Poly-γ-glutamic Acid Hydrogels as Electrolyte for Poly(3,4-ethylenedioxythiophene)-Based Supercapacitors

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** Supporting Information

ABSTRACT: Biosynthetic poly-γ-glutamic acid (γ-PGA) has been used to produce hydrogels using cystamine as cross-linker and 1-[3-(dimethylamino)-propyl]-3-ethylcarbodiimide methiodide (EDC methiodide) as condensing agent. Eight different hydrogels with different properties were formulated by varying both the molecular weight of γ-PGA and the γ-PGA/EDC/cystamine ratio and subsequently characterized. The most appropriate γ-PGA hydrogel was selected to perform as solid electrolytic medium in organic electrochemical supercapacitors (OESCs) using poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes based on their mechanical behavior (consistency and robustness to hold the PEDOT electrodes), morphology, and influence on the electrochemical response of the organic electrode (i.e., specific capacitance and both maximum energy and power density values). Hence, PEDOT/γ-PGA energy storage devices fabricated using the most adequate hydrogel formulation displayed a supercapacitor response of 168 F/g and a capacitance retention of 81%. Moreover, after evaluating the maximum energy and power densities (Ragone plot), cyclability, long-term stability, leakage current, and self-discharging response of PEDOT/γ-PGA OESC devices, results allow us to highlight the merits and great potential of γ-PGA hydrogels as sustainable ion-conductive electrolytes for environmentally friendly energy storage technologies.

INTRODUCTION

Our daily activities have become dependent on the available energy supply. Indeed, portable energy storage devices have become essential, not only for operating laptops and smart cell phones, but also for other electronic and electrical systems used in motor vehicles, satellites, sensors, or medical and military equipment. Among other features, these applications require energy storage devices to be cost-affordable, lightweight, durable (long-term stability), and, if possible, sustainable by using eco-friendly materials.

Although electrolytic/ceramic batteries and capacitors are both used for energy storage applications, these devices differ in the power and energy densities they can provide. Thus, batteries are characterized by high energy density values (10–100 Wh/kg), while capacitors display high power density values (i.e., they can release the stored energy much faster). In low-energy applications (e.g., motor starting, signal processing, and sensing) or when fast pulsed power supply is needed (e.g., electromagnetic forming, Marx generators, pulsed lasers, and particle accelerators, among others), capacitors offer a series of advantages, such as cost-effectiveness, faster charging–discharging times, and long-lasting cycling stability.

Electrochemical supercapacitors (ESCs) have emerged as promising energy storage devices displaying higher energy values (i.e., 1–10 Wh/kg for carbon ESCs) than conventional capacitors (i.e., <0.1 Wh/kg), evidencing a potential future use in large-scale high-energy applications. In ESCs, the electric double layers formed at the electrode–electrolyte interface (i.e., Helmholtz and diffuse layers) contribute to the magnitude of the capacitance, which strongly depends on the electrode surface. In order to increase the capacitance, faradic charge transfer reactions are frequently employed by applying electrochemically active materials, such as metal oxide materials or conducting polymers (CPs). Similarly to metal oxides, CPs display competitive capacitance values (from 60 up to 1000 F/g, depending on the CP) with a potential range of 0.8 V but offering advantages in cost, processability, and lightweight. On the other hand, the charge storage mechanism of CPs requires ions to be intercalated into the polymeric 3D network, which causes chemical degradation and swelling, and thus a possible reduction in the cycle life of the electrode. For example, poly(3,4-ethylenedioxythiophene) (PEDOT) has been reported as an adequate electrode in organic ESCs (OESCs). In addition to showing capacitance values in the range between 60 and 250 F/g, this electrochemically active material is electrostable and biocompatible.

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Recent research in OESCs has been focused on improving their energy density, which is the limiting specification that restricts their application in large-scale energy storage systems, by increasing the capacitance of the device, the operation voltage window, or both. The approaches followed to reach such purpose include: nanostructuring and increasing the electrode porosity, designing electrodes with a gel-like morphology, or combining the CP with metal oxides (e.g., MnO₂ or V₂O₅), carbon nanotubes, graphene oxide, or redox biopolymers (e.g., lignin).21 Nevertheless, even though pseudocapacitance depends primarily on the electrode conductivity, porosity, size, and surface shape, it is also affected by the ion movement speed in the electrolyte. Dopant ion transport represents a critical factor, especially for thick electrodes (>100 μm), since it determines the fraction of electrodes accessible electrochemically and, thus, contributing to the pseudocapacitance of the system.22 Bearing this idea in mind, new electrolytes, such as ionic liquids or gels have been used to provide high potential stability windows and improve the electrochemical stability of the electrodes.

