Biohydrogel from Unsaturated Polyesteramide: Synthesis, Properties and Utilization as Electrolytic Medium for Electrochemical Supercapacitors

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ABSTRACT

The utilization of hydrogels derived from biopolymers as solid electrolyte (SE) of electrochemical supercapacitors (ESCs) is a topic of increasing interest because of their promising applications in biomedicine (*e.g.* for energy storage in autonomous implantable devices). In this work an unsaturated polyesteramide that contains phenylalanine, butenediol and fumarate as building blocks has been photo-crosslinked to obtain a hydrogel (UPEA-h). The structure of UPEA-h, which is characterized by a network of open interconnected pores surrounded by regions with compact morphology, favors ion transport, while the biodegradability and biocompatibility conferred by the α -amino acid unit and the ester group are appropriated for its usage in the biomedical field. Voltammetric and galvanostatic assays have been conducted to evaluate the behavior of UPEA-h when used as SE in ESCs with poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes. Hence, PEDOT/UPEA-h devices displayed supercapacitor response of up 179 F/g and capacitance retention higher than 90%. Moreover, the long-term stability, leakage-current, and self-discharging response of PEDOT/UPEA-h ESCs reflect the great potential of UPEA-h as ion-conductive electrolyte. Indeed, the performance of PEDOT/UPEA-h is higher than found in analogous devices constructed using other biohydrogels as SE (*e.g.* κ -carrageenan, poly- γ -glutamic acid and cellulose hydrogels).

Keywords: Energy storage; Hydrogel electronics; Ion conductivity; Photo-crosslinking; Wearable electronics

1. Introduction

The demand of flexible energy storage devices, including electrochemical supercapacitors (ESCs), increases with the development of flexible and wearable electronics [1-4]. Generally, the stretchable properties of energy storage devices are provided by elastic electrodes and/or electrolytes [5-7]. Within this context, cross-linked polymer hydrogels with high ionic conductivity and stretchable properties have been postulated as very promising electrolytes for multifunctional ESCs, even though not too much research has been carried out to address this issue yet [8-20]. The hierarchical porous structure of hydrogels makes them useful for other applications. Within this context, hydrogels from biopolymers (*i.e.* biohydrogels) are particularly attractive since, in addition of their demonstrated good performance as electrolytic media of ESCs [13-19], their biodegradability and biocompatibility are uniquely suitable for biological applications such as drug delivery vehicles and cell culture scaffolds. Consequently, such biohydrogels can be potentially used not only to power implantable medical devices (*e.g.* pacemakers) but also to fabrication multifunctional ESCs for biomedicine (*e.g.* self-powered drug release devices).

In recent years, the capabilities of some DNA [15,16], protein [17,18], and polysaccharide [17,19] biohydrogels as solid electrolytes (SEs) for multifunctional ESCs have been demonstrated. DNA biohydrogels made by enzymatic crosslinking of branched DNA monomers [21] were operative in cell culture media without exhibiting any cytotoxic effects. Accordingly, these devices showed potential interest as SEs for implantable energy storage devices able to operate in bioenvironments [15,16]. On the hand, the utilization as SE of gelatin biohydrogels, which were prepared using a mixture of water-soluble proteins, was hampered by their compact morphology [17]. In contrast, poly- γ -glutamic acid (γ -PGA) biohydrogels, which were obtained by crosslinking this

polypeptide naturally synthesized by a variety of members of the genus *Bacillus*, showed excellent properties not only as SE [18] but also as flexible electrode when combining with poly(3,4-ethylenedioxythiophene) (PEDOT) particles [22,23]. Regarding polysaccharides biohydrogels, the better response as SE was found for κ -carrageenan [17] and cellulose [19], whereas chitosan and alginate exhibited a poor behavior because of its poor mechanical integrity and water release, respectively [17].

In this work we explore a new strategy for the fabrication of biodegradable and biocompatible hydrogels as SEs for ESCs, using an unsaturated polyesteramide (UPEA) previously reported by Katsarava and co-workers [24]. This UPEA, which contains phenylalanine, butenediol and fumarate as building blocks, has been successfully photocrosslinked to obtain a hydrogel (UPEA-h), as proved by FTIR and NMR characterizations. The α -amino acid unit and the ester group of the UPEA are expected to ensure the biodegradability and biocompatibility of the hydrogel. The work is organized as follows. After report on the synthesis of the UPEA and of the photocrosslinking reaction used to produce the hydrogel, the morphological, topographical and thermal properties of UPEA-h are discussed. Then, the biodegradability and biocompatibility of the hydrogel are examined. Finally, the performance of UPEA-h as novel and sustainable SE for compact ESCs manufactured with PEDOT electrodes, hereafter denoted PEDOT/UPEA-h ESCs, has been analyzed. For this purpose, the electrochemical and electrical response of PEDOT/UPEA-h ESCs have been examined and compared with those previously obtained for ESCs prepared combining identical PEDOT electrodes with hydrogels derived from biopolymers as SEs.

