

SUPPORTING INFORMATION

Towards sustainable solid-state supercapacitors: Electroactive conducting polymers combined with biohydrogels

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METHODS

Preparation of PEDOT electrodes

All electrochemical assays were performed using a PGSTAT302N AUTOLAB potentiostat–galvanostat. PEDOT electrodes were prepared by chronoamperometry (CA) using a constant potential of 1.40 V under nitrogen atmosphere and at room temperature. A three-electrode one-compartment cell was filled with 50 mL of acetonitrile containing EDOT monomer (10 mM) and LiClO₄ (0.1 M) as supporting electrolyte. Stainless Steel (SS) AISI 316 sheets with an area of 6 cm² were employed as working and counter electrodes. The reference electrode was an Ag|AgCl electrode containing a KCl saturated aqueous solution ($E^0 = 0.222$ V vs. standard hydrogen electrode at 25 °C). The polymerization time (θ) was adjusted to obtain PEDOT electrodes with a polymerization charge of 2.67 C (445 mC/cm²). The mean θ value was 358.0 ± 50.7 s after averaging 58 samples. The mass of PEDOT deposited onto the WE was determined as the weight difference between coated and uncoated steel sheets ($n = 10$) using a CPA26P Sartorius analytical microbalance with a precision of 10⁻⁶ g. The exact amount of electrochemically polymerized PEDOT onto the electrode was $m_{pol} = 1.69 \pm 0.23$ mg.

Description and preparation of biohydrogels

In a first screening, four biopolymers were chosen to be applied as hydrogel-based electrolyte: Na-alginate, κ -carrageenan, chitosan and gelatin (Scheme 1). They display different functional groups in their chemical structure and also varying mechanical integrity. Bulk biohydrogels, which are displayed in Figure S3a, were obtained as follows:

Na-Alginate. Anionic linear polysaccharide very abundant in nature that is synthesized by brown seaweeds and by soil bacteria. It is a biocompatible, non-toxic, non-immunogenic and biodegradable copolymer formed by blocks of mannuronic acid and guluronic acid residues. As it has been reported, this polysaccharide undergoes gelation in the presence of divalent cations (*e.g.* Mg²⁺, Ca²⁺, Zn²⁺, Sr²⁺ and Ba²⁺), which form a cross-linked structure after binding the functional groups of alginate chains. Besides, alginates can also form high-viscous acid hydrogels at a pH below the pK_a value of the uronic acid residues, thus displaying a pH-sensitive gel-forming ability.¹⁻³

In this work, Na-alginate was dissolved in H₂O at 2% w/v at *ca.* 50 °C. Then, once it was a completely viscous liquid solution, it was cooled down to 2-3 °C in an ice bath. Finally, maleic anhydride (MA) (2% w/v) was added as fine powder (*i.e.* MA was grounded and converted into a very fine powder to improve its dissolution), and the solution was stirred vigorously for several minutes at 2-3 °C. The gel was let to form at room temperature overnight. Although it was not possible to dissolve MA completely, it was not a major inconvenient because the mixture homogenized by itself during gelation.⁴

κ-Carrageenan. Linear sulfated polysaccharide that is obtained from red edible seaweeds. It has a high molecular weight and is formed by an alternation of D-galactose and 3,6-anhydro-galactose units linked by an α-1,3- and β-1,4-glycosidic bond. Depending on the number and position of the ester sulfate groups on the repeating galactose units, different types of carrageenan are distinguished. Specifically, κ-carrageenan has one ester sulfate group in the repeating unit, and forms strong and rigid gels in the presence of K⁺. Moreover, because of its biocompatibility, biodegradability, high capacity of water retention and mechanical strength it is widely used in food and cosmetics formulations as a gelling, stabilizing and thickening agent.^{5,6} The gelation

mechanism of this biopolymer is based on a two-step process in which a random coil-helix conformational transition takes place (*i.e.* aggregation of helical dimers).

In this work, κ -carrageenan was dissolved in H₂O at 2% w/v at *ca.* 75-80 °C. Thus, solution needs to be heated to properly dissolve the biopolymer. Then, the corresponding volume of 1 M KCl (10% v/v) was added, and the solution stirred vigorously. Finally, the gel was formed at room temperature for several hours. It should be noted that the cooling of hot κ -carrageenan aqueous solution produced a 3D polymeric network in which segments of double helices form junction points, these segments being further cross-linked by K⁺.⁷

Gelatin. Heterogeneous mixture of water-soluble proteins of high average molecular masses, present in collagen, which are extracted by boiling in water relevant skin, tendons, ligaments, bones, etc. Gelatin has been used in many applications in both food and pharmaceutical industries.^{8,9}

In this work, 10 g of gelatin were dissolved in 100 mL of water, and heated gently between 35 °C and 40 °C to facilitate the dissolution process. Then, 2 mL of a hardening solution (1 mL of formaldehyde solution + 1 mL of ethanol) were added and the solution was mixed properly.¹⁰ The gelation took place at 4-5 °C (in the fridge) for 4-6 hours.

Chitosan. Linear polysaccharide composed of randomly distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is obtained after treating shrimp and other crustacean shells with alkali sodium hydroxide. It has been widely used in agriculture, food and biomedical applications.¹¹

In this work, chitosan was dissolved in 2 vol.% acetic acid aqueous solution in a glass container. The mixture was stirred for 1 hour approximately to completely dissolve the biopolymer. After complete dissolution, the container was immersed in a

coagulation bath (10 wt.% NaOH aqueous solution) for several hours (at least 12 h) until the gelation was completed. Basically, the top surface of the chitosan mixture was gelled after being in contact with the NaOH for several minutes. Diffusion of the NaOH solution through the rest of the biopolymer mixture resulted in a layer-by-layer gelation. Once the gel was set, it was washed carefully with deionized water repeatedly until the washing water reached a neutral pH.¹²

Synthesis of polyaniline nanofibers (PAni-nfs)

The procedure followed to prepare PAni-nfs has been described by Kraner *et al.*¹³⁻¹⁵ Briefly, an aqueous solution of aniline (3.2 mmol) in 1 M of HCl as doping acid (10 mL) and another solution of ammonium peroxydisulfate (APS, 0.8 mmol) in the same doping acid (10 mL) were prepared and rapidly mixed by pouring the two solutions together and immediately stirring or shaking to ensure sufficient mixing before polymerization begins. Polymerization takes place properly when the characteristic green color of PAni emeraldine salt appears after several minutes. Reactions were performed at room temperature (*ca.* 20 °C). The product was purified by centrifugation using the reaction solvent until the suspension reached a neutral pH value.

Characterization techniques

Optical profilometry. The thickness of the electropolymerized PEDOT films was determined using a surface profilometer Dektak 150 (Veeco). Several scratches (minimum 4) were intentionally made throughout the surface of polymeric samples ($n = 3$). Then, the step at several positions along the scratches was measured by the computer software Dektak (version 9.2, Veeco Instruments Inc.) to allow statistical analysis of data.

