

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Sample Preparation

3.1.1 Samples to be prepared

- a) lithium nickel cobalt oxide,
- b) manganese rich lithium nickel cobalt manganese oxide,
- c) cobalt rich lithium nickel cobalt manganese oxide, and
- d) lithium nickel cobalt manganese aluminium oxide

The purity of the chemicals used in this work is at least 95%.

3.1.2 Chemicals Used

Chemical Name	Chemical Formula	Molecular Weight
a) Lithium Acetate Dihydrate	$\text{LiCH}_3\text{CO}_2 \cdot 2\text{H}_2\text{O}$	102.02g
b) Nickel Nitrate Hexahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	290.81g
c) Cobalt Nitrate Hexahydrate	$\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$	291.03g
d) Manganese Acetate Tetrahydrate	$\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$	245.09g
e) Aluminum Florida Trihydrate	$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$	138g

3.1.3 Sample Preparation

- i) Amounts of chemicals used

Chemical	Sample	S1	S2	S3	S4
$\text{LiCH}_3\text{CO}_2 \cdot 2\text{H}_2\text{O}$		24.48g	16.32g	8.16g	16.32g
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		12.21g	8.14g	4.07g	8.14g
$\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$		5.238g	1.164g	1.264g	1.164g
$\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$			1.96g	0.49g	0.98g
$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$					0.552g

In terms of atomic percentage, the ratio of Li:Ni:Co for sample S1 is 80:14:6, the ratio of Li:Ni:Co:Mn for sample S2 is 80:14:2:4 and for sample S3 is 80:14:4:2 and the ratio of Li:Ni:Co:Mn:Al for sample S4 is 80:14:2:2:2. The procedure to synthesize these samples is as shown in the Flow Chart (Figure 3.1).

The chemical required are weighed and dissolved in distilled water. To minimize the heating time to evaporate water in the mixture solution, the distilled water used is minimum in volume (just enough to dissolve all the salts)

The chemical solution are then mixed to form a homogeneous solution. To this homogeneous solution is then added 1M tartaric acid, until a colloidal precipitate is obtained. The colloid was heated at 100°C with a heater and magnetic stirrer to ensure a homogeneous heating. Water in the colloid will evaporate and leave the solid to form a powdery precursor.

The precursor was then baked for 5 hours. This is to ensure a homogeneous heating. Three baking temperatures 400°C, 800 °C and 950°C were used. Heating will make the precursor powder black.

3.2 Materials Characterization

The precursor will be subjected to a series of characterization. The characterization tests are X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and Fourier Transfer Infrared Spectroscopy (FTIR). The products will also undergo a series of characterization test. The tests are XRD, DSC, IR, Energy Dispersive Analysis of X-rays (EDAX) and Cyclic Voltammetry (CV).

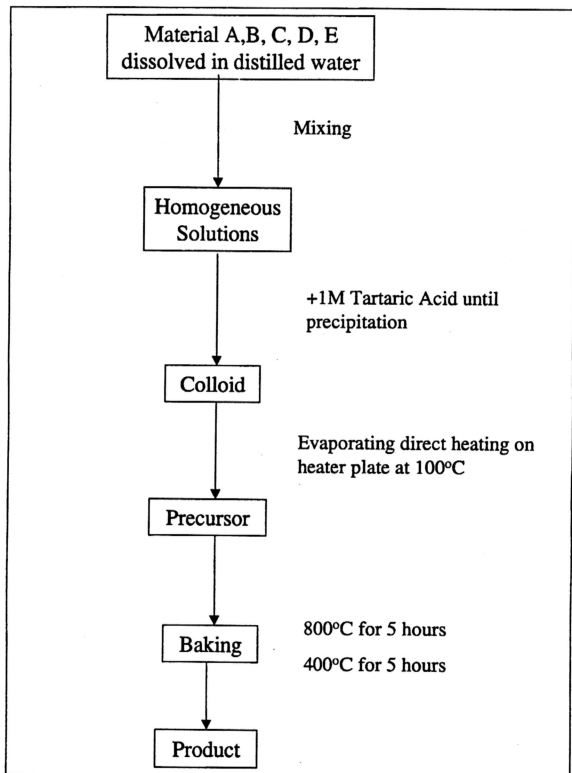


Figure 3.1' Flow chart for synthesis of samples

3.2.1 Differential Scanning Calorimetry (DSC)

3.2.1.1 Use

Differential scanning calorimetry can provide quantitative information about heat changes experienced by a material.

3.2.1.2 Sample

Samples may be examined in the solid or liquid state. Some information may be obtained with samples as little as 0.1 mg, but quantitative studies usually require at least 1mg.