2. Methods

2.1. Characterization

Description of the materials, chemical and physical characterization, enzymatic degradation assays and of cell adhesion and proliferation assays is provided in the Supplementary Information. The methodologies used for the electrochemical and electrical characterization, which are also provided in the Supporting Information, are identical to those previously reported for the evaluation of κ -carrageenan-, γ -PGA and cellulose-based hydrogels as SEs [17-19].

2.2. Synthesis of UPEA

The preparation of the di-*p*-toluenesulfonic acid salt of L-phenylalanine butene 1,4-diester (M1) and di-*p*-nitrophenyl fumarate (M2) monomers, as well as their solution polycondensation to produce the UPEA were adapted from Katsarava and co-workers [24].

Di-p-toluenesulfonic acid salt of L-phenylalanine butene 1,4-diester (M1). 0.03375 mol of L-phenylalanine (Phe), 0.03375 mol of *p*-toluenesulphonic acid monohydrate (TosOH) and 0.01687 mol of butenediol were dissolved in 90 mL of toluene. The solution was heated to 135 °C and kept during at least 24 h in a Dean-Stark trap until reaching the maximum volume of distilled water (*i.e.* 1.5 mL; 0.0669 mol) that the condensation makes. After this, the reaction mixture was cooling down and the obtained solid was filtered, dried and re-crystalized at least three times in dimethyl sulfoxide (DMSO). The obtained ¹H NMR and FTIR spectra are displayed in Figure S1.

Yield: 40 %. M.p.: 239 °C. IR (cm⁻¹): 1737 (O=C), 1456 (=C–H).and 1191 (COO–).
¹H NMR (DMSO-*d*₆, ppm, δ): 8.41 (s, 3H, NH₃), 7.46, 7.09 (dd, 5H, arom), 7.31-7.22

(m, 5H, Phe), 5.54 (t, 1H, CH), 4.66 (d, 2H, CH₂), 4.33 (t, 1H, CH), 3.07 (m, 4H, CH₂), 2.28 (s, 3H, CH₃).

Di-p-nitrophenyl fumarate (M2). A 40 mL solution of fumaryl chloride (0.03 mol) in acetone was added dropwise to 100 mL of acetone with *p*-nitrophenol (0.06 mol) and triethylamine (0.06 mol) at -78 °C using an acetone and dry ice bath. The system was kept under vigorous stirring at room temperature for 24 h. The resulting product was purified by recrystallization in acetonitrile. The obtained ¹H NMR and FTIR spectra are displayed in Figure S2.

Yield: 70 %. M.p.: 123 °C. IR (cm⁻¹): 3101 (C=CH-), 1734 (C=O), 1615, 957 (-CH=CH-CO-), 1519, 1345 (-NO₂), 1212 (COO-). ¹H NMR (DMSO-*d*₆, ppm, δ): 8.34 (d, 2H, arom), 7.59 (d, 2H, arom), 7.24 (s, 1H, =CH).

UPEA. 1 mmol of M1 and 1 mmol of M2 were mixed in 4 mL of dry dimethylacetamide. Then, 2.2 mmol of trimethylamine were added dropwise and the solution was heated to 60 °C with stirring for at least 96 h (*i.e.* until the complete dissolution of M1 and M2). The resulting solution was precipitated with cold ethyl acetate. The solid was filtered and extracted with ethyl acetate in a Soxhlet apparatus for 96 h, and finally dried. The obtained ¹H NMR and FTIR spectra are displayed in Figure S3.

Yield: 75 %. M.p.: 128 °C. *M_w*: 60400 g/molPDI: 2.50. IR (cm⁻¹): 3315 (Amide A), 1736 (C=O), 1623 (Amide 1), 1530 (Amide 2), 1455 (=C-H, alkyl), 1170 (COO-). ¹H NMR (DMSO-*d*₆, ppm, δ): 8.93 (d, 1H, NH), 7.22 (m, 5H, arom), 6.84 (s, 1H, CH), 5.58 (s, 1H, CH), 4.65 (s, 2H, CH₂), 4.58 (t, 1H, CH), 3.04 (m, 2H, CH₂).

