CHAPTER 2- Theoretical details

In this chapter, theoretical details of different experimental techniques and formalisms used in the impedance spectroscopy are discussed.

2.1 Theory about Solid State Reaction

2.1.1 What are Solid State Reactions?

The method of reaction amongst inert solids by heating at higher temperatures, and (generally) normal atmospheric pressure is called the Solid State reaction [1]. Thermodynamic factor like exchange of free energy (called reaction enthalpy) and kinetic factors like reaction rates etc play an important role in the study of solid state reactions.

2.1.2 What is its relevance in Solid State Chemistry?

In solid state chemistry, the solid state reactions play a vital role. Generally solids do not react with each other until they are well grinded, mixed and exposed to elevated temperature and sometimes high pressure conditions. The microstructure study of reactants and the final products in a chemical reaction is of primary importance in solid state chemistry. This study is carried out using techniques like X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR) and Infra Red Spectroscopy to name a few.

2.1.3 Why are Solid State Reactions Difficult?

The solid reactants differ from each other in terms of their structure and composition. Unless and until high enough temperatures or pressures are applied, their bonds and structure do not break. They cannot come in close contact with each other. Thus, the solid state reaction step is difficult. Nucleation is said to be initiated when a seed molecule is formed around which molecules accumulate and form larger structure of the product. Nuclear molecules are formed as a result of structural re-organization between reactants. Nucleation is difficult because (a) there is a difference in structure of reactants, (b) large amount of structural reorganization in terms of breaking bonds, migration of atoms over distances etc is required by the reactants, formation of intermediate phases and products. The formation of final products is influenced by: (1) reaction rates: In simple cases, diffusion of ions in lattice planar layers is governed by parabolic rate law:

$$dx/dt = (kx)^{-1} \qquad \text{……… (2.1)}$$

where k is the reaction rate, x the extent of reaction formation, t is time

$$x = (k'k)^{1/2} \qquad \ldots\ldots\ldots (2.2)$$

Factors like exposed surface area of the reactants also affects the reaction rate. Before heat treatment, grinding of the particles helps in enhancing the surface area of the reactant products. Thus, for the same amount of product, the surface area increases. This encourages the speedy reaction. The method of using markers to find the extent or progress of reaction is called ***Kirkendall effect.***

Some of the factors that affect the microcrystalline structure of the final product are: rate of cooling compounds, the basic bond composition and type of parent compounds, the temperature and pressure conditions for the solid state reaction steps, the method adopted in solid state reaction (example: grinding, heating cycles).

2.2 Experimental Techniques

In the below sections, we elaborate the experimental techniques that have been used in our work:

2.2.1 X-ray Diffraction

X-rays were discovered by Wilhelm Rontgen in 1895. X-rays have wavelength in the range 0.001 Å to 1 Å which corresponds to energy range of 100 keV to 100 eV. Since the wavelength of x-rays corresponds approximately to the atomic and molecular dimensions (example the atomic layer spacing in graphite is in the range of 3.354 Å). Hence, x-rays are used extensively to study the microstructure of solids. Von Laue and William Lawrence Bragg did pioneering research in using x-rays to determine the solid state structure. They received Nobel prize in 1914 and 1915 respectively for their contribution. NaCl was the first molecule whose crystalline structure was resolved using x-rays; further the presence of ionic bonds (and not covalent bonds, as was believed then) in NaCl was established using the x-rays.

In solid state crystallography, the x-rays are produced by striking a high energy electron beam (100 keV) on a Tungsten or Copper target plate (anode). This high energy incident electron strikes one of the electrons in the **K**-shell ($1s^2$, $2s^2$, $3s^2$ ….) of the target anode atoms. This is an inelastic collision in which energy is exchanged between the two electrons. As the **K**-shell electron is knocked off its orbital, an electron from higher **L**-shell (***p***-orbital) rushes to fill in the gap. It emits an x-ray photon of energy equivalent to the difference between the energies of ***s*** and ***p*** orbitals. For investigations in solid state materials, x-rays of wavelength 1.54 Å is preferred from the Copper (Cu) target as anode. Such lines are called Cu Kα_1, Cu Kα_2 and Cu K_β which correspond to wavelengths 1.54051 Å, 1.54433 Å and 1.3922 Å, respectively (see Fig. 2.1). As seen in Fig. 2.2, an x-ray photon when incident on a crystal sees point like atoms. Depending on the angle of incidence, the photon can either be reflected or diffracted from the atomic point source. This results in either constructive or destructive interference of reflected and diffracted x-rays which is described by the following **Bragg's law** [2]**:**

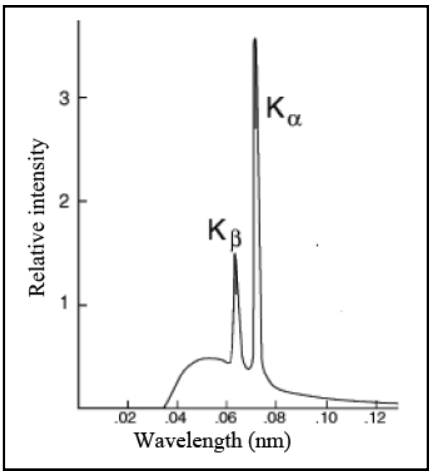


Fig. 2.1 Characteristic x-ray spectrum.

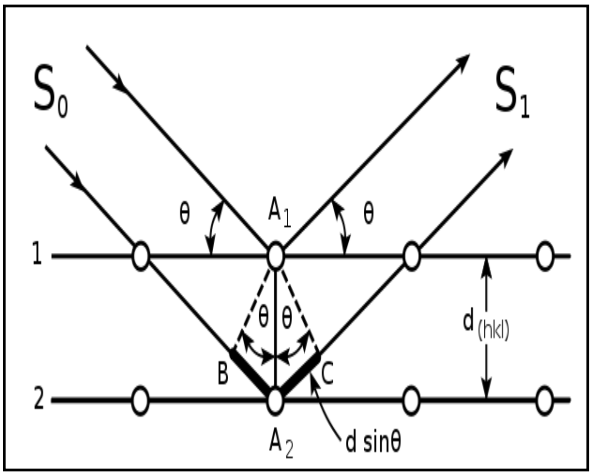


Fig. 2.2 Constructive interference and Bragg's law.

$$2d\sin\theta = n\lambda \qquad \text{……… (2.3)}$$

Here d is the spacing between the atomic layers, θ is the angle of reflection of the incident x-ray beam, λ stands for the wavelength of the incident x-rays and integer n = 1,2,3 ... Constructive and destructive interference fringes, are formed due to periodic microstructure arrangement of the atoms and their inter-planar d-spacing of the atomic layers etc. Fig. 2.2 depicts the arrangement in which constructive interference is produced when the Bragg condition (Eq. 2.3) is satisfied by the incident monochromatic x-rays. The angle of diffraction (θ) is related with the lattice spacing (d) of the crystal by the Bragg's condition. Hence based on the angle of diffraction detected, the orientation of the arrangement within the crystal varies. On accurately detecting the intensity of x-rays at a particular angle, the step size of detection of the diffracted x-rays etc. can reveal important characteristics of the micro structure or the atomic arrangements in a solid. Crystallographers have identified 32 basic arrangements (space groups) in which the atoms can arrange in a solid. From the angles at which the reflected x-ray photons are received on a detector the microstructure information like type of space group and the arrangement of the atoms, the inter-planar distance or the d-spacing, the type of bonds (whether ionic or covalent) and the quantity of a given phase can be determined using the peak height, peak broadening of the x-ray patterns. Thus the angles at which the x-rays are received indicate the innate structure of the solid. X-ray diffraction is a cumulative technique. In a typical x-ray diffractogram, points are plotted at the angle at which the x-rays are received.

