Chapter 5

Electrochemically Synthesised Cu-BDC MOF and Its Application as a New Anode Material for Lithium ion Battery
5.1. Introduction

Alternative energy storage devices are required to replace the fossil fuels which are non-renewable and create CO$_2$ pollution leads to global warming. Rechargeable batteries are one of the possible solutions to overcome the energy demand. Recently lithium ion batteries are employed as a power sources for electric vehicles and hybrid electric vehicles.\textsuperscript{1,2} These electric vehicles require high energy and high power density lithium ion batteries for its operation and long service hours. Numerous electrode materials are investigated to increase the energy and power density of lithium ion batteries.\textsuperscript{3-8} However, the commonly used anodes such as graphite,\textsuperscript{9} metal\textsuperscript{10} and metal oxide\textsuperscript{11} based materials suffered from severe volume expansion results poor capacity retention and cell failure. In addition to these issues, synthesis of the above mentioned inorganic anode materials in nanometric size usually required tedious steps and large energy consumption.

Recently organic electrode materials have gained more attention towards energy storage applications.\textsuperscript{12} However, small organic molecules have several drawbacks such as solubility in organic electrolyte and low thermal stability as compared to inorganic molecules.\textsuperscript{13} Metal-organic frameworks (MOF) overcome the above challenges because they are the new class of porous crystalline materials in which metal ions and cluster ions are linked by organic units.\textsuperscript{14} They exhibit many advantages viz., high surface area, high thermal stability and adjustable pore size in which the pore size can be tuned in such a way that it can be well suited for lithium ion intercalation and deintercalation. X. Li et al\textsuperscript{15} first investigated the Zn$_4$O (1, 3, 5-tribenzoate)$_2$ for lithium storage and they suggested that the storage of Li occurs through conversion reactions however, its capacity falls off rapidly in the subsequent cycles because of the irreversible structural destruction of MOF.
network. Another one potential candidate (MOF) Zn$_3$(HCOO)$_6$ with diamondoid structure for Li storage was reported by Saravanan et al.,$^{16}$ in which they suggested that suitable choice of ligand plays vital role for reversible lithium ion storage. Further, the reversible formation or regeneration of MOF during alloying/dealloying reactions and conversion reactions mainly depends upon the choice of appropriate ligand in the MOF networks. Therefore the above mentioned MOF networks provide an option to the researchers in lithium ion battery for finding out new MOF materials with large reversible storage of Li.

In the present chapter, for first time we report the Cu$_2$(C$_8$H$_4$O$_4$)$_4$ network based MOF for lithium ion battery applications. This MOF network has two main advantages (i) high stability towards organic solvents (ii) ligand [C$_8$H$_4$O$_4$]$^-$ easily forms network with Cu$^{2+}$ ion and we expect these two merits beneficial for reversible lithium ion intercalation/deintercaltion reaction. In this paper we present the versatile electrochemical route for synthesis of Cu-BDC MOF and its preliminary investigation for lithium ion storage.

**5.2. Experimental Details**

**5.2.1. Materials**

Copper plates (John Mathew, India) with 99.9 % purity were used as electrode materials. Benzene dicarboxylic acid (BDC), tetrabutylammonium tetrafluoroborate (TBATFB, Acros organics, India) of analytical grade. Potassium chloride, acetone are of analytical grade (Sisco Research Laborotories), N,N-dimethyl formamide of HPLC grade (Sisco Research Laborotories), acetylene black (Shawinigan Black AB50, Chevron Corp., USA) and 1-methyl-2-pyrrolidone (NMP, Aldrich) were used as received.
5.2.2. Experimental Procedure for the Synthesis of Cu-BDC MOF

Two copper electrodes having similar area (10.5 cm$^2$) were used as an anode and cathode for the synthesis of Cu-BDC. The organic linker (0.1 M BDC) and supporting electrolyte (TBATFB) were dissolved in 50 ml DMF 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 for 2.5 h to complete the reaction. Finally the sky blue colour precipitate of Cu-BDC was collected from the electrolysis cell and allowed to dry in a hot air oven at 120 °C for 12 h and activated at 200 °C for 2 h. Further, optimisation of experimental parameters like supporting electrolyte concentrations, applied voltage and reaction time were carried out in order to get good yield and highly crystalline Cu-BDC. The yield of the product corresponding to the amount of weight loss in the copper anode is 94.63%.

