CHAPTER - III
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3. MEASUREMENT TECHNIQUES USED FOR THE CHARACTERIZATION OF “ITSOFC” MATERIALS

The cathode and electrolyte materials prepared by combustion synthesis in the present work are characterized by the following techniques.

1. Powder X-ray diffraction Analysis
2. Thermal Analysis
3. FTIR Spectroscopy
4. Particle Size Analysis
5. BET Surface Area Measurements
6. Density Measurements
7. Electrical Conductivity Measurements
8. Scanning Electron Microscopic(SEM) Studies
9. Percentage Porosity Measurements

3.1 Powder X-ray diffraction analysis

In crystallized solids, atoms (and molecules) are arranged in a periodic and regular fashion conforming a standard geometry called crystal lattice. In this crystal lattice, the atoms can be thought of as forming different planes taking part in the coherent scattering process. The samples are characterized using JEOL model JEOL-8030 X-ray diffractometer with 2θ scan mode at an operating rate of 40 KV, 20 mA; the characteristic X-radiation is CuKα (Ni filter) possessing the wavelength, \( \lambda = 1.5418 \). The ‘Peak Search’ to tabulate the XRD data and ‘Search Match’ softwares for the comparison of observed data with the standards are available. The photograph of the computer controlled X-ray powder diffractometer used in this study is shown in Fig. 3.1.

When a X-ray beam is incident on a set of parallel planes (within each crystal) of the crystalline bulk, the electron clouds of these atoms diffract the X-ray beam in a rational approach as shown in Fig. 3.2. From the geometrical consideration, the basis Bragg equation is formed as \( 2d \sin \theta = n\lambda \), where \( d \) is the interplanar distance (or lattice constant), \( \lambda \) is the wavelength of the characteristic X-rays, 2θ are the incident and diffracted angles and \( n \) is the order of the scattered beam. This famous Bragg’s law provides the basic pattern for the XRD methods.
Fig. 3.1 – Photograph of the computer controlled X-ray powder diffractometer (Model JEOL-8030)
AÔB = BÔC = \theta

Path Difference = AB + BC = d\sin\theta + d\sin\theta

2d\sin\theta = n \lambda

Fig. 3.2 – Principle of X-ray diffraction

XYZ --> Three dimensional crystallographic axes

a, b, c, \alpha, \beta, \gamma --> Unit cell parameters

Fig. 3.3 – The general configuration of the unit cells and dimensions
A crystal is a complex solid, although orderly arrangement of atoms, all the atoms in the path of the X-ray beam scatter the X-rays simultaneously. In general, the scattered waves interfere and destroy one another, but in certain specific direction (2θ) they combine to form new wavefronts. This cooperative scattering is known as ‘diffraction’ and instruments that are used to study the diffraction of polycrystalline materials are called powder X-ray diffractometer.

There are seven basic unit cells (an unit cell is the smallest figure the repetition of which in three dimension give the actual crystal structure) and they are popularly called as the seven crystal systems. The general configuration of the unit cells and dimensions are brought in Fig. 3.3. The three repeat distances are the three axes of the cell and are given the symbols a, b and c. The angles between the axes are α, β and γ. The distances and angles define the type of cell. If for the example a=b=c and α=β=γ=90° then the cell is a cube and crystal is cubic. Similarly, a=b=c and α=β=γ≠90° produces a rhombohedral cell, which is a cube which has been uniformly deformed along a body diagonal; a≠b≠c and α=β=γ=90° produces a tetragonal cell; a≠b≠c and α=β=γ=90° is orthorhombic, a≠b≠c and α=γ=90°, β≠90° in monoclinic, while a≠b≠c and α≠β≠γ is triclinic. The hexagonal cell is a special case of the monoclinic system where a=b≠C and α=β=90°, γ=120°; this cell however is also related both to an orthorhombic and a rhombohedral cell.

There are fourteen Bravais lattices (in the seven crystal classes) among which all crystalline materials can be classified. Face centered cubic (FCC), body centered cubic (BCC), hexagonal close packed (HCP), body centered tetragonal (BCT) etc. are some of the examples of Bravais lattices. These Bravais lattices and their parameters identify the materials and the lattice planes with specific hkl values and are understood as “finger prints” of the materials. The (h,k,l) are called the Miller indices which are defined as the reciprocals of the intercepts made by the planes on three rectangular axes.

The X-ray powder pattern of a compound provides a convenient and characteristic finger print which can be used in qualitative analysis. Precise values of the α spacings (which are properties of the materials itself, independent of the X-ray wavelength) and of estimated line intensities can be compared with the listed values in the JCPDS file which contains entries of approximately 30,000 inorganic materials [1-2].
a. Quantitative analysis of mixtures

Conventional chemical analysis will yield the bulk composition of a mixture, but it does not reveal the identity and proportions of the component phases. With powder X-ray diffractometer methods, the phases can be identified using the procedure described above and their properties can be determined by comparing the intensities of characteristic lines from each phase, standards are usually necessary.

b. Phase diagrams

Powder diffraction measurements are very useful in the elucidation of phase diagrams both for identifying the compositions of line phases by measuring X-ray patterns for samples at regular intervals of composition and for determining the solubility limits of non-stoichiometric phases.

3.1.1 Crystallite size determination

The crystallite size of the powder can be calculated from the X-ray diffraction peak intensity analysis using the Scherrer formula [3]:

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

--- (1)

where \( D \) is crystallite size in nm, \( \lambda \) is the radiation wavelength (for CuK\( \alpha \) radiation, \( \lambda = 1.5418 \) Å), \( \theta \) is the diffraction peak angle and \( \beta \) is the broadening of the line ("half width") measured at half its maximum intensity (in radians); and in case of sufficient instrumental broadening,

\[
\beta = (\beta_s^2 - \beta_{std}^2)^{1/2}
\]  

--- (2)

Where \( \beta_s \) and \( \beta_{std} \) are half-widths of the sample and standard specimens (at almost same Bragg angle position) respectively.