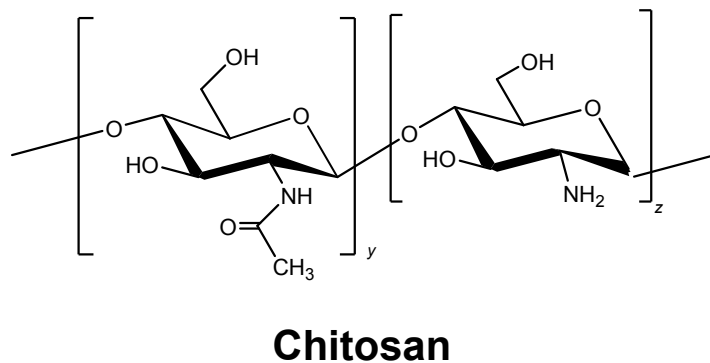
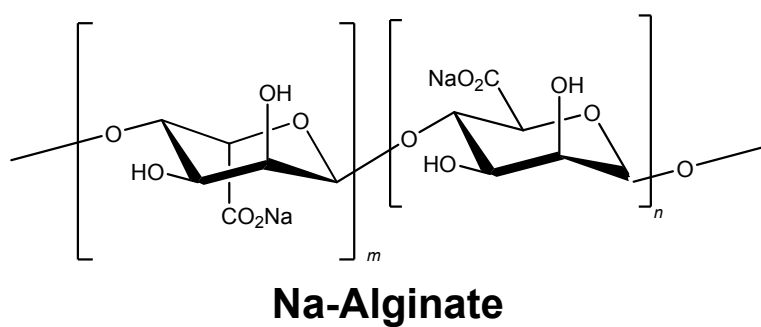
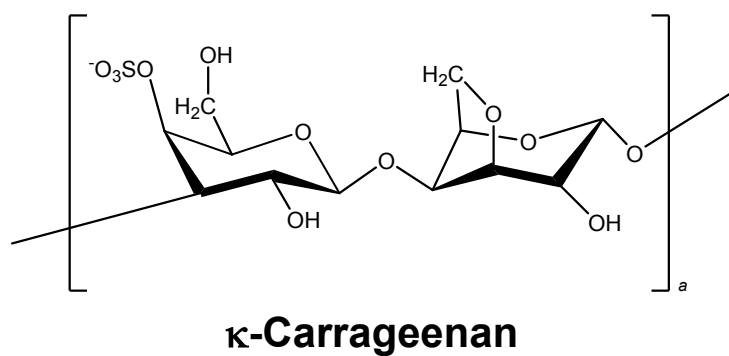
Electrical conductivity. In order to measure the electrical properties of PEDOT electrodes, electropolymerized films were partially coated with silver paint to yield two electrodes for two-probe conductivity measurements.

UV-vis spectroscopy. UV-vis absorption spectra were obtained using a UV-vis-NIR Shimadzu 3600 spectrophotometer equipped with a tungsten halogen visible source, a deuterium arc UV source, a photomultiplier tube UV-vis detector, and a InGaAs photodiode and cooled PbS photocell NIR detectors. Spectra of PAni-nanofibers solution was recorded between 200 and 800 nm in the absorbance mode. Measurements, data collection and data evaluation were controlled by the computer software UVProbe version 2.31.

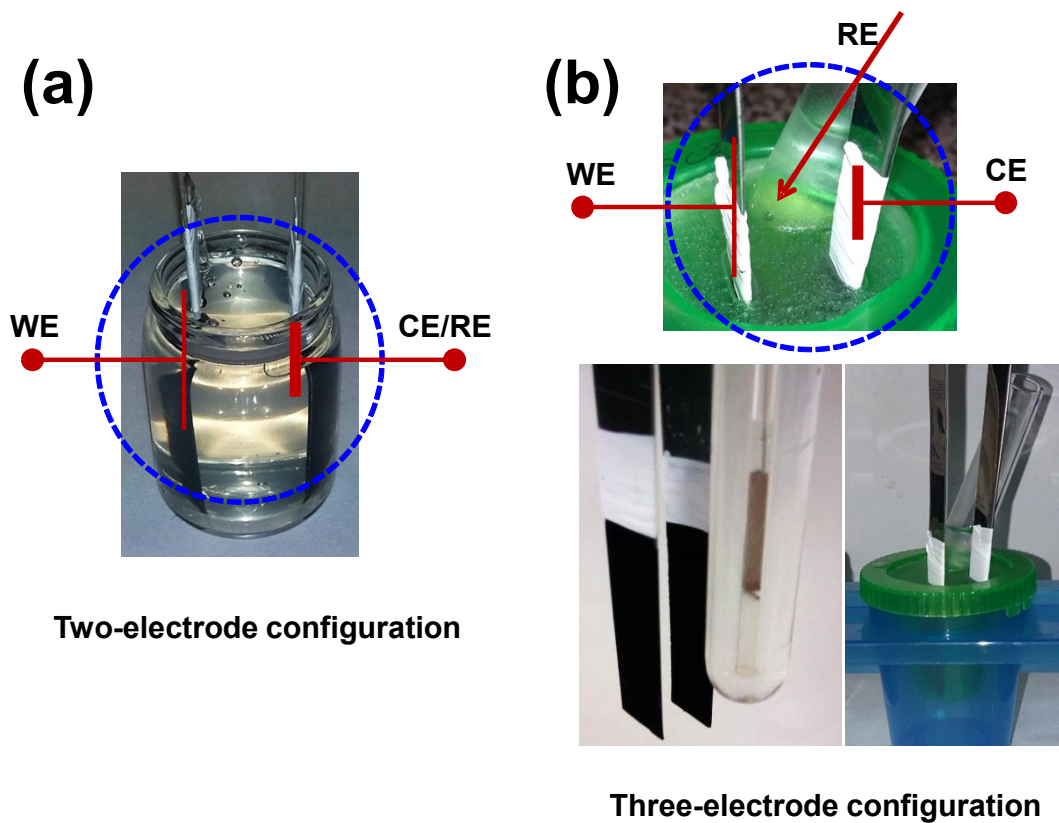
Scanning electron microscopy (SEM). The morphology of PEDOT films, PAni-nanofibers and biopolymer hydrogels was examined by SEM using a Focused Ion Beam Zeiss Neon40 scanning electron microscope equipped with an energy dispersive X-ray (EDX) spectroscopy system and operating at 5 kV. All samples were sputter-coated with a thin carbon layer using a K950X Turbo Evaporator to prevent electron charging problems. Prior to SEM observation, biopolymer hydrogels were lyophilized (*i.e.* freeze-drying) using liquid nitrogen.

