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Javed Hussain Shah

Government College University, Lahore

Ali Hamza

Government College University, Lahore

Muhammad Shahbaz

Government College University, Lahore

Saeed Ahmad

saeed_a786@hotmail.com

University of Engineering and Technology Lahore

Maham Saeed

Government College University, Lahore

Shahzad Sharif

Government College University, Lahore

Nosheen Kanwal

Qassim University

Muhammad Rizwan

Government College University, Lahore

Khurram Shahzad Munawar

University of Mianwali

Onur Şahin

Sinop University

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Crystal structure and electrochemical analyses of a multi-component cocrystal of cobalt(II) complexes of pyridine-2,6-dicarboxylic acid: Improving energy storage performance of hybrid device using redox active Electrolyte

Javed Hussain Shah^a, Ali Hamza^a, Muhammad Shahbaz^a, Saeed Ahmad^{b*}, Maham Saeed^a, Shahzad Sharif^{a*}, Nosheen Kanwal^c, Muhammad Rizwan^a, Khurram Shahzad Munawar^{d,e}, Onur Şahin^f

^a*Materials Chemistry Laboratory, Institute of Chemical Sciences, Government College University Lahore, 54000 Pakistan*

^b*Department of Chemistry, University of Engineering and Technology, Lahore, Pakistan*

^c*Department of Chemistry, College of Science, Qassim University, Almolaydah, Buraydah Saudi Arabia*

^d*Institute of Chemistry, University of Sargodha, Sargodha, 40100, Pakistan*

^e*Department of Chemistry, University of Mianwali, Mianwali, 42200, Pakistan*

^f*Department of Occupational Health & Safety, Faculty of Health Sciences, Sinop University, TR-57000, Sinop, Turkey*

Corresponding authors: mssharif@gcu.edu.pk; saeed_a786@hotmail.com

Abstract

A cobalt(II) cocrystal consisting of mononuclear, dinuclear and trinuclear complexes, with the overall composition, $[\text{Co}_{13}(\text{Pydc})_{10}(\text{PydcH})_6(\text{H}_2\text{O})_{24}]\cdot 14\text{H}_2\text{O}$ (**1**) (Pydc^{2-} = Pyridine-2,6-dicarboxylate) has been synthesized and its structure been established by single-crystal X-ray diffraction. The crystal structure of the compound shows that it is an aggregate of seven complexes, including: two mononuclear $\{[\text{Co}(\text{Pydc})(\text{Pydc-H})]^{-}\}$ complexes, four dinuclear species {two of each type, $[\text{Co}_2(\text{Pydc})_2(\text{H}_2\text{O})_5]$ and $[\text{Co}_2(\text{Pydc-H})_2(\text{H}_2\text{O})_5]^{2+}$ } and a trinuclear $\{[\text{Co}_3(\text{Pydc})_4(\text{H}_2\text{O})_4]^{2-}\}$ complex. To unearth the practical electrochemical applications of compound **1**, three and two-electrode assemblies were utilized to construct the cell. Fabrication of a battery device, constituting of Co cluster with activated carbon (AC) demonstrated the specific capacity of 99.3Cg^{-1} , energy density 20.4Whkg^{-1} and power density 825Wkg^{-1} . Dunn's method was employed to distinguish between capacitive and diffusive controlled mechanisms. The capacitive behavior of asymmetric Co//AC cell was enhanced by adding a redox active species, such as $\text{K}_4[\text{Fe}(\text{CN})_6]$, which exhibited the specific capacity of 99.3Cg^{-1} , energy density 35.3Whkg^{-1} and power density 1280Wkg^{-1} . The cyclic stability of 97% was achieved even after 5000 GCD cycles. Depending on the good initial findings of the electrochemical analysis, the electrode qualifies as a promising candidate for an efficient electrode material for ultra-modern reserves of energy application.

Keywords: Cobalt(II), multinuclear cluster, redox active electrolyte, hybrid energy storage.

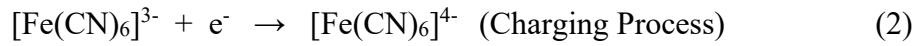
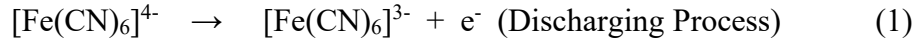
1. Introduction

Transition metal complexes have been explored as promising candidates for energy storage devices due to their high redox activity and excellent electrical conductivity. They are known to possess well-defined composition, good structural stability and redox capacity, fast multi-electron conversion and improved electrochemical conductivity [1-6]. These features grabbed the attention of the scientific community to utilize them in energy storage devices [3-5], in electrocatalysis [6,7] and for magnetic applications [8].

Metal centers play a pivotal role in electrochemical devices as they impact the electrode's charging and discharging efficiency, cycle stability, Li storing characteristics and rate performance [9]. Cobalt-based materials are important in this regard because of the oxidation and reduction characteristics of Co sharp spots, chemical stability and higher redox activity due to various oxidation states of cobalt metal (+1 to +4) and effective faradic reactions [10,11]. Metal complexes, clusters and composites, comprising of cobalt metal offer faster electron transfer rates, lower internal resistance, higher stability, more active sites and high capacitance [12]. Electrocatalysis [13], ferromagnetism [14] and thermopower [15] are just a few of the sectors where significant performance has been shown by the cobalt compounds.

The energy density, power density, rate performance and cyclic stability of an energy storage system is greatly influenced by the effective combination of the right electrode with proper electrolyte. But much attention has not been paid on the selection of electrolytes, which leads to overall low electrochemical efficiency of the energy storage devices [16,17]. Electrolytes modulate the operating potential window, transfer and balance charges between electrodes and, provide ionic conductivity and electrochemical stability. Therefore, electrolytes play a crucial role in determining the electrochemical performance of energy storage devices [18-21]. Bilal *et al.* reported a cobalt pentacyanido(methylaniline)ferrate(II) (CoPCF) complex and determined its best capacitance in various aqueous electrolytes. It was found that CoPCF delivered its best capacitance value at 390 Fg^{-1} in the PVA/KOH gel polymer electrolyte [22]. Electrode-electrolyte compatibility can be optimized to improve the efficiency of supercapacitors [23]. However, the efficiency of various reported supercapacitors could not be improved beyond a certain limit. Unlike aqueous electrolytes, application of electrolytes comprising of additives and redox active species in supercapacitors, is responsible for a wider potential window. To prepare redox additive electrolytes, an optimized concentration of redox active materials (*e.g.*, halide ions, hydroquinone, potassium iodide and $\text{K}_3[\text{Fe}(\text{CN})_6]$) is added to aqueous electrolyte. The redox active species increases the rate of redox reaction occurring at the electrode surface [24-26]. It

is assumed that introducing the redox sensitive compounds, like $K_4[Fe(CN)_6]$ in aqueous electrolytes, produce ionic species ($[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$), because of which the process of electron transfer is catalyzed (eq. 1 & 2).