3.1.2 Theoretical density (X-ray Density) calculation

Theoretical or X-ray density has been calculated (in gcm\(^{-3}\)) using the lattice parameters with the formula [4]:

\[
D_{th} = \frac{M}{z \cdot N \times V}
\]  

--- (3)

Where \( M \) (in atomic-weight units) is the mass of atomic ensemble constituting one unit of the chemical formula, \( z \) is the number of such chemical units in one unit cell of the crystal, \( N \) is the Avagadro’s number and \( V \) (in Å\(^3\)) is the volume of the crystalline unit cell as determined by X-ray diffraction.
3.2 Thermal analysis

The term thermal analysis refers to a group of techniques in which some physical or chemical property of a system is measured as a function of temperature. All materials, as they experience changes in temperature, undergo changes in their physical and/or chemical properties. They changes can be detected by suitable transducers which convert the changes into electrical signals which are collected and analysed to give ‘thermograms’ showing the property change as a function of temperature. Thermal analysis includes thermogravimetry analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), dilatometry etc. The principles of various techniques have been discussed in the literature[5]. The TG and DTA are briefly outlined here. The TG and DTA curves of materials were obtained in air using PL Thermal Sciences Model STA 1500 Thermal Analysis System. The photograph of automated thermal analysis system used in this study is shown in Fig. 3.4.

3.2.1 Thermogravimetry analysis (TGA)

Thermogravimetry analysis is a technique for measuring the change in weight of a substance as a function of temperature or time. The results usually appear as a continuous chart record; a schematic, typical, single step decomposition reaction is shown in Fig. 3.5. The sample, usually a few milligrams in weight, is heated at a constant rate, typically in the range 1 to 20 K.min^{-1}, and has a constant weight W_i, until it begins to decompose at temperature T_i. Under conditions of dynamic heating, decomposition usually takes place over a range of temperatures, T_i to T_f, and a second constant weight plateau is then observed above T_f, which corresponds to the weight of the residue W_f. The weights W_f, W_i and the difference in weight ΔW are fundamental properties of the sample and can be used for quantitative calculations of compositional changes etc. By contrast, the temperatures T_i and T_f depend on variables such as heating rate, the nature of the sample (e.g. its particle size) and atmosphere above sample.

3.2.2 Differential thermal analysis (DTA)

Differential thermal analysis is a technique in which the temperature of a sample is compared with that of an inert reference material during a programmed change of temperature. The temperature of sample and reference should be the same until some thermal event, such as melting, decomposition or change in crystal structure, occurs in the sample, in which case the sample temperature either lags
Fig. 3.4 - The photograph of the automated thermal analysis system
(PL Thermal Sciences Model STA 1500)
Fig. 3.5 – Schematic thermogram for a single step decomposition reaction

Fig. 3.6 – The DTA method. Graph (b) results from the set-up shown in (a) and graph (d), a typical DTA trace, results from the arrangement shown in (c)
small enthalpy changes may be detected. Fig. 3.6(d) is clearly, therefore, a much more sensitive and accurate way of presenting data than Fig. 3.6 (d) and is the normal method for presenting DTA results.

The shape and size of the peaks in DTA curve can give a lot of information about the nature of the test sample. Thus endothermic peaks often signify changes in crystallinity or fusion processes whereas broad endotherms arise from dehydration reactions. Physical changes usually result in endothermic peaks whilst chemical reaction particularly those of an oxidative nature are predominantly exothermic [6].

3.3 Fourier transform infrared (FTIR) spectroscopy

Infrared (IR) spectroscopy is useful in the elucidation and identification of molecular structure and in applications of quantitative analyses. IR radiation is usually defined as that electromagnetic radiation whose frequency is between ~ 12800 and 10 cm\(^{-1}\) (0.78 and 1000 μm). Within this region of the electromagnetic spectrum, chemical compounds absorb IR radiation provided there is a dipole moment change during a normal molecular vibration, molecular rotation, molecular rotation-vibration or a lattice mode, or from combination, difference and overtones of normal molecular vibrations. IR spectroscopy is unique in that spectra can be recorded for materials in any physical state(solid, liquid, vapour) and in solution over a wide temperature range. Each material exhibits its own unique IR spectrum under a specified set of conditions.

There are three general types of commercial IR instrumentation: dispersive, filter and Fourier transform (FT) spectrometers. The principles of various spectrometers have been discussed in the literature[7-8]. The principle of operation of Fourier transform infrared spectroscopy is briefly illustrated here. The materials are characterized in this work with Perkin Elmer 500 FTIR Spectrometer and the photograph of this instrument is shown in Fig. 3.7.