In solid state chemistry, the x-rays are used to extract the information [1] in the following areas:

1) To identify the phase
2) To quantify the phase
3) To determine unit cell parameter
4) To determine the crystal structure
5) To find the d-spacing between the atomic layers
6) To find the particle size
7) To find short range order in non crystalline solids like glasses and gels
8) To determine the crystal defects and disorder

2.2.2 Density Measurements

Density is defined as a ratio of mass to volume of a material. Density measurements (of generally an irregularly shaped) solid material are useful to know as supplementary evidence for the changes in internal microstructure of a solid material. The changes in the microstructure can occur due to doping another material, sintering, corrosion etc. The density can vary due to change in mass (doping heavier material), volume (malleable or ductile material) or both. The material if subjected to prolonged heat treatment at appropriately high temperatures also densifies the internal structure in due course of time.

Archimedes' method is reliable to measure the density of the samples. According to this principle, the volume of the immersed solid is equal to the amount of liquid displaced due to the solid. From the ratio of mass to volume the density of the solid can be measured.

In the present method, we measure the mass of sample in air and then measure the mass of the sample in liquid using a high resolution digital weighing balance (micro balance). The ratio of difference of mass of the sample in air and in liquid to the density of the liquid gives the volume of liquid displaced by the sample. The ratio of mass of solid in air to that of volume displaced by sample will provide the density of the solid.

$$\frac{\boldsymbol{Weight\ of\ Sample\ in\ Air}}{(\boldsymbol{Weight\ of\ sample\ in\ air - Weight\ of\ sample\ in\ Methanol})}\times(\boldsymbol{Density\ of\ Methanol}) \quad \ldots\ldots\ldots (2.4)$$

$$\frac{\boldsymbol{W_{air}}}{\boldsymbol{W_{methanol} - W_{air}}} \times \boldsymbol{Density\ of\ Methanol} \quad \ldots\ldots\ldots (2.5)$$

The samples were weighed in cool and moisture free atmosphere. Methanol is generally chosen since it does not react with the sample material. Besides, its density (0.79 g cm^{-3}) is less than water. Hence any material with lesser density than water can be measured in methanol. It also does not cause hygroscopic damage to the sample. To arrest higher rate of evaporation of methanol, all measurements have to be carried out in a cool atmosphere at 18-20° C.

2.2.3 Scanning Electron Microscopy (SEM)

A Scanning Electron Microscopy is a tool which is capable of magnifying and imaging specimen in micro (10^{-6} m) and nano meter (10^{-9} m) regime. It is capable of producing digital images with 3D details. The SEM is used to characterize microstructural and morphological details of are organic, inorganic, biological, metallic, ceramic etc specimen. Max Knoll [1] and Ernest Ruska (Germany) in 1931 and later Manfred von Ardenne (Belgium) [3, 4] in

1937-38 were amongst the earliest pioneers who attempted to make prototypes and working models of scanning electron microscopes.

The working principle of a scanning electron microscope is as follows: an electron beam is generated from a source (a Tungsten filament) by heating it (Fig.2.3). The beam is collimated using coils of electromagnets at various levels. This beam optics is maintained in high vacuum tube to avoid interaction of electrons in the beam with the air molecules. The energy of electrons (generally in the range 0.5–30 keV) and beam dimensions are adjusted with voltage on electron gun and on collimator lens. The collimated beam which has diameter of 0.5 to 5 nm (depending upon the requirement) is focused on a specimen and scanned in raster mode. The electrons interact with first few layers of the specimen and produce: (1) secondary electrons, (2) backscattered electrons (3) characteristic x-rays, (4) specimen current and (5) transmitted electrons. These secondary electrons or back scattered electrons, or x-rays are detected by appropriate detectors. The secondary or backscattered electrons generally have very low energy when they emerge from the specimen. The detectors consist of coils (grids) at +300 V potential, placed in specific geometry which pick up any electrons. These electrons are then directed to phosphor scintillator at +2000 V, which produces scintillations corresponding to the energy of secondary electrons. These scintillations are then transferred to photomultipliers in a light pipe (Fig.2.4).

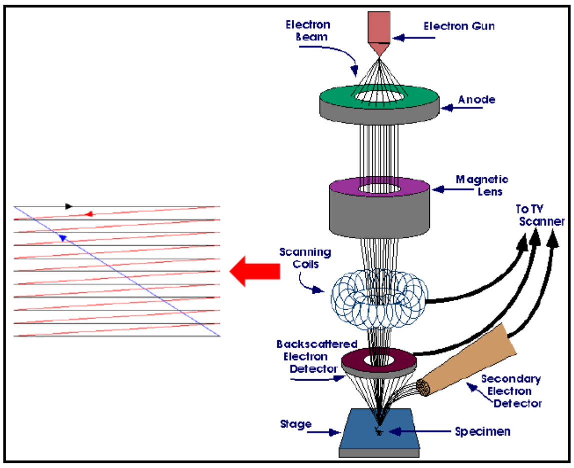


Fig. 2.3 **A schematic view of working of a scanning electron microscope.**

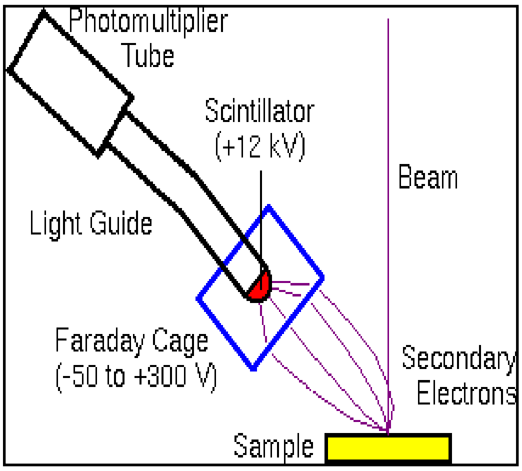


Fig. 2.4 **Working principle of a detector in a scanning electron microscope.**

This assembly of scintillator – photomultiplier system is also called Everhart-Thorley detector [4]. The signals are converted from analog to digital and stored as digital images. Based on the angle of incidence the number of secondary electrons with different energy varies. For a steep angle of incidence at edge on the surface the energy distribution of secondary electrons increases – resulting in an image which has a 3D character.The SEM is capable of a resolution of 10 to 500,000 times. Generally based on the requirements of the samples the SEM is operated in secondary electron, backscattered electron, characteristic x-ray mode etc. Secondary electron mode with an adjustment of inclination is considered to be the best and easiest mode to obtain good quality 3D images upto 1 nm resolution. The primary limitation in resolution in the SEM images is the size of the electron beam spot and its governing electron optics. Since the spot size cannot be less than a few nm, it can resolve a topographical artifact less than this dimension.

