CHAPTER 7 GENERAL DISCUSSION

7.1 Hypothesis of proton-assisted electron transfer (PAET) process of eumelanin

This section builds the basic hypothesis on factors determining the values of the electrochemical potentials of eumelanin before critically discussing the literature (Section 2.2) and experimental data of this work (Section 7.2 to Section 7.6). First of all, *local pH* is induced by the electrical bias (Section 7.1.1). Proton-assisted electron transfer (PAET) processes of eumelanin are proposed based on its deprotonation/protonation of the functional groups (Section 7.1.3). Equations for such PAET processes corresponding to electrochemical potentials are deduced based on the Nernst equation (Section 7.1.4.1). Indeed, due to the control of PAET processes by local pH, the dependence of electrochemical potentials on sweeping rates can be explained (Section 7.1.4.5). Following this section, the effect of unbuffered electrolytes are included in Section 2.2.3 to critically discuss the literature data.

7.1.1 Local pH induced by electrochemical potential

Literature data of electrochemical polymerization by the constant potential technique are listed in Table 2.3. In basic pH (pH 13), a very negative potential (-0.96 V) is required, whereas a positive potential (0.5 V) is required for pH 7 [36][105]. There seems to be a correlation between the bulk pH and the electrochemical potential.

To our knowledge, an electrolyte of pH 13 does not favor synthesis (Section 7.5.6.3). Instead, decompositions are reported at pH 13 [172]. Does it mean that the negative potential brings a local pH close to the synthetic pH range ($6.5 \leq pH < 13$)? Here, *local pH*, also noted as pH_{local}, is defined as the pH value in a small space surrounding the interface of electrode/electrolyte. The pH of the solution is named the *bulk pH* or pH_{bulk}.

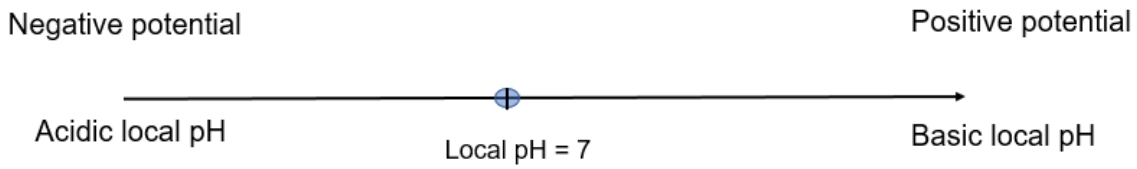

Figure 7.1 The relation between the local pH and the electrochemical potential. The *local pH* is defined as the pH value in a small space around the interface of electrode/electrolyte.

Therefore, based on the electrostatic considerations, we propose a simple hypothesis as follows. There is a potential that we set as E^*, where $pH_{local} = 7$. When the electrode is negatively biased vs. E^*, H^+ in the solution are attracted to the electrode and the local pH becomes acidic. At a positively biased potential vs. E^*, OH^- or the anions of buffering salt A^- for the deprotonation of eumelanin are attracted to the electrode and the local pH becomes basic (Figure 7.1).

7.1.2 Notations of pK_a and electrochemical potentials

In this work, a pK_a value corresponding to a protonation/deprotonation is noted as *pK_a(deprotonated form/protonated form)*. Oxidation peaks/features are noted as *protonated form/deprotonated form* and reduction peaks/features as *deprotonated form/protonated form*. The oxidation and reduction features are paired according to the reversible proton-assisted electron transfer (PAET) process. Here we name them *redox couples* and note them as *redox couple deprotonated form/protonated form* (Section 7.1.4.4).

7.1.3 PAET processes of eumelanin

Possible redox routes of eumelanin corresponding to local/bulk pH = pK_a are described in Figure 7.2. Different from other quinone-based materials, eumelanin has amine groups that can be deprotonated/protonated that also leads to redox activities of quinone groups (pK_a(HQI/H2Q) ca 6.3). Here we name HQI as *protonated quinone imine* that has amine group deprotonated but with quinone groups protonated. At local/bulk pH ca 6.3, the H2Q deprotonates to form HQI that can tautomerize and lose an electron to form SQ. Tautomerization means that proton of an organic compound moves from one functional group to another functional group. Here the proton moves between one hydroquinone group and the amine group (Figure 7.2).

