Electropolymerization of Aniline

47338 Organic Energy Materials

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1   Introduction

With the current energy crisis and continual transition to renewable energy, there is a growing need for satisfactory energy storage. Electropolymerization of conducting polymers is a promising route to support this transition. Conducting polymers are of great interest since they are easily synthesised, affordable, tunable and environmentally stable. One of the most propitious conducting polymers is polyaniline (PANI).

This report aims to investigate the formation of PANI on a transparent conducting electrode. The polymers optical absorbtion, redox states, and oxidative stability will be studied, in order to gain a deeper understanding of the electrodeposition and electrochemical synthesis. Results were obtained through cyclic voltammetry (CV), chronoamperometry (CA) and ultraviolet-visible (UV-Vis) spectroscopy experiments.

2   Methodology

In this section relevant information about the instruments and materials used for the experiments along with theory of electrochemicalpolymerization of PANI will be presented. Furthermore, a description of the experiment setup is presented.

2.1   Aqueous Electropolymerization principle

Aqueous electrochemical polymerization in the presence of H_2SO_4, as used in this study, is a well known method for the synthesis of PANI. This process is based on the deposition of a polymer onto the surface of a solid electrode material. This occurs through the formation of a cationic radical by the oxidation of the monomer on the solid electrode material [1] as can be seen on figure 1.
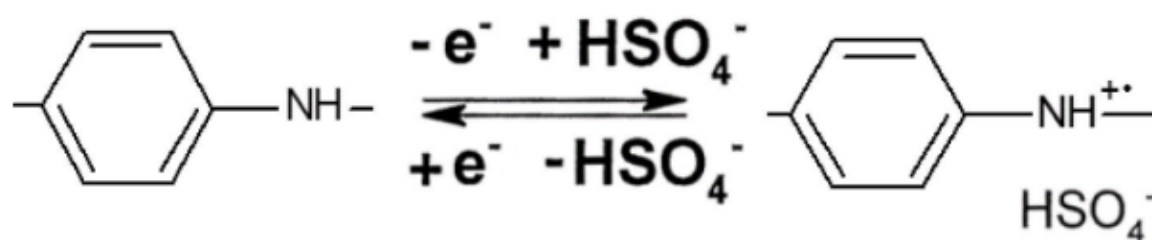

Figure 1: Formation of a cationic radical by oxydation of the monomer. The latter can also be reveresed through reduction.

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[1]T. A. Saleh, Polymer Hybrid Materials and Nanocomposites: Fundamentals and Applications. William Andrew, 2021.

2.2   Electrochemical methods

Cyclic voltammetry
Cyclic voltammetry or CV is a reversal scan technique consisting of a positive and negative potential sweep. The potential of a working electrode is changed linearly with time between two potentials. The resulting current from the changing potential is plotted against the potential for a cyclic voltammogram. CV is widely used in the studies of electrochemical systems.

Chronoamperometry
Chronoamperometry, which will be referred to as CA from this point, is a time dependent technique, where a potential is stepped to a constant for the duration and then the current is measured for the duration. CA is often used to investigate redox couples at a set potential, and for bulk electrolysis.

To analyse the results in terms of deposited mass, film thickness and surface coverage, the following equations were applied.

The deposited mass of the polymer can be calculated with equation 1 in which m_i is the mass of species i, M_i is the molar mass of species i, Q is the charge, F is Faradays constant and n is the number of electrons used per unit.

$$m_i = \frac{M_i Q}{nF} \tag{1}$$

The oxidation or reduction charge can be found from a CV. By integrating the area of the anodic or cathodic current on the forwards or backwards scan respectively and then dividing with the scan rate utilised in the experiment.

