CHAPTER- II

TECHNIQUES AND EXPERIMENTAL PROCEDURES

2.1. Introduction:

The current work on electrode materials for Li-ion batteries involves a range of experimental work, from synthesis and characterization of electrode materials to fabrication of electrodes and assembly of cells for electrochemical measurements. This chapter summarizes a variety of physical and chemical methods used for material characterization. It also describes a detailed electrode preparation procedure and assembly of coin cells. In addition, electrochemical techniques used for performance evolution of fabricated Li-ion cells are discussed.

General synthesis methods commonly used are described in chapter- I. Some of the specific methods we have adopted for the synthesis (nitrate melt decomposition, sol-gel, flux and combustion method) are discussed in the relevant chapters. The powder samples synthesized are analyzed using various physical characterization techniques like powder X-ray diffraction, SEM, TEM, IR, BET, etc.

2.2. Characterization techniques used for structural and morphological analysis:

2.2.1. Powder XRD and Rietveld refinement:

X-ray diffraction is the most important technique for crystal structure analysis. It is mainly used for determining the internal structure and provides details about electron distributions in the molecule, bond length, bond angle etc. The X-ray diffraction process is non-destructive and it is conveniently used for routine analysis.

**Principle:** When X-rays interact with a solid material, the scattered beams reinforce each other in few directions due to the regular arrangements of atoms in the crystal structure. This constructive interference results in diffraction patterns.
The relationship describing the angle ($\theta$) at which a X-ray beam (wave length $\lambda$) diffract from a crystalline surface is known as Bragg’s law,

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

Where,

‘$d$’ is the distance between adjacent planes in a crystal (inter-planar distance),

‘$n$’ is the integer representing the order of diffraction peak.

Figure 2.1, Schematic representation of Bragg diffraction in a crystal lattice. Each lattice plane in a crystal behaves to X-rays just as does a line in diffraction grating. Nature of the X-ray diffracted beam by a crystal is determined by spacing between successive planes‘$d$’.

Fig. 2.1, shows the diffraction from a three dimensional periodic structure (Bragg diffraction) such as atoms in a crystal. Bragg diffraction is a consequence of interference between waves reflecting from different crystal planes. Thus by knowing the wavelength of X-ray used and measuring the diffraction angle ‘$\theta$’, the distance between different lattice planes‘$d$’ can be calculated. No two chemical substances would be expected to form crystals in which all crystal spacing’s are same. Thus X-ray diffraction pattern is like finger print for the definite structure and hence useful to analyze the crystal structure of the compound. Intensity of diffracted beam is dependent on the quantity of the crystalline material in the sample. Thus quantitative determination of the amount of constituent mixture is also possible using XRD pattern.
**Method:** Powder X-ray diffraction of the samples were recorded on either Philips X’pert pro diffractometer or Bruker D8 advanced diffractometer employing Cu-K$_\alpha$ radiation ($K_{\alpha1}=1.5406\text{Å}$) and nickel filter. X-rays are produced in a sealed tube under vacuum when a current is applied to the heating filament that emits electron when it gets heated up. The electrons are accelerated towards an anode (copper plate) by a potential difference of 30 kV. These high energy electrons when bombard the metal copper plate ionize copper 1s K shell, thereby electron from 2p ($K_{\alpha}$) or 3p ($K_{\beta}$) drops down to occupy the 1s and release energy as X-rays of particular wavelength (Cu $K_{\alpha}=1.5406$). Cu $K_{\beta}$ is removed by using nickel filter. This X-rays are allowed to fall on the material under analysis and the diffraction pattern was recorded.