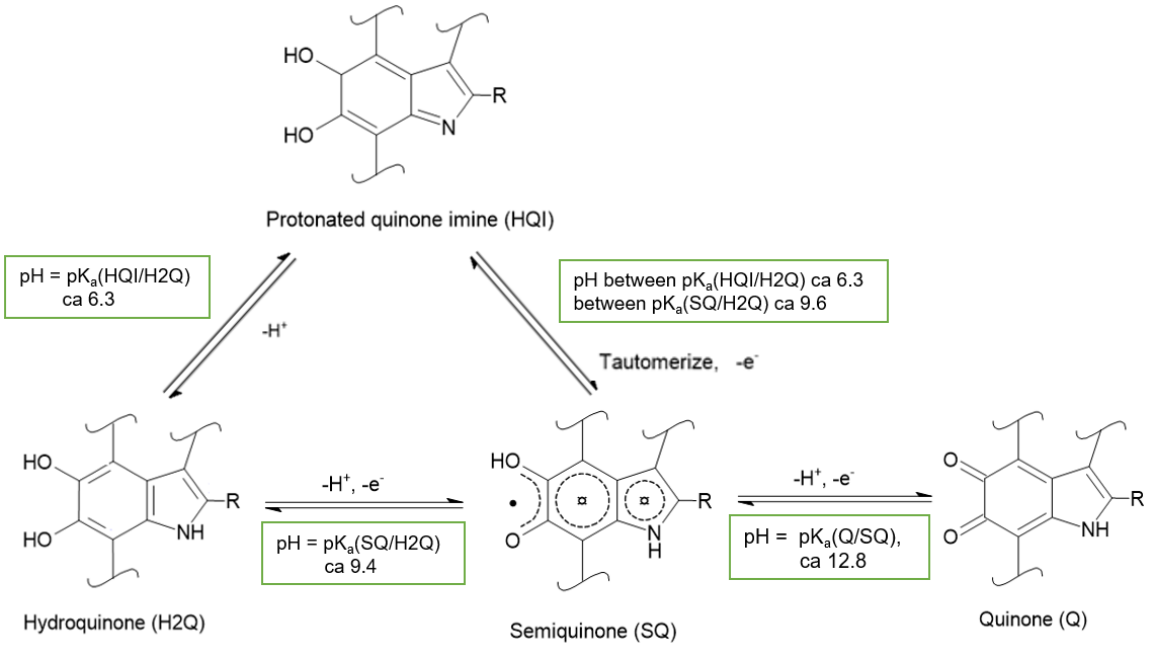

Figure 7.2 Redox processes of eumelanin corresponding to local/bulk pH = pK_a. -R is -H in DHI and -COOH in DHICA.

Throughout this work, we have noticed from literature data and experimental evidence that pH seems to be a key to control the oxidation processes of eumelanin (Section 7.5.2.1 and Section 7.4.4). Therefore, for *proton-assisted electron transfer (PAET) processes*, we hypothesize that during anodic potential sweeps of cyclic voltammetry, the oxidation processes of eumelanin happen after deprotonation, i.e. $pH_{local} \geq pK_a$. The potential corresponding to $pH_{local} = pK_a$ is hypothesized as the onset potential for oxidation (Figure 7.3).

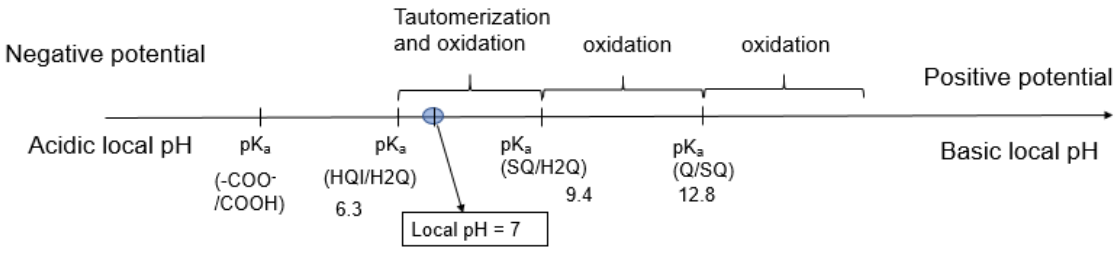

Figure 7.3 The local pH ranges for the oxidation processes of eumelanin.

