CHAPTER 111

EXPERIMENTAL PROCEDURE

3.1 materials

3.1.1 Monomers

Monomers such as Aniline, Toluidine, O-Anisidine and Ethyl-aniline were produced from E.Merck, (India), Mumbai.

3.1.2 Solvents

Since all the experiments were carried out in aqueous medium, water was the only solvent used.

3.1.3 Electrolytes

Sulphuric acid (H$_2$SO$_4$), Hydrochloric acid (HCl), Hydro-fluoboric acid (HBF$_4$) and Perchloric acid (HClO$_4$) were sourced from Rankem., Mumbai, India and used for preparation of the saturated calomel electrode (SCE).

3.1.4 Cell design used

The design of electrochemical cells used for voltammetric experiments depends on technique and on the requirements of the electrochemical system being studied (96). Here, a standard three-electrode cell configuration was used. A small glass cell body is clamped to a Teflon top provided with ports for the electrodes. The electrodes used were,

a) Working electrode - Custom made BAS platinum electrode of area 0.02 cm$^2$

b) Reference electrode - Saturated calomel Electrode (SCE) and

c) The counter electrode - a platinum electrode of area 5 cm$^2$
3.2 Method of purification employed

All the monomers used for experiment, Aniline, Toluidine, 0-Anisidine and ethyl-aniline were triply distilled under vacuum and the distillates were kept in an airtight bottle covered with a black paper under refrigeration to avoid decomposition. Water used in all the investigation was obtained from the Millipore apparatus. Prior or each experiments, the working platinum electrode was cleaned as per the standard procedure (97) and polished to a mirror finish using emery graded sheets.

3.3 Instrumentation used

3.3.1 Cyclic voltametry

Cyclic voltametry is performed using a Bio-analytical system, BAS 100A(U.S.A), which has the features, as described in the Fig.3.1. The data were readable in the monitor and can be plotted as shown in the following block diagram.
Figure 3.1 Block Diagram of the BAS-100A Electrochemical Analyzer.
3.3.2 AC Impedance

AC impedance measurement were done using the EG & G instrument. Princeton Applied Research Model 6310 Electrochemical impedance Analyzer, which can measure the response of an electrochemical system to ac excitations at frequencies ranging from $50^\text{Hz}$ to $100 \text{KHz}$, and the results can be stored on a disk and processed. This analyzer was interface with HCL busy bee IBM 513M model no 486 through an IEEE-488 (GPIB) interface. The output data was collected and graphs was printed using an Inkjet printer of HP Model 690C.

The model 6310 allows us to use two different measurement techniques: single-sine and multi-sine. Single-sine measurement technique covers the frequency range from 10Hz to 100KHz. During very low frequency experiments, which take a very long measurement times, the electrochemical system that we are observing may drift or even actively corrode. To avoid such erroneous data multi-sine techniques can be used. Multi-sine technique covers the frequency range from $50^\text{Hz}$ to 10Hz and which run approximately half the time of the single-line technique.

3.4 Method of Electropolymerization

3.4.1 Potentiodynamic mode

Thin films (thickness $\leq 1\mu m$) of various polymers were thus grown by cyclic voltammetric technique from the respective monomers aniline, toluidine, o-anisidine and ethyl-aniline on a Pt electrode of area 0.02 cm$^2$. The electrolytic solution for the polymerization contained monomer of concentration 1M (aniline,
toluidine, O-anisidine and ethyl aniline) in 2M concentration of H₂SO₄ / HCl / HBF₄ and HClO₄ in a three electrode cell arrangement as described previously. The counter electrode was a Platinum electrode (area 5cm²) and the reference electrode was a saturated calomel electrode. The solutions were prepared using Millipore water and all experiments were performed at room temperature. The potential of the electrode was cycled from 0V to 0.8V vs see for the first cycle and subsequent cycle was excursioned up to 0.7V throughout electropolymerization. Variation of Potentiodynamic cycles was effected to produce the film of particular thickness 119 nm, 159 nm, 199 nm, 399 nm and 1000 nm. A scan rate of 50mV/s for all the Potentiodynamic experiment was run. At the end of the experiments, the deposited films were washed thoroughly with Millipore water and dried prior to further measurement.

Cyclic Voltammetry consists of cycling the potential of an electrode, which is immersed in an unstirred solution and measuring the resultant current. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to the potential excitation signal. The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (ipa), cathodic peak current (ipc), anodic peak potential (Epa) and cathodic peak potential (Epc). One method for measuring ip involves extrapolation of a baseline current as shown in Fig 3.2. The establishment of a correct baseline is essential for the accurate measurement of peak currents. A representation of CV response is shown in Fig 3.2.
3.4.2 AC Impedance Technique

The dried films that were obtained through potential dynamic technique were then transferred to a monomer-free electrolyte. Before making impedance measurements the conducting polymer films which were kept in monomer-free electrolyte was equilibrated at the potential at which the Ac Impedance response were to be collected for 5 minutes. This procedure was repeated for all the potentials at which response of Ac Impedance spectra were required.