Atomic force microscopy (AFM). AFM was conducted to obtain topographic images of PEDOT films surface using a silicon TAP 150-G probe (Budget Sensors, Bulgaria) with a frequency of 150 kHz and a force constant of 5 N/m. Images were obtained with a AFM Dimension microscope using a NanoScope IV controller under ambient conditions in tapping mode. The row scanning frequency was set between 0.6 and 0.8 Hz. The root mean square roughness (Rq), which is the average height deviation taken from the mean data plane, was determined using the statistical application of the NanoScope Analysis software (1.20, Veeco).

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Scheme S1 Chemical structure of three of the four biopolymer-based hydrogels tested as electrolyte. Since gelatin is a heterogeneous mixture of water-soluble proteins of high average molecular masses present in collagen, no chemical structure has been depicted.



Scheme S2. Images of the OESC- κ C device in both two- and three-electrode configurations that have been used for the electrochemical characterization.

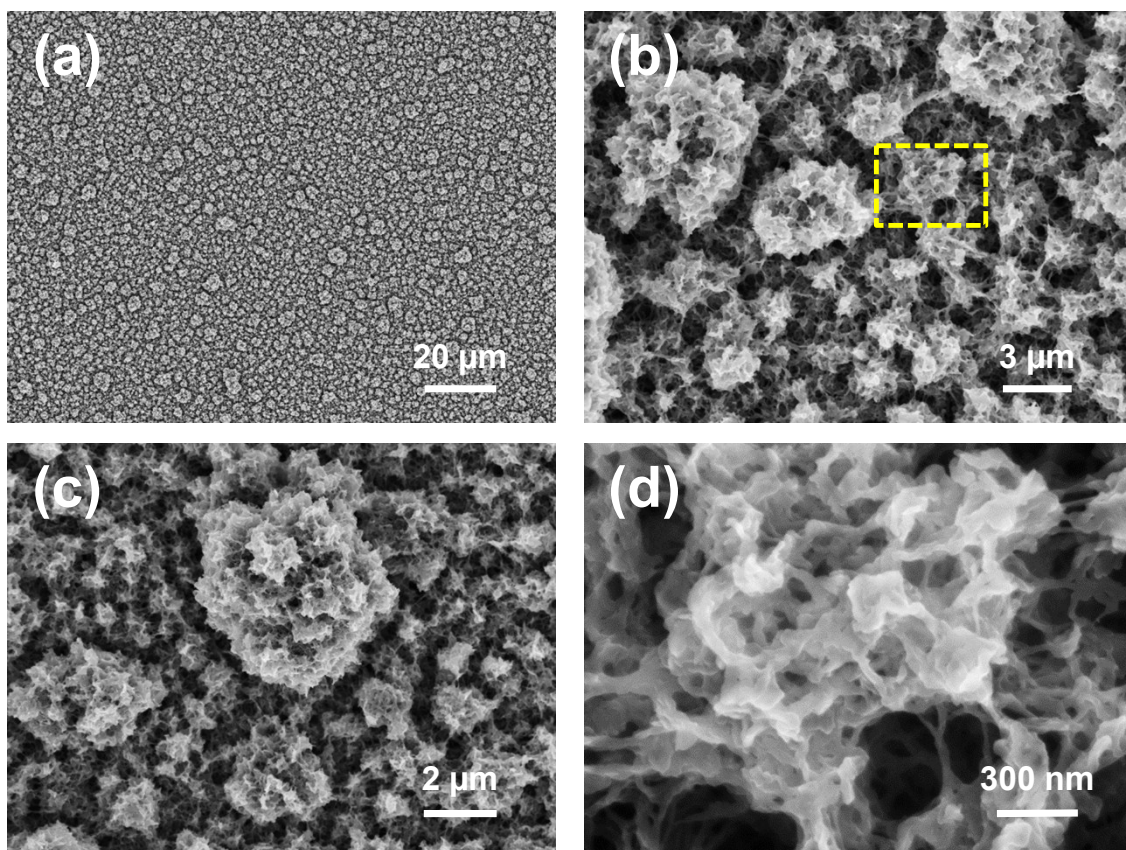


Figure S1. Morphology of PEDOT electrodes. SEM images recorded at different magnifications: (a) 2 kX, (b) 25 kX , (c) 20 kX and (d) 150 kX. Micrograph displayed in (d) corresponds to the yellow box marked in (b).