The pattern obtained is analysed preliminarily by comparing with reported standard patterns of related compounds. Standard JCPDS data was used to compare the experimental pattern using X’Pert high score plus software. Detailed structural analyses of the material are carried out by Rietveld structural refinement using GSAS analytical suit. The Rietveld method is a mathematical technique used for the processing and analysis of powder diffraction data. A crystal structure matching with the one under analysis, together with instrumental information is used to generate a theoretical diffraction pattern that can be compared with observed XRD pattern. Then both patterns were refined using least square analysis in order to minimize the difference between the observed pattern and pattern calculated theoretically by adjusting model parameters. Once the observed pattern fits well with the calculated pattern, refined values of the calculated structural parameters are taken as the parameters of the observed pattern. This way, the Rietveld refinement was used to know the exact atomic positions, lattice parameter values and other structural details.

**2.2.2. Electron Microscopy:**

Microscopy is a technique that is mainly used to produce the magnified image of the specimen under study. If electron source is used to illuminate the specimen, then it is represented as electron microscopy. When a beam of electron is focused to fall on the specimen, they can scatter elastically or in-elastically or interact with the atoms in the sample to produce light, X-rays, Auger electrons etc (See Fig. 2.2). Some of them are used for various microscopic analysis of the sample.
Among different varieties of electron microscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are used in the present study to analyze the surface morphology and related properties.

2.2.2.1. Scanning Electron microscopy:

SEM uses high energy beam of electron in a raster scan pattern to produce the magnified image of the sample. SEM is mainly a reflection instrument and use radiation reflected from the sample for producing the magnified image. Particles up to nanometre size could be viewed using scanning Electron Microscope.

**Method:** SEM images were recorded on HITACHI Model S-3000H Scanning Electron Microscope. An electron beam is produced by the thermionic emission of tungsten filament cathode. The electron beam of energy from 0.2 keV to 40 keV is focused by 2 condenser lenses to a spot on the sample. It scans the sample in raster scan mode over a rectangular area. When the electron beam falls on the sample surface, it emits secondary electrons due to inelastic interaction. These secondary
electrons are attracted towards an electrically biased grid and accelerated towards a phosphor or scintillator. The secondary electron when falls on a scintillator produces flashes of light that are conducted to a photomultiplier outside the SEM column. The amplified electrical signal from the photomultiplier can be viewed as a two dimensional intensity distribution and photographed using analog to digital converters.

2.2.2.2. Transmission Electron Microscope (TEM):

Transmission Electron Microscope is a technique in which a high voltage, high energy electron beam is used to irradiate the sample and the transmitted electrons from the sample are analyzed. An image produced by the transmitted electrons is magnified and used to acquire information about the size and morphology of the material. TEM consists of an emission source made up of tungsten filament, or a lanthanum hexaboride (LaB$_6$) that emits electron by thermionic or field electron emission into the vacuum. The incident electrons are accelerated with a potential of 100-1000 kV to a velocity approaching the speed of light. Therefore the associated wavelength of the electron beam is five orders magnitude smaller than light wavelength. Hence resolutions (resolution $\rho = 0.61\lambda/\sin\alpha$; where, $\alpha$ is the angle between incident and deflected beam) of few nm to Å are possible with TEM.\(^5\) This high resolution of TEM technique enables imaging of material up to nano or sometimes in atomic level. Manipulation of the electron beam is performed using electromagnets and electrostatic fields. The powder sample is dispersed in acetone/ethanol followed by deposition onto support grids or films. High energy electron beam produced from the source made to pass through ultra high vacuums in the range of $10^{-7}$ to $10^{-9}$ Pa and directed to fall on the sample. The transmitted radiations produce an image that is recorded by CCD camera.

Selected Area Electron Diffraction (SAED) is an experimental technique that can be performed using TEM. Electron diffraction of the specimen in a selected area is recorded by inserting an aperture into the incident electron beam path. Selected area aperture is a thin strip of metal that could block the beam. It contains different sized holes to allow passage of electron beams. The aperture is moved in order to select a particular area in the specimen (hence the name ‘selected area’), and only
this portion will interact with the electrons. Since the wavelength of the incident high energy electron beam (few thousands of nanometer) is about 100 times smaller than the spacing between atoms in a solid, the atoms act as a diffraction grating to electrons and diffract it to a particular angle. The obtained diffraction pattern is just similar to X-ray diffraction, but unique in that particular area of the sample and is used to analyze the phase purity, structure etc. SAED pattern consists of dots for single crystals and a series of rings in case of polycrystalline or amorphous solids. On a single crystal, the SAED pattern could also be used to analyze the information’s about the space group.

