Chapter 3

Materials and Methods
3.1. Introduction

This chapter deals with the procedure for electrochemical synthesis of various metal organic frameworks and details about the analytical instruments used for the characterisation of synthesised materials. The electrochemical reaction cell set-up and general experimental procedure for the above synthesis are presented in Fig. 3.1. and Scheme 3.1. respectively.

Electrochemical Cell Set-up

![Electrochemical reaction cell set-up for synthesis of MOFs.](image)

Fig. 3.1. Electrochemical reaction cell set-up for synthesis of MOFs.

3.2. Materials

Metals like copper, aluminium, iron, nickel and magnesium plates with 99.9 % purity (procurred from John Mathew, India) were used as electrode material. 1,4-Benzene dicarboxylic acid (BDC), 1,3,5-Benzene tricarboxylic acid (BTC), 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) (Acros organics, India) were employed as ligands for synthesis of MOFs. The structure of organic ligands are presented in Fig. 3.2. Tetrabutylammonium tetrafluoroborate (TBATFB), tetrabutylammonium perchlorate (TBAPC) (Acros organics, India) pottassium chloride (Sisco Research Laborotories, 30
India) of analytical grade, methanol and N,N-dimethylformamide (Sisco Research Laboratories, India) of HPLC grade, were used as received.

Fig. 3.2. Structure of organic linkers.

3.3. Synthesis of Metal Organic Frameworks

Several research articles deal with different procedure for the synthesis of MOFs including the hydrothermal, solvothermal, solid state synthesis, chemical synthesis, gel-layer, galvanic displacement and electrochemical method. The conventional hydrothermal routes have several limitations on scaling than fast and more efficient microwave synthesis and sonochemical synthesis. Only few reports are available for electrochemical synthesis and patterned film growth on metal surface by anodic
oxidation or by galvanic displacement method, which are less complicated, avoid multi steps and less cleaning procedure. Among these, electrochemical method is having more advantages, due to its simple procedure, ease of handling at ambient operation conditions, higher yield efficiency and high purity of products with very short reaction time. The electrosynthesis of MOFs in non-aqueous medium was reported by Muller et al., and also synthesised a series of MOFs using metal ion with various linkers particularly terephthalic acid, naphthalene dicarboxylic acid and benzene tricarboxylic acid. However, the above studies have limitation over the yield, particle size and surface area. Based on the advantages, this research work mainly concentrates on the electrochemical synthesis of number of MOF materials.

3.4. Experimental Procedure for Electrochemical Synthesis of MOFs

Two metal electrodes having similar area were used as an anode and cathode for the synthesis. The organic linker and supporting electrolyte were dissolved in respective electrolyte solution in the electrolysis cell and stirred for 15 min for complete dispersion. Electrolysis was carried out in an electrochemical cell under constant voltage electrolysis (by adjusting the applied DC current in order to keep the constant voltage) for more than 2.5 hours to complete the reaction. Finally, precipitate of MOFs was collected, washed with suitable solvents and allowed to dry in a hot air oven at 120 °C for 12 h and activated at 200 °C for 2 h. A detailed general flowchart is presented as Scheme 3.1. Further, optimisation of experimental parameters like supporting electrolyte concentration, applied voltage and reaction time were carried out in order to get good yield and crystallinity. The yield of the product corresponding to the amount of weight loss in the metal anode is in the range of 93-98 %. In this work thirteen metal organic frameworks were synthesised and listed in Table 3.1. Among these, only four metal organic framework compounds with
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high surface area, pore size and catalytic nature were chosen for further applications. The detailed discussions about synthesis, characterisation and their suitable applications are presented in the following respective chapters.

Table 3.1. Experimental Conditions for the Electrochemical Synthesis of Various Metal Organic Frameworks

<table>
<thead>
<tr>
<th>S.L No.</th>
<th>Sample</th>
<th>Anode</th>
<th>Cathode</th>
<th>Area (cm²)</th>
<th>Ligand</th>
<th>Supporting Electrolyte</th>
<th>Solvent</th>
<th>Electrolyte (ml)</th>
<th>Yield Eff. (%)</th>
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<tr>
<td>1</td>
<td>Cu-BTC</td>
<td>Cu</td>
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3.5. Characterisations and Its Instrument Specifications

