 2-6 Typical shapes of charge/discharge curve were observed for the different bending states of transparent and ultra-bendable supercapacitor with interdigitated patterned electrode system; flat, compressive and tensile bending state. Current density is $150\mu$A cm$^{-2}$ and bending radius is 1.5 mm (curvature is 6.7 cm$^{-1}$).

Figure 2-7 (a) Photograph and (b) Cyclic voltammogram for a conventional sandwich type supercapacitor based on the same hierarchical MnO$_2$ structure.

Figure 3-1 (a) and (b) Schematics for the all-solid-state origami-type supercapacitor with series circuit analogues. It has periodically isolated electrodes (IEs) and sectionalized electrolytes alike with overlapping odd and even functions. (c) Two half-IEs and one sectionalized electrolyte compose a primitive cell. In a charged reaction, each IE forms opposed poles along the x direction. (d) The potential window versus number of IEs, which shows a linear relationship. The red lines show the H$_2$O electrolysis voltage and the electrolyte decomposition voltage calculated by density functional theory (DFT).

Figure 3-2 (a) Discharged and (b) charged equivalent circuits of capacitor systems with series connection. (c) Potential diagram versus location (x-axis) of charged capacitor system with series connection. The blue boxes represent conventional energy storage units. (d) and
(e) equivalent circuits of isolated electrodes (IEs) system. The red boxes represent IEs and the yellow boxes represent sectionalized ion transferring papers (SITPs). (f) Potential diagram versus location (x-axis) of IEs system. Potential gap between neighboring IEs are the same with the limited potential of conventional system.40

Figure 3-3 Potential gap between near isolated electrodes (IEs) in fully charged three IEs system (Fully charged potential is about 3.2 V). Each potential windows between near IEs is about 0.8 V, which proves the IEs are polarized well. .................................................41

Figure 3-4 Sectionalized ion transferring paper (SITP). (a) Process flow for fabricating SITP: (1) mask attached to the porous paper substrate, (2) gel polymer electrolyte (GPE) adsorbed and doctor-bladed on the same substrate, (3) mask lifted off after solidification of GPE. (b) Scanning electron microscope (SEM) image of cross section for the SITP and energy dispersive spectrometer (EDS) element mapping results for O, C and P species of poly(vinyl alcohol)/H$_3$PO$_4$. ..........42

Figure 3-5 Photographs of IEs systems. (a) Front sides of conventional type (without IE) and IEs systems with 1, 2 and 3 IEs, respectively. The red boxes enclose each IEs. (b) Back sides of the conventional type (without IE) and IEs systems with 1, 2 and 3 IEs, respectively. The sectionalized electrolytes are absorbed on the back side of the system and the yellow boxes represent each of the sectionalized electrolytes. .................................................................43

Figure 3-6 Electrochemical properties of isolated electrodes (IEs) system. Density functional theory (DFT) calculation for the decomposition voltage of Poly(vinyl alcohol) (PVA): (a) three transition states of PVA in the decomposition reaction and charge density for the carbon back-bone of the same transition states, and (b) energy profiles for the decomposition reaction of PVA. (c) Cyclic
voltammogram (CVs), (d) Charge/discharge curve (C/Ds) and (e) Ragon plot of energy system without IE and with 1, 2 and 3 IEs. Scan rate is 5 mV s\(^{-1}\) in CVs, specific current is 0.5 µA cm\(^{-2}\) based the total area of system in C/D analyses (in (d), red line denotes the thermodynamic decomposition voltage of PVA). ..................................44
Figure 3-7 Cyclic voltammograms (CV) of isolated electrode (IEs) energy storage systems with (a) 7 and (b) 11 IEs. Scan rate is 5 mV s\(^{-1}\). The system have 6.4 V and 9.6 V of potential window respectively, which proved the linearly increasing potential window with the number of IEs based on the same area systems............................46
Figure 3-8 Galvanostatic charge/discharge (C/D) curves of system with 7 and 11 isolated electrodes (IEs) with same-sized substrate. The specific currents are (a) 0.2, (b) 0.3, (c) 0.4 and (d) 0.5 µA cm\(^{-2}\), respectively. (e) Ragon plot of IEs system with 3, 7 and 11 IEs. .........................47
Figure 3-9 Galvanostatic charge/discharge (C/D) curves of system with zero, one, two, and three isolated electrodes (IEs). The specific currents are (a) 0.2, (b) 0.3 and (c) 0.4 µA cm\(^{-2}\) based the total area of system, respectively. The red lines show the decomposition potential of poly(vinyl alcohol) \(\times\) \(n\) V (\(n = \text{number of IEs} + 1\))..........................48
Figure 3-10 Nyquist impedance plots of energy system without isolated electrode (IE) and with 1, 2 and 3 IEs. Applied potential is 0.4, 0.8, 1.2 and 1.6 V, respectively. Ac amplitude is 10 mV and frequencies of 100 mHz – 50 kHz. The curves for the various IEs systems have tangent line that intersects the real axis, which caused by synergetic effect of capacitance and mass transfer resistance caused the electrode system with vertical formation...........................................49
Figure 3-11 Origami-based stretchable energy storage system. Photographs of an origami-based stretchable energy system with three IEs for stretching at (a) –60 % (compressible), (b) 0 % and (c) 30 % (tensile)
along the x direction. Cyclic voltammogram (CVs) of the system at (d) –60 % (compressible), (e) 0 % and (f) 30 % (tensile). Three dimensional finite-elemental method (3D FEM) modeling of the stress distribution for the same system in the same (g) compressible and (h) tensile deformation states.

Figure 3-12 3D finite-elemental method (FEM) analyses of origami-based stretchable energy storage system. (a) and (b) Deformation analyses at compressive (- 60 %) and tensile (30 %) decomposition states. (c) and (d) Strain analyses at the same decomposition state, respectively.

Figure 3-13 Safety factor analysis of origami-based 7 folding 3 isolated electrodes (IEs) system. (a) -60 % compressive and (b) 30% tensile decomposition states.

Figure 3-14 Capacitance retention versus cycle number for the origami-type three isolated electrodes (IEs) system septuple-folded in a zigzag formation at various deformation states.

Figure 4-1 Atomic-scale properties of graphene–CNT and actin–myosin interactions. (a) SEM image of graphene–CNT interface. (b) Models for the progressive movement of myosin along actin in a living cell and of CNTs along graphene in an inorganic system. (c) The minimum energy path for the movement of myosin (or CNT) on actin (or graphene) for a living cell and inorganic system. (d) Differential charge densities $\rho_{\text{diff.}} = \rho_{\text{total}} - (\rho_{\text{graphene}} + \rho_{\text{CNT}})$ of graphene–CNT interface with AB and AA stacking between hexagonal carbon chains. Positive (yellow) and negative (blue) values are plotted on the same isosurfaces.

Figure 4-2 (a) Top views of the graphene-CNT structures at AB and AA stacking after the optimization by DFT calculation. The C atoms in
graphene and CNT are represented by smaller brown and larger yellow spheres, respectively. The black square represents the unit cell of the structure for the calculations. Side views of AB and AA stacking are shown in (b).

Figure 4-3 Microscale structure of graphene–CNT stretchable electrode. (a) Compressing and releasing of muscle in a human body through actin–myosin interaction. (b) Optical images and equivalent stress simulation (finite element model (FEM) calculation) of graphene–CNT electrodes at uniaxial, biaxial, and twisted deformation. (c) SEM images of graphene–CNT-layered structure at biaxial stretching (80%) and releasing. (d) High-resolution SEM images of individual crumpled structures in graphene–CNT networks at the point of stretching and releasing. The graphene layers are undeformable and separated from each other. The CNT cluster under the graphene flakes are randomly bending and stretching.

Figure 4-4 Schematics of (a) drifting graphene on the surface of CNT cluster with an actin-myosin coupling analogue and (b) a conventional stretchable circuit without the coupling effect. The upper surface of the CNT cluster is in a state of stretching, with drifting motion of undeformable graphene flakes.

Figure 4-5 Fabrication of graphene-CNT networks with crumpled structures. i) Two dimensional stretching of elastic substrates. ii) Loading of CNT cluster and graphene flakes. iii) Releasing of the substrate and generated crumpled structure.

Figure 4-6 Safety factors for various stretching deformations. Inorganic actin (graphene)-myosin (CNT) at i) uniaxial, ii) biaxial and iii) twisted deformation. The safety factors over 1 indicate that the models are physically feasible.

Figure 4-7 Optical images of graphene-CNT electrode surface. (a) Released structure and (b) uniaxial stretched structure.

Figure 4-8 Graphene–CNT-layered structure on various substrates. (a) Sheet conductivity and normalized resistance of graphene–CNT-layered
structure on rubbers at different strain levels during 100 stretching–releasing cycles. (b) Differential sheet conductivity of graphene–CNT-layered structure, which shows the percolation threshold. (c) Normalized sheet conductivity of graphene–CNT-layered structure constructed on balloon during 100 expansion–deformation cycles. (d) Optical images of graphene–CNT-layered structures on the balloon without and with 140% stretching and shear deformation. (e) Equivalent strain, stress, and shear stress in the $x$–$y$ plane of balloon with graphene–CNT-layered structure by three-dimensional (3D)-finite element model (FEM). Black dotted boxes indicate the location of graphene–CNT layers. (f) Optical images of a light-emitting diode (LED) mounted on a surgery glove without and with finger bending. The images were obtained without external illumination. (g) Optical images of contact lens with LED circuit, collected with (up and left) and without (up and right) external illumination. Photographic images at different focal lengths as captured by CMOS image sensor with and without the electric lens.78

Figure 4-9 (a) Side views and (b) top views of the strained graphenes with identical isosurfaces of calculated total charge densities. (c) The relative energy versus uniaxial strain of graphene in $x$ direction. ... 80

Figure 4-10 Dielectric energy storage properties of a graphene–CNT-layered structure. (a) The galvanostatic charge/discharge curve (C/D) of graphene–CNT layers on PVA/H$_3$PO$_4$ film at a constant current of 0.15 A g$^{-1}$ while the structure was stretched at a constant speed of 0.4% strain per minute. (b) Representative C/Ds at various current densities (0.15–0.75 A g$^{-1}$) without strain and with stretching (80%) and twisting (360°). (c) Representative cyclic voltammetry curves (CVs) at various scan rates (1–10 mV s$^{-1}$) without strain and with stretching (80%) and twisting (360°).
Figure 5-1 X-ray photoelectron spectroscopy (XPS) spectra for the C1s regions of carbon wire a) before and b) after elimination of the sizing agent. The XPS spectra are composed of three contributions at ca. 284.6, 286.7, and 288.6 eV which correspond to carbon sp2 bonding (C−C), epoxide/hydroxyl groups (C−O), and carbonyl/carboxyl groups (C=O), respectively. (a) Before the elimination of the sizing agent, the carbon wire showed a characteristic peak consistent with C−O bonds, which attribute to the presence of oxygen containing functional groups in epoxy resin. (b) After the elimination step, the peak associated with C−C bond becomes predominant while the intensity of the peaks related to oxidized carbon are significantly decreased. The results indicate that most of the epoxy resins used as sizing agent had been removed...

Figure 5-2 Illustrative description of the distribution in the electric field around charges spaces of (a) plane type and (b) cylindrical type. The electric field vectors resulting from both types of charged spaces can be approximated to be uniformly distributed. The vectors are directed normal to the charged surface of electrodes.............

Figure 5-3 Schematics of an electrical-double-layer (EDL) on a planar electrode and a cylindrical electrode. (a, b) The sophisticated pictures of EDL on (a) planar electrode and (b) cylindrical electrode. (c, d) Schematics of (c) dual planar-helix and (d) double helix wire-type supercapacitors. (e, f) Optical images of (e) dual planar-helix and (f) double helix wire-type supercapacitors. The scale bars are 10 mm in length. .................................................................

Figure 5-4 The relationship between potential (ψ) and dimensionless location of electrodes in planar and cylindrical supercapacitors. (a, b) Cross-section of potential distribution in (a) plane and (b) cylindrical type electrodes. (c) Representative spatial voltage profile between two
electrodes in high concentration of electrolyte. Each dotted line shows the border limit of stern layer and diffuse layer from GCS model. Voltage profiles are symmetrical around both electrodes and become constant in the diffuse layer. ........................................... 97

Figure 5-5 Sectionalized schematics of (a) planar electrode and (b) cylindrical electrode for analytic calculation. The distance between Gaussian surface and electrode is the same as the stern layer thickness and the radii of solvated counter ions in the electrolyte. ................................. 98

Figure 5-6 Process flow of twisting method for a dual planar-helix wire-type supercapacitor. The scale bar is 4 cm. .................................................. 99

Figure 5-7 Structure difference of dual planar-helix and double helix wire-type supercapacitors. (a-d) Scanning electron microscope cross-sectional images of (a, c) dual planar-helix and (b, d) double helix wire-type supercapacitors. (c) and (d) are high resolution images. The scale bars are 100 μm in length. ............................................ 100

Figure 5-8 Linear sweep voltammograms of planar and cylindrical-type electrode. The resistances of planar and cylindrical electrode are 3.03 Ω and 2.94 Ω, respectively. ............................................ 101

Figure 5-9 Electrochemical properties of dual planar-helix and double helix wire-type supercapacitors. (a) Cyclic voltammograms of dual planar-helix and double helix wire-type supercapacitors at various scan rates (3, 5, 10, 20, 30 and 50 mV s$^{-1}$). (b) Galvanostatic charge-discharge profiles of dual planar-helix and double helix wire-type supercapacitors at various current densities (4, 6, 8, 10, 15 and 20 mA cm$^{-3}$). ................................................................. 102

Figure 5-10 Long cycle stability test of the carbon based dual planar-helix wire-type supercapacitor during 10,000 charge-discharge. Retention of 90% was obtained after 10,000 cycles. .......................................... 103

Figure 5-11 Cyclic voltammograms of dual planar-helix wire-type
supercapacitor before and after twisting at various scan rates (5, 10 and 30 mV s\(^{-1}\)). ................................................................. 104

Figure 5-12 Woven textile composite with warp and weft electrodes. (a, b) schematics of \(n \times n\) warps or wefts connected in (a) parallel and (b) series and optics images of woven textile composited with 6 × 6 warps or wefts. In the schematics, the red lines and blue lines show positive and negative charged yarns, respectively. In (b), center line appears location of cutting line of sectionalized electrolyte. (c, d) Cyclic voltammograms and charge/discharge curves of the textile supercapacitor with (c) parallel and (d) series circuit analogues. In c), the red dots indicate the characteristic in bending deformation and the gray dots show that in flat. The blue lines in (d) show the stable potential window (0.8 V) of single supercapacitor wires. . 105

Figure 5-13. Three dimensional finite-elemental method analyses of bent carbon wire. (a) Design of mesh for un-deformed carbon wire. (b) Equivalent stress, (c) equivalent strain and (d) safety factor analyses of the bent carbon wire. The scale bar is 2 mm in length and the curvature of bending deformation is 4 cm\(^{-1}\) ........................................ 106

Figure 5-14. Electrochemical performance of the textile supercapacitor with parallel circuit analogue (6 × 6 warps or wefts). Comparative analyses were conducted between flat and rolled textiles. The red and dark lines indicates flat and bent one, respectively. The figure on the right is the rolled textile supercapacitor. a) Cyclic I for different scan rates. The \(C_{sp}s\) calculated from the CV curves are 1.54, 1.37, 1.16, 0.95, 0.85, 0.70 F cm\(^{-3}\) in flat (gray) and 1.76, 1.55, 1.30, 1.07, 0.94 and 0.78 F cm\(^{-3}\) in bended textile (red), at the scan rates of 3, 5, 10, 20, 30 and 50 mV s\(^{-1}\), respectively. The latter exhibited a slightly increased capacitance. This enhancement can be attributed to more intimate contact between compressed interfaces.
of each electrode due to the bending status. b) Galvanostatic charge-discharge curves for different current densities. The $C_{sp}$s calculated from the charge-discharge curves are 2.40, 2.15, 1.98, 1.86, 1.64 and 1.50 F cm$^{-3}$ in flat (gray) and 2.78, 2.46, 2.23, 2.07, 1.79 and 1.62 F cm$^{-3}$ in bended textile (red), at the current densities of 4.43, 6.63, 8.85, 11.07, 16.6 and 22.13 mA cm$^{-3}$, respectively. (c) Optics image of textile supercapacitor with a bent structure (The curvature is 4 cm$^{-1}$).