TEM images and SAED pattern for the present study have been recorded using Technai-20 G2 transmission electron microscope. TEM is used to obtain information about crystallite size, phase purity, phase boundaries, arrangement of atoms in the crystal, etc.

2.2.2.3. Energy-dispersive X-ray spectroscopy (EDS or EDX):

EDX is generally used for the quantitative analysis of various elements present in the specimen. When a beam of high energy electron is allowed to fall on a sample, the atoms within the sample acquires high energy; the electrons in the inner shell of the atom may get excited and could be ejected from the shell. Thus, an electron hole is produced in the inner shell of the atom that is filled by an electron from the outer hole. The difference in energy between the higher energy shell and low energy shell is then emitted in the form of X-rays. As this energy is characteristic of the atomic structure of the element, these X-rays are used for identifying the element. Further, quantitative estimation of various elements present in the sample are calculated by measuring the total number of emitted X-rays of that particular element. The number and energy of the emitted X-rays is measured by an energy dispersive spectrophotometer. EDAX system is most commonly combined with scanning electron (SEM-EDS) and transmission electron (TEM-EDS) microscope. A detector is used to convert the X-ray energy into voltage signal and passes them to analyser for analysis.
2.2.3. X-ray photoelectron spectroscopy (XPS):

XPS is a quantitative technique used for the analysis of chemical and electronic state of the elements present in the material.

**Principle:** When a material is irradiated with a beam of high energy photon (X-rays), the element present in it may get ionized and emits electron. If the energy of the X-ray photon \( E_{(\text{photon})} \) is higher than the binding energy of the electron \( E_{(\text{binding})} \), then the remaining energy will be utilized as the kinetic energy of the ejected electron.

Kinetic energy of the ejected electron,

\[
E_{(\text{Kinetics})} + \phi = E_{(\text{photon})} - E_{(\text{binding})};
\]

Where, \( \phi \) is the work function.

By measuring the kinetic energy of the electron, its binding energy can be calculated. Binding energy of the electron is characteristic of the element and its electronic configuration within the atom (1s, 2s, 2p, etc.).

Typical XPS spectrum consists of kinetic energy plotted vs. number of electrons. Number of electrons with particular kinetic energy is directly proportional to the amount of that particular element. Thus XPS can be used for quantitative measurement of the chemical composition of various elements in the material. The electrons detected by XPS are those electrons originated from the surface of material (10- 12 nm) which are escaped to vacuum in the instruments. XPS is mainly a surface technique and is particularly useful for the analysis of surface chemistry of a material.

XPS is used for,

- Identification of elements present within the top 1-12 nm of the sample surface
- Identification of chemical and oxidation state of the various elements
- Quantitative separation of various oxidation states of the particular element.
• Analysis of binding energy and density of various electronic states.

**Method:** X-ray photoelectron spectra were recorded on a ESCA lab-2000 spectrometer equipped with Al Kα source. Monochromatic Al Kα produces X-rays of wavelength 0.8339 nm that corresponds to photon energy of 1487 eV. The produced X-rays are allowed to fall on the sample mounted on the sample stage. Electron collection lens, electron detector system and electron energy analyzer are used to analyse the kinetic energy of the ejected electron and to count the electrons with particular kinetic energy. XPS analysis is performed under ultra high vacuum in order to avoid the loss of electron energy by interacting with residual gaseous molecule.

2.2.4. Brunauer Emmett Teller surface area measurement:

Surface area and pore size measurement of the samples are done using Brunauer-Emmett-Teller (BET) analysis.