The redox couple in electrolytes also helps in decreasing important resistance parameters at the electrode surface, *i.e.*, charge transfer resistance and solution resistance [27]. Hence, there is an ongoing search for a suitable redox active electrolyte for enhancing the overall electrochemical performance. The literature studies have shown that application of $K_4[Fe(CN)_6]$ redox additive improved the overall effectiveness of the equipment that helps to preserve energy [26-29].

In the past, some cobalt-based systems have been employed in energy storage devices; for example, Shi et al. synthesized a tertadecanuclear cobalt nanocage cluster as a precursor using cobalt chloride hexahydrate, thiacalix(4)arene and tetrazole by solvothermal method, and used it to fabricate the $CoO/Co_9S_8@CN$ composite. This composite was then coated onto nickel foam ($CoO/Co_9S_8@CN/NF$) and was applied as the electrode material in supercapacitors, which showed a specific capacitance of 303.3 Fg^{-1} and capacity retention of 96.3% after 1000 charge discharge cycles [30]. In another work, cobalt nanoclusters (CoNCs) consisting of cobalt metal and thiol-based ligands namely glutathione (GS), 3-mercaptopropyl sulfonate (MPS) and 3-mercapto propionic acid (MPA) had been reported as the electrode materials for supercapacitor applications. Among them, GS-CoNCs demonstrated superior capacitive behavior with the specific capacitance of 540 F g^{-1} and a capacity retention of 79% after 5000 GCD cycles [31]. Similarly, Nguyen *et al.* synthesized 3D hierarchical cobalt vanadate nano sheet arrays and examined their electrochemical behavior in presence of $K_3[Fe(CN)_6]$. The specific capacitance for supercapacitor assembly came out as 1584 Fg^{-1} at 0.5 Ag^{-1} , whereas the recorded energy and power densities were 55.5 Whkg^{-1} and 800 Wkg^{-1} respectively. After 10,000 cycles, it retained the 82.1% capacitance retention [32]. The present research focuses on highlighting the importance of using a redox active electrolyte ($K_4[Fe(CN)_6]$) in an electrochemical system based on cobalt(II) cluster of pyridine-2,6-dicarboxylic acid.

Herein, we have synthesized a seven-component cobalt(II) cocrystal utilizing pyrdine-2,6-dicarboxylic acid ($PydcH_2$) as a ligand. The co-crystalline cluster having the general formula $[Co_{13}(Pydc)_{10}(PydcH)_6(H_2O)_{24}].14H_2O$ (**1**), contains four types of complexes, which

include: $2\{[\text{Co}(\text{Pydc})(\text{Pydc-H})]^{-}\}$ (**1a** - mononuclear), $2[\text{Co}_2(\text{Pydc})_2(\text{H}_2\text{O})_5]$ (**1b** - dinuclear), $2[\text{Co}_2(\text{Pydc-H})_2(\text{H}_2\text{O})_5]^{2+}$ (**1c** - dinuclear) and $\{[\text{Co}_3(\text{Pydc})_4(\text{H}_2\text{O})_4]^{2-}\}$ (**1d** - trinuclear). The crystal structure of the compound was analyzed by X-ray crystallography and its electrochemical attributes were divulged through two-electrode and three-electrode assemblies in 1M KOH solution. The addition of the redox active electrolyte $\text{K}_4[\text{Fe}(\text{CN})_6]$ (KFCN) enhanced the electrochemical performance of the material. The structure of a quite similar compound $[\text{Co}_{13}(\text{Pydc})_{16}(\text{H}_2\text{O})_{24}] \cdot 7\text{H}_2\text{O}$ has been reported earlier [33], but it seems that the structure was not properly solved because the charges are not fully satisfied. The significant values of specific capacity, energy density, power density and excellent stability advocate the fabrication of the material in futuristic energy storage devices.

2. Experimental

2.1 Materials

Cobalt(II) nitrate hexahydrate, pyridine-2,6-dicarboxylic acid, potassium hydroxide and $\text{K}_4\text{Fe}(\text{CN})_6$ were purchased from Sigma-Aldrich. Activated carbon (AC) was purchased from Alfa Aesar. Nickel foam having specification (1.0 x1.0 cm, China) was first washed and cleaned by 3M HCl, distilled water and ethanol, and then dried overnight in oven at 60 °C.

2.2 Synthesis of cobalt(II)- pyridine-2,6-dicarboxylate multinuclear complex

Cobalt(II) nitrate hexahydrate (87 mg, 0.3 mmol) was dissolved in a 2 mL mixture of MeOH and H_2O (50:50 v/v), while pyridine-2,6-dicarboxylic acid (100 mg, 0.60 mmol) was solvated in 10 mL MeOH. The ligand and metal salt solutions were then mixed and the pH of the resulting mixture was adjusted at 4.0 by addition of 0.1 M NaOH. The mixture was then sonicated (MSE Sanyo, Soni prep 150) for 30 minutes at 15 microns amplitude and frequency of 23 KHz. Violet-red block like crystals were obtained after three weeks. The resultant product was washed with MeOH and air dried. The schematic representation of the synthetic procedure is presented in Figure 1. Elemental analysis, % Calculated (Found) for $\text{C}_{112}\text{H}_{130}\text{N}_{16}\text{O}_{102}\text{Co}_{13}$ (4098.41 g/mol): C, 32.82 (32.70); H, 3.20 (3.12); N, 5.47 (5.32).

