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Eumelanin Electrodes in Buffered Aqueous Media at Different pH

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Abstract

Eumelanin, a quinone-based biomacromolecule, is the most common form of the biopigment melanin in the human body. Eumelanin has attracted a great interest due to its physicochemical properties, such as metal-ion chelation, free radical scavenging, hydration-dependent (photo) electrical response and redox activity. Investigating the electron transfer properties of eumelanin is the key to exploit the electrochemical energy storage properties of the pigment. In this work, we investigated the redox behavior of chemically controlled melanin in $NaCH_3COO$ buffer solutions, at different pH values. For our study we used Cyclic Voltammetry, Electrochemical Impedance Spectroscopy and Galvanostatic Charge and Discharge, after characterization of the samples by Scanning Electron Microscopy. Eumelanin, in combination with aqueous electrolytes, provides for an attractive case of study for eco-designed storage devices based on abundant and environmentally benign materials and interfaces.

Keywords: Eumelanin, Quinones, Buffers, Charge transfer, Electrochemical energy storage.

1. Introduction

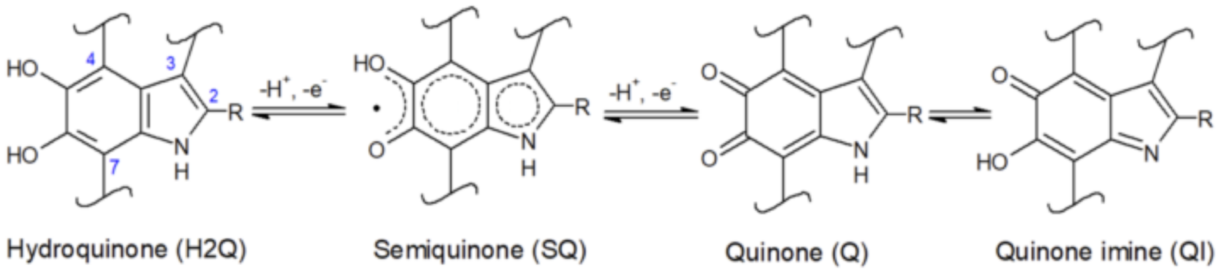
The increasing demand for electricity generated from renewable energy sources, such as the Sun, call for environmentally friendly, safe, low-cost, and robust energy storage devices, such as batteries and supercapacitors [1, 2].

Abundant, bio-sourced organic redox materials, potentially biodegradable, are of primary importance to limit the environmental footprint of electrochemical energy storage devices [3-5]. In combination with those materials, environmentally benign, non-flammable and low-cost aqueous electrolytes are investigated for eco-designed storage devices.

Molecules including redox active quinone groups play a key role in nature, for instance in the metabolism of plants and bacteria (as electron/proton transport agents) and mitochondrial ATP synthesis [6, 7]. They have been used in different electrochemical energy storage devices, such aqueous batteries [8-14] and supercapacitors [15-17].

Eumelanin is a brown-black quinone-based macromolecular pigment widespread in the biosphere, belonging to the melanin family [18]. During the last decades, it attracted the attention of the scientific community because of its unique physicochemical properties, such as broadband optical absorption [19], metal-ion chelation [20, 21], free radical scavenging [22], hydration-dependent (photo)electrical response [23, 24] and redox activity [25, 26].

Eumelanin originates from the oxidative polymerization of tyrosine via the 5,6-dyhidroxindole (DHI) and 5,6-dyhidroxindole-2-carboxylic acid (DHICA) building blocks. The presence of different molecular polymerization sites in the building blocks, co-existing redox states in the macromolecule (hydroquinone (H2Q), semiquinone (SQ) and quinone (Q), Scheme 1) and oligomers with different sizes are the main sources of the chemical heterogeneity of bio-sourced (natural) eumelanin [19, 27].

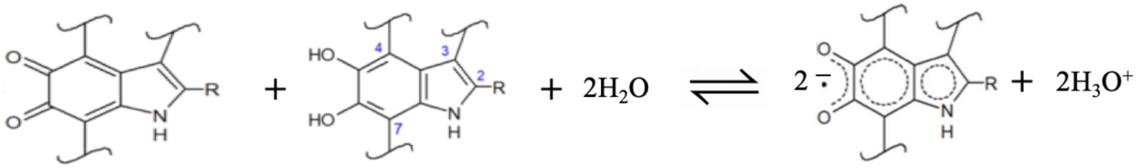


Scheme 1. Hydroquinone (H2Q), semiquinone (SQ) and quinone (Q) redox forms of the building blocks of eumelanin, namely 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA). R is –H in DHI whereas R is the –COOH group in DHICA. The quinone imine form (QI) is the tautomer of Q.