7.1.4 Calculations of potentials from pH/pK_a values in the buffered electrolytes

7.1.4.1 Calculation of onset oxidation potentials from pK_a

We can tentatively calculate the corresponding potentials as follows.

We start with the Nernst equation regarding bulk pH

$$E_{redox}\,(pH_{bulk}) = E_{redox}\,(pH_{bulk} = 0) - 0.059\ pH_{bulk} \qquad \text{Eq. 7.1a (V vs. NHE)}$$

where E_{redox} (vs. NHE, pH_{bulk}) is a redox potential as a function of the bulk pH. NHE (normal hydrogen electrode) is a reference electrode. Eq. 7.1a means that changing the bulk pH shifts the redox potentials E_{redox} by a factor of 0.059. Eq. 7.1a also applies to an onset oxidation potential $E_{ox(onset)}$, by

$$E_{ox(onset)}\,(pH_{bulk}) = E_{ox(onset)}\,(pH_{bulk} = 0) - 0.059\ pH_{bulk} \qquad \text{Eq. 7.1b (V vs. NHE)}$$

From Section 7.1.3, we understand that an oxidation process happens at $pH_{bulk} \geq pK_a$. Therefore, we here hypothesize that the oxidation process happens at $pH_{bulk} \geq pK_a$ without the applied bias, that is,

$$E_{ox(onset)}\,(pH_{bulk} = pK_a) = 0\ V\ (vs.\ NHE) \qquad \text{Eq. 7.2}$$

therefore

$$E_{ox(onset)}\ (V\ vs.\ NHE,\ pH_{bulk} = 0) = 0.059\ pK_a \qquad \text{Eq. 7.3a}$$

Using another reference electrode Ag/AgCl, where

$$E\ (V\ vs.\ Ag/AgCl,\ pH_{bulk}) = E\ (V\ vs.\ NHE,\ pH_{bulk}) - 0.2 \qquad \text{Eq. 7.4}$$

therefore

$$E_{ox(onset)}\ (V\ vs.\ Ag/AgCl,\ pH_{bulk} = 0) = 0.059\ pK_a - 0.2 \qquad \text{Eq. 7.3b}$$

E (vs. Ag/AgCl, pH_{bulk}) at different bulk pHs can again be calculated with the Nernst equation

$$E_{ox(onset)}\ (pH_{bulk}) = E_{ox(onset)}\ (pH_{bulk} = 0) - 0.059\ pH_{bulk} \qquad \text{Eq. 7.1c (V vs. any reference electrode)}$$

Therefore, the onset oxidation potential is expressed as

$$\boxed{E_{ox(onset)}\ (pH_{bulk}, pK_a) = 0.059\ (pK_a - pH_{bulk})} \qquad \text{Eq. 7.5a (V vs. NHE)}$$

which reveals the relation between the onset oxidation potentials and the pK_a values (Figure 7.3). Based on discussions later in Section 7.1.4.4, Eq. 7.5a will be assigned later as both *onset oxidation potentials* and *end reduction potentials* in the buffered electrolytes. From pK_a(Q/SQ) ca 13 and pK_a(SQ/H2Q) ca 9.3, we can calculate from Eq. 7.5a that the expected potential difference between these two electron transfer processes is ca 0.38 V, as estimated by Kim et al. [50]. The onset potentials predicted by Eq. 7.5a are found to fit the results in this work (Section 7.2.2). However, the predicted data by Eq. 7.5a do not fit the literature data. The major reason can be the use of unbuffered electrolytes (Section 2.2.3).