3. Results and discussion

3.1. Synthesis of the UPEA-h

The preparation of the hydrogel involved three different steps: (a) the synthesis of the di-*p*-toluenesulfonic acid salt of L-phenylalanine butene 1,4-diester (M1) and di-*p*-nitrophenyl fumarate (M2) monomers (Schemes 1 and 2, respectively); (b) the solution polycondensation of M1 and M2 to produce UPEA chains with C=C double bonds in the backbone (Scheme 3); and (c) the photocrosslinking of the unsaturated bonds in UPEA. The synthesis of M1, M2 and UPEA (*i.e.* steps a and b), which were already described by Katsarava and co-workers [24], are reported in the Methods section.

Scheme 1. Synthesis of the di-*p*-toluenesulfonic acid salt of L-phenylalanine butene 1,4-diester (M1).

Scheme 2. Synthesis of di-*p*-nitrophenyl fumarate (M2).

Scheme 3. Synthesis of the UPEA.

UPEA was used to produce UPEA-h using functionalized polyethylene glycol (*f*PEG) as cross-linker. The synthesis of *f*PEG (Scheme 4) and the hydrogel (Scheme 5), which was prepared to achieve the maximum cross-linking degree, are described below.

Scheme 4. Synthesis of the cross-linker (*f*PEG).

Scheme 5. Synthesis of the UPEA-h.

*f*PEG. 12 g (1.5 mmol) of PEG were dissolved in 150 mL of toluene at 45 °C. The solution was cooled to room temperature and 1.67 (12.0 mmol) mL of triethylamine were added. Then, 0.97 (12.0 mmol) mL of acryloyl chloride were added dropwise. The

mixture was heated to 80 °C and kept for 3 h under nitrogen atmosphere. The obtained *f*PEG was precipitated in 700 mL of cold hexane (4 °C), filtered and stored at 4 °C. The obtained ¹H NMR and FTIR spectra are displayed in Figure 1.

Yield: 90 %. M_w = 32604 g/mol; PDI= 2.55. IR (cm⁻¹): 2885 (CH₂), 1724 (C=O), 1096 (C–O). ¹H NMR (DMSO-*d*₆, ppm, δ): 6.45, 5.82 (dd, 1H, H_b), 6.37, 5.85 (dd, 1H, H_a), 6.16 (m, 1H, CH), 4.31 (t, 2H, CH₂), 3.64 (t, CH₂).

Figure 1. (a) FTIR and (b) ¹H-NMR spectra of the synthesized cross-linker, *f*PEG.

UPEA-h. 0.08 g of UPEA and 0.32 g of *f*PEG (*i.e.* 1/4 UPEA/*f*PEG w/w ratio) were dissolved in 2 mL of dimethylacetamide. The reticulation reaction was conducted by adding the photoinitiator irgacure 2959 (0.016 g, 5% wt. with respect to the total mass of the precursors). The solution was exposed to an UV lamp (230 V, 0.8 A) for 8 h at room temperature. The resulting gel was washed with distilled water, which was periodically replaced, during 3 days and afterwards lyophilized for its characterization. The obtained FTIR spectrum, a photograph of the hydrogel (hereafter denoted UPEA-h) and the ^{13}C CP/MAS spectrum are displayed in Figure 2.

Figure 2. (a) FTIR and (b) ^{13}C -NMR spectra of the synthesized UPEA-h. A photograph of the hydrogel is displayed in (a).

Yield: 90 %. IR (cm^{-1}): 1096 (C–O). ^{13}C CP/MAS (100kHz, $\delta_{\text{CP/MAS}}$, ppm): 172.16 (COO), 166.10 (NH–C=O), 137.99, 129.93 (arom), 72.08 (polyethylene glycol; PEG), 64.25 (O=C–CH₂–N), 60.66 (O–CH₂), 57.40 (CH–CO–NH), 43–37 (CH₂).

3.2. Morphological, topographical, thermal and mechanical properties

As shown in Figure 3a, which displays scanning electron microscopy (SEM) micrographs, the lyophilized UPEA-h presents a homogeneous network structure with abundant pores. The size distribution of the pores, which tend to adopt an elliptic shape, is not uniform and ranges from 9 to 30 μm . This variability confers a relatively large standard deviation to the average diameter of pores, $17 \pm 7 \mu\text{m}$. From the perspective of SE for ESCs, the structure of UPEA-h contains open interconnected pores surrounded by regions with compact morphology, which favors ion transport and provides mechanical stability and robustness to keep the electrodes at their positions.

