Synthesis and characterization of mesoporous crystalline copper metal–organic frameworks for electrochemical energy storage application

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Abstract

The mesoporous nanostructure Cu-metal organic frameworks (Cu-MOF-1 and Cu-MOF-2) have been synthesized by a high temperature solvothermal route. The products were characterized by X-ray diffraction, Brunauer–Emmett–Teller surface measurement, Thermo gravimetric analysis, scanning electron microscope and Single crystal XRD. The electrochemical properties of these MOF electrodes were examined by using of cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopic techniques. Comparing the results of CV and GCD studies, both those MOFs have shown significant charge storage capacity, while Cu-MOF-2 has showed a specific capacitance greater than Cu-MOF-1. The Cu-MOF-1 and Cu-MOF-2 electrodes showed a maximum specified capacity of 181 and 248 F g^{−1} respectively at a current density of 1 A g^{−1} and an extensive cyclic stability of up to 2000 cycles with capacity retention of ~ 90.1%. The electrochemical studies with Cu-MOF electrodes were conducted in 6 M KOH electrolytes. The excellent electrochemical properties of Cu-MOFs can be credited to the large surface area with a high microporous volume of structurally implanted electro-active metallic centres and the rapid transport of ions into electrolytes/electrodes. The results imply that the Cu-MOFs electrode could be the potentially high- performance electrode materials for super capacitor applications.

Keywords Mesoporous Cu-MOFs · Crystal structure · Cyclic voltammetry · Super capacitor · Specific capacitance

1 Introduction

Metal organic frame works (MOFs) are a recent type of crystalline porous materials that can be formed by the cluster of organic ligands and metallic ions from simple room temperature stirring to high temperature solvothermal/hydrothermal heating methods [1–6]. Accordingly by careful selection of metal ions and organic ligands with distinct coordination geometries can play major role in design to synthesize the MOFs. In the earlier few years, polycarboxylate organic ligands can function as exceptional organic building blocks, pertaining to their strong coordination abilities and variable coordination modes.

On the other hand, the MOFs have received considerable attention in recent years due to their highly porous and three-dimensional hybrid structure possessing interesting electronic properties [7, 8]. The redox behaviour of metal cation in MOFs makes electrode materials promising in energy storage devices such as lithium ion batteries and supercapacitors, especially pseudo capacitors [9, 10]. Supercapacitors are one of the promising energy storage devices with high power density, long service life and low cost correlated to conventional batteries and long cycle life. One specific type of supercapacitor is called double-layer electrical supercapacitors (EDLCs), which usually use carbon electrode materials with increased surface

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Scheme 1 Scheme for the formation of Cu-MOF-1 and Cu-MOF-2

area and porosity. However, both the physically stored charges and the energy density of EDLCs are very low. In addition, pseudo capacitors with electrochemically active materials, including metal oxides/sulphides with increased energy density, have received greater attention in recent years [11, 12]. Unfortunately, due to their poor conductivity [13, 14], the electrochemical application of MOFs is still less. Copper-1,3,5-benzenetricarboxylate ($\text{Cu}_3(\text{BTC})_2$, also called MOF-19 or HKUST-19), showed an exciting behaviour in electrochemically centred supercapacitors because of its high surface area and huge pore volume [15–18]. So far, only some reports for supercapacitors exist based on Cu-MOF, Srimuk et al. [19]. Electrochemical behaviour published for supercapacitors of HKUST-1 with a specific capacity of less than 50 F g^{-1} . Saraf et al. [20]. Later on the Cu-MOF was used as a supercapacitor electrode material and attained a specific maximum capacity of 85 F g^{-1} at current densities of 1.6 A g^{-1} . Both have been based on $\text{Cu}_3(\text{BTC})_2 \cdot 3\text{H}_2\text{O}$. Cu-MOF is used as water/ethanol solvent and water/DMF solvents [21, 22]. This paper represents for the synthesis of new Cu-MOFs with DMF mixed ligands as a single solvent [$\text{Cu}(\text{BDC})(\text{MI})(\text{DMF})$] (BDC = benzene-1,4-dicarboxylic acid, MI = 1-methyl imidazole and DMF = *N,N*-dimethylformamide). Benzene-1,4-dicarboxylic acid (BDC) are considered to be hard ligands, so form strong bonds with hard metal centres. The main choices of metals used to bind to carboxylate are transition metals, which can form a wide variety of coordination geometries affording many different network architectures. Carboxylic acids are also attractive as framework-forming reagents because their high acidity ($\text{pK}_a \sim 4$) allows facile in situ deprotonation. The solvent DMF used in the assembly process may participate in coordination with metal ions or can also act as a guest molecule in the final lattice structure. Although most often the solvents may not be incorporated in the

