CHAPTER - 3
CHAPTER - III
Experimental

3.1: An Outline of the present work

Photoelectrochemical (PEC) splitting of water is a possible means of converting solar energy to a directly usable chemical energy, viz., Hydrogen. The effectiveness of a PEC cell in harnessing solar energy depends upon the efficiency with which light is absorbed by the semiconductor electrode, the number of charge carriers photo-generated within the depletion layer (which of course depends on the incident photon flux as well), effective separation of charge carriers and their migration across electrode-electrolyte interface, and the chemical/electrochemical stability of the semiconductor electrode (Nowotny et al 2005). The semiconductor used in the process and its properties, thus, can have a major influence on the overall operational efficiency of the cell. A majority of research efforts, in the past and present, remained focused on developing new/modified materials (semiconductors) for this purpose. However, the success is still eluding the scientists. The main hindrance comes from the lack of complete understanding on the phenomenon; many aspects of which are still shrouded in mystery. One such, so far, poorly understood aspect is the role played by the electrolytes. It is clear from literature survey that different workers have used different electrolytes leading to varied observations.

In this study the efforts have been made to synthesize nanostructured ZnO and Fe – ZnO thin films which were then employed as a semiconductor photoanode in PEC splitting of water. The main thrust of the present study is, however, on exploring the role of electrolyte and electrolyte – variables, viz., concentration, composition, ionic strength, pH, temperature, sensitizers etc. in the process. The study had three different aspects/stages of investigation. In the first stage, nanostructured thin film samples of undoped ZnO and Fe – ZnO were synthesized by sol – gel spin coating. While undoped ZnO samples were prepared at three different sintering temperatures, 400, 500 and 600 °C, in the case of Fe – ZnO samples sintering was done only at 600 °C. In the second stage of study, prepared thin film samples were characterized for physical, structural and optical characteristics by employing standard methods and techniques.
In the last leg of the study, PEC studies were conducted by using the films as a working electrode. A detailed outline of the work done has been presented in Table 3.1.

Table 3.1: An outline of the present work

<table>
<thead>
<tr>
<th>Stage of the work</th>
<th>Parameters investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Preparation of thin film samples:</td>
<td>• Sintering:</td>
</tr>
<tr>
<td></td>
<td>✓ One-stage: 400/500/600 °C</td>
</tr>
<tr>
<td></td>
<td>✓ Two-stage: 250 → 400/500/600 °C</td>
</tr>
<tr>
<td></td>
<td>• Added concentration of Fe in the case of Fe-ZnO samples:</td>
</tr>
<tr>
<td></td>
<td>0.5, 1.0, 3.0, 5.0 and 7.0 % at.</td>
</tr>
<tr>
<td></td>
<td>• Crystal phase analysis; lattice parameters, dislocation</td>
</tr>
<tr>
<td></td>
<td>density and microstrain.</td>
</tr>
<tr>
<td></td>
<td>• Average crystallite size by Scherrer’s calculations.</td>
</tr>
<tr>
<td></td>
<td>• Surface morphology, topography and surface roughness by</td>
</tr>
<tr>
<td></td>
<td>SEM and AFM analysis.</td>
</tr>
<tr>
<td></td>
<td>• Bandgap energy ($E_g$) by optical characterization.</td>
</tr>
<tr>
<td></td>
<td>• Flat band potential ($V_{fb}$) and Charge carrier density</td>
</tr>
<tr>
<td></td>
<td>($N_d$)</td>
</tr>
<tr>
<td></td>
<td>• Current – Voltage characteristics of the cell under</td>
</tr>
<tr>
<td></td>
<td>darkness and illumination.</td>
</tr>
<tr>
<td></td>
<td>• Photocurrent density ($I_{ph}$)</td>
</tr>
<tr>
<td></td>
<td>• Open circuit voltage ($V_{oc}$)</td>
</tr>
<tr>
<td></td>
<td>• Short circuit current ($I_{sc}$)</td>
</tr>
<tr>
<td></td>
<td>• Composition and concentration of electrolyte</td>
</tr>
<tr>
<td></td>
<td>• Ionic Strength</td>
</tr>
<tr>
<td></td>
<td>• pH</td>
</tr>
<tr>
<td></td>
<td>• Presence of hole scavengers</td>
</tr>
<tr>
<td></td>
<td>• Temperature</td>
</tr>
</tbody>
</table>