**Principle:** Principle of the pore size measurement is based on the multilayer adsorption of gaseous molecule on the surface of the solid under study. It’s a multilayer extension theory of Langmuir’s concepts which is based on the monolayer adsorption. Assumptions made here are, (i) gas molecules physically adsorb on the surface of the solids by infinite layers. (ii) There is no interaction between the each adsorption layer. (iii) Langmuir monolayer theory can be extended to multilayers. Thus BET equation can be represented as,

\[
\frac{1}{v \left( \frac{P_0}{P} - 1 \right)} = \frac{c - 1}{v_m c} \left( \frac{P}{P_0} \right) + \frac{1}{v_m c}
\]

Where,

\(P\) and \(P_0\) are the equilibrium and saturation pressure of adsorbents at the temperature of adsorption,

\(v\) is the adsorbed gas quantity (volume units),

\(v_m\) is the monolayer adsorbed gas quantity.

The term \(c\) is the BET constant expressed as,

\[c = \exp \left[ \frac{E_1 - E_L}{RT} \right]\]
Where, $E_1$ is the heat of adsorption for the first layer, and $E_L$ is heat of adsorption for the second/ higher layers (also known as heat of liquefaction).

Surface area is measured by measuring surface roughness and size distribution of open pores. Total surface area $S_{\text{total}}$ and specific surface area $S_{\text{BET}}$ are evaluated by following the equations: $S_{\text{total}} = \frac{V_mN_s}{V}$

$$S_{\text{BET}} = \frac{S_{\text{total}}}{a}$$

$N$ is the Avogadro’s number

‘s’ is adsorption cross section

$V_m$ is the molar volume of adsorbent gas

$a$ is molar weight of adsorbed species

**Method:** The surface area for powdered samples is measured by BET method using Surface Area Analyzer (Belsorp, Japan). The powder samples were evacuated at 383 K and $10^{-4}$ Pa for 4 h, prior to the BET analysis using surface adsorption of N$_2$ (at 77 K). Multipoint BET analysis was performed using a total of 55 data points between pressure ranges of 7 to 760 mmHg. The BET surface area and micropore area were calculated using BET equation and $t_{\text{plot}}$ method respectively. The BET area ($S_{\text{BET}}$) is calculated with the formula:

$$S_{\text{BET}} = \frac{V_mN_s}{aV}$$

where, $v_m$ is the monolayer adsorbed gas quantity, $N$ is Avogadro’s number, ‘s’ is adsorption gas cross section, ‘a’ is molar weight of adsorbed gas and $V$ is the molar volume of adsorbed gas.

Gas molecules of known sizes are condensed onto the sample surface. By completely covering the surface and opening the pores of each particle with a condensed gas, the surface area analyzer can characterize the surface, including irregularities and pore
interiors down to atomic level. The total pore volume was calculated from the nitrogen adsorption value at relative pressure ($p/p_0$) of 0.95. The external surface area and mesopore size distribution was estimated by using Barrett-Joyner-Halenda (BJH) method on $N_2$ isotherm.

2.2.5. **Infrared spectroscopy:**

Infrared spectroscopy is a versatile technique for the qualitative and quantitative characterization of materials. IR is mostly equipped with Fourier transform analysis and is represented as FTIR. It deals with vibrational motion of atoms in a molecule. The molecules absorb IR radiations of specific energy when their motion is associated with the dipole change. The energy of the absorbed IR radiation is unique for particular bond (functional groups) and useful for qualitative and quantitative analysis of that functional group present in the molecule. FTIR spectra were recorded using Thermo electron corporation Model: Nexus 670 FTIR spectrophotometer in the frequency range of 400-4000 cm$^{-1}$. In the present study, FTIR spectrum is mainly used to acquire information about metal-oxygen bonds, trapped water, carbonates, hydroxyl group etc.

2.2.6. **Chemical methods:**

The chemical compositions of the prepared samples are obtained using atomic absorption spectroscopy (AAS) or inductively coupled plasma (combined with mass spectrometry-ICPMS) analysis.