as-synthesized MOF, they act as a structure directing agent or a medium for the crystal growth process, i.e., the extent of deprotonation of organic carboxylate ligands can be controlled by selecting suitable solvents such as DMF, DEF and DMA or by adjusting the basicity of solvent medium. These solvents can be converted to its corresponding amines at higher temperatures and thus lead to deprotonation of carboxylate.

The electrochemical and electro catalytic properties of these Cu-MOF are investigated in 6 M KOH (alkaline media) solutions. Because of the improved electrochemical behaviour of copper, benzene-1,4-dicarboxylic acid and imidazole, the synthesis of Cu-MOF-1 and Cu-MOF-2 using solvent DMF is reported using a solvothermal method. To the best of our knowledge, the synthesized Cu-MOF-1 and Cu-MOF-2 have been analyzed as high-performance electrode materials. These results show that as—synthesized Cu-MOF-1 and Cu-MOF-2 can be used as a new material for the storage of energy (Scheme 1).

2 Experimental

2.1 Materials

All chemicals used in this research work, such as copper nitrate hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), benzene-1,4-dicarboxylic acid (H_2BDC), methyl imidazole (MI) and *N,N*-dimethylformamide (DMF), were analytical grade and obtained from SDFCL (SD fine chemistry limited). Methylimidazole and chloroform were reagent grade chemicals obtained from Spectrochem Private limited. All these chemicals were used without further purification as received.

Fig. 1 **a** Crystal structure and **b** space filled diagram of Cu-MOF-1

2.2 Synthesis procedure

2.2.1 Cu-MOF-1

The solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 gm), Benzene-1,4-dicarboxylic acid (0.70 gm) were prepared separately by dissolving in 15 ml DMF each under mild stirring until the formation of a clear solution. The mixture of the above

solutions was then transferred to a steel autoclave fitted with Teflon (capacity 60 ml) inner vessel. The tight sealed autoclave was heated to 110 °C and maintained for 36 h and later it was left to cool naturally to room temperature. The product formed was washed sequentially with DMF, ethanol and chloroform and dried in a vacuum oven 70 °C for 12 h.

2.2.2 Cu-MOF-2

The precursors such as $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 gm), Benzene-1,4-dicarboxylic acid (0.70 gm) were dissolved in 15 ml of DMF separately under mild stirring. To the above mixture added about 0.5 ml of 1-methylimidazole to obtain a clear solution. The mixture was subsequently transferred to a 60 ml Teflon lined steel autoclave. The sealed autoclave was heated at 110 °C for about 36 h and cooled naturally to room temperature.

2.3 Characterization techniques

The above products were characterized by vibrational properties of the functional groups were studied by the