Table 3.2: Synthesis of semiconductor films

Several deposition techniques are reported in literature for the preparation of metal oxide thin film coatings, many of which have been used to produce pure ZnO films. These include RF sputtering, molecular beam epitaxial growth, metal-organic chemical vapor deposition, pulsed laser deposition, and spray pyrolysis. The limitations with most above techniques are the involvement of high cost equipment, smaller product yield, large time requirement, and the complexity of operation. Compared to above methods, sol–gel process has some distinct advantages as these offer excellent compositional control, homogeneity at the molecular level due to the
mixing of liquid precursors, lower crystallization temperature, ability to tune microstructure via sol-gel chemistry, and large surface area coating resulted. Considering above advantages, in this study the thin films of ZnO and Fe – ZnO were synthesized by sol-gel spin coating.

In most sol-gel processes metal alkoxides are used as raw material. But the preparation of their stable sol is sometimes problematic and time consuming besides the fact that most metal alkoxides are very expensive. Hence, in this study, zinc acetate dihydrate (ZAD; (CH₃COO)₂Zn.2H₂O) was used as precursor for preparing zinc oxide films. Zinc acetate is inexpensive and easy to handle. For the sol-gel synthesis of ZnO thin films, a solution was prepared by dissolving ZAD in isopropanol and appropriate amount of monoethanolamine was added. To synthesize Fe doped ZnO, iron nitrate was used as a source for metallic iron. Calculated quantity (% at., at five different concentrations) of iron nitrate was added in the precursor solution, which was stirred for 2 h at 40°C to get a spinnable colloidal solution. Conducting glass slides (TCO plates, resistivity approximately 10 Ω cm, dimensions: 4 cm × 3 cm, were used as substrate for film deposition. Before use, the substrates were cleaned by soaking for 1-2 minutes under mild stirring in following solvents in the order given: dilute HCl, double distilled water and acetone. Cleaned substrates were dried in oven at 40 °C and were stored in dust and moisture free environment, by placing inside an air-tight container. The films were obtained by spin coating method. Spin coating is the preferred method for obtaining thin and uniform films on flat substrates. A drop of sol was placed on the substrate, which was then rotated at 2500 rpm using a photo-resist spinner. In order to spread the solution uniformly, centrifugal force was applied by continued rotation for 20 s, during which excess solution spun off the edges of the substrate. For each film deposition 5 layers were coated, one over the other. Between successive coatings, samples were placed for 10 min. on hot plate for drying, but no annealing was done at this stage. The films were deposited in approximately 3/4th length of the substrate only. The remaining 1/4th length of the substrates was later utilized to develop electrical contact, when the films were used as electrode in PEC cell. After final deposition, the deposited coating was sintered in air. As per details given in Table 3.2, few samples of undoped ZnO films were subjected to just one stage sintering, which involved sintering at 400/500/600 °C for 1 h. While
Plate 1: Few samples of ZnO films prepared
other samples of undoped ZnO and Fe – ZnO were sintered in two stages. In two stage sintering samples were placed in a furnace at 250°C for 30 min. to remove organic contaminants. Subsequently, these were sintered in air at temperatures 400/500/600°C for 1 h to complete the cycle of crystallization. After sintering, films were allowed to slowly cool for 15-18 h inside the furnace itself.