**AAS:** In a typical experiment, test sample is digested in concentrated acid and the solution thus obtained is sprayed into the flame. The ions in the solution acquire energy from the flame and atomised. When light of resonance wavelength is passed through the flame containing the atoms, then part of the light will be absorbed. Atoms of particular wavelength absorb radiation of their own characteristic wavelength. Further, the extent of absorption is proportional to the number of ground state atoms present in the sample. Hence, quantitative analysis of atoms in the sample is possible using atomic absorption spectroscopy. AAS analyses were carried out using Varian model spectra-220 with acetylene-air mixture as carrier gas.
**ICPMS:** If plasma is used as an atomisation source, it is represented as ICP. Plasma is a cloud of highly ionised gas composed of electrons, ions and neutral particles. In a typical application, the compound is completely dissolved into its constituent ions by acid digestion. The solution is sprayed into flowing argon and heated to \( \sim 10,000 \, ^\circ C \). At this temperature, the ions in the sample atomised to form a plasma containing excited and ground state of atoms. The atoms thus obtained are then analysed using mass spectrometer (ICPMS) or emission spectrometer (ICPOES). Detection limit below 1 \( \mu g/L \) is possible with ICP.

**Oxygen estimation:** Oxidation state of transition metals in LiMO\(_2\) materials are quantitatively estimated by iodometric titration.\(^8\) In this analysis, weighed amount of LiMO\(_2\) material is dissolved in 5-10 ml of conc. HCl and is added to a solution containing 1 g potassium iodide and 0.25 g Na\(_2\)CO\(_3\). Here sodium carbonate produces CO\(_2\) atmosphere and helps to avoid I\(_2\) liberation by oxygen in air. On reaction with KI, the metal ion M\(^{3+}\) in the LiMO\(_2\) material gets reduced to form M\(^{2+}\) and liberates iodine. The iodine thus liberated is measured by titration with standardised sodium thio sulphate (thio) and the end point is the disappearance of blue colour. Thio solution is standardised priorily using standard K\(_2\)Cr\(_2\)O\(_7\) solution.

Let LiMO\(_2\) consists of ‘x’ metal ions in +2 state and (1-x) in +3 oxidation state, therefore represented as LiM\(_x\)\(^{2+}\)M\(_{(1-x)}\)\(^{3+}\)O\(_{(\frac{4-x}{2})}\).

All M\(^{3+}\) reduces to M\(^{2+}\) during estimation; hence total number of electron change during reaction is 1-x.

Strengt of thio \( \times \) volume of thio \( \times \) M. Wt/ Wt(g)= (1-x) \( \times \) 1000. From this ‘x’ was calculated and hence oxidation state of the metal ion and the oxygen nonstoichiometry in the material.

**2.3. Electrode preparation and cell assembly:**

Electrochemical tests were conducted using Swagelok-type\(^{\text{TM}}\) cells assembled in an argon-filled glove box. The electrode comprised the milled (hand grinding for 1 hour/ ball milling) mixture of 85 wt. % active material with 15 wt. % Super-P Li Carbon (Timcal Belgium) as the conducting additive. Lithium electrode was prepared by
pressing a piece of lithium metal onto a thin stainless steel disc. Electrolyte used was
1M LiPF$_6$/ LiClO$_4$ solution in a mixture of ethylene carbonate and dimethyl
carbonate in 1:1 ratio by volume. For impedance measurements, three electrode cells
were assembled with lithium as reference and counter electrode.

For long term cell cycling and rate capability experiments, CR 2032 coin
cells were assembled. The electrodes for coin cells were made by dispersing a
mixture of 80% active material, 15% carbon and 5% PVDF binder into NMP. The
slurry thus obtained is coated over an aluminium foil for cathode and onto copper for
anode. The films were then dried at 100 °C overnight in a vacuum oven and cut into
small discs of 18mm dia and finally transferred to a glove box. The cells were made
vs. metallic lithium as described above.

2.4. Electrochemical characterization

Electrochemical performance of the cells assembled as above are studied using
VMP3Z (Biologica) Multi-channel potentiostat/ Galvanostat and analysed using EC-
Lab® software. The impedance data were analyzed using ZSimpWin software with
complex nonlinear-least-squares fit.