Table 1 Crystal data and structure refinement for Cu-MOF-1 and Cu-MOF-2

Empirical formula	$\text{C}_{12}\text{H}_6\text{CuO}_5$	$\text{C}_{16}\text{H}_{16}\text{CuN}_4\text{O}_4$
Formula weight	293.71	391.87
Temperature/K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$P2_1/c$
$a/\text{\AA}$	12.820(1)	5.3043(7)
$b/\text{\AA}$	15.649(1)	14.720(2)
$c/\text{\AA}$	6.8289(5)	11.0659(9)
$\alpha/^\circ$	90	90
$\beta/^\circ$	111.366(9)	104.90(1)
$\gamma/^\circ$	90	90
Volume/ $\text{\AA}^3$	1275.86(17)	834.97(18)
Z	4	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.529	1.559
μ/mm^{-1}	1.719	1.337
$F(000)$	588.0	402.0
Crystal size/ mm^3	$0.160 \times 0.160 \times 0.080$	$0.440 \times 0.080 \times 0.060$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	5.206 to 52.732	6.72 to 52.742
Index ranges	$-15 \leq h \leq 16, -13 \leq k \leq 19, -8 \leq l \leq 7$	$-6 \leq h \leq 6, -16 \leq k \leq 18, -13 \leq l \leq 13$
Reflections collected	2437	3091
Independent reflections	1356 [$R_{\text{int}} = 0.0188, R_{\text{sigma}} = 0.0333$]	1711 [$R_{\text{int}} = 0.0207, R_{\text{sigma}} = 0.0348$]
Data/restraints/parameters	1356/9/89	1711/0/116
Goodness-of-fit on F^2	1.099	1.044
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0559, wR_2 = 0.1691$	$R_1 = 0.0381, wR_2 = 0.0820$
Final R indexes [all data]	$R_1 = 0.0675, wR_2 = 0.1776$	$R_1 = 0.0608, wR_2 = 0.0896$
Largest diff. peak/hole/ $e \text{\AA}^{-3}$	1.16/−0.66	0.30/−0.41

Fig. 2 **a**, **b** and **c** are the views of the coordination environment of Cu-MOF-1 with different axis X, Y, Z (symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+1$ #2 $-x+1, -y, -z+1$ #3 $x, -y, z$ #4 $-x+1/2, -y+1/2, -z$)

Shimadzu 8400S FTIR spectrophotometer with IR grade KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$. Powder X-ray diffraction (PXRD) to obtain information on phase structure, purity, nature (crystalline or amorphous), etc. A Bruker D8 Advance X-CuK α radiation diffractometer was used and the $\mu=0.1541874\text{ nm}$. The FE-SEM images were taken on the Zeiss FESEM instrument. The pore size,

the pore volume and the specific material surface area were calculated using the data obtained by Nova1000 BET instrument. Thermo gravimetric analysis (TGA) on a Perkin-Elmer thermal analyzer was carried out in the N_2 atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$. The crystal data was collected at the Xcalibur, Eos and Nova diffractometer. During data collection, the crystal was maintained at $293(2)\text{ K}$. The structure was solved using Intrinsic Phasing with the ShelXT structure solution program using

Fig. 3 **a** Crystal structure and **b** Space filled diagram of Cu-MOF-2

Olex2 and refined using the ShelXL refining package to CGLS minimization.

2.4 Electrochemical measurements

All electrochemical tests have been performed at the CHI 660E electrochemical workstation. The working electrode was prepared with a known quantity of active material (80 wt% or ~2 mg) was prepared with graphite powder (15 wt%) and polytetrafluoroethylene (PTFE) binder (5 wt%) along with an ethanol. This mixture was consequently hand pressed on nickel mesh from all sides. Copper wire was used as the current collector. This electrode was left for drying at room temperature for about 24 h. The cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy were conducted under atmospheric conditions in 6 M KOH electrolyte solution. The saturated calomel electrode (SCE), platinum electrode and prepared Cu-MOF-1 and Cu-MOF-2 electrodes were used as the reference, counter and working electrodes respectively.

3 Results and discussion

3.1 Crystal structure of Cu-MOF-1 and Cu-MOF-2

3.1.1 Single crystal X-ray diffraction (SXRD) studies of [Cu-MOF-1]

The SXRD study of Cu-MOF-1 has revealed that Cu (II) ion forms paddle-wheel units in which the four carboxylate groups are equatorial and two water molecules are axial. Therefore, each unit exists of two Cu(II) six-coordinated units with distorted octahedral geometries. Each Cu(II) dimeric unit co-ordinates with eight oxygen's from four carboxylate groups of four bdc ligands that can be

unraveled as a 4-connected dimeric copper unit (Fig. 1a) and space filled diagram of Cu-MOF-1 (Fig. 1b).

