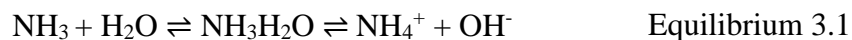on sample holders. When the synthesis starts, the NH_3 and H_2O evaporate from the vial and fill the chamber. Eumelanin samples absorb H_2O and NH_3 and form NH_3H_2O on the sample, by

$$NH_3 + H_2O \rightleftharpoons NH_3H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{Equilibrium 3.1}$$

with a dissociation constant of the base

$$K_b(NH_3H_2O) = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \qquad \text{Eq. 3.1}$$

Due to the dissociation constant, the pH value on the eumelanin sample is expected to remain almost the same throughout the synthesis. We hypothesize that, after a certain amount of time, the equilibria of the concentrations $[H_2O]$ and $[NH_3]$ are reached in each part of the chamber (eumelanin samples, the atmosphere, and the ammonia water in the vial). Therefore, the concentration of NH_3 in the eumelanin sample and the ammonia water in the (initial) vial are expected to be almost the same, and further the pH values.

Here we estimate the initial pH value of the ammonia water in the vial as follows. The NH_3 water with 28% w/v means 28 g NH_3 in 100 ml H_2O, i.e. ca 16 M. We set the concentration of generated $[NH_4^+]$ and $[OH^-]$ as x (M), then the $[NH_3]$ after reaching Equilibrium 3.1 is $(16 - x)$ M. $K_b = x^2/(16 - x)$. Assuming this, because $K_b \ll 1$, $(16 - x)$ M ≈ 16 M, we obtain $x = 0.01697$ M and thus pH value is ca 12.2. Therefore, the synthetic pH is ca 12.

3.2 Cyclic Voltammetry

Cyclic voltammetry is an electrochemical technique commonly employed to investigate the oxidation and reduction processes undergone by the material as the working electrode interfaced with an electrolyte. By both cyclic voltammetry and galvanostatic charge-discharge techniques, we are able to obtain the capacity/capacitance, potential limit, as well as the cycling stability of the material electrode.

3.2.1 Three-electrode setup

A three-electrode setup is used for cyclic voltammetry measurements, including a working electrode, a counter electrode, and a reference electrode (Figure 3.1). The working electrode material is loaded on a current collector. Electrodes are immersed in an electrolyte, which can be

an aqueous or organic solution of salts. In this work and the related literature, aqueous electrolytes are used (Section 2.2). A potentiostat is used to control the applied potential of the working electrode with respect to the reference electrode potential. The potential at the working electrode is measured against the potential of the reference electrode and noted as "vs" the reference electrode [53].
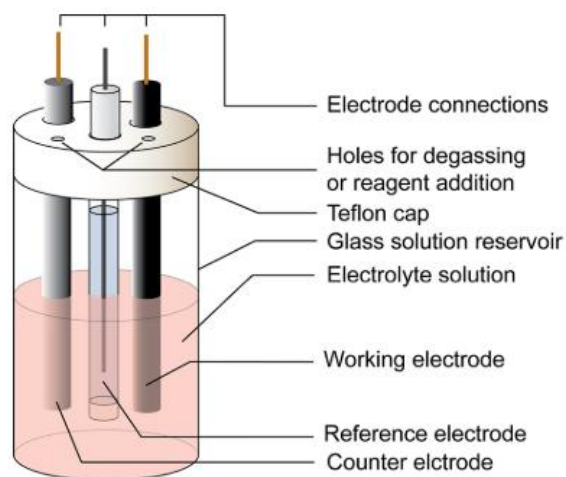

Figure 3.1   Electrochemical set-up for cyclic voltammetry [117].