In addition, due to the global concern regarding sustainable technology, efforts are being made to replace organic solvents usually used in electrolytes for ESC devices by aqueous solutions. Besides, when the electrolyte is presented in solid form (i.e., solid electrolyte, SE) further advantages are obtained: compactness, reliability, reduced leakage risk, flexibility, and ease of handling. Very recently, Armelin et al. reviewed the use of biohydrogels for supercapacitor applications. These materials, which can be extracted directly or eventually synthesized/recycled from biomass and renewable sources, represent the next stage toward a more sustainable energy storage technology. Within this context, we prepared and evaluated the supercapacitor performance of OESC devices using PEDOT as electrodes and four different bihydrogels as SE (i.e., sodium alginate, κ-carrageenan, gelatin, and chitosan). In order to exploit at maximum the pseudocapacitance of PEDOT electrodes, these SEs were expected to present not only mechanical robustness to keep the electrodes at their positions, but also an open porous structure able to favor ion movement and transfer. We found that κ-carrageenan was the most suitable bihydrogel to perform as SE electrolyte due to the appropriate combination of properties: mechanical integrity, lack of water leaking, and structural suitability to favor the electrochemical response of PEDOT. Nevertheless, it should be noted that the pores in those biohydrogels were only mechanical robustness to keep the electrodes at their positions, but also an open porous structure able to favor ion movement and transfer. We found that κ-carrageenan was the most suitable bihydrogel to perform as SE electrolyte due to the appropriate combination of properties: mechanical integrity, lack of water leaking, and structural suitability to favor the electrochemical response of PEDOT. Nevertheless, it should be noted that the pores in those biohydrogels were based on physical cross-links (i.e., polymeric chains were cross-linked by monovalent or divalent metallic ions), hindering the control/tuning of their structural characteristics.

Therefore, herein, we explore the use of hydrogels based on poly-γ-glutamic acid (γ-PGA) as SE in OESC devices. γ-PGA is a poly(γ-peptide) derived from glutamic acid (Glu), in which peptide bonds involve the γ-carboxyl group and α-amino groups (Scheme 1). This compound is naturally synthesized as a slime layer by a variety of members of the genus Bacillus. For instance, the molecular weight of γ-PGA produced by Bacillus subtilis isolated from “chungkookjang”, a traditional Korean fermented soybean food, is much higher than that obtained using Bacillus subtilis natto, which allows its functional application in cosmetics, medicine, and industrial products (e.g., water absorption agents, moisturizing agents, thickening agents, absorption enhancers of minerals, sustained release drug delivery systems, and biodegradable agglomerated detergents). In addition, in its free-acid form, γ-PGA can be chemically cross-linked producing biohydrogels. Most importantly, the structure and content of the cross-linker agent regulate the cross-linking density, pore size, water absorption, and degradation profile of the resulting γ-PGA hydrogels.

In this work, up to eight γ-PGA hydrogel formulations have been prepared by varying the molecular weight of the biopolymer and the cross-linking degree. These parameters affected the morphology, swelling ratio, thermal properties, and mechanical integrity of the hydrogels. After selecting those γ-PGA hydrogels with the most appropriate properties to perform as electrolytic medium in OESC devices, the electrochemical response of PEDOT electrodes has been evaluated in terms of specific capacitance (SC), maximum energy density (Eₘₐₓ) and power density (Pₘₐₓ). Finally, features directly related to the application of the system, such as cyclability, long-term stability, and the lighting of a LED bulb, have been further examined for the optimum PEDOT/γ-PGA OESC.

EXPERIMENTAL SECTION
Preparation of PEDOT/γ-PGA OESC Devices. Specific experimental details for the synthesis of PEDOT films and γ-PGA hydrogels are provided in the Supporting Information. As a general procedure, γ-PGA hydrogels used as SE were prepared 24 h before testing and without applying the washing
step. The response of PEDOT is not hindered by the presence of 1-[(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC methiodine) or cystamine but by the lack of electrolyte, NaHCO$_3$. Therefore, ca. 1.4 mL of the reaction solution was placed into the wells of a 24-well plate and let to gel at room temperature. Before the electrochemical characterization, PEDOT films electropolymorized onto SS sheets were carefully introduced into the γ-PGA hydrogel at a distance of 1 cm and fixed with tape to prevent movement during testing (Figure S1).

**Characterization.** Details on all physical and chemical characterization tests are provided in the Supporting Information with the exception of the electrochemical characterization, which is described here. Although the three-electrode electrochemical cell configuration is adequate for a fast screening of the electrode material, the two-electrode configuration confirms the supercapacitor performance under specific working conditions since the response of the whole cell is under investigation. Accordingly, the electrochemical response of PEDOT electrodes was first studied using three different γ-PGA hydrogels as SE (compositions LPGGA-2, LPGGA-4, and HPGGA-6 in Table S1) in a two-electrode configuration.