Frequencies and intensities of the IR bands exhibited by a chemical compound uniquely characterize the material, and its IR spectrum can be used to identify the particular substance in an unknown sample. Different classes of chemical compounds contain chemical groups which absorb IR radiation at identical frequency(ies) and have the same band intensity(ies). These bands are termed 'group frequencies'. Group frequencies are predictable and allow the analyst to identify molecular structures through functional group identification. Modern instruments allow spectra to be recorded for nanogram samples. No other technique allows examination and
Fig. 3.7 – Photograph of the Perkin Elmer 500 FTIR spectrometer
identification of materials under such a wide variety of physical conditions. With the recent development of Fourier transform infrared spectroscopy, it is now possible to rapidly record IR spectra of even coloured substances and also short living compounds. The Block Diagram, Fourier transform and spectrum formation are represented in Fig. 3.8, Fig. 3.9 and Fig. 3.10.

a. Principle

Fourier transform IR spectrometer uses Michelson interferometer to produce an interferogram. The interferogram is related to the IR spectrum by a mathematical operation known as Fourier Transformation. A computer algorithm that was developed to do the operation very fast in the FFT (Fast Fourier Transform) program. FT instruments takes hardly 0.2 to 0.3 sec to get a spectrum. The schematic of Fourier transform spectrometer is shown in Fig. 3.11.

b. Instrument design

Energy from a source (heated element or glower) falls on beam splitter which reflects 50% and transmits 50%. In one path the beam is reflected by a fixed mirror and reaches the detector. In the other leg of the interferometer, the beam is reflected by a movable mirror that can translate back and forth. But that is always maintained parallel to itself (i.e. without tilt or wobble). The beam from movable mirror is also returned to the beam splitter and partially transmitted to the detector. Energy that reaches the detector is sum of these two beams.

If the two mirrors are equidistant from the beam splitter then the two beams will have traveled equal distances. When the second mirror is moved the optical path lengths become unequal. The path difference is known as optical path difference (OPD). The phase difference and change in intensity with respect to the mirror displacement is shown in Table 3.1.

<table>
<thead>
<tr>
<th>Mirror displacement</th>
<th>Phase difference</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>Zero</td>
<td>Maximum</td>
</tr>
<tr>
<td>Quarter of wavelength</td>
<td>180 deg</td>
<td>Minimum</td>
</tr>
<tr>
<td>Another quarter of wavelength (total half wavelength)</td>
<td>360 deg</td>
<td>Maximum</td>
</tr>
</tbody>
</table>
Fig. 3.8 – The block diagram

Fig. 3.9 – Fourier transform

Fig. 3.10 – Spectrum formation
Fig. 3.11 – The schematic of Fourier transform spectrometer
c. Spectrum analysis

An interferogram is intensity vs. time graph that is measured physically. However spectroscopists are generally interested in intensity vs. wave number spectra which can be obtained from interferogram through Fourier transformation.

A single translation of movable mirror is adequate to produce an interferogram that can be transformed into a spectrum. Better S/N ratios can be obtained by averaging a number of scans. Noise is reduced in proportion to the square root of the number of scans averaged. Reducing mirror velocity also improves S/N ratio.

d. Different designs

Various models are available depending on the wave number range such as:

1. 5000/4000 – 600 cm\(^{-1}\) ----- mid IR only
2. 5000/4000 – 400 cm\(^{-1}\) ----- extending to far IR
3. 5000/4000 – 200 cm\(^{-1}\) ----- extending still further
4. 14000 – 10 cm\(^{-1}\) ----- near IR, mid IR and far IR

Different models will have suitable detectors, beam splitters and window materials as detailed below.

e. Detectors

*Deuterated Tri Glycine Sulphate (DTGS):*

Thermocouples commonly used in dispersive instruments cannot be used in FTIR because its response time is too slow for the rapid scan times used in the interferometer. Hence pyroelectric detectors (DTGS) are used in FT instrument

*Mercury Cadmium Telluride (MCT):*

For very low signals encountered in infrared microscope and FTIR-Gas chromatography, MCT detector increases S/N ratio by an order of magnitude.

f. Beam splitters

Potassium Bromide (KBr) ----- Above 400 cm\(^{-1}\)
Cesium Iodide (CsI) ----- Upto 180 cm\(^{-1}\)
Mylar films ----- Upto mm region

g. Window

Cesium Iodide (CsI) is the most common window

h. Interferometer

*Air Bearing Drive:*

Moving parts ride on a thin cushion of dry gas

*Pivoting Base Plate:*
Rotation of pair of parallel mirrors rigidly mounted on a pivoting base plate

Transept Design:
Abandons the moving mirror entirely and changes pathlength by driving a wedge of refractive material (KBr/CsI) into one leg of optical path.

3.3.1 FTIR applications

FT-IR spectrometer is preferable when we are energy limited and when we need increased signal to noise ratio. With the availability of FTIR, many analyses that we used to avoid have become routine. New group of accessories are available to take advantage of FT-IR capabilities.

Spectra of aqueous solutions, micrometer sized particulates and low transmission samples are now run both rapidly and routinely. The techniques of internal reflection, diffuse reflectance, photoacoustic detection, infrared emission, infrared microscopy and GC-IR are described below.

a. Aqueous solutions

Infrared spectroscopists were avoiding aqueous solutions because of very strong absorption bands of liquid water at about 3400 cm\(^{-1}\) (OH Stretch) and 1640 cm\(^{-1}\) (OH bend). Further, there is total absorption below 800 cm\(^{-1}\). The extremely high signal-to-noise ratios obtained so readily by the FTIR technique make spectral substraction and subsequent ordinate expansion of the difference spectrum quite feasible even over the region of 1640 cm\(^{-1}\).

b. Internal reflection

To work effectively over the entire 3000-800 cm\(^{-1}\) window, we must operate with a cell thickness that transmits reasonable energy across the 1640 cm\(^{-1}\) water band. The solution to this problem is the use of internal reflection or attenuated total reflection or multiple internal reflection attachment. In this technique, the sample beam of the spectrometer is directed into one end of a long, thin crystal of high refractive index. KRS-5, germanium and zinc selenide (Infran-4) are the commonly used crystals. Sample is now placed in close optical contact with the exterior surface of the crystal. At frequencies where the sample has no infrared absorption, the beam passes through the accessory undiminished. But at those bands, where there is interaction at each reflection along the crystal-sample interface, the intensity of the internally reflected beam is attenuated.

