CHAPTER-2

Experimental
This chapter describes the instrumentation, devices and the electrode systems used, in cyclic and stripping voltammetric experiments, and the procedures followed in the present work.

CYCLIC VOLTAMMETRY

2.1. Potentiostat

A potentiostat is an electronic device that controls the voltage difference between a working electrode and a reference electrode. The potentiostat implements this control by injecting current into the cell through an auxiliary, or counter, electrode. All the three electrodes are contained in an electrochemical cell. In almost all applications, the potentiostat measures the current flow between the working and auxiliary electrodes. The controlled variable in a potentiostat is the cell potential and the measured variable is the cell current [1].

Basically, a potentiostat must be able to bring the potential of the working electrode (with respect to the reference electrode) to the desired level in a short enough time. The time taken by the potentiostat for controlling the working electrode potential is called the rise time (Fig. 2.1).

2.1.1. The current to voltage converter

The Current to Voltage (I/E) converter in the simplified schematic measures the cell current. It forces the cell current to flow through a current measurement resistor, $R_m$. The voltage drop across $R_m$ is a measure of the cell current.

The I/E converter's bandwidth depends strongly on its sensitivity. Measurement of small currents requires large $R_m$ values. Stray (unwanted) capacitance in the I/E converter forms an RC filter with $R_m$, limiting the I/E bandwidth. No potentiostat can accurately measure 10 nA at 100 kHz.
2.1.2. The Signal

The signal circuit is a computer controlled voltage source. It is generally the output of a Digital to Analog (D/A) converter that converts computer generated numbers into voltages. Proper choice of number sequences allows the computer to generate constant voltages, voltage ramps, and even sine waves at the signal circuit output. When a D/A converter is used to generate a waveform such as a sine wave or a ramp, the waveform is a digital approximation of the equivalent analog waveform. It contains small voltage steps. The size of these steps is controlled by the resolution of the D/A converter and the rate it at which it is being updated with new numbers (Fig. 2.2).

Voltammetric experiments were performed with Autolab PG STAT 20 (The Netherlands) coupled to a Metrohm make VA stand 663 electrode system comprising glassy carbon as working electrode, Platinum as auxiliary electrode and SCE as reference electrode. The PG STAT was driven by GPES software, at Analytical Chemistry Division, Bhabha Atomic Research Center, Mumbai, India. The instrument incorporates a high speed, high accuracy and an electrolysis mode that consists of high-gain operational amplifier with circuits for controlled potential. Also the electrochemical experiments were carried out using potentiostat Electroanalyser model EA 201 from Chemilink Systems, Mumbai, India.

2.2.1 Electrodes and Electrolysis Cell

In the present work conventional three electrodes system was used i.e. working/auxiliary/ reference electrodes. The reference electrode used is saturated calomel electrode (SCE) or silver/silver chloride (Ag/AgCl), which is often isolated from the solution by a salt bridge to prevent contamination by leakage from the reference electrode. The platinum foil used as auxiliary and working electrodes used are, HMDE,
carbon paste electrode, CPE modified with fullerene or carbon nanotube paste electrodes. The temperature of cell solution was maintained at 25.0 ± 0.1°C.

2.2.2. Electrolysis Cell

Electrochemical cell consists of a glass container with a cap having holes for introducing electrodes and nitrogen. The cell is then maintained oxygen free by passing nitrogen over the solution. The auxiliary, working electrodes and reference electrodes are placed directly into the solution. Since the limiting (or peak) current in any type of voltammetry is temperature dependent, the cell is thermostated for the required temperature (295 K) (Fig.2.3).

2.2.3. Pretreatment of carbon nanotubes

Before use, the CNT material was submitted to various chemical-physical procedures to remove graphitic nanoparticles, amorphous carbon, and catalyst impurities [2-4]. Following one of the purification methodologies and to eliminate metal oxide catalysts, the oxidized amount of carbon nanotubes was dispersed in 60 mL of 6.0 M HCl for 4 h under ultrasonic agitation, washed until the pH of the solution was neutral and finally dried.