As defined by Stoller and Ruoff,$^{35}$ the SC (F/g) is the capacitance per unit of mass for one electrode and can be expressed as

$$\text{SC} = 4 \times \frac{C}{m}$$

where $C$ is the measured capacitance for the two-electrode cell and $m$ the total mass of the active material in both electrodes (i.e., 0.8226 mg). The multiplier 4 adjusts the capacitance of the cell and the combined mass of the two electrodes to the capacitance and mass of a single electrode.

Galvanostatic charge/discharge (GCD) evaluation is the most commonly used procedure to determine the cell capacitance ($C, F$) of a pseudocapacitor

$$C = \frac{I}{dV/dt}$$

where $I$ is the discharging current applied to the device, and $dV/dt$ should be calculated as $(V_{\text{max}} - 1/2V_{\text{max}})/\left(t_2 - t_1\right)$, where $V_{\text{max}}$ corresponds to the highest voltage in the GCD curve after the voltage drop ($V_{\text{drop}}$) at the beginning of the discharging process.$^{35}$

Consequently, GCD curves (5 cycles) between 0.0 and 0.8 V were run at different current densities (i.e., charge and discharge rates are specified in units of current per electrode mass): 0.30, 0.44, 0.61, 1.22, 2.43, and 4.86 A/g that corresponded to 0.125, 0.18, 0.25, 0.5, 1, and 2 mA, respectively. Besides, the Coulombic efficiency ($\eta$, %) was evaluated as the ratio between the discharging and charging times for the electrochemical window between 0 and 0.8 V

$$\eta = \frac{t_2}{t_1}$$

Finally, cyclic voltammetry (CV) measurements can also provide information regarding the cell capacitance ($C, F$) of a system by applying eq 2. In this case, $I$ corresponds to the average current during discharging (i.e., PEDOT reduction from 0.7082 to 0.1012 V), while $dV/dt$ is the scan rate. Specifically, for PEDOT/γ-PGA OESC devices, CV curves (5 cycles) were recorded from 0 to 0.8 V at several scan rates: 10, 25, 50, 75, 100, 150, and 200 mV/s.

All electrochemical experiments (GCD and CV curves) were run in triplicate, and the results presented are the average data (mean ± SD). In addition, NaHCO$_3$ solution (0.5 M) was tested as control electrolyte.

After selecting the most appropriate γ-PGA hydrogel system as electrolyte, the cycling stability of the corresponding PEDOT/γ-PGA OESC device was tested by two approaches. First, the system was submitted to 2000 GCD cycles at a current density of 1.22 A/g from 0 to 0.8 V, which corresponds to $t_1$ and $t_2$ values of approximately 40–60 s. Second, 1000 CV cycles were run from 0 to 0.8 V at 50 mV/s. The time-dependence evolution of the supercapacitor response was determined after 1 week by repeating the GCD test (2000 cycles) for the same sample. From the CV curves, the electrostability of PEDOT electrodes was quantified as the loss of electroactivity (LEA; in %)

$$\text{LEA} = \frac{\Delta Q}{Q_2} = \frac{Q_1 - Q_2}{Q_2}$$

where $\Delta Q$ is the difference between the oxidation charge (in C) of the second ($Q_2$) and the evaluated oxidation–reduction cycle ($Q_2$).

Moreover, the leakage current (LC) and self-discharging (SD) response of PEDOT/γ-PGA devices was evaluated by applying methods previously described.$^{35}$ For the former, after charging the device to 0.8 V at 0.25 mA (i.e., 0.61 A/g), it was kept at 0.8 V for 5–10 min while recording the current. For the latter, PEDOT/γ-PGA devices were charged to 0.8 V at 0.25 mA and kept at 1 $\times$ 10$^{-11}$ mA for 10 min (self-discharging). After that time, the device was discharged to 0 V at $-1$ mA. Data were obtained from three different devices.

Finally, the $E_{\text{max}}$ (Wh/kg), which is the amount of energy stored per unit of mass, and $P_{\text{max}}$ (W/kg), which describes the speed at which the energy stored can be delivered, can be calculated by applying the following equations$^{37}$

$$E_{\text{max}} = \frac{1}{2} \times V_{\text{max}}^2 \times \text{SC}$$

$$P_{\text{max}} = \frac{1}{4m} \times \frac{V_{\text{max}}^2}{R_i}$$

$$R_i = \frac{V_{\text{drop}}}{2 \times I_{\text{discharge}}}$$

where $V_{\text{max}}$ corresponds to the highest voltage in the GCD curve after $V_{\text{drop}}$; $m$ is the total mass of the active material in one electrode (i.e., 0.4113 mg); and $R_i$ is the internal resistance.

### RESULTS AND DISCUSSION

#### Preparation of PEDOT Electrodes

This work focuses on the role of γ-PGA hydrogels as green and aqueous-based SE for OESC devices. Hence, PEDOT electrodes were prepared by applying an optimized procedure previously reported in the literature.$^{35}$ Chronoamperometry (CA) under a potential of 1.25 V and a polymerization charge of 0.5 C/cm$^2$. The resulting PEDOT films exhibited a thickness of 4.12 ± 0.83 μm, an electrical conductivity of 33.2 ± 4.1 S/cm, and a mass of 0.4113 ± 0.057 mg.