3.5.1. SEM and EDX Analysis

The surface morphology and microstructure of synthesised MOF samples were characterised using scanning electron microscope (SEM) using Tescan instrument (Model VEGA3) with 15 kV acceleration voltage or Hitachi instrument with 10 kV acceleration voltage (Model S-3000H from Japan). Prior to SEM analysis, the samples were gold sputtered for conductivity purpose. The elemental composition of the synthesised MOFs were obtained from the analysis of Energy Dispersive X-ray (EDX) Spectroscopy (Thermo Electron Corporation, USA) which was collected at an accelerating voltage of 20.0 kV and a magnification of ×700.
3.5.2. *FT-IR Analysis*

Fourier Transform Infrared (FT-IR) Spectroscopy is an important technique to identify the presence of functional groups and or the interaction between the metal and organic ligand in MOF samples. Such a solid MOF samples were typically had to be highly diluted with the IR-inactive KBr substance and pressed to the well-known form of “KBr-pellet” and recorded on a Nicolet 5DX-FT-IR spectroscopy in the wavenumber range of 400 - 4000 cm\(^{-1}\). The background spectrum scan was corrected with pure KBr pellet. FT-IR analysis was extensively used in the identification and structural analysis of inorganic, organic and organometallic compounds, natural products, polymers, composite materials etc.

3.5.3. *TEM Analysis*

Transmission electron microscopy (TEM) is the most powerful microscopic technique, which utilize energetic electrons to provide morphologic, compositional and crystallographic information on samples at a maximum potential magnification of 1 nanometer level. It produce high-resolution and two-dimensional images, allowing for a wide range of educational, science and industry applications. In this study the surface topography and particle size of the MOF samples were characterised using transmission electron microscopy (Model Philips CM 200 instrument).

3.5.4. *XRD Analysis*

X-ray diffraction (XRD) analysis is a non-destructive analytical technique which reveals the information about the nature of crystal structure, chemical composition and phase purity of the sample. This technique is based on observing the scattered intensity of an X-ray beam when hitting a sample as a function of incident and scattered angle,
polarisation and wavelength or energy. In this study the synthesised MOF samples were characterised by X-ray powder diffraction analysis (‘XpertPROPANalyticalPW3040/60’X’PertPRO’) using Cu–Kα1 radiation (λ = 1.5418˚ A), with the voltage and current were held at 40 kV and 30 mA (2θ = 5–50˚) at a scan rate of 1.5˚ min⁻¹.

**3.5.5. Surface Area Analysis**

The surface area of the samples were determined by the physical adsorption of a gas onto the surface of the sample at liquid nitrogen temperatures. Generally nitrogen or krypton gas is employed as adsorbent for surface area analysis. The amount of adsorbate has been measured either by a volumetric (Static pressure) or continuous flow (Dynamic flow) technique. Based on the amount of adsorbed gas to calculate the specific surface area is expressed in units of area per mass of sample (m² g⁻¹). Prior to analysis the physically bonded moisures or impurities are removed from the sample surface by repeated preconditioned steps. In our study the surface area of the MOFs are determined from BET (Brunauer–Emmett–Teller) adsorption-desorption isotherms, pore volume and pore size are determined from BJH (Barrett-Joyner-Halenda) adsorption-desorption of nitrogen at 77 K using a static volumetric apparatus Micromeritics, ASAP 2020 V3.00H model instruments.

**3.5.6. XPS Analysis**

X-ray photoelectron spectroscopy (XPS) is a quantitative as well as qualitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. In this work X-ray photoelectron spectroscopy (Multilab 2000, Thermoscientific, UK) was employed to study the oxidation state of central metal ion present in the MOFs using an
X-ray source of Al Kα radiation. The sample was scanned in the range of 0–1200 eV (binding energy). The energy scale was adjusted with respect to carbon peak, C1s spectra at 284.5 eV. Peak fitting was carried out for high resolution signals according to Shirley-type background subtraction using curve fitting XPSPEAK 4.1 software program with Gaussian-Lorentzien 60% / 40%.

3.5.7. TGA-DTA Analysis

Thermogravimetric analysis (TGA) is a technique performed on a sample to determine the changes in sample weight with respect to temperature under air (oxidative) or nitrogen (inert) atmosphere. This technique is effective for quantitative analysis of thermal reactions that are accompanied by mass changes, such as evaporation, decomposition, gas absorption, desorption and dehydration. TGA-DTA analysis was performed using a Q 500 instrument manufactured by TA Instruments and experiments were conducted with a constant heating rate of 5 °C min⁻¹ in nitrogen atmosphere.

