Stretchable Transparent Supercapacitors for Wearable and Implantable Medical Devices

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Recent advances in wearable bioelectronics have driven various healthcare applications, such as the monitoring, sensing, and treating of various diseases. However, unsustainable batteries and toxic power solutions hinder their use at the skin interface or in vivo. As a promising power solution, supercapacitors have attracted the attention of researchers. However, there are still several drawbacks, such as the transparency, stretchability, biocompatibility, and flexibility of these materials, when these energy reservoirs are used as power supplies for skin-interfaced electronics. In this work, a novel microfabrication approach for fabricating supercapacitors using anodic aluminum oxide templates is presented. In this work, a large capacitance value of 15.02 mF cm\(^{-2}\), as well as good transparency, stretchability, and biocompatibility are obtained. Thus, it is verified that the proposed supercapacitors are suitable as skin-interfaced power solutions.

1. Introduction

Wearable microsystems offer a considerable amount of health information, such as heart rate, electrocardiogram (ECG), and activity data,[3] and these devices are rapidly gaining market approval.[2] In multifunctional applications of biocompatible devices,[3] particularly in electronics that gather physiological activity data,[1] and these devices are rapidly gaining market approval. In this work, a transparent and stretchable solid-state supercapacitor was fabricated using a novel microfabrication approach for stretchable, biocompatible, flexible, and transparent supercapacitors, based upon polypyrrole (PPY), sodium alginate (SA), and a metal mesh. Our proposed structure combines the following parts. First, we utilized a transparent and stretchable solid-state supercapacitor by utilizing PPY as a positive material, due to its transparency, high current density capability, and biocompatibility. In addition, we used SA and Na\(_2\)SO\(_4\) as electrolytes, as these materials are transparent, stable, biocompatible, and safe (it can be as a food additive), and exhibit fast charging and discharging rates. Lastly, we used metal templates to precisely fabricate electrodes. The metal mesh in this work consists of an orderly and uniform nanoscale porous structure. It differs from previously reported metal mesh structures. The later consists of random pores based on a specific tree leaf.[13] The leaf venation has boughs and is ramose, leading to imbalance and non-stretchability. By precisely controlling the pore density, pore architecture, and pore size distribution of the metal mesh, an increase in the stretchability and power density of the supercapacitors, as well as transmittance of the mesh metal, reached 75% when the porous diameter was 500 nm.[14] Furthermore, the mass production of a metal mesh may be easier than a tree leaf-based process. The solid-state supercapacitor was also based upon a polydimethylsiloxane (PDMS)[15] substrate, as this material exhibits stable electrochemical performance,[16] minimal thermal shrinkage, good transparency, good biocompatibility, and good flexibility,[17] thus broadening the range of potential of this material for industrial and medical applications.

2. Results and Discussion

2.1. Supercapacitor Fabrication and Properties

The metal mesh template was based on anodic aluminum oxide (AAO),[18] due to its highly ordered and high specific surface...
area. The AAO fabrication process is described in Section 4. Figure 1a shows the structure and detailed fabrication process of the supercapacitor, which consisted of three parts. First, the surface of the AAO template was coated with 2 and 15 nm layers of Ni and Au (Figure S1, Supporting Information), respectively, and the Ni and Au layers were used to electrodeposit the conductive PPY polymer. Additional information is also provided in Section 4. In this work, we used PPY due to its stability and biocompatibility as an electrochemical polymer, making it a promising active electrode material. The Au layer was bonded to the pad using a wire bonder, and the solidified PDMS was used to cover and protect the Au layer and connector wire. Relevant information is presented in Section 4. The AAO template was then dissolved by immersing the material in 5% HCl for 2 days. Then, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) polymers and a triton100 mixture were used to coat the Au mesh film, and the PPY was deposited on the Au mesh film by cyclic voltammetry (CV). After deposition, two of the electrodes were packaged together, face to face, and the electrolyte was injected between the two electrodes. Scanning electron microscopy (SEM) was used to observe the morphologies of the Au mesh and PPY layer surfaces, as shown in Figure 1. The top view of the Au mesh, after AAO was dissolved with HCl, is shown in Figure 1b. The top view of the PPY layer was formed using different CV electrodeposition cycles, as shown in Figure 1c–g. The figure also shows the PPY layer that formed after three CV cycles, and the mesh was coated with thicker and more continuous layers of PPY with more time. After 20 cycles of CV, the Au mesh surface contained numerous PPY cores corresponding to the AAO pattern, which became a continuous thin film after 50 CV cycles. This implied that the surface area decreased with an increasing number of CV cycles. We also observed that the PPY of the supercapacitor electrodes formed after 20 CV cycles. FTIR analysis of the PPY layer is provided in Figure S2, Supporting Information.