Figure 3b displays a representative height atomic force microscopy (AFM) image and cross-sectional profiles of UPEA-h. The surface topography of the hydrogel is defined by the micrometric size of the pores that are separated by compact regions, which is fully consistent with SEM observations. The R_q determined for the hydrogel as a whole is $1.05 \pm 0.12 \mu\text{m}$, this value decreasing to $119 \pm 29 \text{ nm}$ when the pores are excluded from the measure and only the compact regions separating them are considered.

UPEA-h was a semicrystalline hydrogel due to the capability of the PEG segments (each one with more than 225 chemical repeat units) to crystallize. Thus, the differential scanning calorimetry (DSC) heating run of the as synthesized hydrogel showed a melting peak at 52.6 °C and a small shoulder around 48.5 °C (Figure 4a). The observed temperatures are in agreement with reported data since they were between the reported

temperature range between 63.0 °C and 44.4 °C that was determined for PEG homopolymers with molecular weights of 10,000 and 1,000 g/mol, respectively [25]. The corresponding melting enthalpy of UPA-h gels was 96.9 J/g, which represents a crystallinity of 49.2 % by considering a melting enthalpy of 196.8 J/g for a 100% crystalline PEG [25]. This crystallinity increased to 61.5% when it was referred to the real PEG content (*i.e.* the presence of non crystallizable UPEA chains was not taken into account).

Figure 3. Representative (a) SEM micrographs at different magnifications and (b) AFM height image with the corresponding cross-section profiles of UPEA-h.

The PEG domains of the hydrogel were able to crystallize after being heated to 150 °C. In fact, the enthalpy of the observed exothermic peak was comparable to that determined in the first heating run (*i.e.* 84.7 J/g with respect 96.9 J/g), a feature that suggest the capacity of preserving the basic mechanical properties after submitting the hydrogel to thermal treatments. The heating run obtained from a melt crystallized

sample revealed also a small difference concerning the narrow melting peak that appeared at 52.8 °C. In this case, the shoulder associated to thinner lamellar crystals disappeared indicating that highly homogeneous crystalline domains could be obtained after the slow cooling process. Despite the significant crystallinity of the sample, a small glass transition signal could be observed around -52 °C, being in good agreement with the values around -67 °C and - 52 °C that are reported for PEG/polyethylene oxide (PEO) with higher molecular weights [26-27]. Note that cross-linking did not play a significant effect on the mobility of PEG chains.

UPEA-h showed a high thermal stability (Figure 4b) since degradation started around 260 °C. Decomposition took place according to two steps that appeared as a small shoulder and a peak at temperatures of 328 and 400 °C, respectively. The main process involved a weight loss close to 80%, which is in concordance with the PEG content. The curves derived from the thermal gravimetric analysis (TGA) its derivative (DTGA) were in relative good agreement with the reported data for the degradation of PEG since a single decomposition step with a maximum DTGA peak at 426 °C or 419 °C was observed at a heating rate of 10 °C/min with samples having molecular weights of 3,400 or 100,000 g/mol, respectively [27]. Note that peak temperature values should increase with the heating rate and consequently thermal stability was clearly lower than observed for neat PEG. The DTGA shoulder observed at 328 °C would probably be related to the decomposition of the UPEA main chain, enhancing the corresponding degradation products the decomposition of PEG segments. Finally, it should be indicated that a char yield close to 6% was determined at 600 °C as consequence of the aromatic content of phenylalanine residues.

Figure 4. (a) Sequence of heating, cooling and reheating runs performed with the as synthesized UPEA-h sample. (b) TGA and DTGA curves of the UPEA-h sample.

The mechanical properties of UPEA-h, which have been determined by measuring stress-strain curves (Figure 5), reveals that the Young modulus and tensile strength are 2.3 ± 0.1 MPa and 66 ± 7 MPa, respectively. Unfortunately, it was not possible to evaluate the elongation at breakage since, in all cases, after reaching a certain elongation (*i.e.* from 24% to 29%, depending on the sample), the water leakage from the hydrogel caused the sliding of the jaws of the test machine and the consequent release of the sample. Obviously, this drawback also affects the numerical values of the Young modulus and tensile strength, which should be considered as rough approximations

only. In spite of this limitation, it should be remarked that the mechanical properties of UPEA-h are high. Thus, the modulus of most hydrogels is of the order of 0.1 MPa [28,29], which greatly limits their use. In recent years, a number of high modulus hydrogels have been developed, as for example, polyampholyte hydrogels ionically cross-linked (7.8 MPa) [30] and dual polyacrylamide–polyacrylic acid hydrogel with covalent and ionic cross-links (3.5 MPa) [31].