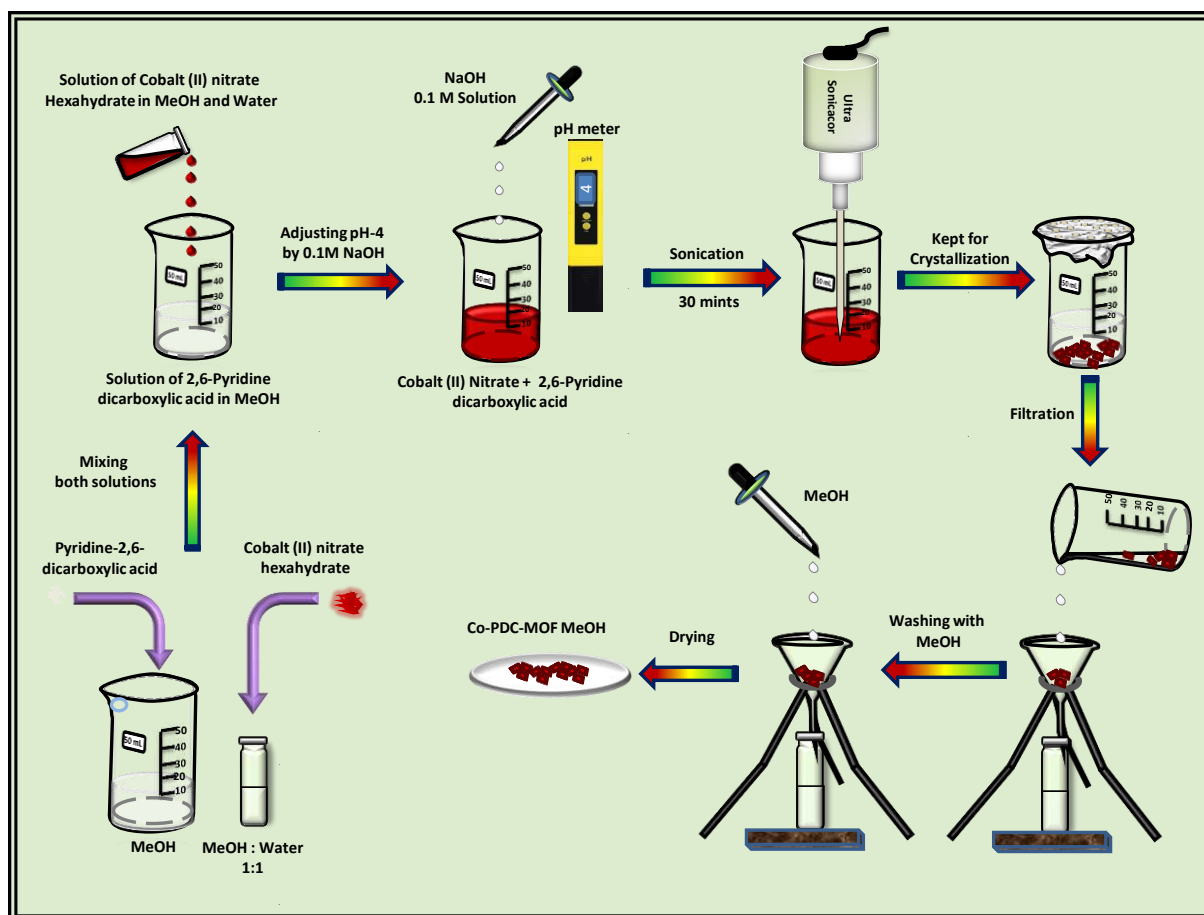


Fig. 1: Schematic diagram for synthesis of the multi-component Co(II) cluster (1)

2.3 X-Ray diffraction analysis

The acquisition of data was carried out using a Bruker diffractometer that was outfitted with a graphite-monochromatic Mo-K α radiation at 296 K, using an appropriate crystal of the complex compound (1). The following measurement methods were employed. Data collection: Bruker APEX2 [34]; solved by direct methods, SHELXS-2013 [35]; refined by full-matrix least-squares techniques, SHELXL-2013 [36]; molecular graphics: MERCURY [37]; solution: WinGX [38]. **Table S1** provides the information on data gathering and crystal structure refinement.

2.4 Electrochemical Tests

A potentiostat/galvanostat (Electrochem Origalys France) was employed to conduct electrical impedance spectroscopy (EIS), galvanostatic charge-discharge (GCD) analysis, and cyclic voltammetry (CV). A three electrodes system of the cell was constituted using the cobalt cluster, **1** (working electrode), Ag/AgCl (reference electrode) and platinum (counter electrode). Compound **1** as active substance (80 wt%) was combined with polyvinylidene

fluoride (PVDF) (10 wt%) and carbon black (10 wt%) in solvent *N*-methylpyrrolidone (NMP). The resultant mixture was stirred for 8 hours before being drop-casted onto active nickel foam having dimensions (1.0 cm × 1.0 cm). It was then evaporated overnight at 60°C. Balancing of the charge and mass is required to get optimal performance of an asymmetric device, which is done through equation 3.

$$\frac{m_+}{m_-} = \frac{C_{s-} \times \Delta V_-}{Q_s} \text{----- (3)}$$

Where, *m* stands for the mass of active material on both electrodes, *Q_s* is specific capacity on negative electrode and ΔV denotes the operating voltage window. The mass acquired for the positive and negative electrodes was around 1:2. Compound **1** was used to represent the positive electrode, while the negative electrode was demonstrated by activated carbon in construction of the asymmetric device, with 0.2 M K₄[Fe(CN)₆] (KFCN) in 1 M KOH as electrolyte. Each electrode was initially stabilized by cycling for 50 times at rate of 50 mVs⁻¹ with potential window of 0 - 1.0 V. In-depth charge storing kinetics was explored for quantitative analysis of pseudocapacitive and diffusion contributions. For this, the power law (equations 4 & 5) can be used to determine the way these two contributions are influenced by CV profiles.

$$i = av^b \text{----- (4)}$$

$$\log(i) = \log(a) + b\log(v) \text{----- (5)}$$

Where, ‘*i*’ is the peak current, ‘*a*’ and ‘*b*’ are variables and ‘*v*’ represents scan rate. The ‘*a*’ and ‘*b*’ values are extracted by fitting the linearity between $\log(i)$ and $\log(v)$. The *b*-value is very important to explain the mass transport character in charge storage mechanism. Dunn’s method to calculate the capacitive and diffusive current contributions is expressed by eq.6 [39] as given below.

$$i(V) = k_1v + k_2v^{1/2} \text{----- (6)}$$

Where, *k₁v* represents capacitive current due to non-Faradaic process and *k₂v^{1/2}* denotes pseudo capacitive current with diffusion-controlled process. Total current contribution for a fixed potential (*V*) is expressed by *i(V)*. A plot of *i/v^{1/2}* against *v^{1/2}* gives the value comprising constant parameters through slope and intercepts (*k₁* and *k₂* respectively). The Specific capacitance (*C_s*, Fg⁻¹), specific capacity (*Q_s*, Cg⁻¹), energy density (*E*, Whkg⁻¹) and specific power density (*P*, Wkg⁻¹) can be evaluated from GCD analysis by utilizing the equations 7-11 [40,41].

$$Cs = \frac{I \times \Delta t}{\Delta V \times m} \text{ --- (7)}$$

$$Qs = \frac{I \times \Delta t}{m} \text{ --- (8)}$$

$$E = \frac{Cs \times \Delta V^2}{2 \times 3.6} \text{ --- (9)}$$

$$E = \frac{Qs \times \Delta V}{2 \times 3.6} \text{ --- (10)}$$

$$P = \frac{E \times 3600}{t_d} \text{ --- (11)}$$

Where, ΔV is potential drop at a specific current density (I/m) and Δt is the time for discharge.

3. Results and discussion

3.1. Synthesis and IR Spectroscopy

The new multi-component cobalt(II) compound (**1**) was prepared by a direct reaction between $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and pyridine-2,6-dicarboxylic acid (PydcH_2) at pH 4 using sonication method. The deprotonation of ligand and its coordination modes with the metal ion highly depend on the pH value. Too low pH will affect the synthesis of complexes due to lack of deprotonation, while the very high pH will not only deprotonate the ligand quickly resulting in low yield but it may also lead to formation of $\text{M}(\text{OH})_2$. So, adjusting pH according to the choice of ligand and its donor sites is important for crystallization growth and optimum yield. The product was air dried, as the air drying is a gentle process in which minimal rise in temperature causes no damage to the product. The composition of the product was established by elemental analysis and the crystal structure was measured by X-ray crystallography.