3.2.1.3 Principle

DSC is a technique for studying the thermal behavior of materials as they undergo physical and chemical changes during heat treatment. When a substance is heated, various chemical and physical transformations occur involving the absorption of heat (endothermic process) or evolution of heat (exothermic process). The DSC technique, on the other hand, measures the amount of heat that is involved as a material undergoes either an endothermic or exothermic transition.

Various environments (vacuum, inert atmosphere or controlled gas composition) and heating rate (from 0.1 C/min to 320 C/min) can be employed for temperatures ranging from -150°C to 2400°C . Qualitative and quantitative measurements are determined with speed and efficiency through automated data analysis and reporting systems. A schematic of a differential scanning calorimeter system is given in Figure 3.2.

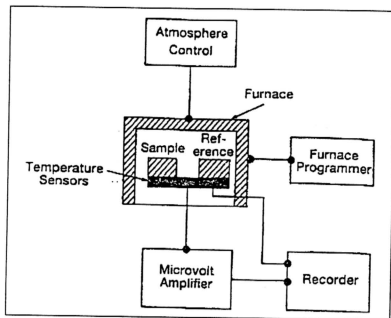


Figure 3.2 : Schematic of a differential scanning calorimeter (DSC) system

3.2.1.4 Application

The DSC technique can be used to investigate the thermal properties of a variety of materials, and are particularly useful tool in the characterization of organics, polymers, biological materials, inorganics and amorphous alloys. Some applications are: qualitative and quantitative evaluation of phase transformation such as glass transition, melting, crystallization; study of polymerization, decomposition and curing processes including a kinetic description; determination of thermal and processing histories, simulation of processing conditions and crystal growth.

Figures 3.3 and 3.4 reveal the polymerization isotherms of pivalolactone monomer using temperature (T) and initiator concentration (C) variables, respectively. The polymerization peak is analyzed for cumulative area (i.e % conversion) as a function of time (t). Data analysis provides the following relationship: $\ln t_{0.75} = 3534/T - 4.157(C)$

– 6.801, where $t_{0.75}$ is the time in minutes, required for 75% polymerization. Thus, the polymerization rate of pivalolactone monomer, e.g. in composite fabrication, may be optimized by the temperature and/or initiator concentration variables.

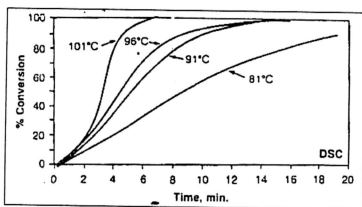


Figure 3.3 : Polymerization isotherms for pivalolactone containing 0.15% initiator

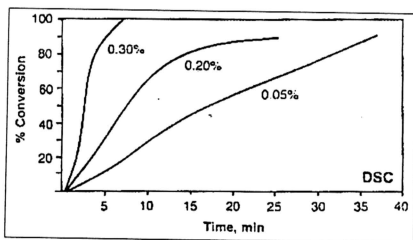


Figure 3.4 : Polymerization isotherms for pivalolactone at 91 °C: initiator concentration dependence

Figure 3.5 shows a DSC scan of an amorphous metal alloy. The first small endotherm (290°C) represents the Curie temperature (magnetic transition) and is followed by a heat capacity change at 490°C due to the glass transition. Devitrification (crystallization) occurs at 535 and 605°C.

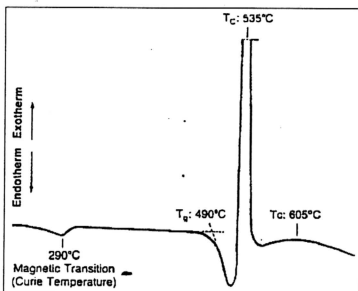


Figure 3.5 : Amorphous metal alloy (ribbon). DSC in argon ($20^\circ\text{C}/\text{min.}$ heating rate)

Figure 3.6 shows the effect of purity on DSC melting peak shapes for benzoic acid. The presence of 2.8% impurity depresses the melting point, significantly broadens the melting range and decreases the melting point, significantly broadens the melting range and decreases the heat of fusion. A computerized program for the DSC determines the purity automatically.

The kinetic of polymerization of diacetylene can be developed by determining the transition peak temperature of the exothermic reaction directly in the instrument as function of heating rate. Figure 3.7 illustrates the difference in the peak shape and temperature for three rates.

Figure 3.8 is a DSC scan of poly(ethylene terephthalate) (PET) indicating the glass transition (T_g), "cold" crystallization (T_c) and melting (T_m) (left to right) temperatures. The automatic data analysis system has also printed out the heats of crystallization (ΔH_c) and melting (ΔH_f).

