A Self-standing Organic Supercapacitor to Power Bioelectronic Devices

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ABSTRACT: The last decade has witnessed rapid progress in the development of implantable and wearable bio(chemical) sensors, which allow for real-time, continuous health monitoring. Among different device configurations, organic electrochemical transistors (OECTs) have shown great potential in transducing weak biological signals with on-site amplification and as components of complex circuits with low power requirements. Yet, a significant technological challenge remains in the way these devices are integrated with power sources that are conventionally bulky and rigid. Here, we present a simple process to assemble a supercapacitor (SC) that is self-standing, lightweight, and biocompatible and made of two identical conducting polymer (poly(3,4-ethylenedioxythiophene) electrodes and an agarose hydrogel comprising alkali metal halides. This SC is distinguished by its high energy and power density (20 Wh kg\(^{-1}\) and 10\(^5\) W kg\(^{-1}\), respectively), moderate gravimetric specific capacitance (70 F g\(^{-1}\)), excellent stability (charge retention of 75\% after 12,000 cycles), operational flexibility (can accommodate various types of aqueous electrolytes), long-lasting self-discharge (>10 h), and fast response time (between 0.1 and 30 s). We use the SC to power a micron-scale OECT, which selectively detects sodium ions in aqueous media. When miniaturized, the SC maintains its high performance and delivers a volumetric capacitance of 240 F cm\(^{-3}\), highlighting the possibility of fabrication in nonstandard form factors to couple with various bioelectronic devices. This low-cost and portable power source instigates the development of robust and biocompatible onboard power sources to be implemented alongside biosensors.

KEYWORDS: organic Supercapacitor, electropolymerization, PEDOT, agarose hydrogel, electrochemical transistor, bioelectronics

1. INTRODUCTION

Bioelectronic devices electronically communicate with living systems to detect or control biological events.\(^1\) This communication led to the development of wearable and implantable devices used for personalized health monitoring and precision therapies.\(^2\) Key to these technologies are functional electronic materials such as conjugated polymers that combine a set of features including mixed electronic and ionic conductivity, softness, mechanical flexibility, and biocompatibility, alongside synthetic diversity and tunability.\(^3,4\) These organic mixed conductors store and transport ionic charges in the bulk of their films upon application of an electrical field through an electrolyte. The voltage-dependent charging (i.e., redox or doping state) of conjugated polymer films has been exploited in the organic electrochemical transistor (OECT) configuration, where the conjugated polymer constitutes the channel in contact with the electrolyte. As a result of the volumetric charging of the channel material gated with an electrolyte solution, OECTs are identified with large changes in the channel current for small gate voltage modulations (i.e., high transconductance, \(g_m\)) and operate within a narrow voltage window (up to ±1 V vs Ag/AgCl).\(^6\)

Because of these features, OECTs are ideal for biosensing applications, where the device converts ionic biological signals into an electronic output while amplifying the input signals.\(^7\) OECTs have thus been used to record physiological signals when interfacing electrically active tissues,\(^8\) detect hormones from the sweat when interfacing the skin,\(^9\) sense minute concentrations of metabolites,\(^10,11,12\) ions,\(^11,12\) and proteins,\(^13\) and monitor the integrity of barrier-forming cells.\(^14\)

Such sensors show great potential at the biological interface, yet one aspect that remains inadequately addressed is the compatibility of their power sources. Power devices that are coupled with biosensors should be portable, low-weight, on-chip integrated, and compatible with the biological environment that the sensor is exposed to. The device components should be low cost and easy to produce and assemble. In this
sense, designing long-lasting and sustainable powering devices should go hand in hand with the advances in sensor development.\cite{15,16} With their capability for on-demand power supply, supercapacitors (SCs) fulfill the criteria set for a powering device.\cite{17} In an SC, electrical power is directly stored as electrostatic power without any energy conversion.\cite{18} As such, they are considered as power sources, with a power density between 5 and 15 kW kg\textsuperscript{−1} (as compared to 150 W kg\textsuperscript{−1} for batteries\cite{19}). While the specific energy is rather low (5–20 Wh kg\textsuperscript{−1}), SCs show a fast charge/discharge rate and long operation life,\cite{20} ideal to switch ON/OFF or monitor the output of a bioelectronic device (e.g., an OECT, identified with low power, <1 μW, requirements). Depending on their charge storage mechanism, SCs are classified as electrochemical double-layer capacitors (EDLCs), pseudocapacitors (PDs), and hybrid capacitors. EDLCs typically use high surface area carbon electrodes, which store/deliver charge by an electrostatic process.\cite{21} PDs are made of conducting polymers and transition metallic oxides that are charged/discharged by fast and reversible redox processes.\cite{20,22} Hybrid capacitors consist of an EDLC electrode and a PD or battery-type electrode, combining the properties of both systems.

