Chapter 2

Materials and methods

Processing of ceramic materials is very important for obtaining product of consistent properties. In this chapter the preparation technique used for the synthesis of the ionic conductors are discussed. Characterization is essential to the systematic development of new materials and understanding how they behave in practical applications. This chapter also includes a brief note on the characterization techniques used in the present study.
1. Synthesis of materials

1.1 Introduction

Ceramics are processing-intensive and processing-sensitive materials. For the processing of ceramic oxides different methods are used such as high temperature solid state reaction technique, sol-gel process and co precipitation techniques. Ceramic components are usually processed through a relatively complicated powder route, where the characteristics of each processing step affect properties of the final product [1-3]. The different steps involved in the process are discussed below.

1.2 Preparation and processing

Conventional ceramic processing of ceramic component requires a number of stages: manufacture of powder, milling and mixing, calcination, incorporating additives, shape forming and densification [4]. The various stages involved in the processing of ceramic materials by solid state reaction are shown in the flow chart (Fig. 2.1). The main disadvantage of solid state reaction is the high temperature needed to form the product which leads to agglomerated particles with poor surface area [5].

1.2.1 Raw materials

The first step involved in the processing by solid state reaction is the selection of the raw materials depending on the properties required in the finished component. Purity, particle size distribution, reactivity and polymorphic form of the raw materials affect the final properties of the ceramic oxide prepared. So high purity raw materials are selected according to the composition and weighed stoichiometrically [6].

Natural raw materials have been used for producing advanced high technology ceramics for several decades. The major problems with natural raw materials are the inability of the user to predict exactly its chemical composition and the alpha emission
from impurities. Nowadays synthetic raw material is used for producing sintered ceramics [7].

![Flow chart for various stages of general ceramic processing](image)

**Fig. 2.1** Flow chart for various stages of general ceramic processing

1.2.2 Mixing and milling

The general objective of beneficiation of ceramic powders (i.e. milling and mixing) is to prepare them to further processing operations: shape forming and sintering. Therefore the objectives of beneficiation are:

- to reduce particle size and modify their size distribution
- to liberate impurities
- to reduce the porosity of particles
- to disperse agglomerates
Even when the material is a single component, if agglomerates are present, they densify more rapidly internally resulting in pores. Hence during mixing process, not only agglomerates are broken but also defects are introduced into the grains that enhance diffusion mechanism [1, 3].

For the mixing a liquid medium such as acetone, distilled water or ethanol is used. After mixing and grinding, the slurry is dried to expel the liquid completely.

Very good mixing on an atomic scale can be achieved by chemical methods. Though these chemical methods yield optimum homogeneity, they are usually more expensive than mechanical mixing. Also, the product consists of small crystals which are bound to agglomerates so that special conditions of calcinations and deflocculation have to be adopted in order to get dense compacts [8].

1.2.3 Calcination

Calcination is believed to be one of the 12 vital process required for the transformation of a substance. It is the process of heating a substance to high temperature, but below its melting or fusing point, to bring about thermal decomposition or a phase transition in its physical or chemical constitution [9]. Calcination is distinguished from drying, in which mechanically held water is driven off by heating, and roasting, in which a material is heated in the presence of air to oxidize materials.

During calcination, the following stages are involved.

- As a result of heat treatment given to powders, sufficient interaction takes place between the constituents to form the compound.
- Volatile impurities like H₂O, CO₂, etc are removed.
- Optimum particle size and desired crystal phase are achieved.
- Coarsening takes place, i.e., particle size of very fine powder that has a poor packing property is increased to a less fine powder with improved packing properties.

The calcination conditions such as temperature, duration of heating and atmosphere are important factors controlling shrinkage during sintering. The final phases of interest may not be completely formed but the calcination yield a consistent product [10].

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1.2.4 Powder consolidation

In ceramic processing, the powder is first consolidated in the desired shape to produce what is called a "green body". This consolidation and shaping step are most widely done by pressing the loose mass of powder in a die at pressures of over 200 MPa. The resulting green body has large porosity (up to 40%). The powder particles are held together by mechanical interlocking and surface forces, aided by small amounts (~ 1%) of some organic binder such as polyvinyl alcohol (PVA). (Binders are particles which form bridges between flocculated ceramic grains). The green body at this stage is very fragile and needs to be handled carefully. The common defect of dry pressed ceramic component is fracture, including laminations, end capping and ring capping. Several innovations such as pressure assisted slip casting, isostatic pressing, injection moulding, gel casting, enzyme catalyzed ceramic forming have made it possible to prepare improved green bodies of complex shapes not achievable by powder pressing [11, 12].