Figure 5-15. Electrochemical performance of the 6 × 6 textile supercapacitor with series circuit analogues. The blue line indicates stable potential window (0.8 V) of a single wire. a) Cyclic voltammograms for different scan rates. Two equivalent sets of supercapacitors in a fabric exactly double the potential window (1.6 V) without any side reactions. The $C_{sp}$s calculated from CV curves are 306, 265, 221, 185, 163 and 140 mF cm$^{-3}$, at the scan rates of 3, 5, 10, 20, 30 and 50 mV s$^{-1}$, respectively. b) Galvanostatic charge/discharge curves for different current densities. The $C_{sp}$s calculated from C-D curves are 800, 673, 599, 555, 483 and 434 mF cm$^{-3}$ at current densities of 2.95, 4.43, 5.9, 7.38, 11.07 and 14.75 mA cm$^{-3}$, respectively. 

.....108
Chapter 1. Introduction

Electronic devices have been surprisingly advanced as follows a Moore’s law. However, there is one electronics that hasn’t changed, energy storage systems, even though the increasing of a future needs for human integrated devices, transport and the storage of fluctuated energy sources. Especially, energy storage is of critical importance because it is a limiting factor in achieving complete and independent stretchable electronics for the next generation. Here, new type electrode architectures were developed to overcome the congested period of the energy storage systems. The strategies proposed here can be directly applied to energy storage systems. To show the application, simple examples were shown as a capacitive energy storage system using an electrical double layer (EDL). The EDL capacitor is one of more promising energy storage systems for the next generation because of its unique properties including a variety of fabrication methods, wide range of operating temperatures, and safety. Moreover, the electrode architectures can be easily extended to the other types of energy storages (e.g. lithium or Sodium ion batteries) by further studies.
1.1 Bendable and transparent electrode architectures

Transparent and flexible electronics are promising devices for the near future. These include multifunctional portable electronics, such as cell phones, electric books and wearable PCs. Elements of novel electronic devices that are transparent and flexible have been fabricated including transistors [1-3], optical circuits [4], displays [5,6], touch screens [7], and solar cells [8], for the various applications. However, fully integrated, transparent and flexible devices have not been realized, because practical reliable energy storage modules with transparency and flexibility have not yet been developed.

To date, some reports have described transparent and flexible supercapacitors and most of these efforts have involved randomly distributed electrode networks on the electrode for achieving transparency, such as nanotubes and nanowires [9-12]. However, reducing the thickness to be appeared the transparency in these systems poses a serious problem, namely percolation. For bulk-like opaque materials, conductivity and capacitance are intrinsic properties. However, when nanostructured films become thin and sufficiently transparent, their electrical and electrochemical properties become thickness-dependent [9]. In practice, this means that the energy densities of systems can progressively degrade as the supercapacitor becomes transparent. It is apparent that, if randomly distributed electrode networks are applied to transparent supercapacitor electrodes, percolation becomes a major factor.

In order to circumvent the percolation problems associated with transparent and flexible supercapacitors, I report herein on my progress in
attempting to produce transparent and ultra-bendable electrode systems without percolation.
1.2 Foldable architecture for high voltage devices

Energy storage systems with patterning-assembly technology have been developed rapidly in recent years because of the need for compact and flexible electronics [13-21]. In fabrication of film type energy storage devices, the patterning approach facilitates the improvement in performance owing to the high surface-to-volume ratio and to the lack of need for binders or separators [13-15,17,18]. Furthermore, the assembly endorses a high degree of bending and stretching [16,19-21]. These characteristics are essential for multifunctional electronics such as wearable computers, electronic books and cell phones with high electrical performance. Representative energy storage performance could be expressed by energy \( E \) and power \( P \). Each of \( E \) and \( P \) is positively related to the stable potential window. The potential window is much more important in a supercapacitor system, as is evident by the following equation:

\[
E = \frac{1}{2} CV^2 \quad \text{and} \quad P = \frac{E}{t} \quad (1-1)
\]

where \( C \) is the capacitance of the material, and \( t \) is time. The potential window is, however, easily ignored in developing a high performance supercapacitor system because the property is limited by the decomposition potential of the electrolytes used. In order to increase the potential window, reports have employed replacement of the electrolyte (from 0.8 V in a Na\(_2\)SO\(_4\), aqueous phase to 2.7 V in BF\(_4\), an organic phase (acetonitrile)) [22,23]. The construction of asymmetric cells also has been proposed as another strategy [24-26]. Despite a slight increase in the potential window, these systems are still limited by the problem of electrolyte decomposition and by electrode selection.
The conventional strategies to increase the electrical performance of supercapacitors have involved a development of materials with high $C$ [26-31]. To realize the material with high $C$, fabrication of a structure with a large surface is necessary. Expressed as an equivalent circuit, the structure can be simplified to an integrated parallel circuit. The intent of parallel circuit analogues is to increase capacitance. However, it also inevitably creates a situation where the $E$ and $P$ of a system are in competition because the specific surface area has a negative association with the diffusion mobility of ions [32-35].

As an alternative, recent research has reported on the development of film-type energy storage devices with series circuits which have high electric performance and especially a high potential window [36-39]. The series circuit, however, requires external circuits including additional resistance and involves an unnecessary volume in the system. Patterned supercapacitors with series connections also have unnecessary building blocks, which means that the systems cannot avoid having additional resistance and a decrease in the volumetric (or area) based electric properties.

To address the above-mentioned issue, I demonstrate an all-solid-state, origami-based, and stretchable electrode system with integrated series circuit analogues. The new energy system is composed of periodically isolated electrodes (IEs) and sectionalized electrolytes which are key factors for densely packed series connections. In charging and discharging, each of the IEs follows the polarization mechanism and the mechanism involves the IEs functioning simultaneously as both a positive electrode and negative electrode in the same region. This results an unlimited increasing potential system without any unnecessary volume in the cell and additional resistive
behaviour.

I prove the system has a linear relationship between the potential window and number of IEs, where no upper limit is associated with this relationship. The IE system permits $E$ and $P$ to be increased simultaneously and also engages in an origami type arrangement that provides highly stable folding. These characteristics are necessary for portable consumer electronics in the next generation.
1.3 Stretchable electrodes with various electronics

Ingenious ideas for fabricating stretchable wavy structures or materials for use in stretchable electronics have been proposed [40]. However, strategies that have been proposed are directed toward only phenomenological characteristics of soft materials with obvious limits, such as the significantly large passive volume of the stretched structure and the low and irreversible performance of stretchable materials [41,42]. Conventional technologies for stretchable electronics are composed of a stretchable bridge and a rigid operating site. Stretchable bridges have successfully conferred deformability to these electronics. However, significant interfacial resistance between the stretchable bridge and the rigid operating site is common, which fundamentally decreases operational stability and durability. Recently, researchers have begun to investigate stretchable supercapacitors in their primary stages [21,39,43-45]. Energy storage is of critical importance because it is a limiting factor in achieving complete and independent stretchable electronics for the next generation. Moreover, supercapacitor is one of excellent alternative energy storage systems because of its high power density and device reliability. However, the system also does not circumvent above general limits of the conventional stretching strategies.

To overcome the limitations of stretchable energy storage systems and electronics, I presented first-principles calculations and experimental proof for graphene–carbon-nanotube (CNT)-layered electrodes, a system inspired by the underlying principle of the motion of human muscles. Graphene is one of the best candidate materials in electronic systems, e.g., printed circuit boards, thin-film transistors, light-emitting devices, solar cells, and various
sensors [46]. Especially, the low-dimensional material is also considered to be the best candidates currently available for use in supercapacitor electrodes because of their high interface charge separation [47-49]. To fabricate a stretchable graphene structure, several studies have made use of conventional techniques: fabrication of a graphene wavy structure and intensification of its stretchable properties. However, the graphene is brittle, and its advantages, i.e., high electric, mechanical, and thermal properties, diminish abruptly and irreversibly in the deformed state [42,50]. In conclusion, the objective of this study was to investigate the use of the rigid and brittle form of graphene as an operating site for stretchable electronics in an attempt to eliminate the interfacial resistance.

A typical cell in living bodies that undergo semi-permanent and reversible stretching is the sarcomere in muscle tissue [51]. Sarcomeres include myosin molecules that function as molecular motors and actin filaments that act as tracks that direct the motion of the motor assembly [51,52]. In the same manner, undeformable graphene can act as a track, and deformation can be accomplished using a stretching component as a motor riding on the graphene track. It is reasonable to use a CNT cluster as the motor because of their significant stretchability and stability [53,54]. CNT cluster can be attached to the graphene surface with van der Waals interactions caused by graphitic AB stacking [55]. In this system, the graphene serves as a floating track and the CNT cluster converts external stress into the stretching motion of the electrode. The graphene and CNT cluster are bonded to form a two-dimensional homogeneous interface, which can solve the problem of inhomogeneous interface stress. The graphene–CNT structure also has negligible slip stress and no passive surface for stretching utilization. Thus,
this structure shows multifunctionality that was previously unachievable, \textit{i.e.}, omnidirectional stretching and energy storage via the formation of a large surface electrochemical double-layer.
1.4 Dual planar helix wire-type electrodes

Wire-shaped energy storage systems are becoming a cutting edge technology in energy-science field within the past decade [56,57]. Such energy systems are taking center stage for application to post-modern electronics and related multidisciplinary fields such as fashion and culture [58-60]. Until now, the mainstream direction in modern electronics (and energy storages) including flexibility, wearability and implantability have involved the use of conventional planar systems [61,62]. However, the two-dimensional structure of the conventional formats has hindered their development in terms of performance and moldability. Compared with two-dimensional planar formats, wire-types can be easily integrated into unique structures such as variety of textiles that can be used in our daily life [57-60].

Although one-dimensional structures can be strong, challenges fundamentally remain in the use of wire-type energy storage. In conventional energy storages, energy is simply improved, either by increasing the specific energy of materials or widening the operational voltage range [63,17]. However, wire-type energy storages still have a low energy density even in cases of the systems that include cutting edge materials in energy-science field, such as high-surface carbon allotropes for improving electrical double layer (EDL) charge and inorganic compounds or conducting polymers inducing faradaic reaction [64-72]. From the standpoint of physics, such a bottleneck is reasonable because the current technologies associated with energy storage wires do not satisfy the theoretical assumptions of electromagnetism that have been in use for the past several decades. For example, in an ordinary charged plane, the electric field is assumed to be
uniform and to have a one dimensional direction. On the other hand, the electrodes in wire-type energy storage have a cylindrical structure which actually causes a two-dimensional and decaying electric field [72]. In spite of the analytical problem, the exact potential distribution and performance model for wire-type energy storage, including a double-helix structure have not been exploited until now days. A theoretical analysis is one of most important aspects for the sustainable development of the energy storage field in next generation.

Here, two possibilities regarding energy storage wires were proposed. (1) The electrochemical performance of universal wire-type electrodes using an analytical derivation was investigated. From the derived equations, a difference existing between wire-type and conventional planar supercapacitors was verified and the fundamental limits of wire-type supercapacitors were identified. I refered to this limit as an ‘energy lag effect’. (2) To exclude the identified limits, thread-type electrode having completely different structure was designed, compared with previous wire-type energy storage systems. The thread type electrode was designed as a dual plane-helix structure and does not show performance limits, experimentally and analytically. Finally, the structure was applied to a flexible textile and an integrated parallel and series circuit analogous to show its structural advantage compared to a conventional wire-types with cylindrical electrodes.
Chapter 2. Transparent and ultra-bendable electrodes without percolation problems

2.1 Experimental

2.1.1 Materials and methods

A positive photoresist layer was spin coated and developed on a PET substrate using a photomask (MA-6, Karl-suss). A Cr layer and Au layer were sequentially thermally evaporated onto the same layer to serve as an adhesion layer and a supercapacitor current collector was applied (ALPS-C03, alpha plus). Vertically oriented hierarchical MnO₂ structure was electrodeposited on the surface of the Au layer. For electrodeposition, the platform was immersed in aqueous solutions of Mn(NO₃)₂ (0.02 M) and NaNO₃ (0.1 M) (WPG100, Wonatech). The platform was used as the working electrode, and a Pt electrode was used as the counter electrode, an Ag/AgCl electrode used as the reference electrode, and a constant current of 100 μA cm⁻² was applied by means of a 10 min deposition time. The remaining photoresist was lifted off the photoresist with acetone followed by an overnight drying at room temperature and pressure. A H₃PO₄/PVA gel electrolyte was prepared by mixing PVA powder with water (1 g of PVA / 10 ml of H₂O), H₃PO₄ (0.8 g) together. The mixture was then heated to around 358K under vigorous stirring until the solution became clear. After cooling down and vaporizing about 48 h under ambient conditions, the electrolyte solidified to form an adhesive gel. After attaching the
interdigitated electrode platform and gel membrane electrolyte, a transparent and flexible supercapacitor with interdigitated electrodes was finally produced.

2.1.2 Characterization

Magnified optical image image and SEM images of micro electrodes in the device were obtained using an optical microscope (HAL 100, Carl Zeiss) and field-emission scanning electron microscope (AURIGA, Carl Zeiss). UV-visible (UV-Vis) spectroscopy (Agilent 8453, HP) is used to determine the transmittance of each elements of device. CV and EIS measurements were carried out using a computer-controlled potentiostat (Iviumstat, Ivium) and C/D measurements were carried out using galvanostat (ZIVE sp2, ZIVE LAB).

2.1.3 Calculation of specific capacitance

The specific capacitances of symmetrical supercapacitors are calculated as follows. The capacitance ($C$) was calculated using the voltammetric discharge integrated from the cyclic voltammogram according to the following equation [86];

$$C = \frac{\int i \, dt}{\Delta E} = \frac{Q}{\Delta E} \quad (2 - 1)$$

where $i$ is the current (A), $t$ the time (s) and $\Delta E$ is the potential window (V).

The specific capacitance ($C_{sp}$) is [87-89];

$$C_{sp} = \frac{4C}{M} \quad (2 - 2)$$
where $M$ is the total weight of both the positive and negative electrodes.

### 2.2 Results and discussion

The characteristics, transparency and flexibility, behind this conceptual supercapacitor can be seen clearly in optical images (Figure 2-1). This prototype device has a capacitance of 405 F g$^{-1}$ and no percolation effects are associated with it. This value is about 5~10 times higher than the values reported for currently available random distribution transparent supercapacitors, such as carbon nanotube electrodes (50 F g$^{-1}$), graphene electrodes (100 F g$^{-1}$), polyaniline/carbon nanotubes as a conducting polymer electrode (55 F g$^{-1}$) and In$_2$O$_3$ nanowires as transition metal oxide electrodes (65 F g$^{-1}$), respectively [9-12]. Moreover, this conceptual system can load more electrode mass than a conventional randomly distributed electrode. All of these capacitance values are based on the electrode mass of the systems.

To produce this energy storage device, I modified a strategy for designing interdigitated patterned electrodes that are used in a large-scale system in my recent research [17]. Interdigitated patterned electrodes have attracted considerable interest, due to their high performance compared to conventional sandwich types. However, little information is available concerning large-scale interdigitated supercapacitor systems before my previous research [14,15,17,34,36]. In the case of a transparent and flexible supercapacitor, large-scale patterned electrodes also have several advantages: (1) the percolation problem can be solved, because the sectionalised pattern does not have an uncombined cluster of active materials that cause a percolation effect in random distribution systems, (2) the pattern assigns a
designated location for the micro electrode, which eliminates depth limitations associated with electrodes for transparency and (3) in the interdigitated system, both the positive and negative electrode are patterned on one substrate, which permits an ultra-bendable system to be easily produced.

In a random distribution sandwich type energy storage system, the purpose of transparency is to reduce the depth of the active materials down to much less than their optical absorption length [9-12]. For the electrode networks having transparency (above the percolation threshold), electrochemical performance, such as conductivity and specific capacitance, follow the percolation scaling law [9]. Transparency is also degradable upon the staking of positive and negative electrodes [9-12,73]. However interdigitated electrode patterns prevent the degradation of electrochemical performance and achieve transparency simultaneously, because both characteristics are not reciprocal in this system; in such a system, transparency involves a horizontal gap in the opaque electrode, not a reduction in the amount of active materials. In addition, this system also provides both stable bending characteristics and no necessity of complicated cell assembly (e.g. accurate alignment). These properties are distinctive points of the system compared to micro grid system batteries with sandwich-type configuration previously reported [35,73].