While carbon-based SCs hold the lion’s share in SC development, large-area electrode production from highly graphitized carbon nanotubes or graphene remains an issue due to difficulties associated with processing in the solution phase. Just as for the field of bioelectronics, conducting polymers are a promising active material to build SCs owing to their ease of processability, softness, flexibility, high pseudo-capacitance, and conductivity.\cite{23} In particular, poly-(ethylenedioxythiophene) (PEDOT) derivatives are uniquely suited for SC development due to their ability to undergo fast and reversible ion uptake and efficient ion-electron coupling.\cite{24} They have a high theoretical conductivity (>500 S cm\textsuperscript{−1})\cite{25} moderate gravimetric specific capacitance (210 F g\textsuperscript{−1})\cite{26}, high chemical and physical stability, and a wide operational potential window. PEDOT-based capacitors are typically made of PEDOT films that are nanostructured to achieve large area surfaces. These PEDOT electrodes are, for instance, in the form of nanotubes polymerized in a porous alumina membrane yielding a specific capacitance of 132 F g\textsuperscript{−1}\cite{27} or fibrous films electrodeposited on graphite foil (184.5 F g\textsuperscript{−1}),\cite{28} porous carbon paper (154 F g\textsuperscript{−1}),\cite{29} or cellulose paper (115 F g\textsuperscript{−1}).\cite{30} Nanofibers were also vapor deposited on a carbon fiber paper (175 F g\textsuperscript{−1})\cite{31} or integrated with flexible 3D carbon fiber cloths (198 F g\textsuperscript{−1}).\cite{32} Some other reports developed high-capacitance composites comprising PEDOT. Such SC electrodes involve PEDOT films mixed with cellulose nanofibers and sulfonated lignin (230 F g\textsuperscript{−1}),\cite{33} hydrogels with polyaniline (112.6 F g\textsuperscript{−1})\cite{34}, and composites with graphene (270 F g\textsuperscript{−1})\cite{35,36} and MnO\textsubscript{2} (1068 F g\textsuperscript{−1}).\cite{37} In addition, freestanding PEDOT materials have been fabricated through various polymerization methods, including an electrochemical rust–vapor phase and in situ chemical polymerization, in the form of nanofibrillar films,\cite{38,39} solid-state nanowire flexible films,\cite{39} and scaffolds\cite{40} all realized into SC devices. The specific capacitance of these SCs varies between 2.5 and 181 F g\textsuperscript{−1}, depending on the fabrication procedure and physicochemical characteristics of the freestanding substrate.\cite{31–33} Apart from its use in SCs, PEDOT has also been the building block of the majority of OECT-based sensors (used in the channel and/or as the gate electrode coating) due to its high electronic and ionic mobilities (~1 to 2 and 1 × 10\textsuperscript{−3} cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, respectively)\cite{41} and electrochemical stability.

A number of ways to prepare the PEDOT films have been reported in the literature such as chemical polymerization, electropolymerization, vapor-phase polymerization, and thermal polymerization.\cite{42} Of these techniques, the electropolymerization of the corresponding monomer, EDOT, embodies a straightforward, robust, and cost-effective route to realize high-quality films on any conducting substrate. This technique combines the polymerization and geometrical patterning steps into one process while providing control over film topography and thickness through several process parameters such as applied deposition charge, counterion concentration, solvent, and electrodeposition method.\cite{43,44} In this work, we developed a self-standing organic SC comprising electropolymerized conducting polymer electrodes to enable
high power energy storage for bioelectronic devices (Scheme 1). The SC has two components: an electropolymerized hydroxymethyl PEDOT, namely, p(EDOTOH), and an agarose hydrogel hosting hydrated ions. The in situ gelation of agarose resulted in a semimflexible, self-standing, water-filled gel with a porous structure, embedded with p(EDOTOH) electrodes. The agarose hydrogel thus fulfilled two tasks in one: it acted as an ion reservoir for the SC electrodes and provided mechanical support to the system. We analyzed the electrochemical properties of SCs built with different concentrations of hydrogels and the chemical composition of the components before and after excessive charge/discharge cycles to engineer an SC with optimal geometry and stability. Our biocompatible SC showed elaborate power density (20 W kg$^{-1}$), long-lasting self-discharge (>10 h), and fast response time (between 0.1 and 30 s). We showed that the SC was lightweight (0.7 g) and robust with a capacitance retention of 75% after 12,000 cycles and that it can also be miniaturized. When integrated with microscale OECTs, the SC provided enough power to operate the device that detects variations in electrolyte concentration in real time. This is the first demonstration of electropolymerized PEDOT films in a self-standing SC comprising agarose. We describe a unique, facile, and fast assembly of the device in a stable electrolyte-bearing hydrogel environment and present how this device can be integrated as a power source for small-power bioelectronics. Focusing on the optimization of an SC for bioelectronic device coupling, this study follows the paradigm of developing green, safe (nontoxic, nonflammable, and no-leakage), and low-cost SCs for low-power bioelectronics.