2.2. Transparent and Biocompatible Electrolyte

Toxic electrolytes are harmful materials when used in skin-interfaced power solutions, as most are acid-based solutions. If a toxic electrolyte containing a solvent, gel, or conductive ions leaks into the body, it can cause serious health problems. Polyvinyl alcohol (PVA) is a polymer gel commonly used in solid-state supercapacitors; however, it is harmful to skin when it is mixed with acids and bases, and it cannot be dissolved using neutral salts. Other gels, such as polyacrylic acid, polyacrylamide, and potassium polyacrylate, may also cause similar issues. Thus, we used a biocompatible and transparent SA material, as a suitable electrolyte for use in skin-interfaced electronics.

The SEM analysis results of the SA with the electrolyte are shown in Figure S3, Supporting Information. To test their
biocompatibility, the supercapacitors and their components were separately co-cultured with HEK293T cells for 3 days, as it is needed for the cell division and proliferation. Then, we used flow cytometry to measure the ratio of live/dead cells, as shown in Figure 2a–d. The selected locations and micrographs are shown in Figure S4, Supporting Information, indicating that the HEK293T concentrations and morphologies did not show any significant differences. Thus, the supercapacitors can be considered safe even if the electrolyte were to leak from the supercapacitor, as the live/dead ratio was around 91%/2% in the labeled locations.

To evaluate transparency, we first measured the transmittance of the two PDMS samples, without a metal mesh but containing an electrolyte. We found that the electrolyte and PDMS were highly transparent with a transmittance of 92%, which did not change with different Na2SO4 concentrations, from 0.1 to 2 M. However, the transmittance decreased slightly when the concentration of SA increased from 0.1 to 2 M (Figure 2f). The transmittance of the electrode containing PPY, Au mesh, and the PDMS substrate was ≈33%, and its transparency is shown in Figure 2g.

2.3. Electrochemical Behavior of the Supercapacitors

CV and galvanostatic cycling with potential limitations were used to characterize the electrochemical behavior of the supercapacitors. The tested supercapacitors contained 1 M Na2SO4 and 1 M CaCl2 mixed with 0.5 M of SA as the electrolyte. Figure 3a shows the CV curves obtained at scan rates of 10–200 mV s⁻¹. The capacitance per unit area of the supercapacitors reached 15.02 mF cm⁻² at 10 mV s⁻¹, while the capacitance values at different charge rates are shown in Figure S5, Supporting Information. As shown in Figure 3b, the charge/discharge cycles revealed charge current densities from 0.8 to 5 mA. Thus, because the electrolyte was highly stable, the supercapacitor could be charged to 1.8 V, with a maximum of 2.5 V (Figure S6, Supporting Information).

Electrochemical impedance spectroscopy was used to characterize the behavior of the supercapacitors. Figure 3c illustrates the impedance testing from 1 Hz to 1 MHz, with a fitting curve. The semicircles in the inset of the Nyquist plot show that the resistance was 11.88 Ω. The curve indicates the charge transfer resistance, with larger semicircles denoting increasing charge transfer resistance values. In Figure S7, Supporting Information, the fitting curve is shown in red, and the Bode plot and fitting data are shown in the Supporting Information. Figure 3d shows the capacitance retention, which was maintained above 92.5% after 1000 charge/discharge cycles. Notably, the resulting leakage from the current was not noticeable, even at a high current density, indicating the excellent capacitive properties of the proposed supercapacitors.