Figure 5. Three representative strain-stress curves of UPEA-h.

The swelling ratio (SR , %) of the UPEA-h was evaluated using the following Eqn:

$$SR = \frac{w_W - w_D}{w_D} \quad (1)$$

where w_W is the weight of the hydrogels as prepared (after the washing step) and w_D is the weight of the hydrogel after freeze-drying (dried hydrogel). The SR determined for the UPEA hydrogels is of 500% only, which is consistent with a high cross-linking degree. This value is comparable to that obtained for γ -PGA hydrogels with a high cross-linking degree (*i.e.* SR decreased from 4000% to 160% when the cross-linker : γ -PGA molar ratio increased from 1: 3.3 to 1:1) [18], but significantly lower than that achieved for sodium carboxymethyl cellulose hydrogels (*i.e.* SR increased from 1064% to 2420% with the concentration of citric acid, which was the cross-linker) [19]. The

low *SR* of UPEA hydrogels is expected to be very advantageous in terms of dimensional stability, which is crucial for the utilization of biohydrogels in the fabrication of energy storage devices [18,19,23].

3.3. Biodegradability and cell viability

Enzymatic degradation studies were conducted as is described in the Supplementary Information, placing hydrogel samples in vials containing lipase *Rhizopus oryzae* in phosphate buffer saline (PBS). Samples were incubated at 37 °C in a shaking incubator set at 100 rpm for a total of three weeks.

Figure 6. (a) Normalized weight loss (Eqn S1) of UPEA-h after 1, 2 and 3 weeks of immersion in Lipase *Rhizopus oryzae*-containing PBS solution. (b) SEM micrograph of the UPEA-h after 2 and 3 weeks of immersion in above mentioned solution (left and right, respectively).

Figure 6a shows that weight loss (Eqn S1) increases with the time of exposition to the degradation medium, reaching $8.1\% \pm 1.0\%$ after 3 weeks. Weight loss has been attributed to the hydrolysis of the ester bonds, which is enzymatically catalyzed by the Lipase *Rhizopus oryzae*. Although the consistency of the hydrogel was apparently maintained during the whole 3 weeks period, the morphology of the hydrogel changed significantly. This is reflected in Figure 6b that compares SEM micrographs of the hydrogel after 2 and 3 weeks of exposition to the degradation medium. As it can be seen, the degraded fragments were retained in the surface of the hydrogel matrix, affecting the pores that were gradually occluded by the degraded material.

The response of the UPEA-h to cellular adhesion and proliferation has been compared with that of tissue culture polystyrene (TCPS), which consists on polystyrene exposed to a plasma gas in order to make it more hydrophilic and facilitate cell adhesion and growth *in vitro*. Assays were conducted using two cellular lines, Vero (green monkey kidney) and MDCK-SIAT (Canine Cocker Spaniel Kidney Sialic Acid Over Expression), which are epithelial-like cells. Quantitative results of cellular adhesion and proliferation assays are displayed in Figure 7a. Results indicate that UPEA-h does not promote cell adhesion with respect to the TCPS, differences being more marked for Vero cells than for MDCK-SIAT cells (*i.e.* the difference between the two substrates amounts to 55% and 23% for Vero and MDCK-SIAT, respectively). This behavior has been attributed to the surface roughness of the hydrogel ($R_q = 1.05 \pm 0.12 \mu\text{m}$), which is much higher and, therefore, less appropriated for cell attachment than that of the TCPS ($R_q = 80 \text{ nm}$). Figure 7b displays micrographs recorded by SEM of Vero and MDCK-SIAT cells adhered onto UPEA-h.

Cell proliferation assays, which were performed by determining the cellular viability on the samples after seven days, reflect a significant enhancement in the cellular

colonization for UPEA-h. Evaluation of this increment with respect to the viability of adhered cells indicates that the preference of Vero and MDCK-SIAT cells is higher for the hydrogel than for the control (Figure 7a). Thus, although cell viabilities are still higher for the control than for the hydrogel, differences decreased to 25% and 8% for Vero and MDCK-SIAT cells, respectively. This growing in the cell viability evidences that the UPEA-h is biocompatible and can be considered as a potential candidate for biomedical applications.

Figure 7. (a) Cellular adhesion and cellular proliferation on the surface of UPEA-h and TCPS plates (control). Vero and MDCK-SIAT cells were cultured during 24 h (adhesion assay) and 7 days (proliferation assay). The experiments were performed using three samples for each substrate. (b) SEM images of Vero and MDCK-SIAT cells adhered onto UPEA-h.