2. EXPERIMENTAL SECTION

2.1. Materials. Hydroxymethyl-3,4-ethylenedioxythiophene (EDOTOH), sodium chloride (NaCl), potassium chloride (KCl), sodium nitrate (NaNO$_3$), lithium perchlorate (LiClO$_4$), sulfuric acid (H$_2$SO$_4$), (3-glycidoxypropyl)trimethoxysilane (GOPS), sodium dodecylbenzenesulfonate (DBSA), ethylene glycol (EG), and phosphate-buffered saline (1× PBS, pH = 7.4), and agarose (MW = 120,000) were purchased from Sigma-Aldrich and used as received. The channel of OECTs is composed of PEDOT:PSS (PH1000, Heraeus). The proton exchange membranes investigated include Nafton 117 (183 μm thickness, Sigma Aldrich) and cellulose (90 μm thickness, GoodFellow Cambridge Limited). The aqueous solutions were prepared using ultrapure water (Millipore Milli-Q).

2.2. Electrodeposition of p(EDOTOH) Films. PEDOT films were deposited on 175 μm-thick flexible Kapton (polyimide) substrates. The substrate was cut with a laser into a specific geometry (either 2.8 or 8 mm in diameter) and subsequently washed in acetone/isopropyl alcohol and deionized (DI) water. We then sputtered a 10/100 nm-thick Cr/Au layer on the substrate followed by cleaning in acetone and soaking in DI water under sonication for 30 min. Prior to electrodeposition, these substrates were electrochemically cleaned in an aqueous solution of H$_2$SO$_4$ (10 mM) using cyclic voltammetry (CV) between −0.2 and 1.2 V for 20 cycles (Autolab PGSTAT128N, MetroOhm). Three-electrode electrodeposition was performed by using a Pt wire as the counter electrode and a Ag/AgCl reference electrode (3 M KCl, $E^\circ$ = 0.22 V vs standard hydrogen electrode at 25 °C). The electrochemical properties and stability of the p(EDOTOH) film were determined by CV and galvanostatic charge-discharge cycling (GCD). CV and GCD curves at different current densities (i.e., charge and discharge rates, which are specified in units of current per electrode mass) were acquired in the potential window between −0.5 and 0.7 V at room temperature (VSP-300, BioLogic, Science Instruments). To determine the double-layer capacitance of the electrode ($C_{dl}$, F), the current density ($j$, mA cm$^{-2}$) in the non-Faradic region (0.3 V vs Ag/AgCl) of an average of three CV curves at different scan rates (5 to 100 mV s$^{-1}$) was selected. $C_{dl}$ was then determined by plotting the difference in the anodic and cathodic current density ($Δj = j_a − j_c$) against the scan rate ($v$) according to the following equation:

$$C_{dl} = \frac{d(Δj)}{2dν} = \frac{d(j_a − j_c)}{2dν}$$

(1)

For the SC, the specific capacitance (F g$^{-1}$), which is the capacitance of one electrode per unit mass for one electrode, was determined from the GCD plots using the following equation$^{27}$

$$\text{specific capacitance} = \frac{4 \times C}{m} = \frac{4 \times I}{m \times \frac{dv}{dt}}$$

(2)

where $I$ is the discharge current applied, $m$ is the mass of the active material, and $dv/dt$ stems from the slope of the discharge curve, equal to $(V_{max} − 1/2V_{max})/(t_f − t_i)$, where $V_{max}$ corresponds to the highest voltage in the GCD curve after the voltage drop at the beginning of the discharging process. The multiplier of 4 adjusts the capacitance of two-electrode cells to the capacitance of a single electrode. The volumetric capacitance was calculated according to the following equation$^{27}$

$$\text{volumetric capacitance} = \rho \times \text{specific capacitance}$$

(3)

where $ρ$ is the apparent density of the films, given by

$$ρ = \frac{m}{A \times d}$$

(4)

where $m$ is the mass of the dry electrode and $A$ (cm$^2$) and $d$ (cm) are the area and thickness of the film electrode, respectively. The Coulombic efficiency ($η_{\text{coulombic}}$) of the SC was evaluated as the ratio between the discharging and charging times, $t_d$ and $t_c$, respectively, for the electrochemical window between 0 V and 0.8 V as displayed below.$^{28}$

ACS Applied Energy Materials www.acsaem.org
ACS Appl. Energy Mater. 2020, 3, 7906−7907

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The cycling stability of the devices was studied by applying charge–discharge cycles at different current densities (i.e., 3.44 and 6.89 A g⁻¹) in a two-electrode configuration from 0 V to 0.8 V, which corresponds to țd and țc of approximately 5 to 20 s. The energy density (E, Wh kg⁻¹), which is the amount of energy stored per unit of mass, and the power density (P, W kg⁻¹), which describes the speed at which the energy stored can be delivered, were derived from the GCD curves by applying the following equations:

\[
E = \frac{1}{2} \times V_{\text{max}}^2 \times \text{specific capacitance}
\]

\[
P = \frac{E}{t_d}
\]

The self-discharge of the SC was monitored by applying 0.4 mA (i.e., 6.89 A g⁻¹ for 5–30 s) followed by an open-circuit potential recording. An SC cell was assembled and charged for 30 s to drive a red (1.35 V) light-emitting diode (LED).

