Chapter 2

Characterization Techniques

Summary

The present chapter gives a detailed description of the characterization techniques, which are employed throughout the research work. The basic principles of the characterization and measurement tools and how they can be applied to study optical properties, crystal structure, surface morphology, elemental composition, particle size distribution, film thickness, electrochemical activity, electrical and magnetic properties etc. are outlined in this section.
Various characterization techniques have been used to study rGO based inorganic composites synthesized employing chemical routes. This chapter is devoted to elucidate the underlying principles and the techniques used for characterization of as-prepared composites. The characterization techniques are mainly divided into two categories namely spectroscopic techniques and microscopic techniques.

### 2.1 Spectroscopic techniques

Spectroscopic techniques are widely utilized to probe the vibrational and electronic energy levels of different materials. UV-Vis-NIR spectroscopy, photoluminescence, infrared and Raman spectroscopy deal with measuring absorption, emission or scattering of light that contain information about the properties of the materials.

#### 2.1.1 UV-Vis-NIR spectroscopy

UV-Vis-NIR spectroscopy is usually used to study the optical properties of transition metal compounds, noble metal nanoparticles, semiconductor nanostructures, highly conjugated organic compounds and biological macromolecules. UV-Vis-NIR spectroscopy consigns to absorption or reflectance in the ultraviolet, visible and near-infrared spectral region. Every molecular system possesses three types of energies namely electronic ($E_{\text{elec}}$), vibrational ($E_{\text{vib}}$) and rotational ($E_{\text{rot}}$). Molecules containing $\pi$-electrons and non-bonding electrons ($n$-electrons), can absorb energy in the form of ultraviolet or visible or near infrared light to excite these electrons to higher antibonding molecular orbitals. The possible electronic transition because of light energy absorption by the molecules is given in the figure 2.1. The more easily excited electrons (lower energy band gap between the HOMO and the LUMO), can absorb the longer the wavelength of light. The absorption peak as a result obtained is broad, smooth and never very sharp due to the fact that the electronic absorption is accompanied by a corresponding change in the vibrational and rotational energies as well. Different molecules absorb radiations of different wavelengths. An optical
spectrophotometer records the degree of absorption at each wavelength in a given range. The resulting spectrum is represented as a graph of absorbance (A) vs wavelength (λ). Absorbance usually ranges from 0 (no absorption) to 2 (99% absorption), and is specifically defined in context with spectrophotometer operation.(1-4)

Figure 2.1. Schematic representation of possible electronic transition during the absorption of light energy by molecules.(1-4)

Monitoring UV-Vis spectra is useful to study the chemical reduction of GO. Absorption spectra of GO give characteristic features corresponding to n-π* transitions of C=O groups that appears as a shoulder at ~320 nm and π-π* transitions of C=C groups that appears at ~230 nm corresponding to sp² carbons. Upon reduction to form rGO, the shoulder at 320 nm disappears as C=O groups get reduced and 230 nm red shifts to ~265 nm due to restoration of conjugation (Fig.2.2a).(5)

Figure 2.2. (a) UV-visible spectra of GO and rGO (b) SPR absorption of Au nanostructures.(5, 6)
UV-visible –NIR spectra provides unique characterization of inorganic nanomaterials as well. Metal nanoparticles show characteristic absorption mostly in the visible region due to surface plasmon absorption. The surface plasmon resonance is the collective oscillation of electrons stimulated by incident light on metal nanoparticles. The frequency of the light photons matches the natural frequency of surface electrons oscillating against the restoring forces of positive nuclei. The surface plasmon absorption is sensitive to the shape and size of the metal nanoparticles and as well as the dielectric medium (Fig. 2.2b). (6) Semiconductor nanoparticles show absorption due to band gap where it matches with the incident wavelength. The extension of band edge absorption can also give insights into defect or dopant levels. Several models are reported for the determination of optical band gap from the optical absorption spectra. Among them, Tauc’s model is the most widespread method, which allows us to derive the band gap energy ($E_g$) from $E (\varepsilon)^{1/2}$ as a function of the incident energy, $E$. The band gap can be determined by extrapolation of the plot (see inset of Fig. 2.3) $(\alpha h\nu)^{1/2}$ over a limited range of photon energies ($h\nu$). (7) The inset of figure 2.3 shows the band gap of ZnO, which is determined by Tauc’s plot method. (8)

![Figure 2.3. Absorption spectra of ZnO nanoparticles; inset shows the band gap calculated by Tauc’s plot method.](image)

Figure 2.3. Absorption spectra of ZnO nanoparticles; inset shows the band gap calculated by Tauc’s plot method. (8)

UV-Vis spectra have also been used in this thesis work to study the catalytic and photodegradation activity of graphene hybrids by monitoring the in situ absorption of...
organic molecule or dye with time. The kinetics of the reaction has been studied by considering the absorbance at a time proportional to the concentration.