3.2.2 Working principle of cyclic voltammetry

In cyclic voltammetry, the applied electrochemical potential *V* is linearly swept/scanned at a certain rate. Such rate is called sweeping rate (mV/s). During a voltammetric cycle, the potential is swept from the initial potential to a spositive potential, called the *switching potential*. It is then swept back to a negative potential, reaching another switching potential, and finally is swept back to the initial potential (Figure 3.2). The *i* vs. *V* plot is called a cyclic voltammogram [53][117]. The potential sweep towards a more positive potential is called an *anodic sweep/anodic scan*. The potential sweep towards a more negative potential is called a *cathodic sweep/cathodic scan* (Figure 3.2). The definition of anodic/cathodic current follows a different principle from the anodic/cathodic sweep in this work. *Anodic current* means positive current, whereas *cathodic current* refers to negative current. The anodic or cathodic current of eumelanin is mainly composed of oxidation or reduction current due to its redox activity.
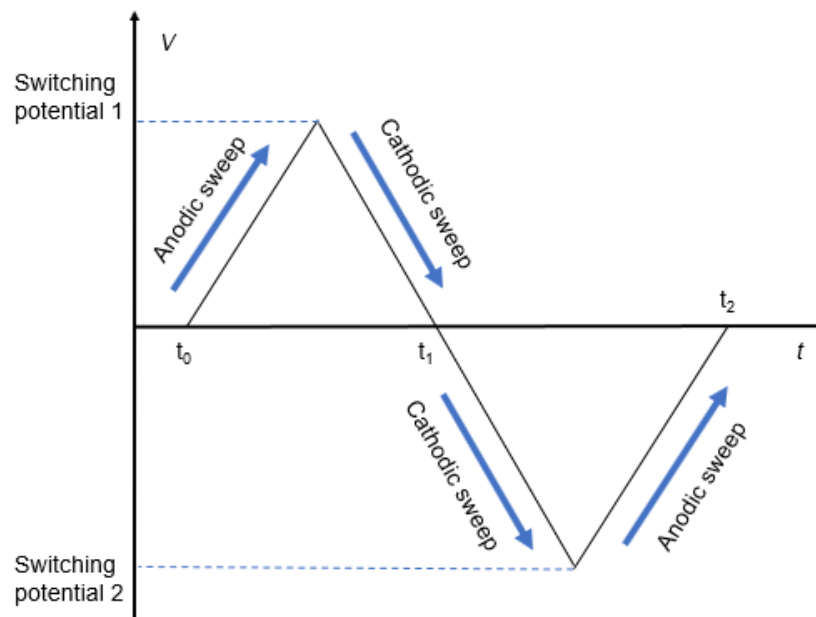
38

Figure 3.2   Scheme of cyclic voltammetry in the plot of potential *V* vs. time *t*.

In this thesis, we often conduct two cycles or more due to two reasons:

- To further observe the stability of the effects of interest. Such effects include the effect of light, transition metal ions, etc.

- The voltammograms of eumelanin can evolve cycle after cycle with the advancement of the polymerization reaction (Section 7.5.1).

3.2.3 Extraction of capacitance and capacity from cyclic voltammograms

3.2.3.1   Extraction of capacity

Capacity *q* (C) is the maximum ability of a material to store charge carriers. Capacitance *C* (F = C/V) describes how much charge carriers can be stored per potential unit, meaning the (maximum) efficiency of a material's charge storage.
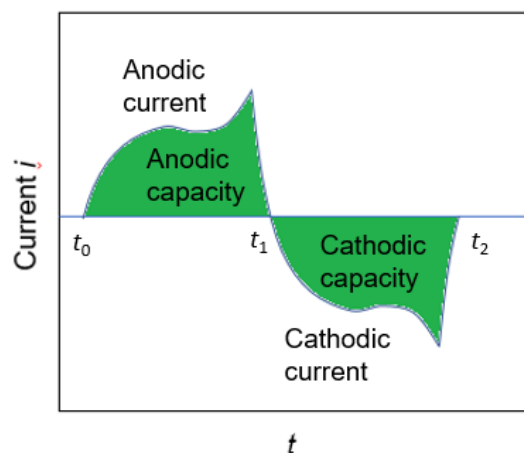
Figure 3.3   Extraction of capacity from cyclic voltammograms of redox-active materials.