Electrochemical impedance spectroscopy (EIS) for the SC was performed at the open-circuit potential using a VSP-300 BioLogic potentiostat. The AC amplitude was 10 mV, while the frequencies varied between 0.01 Hz and 100 kHz. The leakage current (I_leak) of the SC was recorded using an electrical instrument analyzer (Keithley 2002, Multimeter) controlled by customized LabVIEW software.

2.5. Physicochemical Characterization. The surface morphology of the electrodeposited p(EDOTOH) film was characterized using an FEI Nova nanoscopy electron microscope (SEM) with an accelerating voltage of 3 kV and a working distance of 5 mm and an atomic force microscope (AFM). The films were deposited onto aluminum stubs and attached with conductive tape. The cross-sectional image was examined with a focused ion beam (FIB)/SEM (FEI Helios NanoLab 400S) using a Ga⁺ ion source. Platinum layers were deposited on the surface region of interest by electron and ion beams for sample protection. AFM images were obtained with a Veeco Dimension 3100 scanning probe system. The images of the dried samples were obtained in tapping mode in air using FESPVA-V2 probes commercialized by Bruker (nominal resonant frequency: 75 KHz, spring constant: 2.8 N m⁻¹). Morphological images in a liquid environment obtained with a Bruker Scanasyst-fluid module and corresponding Scanasyst-fluid probes (nominal resonant frequency: 150 KHz, spring constant: 0.7 N m⁻¹). Statistical data were collected on the surface using the Gwyddion software. The chemical composition of the p(EDOTOH) before and after the electrochemical measurements was characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), and ultraviolet-visible spectroscopy (UV–vis). XPS was carried out using a KRATOS Analytical AMICUS instrument equipped with an Al Kα X-ray source (1468.6 eV). The source operated at a voltage of 10 kV and a current of 10 mA generating a power of 100 W. The high-resolution XPS spectra were acquired with a step of 0.1 eV. The FTIR spectra were recorded in the range 500–4000 cm⁻¹ at room temperature using a Thermo Scientific Nicolet iS10. Attenuated total reflection (ATR) FTIR mode was used to obtain the reflectance infrared spectra of the polymer film. We signal-averaged 32 scans to form a single spectrum, which was then displayed in terms of transmittance. The baseline was corrected using OMNIC FTIR software. For the UV–vis measurements, the polymer film was electrochemically deposited onto an ITO-coated glass substrate, and the spectrum was acquired using a UV–vis spectrometer (Ocean-Optics USB 2000+) in 0.1 M NaCl.

2.6. OECT Fabrication, Characterization, and Integration with SCs. The OECTs were fabricated on glass wafers (D 263 T eco, Schott) using photolithography based on a previous protocol.13 The device fabrication started with the patterning of Au contacts and interconnects. The photosist S1813 was deposited on cleaned substrates followed by exposure to UV light using a contact aligner and development with an MF-319 developer. A 10 nm layer of Cr and a 100 nm layer of Au were then sputtered on the substrates and patterned the metal through a standard lift-off process. The second layer of photosist AZ9260 was spin-coated on the substrate and developed using an AZ developer to define the channel areas. The channel patterns (width = 100 μm, length = 10 μm, thickness = 170 μm) were deposited on the surface region of interest by electron and ion beams for sample protection. AFM images were obtained with a Veeco Dimension 3100 scanning probe system. The images of the dried samples were obtained in tapping mode in air using FESPVA-V2 probes commercialized by Bruker (nominal resonant frequency: 75 KHz, spring constant: 2.8 N m⁻¹). Morphological images in a liquid environment obtained with a Bruker Scanasyst-fluid module and corresponding Scanasyst-fluid probes (nominal resonant frequency: 150 KHz, spring constant: 0.7 N m⁻¹). Statistical data were collected on the surface using the Gwyddion software. The chemical composition of the p(EDOTOH) before and after the electrochemical measurements was characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), and ultraviolet-visible spectroscopy (UV–vis). XPS was carried out using a KRATOS Analytical AMICUS instrument equipped with an Al Kα X-ray source (1468.6 eV). The source operated at a voltage of 10 kV and a current of 10 mA generating a power of 100 W. The high-resolution XPS spectra were acquired with a step of 0.1 eV. The FTIR spectra were recorded in the range 500–4000 cm⁻¹ at room temperature using a Thermo Scientific Nicolet iS10. Attenuated total reflection (ATR) FTIR mode was used to obtain the reflectance infrared spectra of the polymer film. We signal-averaged 32 scans to form a single spectrum, which was then displayed in terms of transmittance. The baseline was corrected using OMNIC FTIR software. For the UV–vis measurements, the polymer film was electrochemically deposited onto an ITO-coated glass substrate, and the spectrum was acquired using a UV–vis spectrometer (Ocean-Optics USB 2000+) in 0.1 M NaCl.
polymide substrates (Figure 1b–d). The films showed a globular surface morphology with nanometer-sized grains, leading to a root-mean-square (RMS) roughness of ~28 nm, as depicted from the SEM (Figure 1e) and AFM images (Figure S1b). These clusters seem to arise from the aggregation of linear segments of polymer chains, increasing the roughness and porosity of the film surface, as observed in previous studies.57 Fourier transform IR (FTIR) spectroscopy was used to further validate the structure of the polymer film (Figure S1c). The bands in the spectrum of the EDOT monomer ascribed to the C–H bending mode (892 cm$^{-1}$) and the C–H vibration (2879 and 2969 cm$^{-1}$) disappear in the p-(EDOTOH) spectrum, indicating the formation of PEDOT chains with α,α’-coupling.60 In the polymer spectrum, the vibration bands appearing at 1508 and 1303 cm$^{-1}$ are ascribed to the stretching mode of C=C and inter-ring stretching mode of C–C in the thiophene chain, respectively. The characteristic band of the stretching vibration of the C=S–C bond in the thiophene chain is also observed at 969, 823, and 991 cm$^{-1}$, confirming the successful formation of the PEDOT derivative upon the electropolymerization reaction.61,62 Additionally, the UV–vis absorption spectra (Figure S1d) of the electropolymerized polymer on top of an ITO substrate reveal a broad absorption band starting from 700 nm extending to the NIR region. The broad peak at 400 to 800 nm is attributed to the π–π* transition of thiophene chains, while the band at ~1060 nm is credited to polaron and/or bipolaron bands, characteristic of oxidized PEDOT.63,64