1.2.5 Sintering

Sintering is the method for making objects from powder; by heating the material (below its melting point) until its particles adhere to each other. It is the most common technique for consolidating powders [9, 13]. Essentially; it is the removal of the pores between the starting particles, combined with their growth and strong mutual bonding. The process is carried out by heating up the "green" part at about 80% of the melting temperature, until full strength is obtained (10 min to several hours). The biggest problem of this technique is shrinkage, which causes cracking and distortion [11].

In most cases, the density of a collection of grains increases as material flows into voids, causing a decrease in overall volume. Mass movements that occur during sintering consist of the reduction of total porosity by repacking, followed by material transport due to evaporation and condensation from diffusion. In the final stages, metal atoms move along crystal boundaries to the walls of internal pores, redistributing mass from the
internal bulk of the object and smoothing pore walls. Surface tension is the driving force for this movement.

The following major changes occur during sintering process:

- strength, hardness
- electrical and thermal conductivity
- average grain number, size and shape
- distribution of grain size and shape
- average pore size and shape
- distribution of pore size and shape
- chemical composition and crystal structure

There are many methods for sintering a component. The most important are: vapour-phase sintering; solid-state sintering; liquid-phase sintering; reactive liquid sintering. The advantages of solid state sintering are increased strength of the material and reduced surface area. In solid state sintering mechanism the bulk material transport can be by volume diffusion, grain boundary diffusion, surface diffusion or evaporation condensation.

The three stages of sintering are given below:

1. Local point of contact formation and neck formation at the contact point. This results in densification of sintering component by ~ 10%.
2. Neck growth, pores forming and particle centers approaching each other.
3. Isolation of pores, elimination of porosity and grain growth.

The principle variables that control shrinkage in each stages of sintering are temperature, time, particle size and chemical composition of ceramic [3].

During sintering, the surface energy is reduced by transferring matter from the interior of grains to adjacent pores. Grain boundaries serve as vacancy sinks. Grain growth also takes place in parallel with densification which is favored by the reduction in the area of grain boundaries. This is because the crystal lattice has a lower free energy.
than the highly defective grain boundary region and the ratio of boundary area to volume for large grain is smaller than that for small grains.

### 1.2.6 Finishing

The ceramic body after firing is strong and should have desired properties. Often a further finishing step such as grinding to final dimensions is needed. In case of electronic ceramics, the application of metallic coating to act as electrodes is the most common finishing step [14].

### 2. Characterization

#### 2.1 Introduction

Characterization is the very foundation upon which the science of ceramics rest. It describes those features of the composition and structure including defects of a material that are significant for a particular preparation, study of properties or use and suffice for the reproduction of the material [15]. There are various stages of characterization of ceramics which corresponds to the sequence of processing steps that a ceramic product undergoes. The characterization techniques used in the present context are briefly discussed below.

#### 2.2 X-ray powder diffraction

X-Ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials. The method has been traditionally used for phase identification, quantitative analysis and determination of structure imperfections. In recent years, applications have been extended to new areas, such as the determination of crystal structures and the extraction of three dimensional microstructural properties [16].

A crystal may be considered as a natural three-dimensional diffraction grating for radiation of suitable wavelength. The distance between particles in a crystal is of the
order of $10^{-10}$ m, which is in the range of X-ray. Hence, X-ray diffraction is extensively used for characterisation of solids.

2.2.1 Theory and methodology

When a focused X-ray beam interact with the planes of atoms that form a crystal lattice, part of the beam is transmitted, part is absorbed by the sample, part is refracted and scattered and part is diffracted. X-rays are diffracted by each mineral differently, depending on what atoms make up the crystal lattice and how these atoms are arranged [17, 18].