3.5.8. Temperature Modulated-Differential Scanning Calorimetry (TM-DSC)

TM-DSC analysis was performed on a Mettler Toledo Star TM-DSC unit (Leicester, UK) under nitrogen flow of 50 ml min⁻¹ with a Refrigerated Cooling System (RCS) unit attached. Samples were measured by carefully weighing ~5–10 mg of powder into a 40 μl aluminium pan, this was then hermetically sealed with a pin-hole in the lid. An empty pin-holed 40 μl aluminium pan was used as a reference. For standard DSC experiments, samples between 5 and 10 mg were heated from 10 °C to 100 °C at a heating rate of 2 °C min⁻¹. The accuracy of the DSC sensor is 0.1 °C and measurements were performed in duplicate with the results analysed using Mettler STAR software. The
instrument was temperature calibrated with indium (Tm 156.61 °C; ΔH = 28.71 J g⁻¹) before data was collected.

3.5.9. Cyclic Voltammetry

Cyclic Voltammetry (CV) is the most widely used electroanalytical technique for acquiring quantitative information about the electrochemical reactions. In CV experiments, the potential of a stationary working electrode (in an unstirred solution) is varied linearly with respect to time from a potential where no electrode reaction occurs to potentials where the redox reaction occurs. Again the direction of the linear scan is reversed to its initial potential. All the cyclic voltammetric experiments were performed using BAS IM6 Electrochemical Analyzer (USA) with Thales 3.18-USB software. A single compartment conventional three electrodes system was used for the above study. MOFs coated on glassy carbon and a platinum foil were used as the working and counter electrodes, respectively. All potentials were recorded against SCE or Ag/Ag⁺ reference electrode at room temperature (300 ± 2 K). Prior to electrochemical measurements, the test solutions were deaerated with nitrogen gas for at least 15 min to eliminate interfering oxygen.

3.5.10. Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a method in which impedance of the system is measured as a function of frequency of applied AC potential. Instead of applying direct current or voltage, these techniques utilise a continuous perturbation to steady state system using a low magnitude AC signal. EIS is usually measured by applying an AC potential (sinusoidal potential excitation) to the electrochemical cell and then measuring the current (AC current) through the cell. The AC amplitude generally
ranging from 5 to 20 mV and is usually centred on the open circuit voltage or a set DC voltage. EIS measurements were performed to determine the AC conductivity of the MOF electrolyte samples. Impedance measurements were made in the range of frequencies from 100 KHz to 10 mHz at an amplitude of 10 mV, by sandwicking the MOFs laded nanocomposite polymeric membrane (1 cm dia.) between two stainless steel (SS304) blocking electrodes contacts, without any electrolyte using BAS IM6 Electrochemical Analyzer (USA) with Thales 3.18-USB software.

3.6. Preparation of MOF Modified Glassy Carbon Electrode for Cyclic Voltammetric Studies

The MOF modified glassy carbon electrode for electrochemical measurements was fabricated as follows. The glassy carbon of 3 mm dia was cut into 2 mm length and embedded in the pyrex glass tube. To take electrical contact, mercury poured into the glass tube and connection was made using copper wire. This homemade electrode was initially hand polished with fine emery papers (1/0, 2/0, 3/0 and 4/0) and washed with deionised water. The emery polished electrode were further polished with alumina gel over an emery paper 5/0 to get mirror finish. This electrode was then sonicated for 5 min in order to remove the adsorbed alumina. Finally the activity of the above electrode was checked with the ferrocyanide/ferricyanide redox system in 0.1 M KCl solution by adopting the procedure described in the literature. The MOF ink was prepared by dispersing 1 mg of MOF in 100 µl of 5% Nafion® solution and 900 µl acetone solution under ultrasonic condition. Drop cast method was adopted to coat the prepared MOF ink onto the glassy carbon electrode surface.
3.7. Conclusions

The general description of the instrumentation and the experimental details pertaining to this research work are described in this chapter. Moreover, the specific experimental details and instrumentation with suitable applications are also discussed in the respective chapters. In this work, almost thirteen different MOFs were synthesised through electrochemical synthetic route and among these, only four metal organic framework compounds with high surface area, pore size and catalytic nature were chosen for further application studies. The detailed discussions are presented in the following respective chapters.
References