Figure 1f shows a typical CV curve of the p(EDOTOH) film. The potential window applied to the film (~0.5 to 0.7 V) was chosen to avoid the interference from the oxygen evolution reaction during the anodic scan and hydrogen evolution on the cathodic scan. The non-perfect rectangular shape (i.e., fill factor (FF) = 77%) stems from the non-vertical shift in current density upon altering the electrode polarity near ~0.5 and 0.7 V, indicating polarization resistance.65 The CV curve shape did not change upon 1000 cycles, with a small reduction in the current magnitude (FF drops from 77 to 73%). Moreover, we observed that, with an increase in the scan rate, the film produces larger current densities (Figure S2a). The film curve shape did not change upon 1000 cycles, with a small reduction in the current magnitude (FF drops from 77 to 73%). Moreover, we observed that, with an increase in the scan rate, the film produces larger current densities (Figure S2a). 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In addition, the pronounced semicircle response (inset of Figure S2c) indicates a higher interfacial charge transfer resistance after cycling.68

The second component of our SC is a hydrogel whose properties are critical to the device performance. Hydrogels are 3D, cross-linked polymeric networks able to absorb and retain aqueous solutions many times over their weight without losing structural integrity and getting dissolved.69 Agarose is a naturally occurring polysaccharide composed of linear chains of agarobiose, which consists of D-galactose and 3,6-anhydro-L-galactopyranose.70 The gelation of agarose involves the cross-linking and self-assembly of molecules via hydrogen bonding.71 The resulting hydrogel is known for its thermoreversible gelling property, porosity, hydrophilicity, low cost, and high ionic conductivity.70,72 To find out the optimal agarose hydrogel properties (e.g., powder content, thickness of the gel) and evaluate the performance of the electropolymerized p(EDOTOH) films in a two-electrode system, we first built an H-cell where the hydrogel is used as the separation membrane (Figure S3a).

This H-cell could accommodate a range of current densities as low as 0.84 A g⁻¹ to as high as 17 A g⁻¹ (Figure S3b). We found that a hydrogel thickness of 2.26 mm at an agarose weight percentage of 8% yielded the best-performing capacitance retention, greater than 95% for 4000 galvanostatic charge–discharge cycles at 3.4 A g⁻¹ (Figure S3c). On the other hand, a 10-fold increase in the NaCl concentration of the operating medium did not cause a significant change in the cell’s performance, suggesting that the porous network retains enough ions for conduction at 0.1 M NaCl (Figure S3d). At the same time, inferior specific capacities were recorded in the presence of more conventional but less hydrophilic membranes such as Nafion and cellulose (Figure S3d). However, the agarose H-cell revealed high equivalent series resistance (ESR), as gleaned from the charge–discharge curves (Figure S3e). ESR describes the overall resistance of the cell and is a crucial
factor determining the power density and energy of the SC. High ESR primarily stems from polymer degradation and mechanical stress on the membrane. Since the electrochemical window chosen here does not allow for parasitic reactions, care was taken for minimal mechanical stress, the temperature was set in ambient conditions, and the electrolyte concentration was adequately high, we attribute the high ESR values to the distance between the anode and cathode electrodes in this particular device geometry (i.e., 2 cm, Figure S3a). Note also that the ESR is independent of agarose thickness, which was varied between 0.6 and 4.3 mm (Table S2). These results advocate for a different architecture that ensures a more compact configuration for a high-performance SC.