The IR spectrum of compound **1** is displayed in **Fig. S1**. It shows a broad band at 3135 cm^{-1} due to $\nu(\text{O-H})$ vibrations of water molecules and Pydc-H ligands. It also covers the C-H stretching vibrations of Pydc groups. The absorptions at 1545 and 1366 cm^{-1} are attributed to the asymmetric and symmetric stretching of carboxyl groups, respectively. They appear at lower energy as compared to that in the free ligand (1688 , and 1375 cm^{-1} , respectively). A decrease in frequency of these bands indicates the binding of ligand to the metal. The medium intensity bands at 1494 and 1424 cm^{-1} represent the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibrations respectively. The peaks at 1289 and 1135 cm^{-1} are related to $\nu(\text{C-O})$ vibrations. The weak band at 445 cm^{-1} marks the Co-O vibration providing a clear evidence of metal-ligand binding.

3.2. Structural characterization

The crystal structure determination of the prepared cobalt(II) complex of pyridine-2,6-dicarboxylic acid revealed that it crystallized as an aggregate of seven $\text{Co}(\text{II})$ complexes along with fourteen non-coordinated water molecules, the overall formula being, $[\text{Co}_{13}(\text{Pydc})_{10}(\text{PydcH})_6(\text{H}_2\text{O})_{24}].14\text{H}_2\text{O}$ (**1**). The molecular structure of the cocrystal showing the four types of component species is presented in Figure 2. The selected bond lengths and angles are presented in **Table S2**. The cluster **1** is composed of seven $\text{Co}(\text{II})$ complex entities with different nuclearity. There are two identical mononuclear complexes $\{[\text{Co}(\text{Pydc})(\text{PydcH})]^{-}\}$ (**1a**) comprising of Co5 atoms. The pairs of Co1 and Co2 as well as Co6 and Co7 atoms form four dinuclear units, with two of each type; $[\text{Co}_2(\text{Pydc})_2(\text{H}_2\text{O})_5]$ (**1b**) and $\{[\text{Co}_2(\text{PydcH})_2(\text{H}_2\text{O})_5]^{2+}\}$ (**1c**) respectively. In the fourth case, two Co3 and one Co4 atoms form a

trinuclear complex $\{[\text{Co}_3(\text{Pydc})_4(\text{H}_2\text{O})_4]^{2-}\}$ (**1d**). Six of the sixteen Pydc ligands are mono-protonated, while the rest of them bind in the dicarboxylate dianion form. The Pydc ligands adopt the chelating and μ_2 -bridging coordination modes. The Co(II) ions possess three types of coordinated spheres. In the first kind, four oxygen atoms along with two nitrogen atoms from pyridine-2,6-dicarboxylate ligands are coordinated to Co1 (**1b**), Co3 (**1d**), Co5 (**1a**) or Co6 (**1c**) atoms (Figure 2). In the second coordination sphere, the Co2 (**1b**) and Co7 (**1c**) atoms are bound to one oxygen atom from carboxylic group and five oxygen atoms from coordinated water molecules. In the third type of environment, the Co4 (**1d**) atom is coordinated by four oxygen atoms from associated water molecules and two oxygen atoms of carboxylic groups. In each case, Co(II) ion exhibits a distorted octahedral coordination geometry as reflected by the bond angles around cobalt (**Table S2**). The Co-N and Co-O bond distances are comparable to the values reported for the other cobalt(II) complexes of pyridine-2,6-dicarboxylic acid [7,33,42-51].

The structural features of these species are very similar to the related structures of the cobalt(II) complexes of pyridine-2,6-dicarboxylic acid [7,33,42-51]. One of these complexes, $[\text{Co}_{13}(\text{Pydc})_{16}(\text{H}_2\text{O})_{24}] \cdot 7\text{H}_2\text{O}$ is analogous to compound **1**, but in that the numbers of protonated and deprotonated Pydc ligands have not been indicated. Therefore, the charges are not fully satisfied [33]. Most of the other known complexes exist in the mononuclear form as $[\text{diaminium}][\text{Co}(\text{Pydc})_2]$ [42-48]. In one case, a dinuclear complex $\{[\text{Co}(\text{H}_2\text{O})_5][\text{Co}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}\}$ has been reported [49]. In two complexes; $\{(\text{Pyridine-H})[\text{Co}(\text{Pydc})(\text{Pydc-H})] \cdot (\text{PydcH}_2) \cdot (\text{H}_2\text{O})\}_n$ [7] and $(\text{Phenylhydrazinium})[\text{Co}(\text{Pydc})(\text{Pydc-H})] \cdot (\text{Pydc-H}_2) \cdot 3\text{H}_2\text{O}$ [50], the cobalt(II) cation is coordinated to one pyridine-2,6-dicarboxylate dianion and one hydrogen pyridine-2,6-dicarboxylate ion. Among these, $[\text{Co}(\text{Pydc})(\text{PydcH}_2)] \cdot 3\text{H}_2\text{O}$ represents the rare example, where the acid is coordinated to the metal ion in the neutral form (PydcH_2) [51]. In all these complexes, cobalt centers are bound to pyridine-2,6-dicarboxylate anions in a tridentate manner assuming a distorted octahedral coordination environment formed by four oxygen atoms and two nitrogen atoms. Complex **1** is isostructural to the corresponding iron(II) complex, $[\text{Fe}_{13}(\text{Pydc})_{10}(\text{PydcH})_6(\text{H}_2\text{O})_{24}] \cdot 13\text{H}_2\text{O}$ [52].

Within the crystal structure of **1**, the C-H $\cdots$ O and O-H $\cdots$ O hydrogen-bonding interactions are present. They involve C-H and O-H groups of Pydc ligands and water molecules. The specifics of these interactions have been presented in **Table S3**. The hydrogen bonding interactions lead to the formation of a three-dimensional supramolecular structure as shown in Fig. 3.

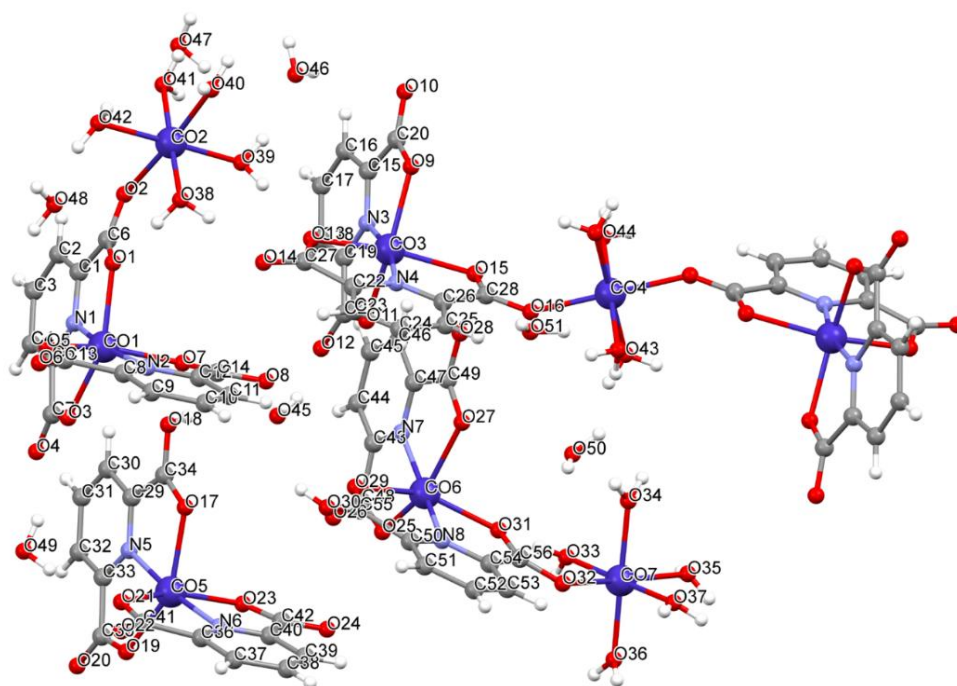


Fig. 2. The molecular structure of the cobalt(II) cocrystal (1) showing four different complexes, along with atomic numbering scheme