2.2.4 Transport Number

The transport number studies are performed to estimate the number of ionic and electronic charge carriers in the solid medium. The transference number measurement helps not only to estimate the percentage of cationic and/or anionic charge carriers in the solid electrolyte or electrode medium, it also gives an estimate of electronic charges that are mobile in the medium [5]. Thus it becomes a useful tool to understand the ion conduction mechanism. Various methods like EMF method, DC polarization method etc are used to find the transference number of a solid electrolyte medium. In the present superionic systems, only Li^+ cation and electrons are mobile charge carriers (and not anions). Transference number is a ratio of current due to ionic charges to the total current (due to ions and electrons) in the system. Generally the ionic transference number of a superionic system is close to unity. Assume that, there are single cationic species (Li^+). Then the current due to ionic charges is given as i_{Li+} and that due to electrons is $\boldsymbol{i_{e^-}}$, then the transference number is given as

$$\boldsymbol{t_{Li^+}} = \boldsymbol{i_{Li^+}} / \boldsymbol{i_{total}} \qquad \text{……… (2.6)}$$

while transference number due to electrons is given as

$$\boldsymbol{t_e = i_e / i_{total}} \quad \text{……… (2.7)}$$

And $\boldsymbol{t_e}$ is generally measured as

$$\boldsymbol{t_{Li^+}} = 1 - \boldsymbol{t_e} \quad \text{……… (2.8)}$$

2.2.4.1 EMF Method

Transference number can also be measured by EMF method [5]. The ceramic pellet (sample) should be placed between two conducting plates with different chemical potentials μ_1 and μ_2. The potential difference across the electrodes is given by

$$E_{Theo.} = \frac{-1}{|M|F} \int_{\mu 2}^{\mu 1} t d\mu = \frac{ti(\mu 1 - \mu 2)}{|M|F} = t_i \frac{\Delta G}{F\,|M|} \quad \text{……… (2.9)}$$

where t_i is the ionic transport number

ΔG is the change in free energy involved for a given pair of electrodes.

|M| is the valence of mobile ion and F is the Faraday's constant. For an ideal electrolyte with $t_i = 1$, the emf generated is given by:

$$E_{Theo.} = \frac{\Delta G}{F\,|Z|} \quad \text{……… (2.10)}$$

$$E_{Obs.} = t_i . E_{Theo.} \quad \text{……… (2.11)}$$

Therefore the transport number is a ratio of $E_{Obs.}$ to $E_{Theo.}$ for a given pair of electrodes in the experiment.

2.2.4.2 DC Polarization Method

This method was developed by Evans [6]. To separate the ionic and electronic contribution, the sample is placed between reverse and blocking electrodes and a uniform DC electric field is applied across this cell. Sometimes two blocking electrodes are used and a small DC voltage is applied across the cell. Thus the cell is constructed to polarize the sample from both sides. The ions are forced to move towards their respective electrodes. Silver paint is applied on both surfaces of the pellet to work as blocking electrodes. The arrangement is as follows: Silver | Sample Pellet | Silver.

2.2.5 Energy Dispersive Spectroscopy (EDS)

Energy Dispersive Spectroscopy is a technique used to carry out the elemental analysis of the surface (or a few layers below the surface). The technique is capable of detecting the elements and also ascertaining their atomic and weight percentage of each element which is detected in its scan. This helps in determining the elemental composition to a high accuracy and is used in fields like geology, solid state chemistry, chip manufacturing to name a few. The working principle (Fig. 2.5) of EDS is as follows: A specimen mounted on a sample holder housed in a sample chamber. This chamber is evacuated up to a pressure of 10^{-4} Torr. Electron tube and related beam optics and the detectors along with the specimen are also enclosed in vacuum. Electrons are generated by heating a tungsten filament. These are collimated into a very thin electron beam of 1 nm spot diameter using an assembly of electromagnetic lens. The beam is focused on a small area (some micron square) of specimen. These primary electrons are energetic enough to knock out the K or L-shell electrons of the atoms in the specimen (Fig. 2.6).

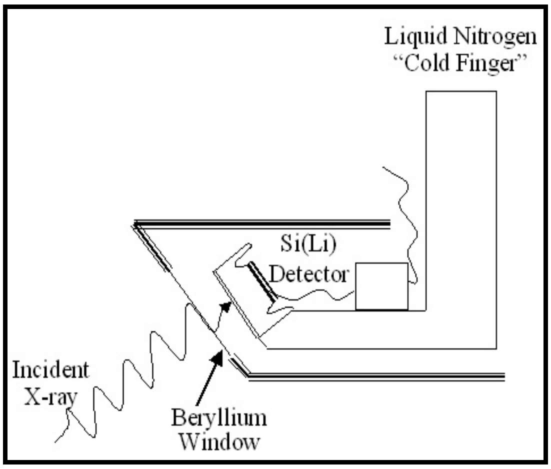


Fig. 2.5 A schematic view of working of a energy dispersive spectrometer.

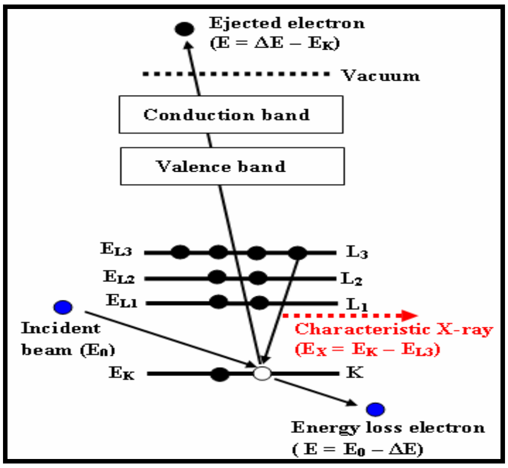


Fig.2.6 Atomic Energy levels principle used in EDS.

This results in formation of secondary x-rays due to photoelectrons. The emitted x-rays characteristic of the elements is detected by scintillation – photomultiplier assembly and/or a sensitive Silicon Drift Detector (SDD). The detector converts the energy and count of the x-rays into electrical signals via a transducer. These signals are stored and compared with the database of characteristic x-rays of different elements. The comparison and data analysis is done using software like ICAN.

The entire operation of mounting the samples to evacuation and grabbing the image and performing the elemental analysis using EDS is done with the SEM measurements, since both the techniques are interfaced. The EDS technique cannot detect elements atomic number (Z) less than 3. Hence Hydrogen (H), Helium (He) and Lithium (Li) elements are not detected by EDS. This is a basic limitation of EDS technique.

2.2.6 Impedance Spectroscopy

Impedance spectroscopy is a tool to study the impedance response of a solid (electrolyte, electrode) material when the latter is subjected to frequencies in microwave (10 Hz to 10^6 Hz) range. Studying the response of a dielectric material to a (small) voltage and measuring the output current response can reveal insight about the material in terms of conduction of charge carriers in it, the presence of capacitance at boundaries etc. Thus impedance spectroscopy measures the dynamical response of a system [7] whereas other techniques like X-ray diffraction give an insight about the static situation within a material. Thus all the dynamical characteristics of a system like, conduction through charge carriers, the dielectric properties of a material, the presence of defects, the presence of grain boundaries etc, can be revealed using impedance measurements. This versatile technique is used in many areas like corrosion engineering and analysis, electrochemical power storage systems like batteries, and many other applications to name a few. In Solid State Ionics and material science, impedance spectroscopy has been used extensively to characterize the ion motion in different samples like polymer films, ceramic pellets, glasses, single crystals etc.