The film thickness of the polymer layer on the electrode can be calculated using equation 2, were d is the film thickness, A is the area of the layer and δ is the density.

$$d = \frac{m_i}{A \cdot \delta} \tag{2}$$

The surface coverage of polymer on each electrode can be calculated with equation 3 were Γ is the surface coverage of species i.

$$\Gamma_i = \frac{Q_i}{nFA} \tag{3}$$

2.3   UV-Vis Analysis

UV-Vis spectroscopy is a technique used to study adsorption by measuring the intensity of the light that is passing through a sample. The results can reveal information about the sample. When it comes to aromatic systems, conjugated double-bonds cause the absorption spectrum to shift towards longer wavelengths (lower frequency and lower energy), this makes UV-Vis a useful tool when studying conjugated systems. Figure 2 shows the principle behind the UV-Vis setup.
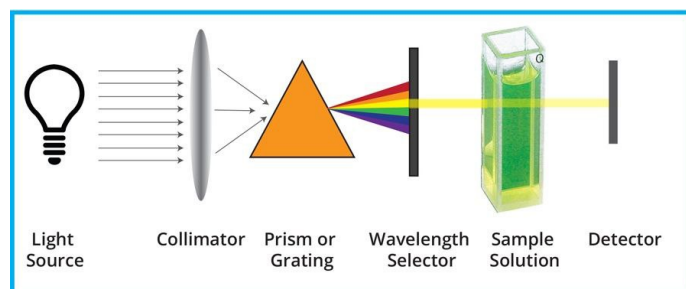

Figure 2: Visual representation of the steps mentioned above

2.4   Experimental setup

The electrode configuration and preparation of electrolyte solutions will be described in the following section, along with the safety considerations for the experiments.

2.4.1   Three-electrode setup

The electrochemical measurements were performed in a three-electrode configuration, consisting of a working electrode (a transparent conducting fluorine doped tin oxide, FTO, electrode), a counter electrode (platinum wire), and a reference electrode (Ag/AgCl with 1 M KCl filling solution). The electrode configuration is shown on figure 3.

Figure 3: Electrode configuration, from left to right we can see; Platinum wire, FTO, Reference Electrode.

2.4.2   Preparation and chemicals

For the experiments two different electrolyte solutions were prepared. H_2SO_4 and aniline were diluted with Milli-Q water for a 25mL 1 M H_2SO_4 solution and a 25 mL 0.2 M aniline and 1 M H_2SO_4 solution. Shown on figure 4.

All chemicals were handled wearing nitrile gloves, safety goggles, and lab coats, as can be seen on figure 4. In addition electrochemical measurements and electrolyte preparation were performed in fume cupboards.

Figure 4:
Left: measuring the right amount of H_2SO_4 before pouring it into the glass.
Right: measuring the right amount of Aniline before adding it to the H_2SO_4

Prior to performing the experiments the electrolyte solutions were degassed with argon for 10 minutes. The argon line was then held above the electrolyte for the duration of the experiments to maintain an inert atmosphere in the glass. The electrodes were then mounted into the electrolyte and connected to the potentiostat. UV-Vis optical absorption spectroscopy measurements were performed outside the fume cupboards, with the setup shown on figure 5.
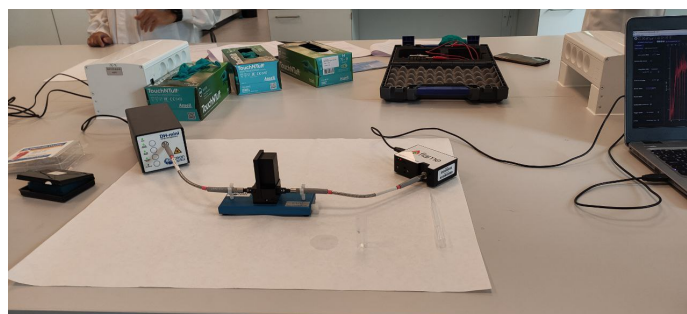

Figure 5: *From left to right;* light source connected to a wavelength selector that shoots light onto the sample submerged into H_2SO_4 which passes through a detector and is finally processed by the computer.

3   Results

All experimental results from the CV and CA, as well as calculations and data plots are presented in the following section together followed by the UV-vis analysis.