The anodic/cathodic current is composed of oxidation/reduction current (peaking current), electrostatic current (box-shaped, Figure 3.4(a)) and ionic current. In this work, the anodic and cathodic capacities are extracted from the anodic (positive) current and cathodic (negative) current, respectively, noted as q_{an} and q_{ca}. The *anodic capacity* is the integration of the anodic current i_{an} vs. time t (Figure 3.3),

$$q_{an} = \int_{t0}^{t1} i_{an}\, dt \qquad \text{Eq. 3.2}$$

and the *cathodic capacity* is the integration of the cathodic current i_{ca} vs. time t,

$$q_{ca} = \int_{t1}^{t2} i_{ca}\, dt \qquad \text{Eq. 3.3}$$

In voltammograms at the same sweeping rate and potential range, higher current means higher capacity.

Oxidation/reduction capacity is defined as the capacity extracted from the oxidation/reduction (peaking) current, noted as q_{ox}/q_{red}.

3.2.3.2   Extraction of capacitance

For an electrical double-layer capacitive material, the capacitance C is defined as

$$C = \frac{q}{V} \qquad \text{Eq. 3.4}$$

which is the slope of the q-V plot (Figure 3.4(a)(b)). For a pseudocapacitor, the q-V plot has different slopes at different potential biases (Figure 3.4(d)). In this case, we find a part of the curve that is close to linear, here called the *quasi-linear curve.* We use the slope obtained from the linear regression of the quasi-linear curve as the capacitance C.
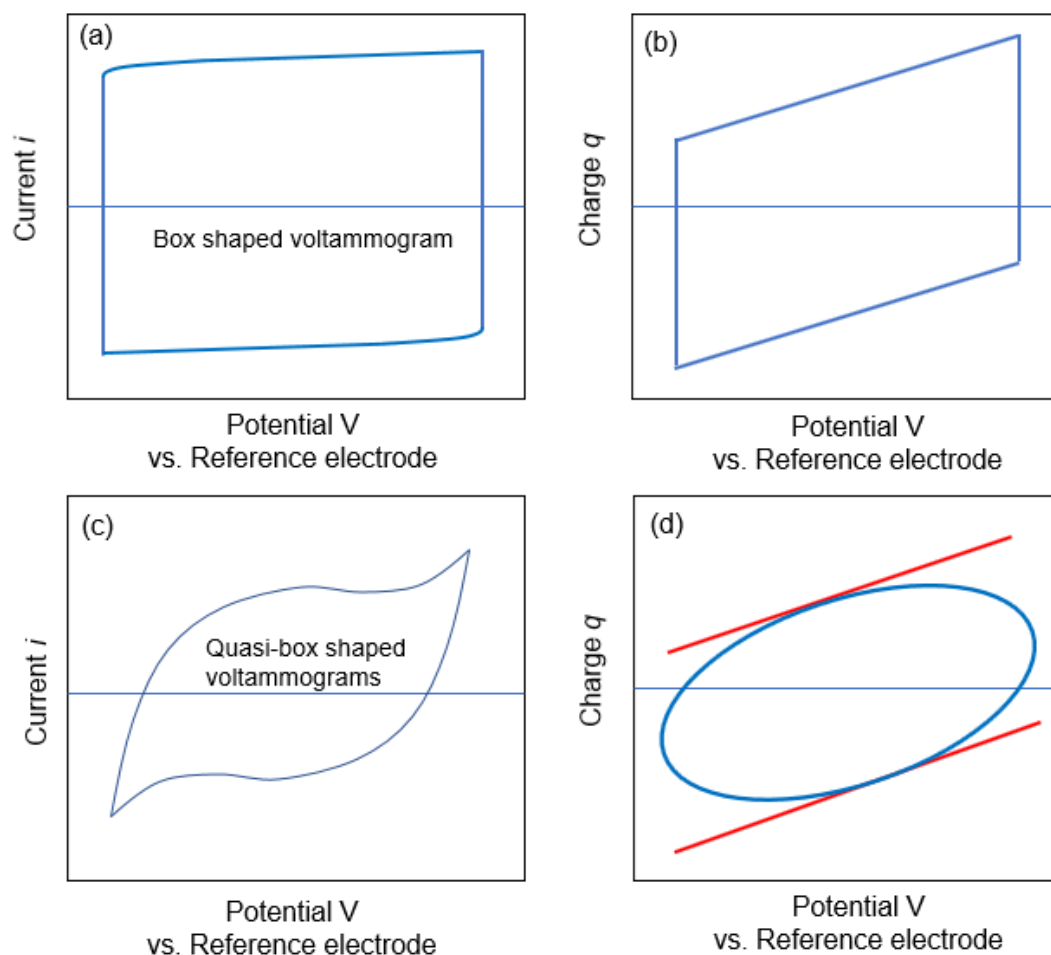