Natural eumelanin (Sepia melanin, extracted from cuttlefish ink) can contain up to 30% DHI, in molecular ratio [28]. The development of synthetic eumelanin only based on one of the two building blocks, such as DHICA- and DHI-melanin, has provided a tremendous tool to the exploration of the poorly understood physicochemical properties of eumelanin [29], in view of its application in electrochemical storage technologies. Considering its molecular structure, DHI-melanin features a more efficient π-electron delocalization over DHICA-melanin [30]. On the other hand, to model the behavior of natural eumelanin, it is pertinent to consider synthetic DHI:DHICA-melanin, where both the building blocks are present.

The pk_a value for the acidic protons belonging to the different eumelanin functional groups is 4.2 for the carboxylic group in the DHICA building block, 6.3 for the quinone imine and within the range 9-13 for the catechol groups [21 , 31]. The pH of the medium also affects the interactions between mono- and multi-valent metal ions and the carboxylic, amine (imine) and catechol groups [21, 25, 32].

Different types of charge transfer are possible for eumelanin, namely quinone-based electron transfer but also intra- and inter-molecular charge transfer, involving the π molecular orbitals of the macromolecule [33]. Further, the presence of a comproportionation equilibrium, where quinone and hydroquinone species react in presence of water to generate semiquinone species and protons, has to be taken into account to understand the electroactivity of eumelanin (Scheme 2) [23, 34].



Scheme 2. Comproportionation reaction of eumelanin in aqueous medium.

The charge transfer properties of eumelanin are expected to be affected by the pH of the electrolyte, the presence of UV-vis light as well as oxidizing or reducing agents [24, 35, 36]. Of all the aforementioned contributions, pH is of primary importance for optimized electrochemical energy storage in aqueous electrolytes. The use of chemically controlled melanins is deemed necessary to devise the effect of the pH on charge transfer, in a well-defined molecular environment.

Here, we report on the electrochemical characterization by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Galvanostatic Charge and Discharge (GCD) of chemically controlled DHI- and DHI:DHICA- (7:3 weight: weight) melanins in buffered aqueous electrolytes, at different pH in the range of 3≤pH≤9, where the material is chemically stable. We selected, as the electrolyte, aqueous solutions of $NaCH_3COO$, considering its low cost and environmentally friendliness [37]. Prior to electrochemical characterization, the melanin samples where characterized for their morphology by Scanning Electron Microscopy, after suitable heavy metal staining.

2. Experimental part

Electrodes preparation (DHI- and DHI:DHICA-melanin on carbon paper): DHI-melanin and (7/3 weight/weight) DHI: DHICA-melanin, were synthesized in situ on carbon paper by ammonia induced solid-state polymerization (AISSP) already reported in the literature [38]. 10 mg/mL solution of DHI was prepared in ambient conditions and used as precursor. For DHI/DHICA-melanin, 10 mg of powder, including 7 mg of DHI monomer powder and 3 mg of DHICA monomer powder, were dissolved in methanol, in ambient conditions, and the solution was used as precursor. Afterwards, the monomer solution of 10 µl was drop casted on the carbon paper (Spectracarb™ 2050A, 10 mils, geometric area 3.0 cm^2). The loading of melanin on each carbon paper current collector was ca. 133µg cm^{-2}. After drop casting, the samples were exposed to NH_3 vapors from $NH_{3(aq)}$ (Sigma Aldrich, 28-30% w/v) for about 72 hours, to catalyze the polymerization reaction.

Preparation of the electrolytes: 0.25 M buffer solutions of $NaCH_3COO$, pH ca. (3, 5, 7) were prepared from $NaCH_3COO$ (Sigma-Aldrich >99%) and CH_3COOH (Sigma-Aldrich >99.7%), dissolved in DI water (18.2 MΩ cm). 0.05 M NaOH was then added to the solution until the desired pH. *The pH of the electrolytes* was measured using Thermo Scientific™ Orion Star™ A215 pH/Conductivity Benchtop Multiparameter Meter.