In X-ray powder diffractometry, X-rays are generated within a sealed tube that is under vacuum. Electrons are emitted from the heated filament and are accelerated by a high voltage. When these electrons hit the target, commonly made of copper, X-rays are produced. The wavelength of these X-rays is characteristic of the target. These X-rays are collimated and directed onto the sample and a detector detects the X-ray signal [19-22]. The signal is processed to a count rate either by a microprocessor or electronically. Changing the angle between the X-ray source, the sample and detector at a controlled rate between preset limits is an X-ray scan [23, 24].

When an X-ray beam hits a sample and is diffracted, the distance between the planes of the atoms that constitute the sample can be measured by applying Bragg’s Law [25].

$$n\lambda = 2d\sin\theta$$  \hspace{1cm} (2.1)
Fig. 2.2 Schematic of an X-ray powder diffractometer [26].

Hence, Bragg’s Law is \( n \lambda = 2d \sin \theta \), where the integer \( n \) is the order of the diffracted beam, \( \lambda \) is the wavelength of the incident X-ray beam, \( d \) is the distance between adjacent planes of atoms and \( \theta \) is the angle of incidence of the x-ray beam. The characteristic set of \( d \) spacings generated in the x-ray scan provides a fingerprint of the material present in the sample. When properly interpreted by comparison with standard reference patterns and measurements, this fingerprint allows for identification of the material [27].

The most widespread use of x-ray powder diffraction is for the identification of crystalline compounds by their diffraction pattern. Phase identification is accomplished by comparing the peaks and relative intensities from the unknown sample with peaks and relative intensities from a very large set of standard data provided by the International Center for Diffraction Data [28].

In the present study, powder method is employed for the identification of the crystalline phases present in the specimen sample. The XRD patterns of the powder after different heat treatment stages have studied by an automated X-ray diffractometer (Philips X’Pert Pro) using CuK\(_\alpha\) radiation with graphite monochromator. This diffractometer is designed to disperse X-rays of a single wavelength by diffracting them
from planes of different spacing. Comparing the patterns with those given in the JCPDS (Joint Committee for Powder Diffraction Standards) files, the phase analysis is done. The relative amounts of different phases are estimated by measuring the integrated intensities of the major XRD peaks of corresponding phases.

Using X-ray diffractometer, X-ray diffraction patterns of the given sample is taken. From the pattern obtained, lattice spacing and hence lattice constants are calculated and the pattern is analyzed making use of the following equations [29].

The interplanar distance between two parallel lattice planes having designation (h k l), is given by,

\[ d_{hkl} = \frac{1}{(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}} \]  

(2.2)

where \( a, b \) and \( c \) are the lattice parameters of the unit cell of the crystal.

Therefore, for a cubic system, \( a = b = c \), \( d = a / (h^2+k^2+l^2)^{1/2} \)

For a tetragonal system, \( a = b \neq c \), \( d = (h^2+k^2/a^2 + l^2/c^2)^{-1/2} \)

For orthorhombic system, \( a \neq b \neq c \), \( d = (h^2/a^2 + k^2/b^2 + l^2/c^2)^{-1/2} \)

For hexagonal system, \( a = b \neq c \), \( d = (2(h^2+k^2+l^2) / 3a^2 + l^2/c^2)^{-1/2} \)

2.3 Scanning electron microscopy

The scanning electron microscopy (SEM) has become an indispensable tool for morphological observation in materials and biological sciences. SEM is a microscope that uses electrons rather than light to form an image. The scanning electron microscope consists of an energetically well defined highly focused beam of electron scanned across a sample [30].
2.3.1 Theory and procedure

The electron beam commonly used in the SEM is accelerated through a voltage of about 1-50kV. The types of signals produced when the electron beam impinges on a specimen surface includes secondary electrons, back scattered electrons, characteristic x-rays and phonons of various energies (Fig.2.3). These signals are obtained in specific emission volumes with in the sample and can be used to examine the characteristics of the sample such as composition, surface topology, crystallography etc. The signals most commonly used are secondary electrons and back scattered electrons [31].