3.1   Electrodeposition

The electrodeposition and formation of PANI film on the FTO electrodes were done both electrodynamically through CV and electrostatically through CA. The voltammograms from the electrodeposition experiments are shown on figure 6 and 7.
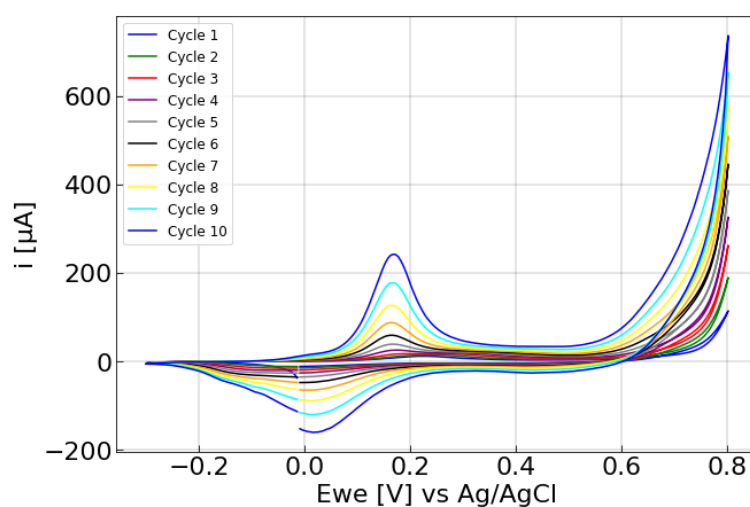

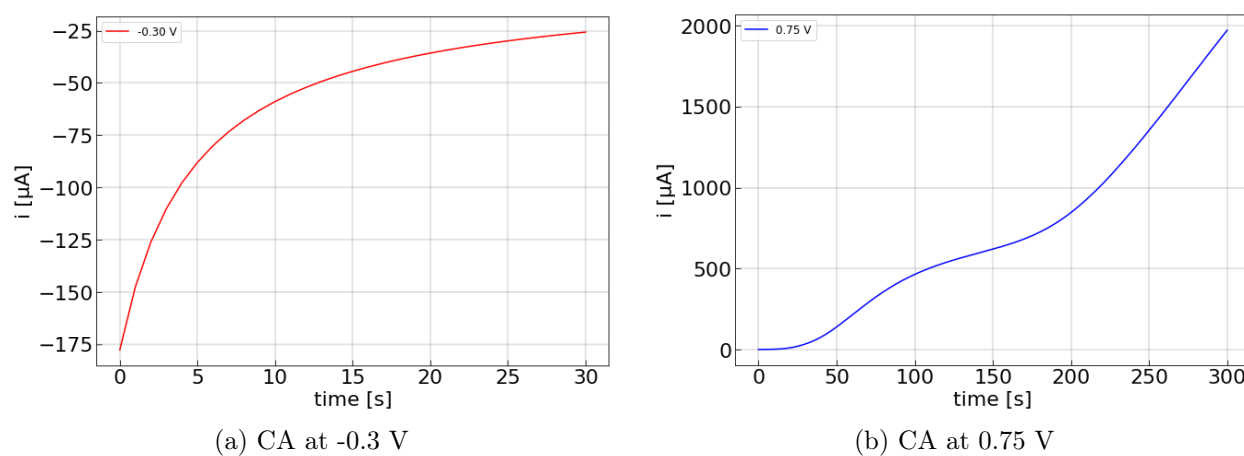Figure 6: Voltammogram from potentiodynamic electrodeposition in 0.2 M aniline and 1 M H_2SO_4 at 50 mV/s.