Our results with the H-cell suggest that instead of using the gel as a membrane, the SC electrodes should be assembled all together within the hydrogel, as depicted in Figure 2a. A compact, self-standing SC was generated in situ while the agarose solution solidified around the electrodes (see Scheme 1 for the assembly procedure). The process of forming the hydrogel is simple (i.e., no functionalization is required), reproducible, and fast (i.e., the hydrogel can be prepared in 20 min under laboratory conditions). Figure 2a shows a photograph of the self-standing hydrogel SC. The distance between the anode and the cathode in this configuration markedly decreased to 1.5 mm, required for low ESR. The scan rate-dependent CV curves of the hydrogel SC (8 wt % agarose) reveal a rectangular pattern (Figure 2b), typical of an electrical double-layer capacitor. The similar shape of this CV curve to that of the electrodes measured in the electrolyte (Figure 1f) highlights that the hydrogel pore diameter is large enough (i.e., 150 nm, see Figure S4) to allow for the transport of ions therein. Moreover, the device retained its rectangular shape even at high scan rates (100 mV s⁻¹) as well as elevated temperatures (i.e., mimicking the physiological temperature of 37 °C, Figure S5), signifying a fast charge storage mechanism independent of speed of voltage applied or temperature. The CV curves reveal an FF of ∼95%, calculated at 100 mV s⁻¹, demonstrating a highly symmetrical charge/discharge behavior of the SC. These results have been anticipated as agarose gels were reported to operate with charged species larger than hydrated Na⁺ or Cl⁻, for example, with DNA for electrophoresis applications. We next estimated the specific capacitance of the all-polymer self-standing hydrogel SC (8 wt % agarose) to be 75 F g⁻¹ at a current density of 8.47 A g⁻¹ and a double-layer capacitance of ∼3.7 mF cm⁻². The specific capacitance value was only marginally affected by agarose weight percentage, as depicted in Figure 2c. Most importantly, the SC had a 10-fold decrease of the ESR (from 340 to 32 Ω) compared to the H-cell configuration (Figure S3a). We attribute the low ESR value to the compactness of the new device architecture, which results in facile ionic transport (i.e., efficient pathways to the p(EDOTOH) sites due to improved interfacial contact) with excellent isolation of electronic flow. In addition, the SC operated similarly when the gel was fed with aqueous solutions other than PBS, such as KCl and NaNO₃ (Figure S6a,b, respectively), evidencing its versatility toward the use of other aqueous salts.

We next evaluated the performance of the SC as a circuit element. The SC charged with 3.44 A g⁻¹ for 30 s readily activated a red LED upon self-discharge (Figure 2d). At the same time, the open-circuit potential stabilized after 4 h at ∼0.31 V, a voltage output large enough to power various bioelectronic devices (Figure 2d). The slow discharge time between 2 and 4 h renders the device suitable as a continuous power supply. In addition, in the absence of the LED and by loading with higher charging currents (i.e., for 30 s at 6.89 A g⁻¹, see charging profile in Figure 2e), the self-discharge lasted for over 1 day, provided that the device was wetted once every 4 h (Figure 2f). The open-circuit potential of this device reached 0.67 V after 25 h, with a 36 mV decrease per hour (measured 4 h after the charging). The main contributors of the potential drop under self-discharge are (i) Faradaic reactions with either activation-controlled or diffusion-controlled mechanism, (ii) ohmic leakage, and (iii) charge redistribution. Leakage current can occur due to redox reactions, ionic charge diffusion, and/or partial electronic discharge through the separator. The corresponding diagnostic test (Figure S7a) revealed a linear dependency of the voltage drop on the logarithm of time, signifying that the 60% decline within 25 h stems from a Faradaic self-discharge initiated by overcharge. The leakage current extracted from Figure 2f was of the order of 1.65 × 10⁻⁵ mA (Figure S7b). These experiments suggest that the device can supply enough voltage for extended periods to low-power bioelectronics as long as it is in a wet environment, which makes it particularly suitable for use in an in vivo setting.

Next, we sought to evaluate the stability of the device upon continuous cycling. Figure 3a displays the variation in specific capacitance and Coulombic efficiency of the SC as a function of cycle number for two different current densities, 3.44 and 6.89 A g⁻¹. Capacitance retentions of 75 and 71% of the devices’ initial capacitance were recorded after 12,000 cycles, indicating good rate capability, associated with the efficient ion transport from the electrolyte to the electrode. Meanwhile, the Coulombic efficiency remained at 100%, further manifesting the robust performance of the device. Nevertheless, we explored further the source of the capacitance loss upon cycling as such analysis could inform which film properties should be improved in the long run and which operation parameters should be avoided. Electrochemical impedance spectroscopy measurements performed before and after cycling revealed sluggish mass transport and a decrease of the capacitance for the cycled SCs.

