



Various Characterization Techniques For Nanomaterials For Energy Applications

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Abstract:

Nanomaterials are very important material for energy applications. For utilising them for different applications, different characterisation techniques need to be performed and studied. In the present manuscript, various surface and electrochemical characterisation techniques have been studied in detail.

Keywords:

Nanomaterials, Characterisation techniques, surface study, electrochemical study

1.Introduction

Nanomaterials have attracted great research interests due to enhanced and unique performance capabilities. They help to grow the society due to technological innovations. But to utilise nanomaterials for various applications, their characteristic properties need to be understood well. For that it is very important to study various characterisation techniques. Nanomaterials have different properties from the bulk materials. They possess high surface-to-volume ratio. This characteristics increase the reactivity of materials exponentially that leads to different electronic, mechanical, optical, chemical or physical properties. These attract material scientists for intensive studies of nanomaterials for potential energy applications. These days, different types of nanomaterials are being synthesized for energy applications. Utilization of the properties of nanomaterials for energy applications require development of various characterization techniques. In fact, quite often a wider characterization of synthesized materials is necessary. In this context, it is advantageous to learn about limitations and strengths of different techniques. Here, the use of different techniques for the characterization of nanomaterials are extensively described. These techniques are at times restricted for the study of only particular properties. Nanomaterials for energy applications are characterized for surface, compositional, and

electrochemical properties. The EDAX is used to identify the elemental contents in the films. Various surface studies i.e. FTIR, BET and XPS have also been discussed in detail. The electrochemical properties of the prepared electrodes are analysed by cyclic voltammetry (Bio-logic electrochemical workstation). The principle, functioning and importance of each instruments are briefly outlined in this section with related theory.

2. Surface study

2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is an important system in the field of material science is shown in Fig.2. It is a simple technique used for identifying functional groups adsorbed on the surface of a material. It's analysis is done on the basis that every molecules have set of different vibrational frequencies[1]. These frequencies take place in the IR region ($\sim 4000\text{ cm}^{-1}$ to $\sim 200\text{ cm}^{-1}$) of electromagnetic spectrum.

When beam of IR radiation falls on the sample, it transmits all other frequencies and absorbs only molecular vibrational frequencies as shown in Fig.1. These absorbed radiation of frequencies are measured using infrared spectrometer[2]. The plot obtained with frequency and absorbed energy is called IR spectrum of material. Detection of a substance has been possible since different materials acquire varied sets of vibrational frequency and give way to different infrared spectra. In addition, from the absorption of frequencies, it is feasible to find out presence of the range of chemical groups in a chemical structure. Also, the features of the absorption, the amount of the absorption in a sample are linked with the concentration of that substance.