5.2.3. Characterisation Techniques

The surface morphology and microstructure of synthesised samples were characterised by scanning electron microscope (SEM Hitachi S-3000H from Japan). The synthesised product was characterised by XRD (‘Xpert PROPAAnalyticalPW3040/60’X’PertPRO’) using Cu–Kα radiation (λ = 1.5418” A), with the voltage and current were held at 40 kV and 30 mA (20 = 5–50°) at a scan rate of 1° min$^{-1}$. Fourier Transform Infrared spectrum has been recorded on a Nicolet 5DX-FT-IR spectroscopy using KBr pellet. The surface area and pore volume of the Cu-BDC were determined from BET adsorption isotherm of nitrogen at 77 K using a static volumetric apparatus Micromeritics, ASAP 2020 V3.00H. The EDX spectrum (Thermo Electron Corporation, USA) was collected at an accelerating voltage of 20.0 kV and a magnification of ×700. Thermogravimetric 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.

For electrochemical evaluation, the anode was prepared by mixing 80 wt.% synthesised MOF, 10 wt.% Super–P carbon and 10 wt.% polyvinylidene fluoride (PVDF) binder in N–methylpyrrolidone (NMP) solvent to form a homogeneous slurry mixture. The mixture was coated over copper foil and dried under ambient condition. 18 mm diameter circular discs were blanked out and dried under vacuum at 120 °C for 12 h. Finally, coin cells of 2016 type were assembled inside an argon filled glove box using the prepared anode as working electrode, lithium as counter and reference electrodes, celgard 2400 as the separator and LiPF₆ in 1:1 EC/DEC as an electrolyte. Charge–discharge studies of the coin cells were carried out using programmable battery tester at a constant current mode in the potential range of 0.01 - 2.5 V vs. Li/Li⁺. Cyclic voltammetric measurements were performed using BAS IM6 Electrochemical Analyser (USA) at a scan rate of 0.1 mV s⁻¹ between 0.01 and 2 V. Electrochemical Impedance Spectra were also measured by using an BAS IM6 Electrochemical Analyser (USA) with an AC amplitude of 5 mV and the frequency range was between 100 KHz and 5 mHz.

5.3. Results and Discussion

5.3.1. Optimisation of Electrolysis Conditions

Fig. 5.1a, b presents the effect of concentration of supporting electrolyte and effect of BDC concentration on the yield of MOF. It is clear that while increasing the concentration of supporting electrolyte and BDC concentration yield increase, but when considering the 0.2 M and 0.25 M BDC concentrations, there is no much change in yield of the product, but higher concentration of TBATFB and BDC affect the surface
morphology. However increasing the applied voltage on the reaction, major change in the amount of yield is observed upto 15 V as shown in Fig. 5.1c, which clearly shows that while increasing the applied voltage the yield also increases, but above 15 V the product was starting to decompose.

**Fig. 5.1.** The graph corresponding to a) concentration of TBATFB vs. yield b) concentration of BDC vs. yield c) applied cell potential vs. yield and d) reaction time vs. yield and reaction time vs. current.

Fig. 5.1d depicts the yield vs. reaction time and current vs. reaction time curve. The yield mainly depends on reaction time but as the reaction goes on, the availability of BDC decreases and thereby current decreases. However, it is worthy to mention that, while increasing the concentration of TBATFB > 0.02 M and if the applied voltage more than 15 V, the particles size are more featureless. Hence, the optimised experimental
conditions are so important to get regular shapes without agglomeration with good yield of crystalline Cu-BDC. Since all the parameters for the synthesis are electrochemically controllable, the above process is said to be scalable. The network structure of Cu-BDC is shown in Fig. 5.2.

![Fig. 5.2. The hypothetical network structure of Cu-BDC MOF (with DMF molecule, red - Oxygen, white - Carbon, grey - Copper and blue - nitrogen).](image)

The criteria for optimised electrochemical condition in order to get maximum yield, high surface area, controlled Cu dissolution and good crystallinity with out agglomeration. The reaction scheme for synthesis of Cu-BDC is presented as Scheme 5.1.
Scheme 5.1. Reaction Scheme for the synthesis of Cu-BDC from 1,4-Benzene dicarboxylic acid.