Table 3.2: Description of thin films samples prepared

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Doping Level (% at.)</th>
<th>Sintering Protocol</th>
<th>Sintering Temperature (°C)</th>
<th>Sample Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>-</td>
<td>One-stage</td>
<td>400</td>
<td>(^{1})Z_{4H}</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>One-stage</td>
<td>500</td>
<td>(^{1})Z_{5H}</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>One-stage</td>
<td>600</td>
<td>(^{1})Z_{6H}</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{4H}</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{5H}</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{6H}</td>
</tr>
<tr>
<td>Fe-ZnO</td>
<td>0.5</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{0.5}</td>
</tr>
<tr>
<td>Fe-ZnO</td>
<td>1.0</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{1.0}</td>
</tr>
<tr>
<td>Fe-ZnO</td>
<td>3.0</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{3.0}</td>
</tr>
<tr>
<td>Fe-ZnO</td>
<td>5.0</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{5.0}</td>
</tr>
<tr>
<td>Fe-ZnO</td>
<td>7.0</td>
<td>Two-stage</td>
<td>250 (Stage 1) → 400 (Stage 2)</td>
<td>(^{2})Z_{7.0}</td>
</tr>
</tbody>
</table>

3.3: Characterization

3.3.1: General physical characteristics

The prepared samples of thin films were characterized for important general physical characteristics, viz, density, electrical resistivity, and film thickness. In PEC response of the semiconductors, resistivity is an important variable that can play decisive role. The \textit{in-situ} resistivity of ZnO thin films was determined by using them as photoelectrode in electrochemical cell. This measurement was based on recording the slope of the linear portion of the current (I)–potential (V) curve (beyond breakpoint potential) under darkness. The gravimetric method, employing a Metler balance
(Metlor AJI 50L) was employed to estimate the approximate density of films coated on substrate. Film thickness values were estimated by UV-Probe 2.21 (Shimadzu, Japan). A close perusal of the I-V curve obtained under darkness and illumination using prepared thin films as electrode revealed photocurrent under anodic reverse bias suggesting n-type nature of the film. Potentiostat (ECDA – 001, Conserv Enterprises) was used to record the I-V curves.

3.3.2: XRD analysis

Analysis of X-ray diffraction data, gives information regarding the solid phase and crystal structure of a material. When a beam of X-ray strikes the sample, it gets scattered in all the directions. Most of the radiations scattered by an atom are cancelled out by the radiations scattered from other atoms. However, X-rays are reinforced rather than annihilated when they strike at certain crystallographic planes at specific angles. This phenomenon is called constructive interference or diffraction (Cullity and Stock, 2001). Wherever a wave meets a barrier with one or more openings that are nearly of the same size as the wavelength of X-ray employed, diffraction takes place. The layers of atoms or ions in crystals are separated by distances of 100-200 pm. This is just the right range to cause diffraction of X-rays. The reason why atoms are able to produce diffraction patterns has much to do with the number of electrons they contain. The electric field of the X-rays interacts with the cloud of electrons around an atom. The diffraction pattern is a result of thousands of such interactions. All large atoms have many electrons and hence they produce the strongest patterns. Small atoms, like hydrogen, may have so few electrons that they have little effect on X-rays (Arora, 2000). Bragg explained the formation of diffraction patterns by his famous equation (3.1), now known as Bragg’s law.

\[
\sin \theta = \frac{\lambda}{2d_{hkl}} \tag{3.1}
\]

Here, \( \theta \) is half the angle between the diffracted beam and the incoming beam, \( \lambda \) the wavelength of the X-rays, and \( d_{hkl} \) the interplanar spacing between the planes that cause constructive interference of the beam (Askland, 1996). The sample films, prepared in this study, are expected to contain many small crystallites and there are always some crystallites/particles which have (hkl) planes oriented in the proper angle to satisfy Bragg’s law (Cullity and Stock, 2001). This will generate a diffracted beam with an angle of \( 2\theta \) with the incident beam. In a diffractometer, a moving X-ray
Plate 2: X-ray diffractometer used in the study
detector records the $2\theta$ angles at which the beam is diffracted, giving a characteristic diffraction pattern. As the wavelength of the X-ray is known, the interplanar spacing and the identity of the planes that cause the diffraction can be determined. Another way of utilizing X-ray diffraction data is to treat the diffraction pattern as a fingerprint. Thus, a sample can be identified by comparing its diffraction pattern with a pre-measured and well-defined diffraction pattern database. In the present work, X-ray diffraction was used as a characterization tool for the sample films. ZnO and Fe-ZnO thin films were subjected to X-ray diffraction analysis by using a Bruker AXS D8 Advance X-ray Diffractometer (Germany), that was equipped with graphite monochromator and CuKα as the radiation source. The angular accuracy was 0.001° and the angular resolution was better than 0.01°.