Another very important characteristic of internal reflection spectroscopy is that only the surface layer of the sample contacting the crystal participates in this
process. Penetration depths into the sample vary with wavelength, angle of incidence and refractive index, but normally it is about 8 to 10 μm. The cell has been designed primarily for use in FTIR spectrometers where good-quality spectra can be routinely obtained even with low energy throughputs.

c. Samples with low transmission

Even when overall transmission is only a fraction of a percent as in the case of engine oil FT-IR techniques can often produce usable spectra. There are two instrumental techniques to improve S/N ratio (SNR). Spectral averaging will reduce noise in proportion to the square root of the number of scans averaged. Reducing the velocity of the moving mirror will also enhance SNR, but now in direct proportion to the reduction in velocity. Improvement in SNR can also be achieved by switching from the normal Triglycine Sulphate (TGS) room temperature detector to a liquid nitrogen-cooled Mercury Cadmium Telluride (MCT).

d. Applications with special accessories

I. Diffuse Reflectance (DRIFT):

Diffuse reflectance measurements are difficult in infrared because the amount of energy that is reflected is so small. While diffuse reflectance can be done with dispersive instruments, the advantages of FTIR spectroscopy makes its use preferable as it gives spectrum with good band intensities.

*Advantages:*
1. The ease of sample preparation;
2. Powdered substances can be run as received;
3. Polymeric changes that may be induced in the pressing of KBr pellets are avoided;
4. Samples give better spectra with less effort when run by diffuse reflectance.

II. Photoacoustic Detector:

It is a good detector accessory for FTIR spectroscopy. The infrared beam from the interferometer is focused on to the sample, heating its surface and causing it to expand. The gas layer above the sample is also heated and expands and all these occur with a modulation frequency corresponding to the product of interferometer’s OPD velocity multiplied by wavenumber. A very sensitive microphone in the gas chamber is used to detect the acoustic signal.

*Advantages:*
1. Simple size and shape are not critical;
2. Sample may be powder, odd-shaped chunks or savings, tablets, fibers, foams and single crystals;

3. Sample preparation is greatly simplified as grinding and dilution are not required

**Infrared Emission:**

The ability of FTIR spectrometer to detect very weak signals makes it possible to study infrared emission, even when the emitting sample is at relatively low temperature.

**Infrared Microscope:**

It is a microsampling accessory. With the higher S/N ratios available in FT instruments one could obtain FT spectra without beam condensers that were as good as those run on dispersive instruments using beam condensers.

It is an energy-efficient accessory and needs the signal to noise advantage of FTIR spectroscopy for viability

**Typical Examples:**

1. Single fibers;
2. Corrosion specks;
3. Occlusions in polymers;
4. Laminates;
5. Paint chips;
6. Minor impurities imbedded in bulk samples

**GC/FT-IR:**

A final example of an application uniquely suited to the capabilities of FTIR spectroscopy is the identification of gas chromatography fractions as they elute from the column, that is, on the fly.

### 3.4 Particle size analysis

The particle size measurements are carried out using Horiba Laser Scattering Particle Size Analyzer (LA-910) (Fig.3.12(a)) using triple distilled water as medium. The system is configured in Fig. 3.12(b). The sample liquid is circulated by the circulation pump while it is dispersed and stirred in the ultrasonic chamber. The computer screen is used for displaying and setting the conditions for both measurement and data display[9].

There are two light sources: a long-life 632.8-nm He-Ne laser expanded by a beam expander and a blue and red monochromed tungsten lamp. The diameter of the
Fig. 3.12 (a) – Photograph of the Horiba Laser Scattering Particle Size Analyser (Model LA-910)
Fig. 3.12 (b) - Configuration of LA-910 system

Fig. 3.13 - Measuring the side and rear scattered light of blue-coloured light
laser beam emitted from the laser and tungsten lamp light source and is radiated on
the particles suspended in the liquid.

After the laser beam has been dispersed and scattered by the particles in the
flow cell, it passes through the condenser lens and is focused on the photo-cell
detector, which contains 18 light-detection elements. The intensity of this scattered
light is converted into electrical signals, which are then used to calculate the size
distribution of the particles.

After the light has been dispersed and scattered by the particles in the flow all,
it is detected by a silicone photo-diode.

3.4.1 Specifications

Principles of measurement -- Based on Mie scattering theory
Range of particle size displayed -- 0.02 to 1000 μm
Required for measurement -- 10 mg to 1 g per measurement, with 215 to
315 ml of dispersant fluid when using the
flow cell
Optical system -- Light source:
632.8 nm He-Ne laser, 1 mW
Tungsten halogen lamp 50 W
Photo-cell detector:
18-division, ring shaped silicone photo-diode
Silicone photo-diode X 6
Proper operation temperature -- 283 to 308 K

3.4.2. Principles of the optical system used in the Model LA-910

The optical system in an ordinary laser-diffraction type analyzer condenses the
front scattering from a laser beam with a condenser lens and forms an image on the
ring-shaped detector located at the focal distance.

Using only this method, it is difficult to measure the range of small particle
sizes, in particular, particles under 0.1 μm. Very small particles cannot be measured
merely by means of the forward scattering using the wavelength of He-Ne laser beam,
i.e., 632.8 nm. To measure such particles, it is necessary to have either information
from the side and back scattering or that from the polarization scattering intensity.
Therefore, as shown in Fig.3.13, the new optical system in the Model LA-910 used
three separate detectors, one each for the side and rear scattering, and third detector
for the front scattering. As the light source for detecting scattered light on the side and
the rear, the Model LA-910 also uses a tungsten lamp. This means: (1) the small angle forward scattered light is conventionally given by the He-Ne laser and detected by the ring detector and (2) the large angle and rear scattered light is given by the tungsten lamp and detected by the photodiode.