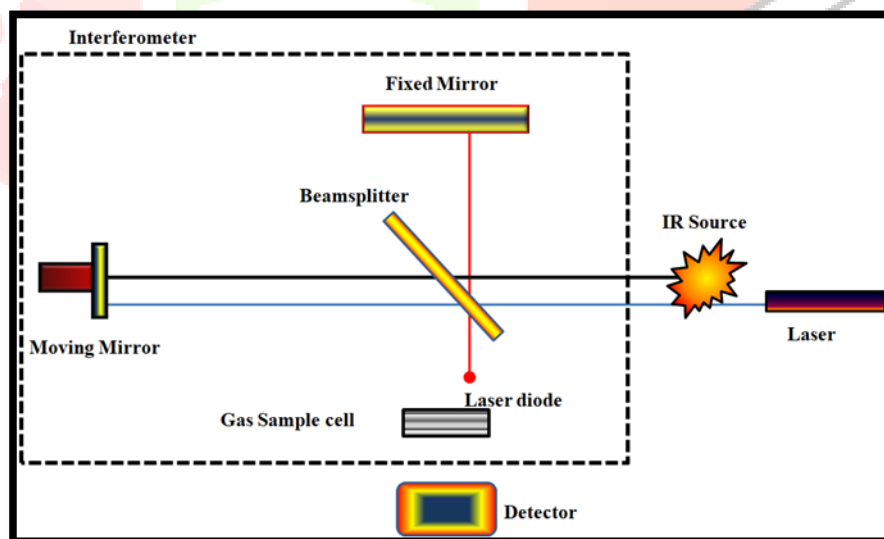


Fig.1 FTIR spectroscopy experimental setup



Fig.2 FTIR spectroscopy instrument

2.2 Energy dispersive X-ray analysis (EDAX)

Energy Dispersive X-ray Analysis (EDAX) is an analytical tool used for study of chemicals and elemental analysis of a sample shown in Fig.4[3]. Since it is type of spectroscopy, so it depends on the study of a sample by interactions of matter with em radiation. It is analyzed by X-rays emitted by the matter after being struck by charged particles[4]. Its characterisation capabilities are limited to larger part of basic principle i.e. each element has a distinct atomic structure. Where these X rays are the characteristic of atomic structure of element which are identified distinctively from each other. Characteristic X-rays emission from a sample are done by focussing high energy beams such as X-rays, electrons, protons or neutrons on sample. In rest state, atom present in sample is present at unexcited level (or ground state) in electronic shells or discrete energy levels are confined to nucleus. Beam incident on specimen excite an electron in the inner shell and eject it from the shell by generating electron hole pairs. An electron present in the outer shell with higher-energy fills the hole shown in Fig.3. This difference in energy between higher or lower energy shell come out as X-ray beam. The number and emitted energy of X-rays from sample are measured by the instrument called energy dispersive spectrometer. Since, the energy and number of emitted X-rays from atomic structure of element and energy shells difference is the characteristic tool to identify elemental compositions in the sample

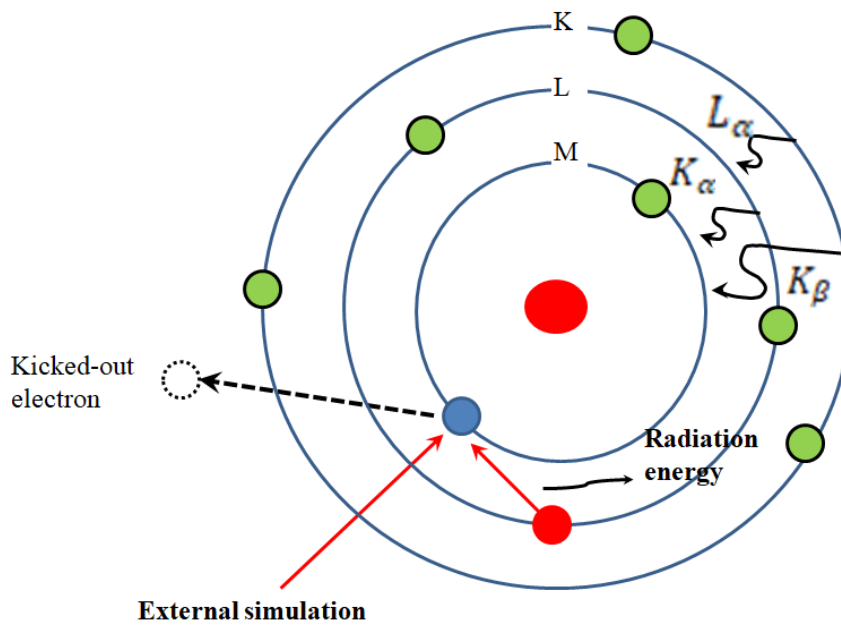


Fig.3 EDAX working principle



Fig.4 EDAX instrument

2.3 X-ray Photoelectron Spectroscopy(XPS)

X-Ray Photoelectron Spectroscopy (XPS) is an important technique in which X-rays are used for bombarding on sample and then electrons are emitted, the energies of these electrons are studied shown in Fig.5. Characteristic X-ray sources used are of $MgK\alpha$ and $AlK\alpha$ at 1253.6 and 1486.6 eV respectively. Also, ultraviolet source (21.2 eV) are used to find high count rates for the low energy region to analyze emitted electrons. This is important as it contains information for valence bands. X-rays penetrate the surface of sample to a depth of few micrometers. But the electrons present near the surface only can be emitted without losing energy due to collisions among different atoms. The kinetic energy (K.E.) and the binding energy (B.E.) of the electrons are determined using simple relationship i.e. $h\nu = K.E. + B.E. + \phi$, here $h\nu$ is energy of X-ray and ϕ represents the work function (generally few eV) for spectrometer. After scanning over the kinetic energy ranging from 0 eV to the incident X-ray energy, an energy spectrum is obtained. The obtained energy spectrum is different for every element and only permits the identification of elemental compositions present in top 1-2 nm. The detection limit is around 0.1% atomic. XPS technique is far more sensitive for elements with higher atomic number.