The general principles of Impedance Spectroscopy in case of ion conducting solid materials are highlighted below:

According to Ohm’s law, the voltage drop $\boldsymbol{V}$ across a resistance $\boldsymbol{R}$ is directly proportional to the current (flow of charge carriers). That is,

$$V = I\,R \qquad \text{……… (2.12)}$$

But the Ohm's law holds only for simple, linear systems following DC circuit. Similarly the capacitance C = QV across the parallel plates of a capacitor

Current is defined as a flow of charges

$$I = \frac{dQ}{dt} \qquad \ldots\ldots\ldots (2.13)$$

Therefore,

$$I = C\frac{dV}{dt} \qquad \ldots\ldots\ldots (2.14)$$

In an AC circuit, where the frequency of the voltage signal is involved, the voltage is represented by the following:

$$V = V_0 \, \boldsymbol{exp(j\omega t)} \qquad \ldots\ldots\ldots (2.15)$$

and current is given by

$$\boldsymbol{I} = \mathbf{C}[\frac{d\,Vo\;exp(j\omega t)}{dt}] = \boldsymbol{j\omega C\, V_0 exp(j\omega t)} \qquad \ldots\ldots\ldots (2.16)$$

The impedance is given by $Z_c(\boldsymbol{\omega}) = \frac{\boldsymbol{V}(\boldsymbol{\omega})}{\boldsymbol{I}(\boldsymbol{\omega})} = \frac{1}{j\omega C}$ and the current which is out of phase (lag) with the voltage signal given by

$$I = I_0 \sin(\omega t - \varphi) \qquad \ldots\ldots\ldots (2.17)$$

Impedance is a complex quantity given by the below formula:

$$Z^* = Z'(\omega) - j\,Z''(\omega) \qquad \ldots\ldots\ldots (2.18)$$

Where $\boldsymbol{Z}'$ = real value of resistance, $\boldsymbol{Z}''$ = imaginary value of resistance, $\boldsymbol{\omega}$ = frequency at time ***t.***

When the charge carriers (ions in our case) within the (ceramic) material are subjected to a (input) voltage $\boldsymbol{V = V_0 \sin\omega t}$, ($V_0$ is the amplitude of signal which is usually 1 – 50 mV AC), the output is measured as current which has a shift in phase and given by $\boldsymbol{I = I_0 \sin(\omega t - \varphi)}$. This is shown in the Fig. 2.7.

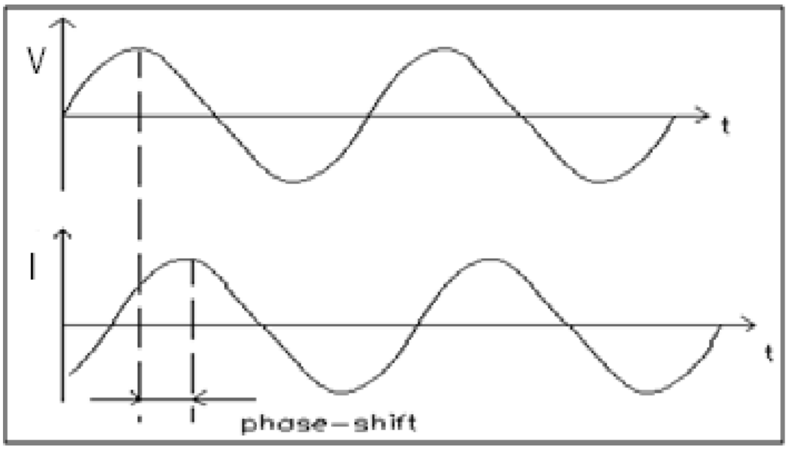


Fig. 2.7 Frequency dependent signal.

The impedance is given by:

$$Z = V_0 / I_0$$

$$Z = V_0 \sin\omega t / I_0 \sin(\omega t - \varphi) = Z_0 e(-j\varphi). \qquad \text{.........} \ (2.19)$$

The behavior of the impedance in a complex plane can be depicted for various situations as follows:

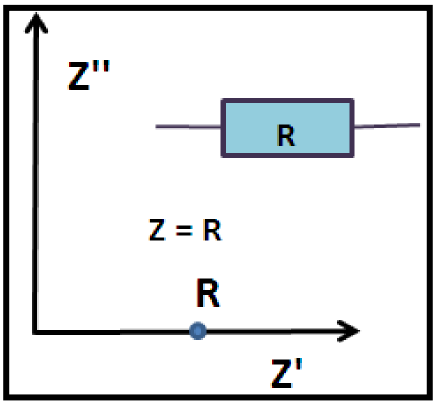


Fig. 2.8 (i) Complex Impedance plots for resistance R only

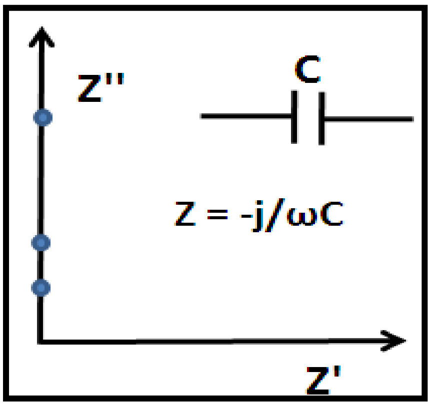


Fig. 2.8 (ii) Complex Impedance plots for capacitance C only

When resistance ***R*** alone is in the circuit, it is depicted as in Fig.2.8 (a). The value of R does not change on the real (Z) axis. While impedance due to capacitor Z_C = $\boldsymbol{-j/\omega C}$ is depicted as in Fig.2.8 (b) for different **ω**.

Series combination of R and C is represented on the complex plane is as follows:

Z_R = R and Z_C = $-j/\omega C$, therefore the impedance $Z^* = Z' - jZ''$ will become $Z^* = R - j/\omega C$. The combination of R and C in a series - results in a line parallel to imaginary (Z'') axis with points on this line representing the value of C for different frequencies (Fig.2.9).

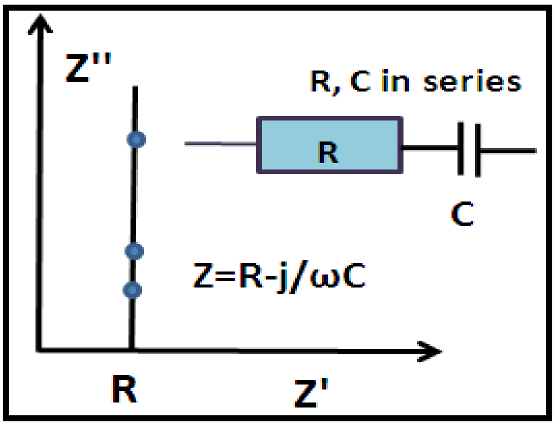


Fig. 2.9 Complex Impedance plot for series combination of R and C elements.

Parallel combination of R and C is represented by the following diagram on a complex plane:

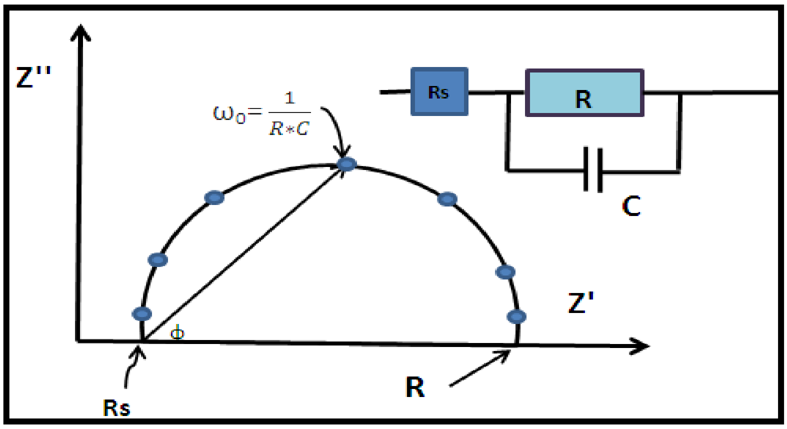


Fig. 2.10 Complex Impedance plot for series combination of R and C elements.