3.4. Electrochemical behavior of UPEA hydrogel as electrolyte

ESCs are electrochemical energy storage devices that operate on the simple mechanism of adsorption of ions from an electrolyte on a high-surface-area electrode. Thus, ESCs differ from ordinary capacitors in two important ways: (i) the electrodes have a much bigger area for the former than for latter; and (ii) the distance between the electrodes is much smaller for the former than for the latter. In an ordinary capacitor, the electrodes are separated by a relatively thick dielectric, as for example mica or plastic film. When the capacitor is charged, positive charges form on one electrode and negative charges on the other, creating an electric field between them. The field polarizes the dielectric, so its molecules line up in the opposite direction to the field and reduce its strength. In an ESC, there is no dielectric as such. Instead, both electrodes are soaked in an electrolyte, which can be liquid or solid. When the electrodes are charged up, charged ions from the electrolyte reorganize, and an electric double-layer is formed in the vicinity of the charged electrode surface (Scheme 6).

Scheme 6. Charging mechanism of ESCs.

In this work, the behavior of UPEA-h as solid electrolyte (SE) was evaluated in ESCs prepared using PEDOT electrodes, hereafter denoted PEDOT/UPEA-h. For this purpose, PEDOT films electropolymerized onto stainless steel sheets were carefully

introduced into the UPEA-h hydrogel, which was previously loaded with NaHCO_3 as supporting electrolytic salt (see Methods section), at a distance of 1 mm and fixed with tape to prevent movement during testing. Complete characterization of PEDOT electrodes was reported in previous work [17]. It is worth noting that PEDOT, which is an electrostable and biocompatible material [32-35], was also employed to prepare the electrodes of the ESCs used to investigate the performance of κ -carrageenan [17], γ -PGA [18], and cellulose [19] biohydrogels as SE. Accordingly, comparison of biohydrogels based on synthetic polyesteramides with those based on natural biopolymers is expected to provide information about the advantages of the former for energy storage applications (e.g. precise control of the photocrosslinking reaction to modulate the pore size and chemical design of the polymer to regulate the biodegradability). The electrochemical response of PEDOT/UPEA-h ESCs was investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements using a two-electrode configuration to evaluate the performance of the whole cell.

Figure 8a compares the cyclic voltammograms recorded at different scan rates for PEDOT/UPEA-h ESCs. Cyclic voltammograms maintain an almost ideal rectangular shape for scan rates up to 100 mV/s, evidencing good capacitive behavior and small contact resistance. Moreover, the electrochemical activity of PEDOT electrodes, which corresponds to the similarity between the cathodic and anodic areas in the voltammograms, is very high, independently of the scan rate. Figure 8b displays the variation of the current density reached at the reversal potential (*i.e.* anodic current density), which measures the amount of oxidized molecules during the charging step, against the scan rate. The observed linear behavior ($R^2 = 0.9927$) indicates that the electrochemical processes are not controlled by diffusion.

Figure 8. Characterization of PEDOT/UPEA-h and PEDOT/NaHCO₃ ESCs by CV. (a) Cyclic voltammograms (2nd cycle shown) recorded from 0 to 0.8 V at scan rates of 10, 25, 50, 75, 100, 150 and 200 mV/s for PEDOT/UPEA-h. (b) Variation of the anodic current density against the scan rate for PEDOT/UPEA-h. (c) Variation of the SC against the scan rate for PEDOT/UPEA-h and PEDOT/NaHCO₃ ESCs. (d) Cyclic voltammograms (2nd cycle shown) recorded from 0 to 0.8 V at scan rates of 10, 25, 50, 75, 100, 150 and 200 mV/s for PEDOT/NaHCO₃. (e) Comparison of the 2nd and 200th consecutive cyclic voltammograms recorded for PEDOT/UPEA-h (scan rate: 50 mV/s).

The specific capacitance (SC; in F/g) values obtained from CV measurements at different scan rates are displayed in Figure 8c. As it was expected, the SC decreases with increasing scan rate, which is fully consistent with the deviation from the ideal

rectangular shape of the voltammograms. Thus, SC decreases from 100 ± 4 F/g to 49 ± 5 F/g when the scan rate increases from 10 mV/s to 200 mV/s. For comparison, these results have been compared with those obtained for a control ESC device prepared using PEDOT electrodes and a NaHCO_3 (0.5 M) aqueous solution as electrolytic medium, denoted PEDOT/ NaHCO_3 . Cyclic voltammograms recorded PEDOT/ NaHCO_3 , which are shown Figure 8d, are more rectangular than those obtained for the same electrodes in UPEA hydrogel. However, the SC values obtained from CV measurements at low scan rates (*i.e.* below 75 mV/s) are higher for PEDOT/UPEA-h than for PEDOT/ NaHCO_3 (*i.e.* the SC increases with the scan rate when the electrolyte is liquid). For scan rates from 75 to 200 mV/s, the SC values are slightly larger for the latter than for the former device (*i.e.* the largest difference is 13 F/g, which corresponds to less than 21%) (Figure 8c).