2.1.2 Photoluminescence

Photoluminescence (PL) spectroscopy is a useful technique for the study of the electronic structure of materials.\(^{(9)}\) Figure 2.4 shows the PL spectra of ZnO NPs, which shows emission in the UV region corresponding to the band edge emission and a broad peak in the visible region that corresponds to the impurity levels due to dopants or oxygen vacancies.\(^{(10)}\)

Recombination mechanisms. Analysis of photoluminescence also provides understanding of the underlying physics of recombination process, which relates to identification of surface, interface and impurity level.

Band gap determination: Most general radiative transitions in semiconductor occur between states in the conduction and valence bands, with the energy gap difference known as band gap.

![Photoluminescence Spectra of ZnO Thin Film](image)

Figure 2.4. Photoluminiscence spectra of ZnO thin film.\(^{(10)}\)

Assessment of the material quality: Material quality can be evaluated by quantifying radiative recombination, keeping in mind that non-radiative recombination is associated
with localised defect levels that are detrimental to material quality and subsequently to device performance.

Detection of defect-impurity levels: Radiative transitions can also involve localised defects and the photoluminescence energy associated with these levels can identify these specific defects.

2.1.3 FT-IR spectroscopy

Fourier transform infrared spectroscopy (FTIR) gives information about chemical bonds in a molecule by probing vibrational levels. An IR spectrum is particularly useful to identify the functional groups in a molecule in the fingerprint region. The FTIR spectrum of a compound is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. The absorption depends on the nature of the functional group and its associated bonding to the rest of the molecule.\(^{(11)}\)

![FTIR spectra of graphene oxide and reduced graphene oxide.](image)

Figure 2.5. FTIR spectra of graphene oxide and reduced graphene oxide.\(^{(11)}\)

The presence of the different functional groups in GO, rGO, and rGO based hybrid films can be evaluated using FTIR spectroscopy (Fig.2.5). GO sheets with oxygen functional groups on its basal plane as well as at the edges should exhibit vibrations characteristic of
hydroxyl (C-OH, 3050-3800 cm\(^{-1}\) and 1070 cm\(^{-1}\)), carboxylic / ketonic species (C=O, 1600-1650 cm\(^{-1}\), 1750-1850 cm\(^{-1}\) including C-OH vibrations at 3530 and 1080 cm\(^{-1}\)), sp\(^2\) hybridized C=C (1500-1650 cm\(^{-1}\), in-plane vibrations) and ether or epoxide (C-O-C, 1000-1320 cm\(^{-1}\)). After reduction of GO, all the characteristic peaks of oxygen functional groups should vanish. The FTIR spectra of rGO show bands near to 3432 cm\(^{-1}\) due to the O-H stretching vibrations and the peak around 1580-1600 cm\(^{-1}\) attributed to the skeletal vibrations of C=C bonds. The presence of surfactants that protect the inorganic nanostructures can also be identified using IR spectroscopy.

### 2.1.4 Raman spectroscopy

Raman spectroscopy is used to observe vibrational, rotational, and other low-frequency modes in a system. This spectroscopy is an essential tool for the characterization of carbon nanomaterials.\(^{(12)}\) Write about confocal Raman working principle, instrumentation etc.