Figure 3.4   Extraction of capacitance in (a), (b) box-shaped cyclic voltammograms of electrostatic capacitive material and (c), (d) quasi-box shaped cyclic voltammograms of pseudocapacitive material. (d) includes linear regression on a quasi-linear curve to obtain capacitance.

Usually, capacity and capacitance have coherent trends of increase or decrease. The comparison of capacity and capacitance should be valid only when the parameters such as sweeping rate, potential range are the same.

3.2.4 Degassing procedure

A small amount of oxygen present in aqueous solutions could lead to ORR features in voltammograms (Section 2.2.6). Therefore, degassing should be conducted strictly throughout the experimental procedures. Pre-purging N_2 in the solution but conducting the cyclic voltammetry in ambient conditions can still result in ORR features in voltammograms of eumelanin.

The suggested degassing procedure is as follows.

1) Using electrolytes with small volumes will make it easier to degas. The larger the volume, the higher the pressure or longer the time required in Procedure 2).

2) Use a high pressure of N_2 gas to purge the aqueous solution. The time for this procedure depends on the quantity of electrolyte. The O_2 in the electrolyte is removed under a given pressure of N_2. For 10 ml aqueous solution, more than 4 min is suggested.

3) Lower the pressure of N_2 and withdraw the pipe above the liquid. This flow of N_2 prevents O_2 from getting into the electrolyte.

In Article 1, the pressure of N_2 does not seem to be high enough in Procedure 2) to exclude the impact of the ORR (Section 2.2.7.3). In Article 2 and Article 3, a higher pressure of N_2 is used in Procedure 2), therefore very little impact of ORR is observed.

3.2.5 Extraction of onset and end potentials

The onset potentials and end potentials are extracted as follows.

- In the case of asymmetric peaks, convoluted symmetric peaks with different onset/end potentials should be considered.

- For the first peak of a potential sweep, the onset potential is found where the slope of the curve initially changes (Figure 3.5). The same applies to the end potential of the last peak of a sweep.

- For the non-first peak of the sweep, its onset potential is usually the local minimum between this peak and the previous peak. If the non-first peak is at a given distance from the previous peak in potential, the extraction is like the first peak's. The same applies to the end potential of the non-last peak.
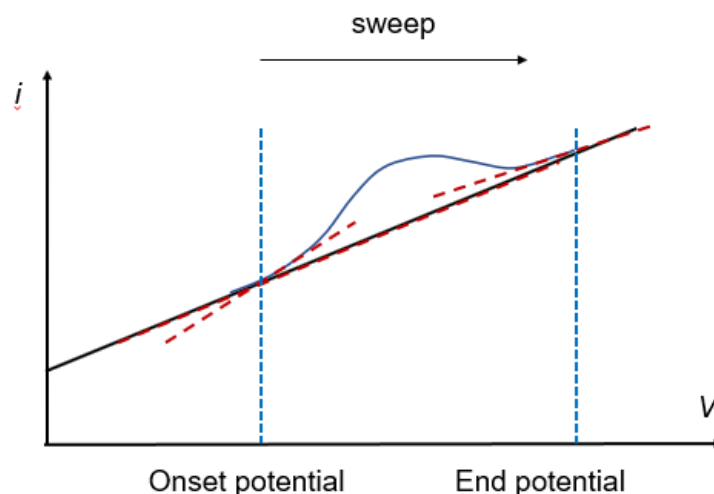
Figure 3.5   The onset and end potential of a peak during a potential sweep.