2.2.4. Preparation of carbon paste electrode

The carbon powder (particle size 50 mm, density 20-30g/100mL) was mixed with the binder, silicone oil, in an agate mortar and homogenized using the pestle. The electrode consisted of a teflon well, mounted at the end of a teflon tube. The prepared paste was filled into the teflon well. A copper wire fixed to a graphite rod and inserted into the Teflon tube served to establish electrical contact with the external circuit. The electrode surface of the working electrode was renewed mechanically by smoothing some
paste off and then polishing on a piece of transparent paper before conducting each of the experiments. The experiments were performed in unstirred solutions.

2.2.5 Preparation of fullerene modified carbon paste electrode

Coating of the C$_{60}$ onto CPE: Fullerene was coated on to the tip of the electrode by physical vapor deposition method using the vacuum coating unit, model 12a 4D; Hind High Vacuum Company Pvt. Ltd Bangalore, India.

Physical vapor deposition of C$_{60}$ Films

Fullerene was coated on to the tip of the electrode by physical vapor deposition method [5 - 10] using the vacuum coating. The electrode and a glass slide were mounted firmly on the substrate holder situated inside the vacuum chamber. The electrode and glass slide was kept at a distance of 4.5 cm from the source to get the uniform coating. About 1 mg of the fullerene sample was taken in the molybdenum boat. A dimple was made to the molybdenum boat to keep the sample to act as a point source. The boat was connected to the electrodes for heating. The vacuum inside the chamber was made to $10^{-5}$ m bar (1 m bar = 0.76 Torr). When high current is applied to the molybdenum boat through the electrodes, the sample gets evaporated. The evaporation was made at the rate of 1 Å/sec, which was controlled by applying the current. The C$_{60}$ was coated to a desired thickness, which was monitored using a quartz crystal microbalance sensitive to mass changes of a thin metal electrode on a piezoelectric quartz crystal. Pure solid C$_{60}$ forms a hexagonal lattice with a nearest neighbor distance close to 10 Å [11, 12].

2.2.6 Preparation of C$_{60}$/CP and MWCNT/CP Electrodes.

The modified electrode was prepared by mixing MWCNT and graphite powder with a given wt% ratio (wt% of MWCNT to graphite powder) in silicone oil was
transferred to the mortar and pestle for hand mixing. The C$_{60}$/CPE was prepared in a similar way by mixing C$_{60}$ and graphite powder with silicone oil. A portion of the resulting paste was packed firmly into the cavity (3.0mm diameter) of a teflon tube. The electrical contact was provided by a copper wire connected to the paste in the inner hole of the tube. The paste was kept at room temperature in a desiccator until used. A new surface was obtained by smoothing the electrode onto a weighing paper.

2.2.7 Preparation of carbon nanotube paste electrode

Carbon nanotube paste electrode prepared from MWCNT (0.22 g) with silicone oil (0.08 mL) and the procedure for making the paste is same as explained above.

2.2.8 XRD Details:

The PHILIPS TW 3710 X-Ray recorder with Cu-Kα (λ=1.54 nm) radiations were used for the XRD studies.

2.2.9 Scanning Electron Microscopy (SEM)

Micrographs of the electrode surfaces were obtained by using a JEOL-JSM-35 LF scanning electron microscopy (SEM).

2.3. Electrochemical measurement procedure

Electrochemical measurements were carried out with a standard electrochemical cell fitted with three electrode system. The supporting electrolyte was placed in the cell and the solution was purged with the flow of N$_2$ gas for 5 min. Background voltammogram for the supporting electrolyte was recorded, to make sure that no impurity or electroactive species in the supporting electrolyte. The electroactive species of under study was added and the first potential sweep was registered.
Fig. 2.1. Experimental representation of instrumentation setup for cyclic voltammetry.