The PEDOT/UPEA-h ESC was submitted to 200 consecutive CV cycles from 0 to 0.8 V at a scan rate of 50 mV/s (Figure 8e). After such amount of cycles, the SC decreased from 68.7 F/g (2nd cycle) to 67.4 F/g, which represents 98.1% of SC retention. Both PEDOT electrodes and hydrogel electrolyte underwent structural changes due to the swelling and shrinkage phenomena induced by the applied oxidation and reduction processes. However, in this case the access (oxidation) and escape (reduction) of dopant ions was only slightly reduced after 200 cycles, as observed from the voltammograms (Figure 8e). It is worth noting that, although voltammetric response of PEDOT/UPEA-h is similar to that reported for other ESCs prepared using PEDOT electrodes and biohydrogels from biopolymers as SE [17-19], the stability against consecutive redox cycles is higher for the device with UPEA-h.

Results from GCD measurements are displayed in Figure 9. Charging-discharging processes at different current densities led to symmetric GCD curves with a typical

triangular shape and a V_{drop} at the beginning of the discharging. Although the triangular shape of the GCD curves is better defined for PEDOT/ NaHCO_3 than for PEDOT/UPEA-h, independently of the current density used, the SC values are systematically lower for the former than for the latter (Figures 9a-c). This is because discharging and charging times are about $\sim 20\%$ higher for PEDOT/UPEA-h ESCs than for PEDOT/ NaHCO_3 ESCs, independently of the current density. The SC of the device with the hydrogel decreases from 179 ± 12 to 114 ± 7 F/g when current density increases from 0.30 to 2.43 A/g, while the SC values of the device with NaHCO_3 remain at around 65 F/g for all the examined current densities (Figure 9b). Moreover, PEDOT/UPEA-h ESCs were submitted to 1,400 GCD cycles at a current density of 0.43 A/g from 0 V to 0.8 V, which corresponds to t_c and t_d values of approximately 17-19 seconds (Figure 9d). After such amount of cycles, the SC decreased from 162 F/g to 149 F/g, which represents 92% of SC retention.

Comparison of the results obtained by GCD for PEDOT/UPEA-h with those achieved for ESCs prepared using identical PEDOT electrodes but κ -carrageenan [17], γ -PGA [18] or carboxymethyl cellulose [19] biohydrogels as SE (PEDOT/ κ -car, PEDOT/ γ -PGA and PEDOT/CMC, respectively) evidences that, in general, the former provides best response. The SC determined for PEDOT/ κ -car, PEDOT/ γ -PGA and PEDOT/CMC by GCD was 79 [17], 159 [18] and 77 [19] F/g, respectively. This represents a reduction in the capacitive performance of more than 50% for the devices with κ -carrageenan and carboxymethyl cellulose hydrogels. Moreover, the retention of the SC after 1,400 consecutive GCD cycles was lower than 90% for PEDOT/ κ -car and PEDOT/ γ -PGA [17,19]. An exception to this behavior was found for PEDOT/CMC, which showed a self-stabilizing behavior. Thus, the SC of PEDOT/CMC ESC increased by 15% after 1400 charge-discharge cycles (*i.e.* from 76.8 to 88.7 F/g). In spite of this

advantageous property, the *SC* of PEDOT/CMC was 40% lower than that of PEDOT/UPEA-h after 1400 cycles.

Figure 9. Characterization of PEDOT/UPEA-h and PEDOT/NaHCO₃ ESCs by GCD. (a) GCD curves recorded from 0 to 0.8 V at different current densities for the PEDOT/UPEA-h (2nd cycle shown). (b) Variation of the *SC* against the current density for PEDOT/UPEA-h and PEDOT/NaHCO₃ ESCs. (c) GCD curves recorded from 0 to 0.8 V at different current densities for PEDOT/NaHCO₃ (2nd cycle shown). (d) Comparison of the GCD curves recorded from 0 to 0.8 V at 0.43 A/g after 2 and 1400 consecutive cycles for PEDOT/UPEA-h.