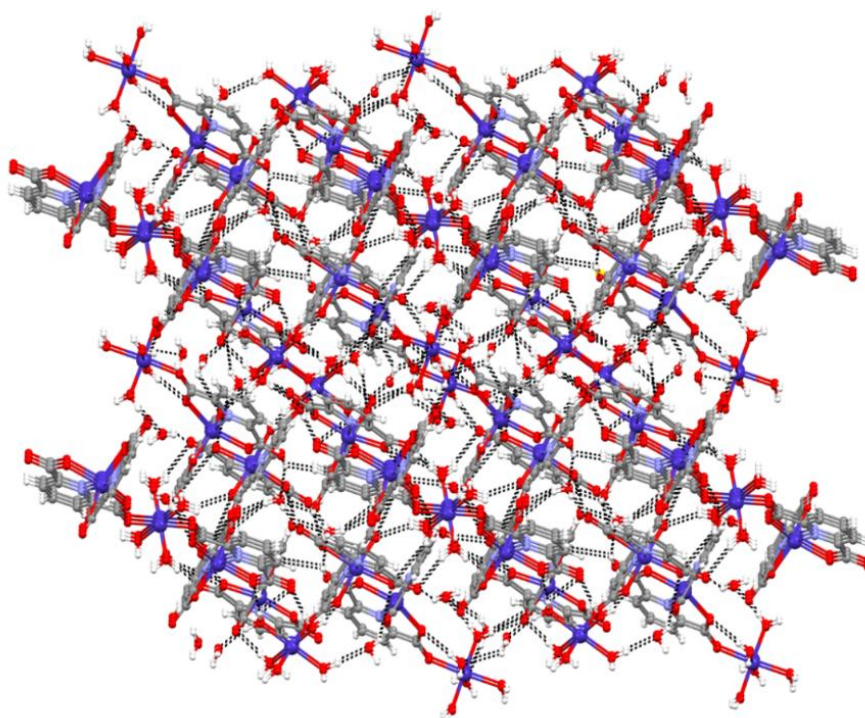


Fig. 3. An infinite 3D supramolecular network in the Co(II) compound 1

3.3. Electrochemical characterization

3.3.1 Half-cell electrochemical analysis

3.3.1.1 Cyclic Voltammetry

The general electrochemical behavior of the synthesized compound was evaluated by cyclic voltammetry in the potential window of 0 to 0.7 V and the scan rates were taken as 3, 5, 10, 20, 30 40, and 50 mV s⁻¹ (Fig. 4A). At all scan rates, the curves exhibited the positive and negative regions representing the dual electron transport process involving the redox active centers within the complexes. The well-defined pair of oxidation and reduction peaks rise with current density and can be assigned to Co⁺²/Co⁺³ pair;



The intercalation and reverse intercalation of cobalt ions happened at working electrode interface as cobalt changed to Co⁺³ during oxidation and it converted back into Co⁺² during reduction indicating reversibility of the compound (**1**). As the scan rate increases, a little change in the maximum potential can be observed in the voltammogram that may be assigned to slow rate of OH⁻ ions' diffusion into electrode material. To further confirm the faradaic nature of **1**, a theoretical analysis was employed in which peak current was plotted against square root of various scan rates. The reversibility of the synthesized material can be confirmed by Randles Sevcik equation (12);

$$I_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} \nu^{1/2} \dots\dots (12)$$

where I_p = the peak current, n = the number of electrons transferred, A = the electrode surface area, C = the concentration of redox active species, e.g., [Fe(CN)₆]^{3-/4-}, D = the diffusion coefficient and ν = the scan rate.

For reversible reaction, peak current (I_p) remains directly proportional to square root of scan rate ($\nu^{1/2}$). Deviation from the linearity is related to complication in the electron transfer kinetics, which is indicative of a homogeneous reaction. Moreover, for reversibility, electron transfer should be fast enough to keep the current function ($I_{p,c}$) constant at all the scan rates so that the equilibrium ratio between the reduced and oxidized ions in a redox couple is maintained. In our case, a straight relationship was observed with a value of regression factor (R^2) 0.99 for oxidation and 0.98 for reduction (Fig. 4B). The R^2 value closer to 1 indicates the excellent reversibility of the synthesized material [53].

The b-value is very useful to distinguish between capacitive and diffusive controlled reactions. The b-value closer to 1, indicates a capacitive process dominated system that involves surface adsorbed electroactive species. On contrary, if the b-value falls around 0.5, it represents a diffusion-controlled process for battery. The value of b in the present system (based on **1**) is 0.56 & 0.64 for oxidation and reduction reactions respectively, which means that a finite diffusion process is happening involving adsorption, desorption or redox reactions. These results indicate that the electrode is redox dominant pseudo capacitive in nature confirming battery-grade material (Fig. 4C).

Kinetic investigation of each mechanism has proven to be very effective to distinguish the total current response quantitatively. Percentage containing the capacitive and diffusive contribution for reduction as well as oxidation occurring at working electrode with different scan rate (3-50 mVs⁻¹) has been shown in Fig. 4D. As the scan rate becomes higher, the capacitive contribution increases from 9% to 28% and the corresponding decrease in the diffusion contribution was observed from 91% to 72%. Moreover, at a scan rate of 3 mVs⁻¹, the percentage contribution of capacitive current is very low as compared to diffusive current with respect to the total current studied (Fig. 4E). It means that at the lower scan rate, sufficient time is given to positive electrode in order to complete the redox reaction whereas in overall device capacity, the diffusive contribution is larger. On the other hand, at a high scan rate, the negative electrode spends the sufficient time for physical adsorption of the charges at interface of electrode and electrolyte. The results demonstrated that the biggest part of total current was dominated by Faradaic process, which came out as 91% whereas percentage of the current contributed by the Electrode Double Layer Capacitor, EDLC (non-Faradaic) was close to 9%. This also strengthens the claim that the synthesized device possesses the features of both a battery and a super capacitor [54]. The specific capacity of the three-electrode system involving complex compound **1** in Cg⁻¹ can be calculated by CV. For different scan rates (3 to 50 mVs⁻¹), the area under the curve was measured, which was divided by the product of scan rate and active mass. The specific capacity for scan rate of 3 mVs⁻¹ was 80 Cg⁻¹ that decreased to 26.90 Cg⁻¹ till 50 mVs⁻¹ scan rate due to the OH⁻ ions slow transit time over the electrode components. The graph of specific capacity against scan rate 3-50 mVs⁻¹ is depicted in Fig. 4F.