The resolution of energy in the spectrometer is enough to resolve differences in the binding energy for different chemical bonds such as, it is likely to separate C-C bond from O-C=O and C-O bonds. The area under the peak for each chemical bond denotes the percentage of that bond present in the sample.

In XPS measurement cleanliness and handling of sample are very crucial steps for obtaining better result since the XPS electrons originate mostly from the first few monolayers. Storage of samples should be done in glass or fluoware containers but not in plastic bags.

The XPS technique has been done to analyze a broad variety of materials. The limitations of this technique are sample used for testing must be a solid and should be compatible to vacuum. Here, powdered samples are mounted with sticky tape and liquid samples are dried on different substrates e.g. silicon.

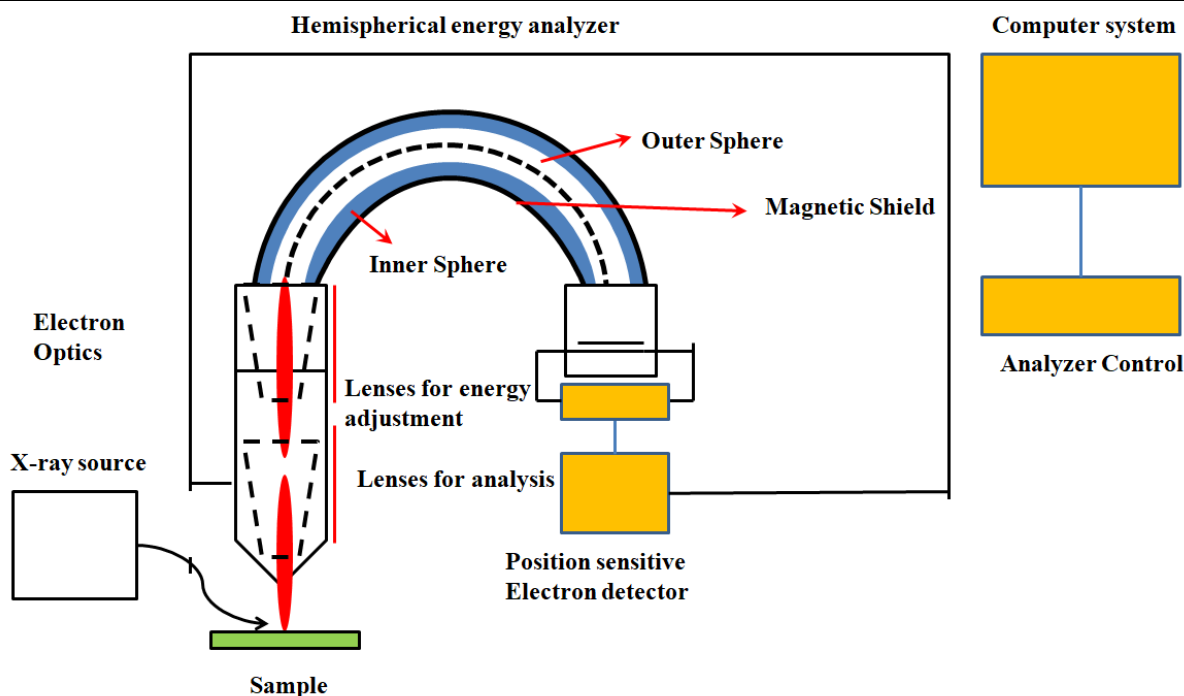


Fig.5 XPS experimental setup

2.4 Brunauer, Emmett and Teller study (BET)

Using Brunauer, Emmett and Teller (BET) instrument, the specific surface area (in m^2/g) and pore size distribution of a sample is determined[5]. It is a key parameter to identify the potential of materials for various applications. Information obtained from BET is used to calculate the dissolution rate, as it is related to specific surface area.