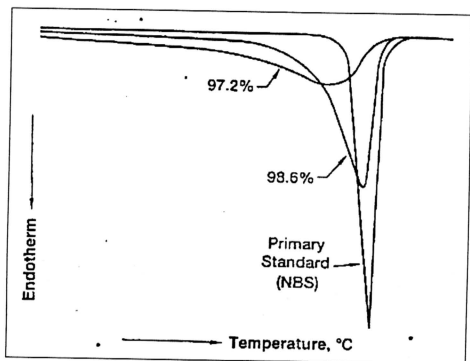


Figure 3.6: Effect of purity on the melting peak shapes (DSC) of Benzoic Acid

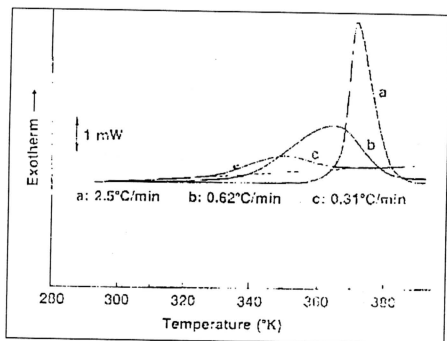


Figure 3.7 : Effect of the heating on polymerization of diacetylene (DSC, in argon)

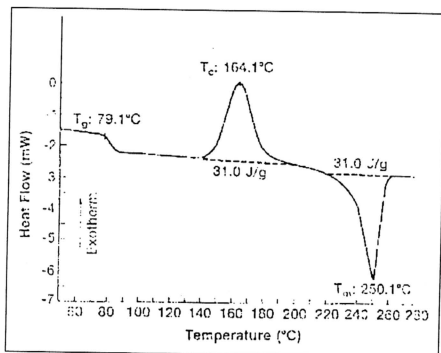


Figure 3.8: Poly(ethylene terephthalate) DSC in Argon ($20^\circ\text{C}/\text{min.}$ heating rate)

3.2.2 X-ray Powder Diffraction

3.2.2.1 Use

X-ray powder diffraction is used to obtain information about the structure, composition and state of polycrystalline materials. The samples may be powders, solid, films or ribbon.

3.2.2.2 Samples

The minimum amount of material required is a few milligrams. However, greater accuracy is achieved if up to a gram of samples is available. In order for a solid sample to be mounted in an automatic sample changer, there are restrictions on its dimensions, depending on the instrument used.

3.2.2.3 Principle

If a beam of monochromatic x-radiation is directed at a crystalline materials one observes reflection or diffraction of the x-rays at various angles with respect to the primary beam, see figure 3.9).

- A: Collimation Assembly
- B: Sample
- C: Slit
- D: Exit Beam Monochromator
- E: Detector
- X: Source of X-Rays

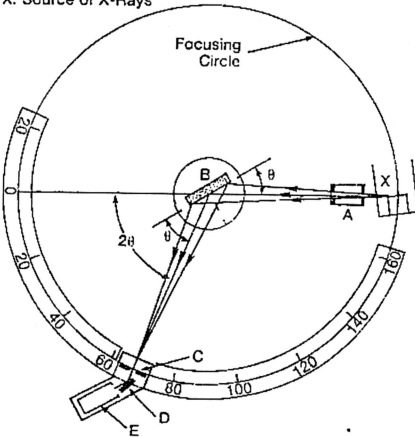


Figure 3.9: Schematic of an x-ray diffractometer

The relationship between the wavelength of the x-ray beam λ , the angle of diffraction 2θ , and the distance between each atomic planes of the crystal lattice, d , is given by the well known bragg condition

$$n\lambda = 2d\sin \theta$$

where n represents the order of diffraction. From this equation we can calculate the interplanar distances of the crystalline material being studied. The interplanar spacings depend solely on the dimension of the crystal's unit cell while the intensities of the diffracted rays are a function of the placement of the atom in the unit cell.

3.2.2.4 Application

The x-ray pattern of the crystalline substance can be thought of as a “fingerprint”, each crystalline material having, within limits, a unique diffraction pattern.

The Joint Committee on Powder Diffraction Standards has published the powder diffraction pattern of some 50,000 compound. An unknown compound is identified by comparing the interplanar spacings and intensities of its powder pattern to the patterns in the powder diffraction file. If x-ray fluorescence data, which describe elemental composition are added, the number of pattern can be reduced. A systematic search (by computer usually leads to an identification in about one hour. Mixtures of up to nine compounds can often be completely identified. The minimum limit of detection for a single phase in a complex mixture is about 1%. Figure 3.10 shows the final step of a typical phase identification in which the stick diagrams of the stored compounds are being compared with the diffraction pattern of the sample. In this example $\alpha\text{-Al}_2\text{O}_3$ (corundum) could be identified as the major crystalline impurity in the preparation of

AlN. In addition to identifying the compounds in a powder, analysis of the diffraction pattern is also used to determine crystalline size, the degree of crystallinity of rapidly solidified materials, the phase composition of the surface region of transformation-toughened ceramics, and other parameters associated with the state of crystalline materials. The diffraction pattern of a solid piece of yttria partially stabilized zirconia is shown in Figure 3.11. The phase composition has been determined quantitatively by an on-line least squares program which permits the separation of overlapping peaks.