My approach for fabricating conceptual transparent and ultra-flexible supercapacitors involved four steps, which are outlined in Figure 2-2 and 2-3 [17]. The first step involved the use of a positive photoresist on a polyethylene terephthalate (PET) substrate for patterning and developing. PET substrates are widely used in optoelectronic devices due to their low
cost, flexibility, and high transparency. The second step involves the sequential deposition of an Au film and an active material film on the PET substrate. My proof-of-concept studies are based on MnO$_2$ as an active material, the most well-known member of electrode for supercapacitor with excellent specific capacitance, although the method is not limited to this material [74-76]. The large area of the Au film serves as a conformable support for the uniform deposition of a MnO$_2$ film. The third step involves creating a lift-off photoresist with a large area of MnO$_2$ film from the PET substrate, which results in a lift-off MnO$_2$ film following the photoresist pattern. This method has some advantages for large area transparent and flexible electronics for practical use [17]. First, the MnO$_2$ structure can be deposited as a large uniform film on an interdigitated pattern and second, the deposited MnO$_2$ film is precisely cut, which eliminates any short circuits [17]. In the last stage, the fabricated platform and a piece of transparent gel electrolyte (poly(vinyl alcohol) permeated with phosphoric acid (PVA/H$_3$PO$_4$)) are assembled. Previous research has documented that the gel membrane is well known to be elastic and highly transparent [24,36,77,78].

Figure 2-4 provides detailed information on the microstructure of electrodes in a full cell of transparent and flexible supercapacitor chips. As shown in Figures 2-4(b) and 2-4(c), the microelectrode is comprised of vertically aligned hierarchical MnO$_2$ structures. These hierarchical structures are produced as the result of the electrochemical deposition [75,76], and would be expected to not only increase electrolyte ion mobility but also be effectively maintained in a severe bending state from the horizontal direction. The image (Figure 2-4(a)) also verifies that the boundary for each MnO$_2$ microelectrode and transparent space between the electrodes is well-defined.
on a micro-scale and the opaque regions cover only a small portion of the overall area of the device, as illustrated in Figure 2-3.

Since the interdigitated electrode is indistinguishable from the transparent substrate, the dimensions of the lines need to be less than the resolution of the human eye [73]. From calculations of the Rayleigh resolution limit, the theoretical angular resolution of the human eye is about $1.22 \times 10^{-4}$ radians, which means that the resolution of the human eye is 37 μm when the distance between the eyes and device is 30 cm (the actual resolution is about 90 μm when the eyesight is 1.0). I prepared interdigitated electrode patterns of 30 μm, which causes the entire device to appear transparent. If the areal portion of the opaque patterned region is $1 - \alpha$, the theoretical transparency of the whole device is $\alpha$ [73]. As shown in Figure 2-4(d), The fabricated supercapacitor showed a transmittance of 50 % in the visible and near infrared, which is 70 % lower than the theoretical value based on the area of the electrode materials in the design (The areal portion of the opaque region is 30 %, indicating a theoretical transparency of 70 %). In this case, the PET substrate is not fully clear, and exhibits a transmittance of 70 % and the transmittance ratio for the full cell supercapacitor and the PET substrate is about 70 %, which is the same as the theoretical value based on the area of electrode materials in the design.

These electrochemical properties and the resistive behavior of the prepared devices were examined by cyclic voltammetry (CV), galvanostatic charge/discharge (C/D) and electrochemical impedance spectroscopy measurements (EIS), and the data are shown in Figures 2-5 and 2-6. The typical sample is prepared by a 10 min period of electrochemical deposition, followed a MnO$_2$ mass loading of 40 μg cm$^{-2}$ in the electrode grid [74]. Its
depth is higher than absorption length of MnO$_2$ therefore the loading of this amount of mass is impossible in conventional randomly distribution method for transparency. According to percolation, the specific capacitance of supercapacitor decreases exponentially when the capacitor becomes transparent [9]. For example, the specific capacitance of previously reported random deposition thin film supercapacitors decreases substantially when these devices have transparency characteristics [9-12]. However, the interdigitated electrode system has a specific capacitance of 405 F g$^{-1}$, which is comparable and even higher than the capacitance of an opaque sandwich type supercapacitor prepared using the same electrode materials (335 F g$^{-1}$) (Figure 2-7). And this value of capacitance is shows good reliability compared with data from previously research of non-transparent MnO$_2$ supercapacitors [74-76]. This proves that the concept of large-scale interdigitated patterned electrodes is an effective method for fabricating transparent supercapacitors without percolation.

When the scan rate was increased from 10 to 50 mV s$^{-1}$, the capacitor exhibited a storage that was approximately 50 % higher than its original capacitance (Figure 2-5(a)). The specific capacitance values were found to be 405, 285 and 195 F g$^{-1}$ for scan rates of 10, 30 and 50 mV s$^{-1}$, respectively. Although the microelectrodes exhibited resistive behavior at a scan rate of 50 mV s$^{-1}$, the measured CVs retained a reasonable shape. This indicates that the rate capability of transparent and flexible large-scale interdigitated supercapacitor chips closely approaches that of conventional film type supercapacitors [79].

Designed for ultra-bendable characteristics, I further evaluated the electrochemical characteristics of the samples under in- and out-of-plane
conformational ultra-bending conditions. Interestingly, the prepared supercapacitor exhibited excellent capacitance stability under in-plane bending conditions (compressive condition). There is actually a small increase (about 1.2 times) in capacitance when a flat supercapacitor is bent to the inside highest curvature of 6.7 cm\(^{-1}\) (bending radius, 1.5 mm), based on data contained in previous reports dealing with transparent supercapacitors (Figure 2-5(c)) [9-12]. This can be attributed to the fact that the compressive bending condition of electrolyte induces pressure in the orthogonal direction from the PVA/H\(_3\)PO\(_4\) electrolyte membrane to the PET substrate, which creates a closer interaction between the electrolyte membrane and electrodes. As shown in Figure 2-5(e), the lower semi-circle can be seen at a high frequency in the Nyquist plot of an in-plane conformation bending system in comparison to a plane system. Such a low semi-circle is mainly due to the higher charge conductivity between the electrolyte and the electrode, a finding that is in good agreement with the CV and C/D analyses (Figure 2-5(c) and 2-6).

In contrast, a noticeable degradation (about 0.4 times) was observed in capacitance when a flat supercapacitor is bent to the opposite side curvature (= 6.7 cm\(^{-1}\)). The out-of-plane conformation can be attributed to the tensile bending conditions of the electrolyte, which can cause a severe expansion of the PVA/H\(_3\)PO\(_4\) electrolyte and it makes a much higher charge transfer resistance between the gel electrolyte and the electrodes (Figure 2-5(d)). The distorted CV behavior and high IR drop of C/D analysis (Figure 2-6) are the result of the large charge resistance, as evidenced by the large semi-circle in the Nyquist plot for the out-of-plane conformation bending system (Figure 2-5(e)).
However, the system recovers its original capacitance to about 80% after out-of-plane bending deformation (Figure 2-5(f)) because the PVA/H$_3$PO$_4$ membrane has characteristics that make it amenable to elastic deformation, typical of organic materials. It is proved in many previous researches of non-transparent ultra-flexible supercapacitor system [24,77,78,80]. As a result, it verifies the flexibility endurance of the prepared supercapacitor under extreme bending conditions. These results also suggest that there were no significant changes in the orthogonally hierarchical structure of the MnO$_2$ electrode on the interdigitated pattern even when the supercapacitor was in severely bent.
Figure 2-1. Photographs of a transparent and flexible supercapacitor with interdigitated patterned electrodes based on vertically oriented hierarchical MnO$_2$ nanostructures; (a) flat and (b) bending state.
Figure 2-2. (a) Process flow for fabricating a transparent and ultra-bendable supercapacitor without percolation: 1) photoresist patterning and developing on the transparent substrate (PET), 2-3) Au/Cr layers sputtering and MnO₂ electrodeposition on the same layer, 4) lift-off photoresist from the substrate, 5) PVA/H₃PO₄ gel membrane electrolyte attaching on the same platform. (b) Schematic illustration of the transparent and ultra-bendable supercapacitor with interdigitated patterned electrodes.
Figure 2-3. Pattern design and linear dimensions of an interdigitated electrode system on a transparent and flexible supercapacitor without percolation. With 150 interdigitated electrodes, each microelectrode was 30 μm in width and 1.5 cm in length. The electrodes were interspaced by a distance of 70 μm. The occupied area of the transparent electrode was 1.5 cm × 1.5 cm. This area can be increased up to an area limit of the electrodeposition method (size of the counter electrode).
Figure 2-4. (a) Magnified optical image and (b–c) SEM images of the interdigitated patterned electrode based on vertically oriented hierarchical MnO$_2$ nanostructure in transparent and flexible supercapacitors; b) boundary of electrode and (c) inside of electrode. (d) Transmittance spectra of a PET substrate and a full cell of the transparent and flexible supercapacitor with interdigitated patterned electrode.
**Figure 2-5.** (a–c) Typical shapes of CV curve were observed for the different bending states of transparent and ultra-bendable supercapacitor with interdigitated patterned electrode system; (a) flat, (b) compressive and (c) tensile bending state. Scan rate is 10mV s\(^{-1}\) and bending radius is 1.5 mm (curvature is 6.7 cm\(^{-1}\)). (d) Cyclic voltammograms (CV, current density versus voltage) for a transparent and flexible supercapacitor with interdigitated patterned electrode based on a hierarchical MnO\(_2\) structure for three different scan rates (10 mV s\(^{-1}\), 30 mV s\(^{-1}\), 50 mV s\(^{-1}\)). (e) Nyquist impedance plots for the transparent and flexible supercapacitor with interdigitated patterned electrode based on a hierarchical MnO\(_2\) structure for three various bending states (flat, compressive and tensile bending state). (f) Capacitance versus cycle for the transparent and ultra-bendable supercapacitor with interdigitated electrode in before, during (compressive and tensile deformed) and after (released) deformation.
Figure 2-6. Typical shapes of charge/discharge curve were observed for the different bending states of transparent and ultra-bendable supercapacitor with interdigitated patterned electrode system; flat, compressive and tensile bending state. Current density is 150\(\mu\)A cm\(^{-2}\) and bending radius is 1.5 mm (curvature is 6.7 cm\(^{-1}\)).
Figure 2-7. (a) Photograph and (b) Cyclic voltammogram for a conventional sandwich type supercapacitor based on the same hierarchical MnO$_2$ structure.
Chapter 3. Origami-type foldable electrode chips with integrated series circuit analogues

3.1 Experimental

3.1.1 Materials and methods

**Patterning of IEs on the substrate.** Graphite was used as the IEs. For the deposition of the IEs, I used a solvent-free drawing method, as described in previous research [81]. IEs were fabricated by simply drawing with a graphite rod on a cellular paper substrate. For accurate characterization, the drawing was finished when the sheet resistance of the deposited electrodes reached $500 \ \Omega \ \text{sq}^{-1}$. Each of the IEs was located periodically by patterning using a mask.

**Patterning of sectionalized ion transferring paper (SITP) substrate.** The SITP substrate is composed of poly(vinyl alcohol) permeated with phosphoric acid (PVA/H$_3$PO$_4$) as a gel polymer electrolyte (GPE) and cellular paper. The back side of the cellular paper includes periodic IEs prepared by the above-mentioned technique, which easily permits IEs and sectionalized electrolytes to be combined. A PVA/H$_3$PO$_4$ GPE was prepared by mixing PVA powder with water (5 g of PVA per 40 ml of H$_2$O), H$_3$PO$_4$ (2 g) together. The mixture was then heated to around 358 K under vigorous stirring until the solution became clear [20]. After attaching the paper substrate with IEs and the mask for sectionalized regions, the GPE was
poured and adsorbed on the paper substrate. After the paper fully absorbed the GPE (1 hour), doctorblading was conducted. After 3 hours under ambient conditions, a lift-off was done to generate localized electrolytes. After cooling down and vaporizing for about 48 hours under ambient conditions, the electrolyte solidified to form the SITP substrate.

**Characterization.** SEM images of SITP substrate were obtained using a field-emission scanning electron microscope (AURIGA, Carl Zeiss). Cyclic voltammetry (CV) was carried out using a computer-controlled potentiostat (Iviumstat, Ivium) at various potential windows (0 V–3.2 V) and galvanostatic charge–discharge (C–D) measurements were carried out using galvanostat (ZIVE sp2, ZIVE LAB) at various specific currents (0.2 mA cm$^{-2}$–0.5 mA cm$^{-2}$). Electrochemical Impedance Spectroscopy (EIS) was carried out using potentiostat (ZIVE sp2, ZIVE LAB) at various applied potentials (0.4 V–1.6 V). The Ac amplitude was 10 mV and frequencies of 100 mHz–50 kHz were used. All CV and C–D curves in the research are representative and each datum was collected at the 10th cycle of CV or C–D analyses.

### 3.1.2 Calculation of properties

**Density functional theory (DFT) calculations.** I performed first principle calculations on the basis of spin-polarized DFT using a generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) functional [82]. I used the projector-augmented wave (PAW) method as implemented in the Vienna ab-initio simulation package (VASP) [83]. A plane-wave basis set with a kinetic-energy cutoff of 400 eV and a 10×2×2
Monkhorst–Pack k-point mesh were used.

**Three dimensional finite-elemental method modelling.** I developed three-dimensional finite-element models for numerical structure analysis. All elements of the model for the origami-based 3 IEs system were designed by means of a 20 node (Serendipity) hexahedral brick. Near the edges of the model, I use an element size under 100 mm for high accuracy.
3.2 Results and discussion

To demonstrate the concept of origami-based supercapacitor chips with a densely packed series circuit analogue, the electrode materials and electrolytes should be precisely located at standardized regions. The location of the patterned electrodes is defined by \( r = na \) for an integer \( n \) in the \( x \) direction (Figure 3-1(a) and (b)), where \( a \) is the width of an electrode and \( n \) is the number of electrodes. The location of the sectionalized electrolytes are defined in a manner similar to that of the electrodes, except that it has a parallel transition with \( 1/2a \) from the location of the electrodes. As a result, the position of the electrodes and electrolytes are an overlap of odd and even periodic functions, analogous to trigonometric functions (Figure 3-1(b)).

Each of the sectionalized electrodes is referred to as IEs. IEs at both ends can be regarded as the positive and negative electrodes in a conventional-type system. The topical part of IEs system is composed of the right half of an IE and the left half of an IE, aligned on the right side of the aforementioned IE. Naturally, it includes an overlapped sectionalized electrolyte. This region is considered as a primitive unit, since it contains the minimum structure that can be used to fully define the whole origami-type supercapacitor chip structure (Figure 3-1(c)). The primitive unit can be repeated \( ad infinitum \) and can be theoretically operated as an independent energy storage system. The density of the primitive units is a key factor for the electrochemical performance of IEs energy storage systems.

In the charged state, each of the IEs is polarized along the \( x \) direction, therefore the IEs are simultaneously charged with different charge carriers (for details see the polarization of isolated electrode part, Figure 3-2 and 3-3).
This is a key factor for a densely integrated series connection. In this case, the two half-IEs of each primitive unit have different roles as positive and negative electrodes and each IE functions simultaneously as a positive electrode/current collector/external circuit/current collector/negative electrode at once. This property allows the avoidance of any connections and additional volume which inevitably appear in conventional cells. In each primitive unit, the limitation of the potential window is applied by the decomposition potential of the electrolyte. In the whole cell, however, the potential window increases in an unrestricted manner with the number of primitive units (Figure 3-1(d)).

An equivalent circuit of the development of materials with high capacity can be shown as an integrated parallel circuit analogue. The integrated circuit results in E and P having a competitive relationship [32-35]. In the IEs system, however, E and P have a linear relationship with number of IEs + 1 because the system incorporates series circuit analogues without any supported circuit and added resistance, theoretically.