(a) CA at -0.3 V

(b) CA at 0.75 V

Figure 7: Potentiostatic electrodeposition in 0.2 M aniline and 1 M H_2SO_4

After the electrodeposition, the electrodes were cycled in the 1 M H_2SO_4 electrolyte to the fully oxidised and reduced state. Shown on figure 8. The calculated charges upon complete oxidation and reduction of the electrodes are presented in table 1.
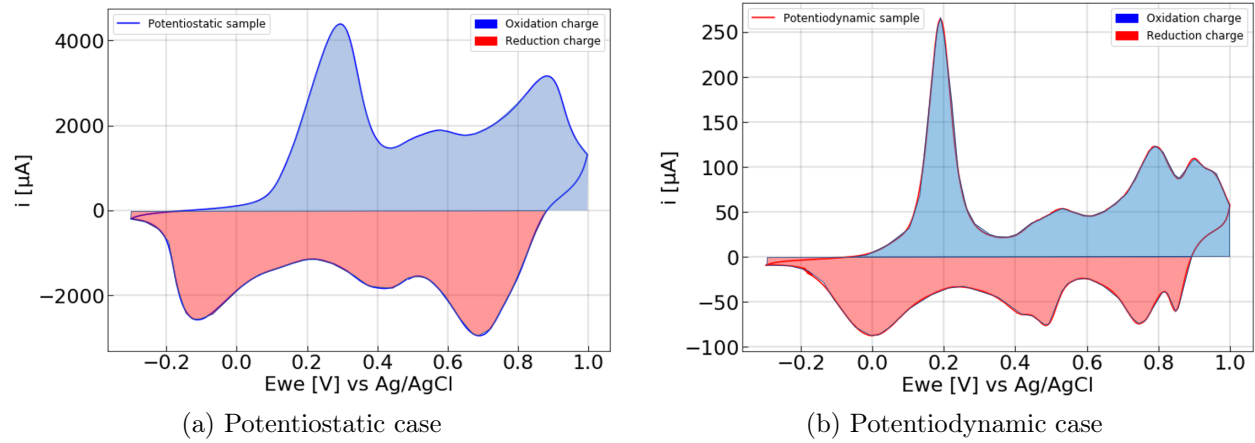

(a) Potentiostatic case   (b) Potentiodynamic case

Figure 8: CVs of the treated electrodes to full oxidation and reduction in 1 M H$_2$SO$_4$ at 50 mV/s, surface charges are represented by shaded areas.

Table 1: Total charge obtained from electrodeposition experiments

	CV	CA
Oxidation charge [μC]	14249	41070
Reduction charge [μC]	11057.6	38193

Based on the calculated charge values the mass, film thickness, and surface coverage of polymer on each electrode were calculated using equation 1 - 3. Calculations were done assuming a density of 1.33 g cm^{-3} for polyaniline.

The following calculations are for the potentiodynamically treated electrode using the oxidation charge obtained from the CV.

The deposited mass, m, of the polymer:

$$m = \frac{93.13 \text{ g/mol} \times 14249\mu\text{C}}{2 \times 96485 \text{ C/mol}} = 6.87674147\mu\text{g} \tag{4}$$

The film thickness, d, of the polymer layer on the electrode:

$$d = \frac{6.87674147\mu\text{g}}{1.2 \text{ cm}^2 \times 1.33 \text{ g/cm}^3} = 43.0873526 \text{ nm} \tag{5}$$

The surface coverage, Γ, of polymer on each electrode:

$$\Gamma = \frac{14249\ \mu\text{C}}{2 \times 96485\ \text{C/mol} \times 1.2\ \text{cm}^2} = 6.15335326 \cdot 10^{-8}\ \text{mol/cm}^2 \qquad (6)$$

Results for the complete set of oxidation and reduction charges are presented in table 2.

Table 2: Calculated values after electrodeposition

	CV		CA	
	Ox charge	Red charge	Ox charge	Red charge
Mass [μg]	6.877	5.337	19.82	18.43
Film thickness [nm]	43.09	33.44	124.2	115.5
Surface coverage [mol/cm^2]	$6.153 \cdot 10^{-8}$	$4.775 \cdot 10^{-8}$	$17.74 \cdot 10^{-8}$	$16.49 \cdot 10^{-8}$