Electrochemical measurements: Electrochemical measurements: Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed using a Biologic bipotentiostat (SP-300) in a three-electrode cell, with eumelanin on carbon paper current collector as the working electrode, a Pt mesh as the counter electrode and $Ag/AgCl_{(aq)}$ in 1M KCl as the reference electrode.

All measurements were conducted under N_2 purge. *Cyclic voltammetry* was performed in the potential range −0.6 V/0.6 V vs Ag/AgCl(aq) at different scan rate (0.1,1,5, 50,100 mV/s) for different pH values (3, 5, and 7), adopting the following protocol: freshly prepared electrode was used for each pH value and cycled at each scan rate for 5 cycles from high to low scan rate.

Electrochemical impedance spectroscopy measurements were conducted within the frequency range 10^5 Hz-10^{-1} Hz, at open circuit potentials (OCP). *Galvanostatic charge-discharge characterizations* were performed with electrodes pre-cycled (5 cycles) in the potential range -0.6 V/0.6 V vs. $Ag/AgCl_{(aq)}$ at 5 mV/s. Galvanostatic charge-discharge were performed, at different current density of 1, 5, 10, 15, 20 and 25 A g^{-1} and a cut-off potential of 0-0.4 V.

Morphology: The morphology of bare carbon paper and the melanin on carbon electrodes was examined by scanning electron microscopy (SEM, JEOL JSM7600F), at an acceleration voltage of 5 kV in backscattered electron (BSE) imaging mode. The melanin on carbon electrodes was stained with uranyl acetate for 1 h, prior to morphology examination by SEM [15, 25, 39].

3. Results and discussion

3.1 Morphology of DHI-melanin and DHI:DHICA-melanin on carbon paper

Melanin and carbon paper are not easily distinguishable by SEM as they are both carbon-based materials. On the other hand, exploiting the chelating properties of melanin, we were able to observe the presence of melanin on carbon paper after melanin staining with uranyl acetate [15, 25, 39]. DHI-melanin is preferentially located on the planar regions connecting the fibers of the carbon paper. On the other hand, DHI:DHICA-melanin is located on the grooves of such fibers.

3.2 Electrochemical characterization in 0.25 M $NaCH_3COO$ buffers at different pH

We carried out cyclic voltammetry investigations on DHI-melanin and DHI:DHICA-melanin in 0.25 M $NaCH_3COO$ buffer solutions, at different pH. In our previous studies, the voltammograms of melanin-based samples generally featured a quasi-box shape, typical of pseudocapacitive materials [15, 25, 40]. Here, in our voltammograms collected at pH 3 and scan rate 5 mV/s, DHI-melanin shows a weak and broad oxidation peak at ca -0.04 V vs Ag/AgCl (Figures 1a and S1). Considering that the peak lasts for more than 10 subsequent scans, we propose to attribute it to the DHI-melanin oxidation (instead to attribute it to oxidative polymerization processes involving monomers that did not react during the solid state chemical polymerization) [35, 41, 42]. If the scan rate is lowered to 1 and 0.1 mV/s, the aforementioned peak is observable even at pH 5 and 7, shifted towards more positive potentials (Figure S1).

In acidic media (pH=3), protons are present in high concentration and, considering the comproportionation reaction (Scheme 2), the density of mobile electronic charge carriers (SQ) decreases. This decrease is expected to be paralleled by a decrease in the voltammetric current. As a consequence, despite oxidation processes being unfavored in hydroquinone-based molecules in acidic media (Scheme 1), the lowering of the voltammetric current in these same media could help to reveal the DHI-melanin oxidation. For this same process, Horak and Weeks [35] reported that, with respect to neutral media, in acidic media a melanoid pigment deposited electrochemically from DHI has a faster charge transfer rate resulting from the decrease of the difference between the energy level of the HOMO of the hydroquinone and the LUMO energy level of the quinone.

For slight acidic and neutral values of the pH (5 and 7), at high scan rates (100, 50, 5 mV/s), DHI-melanin does not have any clearly distinguishable peak (Figures 1a and S1). On the other hand, as already mentioned, at those pH, at low scan rates (1 and 0.1 mV/s), DHI-melanin shows an oxidation feature similar to the aforementioned one, shifted towards more positive potentials (Figure S1). This suggests the slow kinetics of the oxidative reaction at mild and neutral pH [35, 41].