Particles of various sizes exist in an actual sample solution, and their scattering light differs according to their size. Equation 4 shows the relationship between the intensity distribution of the scattering light and the particle size distribution.

\[
g(\theta) = \int_{0}^{\alpha} K(\theta, D) F(d) dD
\]

where
\(- g(\theta) : \) The intensity distribution of the scattering light
\(- K(\theta, D) : \) Response coefficient of scattering light
\(- F(d) : \) Particle size distribution coefficient
\(- D : \) Particle diameter
\(- \theta : \) Scattering angle

In reality, measurement is performed by \( n \) number of detectors. As the Mie scattering theory is used in combination for the response function, the equation corresponding to equation 4 becomes equation 5.

\[
g(N) = \sum_{i=1}^{n} K(N, D_i) F(D_i) \Delta D
\]

where
\(- g(N) : \) Output of \( N \)-th detector
\(- K(N, D_i) : \) Response coefficient of \( N \)-th detector
\(- F(D_i) : \) Particle size distribution
\(- D_i : \) \( i \)-th representative radius
\(- \Delta D : \) Particle size segment number

The particle size distribution \( f(D_i) \) is calculated from the relationship between the output of the detector (expressed by equation 5) and the response function of the detector. \( f(D_i) \) is calculated on the basis of volume.
The particle size distribution by area length and number basis are calculated by equation 6 to 8.

\[
\frac{f(D_i)}{D_i}
\]

Distribution by area basis = \[ \sum_{i=1}^{m} \left\{ \frac{f(D_i)}{D_i} \right\} \] \[ \frac{f(D_i)}{D_i^2} \] Distribution by length basis = \[ \sum_{i=1}^{m} \left\{ \frac{f(D_i)}{D_i^2} \right\} \] \[ \frac{f(D_i)}{D_i^3} \] Distribution by number basis = \[ \sum_{i=1}^{m} \left\{ \frac{f(D_i)}{D_i^3} \right\} \]

3.5 BET surface area measurements

The surface area of all the synthesized oxides are measured by Quantasorb BET surface analyzer. The basic flow diagram is shown in Fig. 3.14. The features of the method of analysis is outlined below in brief [10].

3.5.1 Pretreatment procedure

As the method is based on gas absorption, the sample should be completely free of adsorbed gases prior to analysis. For this, the sample is taken in a sample cell and heated in a stream of Hydrogen. On heating, the sample will desorb all the gases it had adsorbed. While the gas entering the sample cell is pure Hydrogen, the gas leaving the sample cell will be hydrogen contaminated by the gases desorbed by the sample. A special kind of detector in the instrument compares the thermal conductivity of the gas entering the sample cell with the thermal conductivity of the gases leaving the sample cell. When all the absorbed gases in the sample have been removed/desorbed, the thermal conductivity of the entering gas and leaving gas will be same. This indicates that the sample is ready for analysis.

3.5.2 Analysis

Hydrogen gas supply to the sample cell is cut off and a mixture of Nitrogen and Hydrogen gas of known composition is passed through the sample cell. The sample cell is immersed in a Dewer flask containing Liquid Nitrogen. The sample will
Fig. 3.14 – The basic flow diagram of Quantasorb BET surface Area Analyser
absorb Nitrogen. So the leaving gas will have less Nitrogen and proportion of Nitrogen to Hydrogen will be different. Here again a special kind of detector in the instrument compares the thermal conductivity of the gas entering the sample cell with the thermal conductivity of the gases leaving the sample cell. When the thermal conductivity of the entering gas and leaving gas is same, absorption of Nitrogen by the sample is over.

At this stage, the sample cell is removed from the Dewer flask, and kept in a beaker containing water at room temperature. As the temperature has increased the sample will desorb all the Nitrogen it has absorbed. So the leaving gas will have more Nitrogen and the proportion of Nitrogen to Hydrogen will be different. Here also a special kind of detector in the instrument compares the thermal conductivity of the gases leaving the sample cell. When the thermal conductivity of the entering gas and leaving gas is same, desorption of Nitrogen gas in the sample is over. The difference in thermal conductivity is converted into Gaussian shape signals by means of a built-in electronic circuit. The total area under the signal-time is proportional to the quantity of gas absorbed. This area is automatically digitally integrated. When absorption is complete, the integrator stops counting.

The integrator is calibrated by mixing a known volume of pure Nitrogen in the gas stream and recording the counts corresponding to the change in thermal conductivity. The volume of nitrogen absorbed by the sample is found by dividing the counts obtained for the sample by calibration counts. Using ideal gas law volume is converted to number of molecules of Nitrogen absorbed. Brauner, Emmet and Teller’s (BET) theory proposed unimolecular absorption layer formation at liquid Nitrogen temperature (183 K). Knowing the area of cross section of a single Nitrogen molecule surface area of the sample taken in calculated. Sample is weighed now and specific surface area is calculated.