For Ac impedance measurements the potential of the electrode is fixed and the frequency range is covered from 100KHz to 0.1 Hz. The applied ac perturbation signal is 5mV in amplitude. The response to the applied perturbation which is sinusoidal, can differ in phase and amplitude from the applied signal. Measurements of the phase difference and the amplitude (i.e., the impedance ) permits analysis of the electrode process in relation to contributions from discussion, kinetics, double layer, coupled homogeneous reactions etc, the impedance is the proportionality factor between potential and current. Since they have phases, we can divide the impedance into a resistive part, R,
where the voltage and current are in phase, and a reactive part, $X_c=1/\omega C$, where the phase difference between current and voltage are out of phase (i.e., 90°)

Once the experiment is complete the raw data at each measured frequency consists of,

1. the real frequency of voltage ($E'$)
2. the imaginary component of voltage ($E''$)
3. the real component of current ($I'$) and
4. the imaginary component of current ($I''$)

From this data it is possible to compute the phase shift of response 0. The real impedance, $Z'$, the imaginary impedance, $Z''$, and the total impedance $|Z|$ for each applied frequency.

A variety of formats can be used to plot these data. The standard plots used to calculate the required data are,

a) Nyquist plot
b) Bode $|Z|$ plot

a) Nyquist plot

This is one of the popular techniques for evaluating ac impedance data. Here, the imaginary component of impedance ($Z''$) is plotted versus the real component of impedance ($Z'$) for each excitation frequency. This plot could be used to compute the values of $R_s$, $R_{ct}$, $C_{diff}$, $R_o$ and $C_o$
R_s – Solution resistance
R_cl – Charge transfer resistance
C_dl – Double layer capacitance
R_o – Low frequency resistance
C_o – Low frequency capacitance (redox capacitance)

R_s is the initial resistance or the solution resistance which is responsible for the initial shift from the origin and can be measured directly from the semi-circle initial point on the impedance real axis.

R_cl is the charge transfer resistance and can be calculated from the radius of the semi-circle.

C_dl is the double layer capacitance and is measured from the maximum frequency on the semi-circle.

R_o is the low frequency resistance and is obtained by drawing a vertical line intersecting the impedance real axis.

C_o is the redox capacitance corresponding to R_o.

b) Bode [Z] plot

In this plot the frequency component is plotted against the |Z| impedance component.
The $|Z|$ Vs. frequency curve can yield values of $R_s$ and $R_{ct}$ from the initial point and the final point in the curve. By extrapolating a straight line drawn on the “break point” region to the $|Z|$ axis at $\omega=1$ we can obtain the value of $C_{dl}$, where

$$
|Z| = \frac{1}{\omega C_{dl}} \quad \text{(1)}
$$

Since $\omega=1$, $C_{dl} = \frac{1}{|Z|} \quad \text{(2)}$

This plot is used to calculate values of only one time constant, i.e., for a simple electrode reaction.

This experimental Ac Impedance response of thin polyaniline film measures, though can be interchanged to any one of the above forms, the analysis was mainly processed from Nyquist plot.

### 3.5 Characterization of films

#### 3.5.1 Cyclic Voltammetry Characterization

#### 3.5.1.1 Thickness measurement

The CV response obtained was used to estimate the thickness of the electro polymerized polymer film grown on Pt as follows; the principle estimation of thickness (98) was based on the faradaic charge involved in the reversible oxidation process as per the standard procedure reported earlier. The formula used for calculating the thickness was,
where $Q_{\text{redox}} = \text{redox charge}$

- $M = \text{Molecular mass}$
- $x = \text{ratio of oxidized polymer units (0.3)}$
- $F = \text{Faraday number (96500)}$
- $r = \text{density}$

$Q_{\text{redox}}$ is obtained from the area under the oxidation and reduction peaks of a cyclic voltammogram.

$$Q_{\text{redox}} = I \times t$$

$I = \text{current (which is measured from the height of the redox peaks)}$

$t = \text{time (scan rate)}$

### 3.5.1.2 Method of redox peak identification

As per the description available in literature as shown in Fig.3.2 the peak current redox peak were identified and used for recording AC Impedance response of the films. Though further analysis of the CV responses observed was possible based on the principles of electrodics (99) the above mentioned analysis alone was focused to generate precursor data needed for the diagnosis of the films through AC Impedance method e.g.: identification of potential window. Moreover, the analysis based on electrodics is beyond the objective of the investigation chosen here.
3.5.2 AC Impedance characteristics of thin film

The AC Impedance response was measured in the form of Nyquist plot but the data are interchangeable to other forms such as bode \([Z]\) plot, bode phase angle plot, capacitance plot, admittance plot etc. The determination of basic parameters like \(R_{ct}\), \(C_{di}\), \(C_0\) and \(R_0\) were all determined from the Nyquist plot of the Ac Impedance response. To localize these parameters custom made Ac Impedance software M398 was provided by EG&G. This facilitated in processing all the data required for various analysis. The basic data obtained in this measurements was further processed using Microcal origin, Microsoft excel to generate data for the study of the influence of redox potential window on the characteristics of thin polymer films. Further these data were also fit into equivalent circuit model using another software by name “Boukamp” provided by the EG&G Instruments. Both simulated and experimental data were compared and appropriate analysis was made as highlighted in Chapter 4.

3.5.2.1 Boukamp software

The data that were obtained from Ac Impedance measurements can be fit together to form an equivalent circuit using the Boukamp software(101). Boukamp is exclusive software used for fitting equivalent circuit models to the measured impedance parameters. After collecting the data, we can assume an equivalent circuit and NLLS fit is made using Boukamp program. The measured data is fitted against the simulated values for that particular equivalent circuit and the fitted error is given. If the measured values and the simulated values do not match properly we have to switch over to other equivalent circuits till the appropriate equivalent circuit is fitted.