5.3.2. Characterisations of Cu-BDC MOF

Fig. 5.3 shows the morphological structure (SEM image) of the electrochemically synthesised Cu-BDC MOF sample. Morphological studies clearly show that the synthesised Cu-BDC is highly porous in nature. Scanning electron microscopic images (Fig. 5.3a) show the synthesised Cu-BDC are formed in featureless shape with particle size 0.2 - 0.5 µm, when using 0.02 M TBATFB and 0.05 M BDC. While increasing the BDC concentration like 0.1 M and 0.2 M the synthesised material are formed in layer like porous structure (Fig. 5.3b & c). While increasing the BDC concentration to 0.25 M, the rods like structure are formed and are presented in Fig. 5.3d.
Fig. 5.3. SEM images of synthesised Cu-BDC Samples a) lower magnification image and b) higher magnification image using 0.02 M TBATFB, 0.1 M BDC, c) 0.04 M TBATFB, 0.1 M BDC and d) 0.02 M TBATFB, 0.25 M BDC.

In order to confirm the nature of bonding between benzene dicarboxylic acid and Cu$^{2+}$, vibrational spectral analysis was carried out and are shown in Fig. 5.4. The band observed around 1695 cm$^{-1}$ can be significantly assigned to acidic C=O stretching vibration present in the BDC, which after complexation with Cu$^{2+}$ is shifted to 1636 cm$^{-1}$ suggesting that deprotonated has happened in acidic C=O. This unambiguously indicates that the carboxylate ion participates in the complex formation. The absence of peaks at 410, 500, 610 and 615 cm$^{-1}$ indicates that the synthesised materials are free from CuO and Cu$_2$O$^{17}$ crystals during the nucleation of Cu-BDC. Moreover, the characteristic vibration at 687 cm$^{-1}$ may be attributed to Cu-O stretching vibration, in which the oxygen atom is co-ordinated with copper ions.
Fig. 5.4. FT-IR spectra of a) 1,4-Benzenedicarboxylic acid and b) Cu-BDC MOF.

Fig. 5.5. Powder X-Ray diffraction pattern of Cu-BDC MOF.
In order to characterise the phase purity, we carried out the powder x-ray diffraction pattern of synthesised copper terephthalate MOF which is shown in Fig. 5.5. This clearly indicates the phase pure and the diffraction pattern is also very consistent with available literature pattern. The chemical composition and the purity of electrochemically synthesised Cu-BDC was determined using energy dispersive X-ray analysis (Fig. 5.6). It clearly shows the Cu without any impurities other than carbon and oxygen. The effective atomic weight percentage of Cu, C, and O are listed in Table 5.1. Since there are no peaks corresponding to boron and fluoride, we have concluded that electrochemically synthesised Cu-BDC does not contain any impurities (like supporting electrolyte as in the case of hydrothermal route).

**Table 5.1.** Element composition obtained from EDX analysis for Cu-BDC MOF

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>% of C</td>
<td>41.57</td>
</tr>
<tr>
<td>2</td>
<td>% of O</td>
<td>25.17</td>
</tr>
<tr>
<td>3</td>
<td>% of Cu</td>
<td>33.26</td>
</tr>
</tbody>
</table>

**Fig. 5.6.** Energy dispersive X-ray analysis spectrum of Cu-BDC MOF.
To find out the exact specific pore volume and surface area of electrochemically synthesised and activated Cu-BDC, the BET nitrogen gas adsorption/desorption isotherm studies were carried out. The nitrogen adsorption data yield a specific pore volume of 2.62 cm$^3$ g$^{-1}$, pore size of 14.06 nm and surface area of 747 m$^2$ g$^{-1}$. Nanoporous nature is confirmed from the steep rise at the high relative pressure in the isotherm and also the average particle size is found to be 8.02 nm.

![Thermogravimetric Curve of Cu-BDC MOF.](image)

*Fig. 5.7. Thermogravimetric Curve of Cu-BDC MOF.*

The nature of thermal stability and the molecules that are desorbed or buried in the synthesised Cu-BDC with respect to temperature was studied in depth by TGA and compared with literature and is presented in Fig. 5.7. The synthesised Cu-BDC was heated in nitrogen atmosphere with a heating rate of 5 °C min$^{-1}$. The thermogram shows three different regions viz., 1) the first weight loss (4%) region between 50 and 200 °C indicating the loss of moisture 2) the region between 200 to 292 °C corresponding to the loss of two DMF molecules from the MOF with the weight loss of 20%. It is interesting to note that Cu co-ordination has been reduced from six to four takes place at this stage.
(Scheme 5.2) and 3) the third region starts at 327 °C, at that temperature the structure of MOF collapse and the organic linker is buried. This weight loss is completed at 359 °C and stable up to 500 °C and the residue is found to be 22%.