Regarding the morphology, PEDOT films display a sponge-like porous structure with a continuous open network and void
spaces (Figure S2a,b). Besides, PEDOT chain entanglements form aggregates of varying size and height (between 1 and 5 μm) that are distributed throughout the surface resulting in $R_q$ values of $633 \pm 22$ nm for $10 \times 10 \mu m^2$ areas (Figures S2c,d). Such matrix features favor fast ion and electron transport during electrochemical redox processes and thus allow for high charge storage and pseudocapacitance of the OESC device.

**Preparation of γ-PGA Hydrogels and Their Preselection as Electrolyte for OESC Devices.** In addition to facilitating an adequate ion movement toward the electrode, a superior electrolyte performance is based on optimized working voltages, nontoxicity, low corrosion, and safety. Accordingly, γ-PGA hydrogels seem an excellent option to be applied as SE in OESC devices. In this work, γ-PGA hydrogels were produced by adapting the procedure described by Matsusaki et al. that uses cystamine as cross-linker (Scheme 1).

Table S1 summarizes the different γ-PGA hydrogels prepared by varying the concentration of the compounds involved in the condensation reaction: γ-PGA, EDC, and cystamine. The prepared hydrogels have been labeled LPGGA-# and HPGGA-# for samples derived from low and high molecular weight γ-PGA, respectively, # being a number used to identify the cystamine and EDC concentrations ([Cys] and [EDC], respectively).

The preselction of the γ-PGA hydrogels for their use as electrolyte in OESC devices was performed according to the following rational:

- The mechanical robustness of suitable γ-PGA hydrogels must be strong enough to keep the PEDOT electrodes at their positions. For this purpose, evaluation of the mechanical properties has been performed by visual inspection.
- The porosity of suitable γ-PGA hydrogels must be adequate enough to maximize the pseudocapacitance of PEDOT electrodes by promoting ion movement at the electrode–electrolyte interface. The morphology of the prepared hydrogels was evaluated by scanning electron microscopy (SEM).

The swelling ratio (SR, %) of the resulting γ-PGA hydrogels, which is a good indication of their cross-linking degree, decreases with increasing content of cystamine (Table S1). Besides, hydrogels prepared with low $M_w$ γ-PGA exhibit lower cross-linking than those prepared with high $M_w$ γ-PGA. The mechanical stability of γ-PGA hydrogels was found to improve with the cystamine concentration (i.e., cross-linking density). For instance, the mechanical integrity of LPGGA-1, a transparent hydrogel with low cross-linking, was poor (Figure S3a), while, in opposition, HPGGA-6 was a robust, opaque, and compact hydrogel (Figure S3b).
SEs are required to present an open porous structure. SEM micrographs of those γ-PGA hydrogels with a stable mechanical integrity (i.e., LPGGA-2, -4, and -6 and all three HPPGA-#) are displayed in Figures 1 and S4. Samples exhibited pore sizes in the range between 1.4 and 25 μm (Table S1) with the exception of LPGGA-2 and HPPGA-6, for which pore/void spaces display diameters higher than 50 μm. Despite these structural differences, LPGGA-2, LPGGA-4, and HPPGA-6 showed adequate consistency and robustness (Figure 1e), holding PEDOT electrodes during electrochemical assays. In general, these three hydrogels exhibit dense plate- or leaf-like interconnected structures, giving place to dense and open macroporous networks. In contrast, the morphology of the rest of the hydrogels resembles that of microperforated polymeric films (Figure S4). Accordingly, LPGGA-2, LPGGA-4, and HPPGA-6 hydrogels were chosen as suitable SEs for OESC devices due to their mechanical stability and open structure.

**Characterization of γ-PGA Hydrogels.** The FTIR spectra of γ-PGA, LPGGA-2, LPGGA-4, and HPPGA-6 are displayed in Figure S5. The spectrum recorded for γ-PGA shows the characteristic peaks expected for this biopolymer: C=O stretch of free carboxylic acid at 1728 cm\(^{-1}\), stretching vibration of the amide carbonyl group (amide I) at 1638 cm\(^{-1}\), asymmetric COO\(^{-}\) stretch at 1589 cm\(^{-1}\), −CONH− bond vibration (amide II) at 1535 cm\(^{-1}\), and C–N vibration at 1215 cm\(^{-1}\). The disappearance of the free carboxylic acid and asymmetric COO\(^{-}\) bands and the significant enhancement of the amide I and II bands reflect the successful formation of −CONH− as a cross-link bond (Scheme 1).