7.1.4.2 Relation between local pH and applied potential

We tentatively expand the calculating method of Eq. 7.5a for obtaining the local pHs in electrolytes of any bulk pHs. From Eq. 7.1b, we set $pH_{bulk} = pH_{local}$ and $E(pH_{bulk} = pH_{local}) = 0$ V vs. NHE. Then we obtain

$$E_{app}\ (pH_{bulk} = 0, pH_{local}) = 0.059\ pH_{local} \qquad \text{Eq. 7.3c (V vs. NHE)}$$

$$E_{app}\ (pH_{bulk} = 0, pH_{local}) = 0.059\ pH_{local} - 0.2 \qquad \text{Eq. 7.3d (V vs. Ag/AgCl)}$$

Eq. 7.3c and Eq. 7.3d reveal the linear relationship between pH_{local} and the potential (Figure 7.1). Combining with the effect of the bulk pH (Eq. 7.3c), we obtain

$$\boxed{E_{app}\ (pH_{bulk}, pH_{local}) = 0.059\ (pH_{local} - pH_{bulk})} \qquad \text{Eq. 7.5b (V vs. NHE)}$$

Eq. 7.5b indicates that at local pH = bulk pH, the potential is 0 V vs. NHE, no matter at which bulk pH. Eq. 7.5b also implies how the change of the local pH is driven by the applied potential. Eq. 7.5b is used in this work to further discuss the effect of unbuffered electrolyte (Section 2.2.3).

7.1.4.3 Reversible PAET process

We here hypothesize that each *reversible PAET process* has capacity equality of reduction and oxidation at each redox potential, that is

$$q_{red} = q_{ox} \qquad \text{Eq. 7.6}$$

which means that, as long as the peak currents of peak capacities of a redox couple are not equal, this redox reaction is not reversible. For example, in Article 1, all the three oxidation peaks of DHICA-melanin at pH 5 are irreversible (Figure 7.6).

As to the relative position of oxidation potential vs reduction potential, first of all, we would like to define an ideal reversible PAET process (Section 7.1.4.4). After that, we derive such situation for the effect of sweeping rates (Section 7.1.4.5).

7.1.4.4 Ideal reversible PAET process

In an ideal PAET process, we expect the same position of the reduction peak as the oxidation peak. To express them in terms of onset potentials ($E_{ox(end)}$ and $E_{red(end)}$) and end potentials ($E_{red(end)}$ and $E_{ox(end)}$), it is $E_{red(end)} = E_{ox(onset)}$ and $E_{ox(end)} = E_{red(onset)}$ (Figure 7.4). In this work, most of the voltammograms are obtained at 5 mV/s. Some redox couples have electrochemical potentials close to the ideal PAET processes as described in this Section, such as Sepia melanin and DHI-DHICA-melanin (Figure 7.11).

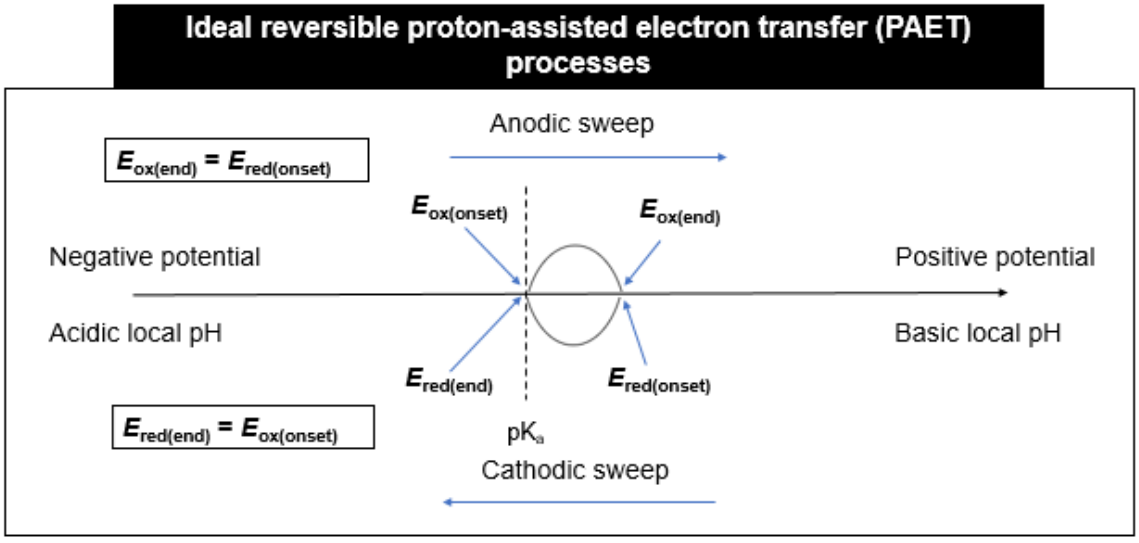

Figure 7.4 Ideal reversible proton-assisted electron transfer (PAET) processes.