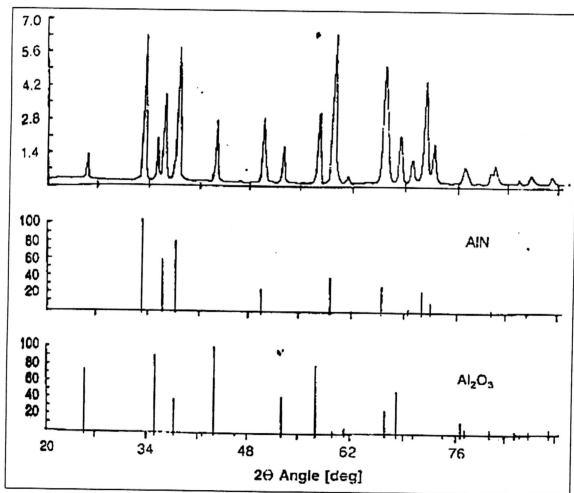


Figure 3.10: Results of computer-assisted phase identification of a two-component system

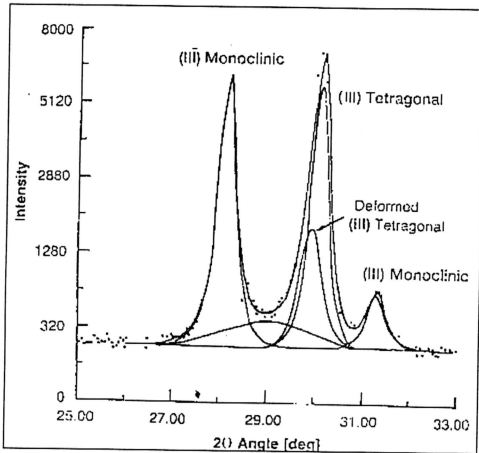


Figure 3.11: Deconvolution of tetragonal and monoclinic phases in a Zr(Y)O_2 ceramic

3.2.2.5 Other Specific Uses

A few of the specialized uses of x-ray diffraction are listed below :

1. Low and high temperature diffractometry (between -100 and 1600°C)
 - a. To determine thermal expansion coefficients
 - b. For phase diagram and phase transition studies
 - c. To study order-disorder transitions.

2. Determination of precise crystallographic lattice constants ($\pm 0.0001\text{\AA}$) in particular for solid solutions, i.e. the incorporation of atomic or molecular species into host lattice without change of symmetry.
3. Structure determination of moderately complex structures by the refinement of the complete XRD pattern. In many cases the results of this technique rival in accuracy a typical single crystal structure determination. It may be required, however, that preferred orientation be eliminated by spray drying technique.
4. The capability to study the state of microcrystalline and amorphous solids. This is accomplished by computer analysis of time-averaged x-ray data. The results can be used to study the spatial relationship or arrangement of atoms in non-crystalline solids.

3.2.2.6 Limitations

Film methods are employed to complement the powder diffraction data for the study of materials with preferred orientation. More detailed characterization may require specialty instruments such as a thin film camera, texture goniometer or a double crystal diffractometer. The lack of spatial resolution can be overcome by microdiffraction for polycrystalline samples and x-ray topography for single crystals.

3.2.3 Infrared Spectroscopy

3.2.3.1 Use

Infrared spectroscopy can be used to identify materials, determine the composition of mixtures, monitor the course and extent of reactions, and provide information useful in deducing molecular structure.

3.2.3.2 Sample

Materials in the solid, liquid or gaseous state may be studied by infrared spectroscopy. A convenient sample size is several milligrams, but spectra can be obtained from as little as 50 picograms with special technique.

3.2.3.3 Principle

Analysis by infrared spectroscopy is based on the fact that molecules have specific frequencies of internal vibrations. These frequencies occur in the infrared region of the electromagnetic spectrum : $\sim 4000\text{cm}^{-1}$ to $\sim 200\text{ cm}^{-1}$.

When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies, but will transmit all other frequencies. The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy versus frequency is called the infrared spectrum of the material.

Identification of a substance is possible because different materials have different vibrations and yield different infrared spectra. Furthermore, from the frequencies of the absorption it is possible to determine whether various chemical groups are present or absent in a chemical structure. In addition to the characteristic nature of the absorption, the magnitude of the absorption due to given species is related to the concentration of that species.

3.2.3.4 Application

Infrared spectroscopy is one of the major tools for obtaining information regarding the structure of molecules. Besides the standard applications of identification and quantitative analysis, there are a number of special technique and applications. Some of these are listed as follows :

3.2.3.4.1 Polymer Chemistry

1. Determination of number average molecular weight through end group measurements in certain polymers.
2. Determine of crystalline index and branching.
3. Estimation of degrees of stereoregularity, conformational analysis and sequence distribution in copolymers
4. Analysis of degradation products to establish mechanisms of degradation.
5. Orientation studies through the application of polarized radiation.
6. Determination of T_g and phase changes through temperatures experiments between -50°C and 400°C .