An electron beam passing through an evacuated column is focused by electromagnetic lenses on to the specimen surface. The beam is then rasted over the specimen in synchronism with the beam of a CRT display screen. The secondary electrons having low energy are omitted from the sample surface and are detected by a scintillator or photo multiplier detector and resulting signal modulates the display screen [32]. These electrons provide a kind of shading that gives a three dimensional appearance
of the image making it easy to visualize the structural relationship of parts of the sample. Back scattered electrons may be used to detect contrast between areas with different chemical composition. But there are only few backscattered electrons than secondary electrons and also their collection efficiency is also very poor [33].

Any solid material can be studied using the SEM; specimen size is limited to less than 10 mm in diameter. As the electron beam consists of electrically charged particles and to yield good images, the sample for SEM observation must either be electrically conducting or must be made to conducting by sputter coating the sample with heavy metals such as gold or platinum. The metal improves specific contrast by promoting electron reflection and providing a homogeneous source of secondary electrons [34].

The spatial resolution of the SEM depends on the size of the electron spot which in turn depends on the magnetic electron optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume. Depending on the instrument the resolution can fall somewhere between less than 1nm and 20nm [9].

When a SEM is used, the column must always be at a vacuum. If the sample is in a gas filled environment, an electron beam cannot be generated or maintained because of a high instability in the beam. Gases could react with the electron source producing random discharge and leads to instability in the beam. The transmission of the beam through the electron optic column would also be hindered by the presence of other molecules. For the use of SEM sample preparation is important. This include removal of all water, solvents etc. that could vaporize while in the vacuum, mounting the sample and making the non metallic sample conducting by sputter coating [35].

2.4 Thermal analysis

Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme. In differential thermal analysis the temperature difference that develops between a sample and an inert reference material is measured when both are subjected to identical heat treatments [36].
2.4.1 Differential thermal analysis

Differential thermal analysis (DTA) may be defined as a technique for recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate [37]. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference. A DTA curve can be used as a fingerprint for identification purposes. The area under a DTA peak can be to the enthalpy change and is not affected by the heat capacity of the sample. DTA can be used to study thermal properties and phase changes which do not lead to change in enthalpy.

The apparatus of differential thermal analysis consists of sample holder, furnace, temperature programmer and recording system. Experiments are frequently performed on powders so the resulting data may not be representative of bulk samples, where transformations may be controlled by the build up of strain energy [38]. The shape of a DTA peak depends on sample weight and the heating rate used. Lowering the heating rate and sample weight leads to sharper peaks with improved resolution.

A simple DTA curve consists of linear portions displaced from the abscissa because the heat capacities and thermal conductivities of the test and reference samples are not identical. The DTA plot provides information on exothermic and endothermic reactions taking place in the sample, temperatures for phase transitions, melting points etc. [39]. In the present case the new system is studied to identify the temperature for phase transition.

2.5 Energy dispersive X-ray spectrometer

Since all elements have characteristic X-ray energy “fingerprints”, these energies can be used both to identify and quantify elements in unknown samples. One technique for doing this is “Energy Dispersive X-ray Spectroscopy” or EDS.

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The Energy Dispersive X-ray Spectroscopy (EDS), also referred to as EDX, is a technique used in conjunction with Scanning Electron Microscopy (SEM). First the area of interest is identified through SEM imaging. X-rays generated by the SEM’s focused electron beam are then collected by the EDS detector where the energy of the X-ray is determined. The number of X-rays are counted for each particular energy and displayed on a graph of counts vs. energy. Since each element releases X-rays with unique energy signatures it is possible to identify the parent atoms from the X-ray spectrum. All elements greater than Beryllium (Be) can generally be detected and its quantitative analysis is possible. Element distribution mapping is another useful technique using EDS. During element mapping, one or more X-ray energies corresponding to one or more elements are collected as the SEM scans the electron beam over a selected area. The X-ray data is synchronized with the SEM image and an ‘element image’ is created showing the presence of the selected element throughout the selected area. This can be a powerful tool for determining the distribution of a contaminant or the structure of a sample [33].

During inelastic scattering of beam electrons, X-rays can be formed by two processes, bremsstrahlung or continuous X-ray process and inner shell ionization process which leads to emission of characteristic X-rays.

2.5.1 Characteristic X-rays

X – Ray spectrum we observe has two distinct different components – a characteristic component, which identifies the specific atoms present in the interaction volume and a continuous component, which is non-specific and forms a background at all energies.