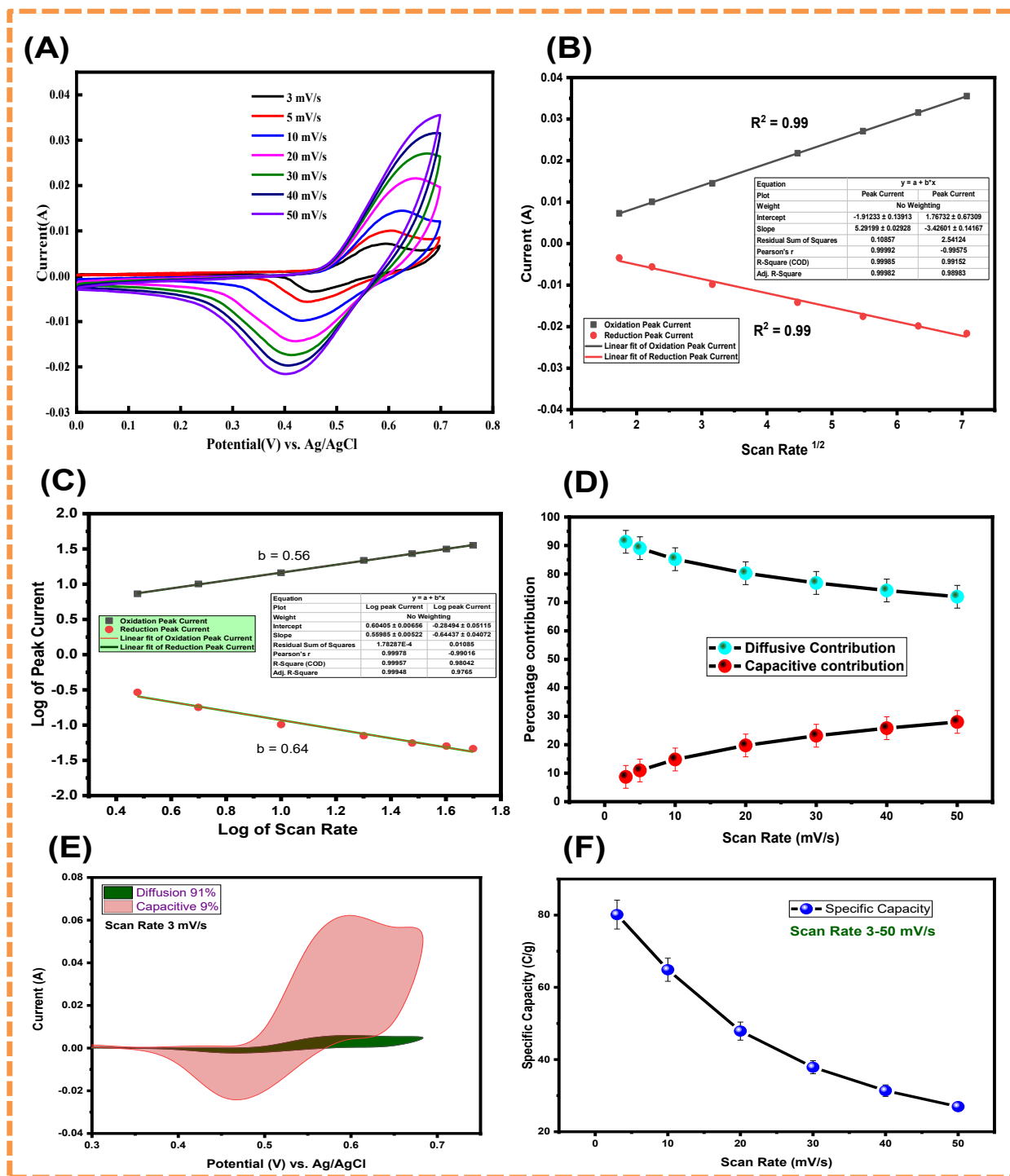


Fig.4. (A) The cyclic voltammograms of cluster 1 at various scan rates (B) Linear fitted graph between peak current and $(\text{scan rate})^{1/2}$ (C) b-value of cluster 1 (D & E) The percentage of diffusive and capacitive contribution at various scan rates (F) Specific capacity trend as scan rate increases.

3.3.1.2. The Galvanostatic Charge-Discharge (GCD) Analysis

GCD of the cobalt cluster (**1**) was studied at 0.6 V with different current densities (0.3 to 3.0 A/g). Maximum discharge time (237 s) was observed at a current density of 0.3 Ag⁻¹ (Fig. 5A). The Qs was calculated from GCD at variable current density ranging between 0.3 to 3.0 Ag⁻¹. A plot of specific capacity against current density (Fig. 5B) showed a decrease in the specific capacity as the current density increased. The maximum value of specific capacity 71.1 Cg⁻¹ was found at a current density of 0.3 Ag⁻¹, which decreased to 45 Cg⁻¹ at a current density of 3.0 Ag⁻¹. The highest specific capacitance was calculated as 118.5 Fg⁻¹ (Fig.5C).

3.3.1.3. Electrochemical Impedance Spectroscopy (EIS)

The EIS studies helped to examine the associated mechanism occurring on the surface of electrode. A straight line from intersection point on real axis in the area of greater frequency speaks about the electrolytic ionic resistance, inherent characteristics of the active material as well as the contact resistance between it and the current collector. The low-frequency semicircle corresponds to charge transfer resistance due to Faradaic responses at the junction of the electrode and the electrolyte. The Electrochemical impedance spectrum of Co-Pydc cocrystal (**1**) displayed in Fig. 5D reflects that the solution resistance (Rs) is close to zero. Additionally, transfer resistance at minimum charge (Rct) is indicated by an insignificant semicircle in the high frequency area. At lower frequencies, the straight line symbolizes Warburg impedance associated with diffusion-controlled process occurring at the electrode-electrolyte interface.