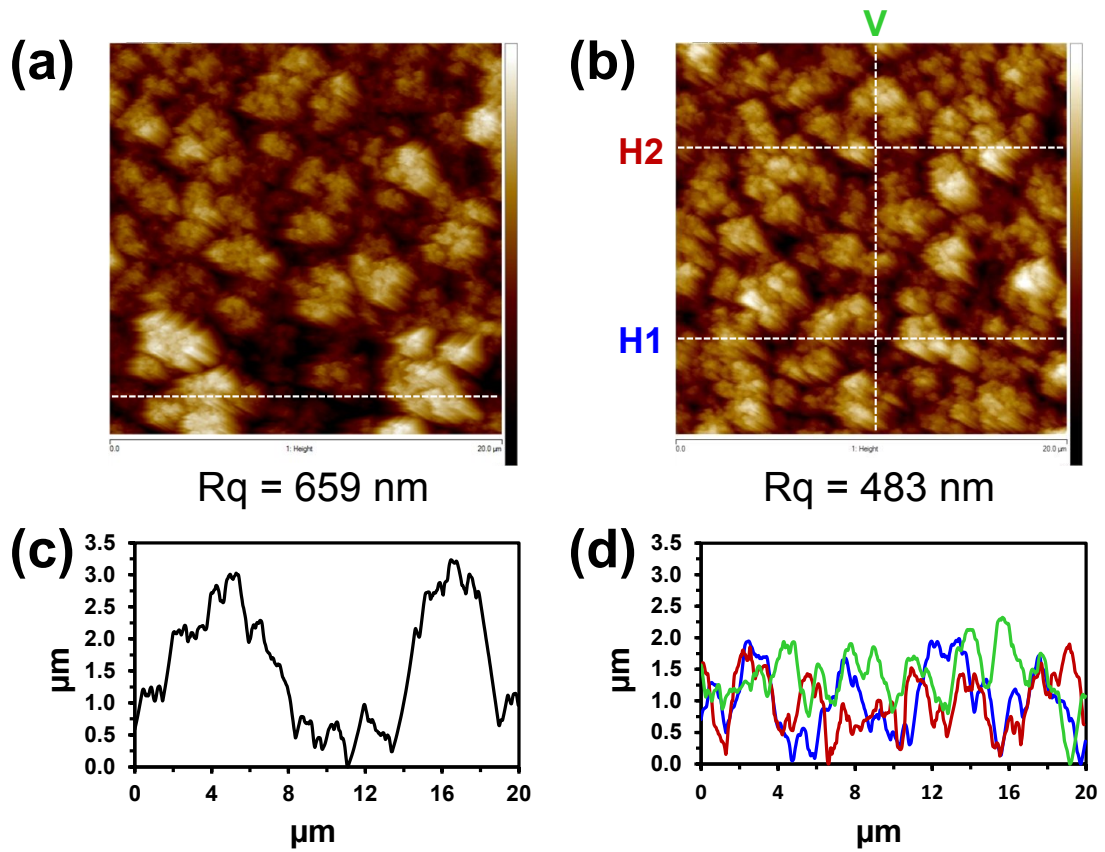


Figure S2. Topography of PEDOT electrodes. (a-b) 2D height images ($20 \times 20 \mu\text{m}^2$) and (c-d) cross-section profiles corresponding to the lines depicted in (a) and (b), respectively. The roughness R_q was determined by scanning different areas: (i) large $20 \times 20 \mu\text{m}^2$ areas, $R_q = 635 \pm 79$ nm ($n = 6$); (ii) medium $10 \times 10 \mu\text{m}^2$ areas, $R_q = 593 \pm 111$ nm ($n = 30$); and (iii) small ($5 \times 5 \mu\text{m}^2$) and homogeneous areas without big protuberances, $R_q = 487 \pm 82$ nm ($n = 6$).

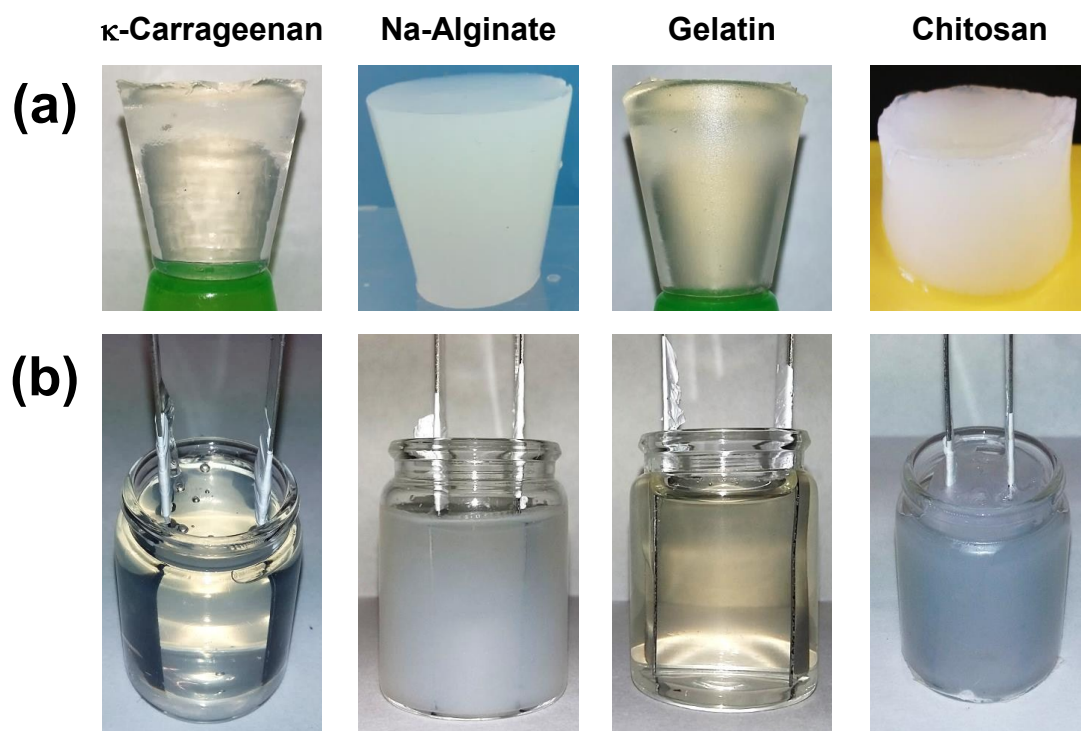


Figure S3. Images of the four biohydrogels tested as electrolyte system: (a) bulk and (b) OESC devices in the two-electrode configuration.