The electrochemical characterizations of DHI-melanin electrodes at pH 5 and 7 show that high voltammetric currents bring about high capacitance and capacity as well as low charge transfer resistance (related to the high density of the SQ species) compared to acidic pH (Figures 1a, 1b, 1c, 1f and S4 respectively).

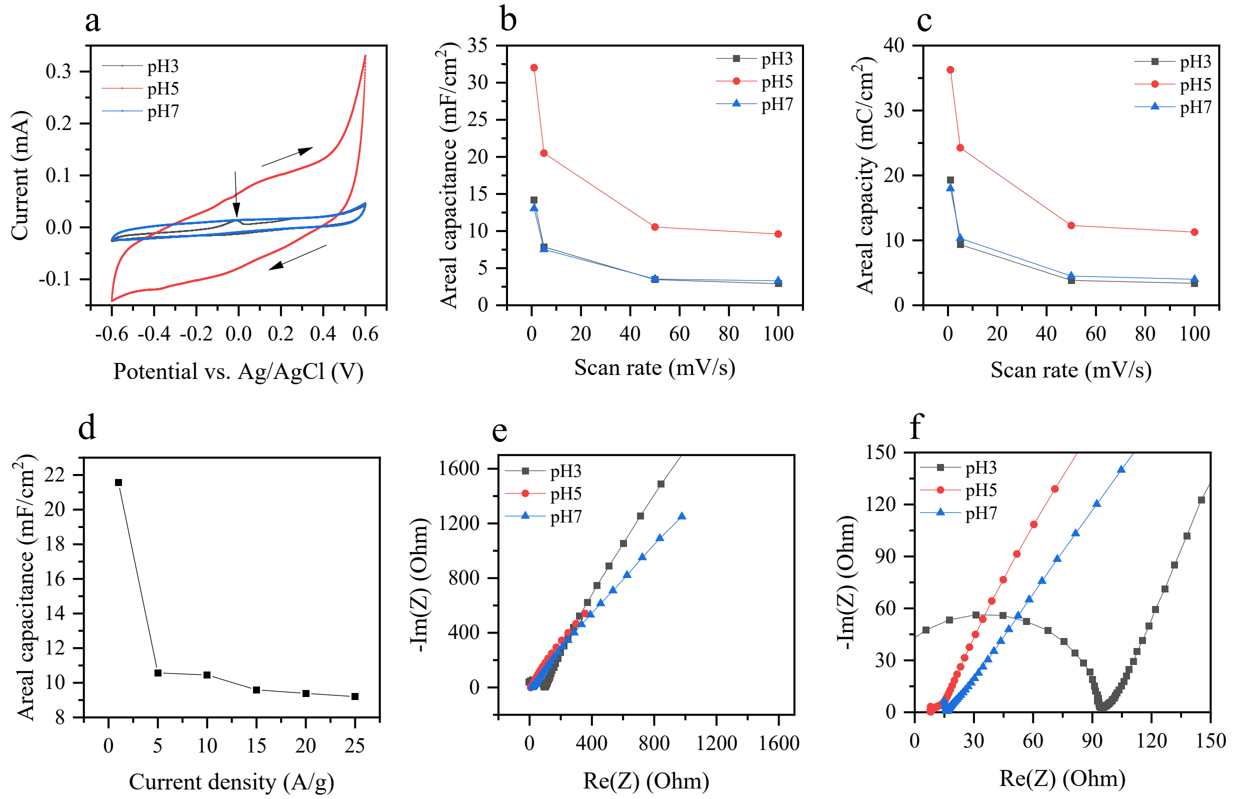


Fig.1 DHI-melanin in 0.25 M $NaCH_3COO$ at different pH: (a) 3rd CV cycle at 5 mV/s. (b) and (c) Areal capacitance and capacity evaluated from 3rd CV cycle vs scan rate. (d) Areal capacitance evaluated from GCD at different current density in 0.25M $NaCH_3COO$ pH 5. (e) Nyquist plot in the frequency range 10^5–10^{-1} Hz. (f) Zoomed Nyquist plot in the frequency range 10^5–5 Hz. In (b)-(f) lines are guides to the eye.