Here the admittance is $Y(\omega) = \frac{1}{Z^*(\omega)} = \frac{1}{R} + j\omega c$ ……..(2.20)

or $Z^*(\omega) = \frac{R}{1+\omega^2R^2C^2} - j\frac{\omega R^2C}{(1+\omega^2C^2R^2)}$ ……. (2.21)

hence we get,

$Z' = \frac{R}{1+\omega^2R^2C^2}$ and $Z'' = \frac{\omega R^2C}{(1+\omega^2C^2R^2)}$ ……. (2.22)

From the above equation $\frac{Z''}{Z'} = \omega RC$ and substituting in Eq. 2.22, we get

$$Z' = \frac{R}{1 + [\frac{Z''}{Z'}]^2}$$

or $$Z'(Z'^2 + Z''^2) - RZ^{2'} = 0 \qquad \text{........} \qquad (2.23)$$

Adding and subtracting by $\frac{R^2}{4}$ in Eq. 2.23, we get

$$(Z' - \frac{R}{2})^2 + Z''^2 = (\frac{R^2}{4}) \qquad \text{........} \; (2.24)$$

On complex impedance plane, the above equation represents a semi circle and intersects the real (Z) at R. The circle has a radius $\frac{\boldsymbol{R}}{\boldsymbol{2}}$ and centre ($\frac{\boldsymbol{R}}{\boldsymbol{2}}$, $\boldsymbol{0}$) as shown in Fig. 2.11 below:

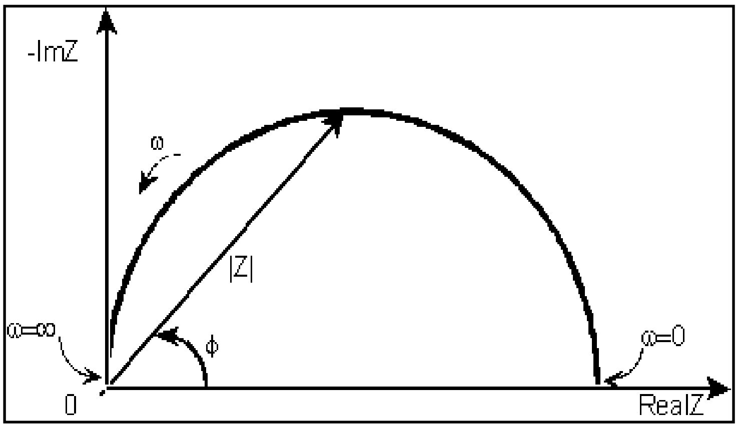


Fig. 2.11 Complex Impedance plot for parallel combination of R and C elements.

The |Z| is absolute value of impedance and φ is the angle, the $\vec{Z}$ forms with Z' or Z (real) axis. As indicated in the figure, the maximum frequency corresponds to ω_0 which is at the upper most tip of the semi circle. Thus a parallel combination of ***R*** and ***C*** corresponds to a semi circular arc in a limited frequency range. Similarly the motion of (ionic) charge carriers in a solid electrolyte material is described in terms of semi circular arcs.

The largest frequency is generally represented at the beginning and lowest at the right most ends. A semi circle is formed as a result of material's dielectric response to frequencies. The behavior can be described by using a combination of ***R*** and ***C*** in lumped circuits which are exposed to microwave frequency range. That is, the charge carriers within a material flow as if they are moving through a series and parallel combination of ***R*** and ***C*** circuits. The values of ***R*** and ***C*** differ due to micro-structural properties of the material under study. The irregular and inhomogeneous distribution of grains causes the semicircle to be depressed on the $Z' - Z''$ plot. In such cases of inhomogeneous aggregation and impurities, an ideal capacitance behavior is not helpful to fit the data of depressed semi circle. It is described by an electrical component called C***onstant Phase Element (CPE)***.

Mathematically, the impedance due to CPE is given as follows:

$$\frac{1}{Z_{CPE}} = A_0 (j\omega)^n = A\,\omega^n + j\,B\omega^n \qquad \text{……… (2.25)}$$

where ***A*** and ***B*** are coefficients given by: $\boldsymbol{A} = A_0 \sin(\frac{n\pi}{2})$ and $\boldsymbol{B} = A_0 \cos(\frac{n\pi}{2})$

When $\boldsymbol{n} = 0$, $A_0 = \frac{1}{R}$ and $\boldsymbol{n} = 1$, $A_0 = C$

Therefore, the equation of the depressed semi circle is given using CPE as follows:

$$[Z' - \frac{R}{2}]^2 + [Z'' + \frac{R}{2}\cot(\frac{n\pi}{2})]^2 = [\frac{R}{2}\operatorname{cosec}(\frac{n\pi}{2})]^2 \qquad \text{……… (2.26)}$$

where the centre of the depressed semi circle is given by: $[\boldsymbol{\frac{R}{2}}, -\boldsymbol{\frac{R}{2}}\cot(\boldsymbol{\frac{n\pi}{2}})]$

and radius is given by: $\boldsymbol{\frac{R}{2}}\operatorname{cosec}(\boldsymbol{\frac{n\pi}{2}})]$

This constant phase element does not exist in real circuit, but is used to fit in the data along with resistance **R**. Sometimes a straight line in an impedance plot also indicates a **CPE**. Surface roughness, chemical heterogeneities, non uniform current distribution etc could be causes of depressed semi circles and the origin of CPE. Another element used commonly in electrochemistry is ***double layer capacitor*** (C_{dl}). When a polarized layer of ions is formed inside an electrode and a corresponding layer of ions is formed at the electrode-electrolyte interface, a capacitance is developed. The separation of the ions between these two layers is a few angstroms (Å). This layer of ions acts as a barrier for the ions that come towards the electrode (from the electrolyte) and does not allow easy intercalation for these ions, into the electrode. Due to this ions or charges the other ions experience electropositive repulsion and get accumulated at the electrode-electrolyte interface. Thus the ion layer acts as a barrier. A double layer capacitance in a complex plane is represented by an almost vertical line in the low frequency region after the depressed semi circle. The Nyquist plots of real $\boldsymbol{Z}'$ *vs*. imaginary $\boldsymbol{Z}''$ were obtained. From the obtained data the variation of impedance (real and imaginary) can be known with frequency. The ionic motion (conduction) can be bifurcated into two types. The DC conductivity refers to the ionic motion when the ions diffuse as they are attracted towards the ionic vacancies over longer distances in a crystal. At this stage the ions are relatively free in the system. Under the effect of externally applied thermal energy, the ions are able to overcome the activation barrier and become relatively free to move about in the crystal. The ions when they leave their parent sites, leave behind them the 'cation' vacancies. Therefore the creation of ions due to thermal energy is synonymous to creating vacancies in the system. The ions even when subjected to externally applied low AC (alternating) frequencies (< 10^3 Hz) diffuse (translational motion) long distances before the next cycle of ac signal takes place. The ions at increasing temperatures and low frequencies travel long distances and accumulate at the electrode – electrolyte interface and form a space charge region there. This is also referred as double layer at the electrodes. In intermediate frequency range they diffuse and hop. At high enough frequencies, the ionic motion is due to hopping motion about their vacancy sites only.

In ceramics the ions move easily in grain region while they have slow and retarded motion along the grain boundary sites [8-10]. Also, at low frequencies, the motion of ions is slow. Hence the (slow) ionic behavior in low frequency regions of the medium represents the grain boundary region while the rapid response of the ions (to the external frequency) is given by the grain region.

Nyquist plot ($\boldsymbol{Z}' - \boldsymbol{Z}''$ plot): A typical Nyquist plot gives an idea of impedance (real and imaginary) at different frequencies. In a single Figure, Nyquist plots for different temperatures can be represented. This gives a fair idea of increasing or decreasing behavior of impedance with temperature.