The quality of graphene obtained by various methods is evaluated from their Raman spectra (Fig.2.6). Raman spectra of monolayer defect free graphene contain (Fig.2.6a) G peak at ~1580 cm\(^{-1}\) and 2D peak at ~2700 cm\(^{-1}\) caused by the in-plane optical vibration (E\(_g\) mode) and second order boundary phonons. The D peak located at ~1350 cm\(^{-1}\) due to first zone phonons is absent in defect-free graphene.\(^{(13)}\) If the D peak is significant, it indicates that there are a lot of defects in the graphene sheet and also edge states corresponding to sp\(^3\) carbons (Fig.2.6b).\(^{(14)}\) The ratio of the intensity of the D peak to G peak gives an estimate of the defects in the graphene layer. The 2D band (Fig.2.6a) is the second order overtone of different in-plane vibrations. 2D peak is always a sharp peak in graphene even when no D peak is present. This band is used to determine the layer thickness. With the increase in the number of layers constituting graphene, a 2D peak broadens with the positional shift. The appearance of the 2D peak is also different, the single layer graphene-containing only one component while bilayer graphene has four parts due to the splitting of the 2D peak. Raman
spectra of GO and rGO are shown in figure 2.6b. The relative intensity of both the peaks such as D and G bands (\(I_D/I_G\)) is a measure of disorder degree and is inversely proportional to the average size of the sp\(^2\) clusters. The \(I_D/I_G\) for rGO (1.70) is larger than the GO (1.21). The band shift in the G band from 1600 cm\(^{-1}\) to 1590 cm\(^{-1}\) indicates the restoration of graphitic structure after reduction of GO.\((14)\)

![Figure 2.6](image1)  
(a) Raman spectra of single layered graphene and multi layered graphene\((13)\)  
(b) Raman spectra of GO and rGO.\((15)\)

![Figure 2.7](image2)  
(a) Pictorial representation of SERS mechanism at noble metal NPs  
(b) SERS spectra of various fluorescent dyes includes methylene blue, rhodamine 6G and rhodamine B.\((16,17)\)

Surface-enhanced Raman scattering (SERS) is a surface sensitive technique and the success of SERS is mainly dependent on the interaction between the adsorbed molecule and surface of plasmon materials or semiconductors, quantum dots, graphene. SERS is mainly of two types namely (i) electromagnetic enhancement (ii) chemical
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enhancement. Increases in the intensity of Raman signal for adsorbents on particular surfaces (Ag, Ag, Cu etc) occurs because of an enhancement in the electric field provided by the surfaces. The chemical enhancement involves by charge transfer between the adsorbed molecule and the surface of semiconductors, quantum dots or graphene. Figure 2.7 shows the illustration of SERS mechanism, (Fig. 2.7b).

2.1.5 XPS spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique capable of providing information regarding the elemental composition, empirical formula, chemical and electronic state of the elements that constitute a material. Photons of energy $h\nu$ impose upon a sample and cause emission of electrons which are collected by an electron lens system and then identified by the energy-selective analyser. According to the excitation radiation and the energy of the excited electrons, this technique has been divided into Ultraviolet photoelectron spectroscopy (UPS) and XPS. In UPS, valence electrons ($E < 40$ eV) are emitted using the UV light (from a noble gas discharge lamp-He-discharge lamp) while in XPS, core level electrons ($E>40$ eV) are excited using soft X-ray radiation. Generally for XPS, a dual anode X-ray gun (Al $K\alpha$, Mg $K\alpha$) is utilised in commercial equipment. The X-rays penetrate a significant distance into the sample ($\sim\mu$m), but due to the strong interaction of electrons with matter, depending on their kinetic energy, their escape depth out of the sample is in the range of 3-30 Å. So it is a suitable technique to probe surface electronic states of a any sample. The kinetic energy of the emitted electrons can be calculated employing a suitable electrostatic or electromagnetic analyser and thus the spectrum of the sample could be recorded as a function of a number of electrons of a particular energy emitted per unit time. A simplistic approach to understanding will be from the equations showing the ionization process of an element.
According to the law of conservation of energy

\[ E (A) + h \nu = E (A^+) + E (e^-) \]  

Since the entire energy of the emitted electron will be kinetic energy (KE), equation can be rearranged as follows,

\[ KE = h \nu - [E (A^+) - E (A)] \]

The term in the bracket represents the energy difference between the ionised and the atomic state of an atom, known as the binding energy (BE), which is characteristic for an atom. The above equation is thus simplified to \( KE = h \nu - \left[ BE \right] \) that contains the Fermi level component and thus this equation is modified incorporating the work function (\( \varphi \)) term for the solids.

\[ KE = h \nu - BE - \varphi \]

Figure 2.8. C1s XPS spectra (a) GO (b) rGO (20)

In the present work, identification of the functional groups present in GO and their extent of reduction can be evaluated by measuring binding energies of carbon (Fig.2.8). C/O ratios can also be calculated from the peak intensities. The oxidation states of elements constituting metal, semiconductor and magnetic nanoparticles in the hybrid systems can also be assessed employing XPS.
2.2 Microscopic techniques

Microscopic techniques for the characterization of nanomaterials mostly give information regarding morphology. Techniques involving the interaction of electron beam with the specimen and the subsequent collection of transmitted or scattered electrons in order to create an image can divulge information on different crystal phases and distribution of a particular phase. This process can be carried out by scanning of a fine beam over the sample (21) or by wide-field irradiation of the sample (22). Atomic force microscopy based on force interaction between a nanometer cantilever-tip and surface gives height information of the nanostructures in addition to high resolution topography.