The total current of the IEs system is the same as the partial current of single primitive unit, as follows:

\[ i_{tot} = i_1 = i_2 = i_3 = \cdots \]  

(3-1)

where, itot is total current of the system and \( i_1, i_2 \) and \( i_3 \) is partial current of each primitive units (the \( i_1, i_2 \) and \( i_3 \) are all the same and represented as \( i \) in the following). The areal capacitances (\( C_{sp} \)) of the symmetrical energy system using an electrical double layer are calculated using the discharge curve integrated from CV or C–D measurements according to the following equation [84-86]:

\[ C_{sp} = \int \frac{dQ}{dV} \]  

(3-2)
\[ C_{sp} = \frac{4C}{A} \]  
where,  
\[ C = \frac{Q}{V} = \frac{i \times t}{V} \]  
(3-2)

and \( A \) is the total area of all of the electrodes in the isolated electrodes (IEs) system, \( Q \) is the amount of charge, \( t \) is the discharge time and \( V \) is the stable potential window. In here, all integrated series circuit systems at various number of IEs are fabricated in the same-sized substrate. Therefore, \( A \) is the same for all IEs systems. In other words, the area of a single IE and the number of primitive units (= number of IEs + 1) are reciprocally proportional in each system. The \( E \) is calculated by integrating the discharge area of the C–D curves as follows [15]:

\[ E = i \int V dt \]  
(3-3)

If I assume the system is an ideal capacitor, the \( E \) is simplified as follows [95,96]:

\[ E = \frac{1}{2} CV^2 \quad \text{or} \quad E = \frac{1}{2} i \times t \times V \]  
(3-4)

And the average \( P \) is also obtained using the following equation [95,96]:

\[ P_{ave} = \frac{E}{t} \quad \text{or} \quad P_{ave} = \frac{1}{2} \times i \times V \]  
(3-5)

where \( t \) is theoretically constant in various IEs systems because \( t \) is proportional to \( V \) and reciprocally proportional to specific current of a single primitive unit (= \( i/\text{area of single IE} \propto \text{number of IEs} + 1 \). \( i \) is a control factor of the C–D analysis and \( V \) is proportional to the number of IEs + 1. Consequently, the \( E \) and \( P \) have a linear relationship with number of IEs + 1. The number of IEs + 1 represents the density of primary units because the various IEs systems were fabricated with the same size substrate.

A technical breakthrough for the energy storage system with IEs is needed.
to combine IEs and electrolytes. For precise sectionalization of electrodes, I used a drawing method [81]. The front side of a substrate was used as the substrate of the IEs and the back side was simultaneously used as the substrate of the sectionalized electrolytes. With this strategy, I could easily combine the IEs and electrolytes and produce primitive cells.

To realize this system, a challenge arises from securing sectionalized conformal electrolytes because the materials are based on ions, not solid atoms [87]. I therefore demonstrated imprintable electrolytes on a cellular paper substrate which is highly stable and has folding characteristics. Generally, GPEs, such as PVA/H$_3$PO$_4$, are prepared via solution casting of liquid state mixtures followed by solidification [87]. The initial liquid-state mixture of GPEs is sorbed into a porous substrate (here, cellular paper) due to their intrinsically fluidic characteristics. In addition, the electrolyte is fixed at a designated location by solidification (Figure 3-4(a)). This unique rheological feature of the gel@paper substrate (here referred to as SITP) facilitates its application in patterned electrolyte systems. In Figure 3-4(b), the SEM images show that the PVA/H$_3$PO$_4$ is fully sorbed and located inside the cellular paper and the SITP is well-realized.

For the experimental proof of IEs systems, I fabricated energy storage systems including one, two and three IEs (Figure 3-5). As a representation of the conventional system, a system without an IE was also fabricated. To realize the system, I used graphite, a well-known conducting material, as the electrode and PVA/H$_3$PO$_4$ as a GPE in view of its non-toxic nature and possible coupling of charge transport [88,89]. The selected materials for the electrode and GPE are replaceable and are not limited to the system.

To identify quantitatively the voltage limitation of the system, I conducted
ab-initio calculations about decomposition reaction for the electrolyte molecule, PVA [90], The overall decomposition reaction for PVA can be expressed as [91]:

\[-\text{CH}_2\text{-CHOH-} \rightarrow -\text{CH}_2\text{-CH-} + n\text{H}_2\text{O} \quad (3-6)\]

For this decomposition reaction, the thermodynamic decomposition voltages (Erxn) can be determined simply by using the following equation [92]:

\[E_{\text{rxn}} = -\frac{\Delta G}{zF}\]

where, \(\Delta G \equiv \Delta E + P\Delta V - T\Delta S\) \quad (3-7)

where \(z\) is equivalents of electrons and \(F\) is the Faraday constant. In the \(\Delta G\), volume effects and entropic effects are neglected due to the low order of \(P\Delta V (10^{-5} \text{ eV})\) and the relatively small value of \(T\Delta S\) compared to \(\Delta E\). By calculating the total energy of the three compounds in the overall decomposition reaction, it is possible to determine the thermodynamic decomposition voltage of PVA. After completion of the decomposition reaction, the carbon chain without hydroxyl groups shows sp\(^2\) conjugated bonds (polyene) (Figure 3-6(a)). In general, conjugated bonds lower the total energy of the polymer and increase its stability. Assuming the half decomposed state of PVA as the transition state, I calculated the decomposition voltage of PVA in the transition state using the decomposition reaction written as:

\n
\[-\text{CH}_2\text{-CHOH-CH}_2\text{-CHOH-} \rightarrow -\text{CH}_2\text{-CHOH-CH-} + n\text{H}_2\text{O} \quad (3-8)\]

I showed the calculated internal energy of the four components and decomposition voltages (Table 3-1). The results show that the decomposition potential of PVA is 0.8 V and the decomposition reaction generates polyene
(C₂H₂) and H₂O (Figure 3-6(a) and (b)). The decomposition voltage is calculated based on thermodynamics and does not account for kinetic limitations such as resistivity effects or activation energy barriers. Nevertheless, the calculated voltage is in good agreement with the experimental potential window of conventional systems with the PVA/H₃PO₄ GPE (~0.8 V, Figure 3-6(c)). This value is also the same as previous data reported for energy storage systems with PVA/H₃PO₄ [36,37,38,88,89].

Compared to a conventional type operated at 0.8 V, the cells with one, two, and three IEs exhibited stable potential windows of 1.6, 2.7 and 3.2 V, respectively (Figure 3-6(c)). A potential window greater than 3.2 V is also obtainable by increasing the number of IEs (Figure 3-7 and 3-8). The potential window and number of IEs + 1 have a linear relationship, which is in good agreement with C–D analyses (Figure 3-6(d)). From the C–Ds, a slight change in the slope is evident near the PVA decomposition potential × n V (n = number of IEs+1). The potential finally reaches 0.8n V as a general limitation potential of PVA/H₃PO₄ (Figure 3-6(d) and 3-9). The E and P of the IEs systems are presented in the form of a Ragone plot in Figure 3-6(e). The non IE system (conventional) has an E of 6.56 nWh cm⁻² and a P of 210.7 nW cm⁻². With the three IEs, the values for both E and P are over 4.0 and 3.5 times higher than the non-IE system, approaching 26.55 nWh cm⁻² and 729.7 nW cm⁻², respectively. Nyquist impedance plots for the IEs systems are presented with various numbers of IEs in Figure 3-10. The various IEs systems show almost the same resistance, about 100 kΩ, regardless of the number of IEs, which is generally consistent with theoretical predictions.
In terms of mechanical properties, the SITP substrate shows stable and folding characteristics which are natural to general papers as well. The properties of SITP enable an origami structure. To design a concept of origami-based system with folding characteristics, I fabricated a three-IEs sample septuple-folded in a zigzag formation and evaluated the electrochemical characteristics of the sample (Figure 3-11). This system shows similar a CV type in the compressive (60%), plane and tensile deformation (30%) conditions and the specific capacitances are 0.94, 0.98 and 0.93 mF cm\(^{-2}\) for each deformation condition (Figure 3-11(d), (e) and (f)). This means that the system is highly stable in mechanical and electrical aspects and this tendency has also been shown in my previous research [20].

From Hooke's law, the stress (\(\sigma\)) and strain (\(\varepsilon\)) of the materials are derived as follow:

\[
\sigma_i = D_{ij} \times \varepsilon_j
\]  

(3-9)

where \(D_{ij}\) is an elasticity matrix, which is determined by following equation under assumption of isotropic materials:

\[
D_{ij} = \frac{E(1-\nu)}{(1+\nu)(1-2\nu)} \begin{bmatrix} 1 & \gamma & 0 & 0 & 0 \\ \gamma & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & \beta \end{bmatrix}, \quad \sigma_i = \begin{bmatrix} \sigma_{xx} \\ \sigma_{xy} \\ \sigma_{xz} \\ \sigma_{yx} \\ \sigma_{yx} \\ \sigma_{zz} \end{bmatrix}, \quad \varepsilon_i = \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \\ \varepsilon_{xz} \\ \varepsilon_{yx} \\ \varepsilon_{yz} \end{bmatrix}
\]

(3-10)

where, \(\gamma = \nu / (1 - \nu)\), \(\beta = (1 - 2\nu) / 2(1 - \nu)\)

where \(E\) is Young’s moduli and \(\nu\) is Poisson’s ratio. The cellular paper substrate has 37 MPa of \(E\) and 0.13 of \(\nu\) [93,94]. The SITP substrate is assumed to be a linearly elastic and isotropic material, which is supported by
physical predictions and experimental properties cited in literature [93,94]. From a finite elemental method (FEM) calculation, the maximum equivalent strain of the origami-based three IEs system is 2.5% (the initial structure is zigzag-type septuple-fold model, as shown in Figure 3-11(a) and the angle of each edge is 90°, respectively) (Figure 3-12). This value is relatively small in comparison with the deformation of the system (-60% of compressive state and 30% of tensile state), which proves that the origami-based structure can result in minimized $\varepsilon$ and $\sigma$ [5,95]. These mechanical properties are clearly evident through a numerical analysis of the stress distribution (Figure 3-11(g) and (h)). For compressive and tensile deformation, almost all areas experience a stress of under 0.4 MPa, and the edge of the origami has a stress of 0.86 (compressive) and 0.45 MPa (tensile). These values are negligible compared to the yield strength of the substrate (45 MPa), verifying the high stretchability of the conceptual system under extreme deformation conditions [93]. To develop an insight into the structural failure of the model, I used the Huber–von Mises failure criteria using the following equation:

$$\text{Safety factor} = \frac{Y}{\bar{\sigma}}$$

where,

$$\bar{\sigma} = \sqrt{\frac{1}{2} \left[ (\sigma_{xx} - \sigma) + (\sigma_{yy} - \sigma) \right] + 3\sigma_{xx}^2 + 3\sigma_{yy}^2 + 3\sigma_{zz}^2}$$

(3-11)

$\bar{\sigma}$ is equivalent stress and $Y$ is yield strength. The safety factor shows whether the model fails or not. The safety factor under 1 means the model is destroyed. In here, $Y$ is 45 MPa and the safety factor is over 15 in all bodies at both folding and stretching, implying that the system is stably maintained in stretching deformation (Figure 3-13). To prove the mechanical stability, long-cycle capacitance retention analysis was conducted (Figure 3-14). After
the first 50 cycles at an initial state with a zigzag formation, the system achieved excellent capacitance retention even slightly higher than capacitance of the first cycles. During the next 100 cycles, the system is compressively folded (~60 %) and stretched (~30 %) compared with the initial state. After the cycles at the deformation, the system achieved over 100 % capacitance retention. The cycling retention analysis is re-conducted and performance fading was not observed. The last 50 cycles were conducted at the initial deformation state and the system maintains its original capacity. It proves that the system shows consistent electrochemical and mechanical performance and it is well correlated with the computational simulation using FEM.
**Figure. 3-1.** (a) and (b) Schematics for the all-solid-state origami-type supercapacitor with series circuit analogues. It has periodically isolated electrodes (IEs) and sectionalized electrolytes alike with overlapping odd and even functions. (c) Two half-IEs and one sectionalized electrolyte compose a primitive cell. In a charged reaction, each IE forms opposed poles along the x direction. (d) The potential window versus number of IEs, which shows a linear relationship. The red lines show the H$_2$O electrolysis voltage and the electrolyte decomposition voltage calculated by density functional theory (DFT).
Polarization of isolated electrodes (IEs)

Conventional series circuit systems are expressed by an equivalent circuit in Figure 3-2(a). At charging state, each capacitor units in series circuit (blue boxes in Figure 3-2(b)) has a charge separation (Figure 3-2(b)) therefore potential profile of the system will be generated as shown in Figure 3-2(c). The conventional series system includes the external lines connecting between each units (black line in Figure 3-2(b)), which inevitably accompanies additional resistance and requires an unnecessary volume in the system.

In this research, I replaced two electrodes including different capacitor units and external line with just one electrode material (isolated electrodes (IEs)). In an equivalent circuit, the IEs are represented by red boxes in Figure 3-2(d). Through the equivalent circuit, IEs are completely isolated and only connected by sectionalized ion transferring papers (SITPs, yellow boxes in Figure 3-2(e)). The narrow middle region of the IEs plays a role as an external line in a conventional series circuit. At charging, the IE materials should be polarized in horizontal direction according to the equivalent circuit in red boxes. In the manuscript, the horizontal direction is expressed by \( x \)-axis in Figure 3-1. The polarization can be proved by the potential profile of the series circuit analogues system (Figure 3-2(f)). From the potential profile, it is known that a limited potential in a conventional energy storage cell is placed between adjacent IEs. I measured the potential between neighboring IEs in the fully charged three IEs system (in the system, fully charged potential is 3.2 V). Each potential window between the neighboring IEs is about 0.8 V in Figure 3-3, which proves that the IEs are polarized.
Figure 3-2. (a) Discharged and (b) charged equivalent circuits of capacitor systems with series connection. (c) Potential diagram versus location (x-axis) of charged capacitor system with series connection. The blue boxes represent conventional energy storage units. (d) and (e) equivalent circuits of isolated electrodes (IEs) system. The red boxes represent IEs and the yellow boxes represent sectionalized ion transferring papers (SITPs). (f) Potential diagram versus location (x-axis) of IEs system. Potential gap between neighboring IEs are the same with the limited potential of conventional system.
Figure 3-3. Potential gap between near isolated electrodes (IEs) in fully charged three IEs system (Fully charged potential is about 3.2 V). Each potential windows between near IEs is about 0.8 V, which proves the IEs are polarized well.
Figure 3-4. Sectionalized ion transferring paper (SITP). (a) Process flow for fabricating SITP: (1) mask attached to the porous paper substrate, (2) gel polymer electrolyte (GPE) adsorbed and doctor-bladed on the same substrate, (3) mask lifted off after solidification of GPE. (b) Scanning electron microscope (SEM) image of cross section for the SITP and energy dispersive spectrometer (EDS) element mapping results for O, C and P species of poly(vinyl alcohol)/H₃PO₄.
Figure 3-5. Photographs of IEs systems. (a) Front sides of conventional type (without IE) and IEs systems with 1, 2 and 3 IEs, respectively. The red boxes enclose each IEs. (b) Back sides of the conventional type (without IE) and IEs systems with 1, 2 and 3 IEs, respectively. The sectionalized electrolytes are absorbed on the back side of the system and the yellow boxes represent each of the sectionalized electrolytes.
**Figure 3-6.** Electrochemical properties of isolated electrodes (IEs) system. Density functional theory (DFT) calculation for the decomposition voltage of Poly(vinyl alcohol) (PVA): (a) three transition states of PVA in the decomposition reaction and charge density for the carbon back-bone of the same transition states, and (b) energy profiles for the decomposition reaction of PVA. (c) Cyclic voltammogram (CVs), (d) Charge/discharge curve (C/Ds) and (e) Ragon plot of energy system without IE and with 1, 2 and 3 IEs. Scan rate is 5 mV s\(^{-1}\) in CVs, specific current is 0.5 μA cm\(^{-2}\) based the total area of system in C/D analyses (in (d), red line denotes the thermodynamic decomposition voltage of PVA).
Table 3-1. Total energy in eV for each molecular structure component and the thermodynamic decomposition voltage of poly(vinyl alcohol) (PVA) at half and full decomposition by density functional theory (DFT) calculation.