Thermogravimetric (TG and DTG) curves of the three selected hydrogels, after drying, are provided in Figure S6. Thermal behavior was highly similar for the three samples. Specifically, TG curves clearly evidenced a small mass loss around 100 °C that increases with the swelling capability of the hydrogel and, logically, corresponds to the evaporation of still absorbed water. The three hydrogels were thermally stable, and a highly complex decomposition process at temperatures higher than 200 °C was observed. Note that DTG curves show different well-defined peaks that slightly change with composition. For example, the most intense DTG peak appears at 400 °C for LPGGA-2 and LPGGA-4, and at 420 °C for HPPGA-6.

**Figure 2.** Electrochemical characterization of PEDOT/γ-PGA OESCs (two-electrode configuration, CE/RE = WE/S = PEDOT) using (a,b) LPGGA-2, (c,d) LPGGA-4, and (e,f) HPPGA-6 as SE. (a, c, e) Cyclic voltammograms (5th cycle shown) recorded from 0 to 0.8 V at scan rates of 10, 25, 50, 75, 100, 150, and 200 mV/s. (b, d, f) GCD curves recorded from 0 to 0.8 V at different current densities (A/g). Solid lines correspond to the second charge–discharge cycle, while the dashed ones correspond to the fifth cycle.
at higher temperatures for the LPGGA-2 sample, which is characterized by a lower content of cystamine cross-links. All samples have a high char yield (20−29%), this yield being higher for the less cross-linked sample (i.e., LPGGA-2 with a higher ratio of γ-PGA).

Selection of γ-PGA Hydrogel As Electrolyte. The electrochemical response of PEDOT in each one of the γ-PGA hydrogels characterized in the previous section (i.e., LPGGA-2, LPGGA-4, and HPPGA-6) was investigated by CV and GCD measurements (Figure 2). Results have been compared with those obtained for an OESC device using NaHCO₃ (0.5 M) as electrolytic medium (Figure S7).

First, five consecutive redox cycles were recorded from 0.0 to 0.8 V at different scan rates to evaluate: (i) the oxidation and reduction charges during the charge−discharge process (Q_{ox} and Q_{red} respectively); (ii) the electroactivity of PEDOT, which corresponds to the similarity between the cathodic and anodic areas in the voltammograms (i.e., ratio between the reduction and oxidation charges, Q_{red}/Q_{ox}); (iii) the current density reached at the reversal potential (i.e., anodic current density, j_a), which indicates the amount of oxidized molecules during the charging step; and, most importantly (iv) the SC of the system.

Figure 2 shows the fifth cyclic voltammogram recorded for each of the three systems at different scan rates. As it can be seen, the PEDOT response using LPGGA-2 is comparable to that of LPGGA-4 (Figures 2a and 2c), displaying similar Q_{ox}, Q_{red}, and j_a values (Figures 3a and 3c), especially at high scan rates. On the contrary, the amount of stored charge and current density obtained when HPPGA-6 is used as SE (Figure 2a,c) is considerably smaller than those reached for LPGGA-2 and LPGGA-4. These features indicate that the higher cross-linking degree of the former biohydrogel induces an excessively compact morphology (Figure 1b), precluding the transport of dopant ions toward the electrode−electrolyte interface during the oxidation and reduction processes of PEDOT. Moreover, cyclic voltammograms recorded for LPGGA-2 and LPGGA-4 almost have an ideal rectangular shape for scan rates up to 100 mV/s, which reflects a good capacitive performance and low contact resistance. Interestingly, the electrochemical behavior of PEDOT in NaHCO₃ 0.5 M (Figure S7) resembles very closely that exhibited by HPPGA-6. Finally, since the current density during the charging step; and, most importantly (iv) the SC of the system.

Figure 3. Electrochemical characterization of PEDOT/γ-PGA OESC devices (two-electrode configuration, CE/RE = WE/S = PEDOT) using different electrolyte media. (a) Variation of the stored charge (Q_{ox}); (b) electrochemical activity defined as Q_{red}/Q_{ox} and (c) current density versus scan rate. The anodic intensity at reversal potential (i.e., 0.8 V, filled symbols) and cathodic intensity at 0.1 V (empty symbols) were taken from the cyclic voltammograms displayed in Figure 2. (d) Coulombic efficiency of GCD curves displayed in Figure 2. Filled symbols correspond to the second charge−discharge cycle, while the empty ones correspond to the fifth cycle. (e,f) Specific capacitance values obtained from (e) CV and (f) GCD measurements (Figure 2).
at the reversal and initial potential (i.e., anodic and cathodic current density, respectively) varies linearly with the scan rate for the three SE γ-PGA hydrogels and NaHCO₃ (Figure 3c). We can conclude that the electrochemical processes are not controlled by diffusion.