7.1.4.5 Effect of sweeping rates

During the anodic sweep, eumelanin is deprotonated by the anions A^- generated by a buffered electrolyte or OH^- by H_2O in an unbuffered electrolyte (Section 2.2.3.1) The sweeping rate means how fast the increase/decrease of potential is. When the sweeping rate is higher than the rate that H^+ or OH^- (or A^-) can accumulate at the interface of electrode/electrolyte, there is a lag between the change of the local pH with respect to the change of the applied potential. From the ideal reversible PAET where $E_{red(end)} = E_{ox(onset)}$ (b), the $E_{red(end)}$ at higher sweeping rate shifts cathodically and $E_{ox(onset)}$ shifts anodically (Figure 7.5). The degree of potential shift is dependent on the sweeping rate. Such phenomenon is shown in the voltammograms in the buffered electrolytes (Figure 6.3, Figure S3 and Figure S4 in Appendix A). For example, in presence of monovalent metal ions, the onset potential of oxidation peak SQ/Q of DHICA-melanin shifts anodically from 0.24 V vs. Ag/AgCl at 5 mV/s to 0.29 V at 100 mV/s (Figure S3(b) in Appendix A).

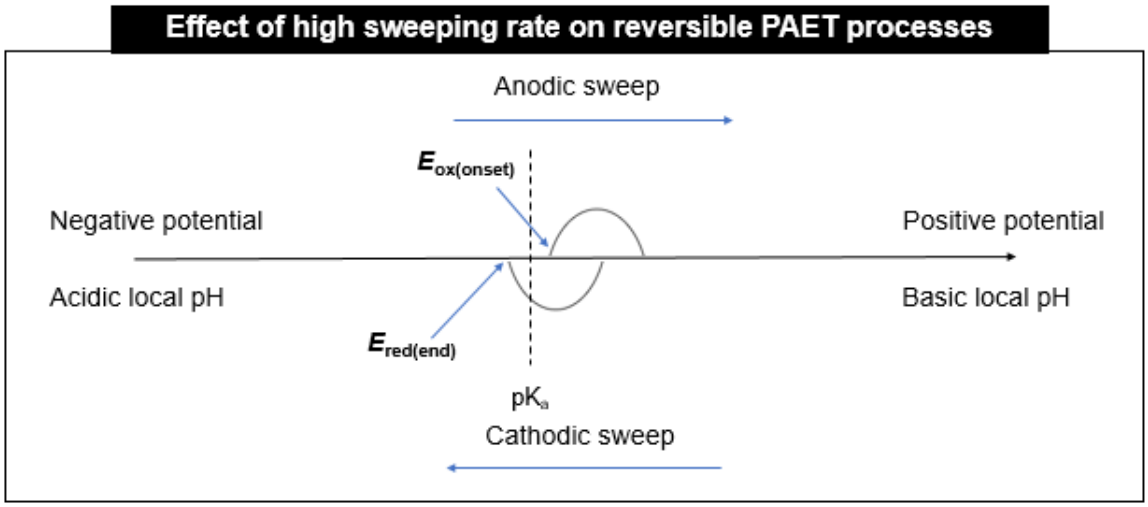

Figure 7.5 The effect of high sweeping rate on the reversible proton-assisted electron transfer (PAET) process.

7.2 Electrochemical potentials and supramolecular structures of DHICA-melanin in presence of monovalent metal ions

7.2.1 Environmental pH vs. pK_a of eumelanin

7.2.1.1 Concept of environmental pH

Before starting the comparison of experimental data and expected data, we would like to define the environmental pH. The *environmental pH* means the pH surrounding the eumelanin sample. It can be synthetic pH (pH 12), storage pH (pH 7), bulk pH of the electrolyte, local pH when electrical biases are applied, etc.