Crystal data for Cu-MOF-1: The Molecular formula is $C_{12}H_6CuO_5$; Analysis made at 293.71 K: monoclinic, space group C2/m with $a = 12.820(1)$ Å, $b = 15.649(1)$ Å, $c = 6.8289(5)$ Å, $\beta = 111.366(9)^\circ$, $V = 1275.86(17)$ Å³, $Z = 4$, $T = 293(2)$ K, μ (MoK α) = 1.719 mm⁻¹ and $D_{calc} = 1.529$ g/cm⁻³. The structure was solved by direct methods and refined to a standard discrepancy index of $R = 0.0188$ and $R_w = 0.0333$ for 2437 reflections with $F 2\sigma(F)$ and a goodness of fit on $F^2 = 1.093$ (Table 1).

In the structure, the Cu(II) ion is connected by two BDC groups and each group connects two dimmers to form a 1D frame works (Fig. 2a), which were specified together with x, y and z axis to form 1D, 2D and 3D channels with a diameter of 12 Å (Fig. 2b, c).

3.1.2 Crystal structure of [Cu-MOF-2]

From the studies, it is found that the structure has Cu(II) ion forming pyramidal units, in which the two carboxylate groups are located in equatorial positions and two imidazole moieties occupy equatorial positions. Each Cu(II) monomer unit co-ordinates with two carboxylate and two imidazole groups with four oxygen atoms in Cu-MOF-2 (Fig. 3a) and the Cu-MOF-2 space filled diagram (Fig. 3b).

Crystal data for Cu-MOF-2: the molecular formula is $C_{16}H_{16}CuN_4O_4$; analysis temperature—293.71 K: monoclinic, space group— $P2_1/c$ with lattice parameters: $a = 5.3043(7)$ Å, $b = 14.720(2)$ Å, $c = 11.0659(9)$ Å, $\beta = 104.90(1)^\circ$, $V = 834.97(18)$ Å³, $Z = 2$, $T = 293(2)$ K, μ (MoK α) = 1.337 mm⁻¹ and $D_{calc} = 1.559$ g/cm³. The structure was solved by direct methods and refined to a standard discrepancy index of $R = 0.0207$ and $R_w = 0.0348$ for 3091 reflections with $F 2\sigma(F)$ and a goodness of fit on $F^2 = 1.093$ (Table 1).

The anisotropic thermal parameters of Cu-MOF-1 and Cu-MOF-2 have been refined for all non-hydrogen atoms. Some of the hydrogen atoms could not be solved, so the analysis was not included. This paper contains additional crystallographic data CCDC number is 1897362 and 1897354.

In Cu-MOF-2, Cu(II) ion is connected by two BDC and imidazole ligands and each group connects two monomer units to form a 1D frame works (Fig. 4a), specified together with x, y and z axis to form 1D, 2D and 3D channels with a diameter of Å12 (Fig. 4b, c).

3.2 FTIR spectroscopy studies

The FTIR spectra of Cu-MOF-1 and Cu-MOF-2 (Fig. 5) show a series of bands of 400–4000 cm⁻¹. The Benzene-1, 4-dicarboxylic acid ring of the MOFs have given

Fig. 4 **a, b and c:** Views of the coordination environment of Cu-MOF-2 with different axis X, Y, Z (Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+1$ #2 $-x+1, -y, -z+1$ #3 $x, -y, z$ #4 $-x+1/2, -y+1/2, -z$)

the signals at 3135 and 3555 cm^{-1} ($-\text{OH}$ stretching); 2977 and 3124 cm^{-1} ($\text{C}-\text{H}$ stretch of aromatic rings); 1607 and 1595 cm^{-1} ($\text{C}=\text{O}$ stretch); 1335 and 1356 cm^{-1} correspond to the asymmetrical and symmetrical stretch of carboxylate groups. The 1100 , 828 cm^{-1} and 1098 , 880 cm^{-1} peaks are corresponding to $\text{C}-\text{C}$ or $\text{C}-\text{O}-\text{C}$ vibrations. The large bands of 3144 cm^{-1} could be assigned to the $\text{N}-\text{H}$

frequency of the Cu-MOF-2 imidazole ring. The vibration of the $\text{C}-\text{C}$ stretch has appeared at 1529 cm^{-1} . The $\text{N}-\text{H}$ vibration stretching mode appeared at 3158 cm^{-1} of the compound. It is a very difficult task to identify the $\text{C}-\text{N}$ stretch frequency because it is possible give mixed bands in this region. The $\text{C}-\text{N}$ stretching vibration modes are appeared at 1463 , 1227 and 1145 cm^{-1} .