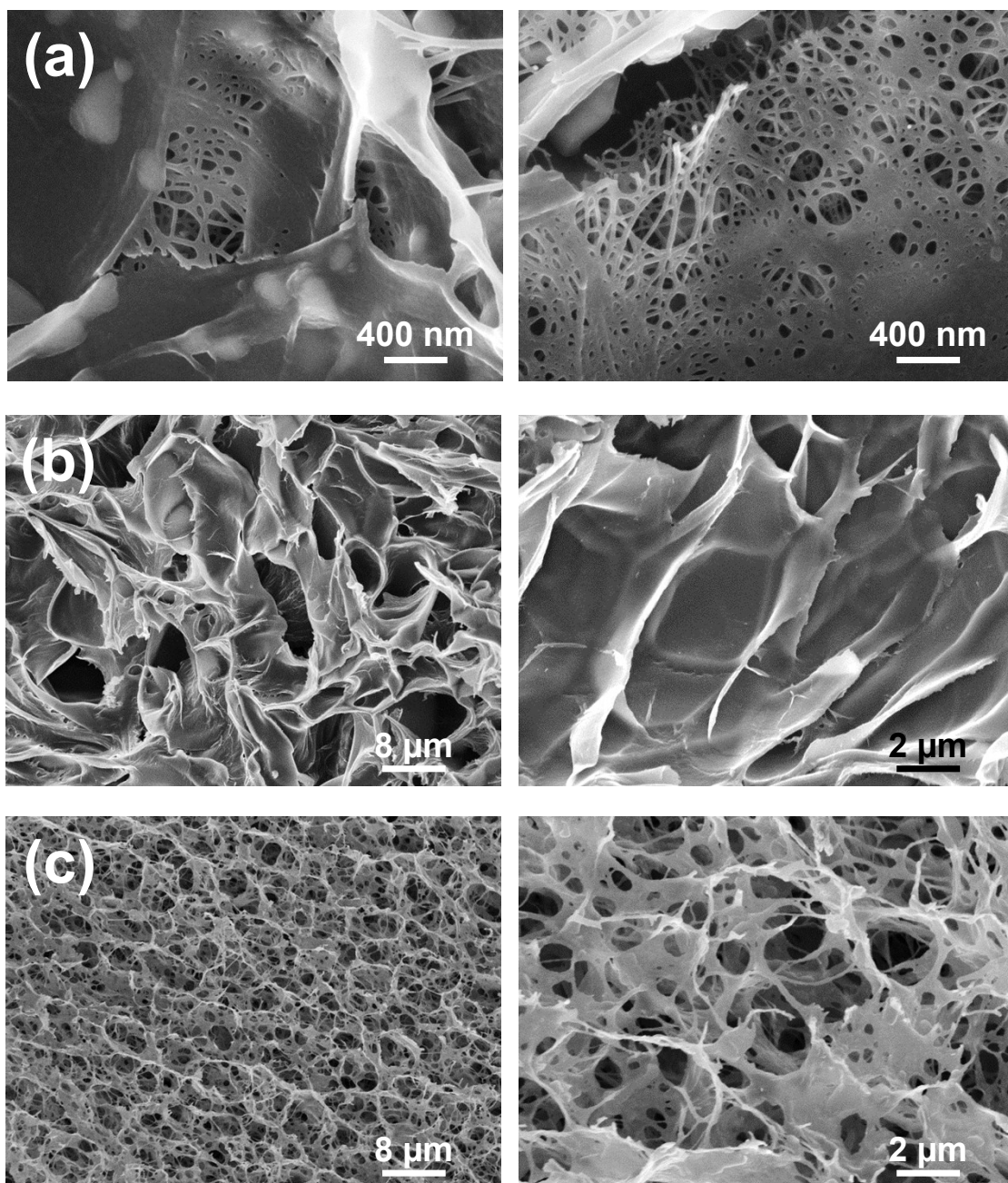


Figure S4. SEM micrographs of biohydrogels: (a) κ -carrageenan; (b) gelatin and (c) Na-alginate.

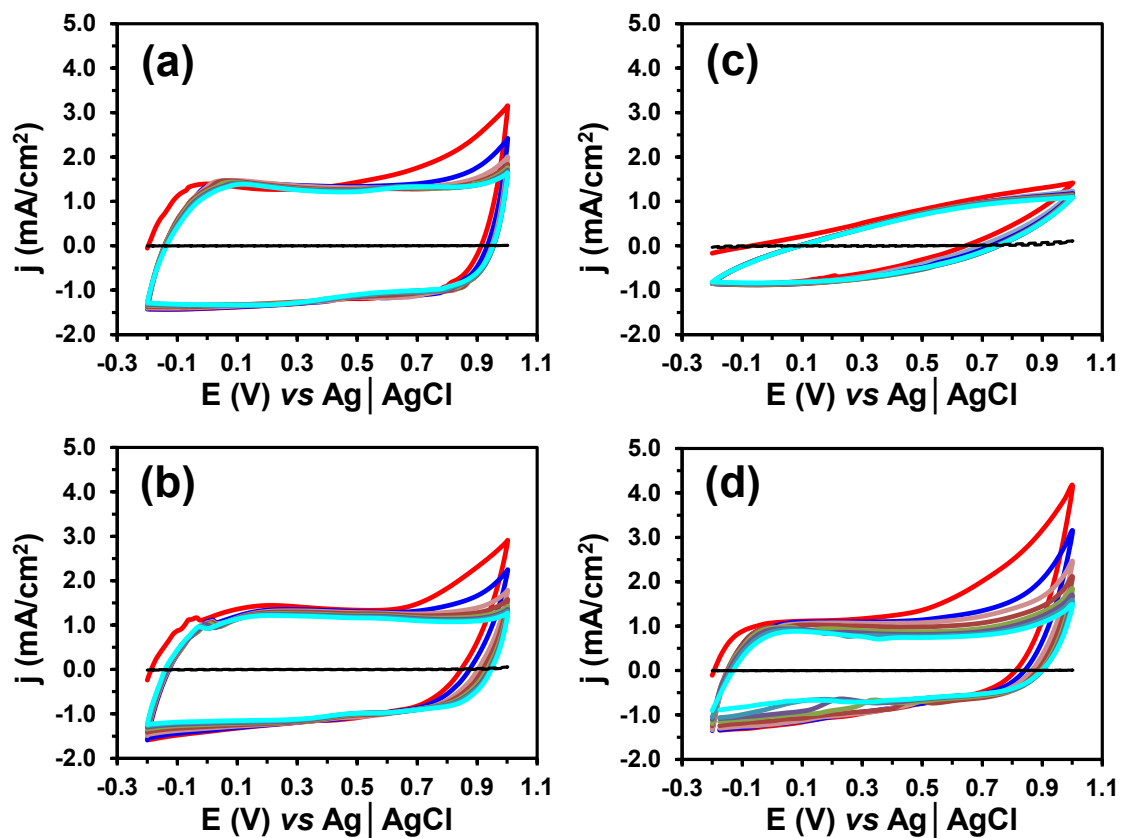


Figure S5. Cyclic voltammograms for PEDOT recorded from -0.2 to 1.0 V at 50 mV/s using: (a) κ -carrageenan, (b) Na-alginate and (c) gelatin as biohydrogel-based electrolyte, and (d) PBS as control electrolyte. A three-electrode configuration, with stainless steel and Ag | AgCl as counter and reference electrodes, respectively, was used for measurements. Displayed voltammograms correspond to the 1st (red), 2nd (blue), 5th, 10th, 20th, 30th, 40th and 50th (light blue) consecutive redox cycles. Tests were run in triplicate, even though only voltammograms for one representative sample are shown. Black line represents the control voltammogram recorded for bare steel electrodes in the corresponding biopolymer-hydrogel based electrolyte.