As mentioned in the earlier sections, the Nyquist plot (Z' vs Z'') consists of one or two semi circles. In real situations the first, smaller depressed semi circle is formed in high frequency region while a larger a semi circle is formed at low frequencies. A depressed semi circle is formed due to impurities and non reactive capacitive effects that the Li^+ encounters during its course of motion. Hence the angle of depression in a fitted Nyquist plot is a measure of inhomogeneities within grain and grain boundary regions [7, 11]. Fitting is generally done using equivalent circuit models in which a parallel and series combination of resistance R, capacitance C, constant phase element (CPE), Warburg element (W), double layer capacitance C_{dl} etc are used to describe the behavior in Nyquist plots. At times, the depressed semicircle shape of a Nyquist plot is not formed in the (microwave) frequency and temperature range (generally above room temperature) studied. That is, the hopping motion of the ions within the bulk of the crystalline material is not adequately seen in the Nyquist plot even in the high frequency region at room temperatures. On the contrary the semi circle is formed partially in high frequency region. Therefore, to get a clearer idea of the ionic hopping motion, within that material, some workers [12] perform the impedance spectroscopy at very low temperatures (below 200 K) and at very high frequencies (1 GHz). Fig. 2.11 relates the region inside the sample (electrolyte), the usage of circuit elements and Nyquist plot. Ideal capacitance exhibited in the below figure to represent the behavior of Li^+ in a system is not found. Instead, CPE are used to mimic the behavior of Li^+ through the solid material. The impedance of CPE is $Z_{CPE} = K(\boldsymbol{j}\omega)^{-\alpha}$ where $0 < \alpha < 1$, is an exponent and K is a fitting parameter [7]. McNealy *et. al.* [13] have recently tried linking impedance data of grain boundary and fitted CPE. They have used a new empirical formula that links the local heterogeneity of grain boundary with variation in the fitted CPE values.

MacDonald [7] has developed extensive theory of non linear fitting and usage of CPE (to describe the depressed semi circle) in circuit of non linear curve fitting procedure. Based on MacDonald’s theory, Boukamp [14] developed a non linear curve fitting package to fit the electrical circuit elements in the impedance plots. The capacitance generally has the property of linear rise in a plot while, using a resistance increases the convex curvature of the plot while fitting. Fig.2.12 relates the region inside the sample (electrolyte), the usage of circuit elements and Nyquist plot.

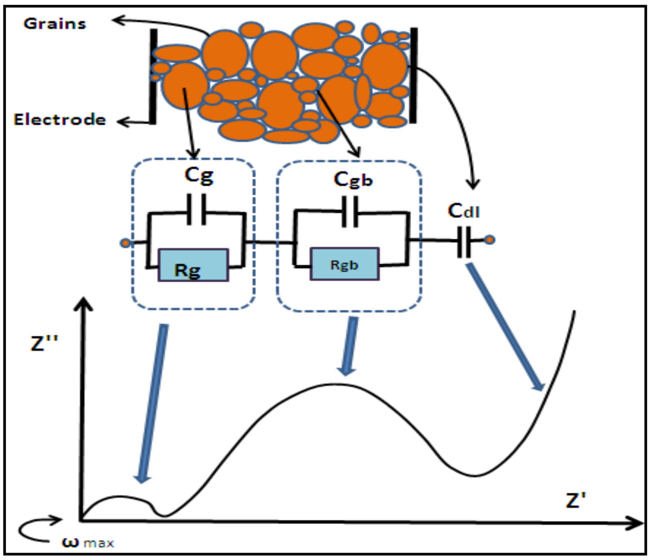


Fig.2.12 Nyquist plot and relation of grain and grain boundary regions in it. (Fitting has been done using equivalent circuit elements as mentioned in the figure)

Here in the Figure, the C_g and C_{gb} denote the grain and grain boundary capacitance, R_g and R_{gb} denote the grain and grain boundary resistance and C_{dl} stands for double layer capacitance which gives rise to a spike or a slant line at the end of the curve. In the below section, the Nyquist plots of different series of samples in our study are highlighted. The fitting of this data is done using the equivalent circuit theory. Generally the fitting in glass ceramics materials is done using a combination of R and CPE. Generally fitting of the conductivity isotherms instead of Z' - Z'' plots can be done using the relation:

$$\sigma^* = [\frac{1}{\sigma_1^*} + \frac{1}{\sigma_2^*}]^{-1} = \sigma_{dc} + \mathrm{B}(j\omega)^n \qquad \ldots\ldots\ldots (2.27)$$

which is derived from the Jonscher's law [15].

As mentioned in the earlier sections, the Nyquist plot (Z' - Z'') consists of one or two semi circles. In real situations the first, smaller depressed semi circle is formed in high frequency region while a larger a semi circle is formed at low frequencies.

The Warburg element is a common diffusion circuit element which is used in equivalent circuit models to describe a linear diffusion for example in a large planar electrode. A Warburg impedance element is associated with capacitance at the interface. The Warburg diffusion element (Z_w) thus describes an imperfect capacitance like a constant phase element

(CPE), with a constant phase of 45° (phase independent of frequency) and with a magnitude inversely proportional to the square root of the frequency by:

$$Z_w = \frac{A_w}{\sqrt{\omega}} + \frac{A_w}{j\sqrt{\omega}} = \sqrt{2}\,\frac{A_w}{\sqrt{\omega}} \qquad \text{………… (2.28)}$$

2.2.7 Dielectric Permittivity

The dielectric permittivity of a material is defined as a tendency of the material to align the dipoles within it to the applied static (DC) or time varying (AC) external electric field. In a typical capacitor a dielectric material is placed between two parallel plates separated by a distance **d**. When an electric field is applied across these plates of area A, the capacitance (the capacity to hold large amount of charge Q at a given voltage V) is given by $\mathbf{C} = \frac{\mathbf{Q}}{\mathbf{V}}$. Thus capacitance depends on geometric dimensions of the system (Area, shape of plates). The above equation can be explained as follows: A strong electric field can ionize the surrounding air and accelerate the charges so produced towards the oppositely charged plates. Due to this 'leakage' of charges, the plates become neutralized. The maximum value of the electric field which the dielectric material (between the plates) can withstand is proportional to the voltage difference between them. Thus, the capacitance depends on the dielectric property of the material kept between the plates.

If there is no material (vacuum) between the plates, then we define the $\mathbf{C_0}$ as the vacuum capacitance. It is expressed as: $\mathbf{C_0} = \boldsymbol{\varepsilon_0}\frac{\mathbf{A}}{\mathbf{t}}$, where $\boldsymbol{\varepsilon_0}$ = 8.85 × 10^{-14} F/cm is the permittivity of free space (constant). The property dielectric behavior of a material can be related to the transport of charges within the microstructure, the defects, the grain boundaries and other faults to which the charges are exposed to.