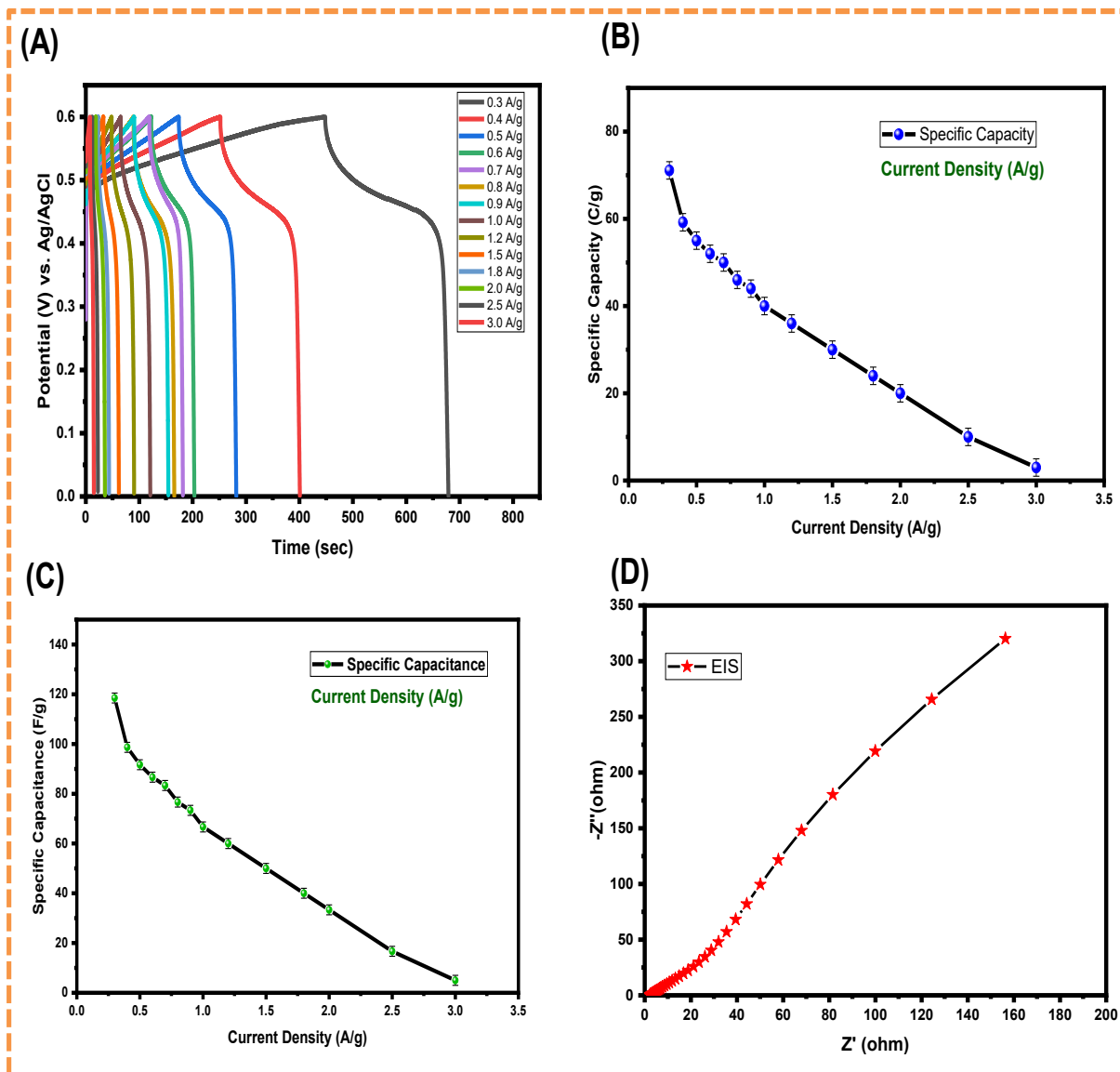


Fig.5. (A) GCD graph of the Co cluster (1) at various current densities (B) Specific capacity and (C) specific capacitance pattern in relation to the current density (D) EIS of 1.

3.3.2. Battery-supercapacitor hybrid assembly

A hybrid supercapacitor was fabricated to validate the practical applications of the multicomponent cobalt cluster (**1**). As prepared electrode of **1** served as a cathode whereas activated carbon (AC) behaved as the negative electrode (Fig. 6A). Operating window of AC was -1.0 V to 0V and cluster **1** worked efficiently between 0V to 0.3V (Fig. 6B). The cyclic voltammograms of **1**//AC was performed with potential window of 0V to 1.6V by increasing scan rate from 5mVs⁻¹ to 40mVs⁻¹ which reflected the hybrid nature of the device (Fig. 6C). Dunn's method was employed to determine the capacitive as well as diffusive controlled contribution of **1**//AC. At scan rate of 10 mVs⁻¹, the capacitive contribution was close to 30.7%. However, with increasing scan rate the capacitive contribution enhanced to 46.9% (Fig. 6D).