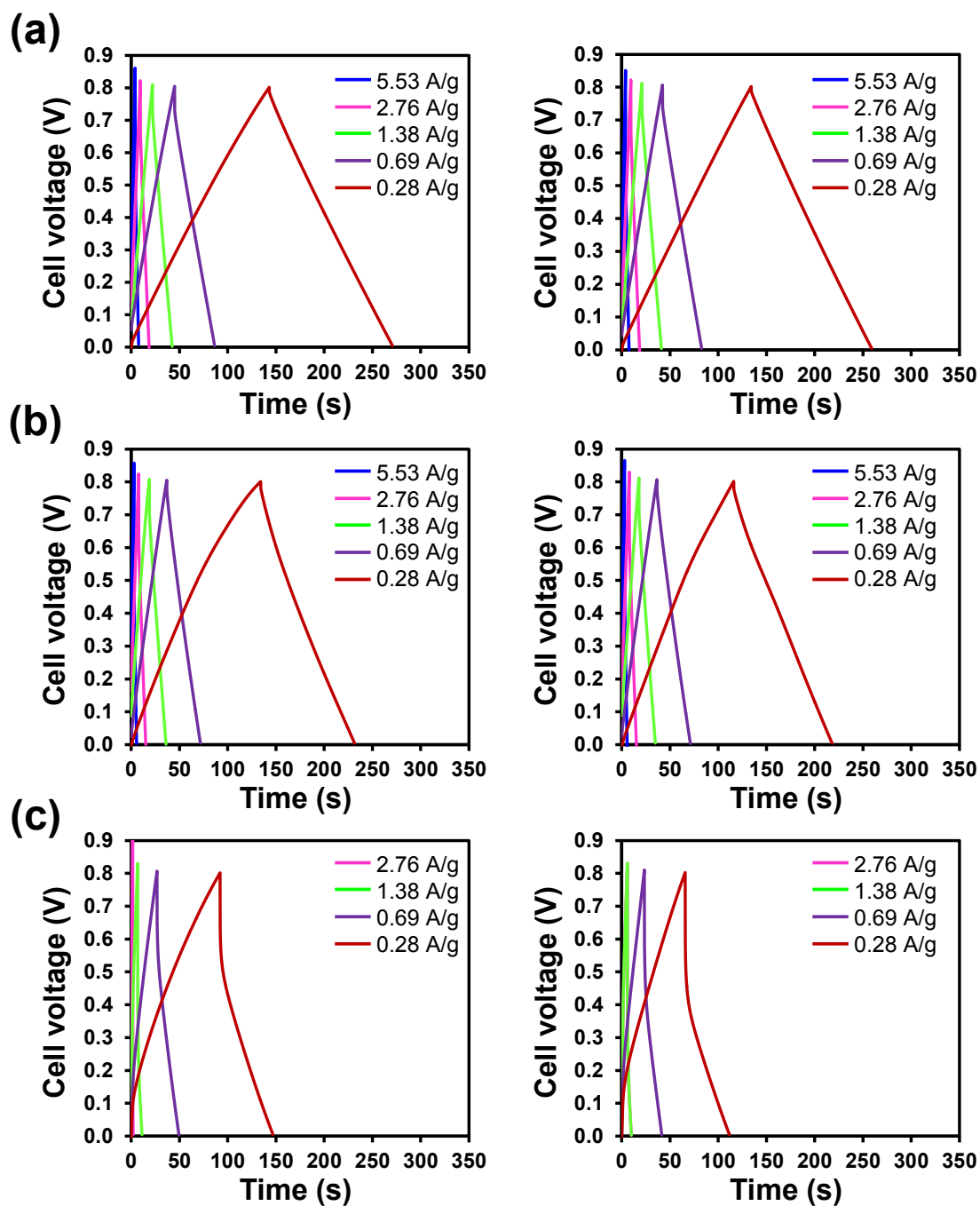


Figure S6. GCD curves (left and right columns correspond to the second and twenty-fifth charge-discharge cycle, respectively) for OESC devices (two-electrode configuration with PEDOT as working and counter electrodes) recorded from 0.0 to 0.8 V at different current densities (A/g) : (a) OESC- κ C, (b) OESC-NaAlg, (c) OESC-Gel.

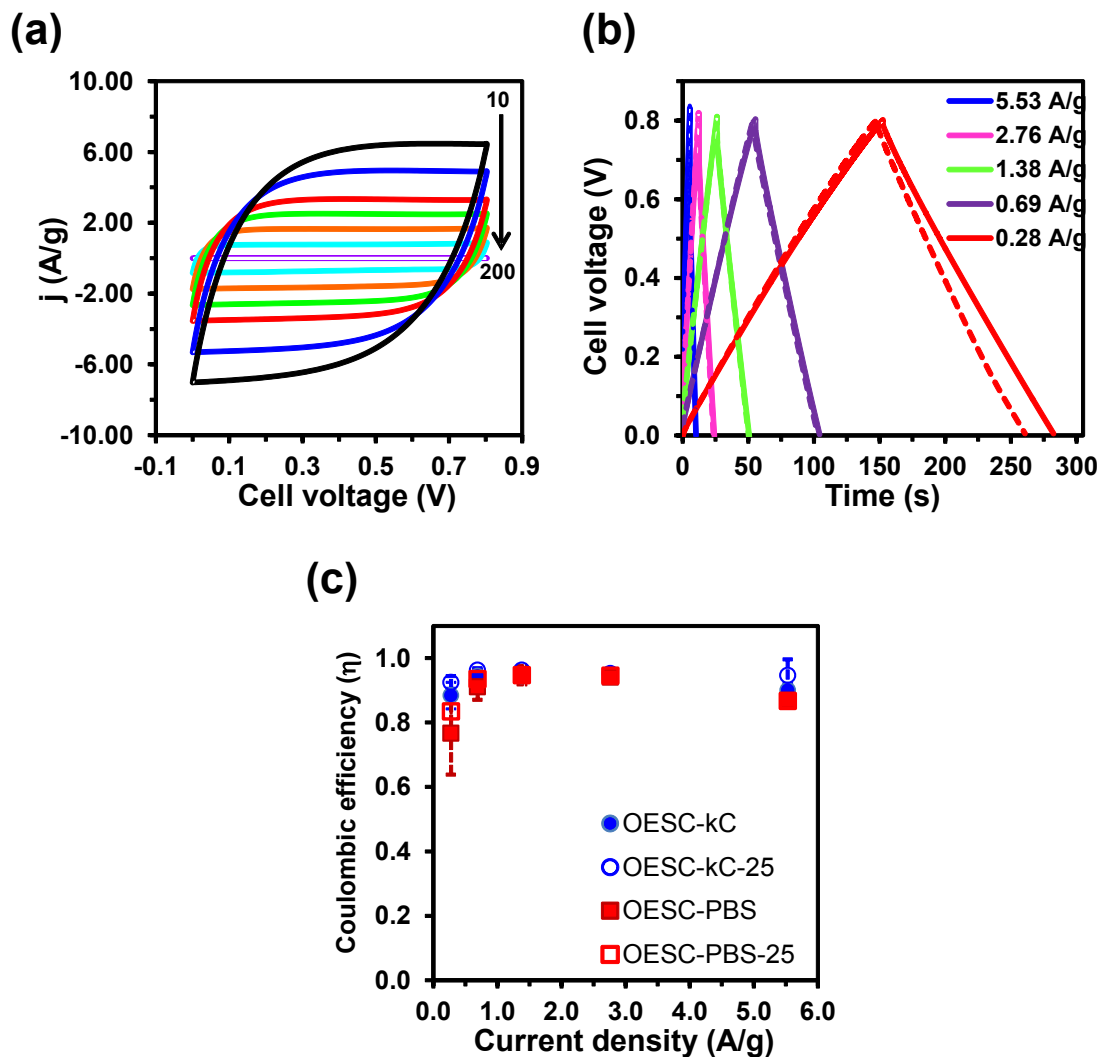


Figure S7. Electrochemical characterization (two-electrode configuration) of OESC-PBS devices, which present both CE and WE made of PEDOT and PBS solution as electrolyte. (a) Voltammograms recorded from 0.0 to 0.8 V after five consecutive redox cycles at scan rates of 10, 25, 50, 75, 100, 150 and 200 mV/s. (b) GCD curves recorded from 0.0 to 0.8 V at different current densities. Solid lines correspond to the first charge-discharge cycle, while the dashed ones correspond to the twenty-fifth cycle. (c) Coulombic efficiency values derived from the GCD curves. Filled and empty figures refer to the SC values determined for the first and twenty-fifth charge-discharge cycles.