Fig. 5 FTIR spectrum of Cu-MOF-1 and Cu-MOF-2

Fig. 6 PXRD patterns for Cu-MOF-1 and Cu-MOF-2

Thus, the FT-IR spectra of as-synthesized Cu-MOF-1 and Cu-MOF-2 yield strong structural confirmation [23–28].

3.3 Powder X-ray diffraction (PXRD) studies

Powder X-ray diffraction (PXRD) is a technique, which reveals the information about the nature of crystal structure and phase purity of the sample. The PXRD patterns of Cu-MOF-1 and Cu-MOF-2 show relatively high intensity peaks indicating the high crystallinity of the compounds (Fig. 6). The peak positions obtained are consistent with the standard parent material. High intensity Bragg

diffraction peaks observed at $2\theta = 9.35^\circ$, 11.31° , 13.78° and 16.16° are correspond to Cu-MOF-1 and those observed at $2\theta = 11.99^\circ$, 16.42° , 18.04° and 24.0° are for Cu-MOF-2. The highest intensity peaks in the x-ray patterns for these MOFs are correspond to $2\theta = 9.35^\circ$ and 11.99° respectively. This indicates the coordination of metal with the ligands to form complex. These results are consistent through the larger crystallite size and also an excellent crystalline nature can be seen.

3.4 FE-SEM analysis

FE-SEM is a technique that enables the microstructure and surface morphology of the product to be studied. Figure 7a–d are the FE-SEM images of Cu-MOF-1 at various magnifications (1, 2, 10 and 20 μm). The Cu-MOF-1 images show the clusters of particles of irregular shapes with angles and sides.

Although Cu-MOF-2 images contain almost flat slabs like structures, they have been shown, the particles are visibly rich in flakes arranged as a cubic number of crystals and possibly have the same phase (as supported by XRD results). The FE-SEM images of Cu-MOF-2 can be seen in various magnifications (1, 2, 10 and 20 μm) in the Fig. 8.

3.5 SEM–EDX analysis

Analysis of the energy dispersive X-ray spectroscopy (EDX) was carried out to identify the elements present in the synthesized Cu-MOF-1 and Cu-MOF-2. The EDX pattern (Fig. 9a) of Cu-MOF-1 shows the C, O and Cu elemental peaks with weight percentage and the Cu-MOF-2 as well along with the nitrogen peaks. The EDX analysis thus confirms the basic composition of the Cu-MOF-1 and Cu-MOF-2. The EDX results are summarized in Table 2.

3.6 BET surface area measurement

The porosity distribution of the Cu-MOF-1 and Cu-MOF-2 samples was analyzed for Barrett–Joyner–Halenda (BJH) method and N_2 adsorption–desorption isotherms at 180°C for 4 h. The Cu-MOF-1 and Cu-MOF-2 isotherm tests provide a distinctive IV- type curve with a different hysteresis loop within the range of 0.8–1.0 P/P_0 (Fig. 10), which indicates the existence of a mesoporous structure that in the two interconnected phases would usually be derived from the voids. The surface area of the BET is 12.9 and $12.7\text{ m}^2\text{ g}^{-1}$ respectively for Cu-MOF-1 and

Fig. 7 FE-SEM micrographs of Cu-MOF-1 at different magnifications (1, 2, 10 and 20 μm)

Cu-MOF-2. This mesoporous nature of Cu-MOF-2 can also play an important role in achieving large specific capacity due to its ability to facilitate the transport of diffusion/ions and ensure a high electrochemical active surface. The high volume of pores is beneficial for the rapid transport and diffusion of ions during the discharge process and therefore provides more electrically active energy storage sites. The Cu-MOF-2 hybrid's porous structure and large surface area is therefore likely to improve its performance in electrochemical applications.