The specific surface measured by BET is related to the total reactive surface area since every porous structure adsorb very small sized gas molecules. The determined surface area from BET is therefore in general are found to be larger than the surface area measured by air permeability. The schematic of instrument is shown in Fig.7

The specific surface area of a powdered sample measured by physical adsorption of gas molecules on sample's surface and then amount of adsorbate gas are calculated related to a monomolecular layer on sample's surface[6]. Physical adsorption process results from the Vander Waals forces (relatively weak forces) between gas molecules of adsorbate and the surface area of adsorbent's testing sample is shown in Fig.6. The measurement is usually carried out at liquid nitrogen temperature. The amount of gas adsorbed may be determined by continuous or volumetric flow procedures. Outgassing is very important before measuring the specific surface area of sample. It is a vital step to remove vapours and gases that may have physically adsorbed onto the surface of sample after synthesis or during sample handling storage and treatment. The specific surface area obtained from BET may be reduced or may be inconsistent if outgassing is not achieved. It happens because an intermediate area of the surface is already covered with previously adsorbed vapours or gas molecules. It is critical step in BET in order to obtain required accuracy and precision in measuring specific surface area due to the sensitiveness of the surface of materials.

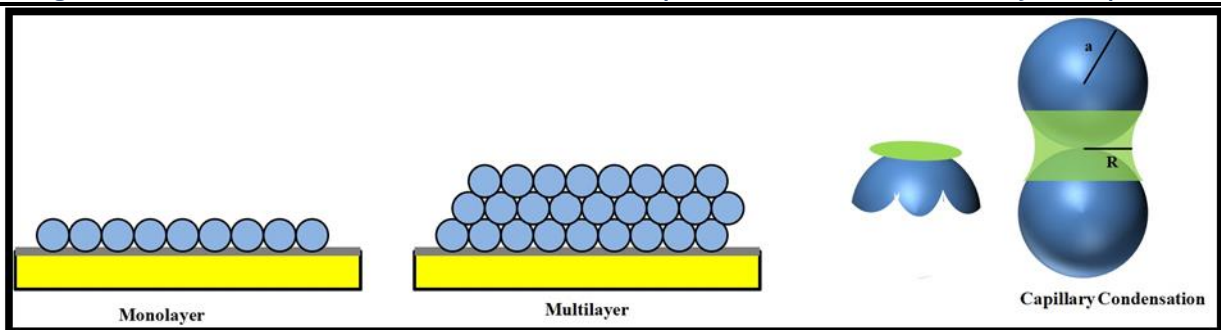


Fig.6 BET working principle

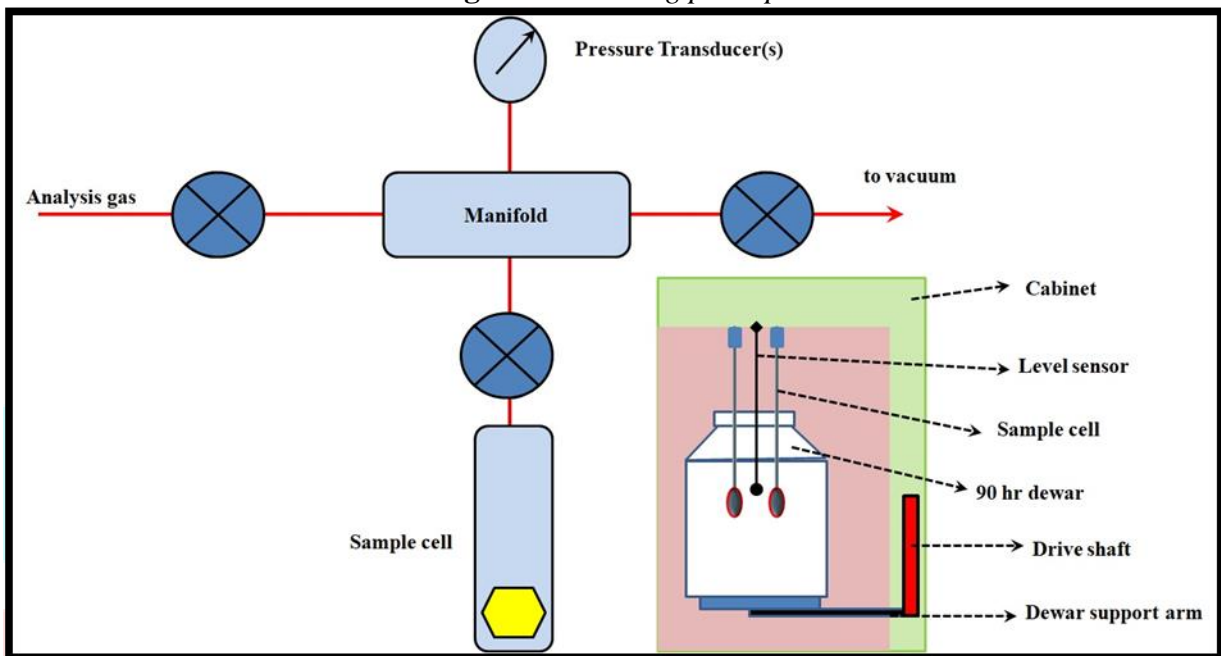


Fig.7 BET experimental set up

3. Electrochemical characterization

3.1 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is commonly used method to study the electrocatalytic properties of a material in electrolyte solution. It is a kind of potentiodynamic measurement for electrochemical properties [7]. In this experiment also as in the case of linear sweep voltammetry (LSV), potential on the working electrode varies linearly with