Using XRD data ($d_{hkl}$ values) and equation (3.2), the lattice parameters ‘$a$’ and ‘$c$’ were also estimated (Caglar et al. 2009).

$$\frac{1}{(d_{hkl})^2} = \frac{4}{3} \{ (h^2 + hk + k^2) / a^2 \} + 1/c^2$$

(3.2)

The average crystallite size in the samples was estimated from broadening of corresponding X-ray diffraction peaks and using Scherrer’s equation (3.3) (Klug and Alexander 1974, Cullity and Stock 2001),

$$B = 0.9 \lambda / t \cos \theta,$$

(3.3)

where, $B$ is FWHM (full width at half maximum) of the broadened diffraction line on the $2\theta$ scale, $t$ average diameter of crystallite, $\lambda$ wavelength of X-ray (for CuKα, $\lambda = 1.542$ Å) and $\theta$ is the half diffraction angle of the centroid. In fact, all X-ray diffraction lines have a measurable width, even when the crystal size exceeds 1000 Å, due to such causes as divergence of the incident beam, size of sample (in Debye cameras) and width of the X-ray source (in diffractometers). Hence, the width $B$ in equation (3.3) refers to the extra width, or broadening, due to particle size effect alone. In other words $B$ is essentially zero when the particle size exceeds about 1000 Å. The main problem in determining particle size from line width is to determine $B$ from the measured width $B_M$ of the diffraction line. Of the many methods proposed, Warren’s method is the simplest (Cullity and Stock, 2001). The unknown sample is mixed with standard having particle size $> 1000$ Å, which produces a diffraction line close to a
line emerging from the unknown sample. A diffraction pattern of the mixture is then recorded through a diffractometer. This pattern will contain sharp line from the standard, and broad line from unknown sample composed of several fine particles. If $B_S$ is the measured width at half maximum intensity of the line from the standard, the $B$ is given by equation (3.4) (Cullity and Stock, 2001).

$$B^2 = B_M^2 - B_S^2$$  \hspace{1cm} (3.4)

As the size of the crystallite increases, the experimental difficulties involved in measuring crystallite size from line broadening increases. Roughly speaking, the measurements provide a good estimate of the size of crystallite, if it lies in the range 0-500 Å. To obtain accurate results in the range 500-1000 Å, a very good experimental technique is needed. The observed XRD diffraction data was also utilized to estimate the dislocation density ($\delta$) and microstrain ($\varepsilon$) in the samples, employing equations (3.5) and (3.6) (Kathirvel et al., 2009).

$$\delta = 1/\ell^2,$$  \hspace{1cm} (3.5)

$$\varepsilon = B \cos \theta/4,$$  \hspace{1cm} (3.6)

Further, attempts were also made to estimate the anion-cation bond length ($L$) in the thin film samples prepared. Equations (3.7) and (3.8) were used for this purpose (Rusu et al., 2011).

$$L = \left[ (a^2/3) + (0.5 - u)^2 \right]^{1/2}$$  \hspace{1cm} (3.7)

$$u = (a^2/3c^2) + 0.25$$  \hspace{1cm} (3.8)

3.3.3: SEM analysis

Optical microscopes have their resolution limited by the diffraction of light to about 1000 diameters magnification. But, electron microscopy takes advantage of the wave nature of rapidly moving electrons. In comparison to the wavelength of visible light, electrons accelerated to 10,000 keV may have a wavelength of 0.12 Å, only. Hence, electron microscopes may easily provide magnifications of around 1,000,000 and the capacity of providing even greater magnifications is restricted only because of spherical and chromatic aberrations (Schroder, 1990). The resolution limit of scanning
electron microscope is, at present, around 25 Å. Thus, observing a sample, particularly the films, through scanning electron microscope is expected to reveal the detailed morphological aspects of samples. In this study few representative samples of prepared thin films were subjected to SEM analysis by using Scanning Electron Microscope (JEOL JSMS 800 LV). This study was made at National Institute of Oceanography, Goa.