The voltammograms for DHI:DHICA-melanin are similar to those of DHI-melanin, at pH=5 and 7 (Figures 2a, S2). The presence of DHICA building blocks in the voltammograms becomes more distinguishable at pH=3. Besides the anodic feature as for DHI-melanin at pH 3, we observe anodic signatures at ca. 0.2 V (broad), 0.48 V (shoulder) and 0.54 V as well as cathodic signatures at 0.41 V, 0.13 V and -0.2 V (extremely broad) (Figure 2a).

In acidic media (pH 3), carboxylic, quinone imine and the catechol functional groups of DHI:DHICA-melanin are protonated. We observe high capacity and capacitance of DHI:DHICA-melanin electrodes in acidic pH with respect to pH 5 and 7 (Figures 2b and 2 c).

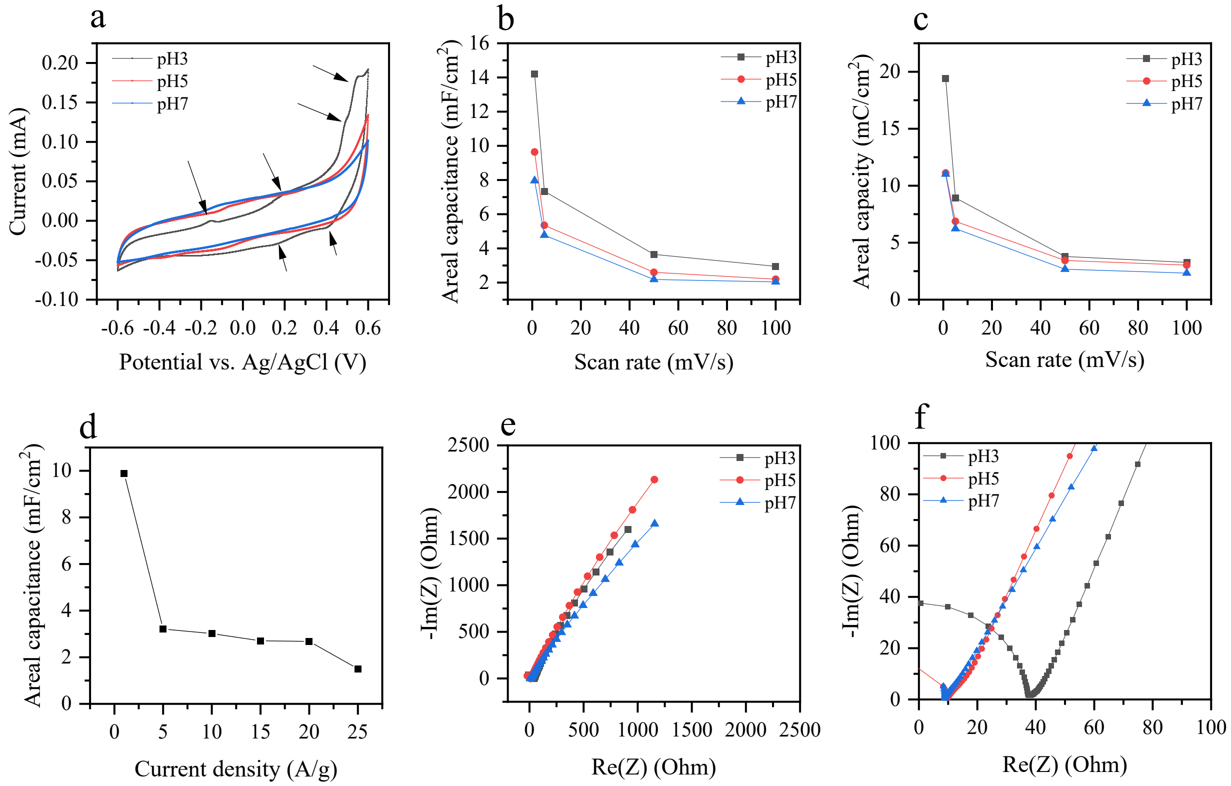


Fig.2 DHI:DHICA (7:3)-melanin in 0.25 M $NaCH_3COO$ at different pH: (a) 3rd CV cycle at 5 mV/s. (b) and (c) Areal capacitance and capacity evaluated from the 3rd CV cycle with scan rate. (d) Areal capacitance evaluated from GCD at different current density in 0.25M $NaCH_3COO$ pH 5. (e) Nyquist plot in the frequency range 10^5–10^{-1} Hz. (f) Zoomed Nyquist plot in the frequency range 10^5–5 Hz. In (b)-(f) lines are guides to the eye.