The Coulombic efficiency was higher than 0.75 for all four electrolytes regardless of the current density employed (Figure 3d). Finally, the SC values obtained from CV measurements are displayed in Figure 3e. For low scan rates (i.e., below 50 mV/s), SC values are higher when using any of the three γ-PGA hydrogels as electrolyte than NaHCO₃ (0.5 M). However, for scan rates from 75 to 200 mV/s, OESC systems based on LPGGA-2 and LPGGA-4 reveal considerably enhanced SC values in comparison to HPGGA-6 and NaHCO₃ (Table 1). A similar behavior was also observed when OESC devices were tested using GCD measurements (Figure 3f and Table 2).

Table 1. Specific Capacitance Values (SC, in F/g) Determined from Cyclic Voltammograms Obtained for PEDOT/γ-PGA OESC and Control Devices Using Different Scan Rates (Figure 2 and Figure S7a)

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<th>scan rate (mV/s)</th>
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<th>LPGGA-4</th>
<th>LPGGA-2</th>
<th>NaHCO₃ (0.5 M)</th>
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<td>75</td>
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<td>62.0 ± 6.3</td>
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Table 2. Specific Capacitance Values (SC, in F/g) Determined from GCD Curves Obtained for PEDOT/γ-PGA OESC Devices and Control Using Different Current Densities (Figure 2 and Figure S7b)

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</table>

this case, charging–discharging processes of PEDOT at different current densities (Figure 2b, 2d, and 2f) led to symmetric GCD curves with a typical triangular shape and a V_dop at the beginning of the discharging. The voltage drop was around 0.03 V for both LPGGA-2 and LPGGA-4, increasing to 0.12 V for HPGGA-6.

Overall, the results described in this section denote both LPGGA-2 and LPGGA-4 as promising biohydrogel-based SE for supercapacitor applications. However, in order to select only one γ-PGA hydrogel composition, the capacitance response of PEDOT in each one of the three tested hydrogel compositions and NaHCO₃ (0.5 M) was plotted in a Ragone graph (Figure S8). This plot indicates the relation between the energy density (how much energy is available, vertical axis) and the power density (how quickly it can be delivered, horizontal axis). The E_max and P_max (eqs 5–7) values were calculated using the SC values obtained from GCD measurements (5th cycle) at different current densities (Table S2). As it was stated by Stoller and Ruoff, both E_max and P_max should be computed by considering the total mass of the device, which also includes electrochemically inert components and the electrolyte. However, in this specific case since the comparison is only within γ-PGA hydrogel systems, m only refers to the mass of one electrode (i.e., 0.4113 mg), and therefore, the values summarized in Table S2 cannot be compared with those reported in other works that rigorously considered the mass of the whole compact OESC device.

Hence, considering that energy storage research focuses on moving the device performance toward higher E_max and P_max values (the upper-right corner of Ragone plots), Figure S8 evidences that devices based on LPPGA-2 are the best option, closely followed by LPGGA-4. However, it is important to bear in mind that Ragone plots only take into consideration one feature of the OESC performance, thus not evaluating other possible determining factors, such as maximum voltage, leakage current, equivalent series resistance (ESR), cycle lifetime, energy efficiency, self-discharging, cost, or processability factors (i.e., size, ease of preparation, and mechanical robustness of the final device). Consequently, with PEDOT as electrodes, LPGGA-4 is the most suitable hydrogel to perform as SE due to both the excellent supercapacitor response obtained (enhanced SC values) and the mechanical stability of the system. Brunauer–Emmett–Teller (BET) analyses of the LPGGA-4 hydrogel reveal a surface area of 6.3 ± 0.1 m²/g, whereas that of PEDOT electrodes prepared using similar conditions was reported to be between 30 and 50 m²/g. The next sections are exclusively focused on further exploring the response of PEDOT/γ-PGA OESC devices using LPGGA-4 as electrolyte (i.e., PEDOT/LPGGA-4 OESC).

PEDOT/LPGGA-4 as Energy Storage Device. This section includes further characterization of the supercapacitor response of PEDOT/LPGGA-4 OESC devices regarding: (1) cyclability and long-term stability; (2) leakage-current (LC) and self-discharging (SD) response; and (3) practical application (LED bulb). However, before discussing these results, the system was analyzed from another perspective. As mentioned above, the LPGGA-4 SE presents some components in excess since it was employed in OESC devices without applying a washing step (i.e., the excess of EDC or cystamine was not removed). Therefore, it would be interesting to understand the influence of EDC, cystamine, and γ-PGA on the electrochemical response of PEDOT.