### 3.5.3 Calculation

\[
\text{Volume of Nitrogen absorbed} = \frac{A \times V_{\text{calibration}}}{A_{\text{calibration}}}
\]

\[
\text{Moles of Nitrogen absorbed} = \frac{P \times V_{\text{nitrogen}}}{RT}
\]

\[
\text{Number of molecules of Nitrogen absorbed} = \left(\frac{P \times V_{\text{nitrogen}}}{RT}\right) \times N
\]

\[
\text{Total surface area (S)} = \left(\frac{P \times V_{\text{nitrogen}}}{RT}\right) \times N \times \text{Area of the cross section of single molecule}
\]

\[
\text{Specific surface area (in m}^2/\text{g)} = \frac{S}{\text{wt of the sample in grams}}
\]

Where
A : Sample counts
A_{calibration} : Calibration counts
V_{calibration} : Calibration volume
P : Atmospheric pressure
V_{nitrogen} : Volume of Nitrogen absorbed
R : Universal gas constant
T : Temperature of measurement
N : Avagadro's number

Area of cross section of single molecule of Nitrogen = \(16.2 \times 10^{-20} \text{ m}^2\)

3.6 Density measurements [11-12]

3.6.1 Bulk density

The as-formed foamy oxide materials were hand crushed in a agate pestle and mortar and the powder was filled into a 10 ml measuring jar. The bulk density of the powder was calculated using the following formula.

Weight of empty measuring jar \(= W_1 \text{ g}\)

Weight of measuring jar with bulk powder \(= W_2 \text{ g}\)

Volume occupied by bulk powder \(= V \text{ cm}^3\)

Bulk density \(= \frac{W_2 - W_1}{V} \text{ g.cm}^{-3}\) \(---(9)\)

3.6.2 Tap density

The as-prepared voluminous oxide samples were hand crushed in agate mortar using a pestle and a known amount of this powder was filled into a measuring jar of 10 ml capacity. The cylinder was tapped until the powder level remained unchanged. The volume occupied by the powder was noted. The tap density of the powder was calculated using the following formula.

Weight of empty measuring jar \(= W_1 \text{ g}\)

Weight of measuring jar with powder \(= W_2 \text{ g}\)

Volume occupied by powder (after tapping) \(= V \text{ cm}^3\)

Tap density \(= \frac{W_2 - W_1}{V} \text{ g.cm}^{-3}\) \(---(10)\)
3.6.3 Absolute density

The absolute density was measured using Archimedes principle with pycnometer and xylene as liquid medium. The pycnometer of volume 25 ml was used. A known quantity of powder was taken in the pycnometer set-up and the bottle is filled with the xylene without any air bubble and after allowing the powder to settle down it is stoppered; the overflowing liquid is wiped out with adsorbent paper and bottle is weighed. The following weights were taken and used in the density calculation:

- Weight of the bottle = \(W_1\) g
- Weight of the bottle + Xylene = \(W_2\) g
- Weight of the bottle + Sample = \(W_3\) g
- Weight of the bottle + Sample + Xylene = \(W_4\) g

\[
\text{Absolute density} = \frac{(W_4 - W_1) \cdot d_{\text{liquid}}}{[(W_3 - W_1) + (W_2 - W_1)] - (W_4 - W_1)} \quad \text{g.cm}^{-3}
\]

Where \(d_{\text{liquid}}\) (density of xylene) = 0.867 g/cc

3.7 Electrical conductivity measurements

3.7.1 Summary of test methods [13]

3.7.1.1 Two probe method

A direct current is passed through ohmic contacts at the ends of a bar specimen and the potential difference is determined between two probes placed along the current direction Fig. 3.15. The resistivity is calculated from the current and potential values and factors appropriate to the geometry.

3.7.1.2 Four probe method

An in-line four point probe is placed on a flat surface of a solid specimen which can be approximated as semi-infinite. A direct current is passed through the specimen between the outer probes and the resulting potential difference is measured between the inner probes (Fig. 3.15). The resistivity is calculated from the current and potential values and factors appropriate to the geometry.

From Two probe method,

\[
\text{Resistivity, } \rho = \frac{V}{I} \frac{WH}{L} \quad \text{(ohm.cm)} \quad --- (12)
\]
FOUR-PROBE METHOD

\[ \rho = \frac{V}{I} \frac{2\pi S}{2} \]

TWO-PROBE METHOD

\[ \rho = \frac{V}{I} \frac{WH}{L} \]

Where:
- \( \rho \) = Resistivity
- \( V \) = Potential Difference
- \( I \) = Current
- \( S \) = Probe Spacing
- \( W \) = Width
- \( H \) = Height
- \( L \) = Length

Fig. 3.15 – Specimen arrangement and probe arrangement for two-probe and four-probe measurements on a rectangular bar
From Four probe method,

\[
\text{Resistivity, } \rho = \frac{V}{2\pi S} \text{ (ohm.cm)}
\]  

--- (13)

Where

V : Potential difference 
I : Current 
S : Probe Spacing 
W : Width 
H : Height 
L : Length 

From the above Resistivity (\(\rho\)) measurements, the conductivity is calculated using the following formula,

\[
\text{Conductivity, } \sigma = \frac{1}{\rho} \text{ (ohm}^{-1}\text{cm}^{-1}) = \frac{S}{\text{cm}^{-1}}
\]  

--- (14)

3.7.2 High temperature electrical conductivity measurements by four probe d.c. technique carried out in the present work

The schematic of the experimental set-up for the present work is shown in Fig. 3.16. The electronic equipment consists of a constant current source, digital voltmeters, IBM compatible desk-top computer and a programmable temperature controller. The computer software has been written to control all the main instrument functions and for data acquisition.