<table>
<thead>
<tr>
<th>Component</th>
<th>Energy [eV]</th>
<th>Decomposition state</th>
<th>Decomposition voltage [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$-CHOH-</td>
<td>-39.78</td>
<td>Half</td>
<td>1.18</td>
</tr>
<tr>
<td>-CH-CH-</td>
<td>-24.97</td>
<td>Full</td>
<td>0.80</td>
</tr>
<tr>
<td>-CH$_2$-CHOH-</td>
<td>-64.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH-CH-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-14.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-7. Cyclic voltammograms (CV) of isolated electrode (IEs) energy storage systems with (a) 7 and (b) 11 IEs. Scan rate is 5 mV s⁻¹. The system have 6.4 V and 9.6 V of potential window respectively, which proved the linearly increasing potential window with the number of IEs based on the same area systems.
**Figure 3-8.** Galvanostatic charge/discharge (C/D) curves of system with 7 and 11 isolated electrodes (IEs) with same-sized substrate. The specific currents are (a) 0.2, (b) 0.3, (c) 0.4 and (d) 0.5 μA cm$^2$, respectively. (e) Ragon plot of IEs system with 3, 7 and 11 IEs.
Figure 3-9. Galvanostatic charge/discharge (C/D) curves of system with zero, one, two, and three isolated electrodes (IEs). The specific currents are (a) 0.2, (b) 0.3 and (c) 0.4 μA cm$^{-2}$ based the total area of system, respectively. The red lines show the decomposition potential of poly(vinyl alcohol) $\times n$ V ($n =$ number of IEs + 1).
Figure 3-10. Nyquist impedance plots of energy system without isolated electrode (IE) and with 1, 2 and 3 IEs. Applied potential is 0.4, 0.8, 1.2 and 1.6 V, respectively. Ac amplitude is 10 mV and frequencies of 100 mHz – 50 kHz. The curves for the various IEs systems have tangent line that intersects the real axis, which caused by synergetic effect of capacitance and mass transfer resistance caused the electrode system with vertical formation [95-98].
Figure 3-11. Origami-based stretchable energy storage system. Photographs of an origami-based stretchable energy system with three IEs for stretching at (a) –60 % (compressible), (b) 0 % and (c) 30 % (tensile) along the x direction. Cyclic voltammogram (CVs) of the system at (d) –60 % (compressible), (e) 0 % and (f) 30 % (tensile). Three dimensional finite-elemental method (3D FEM) modeling of the stress distribution for the same system in the same (g) compressible and (h) tensile deformation states.
**Figure 3-12.** 3D finite-elemental method (FEM) analyses of origami-based stretchable energy storage system. (a) and (b) Deformation analyses at compressive (-60%) and tensile (30%) decomposition states. (c) and (d) Strain analyses at the same decomposition state, respectively.
Figure 3-13. Safety factor analysis of origami-based 7 folding 3 isolated electrodes (IEs) system. (a) -60 % compressive and (b) 30% tensile decomposition states.
**Figure 3-14.** Capacitance retention *versus* cycle number for the origami-type three isolated electrodes (IEs) system septuple-folded in a zigzag formation at various deformation states.
Chapter 4. Omnidirectionally stretchable, high performance electrodes based on a graphene-carbon-nanotube layered structure

4.1 Experimental

4.1.1 First-principles calculations and three-dimensional finite-element method modeling

First-principles calculations were carried out on the basis of density functional theory (DFT) using a generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) functional [82]. I used the projector-augmented wave (PAW) method as implemented in the Vienna ab-initio simulation package (VASP) [83]. The van der Waals interactions are described via the DFT-D2 Method of Grimme [99]. A plane-wave basis set with a kinetic-energy cutoff of 600 eV and a $2 \times 2 \times 10$ Monkhorst–Pack k-point mesh was used. The CNT was built into a single-walled armchair nanotube with a (10,10) index (diameter, 13.7 nm), as shown in Figure 4-1(a). The structures are located in the orthorhombic unit cell with a vacuum gap. Lattice constants are $a = 34.08$ Å, $b = 45.00$ Å, and $c = 2.46$ Å (Figure 4-2). Before calculating the binding energy of the graphene–CNT interface, I calculated the variation of the energy along the $z$-axis by modifying the distance between the graphene and CNT from 5 to 2 Å in steps of 0.2 Å, and the binding energy was maximized at 3.1 Å with structure relaxation (Figure
The structure relaxation well represented the covering state of graphene on the CNT. Calculated energy values were summarized in Table 4-1. I also developed three-dimensional (3D)-finite element method (FEM) models for numerical structure analysis [100]. All elements of the models were designed by means of a 20-node (Serendipity) hexahedral brick. Near the edges of the model, I used an element size under 2 μm for high accuracy.

### 4.1.2 Fabrication of graphene–CNT stretchable electrodes

To fabricate the graphene–CNT-layered structure, various elastic supports [rubber, latex, poly(vinyl alcohol) (PVA), etc.] were initially stretched in two dimensions and fixed. Then ten layers of a 0.5 g/L solution of CNT (ILJIN Nanotech.) ink dissolved in 200 μL of ethanol was spread onto the prestrained substrate. The CNT was pretreated in a 70% HNO₃ solution at 110 °C for 8 h, which resulted in the surface of the CNT being slightly hydrophilic. The HNO₃ treated CNT contains some O-functional groups (8.15 wt%). However, the presence of these did not affect the major interfacial characteristics of the system. Following this process, three layers of a 0.5 g/L graphene ink solution in 200 μL of ethanol was spread onto the CNT layer. The graphene was synthesized from graphene oxide in a microwave oven for 2 min, as suggested in a previous study [101]. The prestrained substrate was then released, resulting in the formation of a wrinkled graphene–CNT layer.

### 4.1.3 Fabrication of electric surgery glove and contact lens
To show the electric circuit on surgery gloves and contact lenses, commercial light-emitting diode (LED) cells [HSMC-C150 (3.2 mm × 1.6 mm), AVAGO Tech.] were mounted and manually bonded to the Ag paste anchor using a conventional soldering method on commercial supports. The applied voltage to the LEDs was a constant 2V, supplied an external power supply. The maximum forward voltage and power dissipation of the LEDs were 2.4V and 60 mW, respectively. A cyclic stretching test using surgery gloves demonstrated that the inserted LED circuit endured 100 cycles with no defects.

4.1.4 Fabrication of stretchable supercapacitor

A PVA/H₃PO₄ gel electrolyte was prepared by mixing 5 g of PVA powder, 4 g of H₃PO₄, and 40 mL of water together [20,100]. The mixture was heated to 358 K under vigorous stirring until the solution became clear. The gel electrolyte was poured onto a petri dish to make the PVA/H₃PO₄ film. After drying, the film was two-dimensionally stretched and fixed. A 200 μL aliquot of the graphene ink (0.5 g/L) was spread three times and 200 μL of CNT ink (0.5 g/L) was spread ten times onto the film. The same amount of ink was spread onto the opposite side. The stretched film was released, resulting in the formation of a stretchable supercapacitor system.

4.1.5 Morphology and electrochemical characterization

Scanning electron microscope (SEM) images of the graphene-CNT structure were obtained using a field-emission SEM (AURIGA, Carl Zeiss).
Cyclic voltammetry (CV) and charge/discharge (C/D) curves were carried out using a computer-controlled potentiostat (ZIVE SP2, ZIVE LAB) at an operation voltage range of 0 to 0.8 V. All CV and C/D curves in this study are representative and each datum was collected at the 10th cycle of CV or C/D analyses.
4.2 Results and discussion

Figure 4-1 schematically summarizes the interfacial interactions of the graphene–CNT-layered structure. The interaction and moving motion of the graphene–CNT electrodes can be demonstrated by comparing them to the actin–myosin interaction in muscles. In living bodies, a single motor in the sarcomere (myosin) moves along the track (actin) and operates via cycling states with different affinities [51,52]. The cycling motion accompanied by a change in affinity also occurs in the graphene–CNT-layered structure [ΔE, 0.08 eV U.C.$^{-1}$ (Figure 4-1(c))]. During biological muscle movement, the head of the myosin forms a chemical bond with an actin molecule on the thin filament (crossbridge). In the graphene–CNT electrode system developed here, the crossbridge is formed by van der Waals interactions between closed chains of six carbon atoms in the CNT filaments and graphene sheets with the graphitic AB stacking [80]. For the calculation of the binding and drifting properties on the graphene–CNT interface, the graphene–CNT structure was simulated with DFT-optimized lattice constants [102,103]. In a graphene structure, the distance between neighboring carbon atoms is 1.423 Å, which agrees with the experimental value of ~1.42 Å [104]. The binding energy, $E_{\text{binding}}$, at the interface of the graphene and CNT was defined by

$$E_{\text{binding}} = (E_{\text{graphene}} + E_{\text{CNT}}) - E_{\text{total}} \quad (4-1)$$

where $E_{\text{total}}$ is the total energy of the system containing the adsorbed CNT and graphene, $E_{\text{graphene}}$ is the total energy for the optimized bare graphene surface, and $E_{\text{CNT}}$ is the total energy for the CNT in the vacuum. With this definition, the positive binding energies correspond to energetically favored states (Figure 4-1(c)). In a sarcomere, as soon as the crossbridge is formed,
inorganic phosphate (P_i), produced by the hydrolysis of adenosine triphosphate (ATP) in the myosin, is released with the concomitant motion of the lever arms (power stroke) [51,52]. In the graphene–CNT-layered system, the shear stress from external pulling or twisting between the graphene and the CNT replaces the chemical energy from hydrolysis of ATP. The binding energy of graphene–CNT AB stacking is 0.49 eV U.C.\(^{-1}\). When the CNT carbon atoms slide on the graphene (hopping mechanism), the activation energy from AB stacking to metastable AA stacking is only 0.08 eV U.C.\(^{-1}\) (Figure 4-1(d)). This value is six times lower than the binding energy of the graphene–CNT network, which induces the CNT motors to move along the graphene layers rather than detach. Especially, the interface stress (slip boundary) between the CNT cluster and the graphene layer has a negligible influence on the overall strain of the inorganic muscle because the energy needed to move the CNT along the graphene track is only 0.08 eV U.C.\(^{-1}\), which is much smaller than the external stress. The graphene–CNT-layered structure is homogeneously located on the two-dimensional surface, which causes uniform strain of the electrode surface, enhancing the durability.

The differential charge density, \(\rho_{\text{diff}}\), of the graphene–CNT interface is defined by

\[
\rho_{\text{diff}} = \rho_{\text{total}} - (\rho_{\text{graphene}} + \rho_{\text{CNT}})
\]

(4-2)

where \(\rho_{\text{total}}\) is the charge density of the graphene–CNT interface, \(\rho_{\text{graphene}}\) is the charge density for the bare graphene surface, and \(\rho_{\text{CNT}}\) is the charge density for the CNT. The charge accumulations (yellow) and charge reductions (blue) around the CNT and graphene are explicitly shown in Figure 4-1(d). The two different charge densities share the same feature: charge accumulations and reductions are vertically superposed between the
CNT and the graphene, which suggests an electrostatic interaction at the graphene–CNT interface. In this system, the interaction energy depends on the van der Waals interaction between the graphene and the CNT. In the case of AB stacking, electronic hybridization was found at the graphene–CNT interface. This induced a charge redistribution, which largely enhanced the strength of the electrostatic interactions. In AA stacking, however, no appreciable electronic hybridization between the graphene and the CNT was detected, indicating that the state was unstable and that the graphene–CNT interface was spontaneously reconstructed in the form of AB stacking. Also, the CNT surface atoms naturally moved from holes in the surrounding carbon atoms of graphene to other holes inside the rings of graphene. As a result, the CNT moved omnidirectionally along the two-dimensional graphene plane by the continuous docking (AB)/undocking (AA) of the CNT edges onto the graphene flake (power stroke, Figure 4-1(d)). In biological systems, after the release of adenosine diphosphate (ADP), the myosin recombines with ATP. The combination induces the collapse of the coupled myosin and actin (Figure 4-1(b)). Simultaneously with the hydrolysis of ATP, the myosin and actin are randomly reconstructed and the crossbridge is shifted by approximately 11 nm, the length of neighboring binding sites of myosin. The result is analogous to the re-docking of the CNT and graphene [52]. In the case of the graphene-CNT power stroke, the distance of the shift in the CNT chains was approximately 2.46 Å, which represents the length between the neighboring holes of the six-membered rings of graphene (Figure 4-2).

To experimentally prove this concept, I obtained optical and SEM images and 3D-FEM simulation of the graphene–CNT stretchable electrode at
various deformation states. Random myosin movement macroscopically appears in the compression and spontaneous release of muscles in the human body (Figure 4-3(a)). In contrast, the movement of the CNT on the graphene track yielded stretching and spontaneous release of the graphene–CNT stretchable electrode. A schematic diagram of the flow process for the drifting motion of graphene is shown as Figure 4-4. The modulus and tensile strength of a single CNT was determined to be ~910 GPa and ~0.15 GPa, respectively, indicating the severe stiffness of a single anisotropic CNT [105]. However, the effective modulus of the CNT cluster was reduced by several orders of magnitude because of the non-coplaner and omnidirectional waviness of the CNTs in a cluster. The morphological characteristics of a CNT cluster is a factor that provides stretchability to the electrode system. Previous research indicates a Young’s modulus of 565 KPa and a tensile strength of 170 KPa for a CNT cluster, indicating a high elasticity with a ~30% yield strain [53]. In addition, the three-dimensional random networks in the CNT cluster enable us to assume nearly isotropic properties [106]. Figure 4-3(b) shows optical images and the corresponding 3D-FEM modeling of graphene–CNT structures formed after 80% uniaxial, biaxial, and twisting deformation. In the graphene–CNT stretchable electrode, the graphene is undeformable and undergoes drifting motion. The slip boundary stress between the CNT cluster and the graphene layer converges to zero based on DFT calculation results, as stated above. Therefore the FEM calculation can be based on the CNT cluster. The value of elasticity shows a relatively low compliance value as compared to my experiments (yield strain, ~75%). This difference is caused by the synergetic effect of the inherent nanostructure of the CNT cluster and the crumpled macrostructure of the graphene–CNT
electrode, which enhances the omnidirectional stretchability (Figure 4-3(b)). The method for fabricating the crumpled structure is shown in the methodology associated in Figure 4-5.

To calibrate the modulus of the graphene–CNT stretchable electrode with combination effects, I used the experimental value for yield strain, ~75%, and the fixed tensile strength of the CNT cluster, 170 KPa. From Hooke’s law, the calibrated Young’s modulus of the system was calculated to be 227 KPa. The graphene–CNT-layered structure had a depth of 2 μm, and I designed the mesh of the structure as a low-density orthorhombic solid. For the FEM calculation, the stress, σ, and strain, ε, of the materials are derived as

\[ \sigma_i = D_{ij} \times \varepsilon_i \] (4-3)

where \( D_{ij} \) is the elasticity matrix, which is determined by following equation for isotropic materials:

\[
D_{ij} = \frac{E(1-\nu)}{(1+\nu)(1-2\nu)} \begin{bmatrix}
1 & \nu & 0 & 0 & 0 \\
\nu & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix},
\sigma_i = \begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz} \\
\sigma_{xy} \\
\sigma_{yz}
\end{bmatrix},
\varepsilon_i = \begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{zz} \\
\varepsilon_{xy} \\
\varepsilon_{yz}
\end{bmatrix} (4-4)

where \( \gamma = \nu/(1-\nu) \), \( \beta = (1-2\nu)/(1-\nu) \), \( E \) is Young’s modulus, and \( \nu \) is Poisson’s ratio. The Poisson’s ratio of the CNT cluster is 0.4 from previous research [106]. From an equivalent stress calculation using 3D-FEM, all structures (biaxial and uniaxial deformation with ~80% strain and twisted deformation with a 360° angle) maintained their elasticity, excluding a small portion of the edges of the structure (Figure 4-3(b)). The results show that the graphene-CNT electrode design is capable of supporting stable and robust operations during large-scale and mixed modes of deformation.
similar to the bending of biological muscle. To develop insight into the structural failure of the model, I used the Huber–von Mises failure criteria as [100]

\[
\text{Safety factor } = \frac{Y}{\bar{\sigma}},
\]

\[
\bar{\sigma} = \sqrt{\frac{1}{2} \left[ (\sigma_{xx} - \sigma_{yy})^2 + (\sigma_{yy} - \sigma_{zz})^2 + (\sigma_{zz} - \sigma_{xx})^2 \right] + 3\sigma_{xy}^2 + 3\sigma_{xz}^2 + 3\sigma_{yz}^2}
\] (4-5)

where \(\bar{\sigma}\) is the equivalent stress and \(Y\) is the yield strength. A safety factor less than 1 indicates that the model is unstable. As shown in Supplementary Figure 4-6, for the most part each calculated model maintained a safety factor of more than 1. Some instability occurred at the edges, which caused a slight decrease of conductivity. However, the calculation results are in good agreement with the optical images (Figure 4-3(b)).