![Diagram](image)

**Scheme 5.2.** Schematic representation of coordinated and de coordinated forms of DMF in Cu-BDC.

### 5.3.3. Electrochemical Behaviour of Cu-BDC MOF

Cyclic voltammetric responses of Cu-BDC coated on GC electrode is crucial in order to find out the electrochemical stability of the compound and is compared with CV response of Cu foil in 0.1 M KCl at a scan rate of 20 mV s\(^{-1}\) under nitrogen atmosphere are illustrated in Fig. 5.8. In general a good experimental reproducibility indicates that the mechanical stability of the frame work structure is high. The resulting cyclic voltammogram (Fig. 5.8a) shows distinct redox peak potentials at -0.004 and +0.112 V vs. SCE indicating the reversible oxidation and reduction of Cu\(^{II}/\)Cu\(^{I}\).\(^{19}\) The another reduction peak at -0.302 V vs. SCE and corresponding sharp oxidation peak at -0.075 V vs. SCE indicates the redox couple of Cu\(^{I}\) to Cu\(^{0}\). The cyclic voltammetric response of Cu-BDC indicated that the copper is in the Cu\(^{2+}\) ionic state, where as such a redox peak behaviour was not observed for Cu electrode in 0.1 M KCl solution (Fig. 5.8b).
Fig. 5.8. Cyclic voltammograms for a) Cu-BDC coated GC (redline represents for GC background) and b) Copper foil recorded in 0.1 M KCl solution at a scan rate of 50 mV s\(^{-1}\) under N\(_2\) atm.

5.3.4. Electrochemical Performance of Cu-BDC MOF as an Anode Material for Li-ion Battery

Fig. 5.9a shows the specific capacity vs. potential curves of Cu-BDC MOF (according to Scheme 5.2, the single unit cell of Cu-BDC can be denoted as Cu\(_2\)(C\(_8\)H\(_4\)O\(_4\))\(_4\) at the current density of 48 mA g\(^{-1}\) when cycled between the potential limits 0.01 and 2.5 V. The first cycle is started from the open circuit voltage (~3.12 V) to 0.01 V vs. Li/Li\(^+\). The discharge profile contains three plateaus around 1.94, 1.39 and 0.72 V vs. Li/Li\(^+\) and the corresponding charge profile shows two plateaus around 0.52 (a small hump) and 1.07 V vs. Li/Li\(^+\) respectively. The first discharge/charge profile delivers the discharge and charge capacities of 1492 and 194 mA h g\(^{-1}\) respectively. The large discharge capacity of the first cycle is due to the large amount of cavities in the MOF network and amorphization reaction of Cu\(_2\)(C\(_8\)H\(_4\)O\(_4\))\(_4\) network.\(^{16}\) According to Li et al.,\(^{15}\) two different kinds of Li\(^+\) ions existed in the MOF network in which the first one derived
from the inserted Li$^+$ ions and another one from the electrolyte. Therefore, these two kinds of Li$^+$ ions can enter and accommodate in the microporous network during discharge process. The accumulation of Li$^+$ ions in the microporous network is irreversible, however, such reactions happened in the first cycle only and it is absent in the second cycle onwards which is evidenced from the charge/discharge curves in the second cycle.

![Fig. 5.9](image)

**Fig. 5.9.** (a) Charge/discharge curves (b) Cycling performance of Cu$_2$[BDC]$_4$ at the current density of 48 mA g$^{-1}$.

Fig. 5.9b shows cycling performance of the Cu$_2$(C$_8$H$_4$O$_4$)$_4$ material at the current density of 48 mA g$^{-1}$ over 50 cycles. The 50$^{th}$ cycle charge capacity is around 161 mA h g$^{-1}$ corresponds to the capacity fade of 16.1 %. The charge/discharge behaviour of Cu$_2$(C$_8$H$_4$O$_4$)$_4$ at different current densities were studied and shown in Fig. 5.10 a & b. The reversible capacity was about 228, 194, 102 and 81 mA h g$^{-1}$ at 24, 48, 120 and 240 mA g$^{-1}$ respectively. From the rate capability measurements we can clearly say that in each current density the reversible capacity remain unchanged during cycling. At the current density of 24 mA g$^{-1}$ we obtained the charge capacity ~228 mA h g$^{-1}$ corresponds to 95% of the theoretical capacity. The above obtained results confirm that terephthalate
ligand in MOF network shows good rate capability and compared with Zn₄O(1,3,5-tribenzoate)₂ MOF network,¹⁵ moreover terephthalate MOF network shows better electrochemical performance. The obtained results are further validated by cyclic voltammetry and electrochemical impedance spectroscopy studies.