The whole assembly was mounted horizontally in an electric-tube furnace made of quartz attached with computer programmable temperature controller. The measurements have been carried out on the new cathode materials. Sintered pellets (Breath = ~0.5cm, Diameter = ~0.5cm and Length = ~2.25cm) were used in this study. Four 0.01 inch diameter silver wires were connected to different points on the sample circumference by means of silver paste as in Fig.3.16. The sample was cured at 1073 K overnight before the measurement. Two of the silver wires (outer) were connected to the galvanostat, which was used to supply constant current to the sample. The other two silver wires (inner) were connected to the data acquisition system, which was used to record the corresponding voltage change. The temperature of the sample was controlled by the electric furnace. Two type R thermocouples in
Fig. 3.16 – Experimental set up for the high temperature electrical conductivity measurements by four probe d.c technique

Fig. 3.17 – The schematic of the rectangular specimen used for electrical Conductivity measurements
separate alumina sheaths were used for measuring the temperature. The thermocouple for measuring the temperature was either in direct contact with, or within 0.5 mm of, the specimen mid-way down its length. The furnace constant temperature zone was 5 cm long (within in ± 1 K). The dimensions indicated for the specimens are commonly used in our work but the equipment is not limited to accepting specimens with these dimensions. All the experiments were carried out in air. The experiments were made from room temperature to 1173 K. The heating and cooling rate was usually 50 – 100 Kh⁻¹. The current passed through the current probes varied between 100nA at low temperatures to 2-5 mA at high temperatures depending on the specimen resistance. The current was kept low to ensure minimal polarization of the current probes and to avoid heating of the specimen as a result of current passage (I²R heating). To minimize the effect of thermal emf between the potential probes, voltages were measured for two different levels of current, and the resistance was determined from the slope of the current-potential plot.

On applying a constant current, i, through the outer contacts, a voltage drop, ΔU, across the two inner contacts was recorded. For every temperature, four (current, voltage)-points were recorded. These four applied currents were chosen as +i, +2i, i, and -2i, where i is of the order of 1 mA cm⁻² so as not to cause any Joule heating effect which would influence the measurement. For the geometry given in Fig.3.17, the conductivity, σ, of the sample at each temperature was calculated through the formula [14-16]

$$\sigma = \frac{1}{\rho} = \left(\frac{I}{\Delta U}\right) \times (bh/l)$$  --- (15)

where ρ is the resistivity, b the breadth, h the height and l the length.

The Arrhenius parameters have been calculated from the following expressions:

$$\sigma T = A \exp \left(-\frac{E_a}{RT}\right)$$  --- (16)

$$\ln (\sigma T) = \frac{E_a}{(RT)} + \ln A$$  --- (17)

where A is the pre-exponential factor, R is the gas constant, and Eₐ is the activation energy of migration. The slope of the plot of ln (σT) versus 1/T gives the activation energy of a sample for the electrical conduction in air.
3.7.3 High temperature electrical conductivity measurements by electrochemical impedance spectroscopy carried out in the present work

3.7.3.1 Definition of complex impedance

The concept of electrical resistance is the ability of a circuit element to resist the flow of electrical current. Ohm’s law (Equation – 18) defines in terms of the ratio between voltage \( E \) and current \( I \).

\[
R = \frac{E}{I} \quad \text{--- (18)}
\]

While this is a well known relationship, it’s use is limited to one circuit – the ideal resistor. An ideal resistor has several simplifying properties:

1. It follows Ohm’s law at all current and voltage levels
2. It’s resistance value is independent of frequency
3. AC current and voltage signals though a resistor are in phase with each other.

The real world contains circuit elements that exhibit much more complex behaviour. These elements force us to abandon the simple concept of resistance. In its place we use impedance, which is a more general circuit parameter. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. Unlike resistance, impedance is not limited by the simplifying properties listed above.

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell.

3.7.3.2 Nyquist plot

Fig. 3.18 has been annotated to show that low frequency data are on the right side of the plot and higher frequencies are on the left. This is true for electrochemical impedance spectroscopy (EIS) data where impedance usually falls as frequency rises (this is not true of all circuits).

Nyquist plots have one major shortcoming. When we look at any data point on the plot, we cannot tell what frequency was applied to record that point.

The Nyquist plot in Fig.3.18 results from the electrical circuit of Fig.3.19. The semicircle is characteristic of a single ‘time constant’. Electrochemical impedance plots often contain several time constants. Often only a portion of one or more of their semicircles is seen.
Fig. 3.18 - Nyquist plot with impedance vector

Fig. 3.19 - Simple equivalent circuit with one time constant
3.7.3.3 Impedance spectroscopy measurements

Two-probe impedance spectroscopy was used to measure the AC conductivity of sintered electrolyte pellets. 'Ag' paste (Dupont, Japan) was applied to each side of the circular electrolyte specimens of area \( \sim 0.785 \text{ cm}^2 \) by using a wire brush and fired at 973 K for 1 h. Pt foils were used as electrodes for impedance measurements as shown in Fig. 3.20. The contact resistance between the Pt and the surface of samples was found to be negligible. The impedance spectra for the electrolyte samples was recorded in between the temperature 773 - 1073 K. The frequency was swept typically from 1 - 100 kHz range using Frequency response analyzer, (Solatron Schlumberger) FRA 1255 attached with a Electrochemical Interface, 1286 (Solatron Schlumberger) to give a characteristic arc response in a Nyquist plot. This arc corresponds to the electrode reduction impedance. The experimental set up is sketched in Fig.3.21.

At the high frequencies, the arc intersects with the real axis. This value corresponds to the electrolyte resistance, \( R_{el} \). For a given geometry, area \( A \) in cm\(^2\), measured thickness of the sample, \( d \) in cm, the conductivity at a given temperature was derived as,

\[
\text{Conductivity, } \sigma = \frac{1}{R_{el}} \times \frac{A}{d} \text{ S.cm}^{-1} \quad \text{--- (19)}
\]

3.8 Scanning electron microscopic studies

Scanning electron microscopy is used primarily for the study of surface topography of solid material. The surface morphology of the sintered components were observed with a S-3000 H, Hitachi Scanning Electron Microscope (SEM) at an acceleration voltage of 20 kV and at the magnification factor ranging between 1000 and 10000. The photograph of the SEM instrument used for this work is shown in Fig. 3.22.