Fig. 2.2. Overview of the potentiostat components connected with three electrode system.

Fig. 2.3. A typical single compartment cell for cyclic voltammetric experiments.
STRIPPING VOLTAMMETRY

2.4. Apparatus

2.4.1. Potentiostat

Voltammetric experiments were performed with Autolab PG STAT 20 (The Netherlands) coupled to a Metrohm make VA stand 663 electrode system comprising HMDE as working electrode, Platinum as auxiliary electrode and Ag-AgCl as reference electrode. The PG STAT was driven by GPES software, at Analytical Chemistry Division, Bhabha Atomic Research Center, Mumbai, India. The instrument incorporates a high speed stirrer to stir electrolytic solution while the metal ions or any electroactive species of interest, deposition on the surface of the working electrode.

2.5.1. Electrodes and Electrolysis Cell

In the present work three electrode system was used i.e. working / auxiliary / reference electrodes. The reference electrode used was Ag/AgCl, Platinum wire used as auxiliary electrode and working electrode was hanging mercury drop electrode (HMDE). Electrochemical cell consists of a glass container with a cap having holes for introducing electrodes and nitrogen. The cell is then maintained oxygen free by passing nitrogen over the solution (Fig.2.4).

2.4.3. Hanging mercury drop electrode (HMDE)

Mercury is widely use in the practice of electroanalytical chemistry both for working electrodes and for reference electrodes, in the latter case usually as electrode of the second kind. The use of mercury is nearly an ideal choice for the construction of working electrodes of several reasons [13]. Mercury has a large liquid range (-38.9 to 356.9° C at normal pressure) and therefore electrodes of various shapes may be
easily prepared. The surface of such electrodes is highly uniform and reproducible if the mercury is clean [14]. One of the most important reason for the application of mercury to the construction of working electrodes is the very high overvoltage for hydrogen evolution on such electrodes. Relative to a platinum electrode, the overvoltage of hydrogen evolution under comparable conditions on mercury will be $-0.8$ to $-1.0$ V. It is therefore possible in neutral or (better) alkaline aqueous solutions to reduce alkali metal cations at mercury electrodes, giving relatively well define voltammetric waves at potentials more negative than $-2.0$ V vs. SCE [15].

The following types of mercury electrodes have been widely used for voltammetry; dropping mercury electrode (DME), hanging mercury drop electrode (HMDE), streaming mercury electrode (SME), and mercury film electrode (MFE) and static mercury drop electrode (SMDE).

**2.5. Electrochemical measurement procedure**

Electrochemical measurements were carried out in the standard electrochemical cell fitted with the VA663 stand. A known amount of acetate buffer was taken as the supporting electrolyte. The solution was purged with the flow of $N_2$ gas for 5 min. The blank voltammogram is recorded by carrying out deposition at $-1.25$ V for 120s followed by scanning the working electrode from $-1.25$ to $0.1$ V in differential pulse mode. The experimental parameters taken in this study were viz; pulse amplitude is $50$ mV. Deposition time 120 s, equilibration time 10 s, step potential 10 mV, modulation amplitude 20 mV, modulation time 0.05 s, interval time 0.2 s. An aliquot of the sample solution (25 ml) containing Cu, Pb, Cd and Zn was taken in an electrolytic cell, Four peaks were observed for Cu, Pb, Cd and Zn respectively. Peak currents corresponding to
the different peak positions were measured. Known volume of standards of Cu, Pb, Cd and Zn were added to the cell and the same procedure as mentioned above was repeated. By repetitive addition of standards, the calibration plots for all the elements were constructed. The peak currents for the samples were also obtained by employing similar procedure as described for standards.

Fig. 2.4. A typical single compartment cell for stripping voltammetric experiments.
References

1. http://chem.ch.huji.ac.il/~eugeniik/electrochemical_tutorials.htm