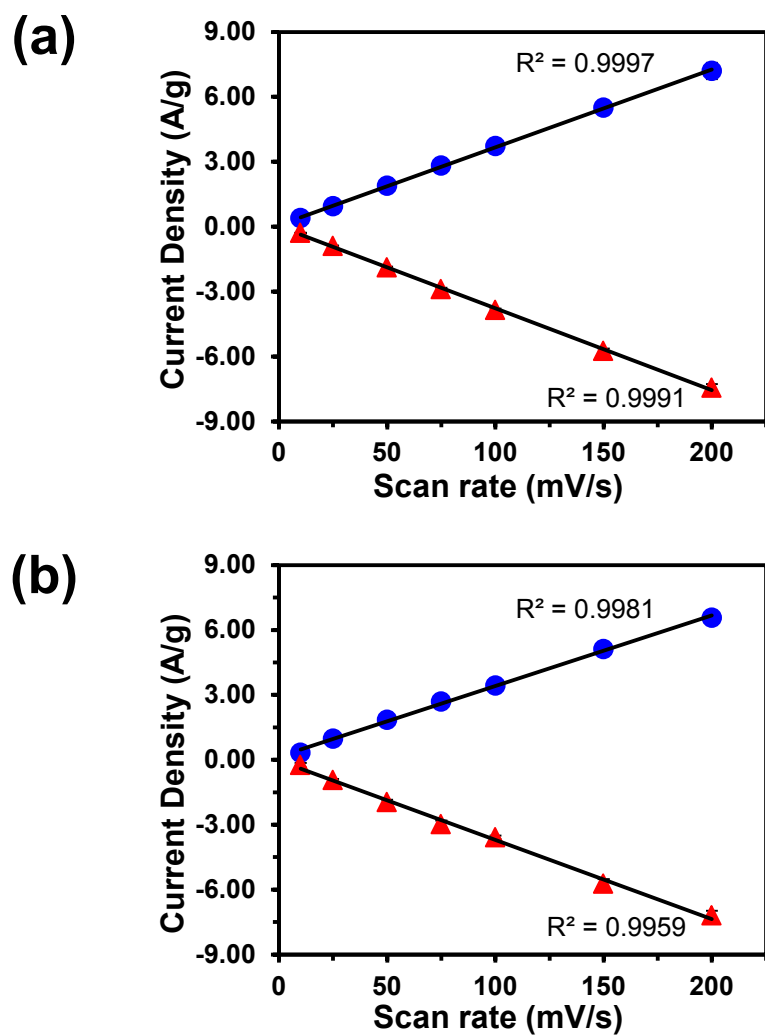


Figure S8. Current density *versus* scan rate of CV curves (two-electrode configuration) recorded for (a) OESC-κC and (b) OESC-PBS. The anodic intensity (●) at reversal potential (*i.e.* 0.8 V) and cathodic intensity (◻) at 0.1 V were taken from the cyclic voltammograms displayed in [Figures 3a and S7a](#).

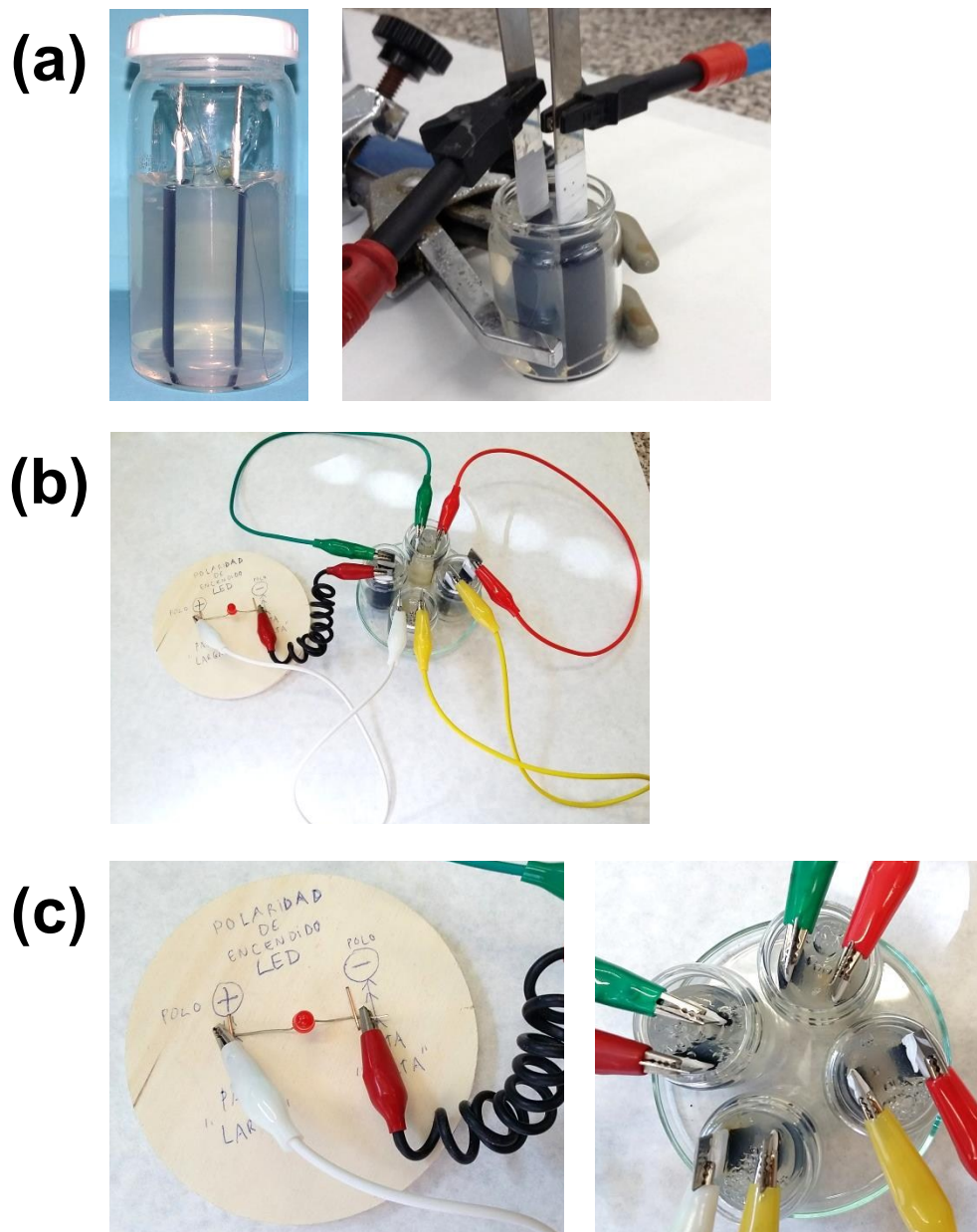


Figure S9. Images of OESC- κ C device: (a) two-electrode configuration; (b) four devices connected in series to power a red LED; (c) details from (b).