3.2 Scan rate dependence and redox states

The potentiodynamically treated electrode was cycled at varying scan rates in order to determine the peak current dependence on scan rate for the first redox process, the results are presented in figure 9.
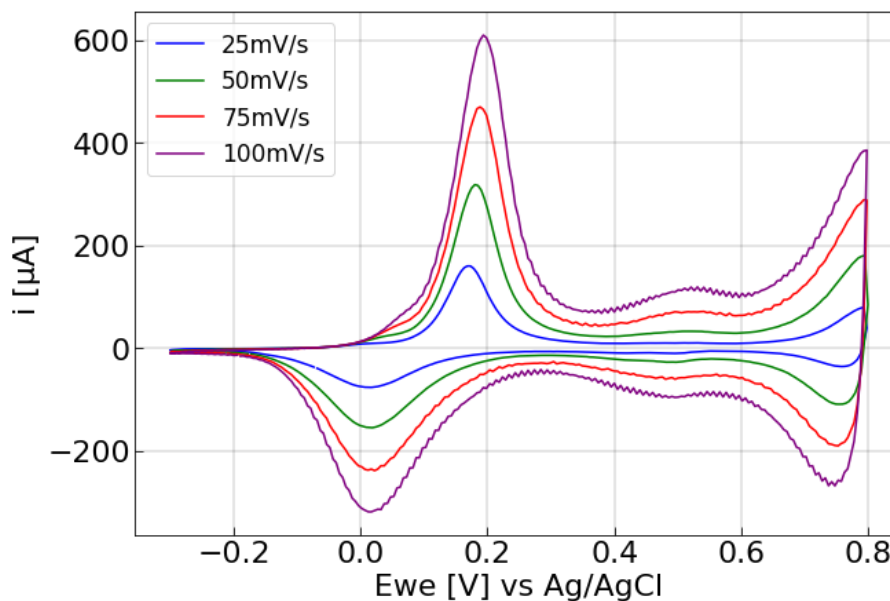

Figure 9: CV of potentiodynamic treated electrode in 1 M H_2SO_4 at varying scan rate.

The peak current was then plotted against the scan rate as shown in figure 10. Based on the points a linear regression was performed giving R-squared values of 0.996 and 0.997 for the oxidation and reduction peaks respectively.
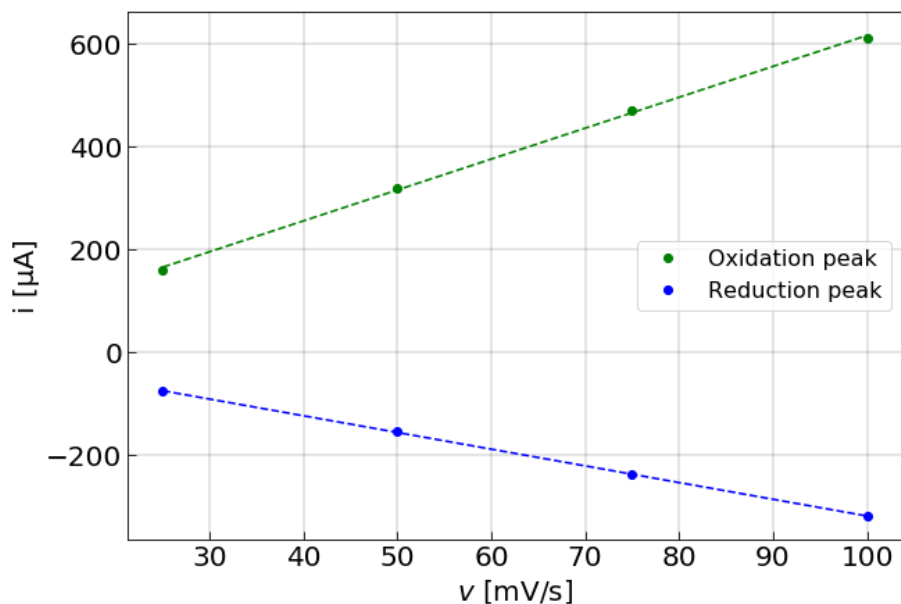
Figure 10: Linear regression of scan rate dependency on peak current