3.7 Thermo gravimetric analysis (TGA)

Thermo gravimetric measurements for the MOFs were made at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ under the N_2 atmosphere without pre-treatment prior to the TG measurement. The Cu-MOF-1 and Cu-MOF-2 (Fig. 11) undergo weight loss at once each. The Cu-MOF-1 undergoes 40%

weight loss between 150 and 300 $^{\circ}\text{C}$, which could be due to the loss of DMF molecule. The weight loss of about 35% was observed in case of Cu-MOF-2 between 150 and 300 $^{\circ}\text{C}$, which could be attributed to the removal of the phenyl ring and carboxylate group. No such weight loss was observed until 500 $^{\circ}\text{C}$ later all the solvent molecules have disappeared and the framework collapsed to yield final product. There is no peak for functional group in the figure showing collapsing of the compound at 600 $^{\circ}\text{C}$ due to the evaporation of solvent molecules. Both Cu-MOF-1 and Cu-MOF-2 are stable in the temperature range of 200 $^{\circ}\text{C}$.

3.8 Electrochemical properties of Cu-MOF-1 and Cu-MOF-2

The electrochemical measurements of Cu-MOF-1 and Cu-MOF-2 electrodes were performed in an electrochemical (three-electrodes) cell containing an electrolyte of 6 M

Fig. 8 FE-SEM micrographs of Cu-MOF-2 at different magnifications (1, 2, 10 and 20 μm)

Fig. 9 Energy dispersive X-ray (EDX) pattern of Cu-MOF-1 and Cu-MOF-2

Table 2 EDX data and elemental composition of Cu-MOF-1 and Cu-MOF-2

Compounds	Elements	Atomic %	Total composition %
Cu-MOF-1	Cu	14.61	100
	C	24.36	
	O	48.73	
Cu-MOF-2	Cu	12.30	100
	C	15.59	
	O	56.88	
	N	27.53

Fig. 10 N₂ adsorption–desorption isotherms of Cu-MOF-1 and Cu-MOF-2 **Fig. 11** Thermogravimetry curve of Cu-MOF-1 and Cu-MOF-2, which shows the weight loss regions

KOH solution. The cyclic voltammetry measurements were performed at different scanning rates (10–100 mV s^{−1}) in the potential range is 0.0–0.5 V is shown in Fig. 12a, b. The strong redox peaks present in each CV curve imply the Faradaic controlled reactions. The fine and sharp redox peaks of Cu-MOF-1 and Cu-MOF-2 can be perfectly related to the faradic reactions of the various oxidation states of Cu²⁺ and the route can be explained by the following reactions.

According to Eq. 3, a high specific capacitance of 976 and 1048.8 F/g^{−1} were attained at the scanning rate of 10 mV/s^{−1}. With increase in scanning rate the oxidation peaks shift towards the positive direction and the reduction peaks shift towards the negative direction, which could be mainly due to the electrode internal resistance.

The CV curve area reflects the amount of charge stored in the electrodes presented in Fig. 12a, b. The specific capacitance can be calculated by the following equation.

$$C_s = \frac{\int I dv}{vmV} \quad (3)$$

If C_s is the specific capacity (F/g), I is the current (A), v is the scanning rate (mV/s), m is the active material weight (g) and v is the potential window (V).

The galvanostatic charge and discharge curves (GCDs) for Cu-MOF-1 and Cu-MOF-2 are shown in Fig. 13a, b respectively. The calculated specific capacities of Cu-MOF-1 and Cu-MOF-2 at the current density of 1 A g^{−1} are 181.65 and 248.44 F g^{−1} respectively. Figure 13 c shows the Cu-MOF-1 and Cu-MOF-2 specific capacitance is decreases, and the current density is steadily increases [29]. The discharge time of the Cu-MOF-2 electrode has increased notably when compared to Cu-MOF-1 electrodes (Fig. 13b). The specific capacitance of the materials can be calculated based on the following equation from the galvanostatic discharge curves.

$$C_s = \frac{I \times \Delta t}{\Delta V \times m} \quad (4)$$

where I is the current (A); t is the discharge time (s), v is the potential (V) and m is the mass of the active material on the electrode [30, 31].

