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論 文 内 容 要 旨

Electronic devices are developing in the direction of thinness, flexibility, and wearability. To realize the requirements of visualization products such as flexibility, slimness, and lightness, and portability, their energy supply components also need to be flexible and high-performance. Therefore, flexible energy storage devices, which are energy supply systems for flexible electronic products, have emerged. As an important member of flexible energy storage devices, flexible supercapacitors are gradually showing their potential market value due to their excellent electrochemical performance and much higher safety than traditional energy storage devices. However, flexible supercapacitors still have problems such as low energy density, poor mechanical stability, and specific capacitance attenuation under high deformation. The essential to solving these problems is to avoid delamination of the flexible substrate with the electroactive material under high deformation and to balance mechanical durability and electrochemical properties. In this thesis, from the perspective of flexible electrode structure design, flexible electrodes with excellent electrochemical properties are obtained by utilizing or preparing a variety of flexible substrates with high electrical conductivity and growing on the surface of the flexible substrates or filling the inside with electroactive materials to prepare flexible supercapacitors with

excellent electrochemical and mechanical properties. The main contents and conclusions of the paper are as follows:

In chapter 3, a flexible supercapacitor was designed and fabricated using a two-step polymerization method based on fiberglass cloth and the unique morphology of polypyrrole (PPy). In this extraordinary nanostructure, not only do PPy tentacles provide high-speed channels for the transfer of electrons and ions, but they also create a larger specific surface area, thus enhancing energy storage. The fabricated PPy/CFC supercapacitor possesses an excellent area-specific capacitance of 549.6 mF cm^{-2} and a remarkable energy density of 48.85 μWh cm^{-2}. Besides, it achieves the high capacitance retention of 92.4% after 10 000 charge and discharge cycles and 96.08% after 1000 bending cycles. Furthermore, it is demonstrated that the PPy/CFC supercapacitor is capable of ensuring a stable power supply for practical applications by driving an LCD electronic watch. The fiberglass cloth-based supercapacitors with PPy tentacles provide a new approach to the practical applications of wearable power supplies.

In chapter 4, a lightweight and compressible all-in-one flexible supercapacitor that can easily extend voltage window was fabricated based on melamine foam (MF) and PPy by the one-step polymerization method. The MF serves as the substrate for depositing PPy and the separator to avoid a short circuit. In addition, the MF can sufficiently absorb and lock in the electrolyte to make the electroactive material fully contact the electrolyte. This device exhibits superior electrochemical performance with a volumetric specific capacitance of 2.86 F cm^{-3} and a volumetric energy density of 0.18 mWh cm^{-3}, outstanding mechanical stability which can work stably under different compressive strains. With the novel design, the output voltage of this device can be adjusted handily by a simple cutting method without connecting several supercapacitors in series. This novel strategy may potentially guide the development of all-in-one supercapacitors for portable and wearable electronics.

In chapter 5, a hybrid polyvinyl alcohol/poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PVA/PEDOT:PSS) hydrogel electrode with 3D interpenetrated network structure is prepared by the freeze-thaw crosslinking and solution immersion method. Due to the strong intermolecular force between PVA and PEDOT:PSS, coupling with the use of liquid phase mixing, this hybrid hydrogel electrode shows uniform interconnectivity and robust mechanical properties. The all-gel-state flexible supercapacitor based on the PVA/PEDOT:PSS hydrogel is fabricated to demonstrate its excellent mechanical durability of which capacitance

retention retains 98.1% after 1000 bending cycles as well as excellent electrochemical performance whose areal specific capacitance is 128.9 mF cm^{-2} and energy density is up to 11.46 μWh cm^{-2}. Moreover, it can continuously power the LCD watch in bending, compression, and low-temperature environments. The outstanding comprehensive performance of this supercapacitor indicates that it has the potential to be used in a new generation of flexible energy storage devices.

In chapter 6, an all-gel-state integrated asymmetric flexible supercapacitor based on poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) and polypyrrole (PPy) composite hydrogel electrodes with an interchangeable positive and negative electrode was fabricated. The device has robust flexibility and mechanical durability, with an elongation at break of 286% at a tensile strength of 22.3 MPa and a capacitance retention rate of 98% after 1000 bending cycles, as well as fascinating electrochemical properties, with an energy density of 397.99 μWh cm^{-3} and a capacitance retention rate of 88.1% for 10,000 charges/discharge cycles. Moreover, the positive and negative electrodes of this asymmetric device can be used interchangeably, and it can power the light-emitting diodes (LEDs) without distinguishing between positive and negative. This design concept will perhaps open a new trend in the design of high-energy-density flexible supercapacitors.

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論文審査結果要旨

本論文では、電極材料、デバイス構造設計、組立方法の 3 つの側面から、フレキシブルな全固体型スーパーキャパシタの設計と創製を目的として、その作製方法、電気化学および機械的性質などを調査している。

第 1 章は緒論として、フレキシブルスーパーキャパシタに関する既存の研究から本研究の背景を述べ、本研究の目的を示している。第 2 章では材料および試験方法として、電極の作製方法および電気化学性能の評価方法について説明している。第 3 章では、市販のガラス繊維布をフレキシブル基板とし、ポリピロール(PPy)を電気化学重合によりガラス繊維布の表面に蒸着することでフレキシブル電極を開発し、フレキシブルスーパーキャパシタを作製している。第 4 章では、スポンジをフレキシブル基板として、PPy を電気活性材料として用いて、一体型の圧縮可能なフレキシブルスーパーキャパシタを作製しており、PPy の気相重合が非導電性基板をフレキシブルな複合電極に応用するための新しいアイデアとなることを示している。第 5 章では、ポリビニルアルコール（PVA）ハイドロゲルをフレキシブル基板として用い、ポリ(2,3-ジヒドロチエノ-1,4-ジオキシン)-ポリ(スチレンスルホナート)（PEDOT:PSS）を電気活性物質として、オールヒドロゲル一体化構造のフレキシブルスーパーキャパシタを作製した。このオールヒドロゲル一体化構造によりスーパーキャパシタの機械的性質および動的変形中のデバイスの安定性が向上することを明らかにした。第 6 章では、PVA/PEDOT:PSS 複合ハイドロゲルと PVA/PPy 複合ハイドロゲル電極を使用して、正極と負極を区別する必要のない非対称オールヒドロゲル一体化フレキシブルスーパーキャパシタを作製しており、今後のエネルギー貯蔵デバイスの開発に新たな方向性を示している。第 7 章は結論であり、研究結果をまとめている。

本論文の成果は、全固体型フレキシブルスーパーキャパシタの設計・製造に重要な学術的貢献をしただけでなく、その高い性能により優れた工学的価値を有している。また、研究業績として、査読付学術論文 4 編、国際会議 2 件、国内会議 1 件を公表している。

よって、本論文は博士（工学）の学位論文として合格と認める。