7. Study of the surface of a material by attenuated total reflection (ATR) and variation of composition with depth by variable angle ATR.

3.2.3.4.2 Organic Chemistry

1. Reaction kinetic studies.
2. Studies of reactive intermediates between -50°C and 400°C .
3. Conformational and configurational studies on both cyclic and acyclic systems.
4. H-bonding, dipolar attractions and solute-solvent interaction studies.

3.2.3.4.3 Inorganic Chemistry

1. the nature of inorganic lattices at different temperatures.
2. Nature of hydration
3. Formation and reaction of $-\text{OH}$ groups in various inorganic glasses.
4. Symmetry properties of the arrangement of atoms through a consideration of group theory.

3.2.3.5 Fourier Transform Infrared Spectroscopy

For many decades, the work-horse of the infrared laboratory has been the light-dispersive spectrometer. While still in wide use for routine analysis, the dispersive nature of these spectrometers, however, severely limits their application in solving "difficult problems"; e.g., microsamples, strong IR absorbers, and analysis of impurities in most samples at levels below ~ 0.1 to 1% without special pre-concentration procedures.

During the past decade, Fourier-transform infrared spectroscopy (FT-IR), coupled with the rapid development during this period of a wide variety of sampling accessories designed to make optimal use of the advantages of FT-IR, has come to the forefront as the technique capable of handling both the “routine” and “difficult” problems. A schematic of an FT-IR spectrometer is given in Figure 3.12.

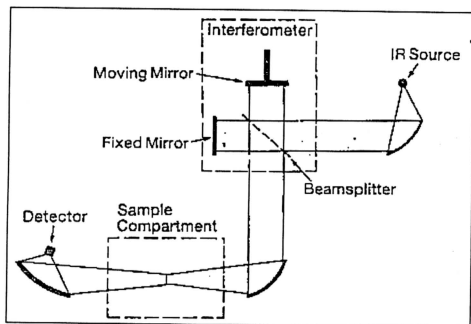


Figure 3.12: Schematic of an FT-IR spectrometer

Fourier transform infrared spectroscopy employ an interferometer in place of a monochromator. This device generates the Fourier transform of the infrared spectrum which is converted to the spectrum itself by a dedicated computer. This approach has the advantages of providing much higher source radiation throughput, increased signal/noise ratio, and higher wavenumber accuracy than is possible with a conventional light-dispersive spectrometer. These advantages can be applied in several ways.

1. Useful spectral information can be obtained from a sample of a microgram or less. Utilizing special techniques, as little as 50 picograms may be analyzed.
2. A spectrum can be obtained in a much shorter time than is possible with a dispersive spectrometer. Thus, spectra can be obtained of transient species or phenomena down to as short a time as $1/30^{\text{th}}$ of a second.
3. A combination of both those advantages makes it possible to obtain infrared spectra of gas chromatographic and high pressure liquid chromatographic cuts as they merge from the chromatograph, thus providing considerable structural information about the material giving rise to each peak in the chromatogram (cf. GC-mass spectrometry and HPLC).
4. The spectrum can be obtained at very high resolution, which has certain advantages in studying small molecules in the vapor phase.
5. Utilizing microscope accessories spectra of individual particles or inclusions of the order of $5\mu\text{m}$ in size can be obtained.
6. The modulation provided by the interferometer allows the use of Photoacoustic spectroscopy (PAS), whereby the spectra of the material may be obtained "as is" (powders, pellets, chunks, etc.). PAS involves infrared absorption in the sample, followed by conversion of the absorbed energy into heat. The subsequent heat-induced thermal expansion in the sample and adjacent media produces a photoacoustic signal when the incident beam intensity is modulated at a frequency in the acoustic range. Microphonic detection of this signal, processed by the normal detector amplification electronics of an FT-IR spectrometer, yields the spectrum.

3.2.3.6 Limitations

Routine analyses using solution, mulls or specialized sampling accessories, for examples, diffuse reflectance or photoacoustic detection, require milligram quantities of material. This requirement has been reduced to the nanogram level with the development of a variety of microanalytical accessories. Infrared detection of chromatographic cuts (both GC and HPLC has been pushed to the nanogram level. Using matrix isolation technique, 50 pg of material can now be detected in GC-IR analyses. These detection limits are achievable with commercially available instrumentation.

3.2.4 Energy Dispersive X-ray (EDAX)

3.2.4.1 Use

Energy Dispersive X-ray is used for determining elemental composition and distribution within a micro volume of material. Elemental detectability extends from B through U. EDAX is most commonly used in conjunction with Scanning Electron Microscope (SEM) imaging thereby allowing analysis to be performed directly on the areas under electron beam observation.