Figure 4a,b shows the CV curves of the supercapacitor after five stretching and bending cycles, at a scan rate of 80 mV s⁻¹.
The CV curves revealed that the three supercapacitors were stable even after bending and stretching. Figure 4c shows the stretching behavior of the electrodes with 5% strain, and when the electrode was stretched more than 8%, it became unstable. Figure 4d presents the 180° bending behavior of the electrode, showing that the resistance was stable after 200 cycles. A capacity comparison of several transparent supercapacitors is shown in Table 1. We found that the capacity obtained in this work reached 15.02 mF cm⁻², which was better than the state-of-the-art supercapacitors listed in Table 1.
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Table 1. Transparent supercapacitor performance.

| Electrolyte       | Stretchable (Y/N) | Specific capacity [mF cm⁻²] | Bending time [mA] | Material       | Reference |
|-------------------|-------------------|-----------------------------|-------------------|----------------|-----------|
| PVA and LiCl      | N                 | 13.02                       | N/A               | PPY            | [13]      |
| PVA and H₂SO₄     | N                 | 3.23                        | N/A               | Au@MnO₂        | [21]      |
| PVA and LiClO₄    | Y                 | 4.02                        | 500               | Au@MnO₂        | [22]      |
| PVA and LiClO₄    | Y                 | 3.68                        | 700               | Au@MnO₂        | [23]      |
| PVA and H₂PO₄     | Y                 | 0.52                        | 100               | Ni@PEDOT:PSS   | [24]      |
| SA and Na₂PO₄     | Y                 | 15.02                       | 200               | PPY            | This work |

*N/A: Non-application.

2.4. Wireless Charging and Powering Light Emitting Diode Circuits

Wearable devices can record electrophysiological parameters such as electromyogram, electroencephalogram, and electrocardiogram data. Implantable devices can also record the in vivo activity of blood and neural cells, offering exact, abundant, and real-time data. In addition, supercapacitors can be used in both wearable and implantable devices because of their biocompatibility. Thus, wireless charging is the best approach for recharging supercapacitors. Figure 4e shows a simplified block diagram of the wireless charging circuit used as an inductive link, while Figure 4f shows a photograph of the electronic module. The circuit was mounted on a printed circuit board (PCB), and a miniaturized version of this PCB could be used for implantable applications, powered by wireless charging. In Figure 4e, L2 is the receiving coil, and load capacitance (CL) denotes the supercapacitor. Thus, in this study, we also verified the functionality of the supercapacitor. When SW1 was closed and SW2 was open, CL would charge. When SW1 was open and SW2 was closed, CL would discharge through the light emitting diode (LED), and the LED would illuminate (Figure 4f). We also implemented a circuit and PCB for tissue stimulation purposes, as shown in Figure S8, Supporting Information. In this study, the implemented circuit delivers up to current of 10 mA and used a stimulation frequency of several dozens of Hz.

3. Conclusions

In this study, we proposed low-cost solid-state supercapacitors that can be easily fabricated with a metal mesh pattern using an AAO template. We determined that these materials can be used as next-generation power solutions at the skin interface due to their transparency, stretchability, biocompatibility, and flexibility. These key properties may be useful for electronic device applications with a skin interface. By precisely controlling the microstructure of the mesh template, we created a structurally diverse material and could tune its transparency, stretchability (Figure S9, Supporting Information), and flexibility. Thus, many types of conductive polymers, such as polyaniline and polypyrrole, could be used to generate supercapacitors with even higher capacitance values, using this approach. In addition, this approach has a high potential for in vivo applications because of its safety, high energy density, ease of charging, and biocompatibility.

4. Experimental Section

Materials/Reagents: In this study, the following materials and reagents were obtained: hydrochloric acid (Macklin, Shanghai, China), CaCl₂ (Macklin, Shanghai, China), PDMS (KangNing, America), pyrrole (Adamas, Shanghai, China), SA (Rhawn, Beijing, China), Na₂SO₄ (Klamar, Beijing, China), sodium p-toluenesulfonate (Rhawn, Beijing, China), PEDOT-PSS (Liantian, Guangzhou, China), Triton100 (jiushan, Nanjing, China), HEK293T (American type culture collection, USA), basic DMEM (Thermo Fisher, USA), 10% FBS (Thermo Fisher, USA), 20 units mL⁻¹ of penicillin, and 20 µg mL⁻¹ of streptomycin (Thermo Fisher, USA).