The deformation of the graphene–CNT connections involves the following steps. First, the system contains non-coplanar wrinkles similar to crumpled paper, and an external force causes the wrinkled structure to physically unfold (Figure 4-3(c) and 4-5) [43,44]. With the physical unfolding, the serpentine CNT cluster is subsequently extended along the graphene track with a negligible interface stress (Figure 4-3(d)). To provide clear evidence of sliding graphene on the CNT stretchable substrate, I conducted in-situ microscopy analyses of the composite structure (Figure 4-7). At the released state, graphene sheets are observable on the surface of the composite. With applied stretching, the graphene sheets become cracked because of their rigidity. In such a situation, the conductivity of the composite is maintained (Figure 4-8(a)), which means that the substrate composed of a CNT cluster provides support between graphene sheets. This
result indicates not only negligible shear stress between the graphene and stretchable CNTs but also tenable conductivity enabled by the CNT substrate. Microscopically, each crossbridge in the interface between graphene and a CNT layer is randomly broken with stretching of the CNT clusters. The crossbridges are continuously reconstructed during the movement of the CNT, regardless of direction, because graphene flakes offer the system a repetitive two-dimensional (2D) track. From a macroscopic viewpoint, the reconstruction process shows that undeformable graphene flakes recede by the stretching of CNT filaments (Figure 4-4). To estimate the deformation of graphene under tension, I applied a series of incremental tensile strains on a unit cell of bare graphene using the simulation based on DFT calculations. Uniaxial tension was applied in the $x$ direction and the Poisson contraction was assumed to be zero under the tension for computational convenience (Figure 4-9(a)). Figure 4-9(b) shows the calculated stress–strain curve of graphene. Strain, $\varepsilon$, is defined by

$$\varepsilon \equiv \frac{L}{L_0} - 1 \quad (4-6)$$

where $L$ is the length of the unit cell at the $x$-axis and $L_0$ is the value at zero stress optimized by DFT calculation. Stress, $\sigma$, is the difference in internal energies from the value of the graphene sheet at zero stress. Up to 20% strain, graphene has an isotropic in-plane elastic response, and the lattice symmetry is broken when this value is exceeded. The findings are in good agreement with the experimental results of the Young’s modulus of graphene sheets, $\sim 1.1$ TPa [107,108]. However, at 2% strain, the stress (0.23 eV U.C.$^{-1}$) already exceeds the activation energy between AB stacking and AA stacking of the graphene–CNT interface (0.08 eV U.C.$^{-1}$). This fact, therefore, verifies that external stress causes the CNT to follow the undeformable graphene
track rather than the deformation of the graphene sheet.

In the experiment, each robust graphene area is indicated by the bright regions in the SEM images of Figure 4-3(c) (Pt-coated area). The size of the graphene flake is approximately 100 μm$^2$ during the stretching and releasing, which is in good agreement with the Supporting Movie of the graphene–CNT electrode at various deformations. The movie shows floating and undeformed graphene flakes that are similar to graphene with cracks at irreversible stretching deformation in previous research [50]. In general, the cracks cause an abrupt and irreversible diminishement in the graphene’s advantageous properties. According to percolation theory, the formation of percolation islands causes an exponential decrease in conductivity and performance [9]. In the case of CNT stretchable motors that connect the graphene islands to one another, however, the unique properties of the graphene surface are maintained, even under conditions of significant deformation (Figure 4-3(d)). Therefore, the graphene flakes are able to reversibly drift with a high degree of strain while its original properties are maintained. A graphene sheet that is not deformed during stretching and release offers many advantages for multifunctional applications. Each drifted and undeformed region of the graphene layer can be used as a conductive location for the installation of microdevices as various types of stretchable electronics, i.e., molecular devices, and for stable energy storage from an electrochemical double-layer, which was previously unachievable in a stretchable system.

The stable connection between graphene flakes was verified by monitoring the conductivity change at various deformed states (Figure 4-8). As shown in Figure 4-8(a), the resistance of the graphene–CNT-layered
structure was nearly unchanged under a tensile strain of 80% in the case of uniaxial deformation, and a gradual increase in sheet conductivity was observed. The limiting strain of the structure was 75%, as indicated by the percolation threshold in Figure 4-8(b). In spite of these limitations, the tendency of conductance of the graphene–CNT stretchable electrode was maintained during 100 cycles of stretching–releasing with a strain of more than 150%, proving the excellent mechanical stability and durability of the graphene–CNT electrode system. To examine the tolerance of the system at extremely mixed deformation conditions, I carried out conductivity measurements during the repeated contraction and expansion of a rubber balloon onto which the graphene–CNT electrode layer was installed (Figure 4-8(c)). The expansion of the rubber balloon by the injection of air induces a significant simultaneous biaxial deformation and shear deformation, which is of interest for practical applications [21,39-44]. Figure 4-8(d) shows the graphene–CNT electrode region in the contracted and expanded states during the measurement of conductivities. The surface extension of the inorganic muscle system on the balloon induced in this manner reached ~140% in the expanded state. In consequence, the electrode maintained ~80% of the original sheet conductivity, and superior electrical conductivity was verified during more than 100 cycles. The results of 3D-FEM simulations indicate that the extension of the graphene–CNT on the rubber balloon (the radius of the balloon was 2 cm) was 136% (Figure 4-8(e)). This observation suggests that the graphene–CNT electrode system provides negligible mechanical loading on the elastic support, which is consistent with the very low effective modulus conferred by the intrinsic properties of the CNT clusters [53].

As a practical demonstration, I used the stretchable electrode as an electric
circuit for various stretchable electronics: electronic surgical gloves and hemispherical contact lenses (Figure 4-8(f) and 4-8(g)). The surgery glove and contact lens were used as substrates, which shows the versatile application of the electrode. LED lamps in the stretchable circuits were integrated onto the drifting graphene flakes by conventional soldering. The unique mechanism of the graphene–CNT-layered system enables the integration and stretching operation realized by the soldering method, which is unavailable when even state-of-the-art stretching circuits are used [109].

Many stretchable electrodes, including electronic devices and power supplies, have recently been reported. However, their practical usage is valid only for ready-made and fixed electronic components. Most of the methods for preparing stretchable electronics demand a sophisticated procedure, because the operating components and stretching bridges need to be precisely separated and fixed on the surface of the system. However, a conventional integrating method for electronics, represented by soldering, is inappropriate for use in such processing and soldering terminals are required for the connection to the electronic components. In this study, the surface of the graphene-CNT electrode was composed of only a graphene sheet. Therefore, the electronic devices were not in separate locations. This means that conventional electronic components can be implanted on the electrode, irrespective of the integration method used. The LED was fixed and operated well at stretching and bending states, which proved that the undeformed regions supporting the device were able to flow freely along the stretching CNT cluster. The stretchable electrode system can also be attached to a curvilinear surface (e.g., contact lenses, without any defects), as shown in Figure 4-8(g). The difference of sight focus with and without the contact lens
proves that the electric lens maintains its sight-correction ability, even after the insertion of an electric circuit. These results show that the system provides a solution for the fusion of electronics and hemispherical photodetector arrays.

The graphene flakes not only provide floating and undeformable regions for active devices on CNT stretchable circuits, they also have significant electrochemical double-layer energy caused by the intrinsic high surface area (2630 m² g⁻¹, theoretically) [23]. From a electrochemical double-layer mechanism, the specific surface area of materials is linearly proportional to the energy storage performance, and graphene is considered to be the best candidate for use in electrochemical double-layer energy storage systems [47,48]. To fabricate the inorganic system for a supercapacitor, I used a PVA gel as a substrate for the graphene–CNT electrodes [100,110]. Specifically, the PVA gel serves as (1) an elastic substrate, (2) glue, (3) a separator, and (4) a solid solvent of electrolytic ions. The graphene–CNT stretchable electrodes were reversibly located on both sides of the PVA gel substrate. The PVA gel used here contained H₃PO₄, which functions as an electrolyte. The stretchability of the energy storage system comes not only from stretchable CNT clusters but also from the pseudo-elastic PVA gel substrate. The PVA gel and the CNT clusters are made up of similar serpentine network chains on the atomic and microscale, respectively. These networks retain the construction of the electrodes and contribute to the reversibility of deformation [111].

Figure 4-10(a) shows C/D curves of the supercapacitor system with graphene–CNT electrodes during the stretching process. The specific capacitance is 329 F g⁻¹ based on the mass of the active component as
graphene layers, which is even higher than the performance of conventional electrode materials without stretchability, as reported in previous studies [47-49]. The mass of the graphene was determined by the volume of graphene ink spread on the substrate. A 600 μl aliquot of graphene ink (0.5 g/L) was used, therefore I calculated the mass of the graphene to be 0.3 mg. Based on the mass of the full cell, including passive components, the capacitance is 58.4 F g⁻¹, which is much more efficient than the capacitance of devices fabricated using conventional techniques, including state-of-the-art stretchable and nonstretchable energy storage systems [21,40,43-45,47-49]. The reason for these improved results is that the stretchable supercapacitor system is designed as a freestanding form and thus does not need a heavy metal current conductor, passive surface blocking active sites for stretching, or an external skeleton, which are used in conventional schemes for structure maintenance. The supercapacitor system possessed stable C/D performance for 3.3 h during the stretching process, suggesting that the system can be stretched up to approximately 80% strain without a decrease in performance. Figure 4-10(b) and (c) show the representative C/Ds and CVs of inorganic muscles upon releasing and 80% stretching at different current and scan rates. The CVs are rectangular in shape within a selected range of potential, even at high scan rates, indicating that the system maintained excellent capacitance behavior under highly strained conditions. The results are also in good agreement with the C/Ds at various current densities. Twisting provides another substantive mode of deformation that is of interest regarding high shear deformation in the axial and width directions. Optical images of 360° twisting deformations and 3D-FEM simulations indicate that the system has strong mechanical stability (Figure 4-3(b)). The C/D and CV values also
indicate stable and high-energy storage characteristics (349 F g\(^{-1}\)) with a twisting angle of 360°, as shown in Figure 4-10(b) and (c). The curves are nearly unchanged in comparison with the original relaxed system and the performance is even higher, indicating the high mechanical and electrical durability of the system.
Figure 4-1. Atomic-scale properties of graphene–CNT and actin–myosin interactions. (a) SEM image of graphene–CNT interface. (b) Models for the progressive movement of myosin along actin in a living cell and of CNTs along graphene in an inorganic system. (c) The minimum energy path for the movement of myosin (or CNT) on actin (or graphene) for a living cell and inorganic system. (d) Differential charge densities $\rho_{\text{diff}} = \rho_{\text{total}} - (\rho_{\text{graphene}} + \rho_{\text{CNT}})$ of graphene–CNT interface with AB and AA stacking between hexagonal carbon chains. Positive (yellow) and negative (blue) values are plotted on the same isosurfaces.
Figure 4-2. (a) Top views of the graphene-CNT structures at AB and AA stacking after the optimization by DFT calculation. The C atoms in graphene and CNT are represented by smaller brown and larger yellow spheres, respectively. The black square represents the unit cell of the structure for the calculations. Side views of AB and AA stacking are shown in (b).
**Table 4-1.** The calculated total energy (eV U.C.\(^{-1}\)) of structure components. Structure components contain the CNT and graphene with various strains and graphene-CNT layered structures (AA and AB stacking).

<table>
<thead>
<tr>
<th>Component</th>
<th>Total energy (eV U.C.(^{-1}))</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>-296.953</td>
<td>Zero</td>
</tr>
<tr>
<td>CNT</td>
<td>-369.552</td>
<td>Zero</td>
</tr>
<tr>
<td>Graphene-CNT (AB stacking)</td>
<td>-666.994</td>
<td>Zero</td>
</tr>
<tr>
<td>Graphene-CNT (AA stacking)</td>
<td>-666.917</td>
<td>Zero</td>
</tr>
<tr>
<td>Graphene</td>
<td>-289.924</td>
<td>10</td>
</tr>
<tr>
<td>Graphene</td>
<td>-273.617</td>
<td>20</td>
</tr>
<tr>
<td>Graphene</td>
<td>-261.061</td>
<td>30</td>
</tr>
<tr>
<td>Graphene</td>
<td>-261.294</td>
<td>40</td>
</tr>
<tr>
<td>Graphene</td>
<td>-261.869</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 4-3. Microscale structure of graphene–CNT stretchable electrode. (a) Compressing and releasing of muscle in a human body through actin–myosin interaction. (b) Optical images and equivalent stress simulation (finite element model (FEM) calculation) of graphene–CNT electrodes at uniaxial, biaxial, and twisted deformation. (c) SEM images of graphene–CNT-layered structure at biaxial stretching (80%) and releasing. (d) High-resolution SEM images of individual crumpled structures in graphene–CNT networks at the point of stretching and releasing. The graphene layers are undeformable and separated from each other. The CNT cluster under the graphene flakes are randomly bending and stretching.
Figure 4-4. Schematics of (a) drifting graphene on the surface of CNT cluster with an actin-myosin coupling analogue and (b) a conventional stretchable circuit without the coupling effect. The upper surface of the CNT cluster is in a state of stretching, with drifting motion of undeformable graphene flakes.
Figure 4-5. Fabrication of graphene-CNT networks with crumpled structures. i) Two dimensional stretching of elastic substrates. ii) Loading of CNT cluster and graphene flakes. iii) Releasing of the substrate and generated crumpled structure.
**Figure 4-6.** Safety factors for various stretching deformations. Inorganic actin (graphene)-myosin (CNT) at i) uniaxial, ii) biaxial and iii) twisted deformation. The safety factors over 1 indicate that the models are physically stable.
Figure 4-7. Optical images of graphene-CNT electrode surface. (a) Released structure and (b) uniaxial stretched structure.
Figure 4-8. Graphene–CNT-layered structure on various substrates. (a) Sheet conductivity and normalized resistance of graphene–CNT-layered structure on rubbers at different strain levels during 100 stretching–releasing cycles. (b) Differential sheet conductivity of graphene–CNT-layered structure, which shows the percolation threshold. (c) Normalized sheet conductivity of graphene–CNT-layered structure constructed on balloon during 100 expansion–deformation cycles. (d) Optical images of graphene–CNT-layered structures on the balloon without and with 140% stretching and shear deformation. (e) Equivalent strain, stress, and shear stress in the \( x-y \) plane of balloon with graphene–CNT-layered structure by three-dimensional (3D)-finite element model (FEM). Black dotted boxes indicate the location of graphene–CNT layers. (f) Optical images of a light-emitting diode (LED) mounted on a surgery glove without and with finger bending. The images were obtained without external illumination. (g) Optical images of contact
lens with LED circuit, collected with (up and left) and without (up and right) external illumination. Photographic images at different focal lengths as captured by CMOS image sensor with and without the electric lens.
Figure 4-9. (a) Side views and (b) top views of the strained graphenes with identical isosurfaces of calculated total charge densities. (c) The relative energy versus uniaxial strain of graphene in $x$ direction.
Figure 4-10. Dielectric energy storage properties of a graphene–CNT-layered structure. (a) The galvanostatic charge/discharge curve (C/D) of graphene–CNT layers on PVA/H₃PO₄ film at a constant current of 0.15 A g⁻¹ while the structure was stretched at a constant speed of 0.4% strain per minute. (b) Representative C/Ds at various current densities (0.15–0.75 A g⁻¹) without strain and with stretching (80%) and twisting (360°). (c) Representative cyclic voltammetry curves (CVs) at various scan rates (1–10 mV s⁻¹) without strain and with stretching (80%) and twisting (360°).
Chapter 5. Dual planar-helix type energy storage wires to circumvent universal energy lag effect

5.1 Experimental

5.1.1 Fabrication of planar and cylindrical shape elongated electrodes.

Commercial carbon wires (TAEKWANG CO.) were used as an electrode for fabricating the supercapacitor wire. The commercial carbon wires have an elongated planar-structure and are composed of micro-sized carbon fibers and sizing agents to maintain the planar-structure [12]. The sizing agent was eliminated by heat and acid treatments before I change the structure. To eliminate the organic sizing agent (epoxy resin) on the surface, the electrode is heated under a $\text{N}_2$ flow at 800°C (2 h), followed by an additional acidic treatment (12 h) using the mixture of sulfuric acid (95 wt%) and nitric acid (60 wt%) in 3:1 (v/v). The acid-treated carbon thread was rinsed with deionized water followed by a complete drying at 60°C in an oven. The elimination of sizing agent was verified by X-ray photoelectron spectroscopy analyses (XPS) (Figure 5-1). After the elimination of sizing agents, the planar structure can be converted to cylindrical-shape by the agglomeration of carbon fibers in water. For the comparison of planar and cylindrical wire structures, the carbon fibers were shaped into planar structures (4.35 mm in width and 144 μm in depth) and cylindrical structures (447 μm of radius).
The effective radii of dual planar-helix and double-helix type supercapacitor devices are 1.19 and 1.12 mm, respectively.