time. But LSV experiment stops after reaching a set potential value but CV takes the experiment an additional step forward. When a set potential is reached on CV, potential trace for working electrodes get inverted. The inversion of potential trace can take place several times during a particular experiment. In this experiment, the current versus applied potential at the working is plotted to get the cyclic voltammogram curve. In CV, the working electrode potential and time are related to each other. This is known as the scan rate of the experiment measured in V/s. A potential value is applied between the working electrode and reference electrode and the current is calculated between the counter electrode and working electrode. The obtained result is plotted as current (i) versus potential (E).

Scan produces a peak current (i) for any materials that can be oxidized or reduced which depends on the

direction of initial scan during the potential(E) scanned range. The current increases when the potential attains the reduction potential of material[8].

If the applied potential is reversed and redox couple is found reversible then it will attain that potential which deoxidises formed product in the first reaction of reduction and generates current with reverse polarity of forward scan. This is the oxidation peak typically have similar shape to that of the reduction peak shown in Fig.8.

Since CV measures the charge-response in view of a changing voltage, so it is a way for evaluating the capacitance. During CV analysis, a series of varying potentials at a constant sweep/scan rate (dV/dt) are applied and the response of current is recorded. An ideal capacitor without resistance show a rectangular shape. CV studies are performed at suitable potential range versus Standard Calomel Electrode (SCE) at different scan rates. The Specific capacitance (SC) is evaluated using half of the integrated area of CV curves to get charge (Q), and then dividing Q by the mass of the working electrode (m) and potential width window. The experimental set up electrochemical characterisation is provided in Fig.9