During CV, the PANI film oxidises and reduces to differet redox states. The different forms of the PANI film is indicated on figure 11.
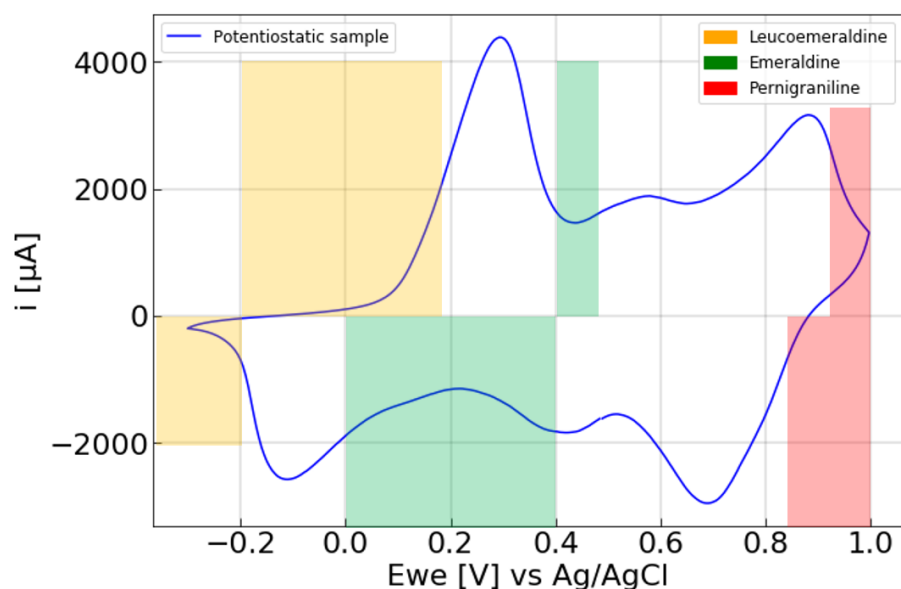

Figure 11: Voltammogram indicating different redox states of the PANI film.

The potentiostatically treated electrode was cycled between 0.3 V and 1.2 V in order to see how high anodic potentials would affect the stability of the sample seen on figure 12.
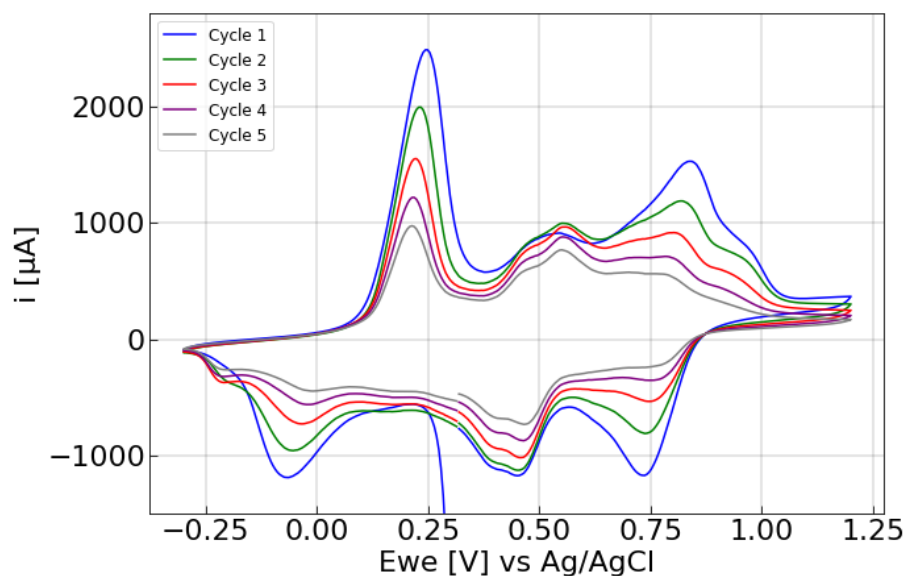
Figure 12: Voltammogram of potentiostatic treated electrode in 1 M H_2SO_4 at 25 mV/s.