Scanning electron microscope permits a depth of field for greater than optical or transmission electron microscopy. The resolution of the scanning electron microscope is about 3 nm (30 Å), approximately two orders of magnitude greater than the optical microscope and one order of magnitude less than the transmission electron microscope. Thus, the SEM bridges the gap between the other two techniques [17].

3.8.1 Principle

An electron beam passing through an evacuated column is focussed by electromagnetic lenses onto the specimen surface. The beam is then projected over the
Fig. 3.20 – Sample holder for impedance measurements at high temperature

EI 1286 – Solatron Electrochemical Interface
FRA 1255 - Solatron Frequency Response Analyser
HP – Hewlett Packard Computer
GPIB – Interface Bus
RE₁, RE₂, CE, WE : Reference, Counter and Working electrode functions

Fig. 3.21 – Experimental set-up for the electrochemical impedance spectroscopy
specimen in synchronism with the beam of a cathode ray tube (CRT) display screen. Inelastically scattered secondary electrons are emitted from the sample surface and collected by a scintillator. In this way the secondary electron emission from the sample is used to form an image on the CRT display screen.

Differences in secondary emission result from changes in surface topography. If (elastically) backscattered electrons are collected to form the image, contrast results from compositional differences. Cameras are provided to record the images on the display screen.

3.8.2 Interaction between electron beam and specimen

Since an electron is a charged particle, it has strong interaction with the specimen (due to coulomb interaction). When an electron beam impinges on specimen, it is scattered by atomic layers near the surface of the specimen. As a result, the direction of electron motion changes and its energy is partially lost.

Once an incident electron (primary electron) enters a substance, its direction of motion is influenced by various obstructions (multiple scattering), and follows a complicated trajectory which is far from a straight line. Also when electrons with a same energy are incident on the specimen surface, a portion of electrons is reflected in the opposite directions (back scattered) and the remainder is absorbed by the specimen (exciting X-rays or other quanta in process). If the specimen is sufficiently thin, electron can pass all the way through the specimen (transmitted electrons, scattered or non-scattered).

The Scanning Electron Microscope permits not only observation of very fine details (high resolution) but also good focus over a wide range of specimen surfaces (large depth of field). If an element of the specimen has a low atomic number, the incident electrons will show a tear-drop shaped diffusion, while if the element has a high atomic number, the incident electrons will show a hemispheric diffusion. Higher accelerating voltages expand the diffusion area much deeper. In the course of diffusion, the incident electrons gradually lose their energy until absorbed by the specimen (detected as absorbed current). In this process, low-energy secondary electrons are reflected outside the specimen, with loosing much of their energy. In addition, the Auger effect causes Auger elements very near the specimen surface. When incident electrons collide with constituent atoms of the specimen, most of the electron energy is converted to heat, but a portion of it is consumed to produce X-rays, visible and infrared cathode luminescence together with secondary and Auger
electrons. Quanta (secondary electrons, backscattered electrons, X-rays and so on, carry information which describes the nature of the specimen (its atomic number, elemental distribution, topography, surface potential distribution, magnetic domain, chemical and crystallographic characteristics, etc.). This information is converted into a video signal and displayed on a CRT as a scanning image. The Table 3.2 below lists the relation between the types of scanning image and obtainable information.

<table>
<thead>
<tr>
<th>Types of scanning image</th>
<th>Major information</th>
<th>Detectors and instruments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Secondary electron image</td>
<td>1. Surface structure, potential distribution, magnetic domain</td>
<td>1. Scintillator, PMT detector</td>
</tr>
<tr>
<td>2. Backscattered electron image</td>
<td>2. Composition, topography, magnetic domain, crystalline state</td>
<td>2. Paired semiconductor detector</td>
</tr>
<tr>
<td>5. Auger electron image</td>
<td>5. Elemental distribution of surface</td>
<td>5. Auger scanning electron microscope</td>
</tr>
<tr>
<td>6. Cathodoluminescence image</td>
<td>6. Visible or infrared luminescence</td>
<td>6. PMT detector</td>
</tr>
<tr>
<td>7. X-ray image</td>
<td>7. Elemental distribution</td>
<td>7. X-ray spectrometer</td>
</tr>
</tbody>
</table>

3.8.3 Limitations of scanning electron microscopy

Samples to be studied must be solids that are not electron-beam-reactive and contain no highly volatile or corrosive components. Special specimen stages can handle specimens up to about 20 cm in diameter although conventional stages can accommodate samples only a few cm in diameter. Resolution limitations of the technique extend down to about 2–3 nm.

3.9 Percentage porosity measurements

The percentage porosity measurements are made for all the components with respect to their sintering temperature using liquid absorption technique with dioxan as medium[18]. This method involves inhibition of a non-wetting and non-reactive liquid by the sample in vacuum. The initially weighed \(W_1\) sample is immersed in dioxan with a closed flask. Dioxan is filled in the pores of the sample by evacuating
the entrapped gases with the vacuum pump. The sample is taken away and weighed \((W_2)\). The percentage porosity of the samples is calculated using the following formula.

\[
\text{Initial weight of the sample (dry)} = W_1 \text{ g} \\
\text{Final weight of the sample (wet)} = W_2 \text{ g} \\
\% \text{ Porosity} = \frac{W_2 - W_1}{\text{Density of dioxan} \times \text{Sample volume}} \times 100 \\
\]

--- (20)

Where, the density of dioxan is \(1.03 \text{ g.cm}^{-3}\)
References


10) *Instruction Manual for Quantasorb Surface Area Analyzer*, Quantachrome Corporation, NY, USA