Figure 4a,b compares the fifth CV and GCD cycles recorded at 50 mV/s and 1.22 A/g, respectively, of PEDOT-based OESC devices using as electrolyte the following five systems: (A) control electrolyte (0.5 M NaHCO₃); (B) as-prepared LPGGA-4 hydrogel; (C) LPGGA-4 washed in distillate water for 3 days; (D) LPGGA-4 washed in distillate water for 3 days and immersed in 0.5 M NaHCO₃ for 24 h; and (E) LPGGA-4 lyophilized after washing and subsequently immersed in 0.5 M NaHCO₃ for 24 h. The SC values obtained from such measurements are summarized in Table S3. Comparison of the
results obtained for the as-prepared and washed LPGGA-4 hydrogels (B and C, respectively) indicates that the elimination of noncovalently linked species, EDC and NaHCO₃, causes a drastic reduction of the SC values (i.e., from 131.8/158.8 F/g to 22/881 F/g determined using CV/GDC curves, respectively). Systems (D) and (E), which were designed to reabsorb the NaHCO₃ dopant after it was washed out, did not result in higher SC values. Overall, results reflect that the NaHCO₃ dopant ions coming from synthesis of the hydrogel must be preserved by avoiding the washing step since its reabsorption is not an easy task.

Regarding the influence of EDC, cystamine, and γ-PGA, Figures S9a,b show the fifth CV and GCD cycles recorded at 50 mV/s and 1.22 A/g, respectively, of PEDOT-based OESC devices using as electrolyte the following three additional systems: (F) low M_w γ-PGA (0.5 M) in NaHCO₃ (0.5 M), (G) EDC (0.5 M) in NaHCO₃ (0.5 M), and (H) cystamine (0.25 M) in NaHCO₃ (0.5 M). The SC values obtained from such measurements, which are summarized in Table S3, were higher than that of the control electrolyte (A) and very similar to that of the as-prepared LPGGA-4 (B), especially for (F) and (G) electrolytic media. These results indicate that the presence of both EDC and γ-PGA in the electrolyte enhances the electrochemical response of the OESC device.

As highlighted by McCloskey, it seems of major importance to identify new electrode and electrolyte materials for obtaining enhanced SC and, in turn, higher energy density, by better understanding electrode–electrolyte interactions. Although this consideration is beyond the scope of the current study, theoretical molecular dynamics calculations are a good strategy to fulfill such a goal by guiding the OESC optimization performance.

Cyclability and Long-Term Stability. PEDOT/LPGGA-4 OESC devices were submitted to thousands of cycles to determine their cyclability, which is an important factor when considering a supercapacitor adequate for practical applications (Figure 5 and Table 3). Specifically, PEDOT/LPGGA-4
OESCs were submitted to 1000 consecutive CV cycles from 0 to 0.8 V at a scan rate of 50 mV/s (Figure 5a). After such amount of cycles, the SC decreases from 161 F/g (5th cycle) to 136 F/g, which represents 84% of SC retention. During oxidation and reduction processes, swelling and shrinkage phenomena derived from consecutive doping–dedoping steps induce structural changes in PEDOT electrodes. Hence, once the equilibrium is reached, the final morphology is more compact, and therefore, the access and escape of dopant ions is reduced in comparison to the first stages of PEDOT response. This explains the reduction in SC values, as well as the LEA value, which is constant at ca. 17% after 1000 CV cycles (Figure 5b and Table 3). However, this response is more related to the electrode material rather than the electrolyte, which further confirms the suitability of LPGGA-4 as electrolytic medium.

Besides, PEDOT/LPGGA-4 OESCs were also submitted to 2000 consecutive GCD cycles from 0 to 0.8 V at a current density of 1.22 A/g (Figures 5c,d and Table 3). GCD curves exhibited a typical triangular shape with a small voltage drop (i.e., 0.06 V) at the beginning of the discharging step. This drop is practically identical to that reported for OESCs prepared by combining PEDOT electrodes and κ-carrageenan hydrogels,25 and similar to that achieved for devices fabricated using graphene/polypyrrole electrodes immersed in porous cellulose.14 The symmetric charge–discharge curves indicate high Coulombic efficiency and good reversibility, reflecting the excellent capacitive properties of PEDOT.6,11,46 The latter is consistent with the high SC value obtained for the second charge–discharge cycle (168 F/g). After 2000 consecutive GCD cycles, the SC decreased to 136 F/g, which corresponds to 81% of SC retention. Again, the structural changes in the morphology induced by the swelling and shrinkage of PEDOT during oxidation and reduction processes slightly reduce the SC of PEDOT/LPGGA-4 after 2000 consecutive GCD cycles. In addition, to examine the lifetime stability of PEDOT/LPGGA-4 OESCs, this galvanostatic assay was repeated to the devices 1 week later. Figures 5c and 5d compare the results obtained for as-prepared OESC devices ($t_{ox}$) with those obtained for devices examined 1 week after ($t_{1w}$), while numerical values are listed in Table 3. After 1 week, the SC of prepared devices decreased from 168 F/g to 148 F/g (2nd cycle) at a constant current density of 1.22 A/g from 0.0 to 0.8 V, which represents a reduction of only 12%, and the voltage drop increases to 0.10 V. More interestingly, after 2000 GCD cycles, the SC value of as-prepared devices (136 F/g) resembles that of devices examined 1 week later (130 F/g). This small difference (4%) corroborates that the structure and morphology of PEDOT is completely stabilized after 2000 GCD cycles and stable for 7 days.