The scanning electron microscope generates a beam of electrons in vacuum. The beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils. The primary imaging method is by collecting secondary electrons that are released by the sample. The secondary electrons are detected by a scintillation material that produces flashes of light from the electrons. The light flashes are then detected and amplified by a photomultiplier tube. By correlating the sample scan position with the resulting signal, an image can be formed that is strikingly similar to what would be seen through an optical microscope (Schroder, 1990).

### 3.3.4: AFM analysis

A powerful technique used for surface profile characterization (i.e. to examine surface topography) of thin film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors is the Atomic Force Microscope (AFM). The AFM is applied for studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. The principle on which the AFM works is very simple. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si₃N₄ or Si, and extended down from the end of a cantilever. The nanoscope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contours on the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode. The photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts to voltage. Feedback from the photodiode
Plate 3: UV-Vis spectrometer used for band gap measurement
Plate 4: Atomic Force Microscope used for surface topography
difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode the piezo-electric transducer monitors real time height deviation. In the constant height mode the deflection force on the sample is recorded. The mode of operation also requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope.

In this study, the thin film samples of ZnO and Fe – ZnO were subjected to AFM analysis by employing (Nanosurf easyscan, Switzerland; Version 1.8) AFM/Surface Profilometer. The set point force was fixed at 20 μN for all the images, which were obtained for 256 × 256 data points for each scan size of 5μm × 5 μm. Obtained AFM data was also utilized to estimate root mean square (RMS) surface roughness in films.

3.3.5: Optical characteristics

The ability of a semiconductor photoelectrode to drive the water splitting is primarily determined by its band gap energy (E_g) and the position of the valence and conduction band edges relative to water redox energy levels for hydrogen and oxygen generation (Aroutiounian et al., 2000). On illumination of the semiconductor electrode in PEC cell, only a portion of the incident radiation having energy greater than band gap is absorbed by the material. This implies that, in PEC cell, photons having energy less than the band gap energy are not available for energy conversion. So, it is necessary that semiconductor used in PEC cell for energy conversion should have small band gap energy. However, too small band gap is also not desirable as it will result in lower photovoltage, and this will further reduce the efficiency of the PEC cell (Nozik, 1978, Gratzel, 2001).

In this study UV-Visible Spectrometer (UV-2450, Shimadzu, Japan) was used to determine the optical absorbance of sample films. The tentative idea regarding the band gap energy values can be obtained from the edge of absorption spectra (Chaudhary et al., 2004). However, this observation provides no clue to the direct or indirect nature of the bandgap. In order to understand this aspect and also to reconfirm the band gap energy values determined from absorption edge measurement, the values of absorption coefficient (α) need to be computed from the reflection and transmission data using equation (3.9),
Plate 5: ZnO films converted to photoelectrode
\[
\alpha = \frac{1}{d} \left/ \log \left\{ \frac{(1-R^2)}{T} \right\} \right.
\]
(3.9)

where, \(d\) is the thickness of the film, \(R\) reflectance, and \(T\) transmittance. Alternatively, the approximate value of \(\alpha\) can also be determined by dividing the observed absorbance data with the sample thickness. In this study the second approach was tried. For single phonon absorption, the \(\alpha\) for direct/indirect transitions is given by equation (3.10) (Pankove, 1971),

\[
\alpha = J \left\{ (hv - E_g \pm E_p)^{n2}/(hv) \right\}
\]
(3.10)

where, \(n\) is an integer and depends on whether the band gap is direct \((n = 1)\) or indirect \((n = 4)\). The negative sign corresponds to phonon emission, while the positive sign indicates phonon absorption. \(J\) is a constant, \(E_g\) the energy gap and \(E_p\) the energy of the phonon assisting in the indirect transition of the electron (Misho and Murad, 1992). For direct band gap determination, based on the use of equation (3.11), a plot is obtained between \((\alpha hv)^2\) and \(hv\), which results in a linear graph. The extrapolation of the linear graph yields an intercept on \(hv\) axis that corresponds to energy equivalent to the band gap energy (Misho and Murad, 1992).