3.2.4.2 Sample

Any solid material containing elements heavier than Be may be studied.

3.2.4.3 Principle

When materials are bombarded by a high energy (10keV-50keV) electron beam, characteristic x-ray fluorescence radiation is produced. By incorporating either energy

dispersive or wavelength dispersive spectrometers directly into the instrument, it is possible to obtain x-ray spectra directly on the area as seen by the electron beam. Thus, it is possible to obtain qualitative and quantitative elemental data from a volume on the order of $1\text{ }\mu\text{m}^3$ for the elements B through U. Data can be obtained from an isolated region of the sample (spot mode), along a pre-selected linear trace (line profiling) or from an area (x-ray distribution mapping).

3.2.4.4 Applications

Because of its capability for qualitative and quantitative analysis on micro volumes, EDAX has been used extensively for impurity and inclusion identification in polymers and cast ingots, as well as compositional determination of amorphous metals, complex garnet films and corrosion deposits. The line profiling and x-ray mapping modes are routinely used for determination of diffusion profiles and elemental distribution in braze joints, electronic components, optical fiber components and plated parts.

3.2.4.5 Limitation

Samples to be studied must be solids that are not electron-beam-reactive and contain no highly volatile or corrosive components. Special specimen stages can handle specimens up to about 20cm in diameter although conventional stages can accommodate samples only a few cm in diameter. The specimen surface should be flat and polished. The lightest element detectable is B. Since the electron beam penetration and x-ray emission are strongly affected by instrument parameters, specimen composition and

specimen characteristics, the analyzed volume can be as large as several cubic dispersive x-ray analysis and about 1000ppm for energy dispersive x-ray analysis. Sensitivity may be poorer depending on the element of interest and it's matrix.

3.2.5 Cyclic Voltammetry

Cyclic Voltammetry is an electrochemical technique. As a material scientist, it is required to apprehend a multitude of disciplines. For example doing cyclic voltammetry one would be able to test and discover the ability of a material to intercalate lithium ion and hence suggest new materials as electrodes in batteries.

3.2.5.1 Electrochemical Reaction

The simplest electrochemical reaction can be divided into three steps, which occur in the interphase between the solution and the electrode.

- a) mass transport of the electroactive species from the bulk solution to the electrode surface.
- b) Charge transfer from the electrode to the electroactive species (reduction) or vice versa (oxidation).
- c) Mass transfer of the electroactive species from the interphase to the bulk solution.

The mass transfer process from the electrode surface to the bulk solution and vice versa can occur in three ways by :

- a) diffusion, which is the transport of electroactive species when there is a concentration gradient between the electrode surface and bulk concentration.

- b) Convection, which is the transport of electroactive species caused by mechanical agitation.
- c) Ionic migration, which is a transport of the electroactive species that is caused by ionic attraction between the charged species and the electrode.

Convection can be avoided by maintaining mechanical stability of the system. Adding an inert salt such KCl that has a much larger concentration than the electroactive species can reduce ionic migration so that the ionic migration to the electrode is largely due to the migration of the inert salt and not the electroactive species. So, the mass transport is mainly due to the diffusion process.

When an electrode reaction is a reversible reaction, there is fast electron transfer process; it is not a rate determining step of the whole reaction but the rate controlling step to be the mass transport of the electroactive species.

3.2.5.2 Technique of Cyclic Voltammetry

Cyclic voltammetry is a useful technique for the investigation of an electrochemical reaction. It is a technique most sought, for preliminary studies of an electrochemical reaction before recourse to other advanced technique. Its versatility is due to the fact that qualitative and also be deduced from this technique as mathematical equation that was derived accurately relates these parameters. Potential profile with time is shown in the Figure 3.13 below :

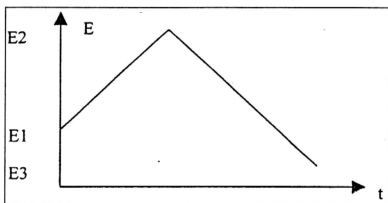


Figure 3.13: Potential profile with time in cyclic voltammetry.

The diagram shows that the initial potential E_1 applied to the working electrode is increased at a constant scan rate of v/mVs^{-1} until it stops a potential E_2 . The potential is then reduced with a constant scan rate v/mVs^{-1} back to the initial potential E_1 or to a lower potential E_3 . This scan can also be repeated to reach E_2 and back to E_1 or E_3 .

Planar diffusion occurs in electrode with large surface area (where electrode dimensions are a few millimetres). In some other cases there can also be hemispherical diffusion, like the case of a microelectrode where the electrode dimensions are in the order of microns (10^{-6} m).