**Leakage-Current and Self-Discharging Response.** The LC corresponds to the stable parasitic current expected when the capacitor is held indefinitely on charge at the rated voltage,36 while the SD is associated with the voltage drop of a charged capacitor after a set period of time and its effects on the power and energy densities.45 Assays to evaluate both the LC and the SD response, which were run using three independent PEDOT/LPGGA-4 devices, were performed by charging the OESCs to 0.8 V at 0.25 mA. The LC was determined by keeping the potential at 0.8 V for 5 min and monitoring the current data through the device. Figure 6a displays that the current rapidly decreases to a minimum value of 51.3 μA, staying at that value for the remaining time. This small LC reflects the good stability of PEDOT/LPGGA-4 devices. On the other hand, the SD response was evaluated by keeping the charged device at 1 × 10−12 mA for 10 min (self-discharge), and after this period of time, the device was discharged to 0.0 V at −1 mA. Figure 6b reveals that in all cases the voltage of the device ends above 0.45 V after the period of time set for self-discharge. Additional SD experiments keeping the charge for 2 h corroborated the low self-discharge tendency of the device (Figure S10), the voltage being 0.41 V after such a period. Such response combined with the small LC corroborates the potential interest of PEDOT/LPGGA-4 OESC devices for practical applications.

**Practical Application (LED Bulb).** In order to show the potential application of PEDOT/LPGGA-4 OESC devices, four units, as the one depicted in Figure S1b, were connected in series and used to power a red LED bulb (lowest working potential = 1.65–1.7 V). The preparation process of the tandem device is illustrated in Figure S11. When connecting four identical capacitors in series, each voltage threshold V and capacitance C is combined to theoretically result in a voltage threshold equal to 4 V and a capacitance of 1/4 C. Nevertheless, combining capacitors in series also leads to a
higher ESR value, and slightly different LCs may induce voltage across each one to differ, thus leading to a resulting voltage threshold lower than the theoretical value.

Before powering the LED, the assembled device was characterized by 25 GCD cycles at 2 mA (charging and discharging times equal to 60 s). Figure 7a shows the stability of the system, which reaches the same final potential after such amount of cycles. Besides, the SD response of the system was also determined through the following procedure: the device was charged to 3 V at 2 mA, held at 0 mA for 5 or 10 min (self-discharge), and after time, the device was discharged to 0 V at −4 mA. This procedure was repeated five times to ensure data reproducibility. Figure 7c reveals the low SD tendency of the four PEDOT/LPGGA-4 OESC devices connected in series: the voltage ends above 1 V after 10 min.

Finally, the assembled device was used to power a red LED bulb. Figure S12 shows the connections during the charging of the system to 3 V at 2 mA (charging time, \( t_c = 30 \) s) as well as during discharging (i.e., red LED bulb ON; Figure 7d). Briefly, during charging, 1 connects the four OESC units in series to the CE/RE, while 2 closes the circuit by connecting them to the WE/S electrode. Once the system is charged, connection 3 between the LED and the tandem device is established, and 1 and 2 are disconnected. The charging/discharging operation was successfully repeated several consecutive times (more than 15), the red LED being ON for 28.3 ± 1.0 s even though it was dimly lit even after 38 s (Figure S13).

### CONCLUSIONS

In summary, we have selected the experimental conditions required to obtain \( \gamma \)-PGA hydrogels with (i) an open internal structure that facilitates the ion diffusion process through dense macroporous networks and (ii) stable mechanical robustness to hold the electrodes, which ensures their use as SE in PEDOT/\( \gamma \)-PGA OESC devices. Although three hydrogels with pore size ranging from 19 to >50 \( \mu \)m and SR varying between 140 and 1800% fulfilled such conditions, the one (LPGGA-4) with the smallest macropores (19.1 ± 7.7 \( \mu \)m) and intermediate SR (450%) induced the best response of PEDOT electrodes. The electrochemical performance of the PEDOT/LPGGA-4 system is significantly higher than that of PEDOT/NaHCO\(_3\) (aq) devices used as a control. Additionally, the utilization of LPGGA-4 as SE provides good capacitor response and cycling stability, small LC, and SD tendency without water loss or evaporation. This work demonstrates the advances that can be achieved by selecting suitable biopolymeric hydrogel formulations as SEs and their substantial potential for other energy devices design. Thus, the selected \( \gamma \)-PGA hydrogel not only maintains the excellent electrochemical response of PEDOT electrodes, but also provides sustainability, a lightweight solid support for the electrodes, and a porous structure that provides effective ion and electron transport.

### ASSOCIATED CONTENT

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b10693.

  Synthetic methods and characterization techniques.
  Figures S1–S12 and Tables S1–S3 as described in the text (PDF)

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