2.4.1. Galvanostatic charge- discharge studies:

Electrochemical performance, mainly charge- discharge cycles of a Li-ion cells are
obtained through a galvanostatic method; in which current is controlled (kept
constant) and the potential is determined as a function of time. Since potential is
determined as a function of time, the technique is also known as
chronopotentiometry. In the actual experiment, constant current is applied between
two terminals of a cell/ battery and the voltage between working and reference
electrode is measured. With the applied current the potential of electrochemical cell
varies according to Ohm’s law (V= IR). The input and resultant output profile of the
constant current experiment is shown in Fig 2.3.
Figure 2.3, (a) Input profile of a galvanostatic experiment showing the applied current with time and the resultant (b) voltage vs. time plot (output profile).

As the current passes through the cell, the electrochemical redox reaction takes place at the electrode-electrolyte interface. The concentration of the active phase varies with the applied current; hence there is a change in the potential of the cell. The time period between the commencement of electroreduction/oxidation and the change in potential is called the transient time. Transient time for a species in presence of supporting electrolyte was first quantified by Sand. The Sand’s equation relates transient time with diffusion coefficient of the electro-active species as,

$$\tau^{1/2} = \frac{\pi^{1/2} nFC_0D^{1/2}}{2i}$$

Hence galvanostatic experiments can be used for the analysis of electrode kinetics. For the routine analysis, galvanostatic experiment is used for measuring the specific capacity, cycle life and rate capability of the material.

A common method to indicate the current used for charging or discharging the electrochemical cell under study is C rate, and is expressed as,

$$I_t (A) = C_n (Ah)/1(h)$$

Where,

‘I’ is the current expressed in amperes

‘C_n’ is the rated capacity in ampere-hours i.e total capacity the cell could deliver in ‘n’ hours.
For example, if a current of 100 mA is used to charge a cell with a rated capacity of 1000 mAh, then the C rate would be expressed as C/10 or 0.1 C.

Theoretical specific capacity of the material under study is calculated for the complete removal of 1 lithium,

In a lithium half cell, if 10 mg (active mass) of LiCoO$_2$ is used as positive electrode, then the total capacity of LiCoO$_2$ is $26.8 \times \frac{\text{Weight of active material}}{\text{Molecular weight}} = 26.8 \times \frac{10 \text{ mg}}{97.87} = 2.738 \text{ mAh}$.

The total capacity is considered as capacity in 1 hour i.e C$_1$ or 1C.

Therefore, the input current for C$_n$ rate is C$_1$/ n.

Specific capacity (mAh.g$^{-1}$) = capacity in mA/Active mass of LiCoO$_2$ in grams.

In a typical experiment, practical capacity (in mA.h) of the material is measured by multiplying the input current and total time for the charge/ discharge process.

2.4.2. Potentiostatic cycling (Cyclic voltammetry):

Cyclic voltammetry popularly known as CV is a potentiostatic or potentiodynamic technique; used for acquiring qualitative and sometimes quantitative information about the electrochemical reaction and analyte concentrations. It involves application of constant potential to the working electrode in a triangular wave form and measurement of its current response. Potential is swept linearly with time and once the set potential is reached the working electrode potential ramp is inverted (forward scan from E1 to E2 and reverse scan to E1). Input and output of cyclic voltammetry is shown in Fig. 2.4. Output graph of current response as a function of voltage is represented as cyclic voltammogram (CV). CV provides information on redox processes, phase transitions associated with the redox processes, heterogeneous adsorption etc. During the potential sweep, electrochemical reaction takes place due to the potential applied to the system: Simple electrochemical reaction can be represented as,

$\text{OX} + n\text{e}^- \leftrightarrow \text{Red}$
Current produced as a result of electrochemical reaction is measured by the potentiostat.