Fabrication of AAO Template: Aluminum sheets were cut into square chips with side lengths of 20 mm. The imprinted chips used a nickel template with a pillar array, which determined the diameter of the array. Later, an aluminum piece was electrochemically etched to form the AAO piece, with a 220 nm pore diameter and a nearest-neighbor pore distance of 200 nm. The ordered array was also characterized via SEM, which showed a nanoscale array of the precise pore diameters and the pore-to-pore distances before and after deposition of the Au mesh film.

Coating the Ni and Au Layers: Thin Ni and Au layers with thicknesses of 2 and 15 nm, respectively, were deposited via physical vapor deposition using a high vacuum thermal evaporation coating machine (KZ-DZ400, Shenyang Kecheng Vacuum Technology Co., Ltd.).

Synthesis of Polypyrrole: After coating the Au layer and PEDOT-PSS and triton100 treatment at a ratio of 10:1 for 30 min, the metal mesh film was soaked in the electrolyte, which consisted of 0.5 m pyrrole and 0.5 m sodium P-benzenesulfonate. The voltage in the CV cycles ranged from −0.5 to 2 V, and the total runtime was under 100 cycles. After the metal was washed with deionized water and dried with N₂, the electrode was packed with the electrolyte.

Solidifying the PDMS Substrate: PDMS components A (substate) and B (curing agent) were mixed at a ratio of 10:1 and dropped on the top of the Au layer, then placed in a vacuum chamber for 5 min. After solidifying the PDMS on a hot plate, the AAO template was dissolved.

FTIR Analysis: A micro-FTIR spectrometer ( Nicolet iS50) was used to measure the PPY spectra. The wavelength ranged from 500 to 3000 nm, and air was used as a reference.

Characterization of Structural Properties of the PPY Layer and Film Template: A field-emission scanning electron microscope (Gemini500) was used to characterize the structural properties at extra high tension at 2 kV, and magnifications of 40 and 100 k.

Characterization of the Structural Properties of SA: A field emission environment scanning electron microscope (Quattro S) was used to characterize the surface of the SA gel, which consisted of 1 m Na₂SO₄, 0.5 m SA, and 1 m CaCl₂. The system was set to a high voltage of 20 kV, with a humidity of 85.3% at 2 °C and pressure of 600 Pa.

Co-Culturing the Supercapacitors with HEK293T: The supercapacitors and their components were co-cultured separately with HEK293T cells for 3 days, as it was needed for the cell division and proliferation. An eBioscience Fixable Viability Dye eFluor 780 was also used in the Beckman CytoFLEX to confirm the live/dead cells, as well as microscopy to monitor the morphologies and concentrations of HEK293T.
Electrochemical Measurements: CV and galvanostatic cycling with potential limitations were conducted using a potentiostat (VMP300), and electrodeposition was performed using two electrodes. The scan rate ranged from 10 to 200 mV s⁻¹ during CV measurements, and galvanostatic cycling measurements were conducted using two electrodes.

Wire Bonder: A wire bonder (West Bond, 7KE) was used to connect the metal template with the Au pad. The Au pad was fixed on the surface of the aluminum foil, and the Au pad was bonded with the AAO template with an aluminum wire. The Au pad was then connected to the potentiostat during measurements.

Transmittance Measurements: A Shimadzu UV–vis–NIR (UV3600Plus) was used to measure the transmittance of the two PDMS materials with the electrolyte but without the metal mesh. PDMS components A (substrate) and B (curing agent) were mixed together at a ratio of 10:1 and dropped on the surface of the silicon wafer. After solidifying the PDMS on the substrate, the material was cut and the electrolyte was placed between the two PDMS pieces. The system was then sealed with plastic tape. Later, the transmittance of the system with air was measured as a reference.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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