Figure S8 denotes the variation of capacitance with frequency, indicative of the electrolyte ion penetration inside the p(EDOTOH) film at each frequency. The value of the real part of the capacitance at low frequencies reflects the bulk capacitance of the SC. Here, we measure a 20% decrease after the film was cycled for 12,000 times, possibly due to an electrochemical degradation mechanism. Furthermore, we observed a reduction in the dielectric relaxation time constant (i.e., τ₁ = 3.03 s vs τ₀ = 1.04 s, see Figure S5b) as the films were cycled, suggesting hindered mass transport. The post-mortem analyses of the SC components showed signs of deterioration with cycling, accounting for this loss in capacitance. A roughened morphology after cycling (12,000 cycles) is evident from the SEM images, which shows the formation of micrometer-size clusters (between 1 and 5 μm) on the surface of the films (Figure S9a,b). We recorded the high-resolution carbon (C 1s) XPS spectra of the pristine p(EDOTOH) electrode as well as those after cycling. Figure S9c shows the typical XPS spectrum of the pristine sample, deconvoluted into three peaks, including the C–C/C=O/C bonds at 284.5 eV, C–O/C–S bonds at 286 eV, and C=S bond at 288 eV. We found, however, an additional peak in the spectrum of the
cycled cathode (5.89%) and anode (6.11%), originating from carboxylate groups (Figure S9d,e). This peak suggests a partial overoxidation of the p(EDOTOH) electrode upon cycling, possibly due to the cleavage of the C−C bond, which is converted into a carboxylic group.80 The decrease of the C=C/−C=O bond contribution (from 56.2 to 48.5 and 51.5% for the cathode and anode, respectively) further corroborates the electrochemical degradations of the CP electrodes (see Table S3 for a summary of XPS signals).

Lastly, these changes are not only confined on the surface of the film, but they are also seen in the bulk of the cycled films. ATR-FTIR spectra in Figure 3b reveal two new bands at 1394 and 1577 cm−1 for the cycled films, stemming from the stretching of the carboxyl group,81 attributed to the over-oxidation of the PEDOT. Electrochemical degradation can lead to chemical bonds in CPs to be broken, leading to the polymer chains being irreversibly oxidized into fragments.78 A band at 866 cm−1 appeared with long-term cycling, attributed to the vibrations of the sulfone group after a part of the thiophene units becomes overoxidized (Figure S10a). Moreover, the shift of the C−O−C bands at 1142 and 1183 cm−1 (Figure S10b) advocates a change in the electrode’s molecular vibrations as the bonds become less stiff and require lower energy. The optimization of operating conditions such as choosing a narrower range for the applied potential and/or current and slower scan rate could avoid the overoxidation of PEDOT electrodes.

An important trait of our capacitor is its flexible form factor thanks to the easy assembly of its components. In the experiments above, the SC had a weight of 1.95 g (±0.12 g), and the gel had a volume of 0.5 mL. These dimensions can further go down as we built a miniaturized version of the device with the active area of the anode and cathode being equal to 0.053 cm², leading to a lightweight, spherical SC (W_total = 0.7 g, ±0.04 g) with a volume of 0.065 cm³ (V_hydrogel = 0.2 mL), as illustrated in Figure 4a and further in Figure S11. The specific capacitance of this “micro-SC” was indistinguishable to the larger SC (shown in Figure 2c) and decreased with increasing current density (Figure 4b) owing to the increase of charge transfer resistance of p(EDOTOH).82 The energy density that the micro-SC provides is between 15 and 20 W kg−1, while the power density reaches a maximum of 70 kWh kg−1 for a discharge time of 0.75 s. The high values of the power density (i.e., how fast the ions can move) are well aligned with surge-power delivery applications and, in turn, small (bio)electronics. The power characteristics of the miniaturized device are illustrated in the Ragone plot in Figure 4c. The performance of the miniaturized all-polymer SC is up to par with other reported systems based on PEDOT electrodes. The notable stability of the SC combined with its high power density and flexible geometry renders this system a promising candidate for both in vivo and in vitro energy storage and delivery applications. As a final point, the micro-SC can deliver a volumetric capacitance of 240 F cm−3 at a current density of 1.07 A g−1 in line with other PEDOT-based supercapacitor devices (Table S4) and can afford a capacitance of 200 F cm−3 at 28.56 A g−1.