Figure 2.4, (a) Input and (b) output profile of a cyclic voltammetry experiment. A constant potential at a fixed scan rate (V/sec) is applied to the cell in a triangular wave form and the current response is studied.

At equilibrium, potential of the system is controlled by Nernst equation,

\[ E = E^0 - \frac{RT}{nF} \ln \left( \frac{\text{red}}{\text{ox}} \right) \]

When the applied potential \( E > E^0 \), the reduced species in the analyte starts getting oxidised. Thus the concentration of reduced species in the interface is less and hence more of reduced species can go near to electrode. That means diffusion layer thickness is less and hence current (ion) flux to the surface (and current) increases. It reaches a maximum as the potential is raised, and then it turns down as the depletion effect sets in. Thus we get a peak in the voltammogram \( (I_p) \). When the potential is reversed, the reduction process sets in and a negative current peak appears in the cathodic sweep. Based on the reversibility of the process, the electrochemical system under study can be classified as reversible, quasi-reversible and irreversible.

When the system remains in equilibrium throughout the potential sweep, the reaction is termed as reversible. The parameters used to characterize the reversible process\(^{12}\) are,
(i) The separation between cathodic \( (E_c) \) and anodic \( (E_a) \) peak potential,
\[ \Delta E_p = E_c - E_a = \frac{58}{n} \text{ mV} \text{ at all scan rates at 25°C.} \]

(ii) The peak current ratio,
\[ \frac{i_a}{i_c} = 1 \]
at all scan rates. Where, \( i_a \) is the anodic peak current and \( i_c \) is the cathodic peak current.

(iii) The peak current function \( i_p/\nu^{1/2} \) is independent of \( \nu \).

Where,
\[ i_p = 2.69 \times 10^5 n^{3/2} AC D^{1/2} \nu^{1/2} \]
\[ n = \text{number of electrons transferred per molecule} \]
\[ A = \text{Electrode surface area (cm}^2) \]
\[ C = \text{Concentration (mol.cm}^{-3}) \]
\[ D = \text{Diffusion coefficient (cm}^2.\text{s}^{-1}) \]
\[ \nu = \text{Scan rate (mV.s}^{-1}) \]

Variation from the above parameters shows departure from the reversible behaviour.

The aforesaid equation for peak current \( i_p \) is known as Cottrell equation\(^{12} \) and is due to the diffusion controlled processes occurring in the electrochemical reaction.\(^{13} \) As the Li-ion intercalation is mainly diffusion controlled, Cottrell equation is highly applicable for the study of Li-ion battery mechanisms.

Cyclic voltammetry is useful for Li-ion battery studies,

(i) For identifying whether the reaction under study is reversible or not.

(ii) As in galvanostatic experiment, CV could also be used to measure the specific capacity of the material. Capacity is calculated by measuring the total
current response (integrating the area under the peak in time vs. current plot of CV) for the complete sweep.

(iii) To find the solid solution regions and biphasic reactions of lithium insertion/deinsertion process. Symmetric peak in the cyclic voltammogram represents solid solution behaviour and asymmetric peaks represent biphasic regions.

(iv) The change in current response ‘i’ with scan rate ‘ν’ is used to differentiate the charge storage mechanism as diffusion controlled and non-diffusion controlled.

\[ i \propto \nu \] for non diffusion controlled process and,

\[ i \propto \sqrt{\nu} \] for diffusion controlled process.

Various kinetic parameters associated with charge/discharge processes can be calculated using SSCV (Slow scan cyclic voltammetry) technique.

2.4.3. Constant power experiments:

Constant power experiments are designed to study the charge- discharge behaviour of a cell at constant power and useful for plotting Ragone plot (power vs. energy density). Ragone plots are curves that relate the power of the energy storage device to the available energy. It is mainly used for the comparison of varieties of devices with respect to their energy, power and efficiency. The actual experiment is carried out by applying constant power \((i \times v\) is constant\) to the system and measuring the time required for charging/discharging the cell. Therefore, the current is lowest at the beginning of the discharge and increases as the battery voltage drops in order to maintain a constant-power output at the level required by the equipment. The average current is lowest under this mode of charge/discharge, and hence, the longest service time is obtained. Fig. 2.5, shows input power and the voltage profile evolution with time during constant power experiments. From the time required for charge/discharge, the energy density of the cell is calculated to be power \(\times\) time. Final plot of power vs. energy density is represented as Ragone plot.
Figure 2.5, Schematics showing the (a) input constant power and the (b) potential evolution of the cell during constant power experiments.