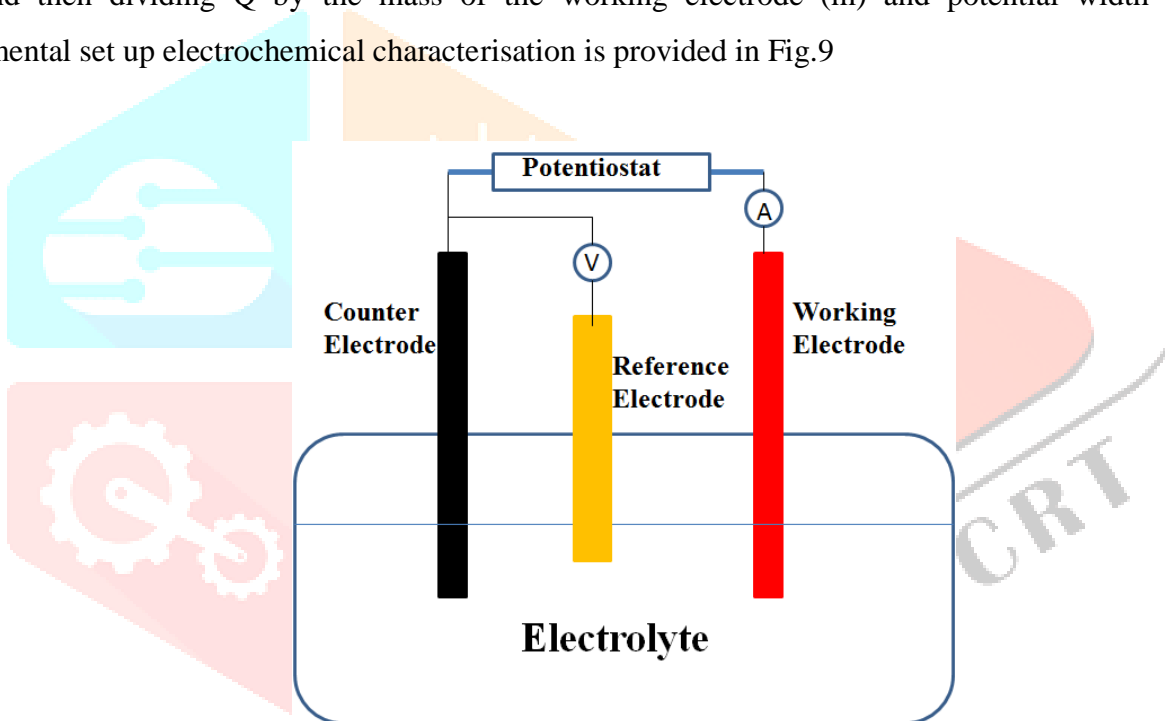


Fig.8 Electrochemical study experimental setup

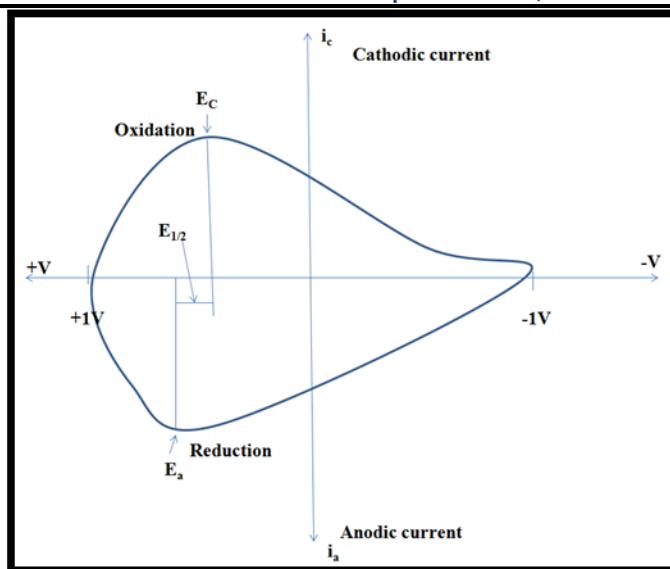


Fig.9 Cyclic voltammetry plot

3.2 Galvanostatic charge-discharge (GCD)

Galvanostatic charge discharge (GCD) is the most useful technique to calculate electrochemical capacitance value for any material under controlled conditions of current [9]. This technique is quite dissimilar than the cyclic voltammetry technique since in the GCD technique, the current value is controlled and voltage is measured as shown in Fig.10. This is in fact an extensively used technique in supercapacitor field since it can be expanded from the laboratory scale to the industrial one. This technique is also known as chronopotentiometry and gives way in to several parameters for example capacitance, cyclability, resistance, etc. [10]. In this technique, current pulse is given on working electrode and the resulting potential is measured as function of time against the reference electrode. The instant when current is applied to the system, the potential value measured suddenly changes due to loss of internal resistance (IR) and then it changes gradually due to the development of over-potential concentration across electrodes. This occurs because the reactant concentration is exhausted at the surface of electrode.