![Fig. 5.10.](a) Charge/discharge curves of Cu₂[BDC]₄ at different current densities (b) Rate capability of Cu₂[BDC]₄ at different current densities.

The cyclic voltammogram of Cu₂(C₈H₄O₄)₄ recorded between 0.01 and 2.5 V vs. Li/Li⁺ at the scan rate of 0.1 mVs⁻¹ shown in Fig. 5.11. We observed three peaks (1.92, 1.40 and 0.73V) in the cathodic region and two peaks (a small hump at 0.57 V and broad peak at 1.1V) in the anodic region respectively. The intense cathodic peaks at 1.92 and 1.4V vs. Li/Li⁺ indicates that amorphization and formation of Cu nano particles and lithium terephthalate as followed by the equation 5.1. This is further supported by the fact that the reduction of Cu(II) to Cu(0) via intermediate Cu(I) at these potentials according to Parzych et al.,²⁰ and Sahay et al.²¹ The broad peak at 0.73 V vs. Li/Li⁺ is due to the various alloying reactions of Lithium with copper (equation 5.2). In the successive anodic region at 0.51 V vs. Li/Li⁺ (a small and broad hump) indicates that the dealloying reaction of Cu and Li. The peak at 1.1 V vs. Li/Li⁺ in the anodic region confirms that the
regeneration of terephthalate ligands. Therefore we expect that the following reaction mechanism may happen during cycling.

\[
\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_4 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow 2\text{Cu} + 4\text{C}_8\text{H}_4\text{O}_4\text{Li} \quad (5.1)
\]

\[
2\text{Cu} + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow 2\text{Li}_2\text{Cu} \quad (5.2)
\]

Thus the full reduction of Cu(II) to Cu(0) requires two lithium per Cu in the MOF network during cycling.

![Cyclic voltammogram of Cu$_2$[BDC]$_4$ at the scan rate of 0.1 mVs$^{-1}$](image)

**Fig. 5.11.** Cyclic voltammogram of Cu$_2$[BDC]$_4$ at the scan rate of 0.1 mVs$^{-1}$.

Fig. 5.12. presents the Nyquist plot of Cu$_2$(C$_8$H$_4$O$_4$)$_4$ before and after cycling. We can clearly observe the depressed semi circle after cycling as compared to the fresh electrodes. The two semi circles in the Nyquist plot of Cu$_2$(C$_8$H$_4$O$_4$)$_4$ (fresh electrodes) is due to the increase of interfacial resistance in the electrodes. This is attributed to the fact that mass transfer occurs in this region i.e the accommodation of Li$^+$ ions in the porous structured cavities of MOF network i.e the reduction of electrolyte species.$^{22,23}$
Further relaxation loop evident at high frequencies may be attributed to the decrease of resistance and increase charge transfer process from the SEI layer.\textsuperscript{24} However, the impedance plot of MOF composite electrode after cycling exhibit the one semicircle followed by well defined tail at 45° angle which is called Warburg diffusion. This indicates that the interfacial resistance decreases after completion of the first cycle which is consistent with charge/discharge studies. The lithium ion diffusion co-efficient could be calculated using the following equation 5.3.

\[
D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad \text{(5.3)}
\]

Where R is the gas constant, T is the absolute temperature, n is the number of electrons per molecule oxidized, A is the surface area, F is the Faraday’s constant, C is the concentration and D is the diffusion co-efficient and \( \sigma \) is the coefficient of Warburg impedance which can be obtained from the intersection of the straight line on the real
axis.\textsuperscript{25} It is equal to \((R_s + R_{ct} - 2\sigma^2C_{dl})\) in which the calculated diffusion coefficient of MOF electrode (after cycling) is \(4.3 \times 10^{-8}\ \text{cm}^2\ \text{s}^{-1}\). The above obtained results from cyclic voltammetry and impedance studies are quiet consistent with charge/discharge studies.

\textbf{5.4. Conclusions}

In this chapter, highly porous, phase pure crystalline copper terephthalate (Cu-BDC) MOF has been prepared via a simple \textit{in-situ} copper ion generating electrochemical route. It was demonstrated that \(\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_4\) as a new class of anode material for Li-ion battery, which can have the ability to store \(\text{Li}^+\) ions reversibly. It delivers \(227\ \text{mA h g}^{-1}\) in the first cycle which is around 95\% of the theoretical capacity. The new anode material \(\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_4\) considers as a candidate for long time energy storage.
References