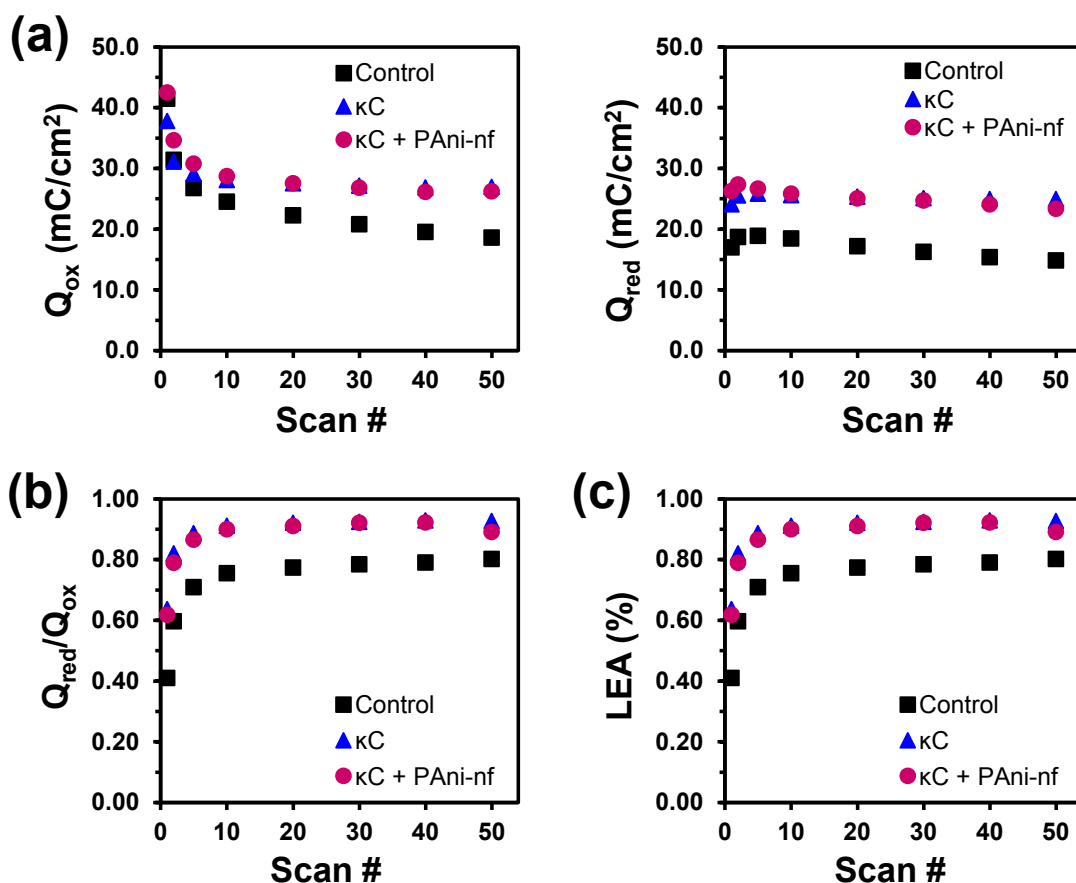


Figure S10. Cyclic voltammetry have been used to determine the electrochemical properties of PEDOT electrodes using different electrolyte systems: κ -carrageenan hydrogel (blue triangle), κ -carrageenan hydrogel loaded with Pani-nfs (red circle) and control PBS (black square). A three-electrode configuration, with stainless steel and Ag|AgCl as counter and reference electrodes, respectively, was used for measurements. Cyclic voltammograms were recorded from -0.4 to 1.0 V using a scan rate of 50 mV/s. The electrochemical properties determined from the recorded voltammograms are: (a) the variation of the stored charge, where Q_{ox} (left) and Q_{red} (right) refer to oxidation and reduction charge; (b) the electrochemical activity, which is defined by the Q_{red}/Q_{ox} ratio; and (c) the loss of electrochemical activity (LEA) against the number of consecutive redox cycles.

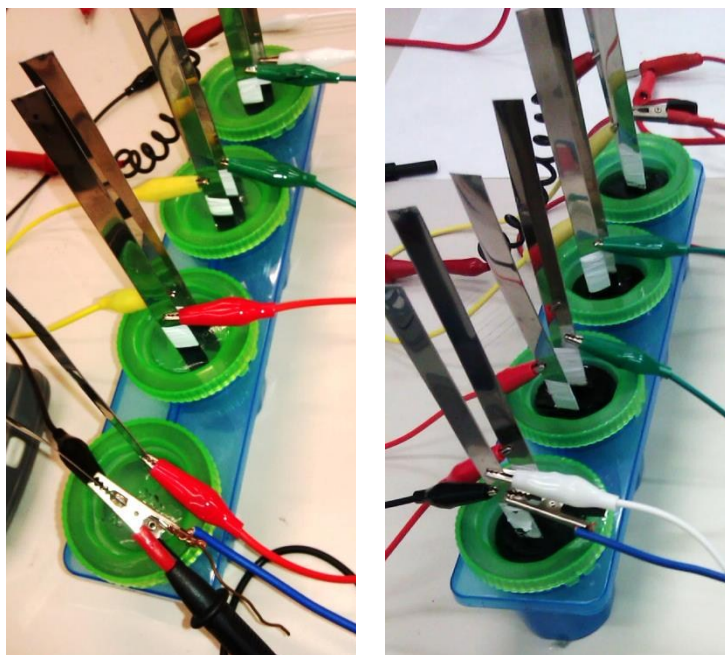


Figure S11. Images of four OESC devices connected in series: (left) OESC- κ C and (right) OESC- κ C:PAni-nfs.

Table S1. Specific capacitance values (SC , in F/g) determined from cyclic voltammograms obtained for OESC-PBS (Figure S7a) and OESC- κ C (Figure 3a) using different scan rates.

Scan rate (mV/s)	OESC-PBS	OESC-κC
10	57 ± 6	51 ± 2
25	62 ± 7	63 ± 3
50	61 ± 3	63 ± 4
75	57 ± 3	61 ± 5
100	55 ± 2	58 ± 5
150	44 ± 6	51 ± 5
200	37 ± 8	44 ± 6

Table S2. Specific capacitance values (SC , in F/g) determined from GCD curves for OESC-PBS (Figure S7b) and OESC- κ C (Figure 3c) using different current densities.

j (A/g)	OESC-PBS		OESC-κC	
	2nd cycle	25th cycle	2nd cycle	25th cycle
0.28	80 ± 5	79 ± 6	80 ± 4	78 ± 5
0.69	84 ± 4	85 ± 3	81 ± 3	75 ± 9
1.38	85 ± 4	87 ± 2	77 ± 2	74 ± 7
2.76	86 ± 3	85 ± 3	77 ± 1	72 ± 6
5.53	81 ± 5	82 ± 5	71 ± 1	67 ± 7