2.2.1 Scanning electron microscopy

A scanning electron microscope (21) is a category of electron microscope that generates images of a sample by scanning the sample with a focused beam of electrons. The electron beam interacts with atoms present in the sample, producing different signals that contain information concerning the samples’ surface topography and composition. The interaction of an electron beam with the sample surface generates various signals (Fig.2.9a) such as backscattered electrons (BSE), X-rays, secondary electrons (SE) and Auger electrons. These different signals are detected in SEM, and the detected signals contain information about the sample. BSE image mode is to show compositional differences (material contrast) in the specimen. (23) BSE have a advantage that they are sensitive to the atomic mass of the nuclei they scatter from. As a result in the BSE image, the heavier or high atomic mass elements can back scatter more efficiently and appear brighter than the lighter elements. The primary signal carrier in SEM is secondary electrons, which are ejected from the k-shell of the sample atoms with inelastic scattering interactions with the beam electrons. They have very low energy and can be detected by the Everhart-Thornley detector. The brightness of the signal depends on the number of secondary electrons
reaching the detector. Working distance has significant effect on the efficiency of the SE mode. A minimum working distance of 4 mm should be used to get better images. The SE detector is mounted at a certain angle to the specimen, so it provides good surface information. The surface morphology of GO and rGO images by SE is shown in the figure 2.9b.

![Figure 2.9. (a) Schematic diagram that demonstrates various signals emitted from the sample surface when illuminated with an electron beam (a) FESEM image of GO.](image)

EDS is a qualitative and quantitative X-ray microanalytical non-destructive technique that can provide information about the chemical composition of the material. In this, an electron beam is focused on the sample in SEM or TEM. Due to the interaction between electrons and sample atoms X-rays characteristic of the constituting elements are generated. These X-rays are detected by a detector and displayed as a spectrum.

### 2.2.2 Transmission electron microscopy

TEM is a microscopy technique, in which a beam of electrons is passed through an ultra-thin specimen. An image is formed from the interaction of the electrons transmitted through the sample. The image is magnified and focused on to an imaging device such as CCD camera. TEM is the ultimate imaging tool for studying nanomaterials. The size distribution and shape of nanostructures can be studied. The high resolution images of the materials
Figure 2.10. HRTEM images of graphene and rGO: insets show the SAED.\(^{(26, 27)}\) provide information about crystal phase, defect planes and interfaces.\(^{(25)}\) Figure 2.10a shows the TEM image of single layer graphene and inset shows the SAED with single crystalline with hexagonal lattice symmetry. Selected area electron diffraction (SAED) gives the information about the nature of the sample such as amorphous (diffuse rings), crystalline (bright spots), polycrystalline (small spots making up rings), each spot arising from the Bragg’s reflection from an individual crystallites. HRTEM micrograph of rGO along with SAED is given in figure 2.10b. The image shows wrinkled morphology with a mixture of single to few layered graphene sheets. The SAED exhibits typical sharp polycrystalline ring patterns with many spots, indicating a loss of long range ordering between the rGO nanosheets.

2.2.3 Atomic force microscopy

Atomic force microscopy (AFM) belongs to the family of scanning probe microscopy, which provides high resolution image of surfaces with height information. The image is gathered by "feeling" the surface with a mechanical probe-cantilever assembly and the force experienced by the probe is detected using an optic lever method. The probe or the sample is mounted on scanner that is capable of moving in X, Y and Z directions with nanometer resolution. A laser is focussed on the cantilever and reflected on to a position
sensitive photodiode. The cantilever deflection will cause a shift in the laser position on to the diode and the intensity difference is mapped as topography contrast. AFM can be operated in various modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) mode and dynamic (non-contact or intermittent contact) modes (Fig. 2.11a).

**Contact mode:** In the static mode operation, the static deflection is employed as a feedback signal using low stiffness cantilevers. However, close to the surface of the sample, attractive forces can be quite strong, causing the tip to snap-in to the surface of the sample. Thus, static mode AFM is always done in contact where the overall force is repulsive. In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection of the cantilever. This mode has also been used for thickness measurement of thin films with respect to the bare substrate.