Figure 10a shows the variation of the Coulombic efficiency (η) against the current density for PEDOT/UPEA-h. The Coulombic efficiency, which ranges from 0.92 to 0.78, decreases with the increasing V_{drop} and, therefore, with increasing current density (Figure 9a). However, the Coulombic efficiency remains higher than 0.90 for low current densities ≤ 0.61 A/g, indicating that these are the most appropriated charge-discharge conditions for the PEDOT/UPEA-h ESC.

Figure 10. (a) Variation of the Coulombic efficiency (η) against the current density and both (b) self-discharge and (c) leakage current curves for PEDOT/UPEA-h ESCs.

Application of ESCs is mainly limited to short-term energy storage due to the self-discharge processes, which cause substantial voltage decay, leakage current and loss of stored energy. Self-discharge, which is typically defined as the voltage drop after a set period of time, affects the electrochemical response of the ESC by decreasing the power and energy densities. Self-discharge is influenced by the chemistry and electrochemistry

of the system, the purity of reagents and electrolyte, and the temperature [36,37]. In this work, the self-discharging (SD) was determined by charging the PEDOT/UPEA-h ESC to 0.8 V at 0.25 mA, keeping it at $1 \cdot 10^{-11}$ mA for 10 min (self-discharging), and discharging to 0.0 V at -1 mA. For most of the cases, the cell voltage ended at voltages comprised between 0.4 and 0.5 V after the set period of time (Figure 10b), which indicates that in the short term the self-discharging tendency of the PEDOT/UPEA-h device is very low.

Another self-discharging parameter is the leakage current, which represents the stable parasitic current expected when the capacitor is held indefinitely on charge at the rated voltage [38]. The leakage current was measured by charging the ESC to 0.8 V at 0.25 mA, keeping that potential for 5 or 10 minutes and, finally, recording the current data through the ESC. Figure 10c shows how the current quickly decreases to a value comprised between 13 and 24 μ A that remained the rest of the time. This small leakage current is associated to a good stability of the PEDOT/UPEA-h ESC, which is crucial for energy storage applications.

The ionic conductivity of the UPEA-h was determined using electrochemical impedance spectroscopy (EIS). Accordingly, the impedance was measured for frequencies ranging from 10 to 10^5 Hz using a previously reported through-plane impedance cell [39]. Figure S5 displays the collected impedance (Z) data for three independent replicas as Nyquist plots. These consist in a capacitive semicircle in the high-frequency range and a straight ascending vertical line (almost 90° to the real axis) in the low-frequency range. This vertical line, which can be described as a “*capacitive spike*”, is consistent with a double-layer porous capacitor and reflects the diffusion of the supporting NaHCO_3 ions.

The hydrogel conductivity (σ , in S/cm) was calculated from Eqn 2:

$$\sigma = \frac{L}{R \cdot A} \quad (2)$$

where L is the thickness of the SE (0.1 cm); A is the area of the electrode (1×1 cm²), and R is the hydrogel resistance. The average conductivity determined for UPEA-h using three independent replicas is 0.039 ± 0.002 S/cm. Although this conductivity is smaller than the ones observed for hydrogels made of conducting polymers [40,41], which are able to exhibit electronic in addition to ionic conductivity, it is higher than that displayed by conventional gel polymer electrolytes (*ca.* 10⁻³ S/cm) under ambient conditions [42] and comparable to those of advanced biohydrogels (*e.g.* cellulose hydrogels prepared using ionic liquids, 0.040 S/cm) [43].

4. Conclusions

To conclude, we have reported the characterization of UPEA-h, which was synthesized by photo-crosslinking UPEA chains that contain phenylalanine, butenediol and fumarate as building blocks. The morphology of UPEA-h is appropriated for its utilization as SE in ESCs while the biocompatibility and biodegradability confers applicability in the biomedical field. ESCs prepared using PEDOT as electrode material and UPEA-h as SE exhibit excellent performance: the SC obtained by CV and GCD extends from 100 to 49 F/g and 179 to 114 F/g, respectively, depending on the scan rate and the current density; high cyclic stability and Coulombic efficiency; low self-discharging tendency; and small leakage current. Our work shows that UPEA-h presents a better behavior as SE than biohydrogels derived from biopolymers, as for example natural and modified polysaccharides (κ -carrageenan and carboxymethyl cellulose, respectively) and polypeptides, without any detriment in the biocompatibility. Therefore, UPEA-h has great potential as SE material for the fabrication of flexible

ESCs for self-powered biomedical implants and represents an excellent alternative to the biohydrogels derived from biopolymers typically used.

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Data availability

The raw/processed data required to reproduce these findings are available upon request to the authors.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/XXXXXX>.

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Graphical abstract