A method analogous to C rate is used to express the charge-discharge rate in constant power experiments and is known as ‘E’ rate.\textsuperscript{11}

\[ P = M \times E_n \]

Where ‘\( P \)’ is the power in watt (W),

‘\( E_n \)’ is the rated energy of the battery in watthours (Wh) at the time duration of ‘\( n \)’ hours (at which the battery was rated).

‘\( M \)’ is the multiple or fraction of \( E \).

For example, the power level at the \( E/2 \) rates for a battery rated at 1200 mWh, is 600 mW.

2.4.4. Impedance spectroscopy:

Impedance spectroscopy is an important electrochemical technique that measures the opposition exerted by the electrochemical system to a sinusoidal alternating current. System under investigation is perturbed from its steady state by applying an external signal. External signal applied is normally a sinusoidal voltage (or current) of known amplitude and frequency. The response to the applied excitation signal i.e the way in which the system follows the perturbation at steady state is analysed in impedance spectroscopy.\textsuperscript{14} Fig.2.6 shows the applied sinusoidal wave (\( I_{AC}^{in} \)) and the current response (\( I_{AC}^{out} \)) of the impedance spectroscopy.
Figure 2.6. General principle employing EIS analysis in a battery unit i.e perturbation of system with an alternating signal of small magnitude ($I_{AC}^{in}$) and study the way in which the systems follows the perturbation at study state.

The output voltage with time is represented as $E = E_0 \sin \omega t$. Where, $E_t$ is the potential at time t, $E_0$ is the equilibrium potential, $\omega$ is the angular frequency (radians/second). $\omega = 2\pi f$ (f= frequency expressed in hertz). In a linear system, current response is shifted by $\phi$. Therefore,

$I = I_0 \sin (\omega t + \phi)$.

Thus impedance analogous to simple resistance is,

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$

Where, $Z_0$ is the magnitude of impedance and $\phi$ is the phase shift. According to Euler’s theorem,

$\exp(j\alpha) = \cos \alpha + j\sin \alpha$

Therefore, $Z(\omega) = Z_0 \cos \phi - Z_0 \sin \phi$,

Where $Z_0 \cos \phi$ is the real part and $Z_0 \sin \phi$ is the imaginary part of the impedance.

Plot of real part vs. imaginary part is known as Nyquist plot. The plot can be analysed by fitting the data with equivalent circuit model.

Various kinetic steps that are responsible for impedance in a lithium ion battery include ionic conduction through the electrolyte, lithium ion migration through the SEI layer, charge transfer resistance on the surface of each particle, solid state
diffusion of lithium ion through the electrode material and other processes such as formation of new crystalline structures. Since, all steps have different time constants, the impedance appears at different frequencies; has been analysed by applying sinusoidal wave of different frequency regions.

Impedance measurements for the present study were carried out using three electrode assemblies with lithium as reference and counter electrode (shown in Fig. 2.7).

![Three electrode assembly](image)

**Figure 2.7, Three electrode assembly used for impedance analysis. Lithium metal is used as both reference and counter electrode.**

In a typical Galvanostatic Electrochemical Impedance Spectroscopy (GEIS), an input current signal of small amplitude is applied between working electrode and reference electrode and the voltage/current response is measured as a function of frequency (400 kHz and 2 mHz). The data were analyzed using ZSimpWin software with complex nonlinear-least-squares fit.
2.5. References:


7. H. Kaur, Instrumental methods of chemical analysis, Pragati Prakashan, Meerut, India.