**Non-contact mode:** In this mode, the tip of the cantilever is not in contact with the sample surface and is oscillated at a frequency slightly above its resonance frequency where the amplitude of oscillation is typically a few nanometers (< 10 nm). The van der Waals forces, which are strongest from 1 nm to 10 nm above the surface or any other long range force which extends above the surface acts to decrease the resonance frequency of the cantilever. This decrease in resonance frequency is combined with the feedback loop system.
Several forces are in operation when a probe approaches that also depend on the sample nature. By choosing suitable probe material and design of electronics to acquire the desired signal, AFM can be used to measure local properties, such as friction, magnetism, and local currents, surface potential etc. It can also be used to perform nanolithography.

2.3 X-ray diffraction

X-ray diffraction (XRD) is a powerful non-destructive technique to study the crystal structure of materials. It provides information on structures, phases, and structural parameters such as grain size, crystallinity, strain and crystal defects. Every crystalline solid has its unique characteristic X-ray diffraction patterns, which can be considered as a fingerprint for the identification of the material. Crystals consists of regular arrays of atoms, and they are arranged in a way that a series of parallel planes separated from one another by a distance d. XRD peaks are produced by a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample (Fig. 2.12). The scattered X-ray is determined by Bragg’s law,

\[ n\lambda = 2d \sin \theta \]

where ‘n’ is an integer, \( \lambda \) is the wavelength of the X-ray beam, d is the spacing between diffracting planes, and \( \theta \) is the incident angle of the beam. The incident angle is mapped against diffraction intensity that gives the various crystal planes involved. XRD patterns are usually identified by comparing obtained data with an international standard database of JCPDs. In the present study, the XRD patterns of as-synthesised hybrid films and composites powders were recorded using Rigaku-SmartLab X-ray diffractometer with Cu K\( \alpha \) radiation (\( \lambda = 1.54 \) Å). Rigaku-PDXL2 software was used for evaluating Full width at half maximum (FWHM) of XRD peaks to calculate the particle size.
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Figure 2.12. X-ray diffraction involves constructive interference of waves being “reflected” by various atomic planes in the crystal. (29)

2.4 Semiconductor characterization system

Figure 2.13. (a) Picture of the semiconductor characterization system (SCS-4200) (b) Schematic presentation of a two-probe method for conductivity measurements.

The current versus voltage (I-V) characteristics of as-synthesized hybrids are studied by semiconductor characterization system (SCS-4200) from Keithley instruments employing two probe method (Fig.2.13). It consists of three SMUs (source-measure unit), one C-V module and a pulse I-V module. It operates in the current range of 1 pA to 100 mA. A basic SMU can act as a voltage source or current source. The I-V measurements, C-V measurements, pulse I-V measurements, FET and various other characteristics can be measured using the semiconductor characterization system. The conductivity of the as-
synthesized GO, rGO and rGO-based hybrid thin films have been studied using the semiconductor characterization set-up through two probe measurements (Fig.2.13b).

2.5 Magnetometer

Magnetic measurements of rGO based hybrids were carried out employing an MPMS SQUID magnetometer, with Superconducting Quantum Interference Device (SQUID) sensor. It contains superconducting loops having Josephson junctions that measure very subtle magnetic fields. The Josephson junction is made of niobium and an insulating layer is a sandwiched between superconducting layers. In the measurement, the sample is moved through the superconducting detection coils and the change in the magnetic moment of the sample induces an electric current in the detection coils. Any change of magnetic flux in the detection coils produces a change in the persistent current in the detection circuit. This signal is proportional to the magnetic moment of the sample, which is magnetized by the magnetic field produced by the superconducting magnet.\(^{(30, 31)}\)

Figure 2.14. Photograph of the MPMS-SQUID magnetometer.

The superconducting quantum interference device (SQUID) magnetometer is one of the most efficient and sensitive ways of measuring magnetic properties. Photograph of MPMS-SQUID image is given in figure 2.14. In particular, it is the only method which allows to directly determining the overall magnetic moment of a sample in absolute units. Using this technique, the magnetization of the materials is measured, as a function of the
magnetic field intensity or temperature. This device allows recording of the Zero-field-cooled (ZFC), field-cooled (FC) magnetization curves and hysteresis curves. From the ZFC and FC curves, one can determine the blocking temperature for nanoparticle domains, domain interactions, magnetic ordering transitions, and M-H hysteresis loop gives information about the type of magnetism in the sample and also about the coercivity, saturation remanent magnetization and exchange bias effects.