When a material is exposed to a time varying external electric field is the complex dielectric (permittivity) function ε^* is given as

$$\varepsilon^*(\omega) = -j/\omega C_0 Z^*(\omega) = \varepsilon'(\omega) - j\,\varepsilon''(\omega) \qquad \text{……..(2.29)}$$

where, the real part (ε') of complex dielectric function is the tendency (readiness) of the ions (charges) to align with the electrical field while the imaginary part (ε'') is considered to be the loss of the electrical field strength when the ions are not able to absorb and re-orient according to the field. If a time varying field V(t) = $V_o exp(j\omega t)$ is applied to a material, then the polarization and induced charge Q are related as $Q = \varepsilon^*(\omega).V_o exp(j\omega t)$

where ε^* is a dielectric constant which is a frequency dependent **(ω)** quantity. It is given by the following:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+j\omega\tau)} \qquad \text{……… (2.30)}$$

ε_∞ is the permittivity corresponding to the highest frequency and $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ where ε_s represents static low frequency permittivity (that is value of ε when time variation t = 0) and τ represents the relaxation time for the ion in the medium. The complex permittivity ε^* is given as $\varepsilon^* = \varepsilon' - j\,\varepsilon''$

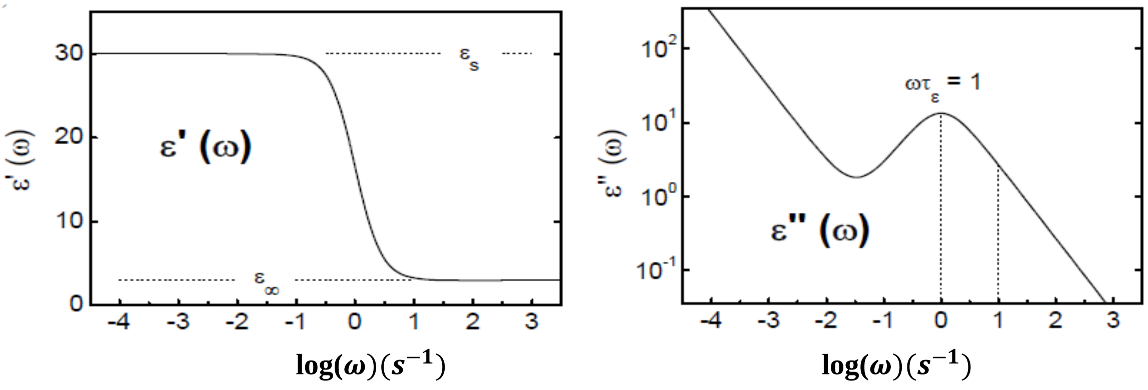
the real and imaginary parts of dielectric permittivity are given as follows:

$$\varepsilon' = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+(\omega\tau)^2)} \quad \text{and} \quad \varepsilon'' = \frac{\Delta\varepsilon.\omega\tau}{(1+(\omega\tau)^2)} \qquad \text{……..(2.31)}$$

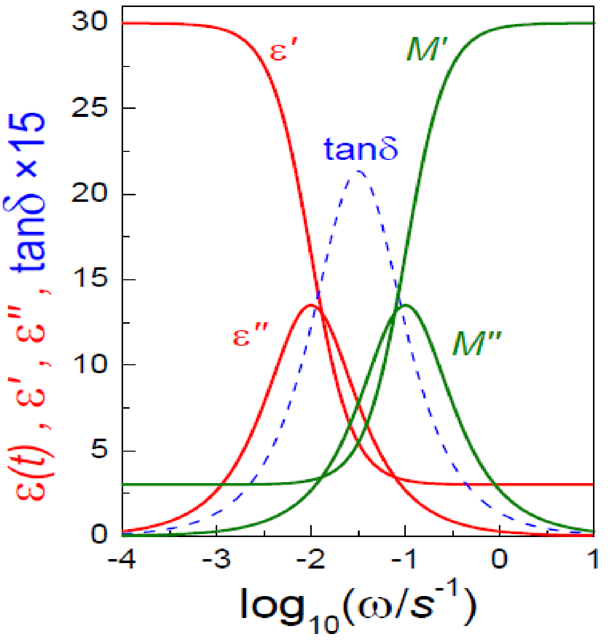
The ratio of imaginary to real dielectric permittivity is called the loss tangent *tanδ*

$$tan\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{\Delta\varepsilon.\omega\tau}{(\varepsilon_s + \varepsilon_\infty(\omega\tau)^2)} \qquad \text{……(2.32)}$$

tanδ indicates the loss of the electric field energy due to inability of the ion to get polarized as fast as the changing field. The above equations describe an ideal behavior, were first proposed by Peter Debye (1915), wherein a dipole oscillates according to externally applied field without interacting with other dipoles or its environment. This ideal behavior is given in Fig.2.13.



(a) **(b)**



(c)

Fig. 2.13 The variation of (a) ε' (b) ε'' and (c) tan*δ* with frequency for an ideal Debye system

In the Fig. 2.13 the real dielectric permittivity ε' attains a maximum value at low frequencies (that is easily orients to the field) and at very high frequencies attains an asymptotic behavior where $\varepsilon' \rightarrow \varepsilon_\infty$. The time during which the ion re-orients itself to the electric field is called the dielectric relaxation time $\boldsymbol{\tau}$. During this time, it is unable to absorb any electric field energy. The maximum of ε″ is given at ωτ = 1 at the peak of the plot. At this point, the oscillator is able to absorb the maximum energy from the electric field. For an ideal Debye oscillator, the peak in the *tanδ vs. log f* plot is symmetric about the mean position and given by $\boldsymbol{\omega\tau} = \left[\frac{\boldsymbol{\varepsilon_S}}{\boldsymbol{\varepsilon_\infty}}\right]^{½}$ represents the maximum frequency.

A deviation from the ideal Debye behavior can be expressed by functions like Cole-Cole, Cole-Davidson and Havraliak-Negami functions which are given by following formulae [16]:

1) The Cole–Cole equation has a functional form as follows:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\boldsymbol{\Delta\varepsilon}}{(\mathbf{1}+(\boldsymbol{j\omega\tau})^{\mathbf{1}-\boldsymbol{\alpha}})} \qquad \ldots\ldots(2.33)$$

where $\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$;

ε_S is a static dielectric permittivity while ε_∞ represents asymptotically increasing dielectric function. This function is often used to describe dielectric relaxation in polymers. The value of exponent parameter α, is between 0 and 1. When α = 0, the Cole-Cole model reduces to the Debye model. When α > 0, the relaxation is *stretched*, i.e. it extends over a wider range on a logarithmic ω scale than Debye relaxation.

2) Cole-Davidson relaxation function: This is described by the following equation:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+j\omega\tau)^{\beta}} \quad \text{..……(2.34)}$$

3) Another type of relaxation function is Havriliak-Negami relaxation which is described by the following formula:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+(j\omega\tau)^{\alpha})^{\beta}} \quad \text{……… (2.35)}$$

where the exponents α and β describe the asymmetry and broadness of the corresponding spectra. If β = 1, the Havriliak–Negami equation reduces to the Cole–Cole equation and if α = 1 to the Cole–Davidson equation. Hence the Havriliak-Negami function is a generalized form and often used to explain the relaxation of ions in complicated systems like polymers.