3.3 Galvanostatic charge-discharge

The galvanostatic charge-discharge electrochemical method is used to evaluate the electrochemical capacitance, resistance and cycling stability of the electrode material.

3.3.1 Working principle of galvanostatic charge-discharge

To evaluate a supercapacitor, two identical electrodes are set as working and counter electrode, respectively. A galvanostatic (constant) current is applied to the working electrode vs. the counter electrode as a function of time. The *cell potential* is therefore the potential difference between the working electrode and counter electrode. A *cut-off voltage* is set to be the potential limit of the cell potential. The resulting plot of galvanostatic charge-discharge is a *V-t* plot. The potential increases with time during the charging process, reaches the cut-off voltage, and then decreases with time during the discharging process. In an ideal double layer capacitor, the increase and decrease of the *V* vs. *t* is linear. In a pseudocapacitor, this plot is not strictly linear (Figure 3.6). In this work, a reference electrode is concurrently used to measure the actual potential at both the working electrode and counter electrode vs. the reference electrode (Figure S5 of Appendix D).
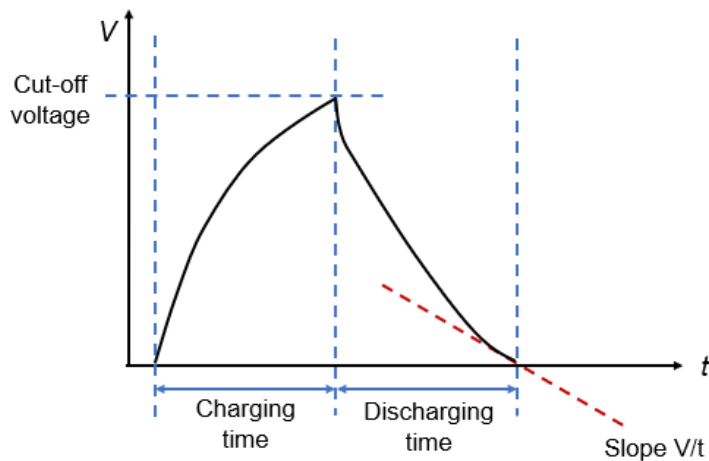
Figure 3.6   Scheme of galvanostatic charging-discharging *V-t* plot for a pseudocapacitor. The slope *V/t* is the linear regression for a quasi-linear part at the end of the discharging time.

Equations to calculate the Coulombic efficiency and equivalent resistance are described and calculated in this work in Appendix B [53], [54]. Extraction of capacitance and capacity are described in Section 3.3.2.

3.3.2 Extraction of capacity and capacitance from the data

The charging capacity and discharging capacity are the products of the constant current and the time for charging and discharging, respectively,

$$q = it \qquad \text{Eq. 3.5}$$

For an electrical double-layer capacitor, capacitance C is defined as

$$C = \frac{q}{V} = \frac{t}{V} \cdot i \qquad \text{Eq. 3.6}$$

which is the result of the constant current divided by the slope (*V/t*) of *V-t* plot. For a pseudocapacitor, where the *V-t* plot does not have the same slope at every point, we find a quasi-linear curve in the discharging *V-t* plot. In this work, the quasi-linear curve in the *V-t* plot is located at the end of discharging time (Figure 3.6). The slope of *V/t* for the calculation of the capacitance is obtained from the linear regression of the quasi-linear curve.