\[
\alpha hv = A (hv - E_g)^{n2}
\]
(3.11)

3.3.6: Mott-Schottky analysis

Flat band potential \((V_{fb})\) is one of the most important parameter to characterize the semiconductor/electrolyte interface. Its value can be conveniently obtained by extrapolating Mott-Schottky (MS) curve, which relates the capacitance of space charge layer at junction to the applied potential. In the present study, using thin films of ZnO and Fe – ZnO as working electrode, capacitance \((C)\) at semiconductor/electrolyte junction in PEC cell was measured under darkness by LCR meter (Model 4263B, Agilent Technologies) at potential \((V)\) measured against SCE, varying from -1.8 to +1.8 V at 1 kHz signal frequency. MS curves were obtained by plotting \(1/C^2\) against potential \((V)\). Flat band potential was then calculated using the following equation,

\[
1/C^2 = \left[ \frac{2}{\varepsilon \varepsilon_0 N_D} \right] \left[ V - V_{fb} - (k_B T/q) \right],
\]
(3.12)
where, \( \varepsilon_0 \) is permittivity of free space \((8.86 \times 10^{-12} \text{ J}^{\text{T}} \text{C}^{\text{m}}^{-1})\), \( \varepsilon_s \) dielectric constant of the semiconductor electrode \((2.1 \text{ for ZnO})\), \( q \) charge on the carriers \((1.6 \times 10^{-19} \text{ Coulombs})\), \( N_D \) charge carrier concentration \((\text{m}^{-3})\), \( T \) temperature \((\text{K})\), and \( k_B \) Boltzmann’s constant \((1.38 \times 10^{-23} \text{ JK}^{-1})\). A straight line is expected from MS plots. The intercept of extrapolated straight line on potential axis at \( C^2 = 0 \) yielded the values of flat band potential \((V_{fb})\). Further, from the slope of Mott-Schottky curves and using the equation (3.13), the charge carrier density \((N_D)\) in samples were also determined,

\[
S = \left| \frac{2}{\varepsilon_0 \varepsilon_s q N_D} \right|, \tag{3.13}
\]

where, \( S \) is slope of MS curve.

### 3.3.7: Estimation of \( V_{fb} \) by Buttler’s Method

If an external potential bias is applied to an n-type semiconductor in contact with an electrolyte such that no space charge layer exists in the semiconductor, the CB and VB are flat at the semiconductor electrolyte interface and the applied potential is equal to \( V_{fb} \), the flat band potential. Ideally, no current flows across the semiconductor at this potential because electron-hole pairs cannot be generated. As more positive bias is applied to the semiconductor electrode, its Fermi level moves toward more negative values of energy (in solid state vacuum scale) and the bands bend upward. In the dark, this establishes a barrier to charge transfer and no current flows. Upon illumination with radiation having energy higher than the band gap of the semiconductor, electron-hole pairs are generated and the holes in the valence band are accelerated through the interface toward the electrolyte, generating an anodic photocurrent. Thus the onset of photocurrent also corresponds to the flatband potential \((V_{fb})\). Its value was, thus, also obtained by using the Butler’s method and equation (3.14).

\[
I_{ph}^2 = (V - V_{fb}) \tag{3.14}
\]

where \( I_{ph} \) is the photocurrent and \( V \) is the applied potential bias. According to this equation, the intercept of the linear portion of the square of \( I_{ph}^2 \) vs \( V \) plot with the abscissa will be \( E_{fb} \). A small anodic photocurrent was observed at \( V_{fb} \), and it could correspond to surface-related trap states (Butler 1977).
Plate 6: PEC set-up with attached potentiostat used in the study
3.4: Photoelectrochemical Studies