5.1.1 Fabrication of dual planar-helix and double-helix type supercapacitor wires.

PVA/H$_3$PO$_4$ gel was used as a gel polymer electrolyte (GPE). 5g of PVA (Sigma, reagent grade, degree of polymerization: 2000-3000) was mixed with 40ml deionized water and 2.4ml of H$_3$PO$_4$ (85 wt%). The temperature was then raised to 358 K on a hot plate with sufficient stirring until a transparent gel was formed. This viscous liquid was poured onto the planar glass bath and allowed to spread to an equal thickness after a minute. As-synthesized carbon wires were placed in the PVA/H$_3$PO$_4$ gel solution for 12 hours to complete the solidification. The other side of the wires was coated in the same way. Finally, the PVA-coated carbon thread electrodes (independent half-cells) were peeled off from the glass bath, combined in pairs by the graft force originated by the GPE and twisted to create a wire-type full cell.

5.1.2 Weaving of energy storage textiles with warp and weft electrodes.

To fabricate textile supercapacitors with parallel circuit analogues, PVA-coated planar thread electrodes are placed together so as to cross over and under each other to produce a fabric with a checkered pattern. In this study, a total of 12 electrodes were used in single textile supercapacitor cell, six in each direction. An additional step is needed to prepare series circuit
analogous. In the middle of the six electrodes laid on the same direction, there were uncoated-GPE lines, one on each single thread. The sectionalized GPE line was fabricated by a lift off method which is has been described in my previous research [100]. As a consequence, each side of textile sectionalized by GPE acts as an independent capacitor unit allowing the entire textile to be two supercapacitors in series.

5.1.3 Characterization and electrochemical measurement.

Cross-sectional SEM images of dual planar-helix and double-helix wire-type supercapacitors were obtained using a field-emission scanning electron microscope operating at 2 kV with an in-lens detector (Sigma, Carl Zeiss). Cyclic voltammetry (CV) was carried out using a computer-controlled potentiostat (Zive sp2, Zive Lab) at various potential windows (0–1.6 V) and galvanostatic charge–discharge (C–D) measurements were carried out using the same equipment at various current densities (4 mA cm\(^{-3}\) – 22.13 mA cm\(^{-3}\) \(^3\)). XPS spectra were obtained using a Kratos AXIS-HIS electron spectrometer equipped with a Mg-Ka X-ray source and a hemispherical electron energy analyzer.
5.2 Results and discussion

From electromagnetism, a charged plane creates one dimensional and uniform electric fields: \( \mathbf{E} = \frac{Q}{\varepsilon_0 A} \). Where \( \mathbf{E} \) is the electric field, \( Q \) the total charge on the charged plane, \( \varepsilon_0 \) the permittivity of free space and \( A \) the vector area of the plane (Figure 5-2(a)). With this equation, it is possible to assume that an ordinary planar electrode also has a homogeneous \( \mathbf{E} \) with the exception of edge effects. On the other hand, a wire-type electrode has a cylindrical structure. Therefore, it makes \( \mathbf{E} \) in a radial direction, and the \( \mathbf{E} \) is inversely proportional along with a radial vector, \( r \). The calculated \( \mathbf{E} \) in a wire structure via Gauss’s law is derived as an Equation (1) with Figure 5-2(b).

\[
\mathbf{E} = \frac{Q}{\varepsilon_0 2\pi r L} \quad (5-1)
\]

The difference of \( \mathbf{E} \) causes a disparity in the charged energy in the electrodes. The ‘energy lag effect’ is defined as the energy density gap between a planar and cylindrical electrode constituting wire-type energy storages. To be specific, we analytically derived an equation for the difference of capacitance densities (\( C_{sp} \)) in planar and wire-type supercapacitors. In the supercapacitor or an EDL capacitor system, the volume between two electrodes is filled with an electrolyte. Therefore, an electrical potential (\( \psi \)) is generated in the system between the surface of the electrode and attractive counter ions in the electrolyte. In conclusion, considering the different structures, plane and wire, it is possible to simultaneously create different EDL models on each electrode in this charge situation.
The sophisticated picture of a conventional planar EDL has been described using the Gouy-Champman-Stern (GCS) model during the past decades [113]. The GCS model is derived from the combination of the von Helmholtz and Gouy-Champman model using a Poisson-Boltzmann (P-B) equation with a Cartesian coordinate. Regardless to the coordinate system, the P-B equation is governed by a differential form as follows [114].

\[
\nabla^2 \psi = -\frac{\rho}{\varepsilon_r \varepsilon_0} \quad \text{and} \quad \rho = e \cdot \left[ z_+ c_\infty^+ \exp \left( \frac{-z_+ e \psi}{k_B T} \right) - z_- c_\infty^- \exp \left( \frac{z_- e \psi}{k_B T} \right) \right] \quad (5-2)
\]

From the Equation (2), the differential form of a \( \psi \) in EDL can be described in Equation (3) with a valence of electrolyte.

\[
\nabla (\varepsilon_r \varepsilon_0 \nabla \psi) = \begin{cases} 
0 & \text{in Stern layer} \\
2 e z c_\infty \sinh \left( \frac{z e \psi}{k_B T} \right) & \text{in diffuse layer} 
\end{cases} \quad (5-3)
\]

Where \( \rho \) is the charge per unit volume, \( \varepsilon_r \) the dielectric constant of the solvent, \( e \) the electron charge, \( z \) the ionic charge, \( c_\infty \) the bulk ion concentration, \( k_B \) the Boltmann constant, and \( T \) the absolute temperature. At low ion concentration, the P-B equation was already solved on a cylindrical coordinate using a numerical method for applications in plasma physics or DNA double-helix structure mixed with liposomes [115,116]. In a supercapacitor system, a simple Stern layer (or a Helmholtz layer) can be used as depicted EDL without a diffuse layer, because it is reasonable for a relatively high ion concentration where a diffuse layer is not expected to play a major role analogous to the schematics in Figure 5-3(a) and (b) [32,117]. The assumption is well operated in a variety of supercapacitor electrolytes, \textit{i.e.}, 1 M \( \text{H}_3\text{PO}_4 \) and 6 M KOH in aqueous solvent or 1.5 M tetraethylammonium tetrafluoroborate in non-aqueous solvent.
(TEABF₄/CH₃CN) [33,34]. In this context, the P-B equation is simplified as a Laplace’s equation ($\nabla^2 \psi = 0$) in supercapacitor systems. The Laplace’s equation expresses $\psi$ related to one electrode in a supercapacitor system. However, $\Delta \psi$ is almost zero in a bulk electrolyte and the $\psi$ has an inverse symmetry on both electrodes, therefore the equation can show the distribution of $\psi$ for the entire system. In Figure 5-4, I showed the relationship between $\psi$ and the dimensionless location of electrodes in planar and cylindrical supercapacitors. In conclusion, it is possible to analytically solve the differential equation and to understand the electrochemical performance of a wire-type supercapacitor.

The capacitances ($C$) of planar and wire-type supercapacitors are depicted as in Equation (4) and (5) with Figure 5-5. $C$ can be determined by the relations; $C \equiv Q/\Delta \psi$. The $\Delta \psi$ is calculated by the integration of Laplace’s equation that arises from Equation (3) with a Cartesian and cylindrical coordinate, respectively. The boundary conditions of the calculation are that if $t = t_0$ and $r = r_0$, $Q = \text{constant}$ in the surface of the electrode. $t_0$ is the half-thickness of the electrode, $r_0$ is the radius of the electrode and $Q$ is a total charge on the charged surface.

$$C \equiv \frac{Q}{\Delta \psi} = \frac{\varepsilon_r \varepsilon_0 A}{t - t_0}$$

if $t = t_0$, $Q = \text{constant}$ in a planar electrode \hspace{1cm} (5 - 4)

$$C \equiv \frac{Q}{\Delta \psi} = \frac{2\pi \varepsilon_r \varepsilon_0 L}{\ln(r/r_0)}$$

if $r = r_0$, $Q = \text{constant}$ in a cylindrical electrode \hspace{1cm} (5 - 5)

The equation (5) is similar to an EDL model in the cylindrical pore structure of carbon as previously researched.\[27,29\] In consequence, the capacitance densities ($C_{sp}$) in planar and wire type electrodes are as follows.
\[ C_{sp} \equiv \frac{C}{\nu} = \frac{\varepsilon_r \varepsilon_0}{t_0(t - t_0)} \quad \text{in planar electrode} \quad (5 - 6) \]

\[ C_{sp} \equiv \frac{C}{\nu} = \frac{2\varepsilon_r \varepsilon_0}{r_0^2 \ln(r/r_0)} \quad \text{in cylindrical electrode} \quad (5 - 7) \]

where \( \nu \) is the volume of electrode. Equation (6) and (7) prove that a \( C_{sp} \) and energy density is closely related to the morphology of the electrode. According to the following Equation (8), it is reasonable that the wire-type supercapacitors would have a lower capacitance compared to that of two-dimensional planar supercapacitors made up identical materials.

\[ \Delta C_{sp} \equiv C_{sp \, plane} - C_{sp \, wire} = 2\varepsilon_r \varepsilon_0 \left( \frac{1}{2t_0(t - t_0)} - \frac{1}{r_0^2 \ln(r/r_0)} \right) \quad (5) \]

I refer to the \( \Delta C_{sp} \) between planar and cylindrical electrodes as the energy lag effect in supercapacitor or capacitance lag effect. In Figure 5-3, the distance between surface of electrode and counter ions \( (d) \) is uniform and it is same with a radii of solvated counter ions. Therefore, \( d = t - t_0 = r - r_0 \) in Figure 5-5. If \( d \ll r \), \( r_0 \ln(r/r_0) \approx r - r_0 \) [33,34]. Most reported wire-type supercapacitor systems satisfy this assumption, therefore the capacitance lag effect is simplified as Equation (9) [64-72].

\[ \Delta C_{sp} = \frac{2\varepsilon_r \varepsilon_0}{d} \left( \frac{1}{2t_0} - \frac{1}{r_0} \right) \quad (5 - 9) \]

The calculated ratio of \( C_{sp \, plane} / C_{sp \, wire} \) using the capacitance lag model (Equation (9)) is \( r_0 / 2t_0 \). This result is independent of the absolute radii in wire electrodes because specific shapes cannot influence the absolute volume of identical materials. To make \( C_{sp \, plane} / C_{sp \, wire} \) to be under 1, the ratio of width and thickness \( (a / 2t_0 \) in Figure 5-5) in plane electrodes must be under \( \pi \) (~3.14). In practice, the ratio in plane electrodes is at least > 10, therefore \( r_0 \gg 2t_0 \). In conclusion, conventional-shaped supercapacitor wires
always have a lower energy density than two-dimensional planar supercapacitors regardless of absolute size when identical materials are used. From the analytic interpretations and schemes, I can not only prove the fundamental limitation of wire-types, but also find a breakthrough to circumvent this geological issue.

In order to solve the capacitance lag effect, supercapacitor wires must not have conventional double-helix structures. I proposed a new design of a supercapacitor wire that contains a dual planar-helix structure (Figure 5-3(c-f)). In the systems, parallel and elongated flat-electrodes are located at opposite sites and twisted together, and both electrodes are separated by a gel-polymer electrolyte (GPE). The twisting is a way to construct wire-type supercapacitors utilizing elongated planar-electrodes. The way of twisting for the elongated planar-supercapacitor was presented in Figure 5-6. In this helix structure, the $z$-axis is symmetrical without considering edge effects. By the symmetry and a superposition law, the electrochemical properties of the supercapacitor are consistent along with $z$-axis. In conclusion, the dual planar-helix type supercapacitor has a complete wire structure and the performance is analytically the same as an ordinary two-dimensional planar supercapacitor, which means that the dual planar-helix types do not show the energy lag effect observed in universal wire-type energy storages.

The proof-of-concept experiments for the planar-helix structure are based on a commercial carbon wires as an electrode and PVA/H$_3$PO$_4$ as a GPE (Figure 5-7). Carbon allotropes were well known members of supercapacitor electrodes [79,118], and PVA/H$_3$PO$_4$ GPE is widely used due to its non-toxic nature and possible coupling of charge transport [88,89]. The GPE in the system serves as a separator, glue, electrolyte and elastic skeleton component
at once. The dual planar-helix supercapacitor wires does not require the additional loading of active materials or post treatment to increase their performance, which is another distinct advantage of this system over conventional wire-type supercapacitors from an engineering view point. The selected materials for the electrode and GPE are replaceable and are not limited in the system.

For a control experiment, I fabricated both dual planar-helix and conventional double-helix supercapacitor wires using identical electrodes and electrolyte. The morphologies of the fabricated supercapacitors can be seen clearly in optical and SEM images (Figure 5-3(e), (f) and 5-7). The electrical resistances of the electrodes were measured as shown in Figure 5-8. The resistances of electrodes with a planar and a cylindrical shape are 3.03 Ω and 2.94 Ω, respectively. Both electrodes showed equivalent values of resistances, which represents that the difference in the performance of two system is determined by a geometry, not a conductivity. These results of electrical conductivity are rational, because the material (carbon wire) and the length (8 cm) of electrodes of both dual planar-helix and double-helix type supercapacitors used are identical. The electrochemical properties and the resistive behavior of the planar-helix and double-helix systems were examined by cyclic voltammetry (CV) and galvanostatic charge/discharge (C-D) analyses shown in Figure 5-9(a) and (b), respectively. The prototype device with planar-helix structure has a 3.14 F cm$^{-3}$ of $C_{sp}$ at a current density of 4 mA cm$^{-3}$ and the value is converted as 19.72 mF cm$^{-1}$ of capacitance per unit length of the wire (See calculation details in Supporting Information). This value is about from three times to two orders of magnitude higher than that of currently available one-dimensional electrodes,
such as carbon fibers (0.504 mF cm$^{-1}$) and carbon nanotubes (CNTs) (0.51 mF cm$^{-1}$) in EDL capacitors [66,67], MnO$_2$/CNT (0.022 mF cm$^{-1}$) and Ni(OH)$_2$/ordered mesoporous carbon (6.67 mF cm$^{-1}$) as transition metal oxides [68,69], polyaniline/CNT as a conducting polymer electrode (0.9 mF cm$^{-1}$) in pseudo-capacitor [70], respectively. In addition, it is further possible to increase the performance of the conceptual system by using cutting edge electrode materials similar to conventional wire-types, i.g., metal oxide hybrids for inducing pseudo-capacitance behavior.

The $C_{\text{sp}}$ of dual planar-helix supercapacitor (1.91 F cm$^{-3}$ at 10 mV s$^{-1}$) is 3.0 times higher than that of a double-helix type prepared using the identical materials (0.66 F cm$^{-3}$ at 10 mV s$^{-1}$). The calculated ratio of $C_{\text{sp dual planar-helix}} / C_{\text{sp double-helix}}$ using the capacitance lag model (the ratio = $r_0 / 2t_0$) is 3.36 which is similar to the measured ratio ($\approx 3$) from experiments. This proves that the analytical model describing the energy lag effects operates well and is rationally applicable to real systems. When the scan rate was increased from 3 to 50 mV s$^{-1}$, approximately 30% of its original capacitance was measured (Figure 5-9(a)). The $C_{\text{sp}}$ values were found to be 2.59, 2.30, 1.91, 1.45, 1.16 and 0.76 F cm$^{-3}$ for scan rates of 3, 5, 10, 20, 30 and 50 mV s$^{-1}$, respectively. Although the system exhibited a slight resistive behavior at a scan rate of 50 mV s$^{-1}$, the measured CVs retained a reasonable rectangular shape [119]. From C-D analyses, the planar-helix type obviously exhibited a longer discharge time than that values based on the double-helix structure. With planar-helix electrodes, $C_{\text{sp}}$ values of 3.14, 2.84, 2.59, 2.43, 2.17 and 1.98 F cm$^{-3}$ were achieved at various current densities of 4, 6, 8, 10, 15 and 20 mA cm$^{-3}$, respectively. Whereas, the double-helix type only showed $C_{\text{sp}}$ of 1.10, 0.91, 0.77, 0.66, 0.46 and 0.34 mF cm$^{-3}$ at same current densities.
All of the above electrochemical results not only prove the correctness of the energy lag effect but also show the advantage of dual planar-helix types in view of performance. The stability of a supercapacitor is also an important parameter for evaluating the suitability of systems for practical applications. Figure 5-10 shows the cycling stability of the planar-type during a repetitive C–D analysis. The structure showed good cyclic stability, and it maintained a capacitance of over 90% of the original value at the initial cycle even after 10,000 charge–discharge cycles. For control experiments, the electrochemical performances of the dual planar-helix wire-type supercapacitor before and after twisting were evaluated. As shown in Figure 5-11, the cyclic voltammetry curves of the supercapacitor before and after twisting were identical, which means that the electrochemical performances are equal irrespective of the twisting deformation.