3.2.5.3 Reversible Reaction

The reaction studied is a reversible reaction when the charge transfer process is much faster than the diffusion process. An example of this type of reaction is the reduction of oxidized specie in solution $\text{O} + e^- \rightarrow \text{R}$.

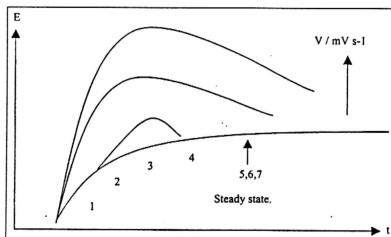


Figure 3.14: A series of voltammogram for various scan rates.

If a very low scan rate is applied to the electrode, then the voltammogram will have a “S” shape as seen in Figure 3.14 and is a steady state condition. But if higher scan rates are used then the voltammogram with peak will be obtained. To understand how this process occurs, the concentration profiles of concentration and the distance from electrode surface must be studied.

For a steady state condition the concentration profiles with the distance from electrode surface is shown in the Figure 3.15 below.

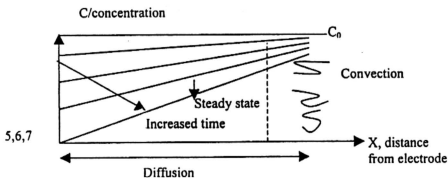


Figure 3.15: Profiles of concentration with distance from electrode for a steady state reaction.

The concentration gradient on the electrode surface is (C_0/d) , and gives a limiting current 5, 6, in the “S” shaped voltamogram in Figure 3.14.

In a reversible reaction, the current is proportional to the concentration gradient of the electroactive species an the electrode surface $(dC/dx)_{x=0}$. Therefore in the steady state condition where the thickness of the Nerst diffusion layer is independent with time, a steady state current will result in a “S” shaped voltamogram.

If the scan rate is increased then the voltamograms will have a peak and the concentration profiles is shown in Figure 3.15. Because the current is proportional to the concentration gradient at the electrode surface then a voltamogram with a peaked response is obtained as in Figure 3.16.

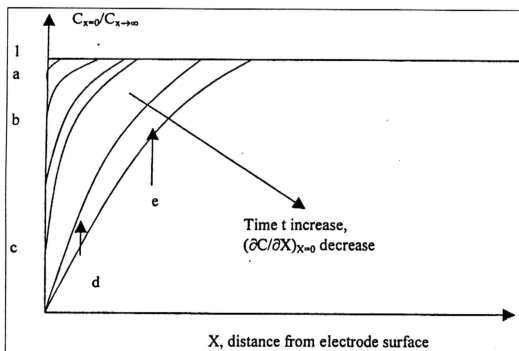


Figure 3.16: Concentration profile C , with distance from electrode X , for a reversible electrode reaction during cyclic voltammetry.

In steady state condition, the electroactive species concentration is constant in the bulk solution as there is natural convection. The region next to the electrode is the Nernst diffusion layer where the concentration profile is linear. For the reversible reaction the concentration of the electroactive species on the electrode surface is $C_{x=0}$ must decrease when the potential is increased to more negative values because of the reduction of O to R. Therefore the increase of the concentration gradient on the electrode surface will also increase the current. The concentration of the electroactive species at the electrode will reach zero and this will result in a maximum current or steady state current because the concentration profiles does not change with time.

If scan rate increased, steady state conditions will not be observed because the diffusion layer will not have sufficient time to reach equilibrium, and the concentration result in a concentration gradient. Therefore the current which is proportional to the concentration gradient on the electrode surface will flow to the external circuit. When the potential is made more negative the concentration of O at the electrode surface will reach zero. The concentration gradient of electroactive species at any potential is always greater than the concentration gradient at the electrode surface in a steady state condition. Therefore the current will be greater than the current of the steady state condition. When the surface concentration of the electroactive species $C_{x=0}$ is zero, the concentration gradient on the electrode surface will slowly decrease because of relaxation, (Figure 3.4) causing the current to decrease. This will result in the peaked response as in Figure 3.4. Also the concentration gradient will increase when the scan rate is increased because the insufficient time does not permit the decrease in the concentration of the electroactive species in the regions close to the electrode to be restored to its bulk value.

For very slow scan rate that are for pseudo steady state conditions, the current will traverse its original path in the front scan as in Figure 3.18.

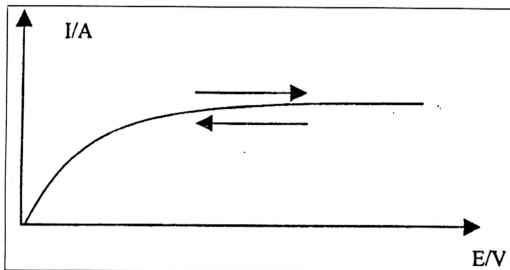


Figure 3.17: The current of the front scan (reduction) and the current for the reversed scan (oxidation) for a steady state condition.