2.2.8 Modulus Formalism

The modulus formalism is used to analyze the relaxation processes in solids [17]. The complex modulus function can be given as,

$$M^*(\omega) = \frac{1}{\varepsilon^*} = j\,\omega C_0 Z^* = M' + j\,M'' \quad \text{……… (2.36)}$$

The complex dielectric analysis provides information about the electrode polarization while the modulus formalism gives the conductivity relaxation effects. Kohlrausch Williams Watts (KWW) stretched exponential function is used to describe the effects of relaxation in modulus formalism. The formula is given as below:

$$\varphi(t) = exp[-(t/\tau)^{\beta}] \quad \text{……..(2.37)}$$

Here $\boldsymbol{\tau}$ represents the relaxation time, $\boldsymbol{t}$ indicates the total time and $\boldsymbol{\beta}$ is an exponential parameter ($0 < \beta < 1$);

When an ion is exposed to changing electric field it tries to orient itself in the direction of applied electric field. There is an interaction of the charge (the charge of electron cloud and that of the nucleus) and spin of the ion, due to which the ion stores some or entire energy of the external electric field. Besides, the ion also orients itself according to the direction of the electric field. This act of re-orientation of the ion to the external field, is called, polarization. During this time, not only the ion but its surrounding charges have to re-orient themselves to retain an electrically neutral character in the local area in accordance with the electrostatic considerations. The relaxation of the surrounding environment the ion and the ion itself happens simultaneously. Thus the ion takes some time to polarize itself. This is called the relaxation time. In relaxation time the ion is not able to gain any electric field energy. Besides, if the electric field direction changes during the time when the ion is still relaxing, the ion cannot respond to this change and a lag is produced in time domain for the ion. Generally the ion has thermodynamic agitations or vibrations (in Infra red region of the electromagnetic spectrum). The frequency of applied electric field has to be greater than the vibration frequency of the atoms or ions. Therefore the ions are exposed to electric field which is in microwave frequency region of the electromagnetic spectrum. If the ion is not able to gain energy from the high frequency electric field it cannot polarize and hence other processes like adjustments in local environment of the ion also cannot happen. To understand the ion conductivity it is important to understand the ionic relaxation at varying frequencies. This variation of the time lag with respect to stretched time, in case of solid materials, is described by the above mentioned Kohlrausch Williams Watts (KWW) stretched exponential function. Since modulus is expressed as inverse of complex dielectric, the dielectric relaxation described by the KWW function is also related to Modulus formalism.

Some authors believe that Modulus formalism is an indirect way of representing dielectric behavior of a system or electrochemical cell. It also suppresses the polarization effects at the electrode-electrolyte interface in an electrochemical cell. Hence modulus formalism is not believed by some authors as a correct means of representing the dielectric behavior of a solid ionic material.

2.3 Jonscher's Power Law

In 1967, A.K. Jonscher [15] from his study of results of dielectric relaxation and conductivity behavior of different class of solids (viz. crystals, glasses, gels, ceramics, polymers etc.) gave the following relation:

$$\sigma(\omega) = \sigma_0 + A\,\omega^n \qquad \text{……..(2.38)}$$

where σ_0 indicates the DC conductivity, A is the pre-exponential constant and n is the exponent term. The expression gives an explanation about the AC conductivity which according to Jonscher is a sum of contribution of the DC conductivity and hopping frequency. The term ω^n is a result of the hopping frequency and indirectly indicates the contribution of mobility of the ion. A typical conductivity isotherm given in the Fig.2.14 can be well described using the above mentioned Jonscher power law equation. The low frequency region in the isotherm indicates the polarization at the electrode-electrolyte interface in which the ions even though they are free to move accumulate near the interface and prohibit the entry of ions into the electrode. The curve in intermediate frequency region is described by the DC conductivity of the ions in the medium. The ions have enough energy to overcome their activation energy barrier. These free ions diffuse through translational and rotational motion and travel large distances in the solid. The diffusion of the ions is governed by the presence of defects in the solid. The defects are typically point defects which include cation vacancies or interstitial atoms/ ions whose presence and charge affect the ionic diffusion within the solid. The other types of 2-D defects include the stacking faults, edge or plane defects. 3-D defects typically include the screw dislocations within the solid. The diffusion is primarily governed by the presence of 1-D defects mentioned above. The cation vacancies are also created when temperature of the solid is isothermally increased. The ions gain enough energy to cross their activation barrier potential, and thus diffuse away. The migration of ions creates vacancy sites which have a deficiency of positive charge.

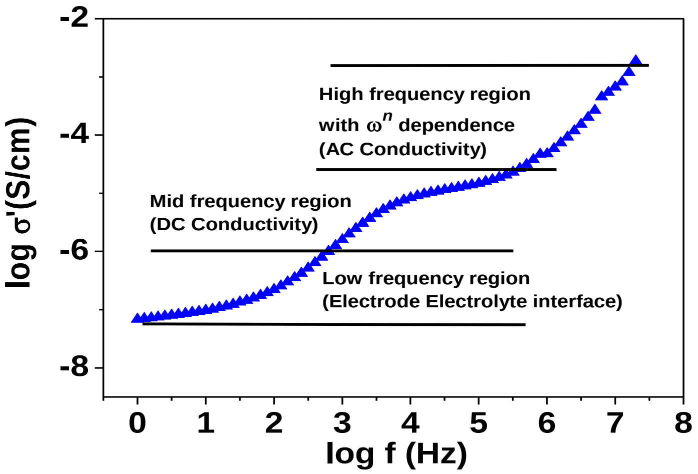


Fig. 2.14 Frequency dependent behavior of conductivity spectrum.

The charge deficient sites try to neutralize their electronic configuration by attracting other migrating ions. Thus temperature acts as an effective means of studying ionic motion in a solid material. Thus, number of defects and diffusion coefficient are directly proportional to the increasing temperature. The relation between DC conductivity and temperature is described by an Arrhenius plot. It is noteworthy to mention here that the frequency of the electric field applied on the solid is not strong enough to polarize the diffusing and migrating ions. The third region described as dispersive region on the conductivity isotherm is strongly dependent on the imposed frequency. Thus the ions which due to higher temperature become free from their site do not become free enough to migrate to the other vacancy sites. The changing direction of the electric field does not permit the ion to hop beyond a few vacancy sites. The conductivity of the ions strongly depends on their hopping and mobility.

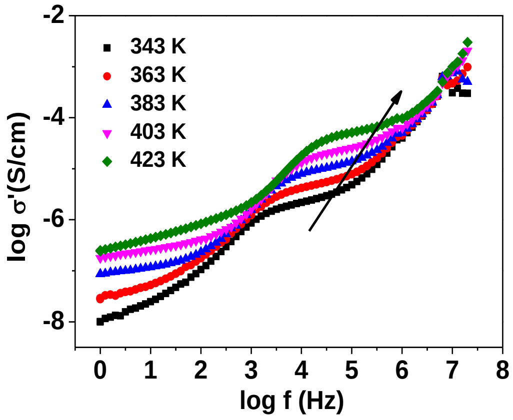


Fig. 2.15 Frequency dependent conductivity behavior at different temperatures.

The presence of the frequency exponent indicates the power law behavior followed by the ions. The Jonscher's law is followed by charge carriers in solids; hence it is called the Universal Dielectric Response (UDR) also. After studying the frequency dependent conductivity isotherms, at increasing temperatures, Almond and West concluded that the frequency at which the DC regime changes to AC regime increases with temperature [1]. This cross over is described by a straight line in the Fig. 2.15. They gave the following formalism to describe the frequency dependent behavior of the ions

$$\sigma(\omega) = \sigma_o [1 + (f/f_p)^n] \quad \text{........ (2.39)}$$

where f_p is the cross over frequency that is the frequency at which there is a cross over from DC conductivity to AC conductivity. From the above equation, an estimate of DC conductivity can be obtained by the below relation:

$$\sigma (f_p) = 2\, \sigma_0 \quad \text{......... (2.40)}$$

The DC conductivity and the cross over frequency are related by the following relation:

$$\sigma_0 T = K f_p \quad \text{......... (2.41)}$$

and

$$K = [\frac{2\pi N e^2 a^2}{k_B}] \gamma c(1\text{-}c) \quad \text{......... (2.42)}$$

where K is the mobile charge carrier concentration factor, c is concentration of charge ions, e is electronic charge, a is the hopping distance, N are the equivalent sites per unit volume.

Here γ is the correlation factor which describes the correlation of the ions in a many-body system (where the concentration of the ions is given by c) and k_B is Boltzmann constant. Thus the correlation of the ions (electropositive repulsion) exerted on each other is influential enough to deviate and disperse the ion from its translational trajectory of diffusion.

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