The rapid transport of electrolytes in large voids between the two phases of Cu-MOF-1 and Cu-MOF-2 can be attributed to this outstanding performance and an extensive cyclic stability up to 2000 cycles with capacity retention of ~90.1%. The better long-term constancy of the Cu-MOFs electrode shows that it can be a good

Fig. 12 **a** and **b** are the CVs of Cu-MOF-1 and Cu-MOF-2 electrodes respectively in a 6 M KOH solution at different scan rates between 10–100 mV s⁻¹, **c** and **d** are the Relationships between the graph of

anodic peak current (I_{pa}) versus square root of scan rate ($v^{1/2}$) was plotted in the Cu-MOF-1 and Cu-MOF-2 electrodes

material for applications for super capacitors. The power density (P) and the energy density (E) can be calculated from the following equations.

$$\text{Energy density } E = \frac{1}{2} CV^2 \quad (5)$$

$$\text{Power density } P = \frac{E}{t} \quad (6)$$

where C (F/g⁻¹), V (V), P (W/kg), E (Wh/kg), and t (s) are the specific capacitance, potential window, power density, energy density and discharge time respectively [32, 34].

3.9 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements were made at a frequency range of 100 kHz to 0.01 Hz with a disturbance potential of 5 mV s⁻¹ as shown in Fig. 13d. The Cu-MOF-1 semicircles in the high frequency range are smaller than the Cu-MOF-2 semicircles. A smaller semi-circle indicate a small charge- transfer resistance (R_{ct}) [32], the straight lines in the low- frequency region show an ideal electrode capacitive behaviour, while the calculated R_{ct} for Cu-MOF-1 and Cu-MOF-2 are 6.23 and 7.4 Ω respectively. The interception of the real axis in the high frequency range of Nyquist plots indicates the equivalent series resistance (ESR), the combined series resistance of electrolytes, electrodes, electrolytes and electrodes [35, 36]. The Cu-MOF-1 and Cu-MOF-2 ESRs are 4.58 and 3.48 Ω respectively (Table 3).

Fig. 13 **a** and **b** Galvanostatic Charge/discharge curves of Cu-MOF-1 and Cu-MOF-2 at different current densities, **c** variation of specific capacitance as a function of current density and **d** Nyquist

plot and Equivalent Circuits of Cu-MOF-1 and Cu-MOF-2 electrodes in 6 M KOH Solution

Table 3 Power density (P) and the energy density (E) of Cu-MOF-1 and Cu-MOF-2 with different current densities

Compounds	Current densities (Ag^{-1})	Energy density (Wh/kg)	Power density (W/kg)
Cu-MOF-1	1	22.62	124
	2	9.25	249
	3	5.55	375
	4	3.60	500
	5	2.87	623
Cu-MOF-2	1	31.0	125
	2	29.12	251
	3	16.45	374
	4	10.13	499
	5	6.53	624

4 Conclusions

The Cu-MOF-1 and Cu-MOF-2 have been successfully synthesized by solvothermal methods. The Cu-MOF crystals are the mass of many thin mesoporous structures bearing a larger surface area. The electrochemical properties of the Cu-MOF-1 and Cu-MOF-2 electrodes have been studied to understand them for the supercapacitor application. The Cu-MOF-1 and Cu-MOF-2 electrode showed a maximum specific capacity of 181 and 248 Fg^{-1} at a current density of 1 Ag^{-1} . Moreover, the materials deliver high energy and power density and excellent rate performance with long cycle life as we studied. The Cu-MOF-2 showed improved electrochemical performance compared to the Cu-MOF-1. Our results show that Cu (bdc) MOFs are highly promising to be used as an advanced electrode material for high-performance super capacitor applications.

5 Supplementary material

Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1897362 and 1897354. The Director, CCDC12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail:deposit@ccdc.cam.ac.uk).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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