2.6 Electrochemical workstation

Figure 2.15. Schematic diagram of an electrochemical workstation; Zoomed view of electrochemical cell with working (Pencil graphite electrode) electrode, Ag/AgCl reference electrode and counter or auxiliary platinum electrode.

The electrochemical activity of the hybrid films were performed using an electrochemical workstation. A three-electrode cell setup consisting of glassy carbon as the working electrode, a platinum electrode as the counter or auxiliary electrode and Ag/AgCl as the reference electrode in a suitable electrolyte is generally used for acquiring current-potential plots (Fig. 2.15). Various electrochemical methods have been employed during the research work such as cyclic voltammetry, differenctial pulse voltammetry, chronocoulometry, galvanostatic charge and discharge, Tafel plots and electrochemical impedance spectroscopy.(32, 33)
2.6.1 Cyclic voltammetry

In cyclic voltammetry, the potential of the working electrode is varied linearly in time with a definite scan rate (mV s\(^{-1}\)) between two potential limits, while the current is measured, resulting in current versus potential (I vs E) plots. During the voltammetry sweep, the measured current consists of a Faradiac and non-Faradiac contribution. The important parameters in a cyclic voltammetry are the peak potential (\(E_{pa}, E_{pc}\)), peak current (\(I_{pa}, I_{pc}\)), of the anodic and cathodic peaks, respectively. In this thesis, cyclic voltammetry is employed for the determination of redox properties of active materials and also for detection of various analytes. We have also employed cyclic voltammetry for the determination of electrochemical surface area by probing \([\text{Fe(CN)}_6^{3-}/4^-]\).

2.6.2 Differential pulse voltammetry

Differential pulse voltammetric (DPV) technique is having better sensitive than the voltammetric measurements. In this method, potential is scanned with a series of pulses and each potential pulse is fixed, of small amplitude (10 to 100 mV), and is overlaid on a gently changing base potential. The current is measured at two points of each pulse, which are at the first point just before the application of the pulse and the second at the end of the pulse. These sampling points are selected to allow for the decay of the non-Faradiac (charging) current. The difference between current measurements at these points for each pulse is calculated and plotted against the base potential. In DPV technique, the measured current is only a product of Faradiac process with the elimination of capacitive charge. Hence, the technique is widely used in sensing of the analytes.

2.6.3 Chronocoulometry

In chronocoulometry, the total charge (Q) that passes following a potential step is measured as a function of time. Here, the Q is obtained by integrating the current (I) during the potential step. In this technique, the experiment starts at a particular potential, where no
reaction occurs and stepped up instantaneously to a potential where either the oxidation or reduction occurs. Chronocoulometry is useful for the measurement of electrode surface area, diffusion coefficients, the time window of the electrochemical cell and adsorption of electroactive species. The mechanisms and rate constants of chemical reaction coupled to electron transfer reaction can also be measured.

2.6.4 Galvanostatic charge and discharge

Galvanostatic charge and discharge (GCD) is performed on capacitors for performance evaluation such as charge capacity and life span. GCD measurements consist of two parts; (1) charging a capacitor at a constant current (2) discharging a fixed current in a specific voltage range. The operating voltage of the capacitor is determined by electrolyte used in the system.

2.6.5 Tafel plots

Tafel plot is a graph of log I versus overpotential (\( \eta \)), that is used to acquire kinetic and mechanistic information about the electrochemical reaction. The analysis based on the Tafel equation, is given as follows.

For cathodic reaction, \( \log (I) = \log I_0 - \alpha_c \, nF \eta / 2.303 \, RT \) and for anodic reaction, \( \log (I) = \log I_0 + \alpha_a \, nF \eta / 2.303 \, RT \), where \( I \) is the total current density, \( I_0 \) is the exchange current density, \( \alpha_c \) and \( \alpha_a \) are the Tafel slopes and \( \eta \) is the over potential. So from the above equation, the slope of the Tafel plot can help determining the number of electrons involved in the rate determining step of the electrochemical process.

2.6.6 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) employed to study a variety of electrochemical phenomena over a wide range of frequency. The EIS plots provides a quantitative information regarding conductance, electric coefficient, properties of interface
of the system, and the dynamic change due to absorption or charge transfer phenomena.

The data obtained in EIS is usually expressed in Nyquist plot or Bode plots.

2.7 References