The beam electrons can interact with a tightly bound inner shell electron, ejecting the atomic electron and creating a vacancy in that shell; the atom is left as an ion in an excited energetic state. The atom releases to its ground state within pico seconds through a limit set of transitions of outer shell electrons to fill inner shell vacancy in an additional way also, the Auger process.
For a specific shell Auger process is favored for low atomic numbers while characteristic X-ray process dominates for high atomic numbers. The energy levels of shells vary with atomic number $Z$, supported by Moseley’s relation

$$\lambda = B / (Z-C)^2$$  \hspace{1cm} (2.3)

where $B$ and $C$ are constants for each family and $\lambda$ is characteristic X-ray wavelength. This relation forms the basis for qualitative analysis, ie the identification of elemental constitution plotted for different X-ray lines (K\(\alpha\), L\(\alpha\), M\(\alpha\)).

When ionization occurs in the K shell, a transition to fill that vacancy can occur from either L shell or M shell. Since electrons in these shells are at different energies, X-rays created from these two shells must have different energies and designated differently. In Siegbahn notation, lower case Greek letters are used to designate X-rays arising from ionization in a particular shell in the general order of observed intensity: \(\alpha, \beta, \gamma\), etc. The advantage of rapid calculation of chemical composition is that the operator has greater flexibility in carrying out analyses and provides repetitive analysis.

2.6 Ionic conductivity measurements

Ionic conductivity can be measured using impedance spectroscopy (IS). Impedance spectroscopy is a powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charges in the bulk or interfacial regions of any kind of solid or liquid material, ionic, semi conducting, mixed electronic ionic and dielectrics.

Impedance spectroscopy is the study of sample resistivity over a wide range of frequencies ranging from several mHz to a few MHz. Each individual spectrum provides information about the resistive, inductive or capacitive elements, which together constitute the electrical behaviour of the sample. Impedance spectroscopy is frequently used in the study of electrochemical systems. The ability of automated high quality frequency response analysis devices to interface with PCs enables the multitude of data to
be recorded and analyzed. These measurements are taken over a large frequency range and enable different circuit elements, to be resolved and have been particularly useful for the study of ionic conduction, grain boundary impedance, electrode/electrode interface characteristics and also mixed conducting solid electrode materials. Semicircles are frequently observed in impedance spectroscopy measurements and are caused by a combination of a sample resistance in parallel with a sample capacitance [40].

2.6.1 Basic impedance spectroscopy experiment

Electrical measurement to evaluate the electrochemical behavior of electrode and/or electrolyte materials are usually made with cells having two identical electrodes applied to faces of a sample in the form of a circular cylinder. The general approach is to apply an electrical stimulus (a known voltage or current) to the electrodes and observe the respond (the resulting current or voltage). The properties of the electrode- material system are time invariant and it is one of the basic purposes of IS to determine these properties, their interrelations and their dependences on such controllable variable as temperature, oxygen partial pressure, applied hydrostatic pressure and applied static voltage or current basis.

A multitude of fundamental microscopic processes take place through out the cell when it is electrically stimulated and it lead to the overall electrical response. These include the transport of electron through the electronic conductors, the transfer of electron at the electrode electrolyte interfaces to or from charged on uncharged atomic species which originate from the cell materials and its atmospheric environment and the flow of charged atoms or atom agglomerates via defects in the electrolyte. The flow rate of charged particles depends on the atomic resistance of the electrodes and the electrolyte and on the reaction rates as the electrode- electrolyte interfaces. The flow may be further impeded by band structure anomalies at any given boundaries present and the point defects in the bulk of all materials [41, 42].

There are three different types of electrical stimuli which are used in IS. First, in transient measurements a step function of voltage may be applied at t=0 to the system and
the resulting time varying current \( t \) measured. The ratio \( v_0/i(t) \), the time varying resistance, measures the impedance resulting from the step function voltage perturbation at the electrochemical interface. Such time varying results are generally Fourier transformed into the frequency domain yielding frequency dependent impedance.

The advantages of this approach are that it is experimentally easily accomplished and the independent variable, voltage, controls the rate of the electrochemical reaction at the interface. Disadvantages include the need to Fourier analyze the results and the fact that the frequency spectrum is not directly controlled, so the impedance may not be well determined overall desired frequencies.