3.3   UV-Vis

From the UV-Vis analysis the following absorption spectra for potentiostatic holds at -0.3 V, 0.35 V and 0.8 V vs Ag/AgCl were recorded and are presented in figure 13. Then, adsorption spectrum for the CV at 1.2 V was recorded and is presented in figure 14. Finally, both UV-Vis adsorption spectra have been merged in a single plot to highlight the results obtained as represented in figure 15.
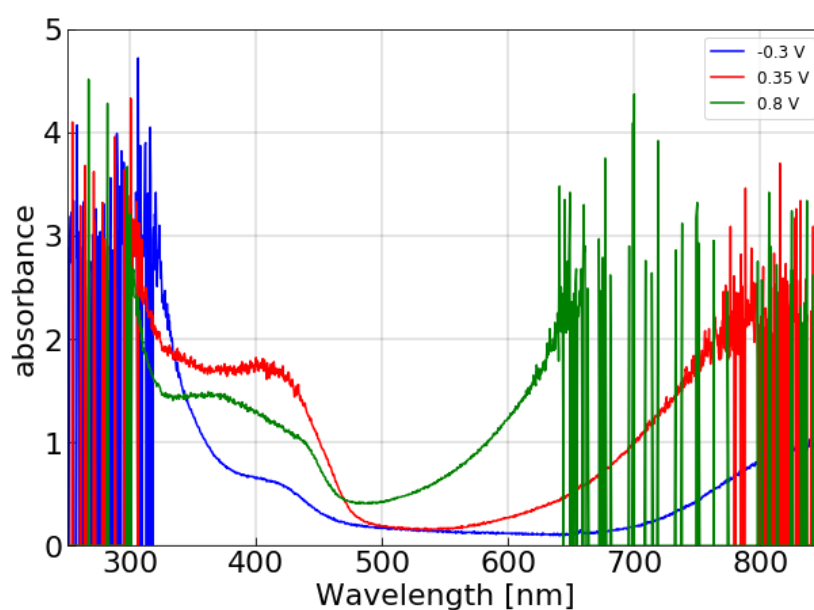

Figure 13: Absorption spectra at potentiostatic holds of 0.3 V, 0.35 V and 0.8 V
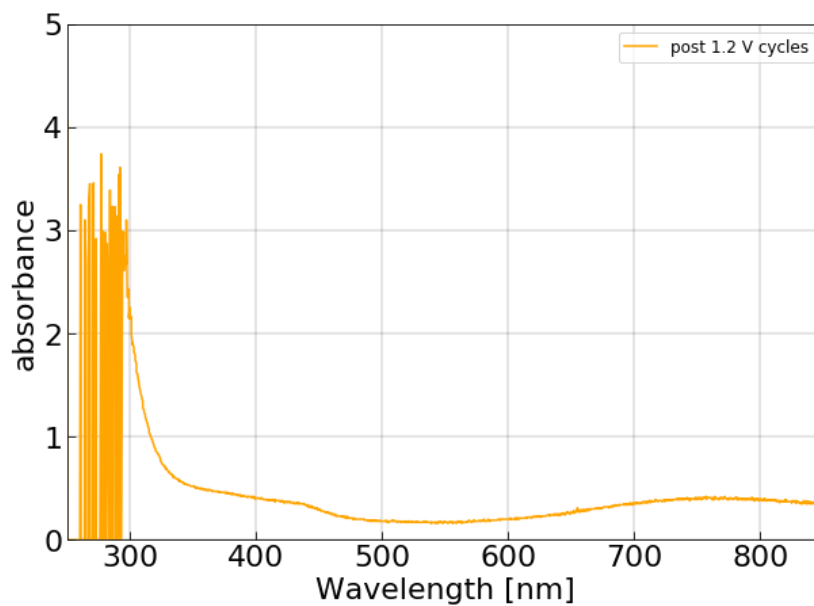
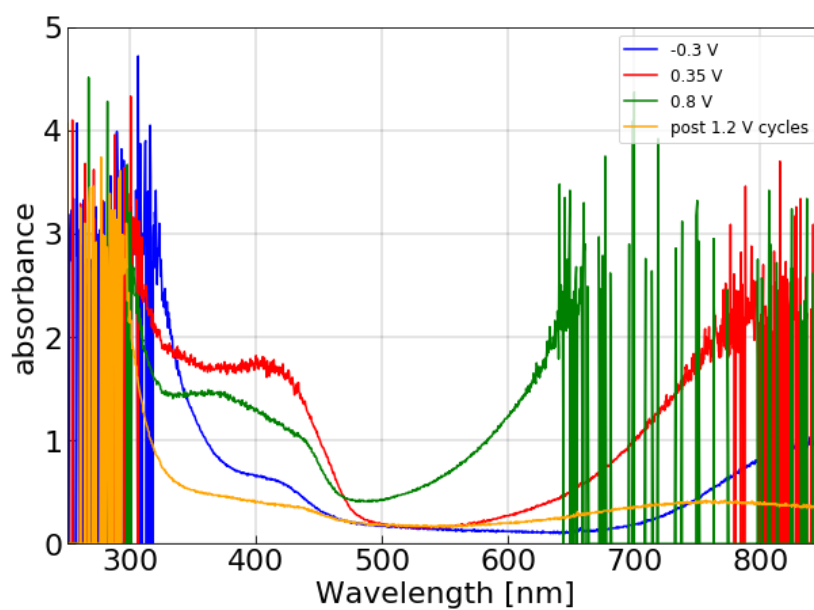Figure 14: Absorption spectrum of CV at 25 mV/S between -0.3 V and 1.2 V vs Ag/AgCl