Concerning the applicability of such systems in wearable devices, many wire-type energy storages have been incorporated into textile products [71,72]. In a further study, we applied my planar-threads as warp and weft yarns themselves and used them to prepare textiles as shown in Figure 5-12. The planar-type carbon thread was first capsulated with GPE, and was then used as a warp or weft. The yarns were in intimate contact, thus guaranteeing a good ion-transport pathway the same as the planar-type supercapacitor. In the energy storage cloth, the extension is easily permitted with parallel and series connections. Figure 5-12(a) and (b) illustrate the schematics of $n \times n$ warps or wefts connected in parallel and series (wire length is 36 mm). From CV and C-D analyses, the output current of parallel connected textiles were increased by a factor of three compared with the single planar-helix supercapacitor wire (Figure 5-12 (c)). I also evaluated the electrochemical
characteristics of the textile under severe bending conditions. There was actually a small increase (about 10%) in capacitance when the systems are bent (the curvature, $k$, is $4 \text{ cm}^{-1}$ and bending radius is 2.5 mm). The improved performance can be attributed to the fact that the bending condition induces pressure in orthogonal direction between GPEs and electrodes as observed in my previous studies [20,100]. This also suggests that there is no significant change in the carbon thread electrode when the supercapacitor was in a severely bent shape, which is in good agreement with the three-dimensional finite elemental modeling (3D-FEM) of the carbon thread in Figure 5-13. In Figure 5-12(d), an enhanced voltage range with the combination of series connection is also provided. In conclusion, the current and voltage range can be easily improved by connecting the wires in parallel or in series analogues to meet the power and energy demands needed. The electrochemical properties are maintained at various rates regardless of the type of circuits and deformation conditions as proved by a series of CV and C-D analyses (Figure 5-14 and 5-15).
The XPS spectra are composed of three contributions at ca. 284.6, 286.7, and 288.6 eV which correspond to carbon sp2 bonding (C=C), epoxide/hydroxyl groups (C−O), and carbonyl/carboxyl groups (C=O), respectively. (a) Before the elimination of the sizing agent, the carbon wire showed a characteristic peak consistent with C−O bonds, which attribute to the presence of oxygen containing functional groups in epoxy resin. (b) After the elimination step, the peak associated with C−C bond becomes predominant while the intensity of the peaks related to oxidized carbon are significantly decreased. The results indicate that most of the epoxy resins used as sizing agent had been removed.
Figure 5-2. Illustrative description of the distribution in the electric field around charges spaces of (a) plane type and (b) cylindrical type. The electric field vectors resulting from both types of charged spaces can be approximated to be uniformly distributed. The vectors are directed normal to the charged surface of electrodes.
Figure 5-3. Schematics of an electrical-double-layer (EDL) on a planar electrode and a cylindrical electrode. (a, b) The sophisticated pictures of EDL on (a) planar electrode and (b) cylindrical electrode. (c, d) Schematics of (c) dual planar-helix and (d) double helix wire-type supercapacitors. (e, f) Optical images of (e) dual planar-helix and (f) double helix wire-type supercapacitors. The scale bars are 10 mm in length.
Figure 5-4. The relationship between potential ($\psi$) and dimensionless location of electrodes in planar and cylindrical supercapacitors. (a, b) Cross-section of potential distribution in (a) plane and (b) cylindrical type electrodes. (c) Representative spatial voltage profile between two electrodes in high concentration of electrolyte. Each dotted line shows the border limit of stern layer and diffuse layer from GCS model. Voltage profiles are symmetrical around both electrodes and become constant in the diffuse layer.
Figure 5-5. Sectionalized schematics of (a) planar electrode and (b) cylindrical electrode for analytic calculation. The distance between Gaussian surface and electrode is the same as the stern layer thickness and the radii of solvated counter ions in the electrolyte.
Figure 5-6. Process flow of twisting method for a dual planar-helix wire-type supercapacitor. The scale bar is 4 cm.
**Figure 5-7.** Structure difference of dual planar-helix and double helix wire-type supercapacitors. (a-d) Scanning electron microscope cross-sectional images of (a, c) dual planar-helix and (b, d) double helix wire-type supercapacitors. (c) and (d) are high resolution images. The scale bars are 100 μm in length.
**Figure 5-8.** Linear sweep voltammograms of planar and cylindrical-type electrode. The resistances of planar and cylindrical electrode are 3.03 Ω and 2.94 Ω, respectively.
Figure 5-9. Electrochemical properties of dual planar-helix and double helix wire-type supercapacitors. (a) Cyclic voltammograms of dual planar-helix and double helix wire-type supercapacitors at various scan rates (3, 5, 10, 20, 30 and 50 mV s$^{-1}$). (b) Galvanostatic charge-discharge profiles of dual planar-helix and double helix wire-type supercapacitors at various current densities (4, 6, 8, 10, 15 and 20 mA cm$^{-3}$).
Figure 5-10. Long cycle stability test of the carbon based dual planar-helix wire-type supercapacitor during 10,000 charge-discharge. Retention of 90% was obtained after 10,000 cycles.
Figure 5-11. Cyclic voltammograms of dual planar-helix wire-type supercapacitor before and after twisting at various scan rates (5, 10 and 30 mV s\(^{-1}\)).
**Figure 5-12.** Woven textile composite with warp and weft electrodes. (a, b) schematics of $n \times n$ warps or wefts connected in (a) parallel and (b) series and optics images of woven textile composited with $6 \times 6$ warps or wefts. In the schematics, the red lines and blue lines show positive and negative charged yarns, respectively. In (b), center line appears location of cutting line of sectionalized electrolyte. (c, d) Cyclic voltammograms and charge/discharge curves of the textile supercapacitor with (c) parallel and (d) series circuit analogues. In c), the red dots indicate the characteristic in bending deformation and the gray dots show that in flat. The blue lines in (d) show the stable potential window (0.8 V) of single supercapacitor wires.
Figure 5-13. Three dimensional finite-elemental method analyses of bent carbon wire. (a) Design of mesh for un-deformed carbon wire. (b) Equivalent stress, (c) equivalent strain and (d) safety factor analyses of the bent carbon wire. The scale bar is 2 mm in length and the curvature of bending deformation is $4 \text{ cm}^{-1}$ (Bending radius is 2.5 mm).
Figure 5-14. Electrochemical performance of the textile supercapacitor with parallel circuit analogue (6 × 6 warps or wefts). Comparative analyses were conducted between flat and rolled textiles. The red and dark lines indicates flat and bent one, respectively. The figure on the right is the rolled textile supercapacitor. a) Cyclic I for different scan rates. The $C_{sp}$s calculated from the CV curves are 1.54, 1.37, 1.16, 0.95, 0.85, 0.70 F cm$^{-3}$ in flat (gray) and 1.76, 1.55, 1.30, 1.07, 0.94 and 0.78 F cm$^{-3}$ in bended textile (red), at the scan rates of 3, 5, 10, 20, 30 and 50 mV s$^{-1}$, respectively. The latter exhibited a slightly increased capacitance. This enhancement can be attributed to more intimate contact between compressed interfaces of each electrode due to the bending status. b) Galvanostatic charge-discharge curves for different current densities. The $C_{sp}$s calculated from the charge-discharge curves are 2.40, 2.15, 1.98, 1.86, 1.64 and 1.50 F cm$^{-3}$ in flat (gray) and 2.78, 2.46, 2.23, 2.07, 1.79 and 1.62 F cm$^{-3}$ in bended textile (red), at the current densities of 4.43, 6.63, 8.85, 11.07, 16.6 and 22.13 mA cm$^{-3}$, respectively. (c) Optics image of textile supercapacitor with a bent structure (The curvature is 4 cm$^{-1}$.
Figure 5-15. Electrochemical performance of the $6 \times 6$ textile supercapacitor with series circuit analogues. The blue line indicates stable potential window (0.8V) of a single wire. a) Cyclic voltammograms for different scan rates. Two equivalent sets of supercapacitors in a fabric exactly double the potential window (1.6V) without any side reactions. The $C_{sp}$s calculated from CV curves are 306, 265, 221, 185, 163 and 140 mF cm$^{-3}$, at the scan rates of 3, 5, 10, 20, 30 and 50 mV s$^{-1}$, respectively. b) Galvanostatic charge/discharge curves for different current densities. The $C_{sp}$s calculated from C-D curves are 800, 673, 599, 555, 483 and 434 mF cm$^{-3}$ at current densities of 2.95, 4.43, 5.9, 7.38, 11.07 and 14.75 mA cm$^{-3}$, respectively.
Chapter 6. Conclusions

The recent boom in miniaturized electronics requires more compact, flexible and high performance energy storage systems. As a result, the growth of energy storage system with novel patterning assembly technologies has been accelerated. Patterning technology related to electrodes for energy storage facilitates improvement in performance by a high surface-to-volume ratio and unemployment of binders or separators in their production. Furthermore, the technique also promotes other advantages, such as bending and stretching. In this thesis, I developed various types of electrodes architectures for the application to flexible energy storage devices.

First, the materials and mechanical concepts reported here for creating transparent and flexible energy storage devices describe design options that are unavailable when conventional schemes are used. In this case, the technology foundation for transparent and ultra-bendable energy storage devices without percolation and depth limitations is introduced, with demonstrated examples in in- and out-of-plane deformation states. This prototype device, built on large-scale interdigitated grid type electrodes, constitutes significant advances over existing methodology for transparent electrodes for supercapacitors in terms of capacitance and the flexibility.

Second, technological break-through was reported, involving the use of a series of analogue circuits and an origami-based structure with an increasing stable potential window and naturally foldable characteristics. The conceptual system, built on IEs and SITP, offers a significant advance over existing methodology for film-type patterned energy storage devices in terms
of energy density, power density and foldable characteristics.

Third, the designed graphene–CNT stretchable electrode provided important and extraordinary capabilities in deformable electrodes, as demonstrated by the integration of circuits on various substrates and based on their application as energy storage materials with significantly high performance. The suggested system, built on a 2D graphene track with a CNT motor, offers significant improvement over existing methodologies for stretchable electronics in terms of stability, multimode deformation, and density of energy.

Finally, I addressed two sequential topics that are of interest for universal wire-type electrode. First, a valid method was analytically designed for calculating the cutting edge wire-type energy storage devices based on fundamental electromagnetism. Second, rationally optimized energy storage threads were fabricated based on this knowledge. The fabricated thread-type electrodes could be transformed into wires, textile, and integrated parallel and series circuit analogous.

These systems has drawbacks to be resolved for the practical applications, such as relatively high fabrication cost. However, I believe that the concepts have noteworthy implications across a number of disciplines toward the development of high-performance and stretchable electronics for the next generation.
Chapter 7. Recommendations for Further Research

The novel strategies for the fabrication of electrode architecture proposed in this dissertation can be extended to the other types of energy storages system (e.g. lithium or Sodium ion batteries) by further studies.

For the further studies, the most important part is the choice of some optimized materials. To fabricate lithium ion battery system, the development of flexible and solid state electrolyte is required. Among the solid state electrolytes, gel polymer electrolyte can be one of the most promising candidate due to its high elasticity. The well-estabilished gel polymer electrolyte (GPE) for lithium ion batteries is PEO-LiX (or PEO-AₓBᵧ) in which the X⁻ are ClO₄⁻, AsF₆⁻, CF₃SO₃⁻ and BF₄⁻. However, the GPE shows low ionic conductivity, therefore, additional plasticizer or ionic liquid should be considered for the development of advanced GPE. Plus, ceramic fillers (i.e. SiO₂, Al₂O₃) can decrease crystallinity, which increases the ionic conductivity of GPE (nano-composite polymer electrolyte, CPE).

For the application to high voltage origami electrodes, it is necessary to select the anode materials with elevated Li insertion potential (over 0.5 V). Because both anode and cathode are located on a single region for the construction of bipolar system. Therefore, TiO₂ or Li₄Ti₅O₁₂ material (plateau voltage, 1.55V (vs Li/Li⁺)) have strong candidacy.

In order to fabricate stretchable electrode system, electrodes should be composed of graphene and active materials. As a cathode part, LiFePO₄-graphene composite is a representative material. Metal oxide-graphene composites (i.e. Mn₃O₄ and NiO) based on conversion reaction are highly applicable to anode part. In addition, Li₄Ti₅O₁₂-graphene composite is also well-developed anode material. Such examples suggest that the anode and cathode materials with high Li electroactivities can be integrated with the high voltage & stretchable energy storage device proposed in this
dissertation.

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요약(국문초록)

인체 삽입형 장치, 운송 장치 및 신재생 에너지 자원의 개발과 맞물려
에너지 저장 장치에 대한 요구가 해마다 증가하고 있다. 그러나 Moor의
법칙에 따라 발전하고 있는 기타 전자장비와 달리, 에너지 저장 장치의
발전은 오늘날까지도 미비한 실정이다. 특히, 플렉서블 일렉트로닉스의
발전과 맞물려 플렉서블 에너지 저장 장치의 수요가 증대되고 있으나,
일반적인 개발 방식에 따른 한계를 여전히 극복하지 못하였다. 이러한
한계를 극복하기 위하여, 이 학위논문에서는 에너지 저장을 위한 위한
새로운 형태의 플렉서블 전극 구조를 개발하였다.

먼저, 유연하고 투명한 에너지 저장 장치의 개발에 활용할 수 있는 각
지 길 형태의 전극 구조를 개발하였다. 일반적인 투명 전극의 경우, 퍼
콜레이션 효과로 인해 전기화학적 성능이 저수함수적으로 감소하는 문제
점을 갖는다. 각지 길 형태의 전극을 이용할 경우, 투명성을 위해 전극
의 두께를 조절하지 않으므로 퍼콜레이션 효과를 방지할 수 있다. 또한
하나의 기판에 모든 전극을 패턴화하여 높은 유연성을 얻는다. 이러한
이유로, 제작된 투명 플렉서블 전극 구조는 높은 응용특성, 투명성 및
유연성을 동시에 갖는다.

장치의 유연성을 극대화하기 위하여, 종이접기 형태의 접을 수 있는 전
극 구조를 개발하였다. 접결 특성은 차세대 휴대 전자 장비에서 가장 각
장 받는 특성 중 하나이다. 제안된 시스템은 고립 전극과 구획화된 이온
투과 막으로 구성되며, 이러한 구성은 초밀집 직렬 구조를 만들 수 있다
는 장점이 있다. 고립 전극의 개수에 따라, 시스템은 제한없이 높은 전
압을 갖는다. 이 시스템에서 장치의 전력과 에너지 밀도는 동시에 증가
할 수 있으며, 이는 고립 전극의 개수에 따라 결정된다. 이온 투과 막과
전극의 유연성으로 인해 접거나 굽혔을 때도 안정적인 특성을 가지며,
이를 제1원리 계산 및 유한요소법 계산으로 증명하였다.

플렉서블 장치가 가질 수 있는 가장 우수한 구조 특성은 스트레처를 특
성이다. 따라서 스트레처를 슈퍼커페시터를 가능하게 하는 그래핀-탄소
나노튜브 적층 구조의 전극을 개발하였다. 전극 내에서 활성물인 그래핀은 움직이는 트랙으로 역할한다. 도전제인 탄소나노튜브는 외부 장력이 있을 시 그래핀 트랙을 따라 늘어나는 움직임을 보인다. 개발된 시스템은 무시할 만한 수준의 패시브 부피를 갖지며, 이방향 변형 및 꼬임 변형에서도 안정적인 전기화학 특성을 유지하는 장점이 있다. 선 형태의 전극구조를 전자 장비의 형태를 가리지 않고 적용가능한 차세대 플랫폼으로 개발하였다. 전극 구조를 최적화하기 위해 이중 평면 나선 구조의 전극을 설계하였으며, 이러한 전극이 기존 원통형 전극 구조의 에너지 저장 효과를 방지함을 증명하였다. 개발된 평면 나선 전극은 선 형 에너지 저장 장치는 물론 적물화가 가능함을 보였고 이를 통해 높은 수준의 에너지 효율을 증명하였다.

주요어: 플렉서블 에너지 저장 장치, 각자 긴 형태 전극, 투명 전극, 퍼콜레이션 효과, 고립 전극, 구획화 된 이온 투과막, 제한 없는전위창, 스트레쳐블 슈퍼커패시터, 그래핀-탄소나노튜브 적층 구조 전극, 이중 평면 나선 전극.

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