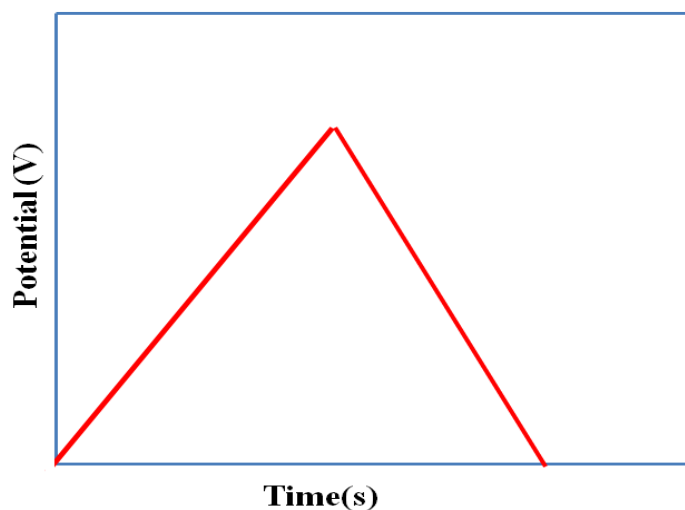


Fig.10 Galvanostatic charge discharge curve

3.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a vital technique for studying the charge transfer characteristics of the working electrodes and cells. It measures the complex impedance of electrochemical cells and electrodes. At low frequency, the real part of the impedance approximately equals to the sum of R_f and R_s while at high frequency, the real part of the impedance equals to R_s .

Electrochemical impedance spectroscopy (EIS) has been done in a particular range of frequency for studying electrochemical activities of materials. In this study, the term spectroscopy is because of the fact that impedance is plotted against frequency but this frequency is not the energy levels. So, it is not possible to get information regarding quantum states from data analysis of impedance curve. Electrochemical characteristics of the system can be done by analysing data of impedance in the applied range of frequency. Complex resistance called as “impedance” is formed, if current flows from a circuit containing capacitors, inductors, resistor etc. In general, inductive property are not obtained in electrochemical characteristics, so equivalent circuit without inductor are explored. Impedance data are analysed by Nyquist curve (Fig.11). In this curve, the imaginary impedance (Z_{im}) are plotted with real impedance (Z_{Re}) [11]. Nyquist curve consists of semicircle and slant line, where ability of charge transfer and diffusion process are explained by semi-circle and slant line respectively in Fig.11.

Analysis of impedance data has been done with the help of equivalent circuit model. It is made using a software called Z fit. This equivalent circuit consists of several components i.e. resistance corresponding to film, solution, charge transfer (R_f , R_s , R_{ct}) respectively, resistance due to diffusion (Z_w), constant elements due to phase (CPE) etc. Here, R_s and R_f represent the capability to gather electrons from the exterior of circuits, the ability of charge transfer is shown by R_{ct} . Lower resistance values denote conductivity and the process of diffusion process is better for electrodes. Where high Warburg impedance value denotes the improved electrocatalytic capacity [12]. Small arc radius in the Nyquist plots indicate smaller value of resistance which causes higher charge transfer [13].

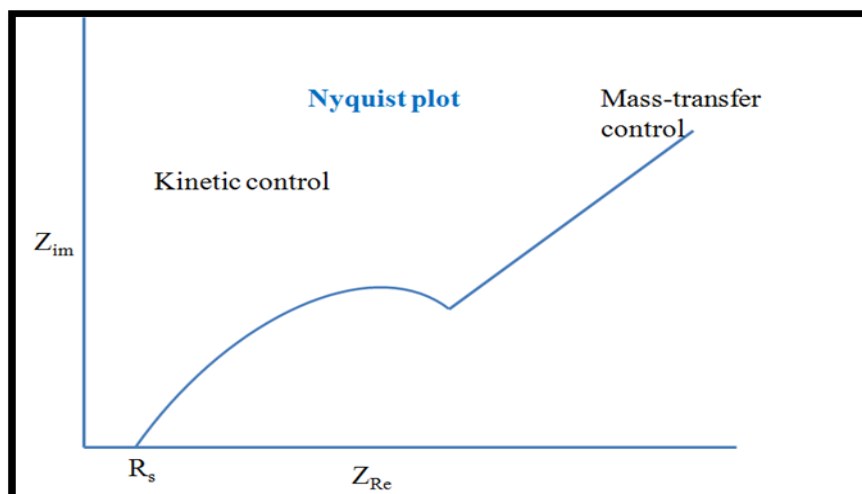


Fig.11 Electrochemical impedance spectrum

4. Conclusions:

In this manuscript, different characterization techniques for energy applications have been studied in detail.

7. Acknowledgement

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