As we verified the performance and stability of the self-standing SC and used it to power an LED, we next integrated it with a microscale OECT. We connected the SC to a Ag/AgCl pellet, which was used as the gate electrode of the OECT comprising PEDOT:PSS-coated channels (width = 100 μm, length = 10 μm, thickness = 170 nm). Our OECT is electrolyte-gated, meaning that it operates in an aqueous salt (100 μL of 0.1 M NaCl). Figure 5a shows a cross-sectional schematic of an OECT, and a photograph of a chip comprising six identical channels is given in Figure S12. In the absence of a gate voltage (V_g), the PEDOT:PSS channel is in the ON state and require electrical gating for OFF state. Figure 5b presents a typical I−V characteristic curve for an OECT with the SC serving as the gate electrode. The specific output power (P) of the OECT is equal to 0.053 cm², leading to a lightweight, spherical SC (W_total = 0.7 g, ±0.04 g) with a volume of 0.065 cm³ (V_hydrogel = 0.2 mL), as illustrated in Figure 4a and further in Figure S11.
displays the current profile of a PEDOT:PSS channel where the gate is connected to the charged, all-polymer SC, monitored for 20 min. We switch OFF/ON the OECT by inserting/taking out the gate electrode (Ag|AgCl pellet) into/from the electrolyte. The gate potential acting on the semiconductor channel is proportional to the open-circuit potential of the discharging SC connected to the transistor gate. As the positive gate voltage supplied by the SC increased, the source−drain current (I_D) decreased, consistent with the depletion mode OECT operation. We used multiple SCs that were charged at different rates to simulate different gating potentials. Here, a source-measure unit was used to supply voltage to the channel (V_G). As for the gate source, an SC can also supply the voltage for the source−drain. Figure 5c shows the channel readout as the SC was connected to the source and drain contact with an output voltage of −0.10 V. The circuit contained an external load to slow down the decay of the voltage output of the SC to have stable drain current outputs over time. Once this load was disconnected, the current first increased and then decayed to lower values as the SC discharged. The discharge rate of the SC and the voltage it supplies to a circuit can be easily manipulated by the integration of such circuit elements.

To further demonstrate the use of the SC in an actual biosensor circuit, we built a Na⁺ sensor. For these experiments, we polymerized ion-selective crown-ether-functionalized EDOT-based films as has recently been reported in our group.54 The OECTs comprising the Na⁺-selective copolymer at the gate electrode was shown to have channel current scaling with Na⁺ content of the electrolyte.54 We deposited the Na⁺-selective copolymer on the laterally patterned gate electrode of the OECT (Figure S12). The channel was based on PEDOT:PSS and had a geometry identical to the one used in the experiments above. We monitored the response of this OECT in aqueous solutions containing different NaCl concentrations while both the drain and gate contacts were connected to two discharging SCs. The supercapacitor upon discharge will release its energy as electric current into the OECT. The V_G and V_D are supplied by two separate SCs with an output voltage of −0.2 and −0.3 V, respectively, after charging them for 1 min at 3.44 A g⁻¹. Figure 5d shows the current profiles of this SC-powered ion sensor in different electrolytes. Note that as the discharging kinetics is preset for the SCs, the voltage that they supply to the OECT gate and channel remains the same for the measurements in three electrolytes. The drain current monitored for 30 s is higher in the concentrated electrolytes compared to the dilute one (I_{D_1M} > I_{D_100mM} > I_{D_10mM}), in agreement with the operation of this type of ion sensor.54

4. CONCLUSIONS

The growing interest in bioelectronics has to be capitalized with compliant powering devices. Powering a biosensor/actuator is of paramount importance for the viability of such devices in everyday life applications. To this end, we presented a simple and straightforward strategy to devise a lightweight,
biocompatible, and cost-effective supercapacitor made from electropolymorized p(EDOT-OH) films embedded in a self-standing agarose hydrogel. The device has the advantage of continually utilizing an external source of biocompatible liquid for energy storage. The hydrogel acted as a mechanical support as well as a source of ions. This conducting polymer-based self-standing hydrogel SC was robust (capacitance retention of 75% after 12,000 cycles) and exhibited high power density (10^5 W kg⁻¹), long self-discharge (>2 h), and fast response time (0.1–30 seconds) while it can afford a specific capacitance of 71 F g⁻¹ and volumetric capacitance of 240 F cm⁻³. The device also possessed operational flexibility (can accommodate various types of aqueous electrolytes), and its geometry was easy to change. When miniaturized, the SC yielded similar power characteristics to larger prototypes. By further optimizing the electrode material, higher performances in terms of specific capacitance and power density can be realized for SCs that are easy to assemble in various forms and shapes compatible with biological media. Stemming from the growing interest in the design and engineering of implantable operational energy generating devices, this research contributes to the technological advancement of cost-effective energy storage devices that can power micron-scale biosensors/actuators.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c01299.

Literature review, electropolymorization route, optical pictures and additional experimental results (AFM, CV, EIS) (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

G.N. and S.I. thank the support by the King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under Award No. OSR-2015-Sensors-2719. Scheme 3, Figure 2a, and the TOC image were created by Heno Hwang, scientific illustrator at KAUST. The authors thank Dr. Craig Combe and Prof. Iain McCulloch (KAUST Solar Center) for the synthesis of the ion-selective EDOT monomer.

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