A second technique in IS is to apply a signal \( V(t) \) composed of random noise to the interface and measure the resulting current. Fourier transforms the results to pass into the frequency domain and obtain impedance. This approach has the advantage of fast data collection. The disadvantages are that it requires true white noise and then the need to carry out a Fourier analysis which can be computationally difficult and time consuming.

The third approach is to measure impedance directly in the frequency domain by applying a single frequency voltage to the interface and measuring the phase shift and amplitude of the resulting current at that frequency. Advantages of this approach are the availability of these instruments and the case of their use as well as the experimentalist can control the frequency range to examine the domain of most interest.

Any intrinsic property that influences the conductivity of an electrode materials system can be studied by IS. The parameters derived from an IS spectrum consists of those pertinent to material itself and those pertinent to an electrode- material interface. The former include conductivity, dielectric constant, mobility of charges etc. and the latter include capacitance of the interface region, absorption reaction rate constants etc.

2.6.2 Theory

A monochromatic signal \( v(t) = V_m \sin (\omega t) \), is applied and the resulting steady state current \( I(t) = I_m \sin (\omega t + \theta) \) is measured. \( \theta \), the phase difference between the voltage and current is zero for purely resistive behavior.
Thus, impedance is defined as, $Z(\omega) = v(t)/i(t)$. Its magnitude is $V_m/I_m(\omega)$ and phase angle is $\theta(\omega)$.

The impedance is an important parameter used to characterize electronic circuits, components and the materials used to make components. Impedance $Z$ is generally defined as the total opposition a device or circuit offers to the flow of alternating current at a given frequency and is represented as a complex quantity [43].

The magnitude and direction of a planar vector in a right handed orthogonal system of axes can be expressed by the vector sum of the components $a$ and $b$ along the axes. i.e. $Z = a + jb$. The imaginary number $j$ indicates an anticlockwise rotation by $\pi/2$ relative to the x axis. An impedance $Z(\omega) = Z' + Z''$ is a vector quantity and can be plotted in the plane with rectangular or polar coordinates. (Fig. 2.4) [44]

![Fig. 2.4 Impedance Z plotted as a planar vector.](image)

The two rectangular coordinate values are

\[ \text{Re} (Z) \equiv |Z| \cos (\theta) \text{ and } \text{Im} (Z) \equiv |Z| \sin (\theta) \]

with phase angle $\theta = \tan^{-1} (Z''/Z')$.

Thus, $Z$ is frequency dependent and IS measures $Z$ as a function of $v$ or $\omega$ over a wide range of frequency. It is from the resulting structure of the $Z(\omega)$ vs. $\omega$ response that one derives information about the electrical properties of the full electrode - material system.
2.6.3 Experimental

IS can predict aspects of the performance of chemical sensors and fuel cells. In polycrystalline solids, transport properties are strongly affected by microstructure and IS contains features that can be directly related to microstructure. Much of the work done on correlating microstructure and electrical properties has been carried out on these materials since the work of Bauerle. The combined use of IS and microscopy is a powerful means of characterizing materials.

Measurement techniques used to characterize materials are generally simpler. The frequency range to be chosen depends on the relaxation frequencies of phases present in the sample under study and on the microstructure. Bulk properties such as conductivity are calculated using the length over area $l/A$ of each sample. Hence, sample should be cut so as to have two parallel faces and a well defined cross section. Electrodes are normally applied to the sample by painting. Silver paints provide good general purpose electrodes for use at moderate temperatures. Platinum painted electrodes are widely used in the IS of ceramics [44].

The schematic of the impedance measurement system used in the present study is shown in fig.2.5.

![Schematic of impedance measurement system](image)

**Fig.2.5** Schematic of impedance measurement system
For the present study the Solatron 1260 Impedance analyzer which measures the impedance over a frequency range of mHz to 32 MHz were used. The Solatron is capable of taking four point measurements, but for normal use two point measurements have been found to be adequate. The frequency response analyzer (FRA) generates a sinusoidal voltage of specified frequency and amplitude which is applied to the sample under test. The results are expressed as two complex voltages and are transmitted to the computer along with the measurement frequency. In the study of solid electrolytes the applied voltage is restricted to a few millivolts.
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