When the scan rate is increased the response will be different from the steady state response because the reduced electroactive species R is close to the electrode surface until the oxidation potential of R is reached where it will be oxidized to O at potential E_e° and the reversed current or oxidation current will flow to the external circuit. With more positive potentials the surface concentration of R will reach zero. Therefore the oxidation current is a peak like reduction current but with opposite sign.

The charge in the oxidation process is less than the charge in the reduction process because there is a concentration gradient that results in the diffusion of R away from the electrode surface to the bulk solution and cannot be oxidized back to O .

A reversible reaction will have a peak current I_p that proportional to the square root of the scan rate which is known as the Randles-Sevcik equation :

$$I_p = -0.4463nF(nf/RT)^{1/2} \cdot (Dv)^{1/2} \cdot C_0, \text{ where}$$

N = number of electrons which is transferred in the electron transfer step.

F = Faraday's constant 96500 /Cmol^{-1} .

R = gas constant $8.3142 \text{ /Jmol}^{-1}\text{K}^{-1}$.

D = diffusion constant $\text{/m}^2\text{s}^{-1}$.

V = scan rate /Vs^{-1} .

C_0 = electroactive species concentration in solution.

3.2.5.4 Irreversible Reaction

In the case of irreversible reaction, the electron transfer rates at all potentials are significantly less than the rate of mass transport and the Nernstian equilibrium is not maintained at the surface of the electrode. At low potential sweep rates, the rate of electron transfer is greater than that of mass transfer and reversible cyclic voltammogram is recorded. But when the potential sweep rate is increased, the rate of mass transport is increased and becomes comparable to the rate of electron transfer. When the potential sweep rates are increased further, then the rate of electron transfer becomes much less than the rate of mass transport.

The peak for an irreversible process is more drawn out, because the surface concentration of the oxidized species O changes more slowly with potential (because of low rates of electron transfer). When the surface concentration of O reaches zero, the concentration profile for O is less steep and the flux to the surface is lower. Because the electron transfer process of the irreversible reaction is slow and can be enhanced by

increasing the potential, then the peak for an oxidation process is shifted to more positive potentials and the peak for reduction process is shifted to more negative potentials for an irreversible process.

Sometimes there is the absence of the reverse peak in a cyclic voltamogram of a irreversible reaction, but such a feature can also imply that a fast chemical reaction that takes place which consumes O before it can be reduced back to R. Other test must be made. For the irreversible case the value of E_p^c is found to vary with the sweep rate as shown below.

$$E_p^c = K - \left[\frac{2.3 RT}{2\alpha_c \eta_a F} \right] \log v$$

where v = potential sweep rate (or scan rate).

α = electron transfer coefficient.

n = number of electrons transferred in electron transfer step.

K is a constant.

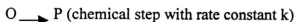
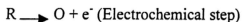
For an irreversible electrochemical system (Southampton Electroanalytical Chemistry Group) at 25°C,

1. There sometimes can be no reverse peak.
2. E_p shift with increasing potential sweep rates.

3.2.5.5 Coupled Homogenous Reaction

Cyclic voltammetry can be used to investigate some coupled chemical reactions that occur with the electrochemical reaction. The voltamogram should be recorded with

varying the sweep rates and over a wide range of potential to determine whether there are other process that are coupled with the one of interest. For example h reaction below is

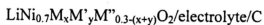


The case where the electron transfer is rapid and P is not electronegative. Then the form of the voltamogram is dependent on both the values of k and potential sweep rates. Three cases need to be considered :

- i) When the potential sweep rates is fast (shorter time scale) compared to the half life of the intermediate O. Then the response can't be influenced by the chemical step and will give a response A in the diagram.
- ii) At intermediate potential sweep rates, the tie scale of the experiments and half life of the intermediate O is comparable to the response as shown at B. the reverse peak will be smaller and clearly I/I will increase with potential sweep rate v .
- iii) At very slow rates and very large rate constant k, all the species O formed during oxidation will be converted to P and none can be reduced back to R in the reverse scan. The reverse does show a peak but this is merely the oxidation reaction is switching off as the potential is scanned into the range where the conversion R to O is no longer favorable.

3.2.6 Battery Fabrication

In order to confirm that intercalation and de-intercalation takes place in a real electrochemical system, an electrochemical cell was fabricated using one of the materials in the following configuration:



where C is the anode and $\text{LiNi}_{0.7}\text{M}_x\text{M}'_y\text{M}''_{0.3-(x+y)}\text{O}_2$ is the cathode. In the assembled state the cell is dead and therefore has to be charged. During charge, Li^+ from the cathode will migrate to the anode. Thus Li^+ de-intercalates the cathode and intercalates the anode. Hence, if the cell can be charged and discharged, the process of intercalation and de-intercalation has been proven.