7.2.1.2 Hypothesis: pK_a values of eumelanin shift towards environmental pH during polymerization

Various experimental evidence points that, when the eumelanin is in a new environment, it begins to (further) polymerize or depolymerize depending on the pH. The main evidence is as follows:

- Yang et al. reported that the adhesion properties of polydopamine vary with pH changes, noted by the detachment ratio [172]. The detachment ratio varies at the change of every pH unit except for pH 4-7.
- Analyzing the experimental data of this work, it seems that pK_a values of DHICA-melanin are more close to the environmental pH that it experienced (Section 7.2.2).

Therefore, we hypothesize that, during the (further) polymerization of eumelanin in a new environment, the pK_a value that is close to the environmental pH shifts towards the environmental pH, so that the polymerization rate decreases until it reaches a given level.

Indeed, eumelanin is prone to be (further) polymerized in hydrated conditions due to the coexisting redox forms H2Q and Q (Section 2.1.1). Even during immersion of the working electrode without electrical bias, when the electrolyte is being degassed, eumelanin can also undergo further polymerization.

7.2.2 Data analysis of DHICA-melanin

In this section, we review the important voltammograms in this work and discuss the pK_a values of the eumelanin and their relation to environmental pH that it experienced.

At bulk pH 5, the oxidation peak H2Q/HQI seems convoluted (Figure 7.6 (a)). The convoluted peaks have onset potentials ranging between -0.14 V and -0.07 V vs. Ag/AgCl, corresponding to ca 6.0 and ca 7.2. The original pK_a(HQI/H2Q) ca 6.3 has shifted towards the storage pH (ca pH 7). The onset potential of H2Q/SQ is ca 0.02 V vs. Ag/AgCl, corresponding to a pK_a value ca 8.7. This probably results from the shift of the original pK_a(SQ/H2Q) ca 9.4 towards the storage pH 7. The onset potential of SQ/Q is ca 0.22 V vs. Ag/AgCl, with pK_a(Q/SQ) ca 12.1 equaling the synthetic pH (Section 3.1.3).

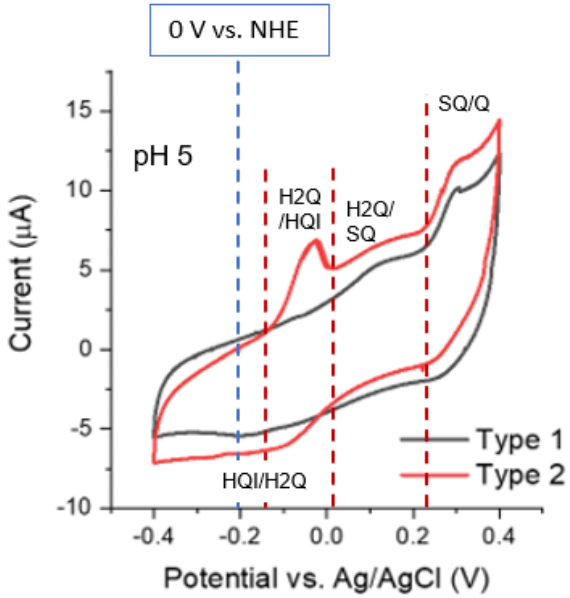

Figure 7.6 Type 1 and Type 2 DHICA-melanin in 0.25 M buffered $NaCH_3COO$ bulk pH 5. Adapted from Figure 6.2.

7.2.3 Supramolecular structures of DHICA-melanin

7.2.3.1 Supramolecular structures of two types of DHICA-melanin

In this work, the oxidation peak H2Q/HQI differentiates Type 1 from Type 2 DHICA-melanin (Figure 7.6). We tentatively explain such a difference as follows.

On a single DHICA monomer, one side has quinone groups and the other side has amine and $-COO^-$. DHICA oligomers form rod-shaped assemblies by hydrogen bonding between these functional groups (Figure 2.2). The cause of the oxidation peak H2Q/HQI is the deprotonation of the amine groups. Therefore, we deduce that, in Type 1 DHICA-melanin, the side with $-COO^-$ and amine groups may form hydrogen bonds inside the rod-shaped structure. In such a situation, the