DHI:DHICA-melanin electrodes feature, at pH 3, a slightly higher charge transfer resistance (37.5 Ohm), compared to pH 5 and 7 (10 Ohm and 9.8 Ohm, Figures 3f and S4).

To evaluate the electrochemical energy storage performance of our melanin-based electrodes, their areal capacitance and capacity at different pH and scan rates were calculated from the voltammetric results reported in Figures S1 and S2 by the following equations:

$$C_{CV} = \frac{\int Idt}{A\Delta V} \tag{1}$$

$$Q_{CV} = \frac{\int Idt}{A} \tag{2}$$

where $\int Idt$ is the area of the voltammetric cycle during the discharge, A is the footprint area of the melanin on carbon paper, and ΔV is the electrochemical potential window.

The capacitance and capacity of melanin-based electrodes extracted from CV decreased with the increase of the scan rate (Figures 1b, 1c, 2b and 2c), likely due to mass transport limitations at high rates [43].

To further investigate the electrochemical energy storage behavior of our melanin-based electrodes, GCD measurements (Figure S3) were performed for different values of the current density (1, 5,10, 15, 20, 25 A/g) and a cut-off potential of 0.4 V, at pH 5. The areal capacitance from GCD curves was calculated using:

$$C_{GCD} = \frac{I_{dis}}{A\,s} \tag{3}$$

where I_{dis} is the discharge current and s is the slope of the plot cell voltage versus time, during discharge. Figures 1d and 2d show the decrease of the areal capacitance with the increase of the current density. Nevertheless, we observed that both melanins work quite efficiently at relatively high current density (5-20 A/g) as the change in the areal capacitance is less than 5%. As expected, DHI-melanin features higher voltammetric current and, in turn, higher capacity and capacitance, in relation to the efficient π-π stacked structure.

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic tool for several electrochemical processes [44]. Nyquist plots show that the low frequency diffusion tail becomes *more vertical* (slope increases) with pH, indicating that slightly acidic (pH=5) and neutral (pH=7) aqueous electrolytes are nearly ideal choice for a capacitive behaviour (Figures 1e and 2e). The change of the charge transfer resistance, evaluated from the semicircle intercepts of the real part of the impedance Re(Z) with pH (Figures 1f and 2f), confirms too the enhanced charge transport in buffer solutions of pH 5 and 7 (ca. 10 Ohms for both melanins) compared to pH 3 (ca. 90 Ohms and 37 Ohms for DHI- and DHI:DHICA- melanins respectively) (Figure S4).

4. Conclusion

We investigated the effect of the pH on the electrochemical properties of eumelanin, a quinone-based pigment, within the current efforts of the electrochemical energy storage community to go for eco-designed storage devices based on abundant and environmentally friendly materials. Considering the chemical and physical heterogeneity of natural (bio-sourced) eumelanin, for our fundamental studies we focused on chemically controlled DHI- and DHI:DHICA-melanins (the latter modeling natural Sepia Melanin), synthesized in situ on carbon paper by solid-state polymerization, in a way to devise the effect of the pH, in a well-defined molecular environment. Our study was conducted in 0.25M $NaCH_3COO$ buffer solutions at different pH values, namely 3, 5 and 7. Mild and neutral media give the optimum capacitance, capacity, and charge transfer resistance for both DHI- and DHI:DHICA melanin, explained within the context of the comproportionation equilibrium regulating the relative concentrations of quinone, hydroquinone, semiquinone (the electronic mobile charge carriers in eumelanin) and protons. All in all, the effect of the pH on the voltammetric properties is more significant on DHI-melanin with respect to DHI:DHICA-melanin. In the former case, the efficient π stacking brings efficient transport, indicated by the high voltammetric currents. We are capitalizing on the results reported in this work to develop fundamental and technological aspects of the research. Fundamental aspects pertain to the possibility to distinguish quinone-based transfer from intra- and inter-molecular transfers; such studies are based on the different role played by proton transport in these different mechanisms. Technological aspects pertain to the fabrication of suitable hydrogels to be interfaced to eumelanin electrodes, for mechanically robust storage eco-designed devices.

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