3.4.1: Preparation of Working Electrode

As stated earlier in Section 3.2, thin films of ZnO and Fe–ZnO were deposited only on 3/4th length of the substrate. From the remaining 1/4th length of the substrate Ohmic electrical contact was developed using silver paint and copper wire. The electrical contact, thus prepared, was tested for its Ohmic behaviour by observing the current (I) – potential (V) characteristics. Once the Ohmic nature of contact was confirmed, the contact side and substrate-edges were perfectly sealed with non-transparent and non-conducting epoxy resin, Hysol (Adhesives Dexter Distributors, Singapore). After the proper sealing and curing of the epoxy, working electrodes (WE) were obtained. The working electrodes were used in the photoelectrochemical cell to investigate their suitability for PEC water splitting under various experimental conditions.

3.4.2: Current (I) – Potential (V) Characteristics: Measurement of Photocurrent

Current – potential (I–V) characteristics of PEC cell, fabricated by using the prepared thin film samples as working electrode, were investigated in three electrode configuration electrochemical cell. The PEC cell was a quartz beaker (150 cm$^3$) fitted with a three-hole cork to accommodate working, counter and reference electrodes. A water jacket, was placed between working electrode and light source at a fixed distance to prevent heating effects. The semiconductor working electrode (WE) was used in association with a platinum counter electrode (CE) and saturated calomel reference electrode (SCE). The Platinum mesh (0.1 mm thick, 99.9%), used in the preparation of counter/auxiliary electrode for PEC studies, was procured from Sigma–Aldrich Corporation, U.S.A. Conductive silver paste (Eltecks Corporation, Bangalore, India) and commercial grade copper wire (1 mm thick) were used for establishing electrical contacts with the zinc oxide thin film.

As the main thrust of this study was to systematically investigate the effect of electrolyte environment on the process, several combinations of aqueous solution of bases and salts (in order to vary the pH, ionic strength, concentration, chemical nature, and temperature) were used as electrolyte. However, unless otherwise stated, the electrolyte conditions in PEC studies were as: Electrolyte – 0.1 M NaOH, pH – 13, ionic strength 0.10 M, temperature – 25 ± 3 °C. The electrolyte solution was purged
Plate 7: LCR meter set-up with attached power supply used in the study
with N₂ for 15-20 minutes just before each PEC measurement. Current – potential (I–V) characteristics of the cell were determined both under darkness and illumination by employing a potentiostat (Model ECDA-001, Con-Serv Enterprises) and 150 W Xenon Arc lamp (Oriel, USA) (used as light source). The photocurrent density at a particular bias was computed from the difference of current recorded under illumination and darkness. The PEC data was further evaluated by estimating Open circuit voltage (Vₜₐ₉) and Short circuit current (Jₜₑ). Since, OR / H₂O, is the only redox couple dominantly present in electrolyte solutions used, any significant gain in photocurrent in this case may be considered as indicative of photoelectrolysis of water. Although, no efforts were made, in this study, to collect and analyze evolved gases. Yet, a distinct evolution of gases in the form of gas bubbles at the electrode surface was observed under high photocurrent conditions, the intensity of which varied in different cases. Moreover, when the applied bias was raised further, there was an increase in the rate of bubble formation.

To prepare reagent solutions, throughout the study, only double distilled deionized water (DDW, specific conductivity < 0.8x10⁻⁶ ohm⁻¹ cm⁻¹ at 25 °C) was used. The concentration of electrolyte (NaOH/KOH) solutions was determined titrimetrically against standard solution of oxalic acid, using phenolphthalein as indicator. Solutions’ pH values were determined employing a Digital pH meter (Systronics). Triplicate samples of thin films were prepared under each investigated experimental conditions and with each sample 3-5 repetitive measurements were recorded. The data recorded were subjected to standard statistical analysis. The standard deviation in such measurements was < 8.6 %.