Figure 15: Absorption spectra of potentiostatic holds combined with the absorption spectrum after CV

4 Discussion

From the results in figure 1 and 3 it can be seen that the induced current from the potentiostatic hold reaches magnitudes 4 times larger than the potentiodynamic electrodeposition. This is reflected once again in the calculated charges for the fully oxidised and reduced forms. This is partly due to the fact that when performing CV, the film is continuously being oxidised and reduced and thus only built upon little by little for every cycle. While the chronoamperometry continuously holds an oxidative potential and the film is then constantly being built up by diffusive species from the solution. After electrodeposition, when rinsing the treated electrodes soluble material was washed off. This could be because oxidation of the reduced form of the PANI film will attract anions and accompanying solvent/electrolyte molecules, these solvent molecules and possible attracted anions could be washed away during rinsing of the electrodes.

Regarding the scan rate dependence, the linear regression depicted in figure 10 show that both the reduced and the oxidized form can be assumed to be directly proportional to the scan rate. From this it can be concluded that the polyaniline is surface confined and fully absorbed onto the surface of the electrode.

On figure 12 it can be seen that the current is lessening with each cycle. This can be attributed the fact that at too high anodic potentials polyaniline starts to over-oxidise leading to degradation of the PANI film, resulting in less polymer on the surface of the electrode and thus fever electrons can be transferred and less current conducted.

The aromatic systems and double bonds in leucoemeraldine, emeraldine, and pernigraniline displays adsorption around the 400-450 nm range. There is noise from the 650, and 800 nm point on the 0.8 V and 0.35 V measurements, respectively. This might be attributed to the electrode being askew inside the cuvette during measurements. From the comparison of the UV-Vis spectra, an increase in the adsorption at short wavelengths for the 0.35 V potentiostatic hold compared to the -0.3 V and the 0.8 V is evident. The adsorption of the 0.8 V measurement might be lower than the 0.35 V because the film is already starting to over-oxide and forming quinone like structures. After the 1.2 V cycles the sample showcased a significant decrease in adsorption at the 400-450 nm range, this can be attributed to the over-oxidation of PANI film, resulting in less molecules with double-bonds and extended conjugation. We also see the noise at the 650 and 800 nm points are gone, which might be because the sample was oriented perpendicular to the light source in this measurement.