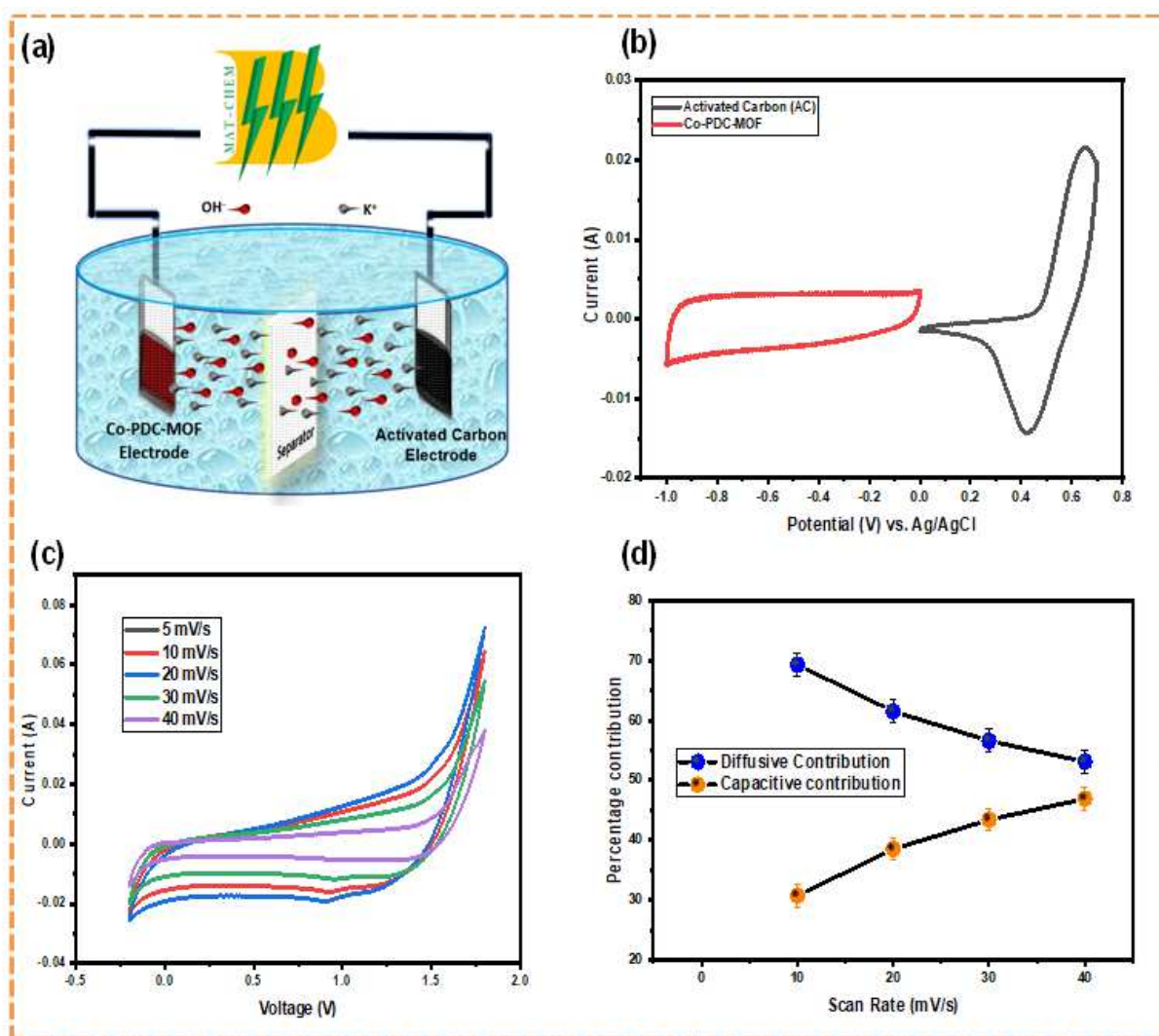


Fig.6. (A) Cluster 1//AC mechanism of electrolyte and ions **(B)** CV pattern of 1 and activated carbon (AC)**(C)** CV graph of 1 at scan rates (10,20,30,40 mVs^{-1}) **(D)** Capacitive-Diffusive percentage pattern.

The power and energy densities are the two important parameters to adjudge the performance of a hybrid device. GCD curves were obtained at different scan rates (1 to 4 Ag^{-1}) as shown in Fig.7b. The specific capacity calculated from GCD came out as 89 Cg^{-1} at a current density of 1 Ag^{-1} , which decreased to 22 Cg^{-1} at a current density of 3 Ag^{-1} (Fig.7c). The energy and power densities were calculated as 20.4 Whkg^{-1} and 825 Wkg^{-1} respectively.

EIS technique helped to analyze the conductivity of the asymmetric device. EIS spectrum confirmed the equivalent series resistance (ESR) of 2.55 Ω , whereas the charge transfer resistance (R_{ct}) was close to 18.4 Ω . The results showed that **1**//AC is suitable for its application as a hybrid device. The experimental and fitting curves with circuit diagram, percent error and chi-squared value are provided in **Fig. S2** and **Table S4**.

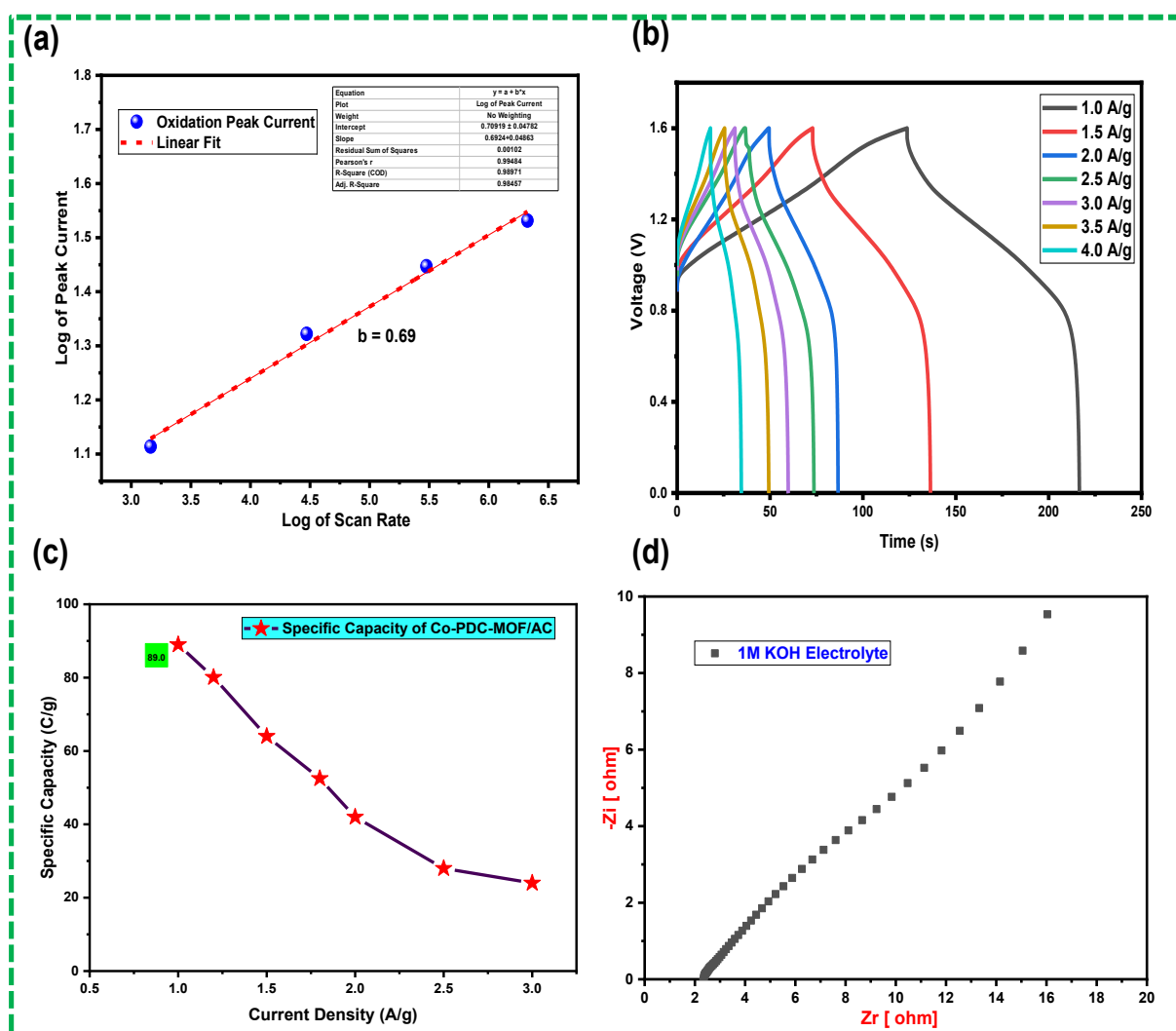


Fig.7. (a) 1//AC b value graph(b) GCD graph of 1//AC with current density (1-4 Ag^{-1})(c) Specific Capacity pattern of **1 and AC(d) EIS pattern of 1//AC in 1M KOH.**

3.3.2.1 Effect of Additive $K_4[Fe(CN)_6]$ (KFCN)

The pseudo capacitance of pseudo capacitors may be increased by adding the redox additives to the electrolyte [26-29]. For example, Su *et al*, noted that the addition of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ into the KOH solution improved the capacitive performance of the Co-Al layered double hydroxide (LDH) electrodes. The Co-Al LDH using combined KOH/ $K_3Fe(CN)_6$ or KOH/ $K_4Fe(CN)_6$ electrolytes at a current density of 2 Ag^{-1} , demonstrated the enhanced capacitances by 712 and 317 Fg^{-1} respectively, which was larger compared to the solution of KOH alone (226 Fg^{-1}). The rise in capacitance is explained by acquisition and disposition of electrons by Co(II/III) ions, while charging and discharging are promoted by $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ [28]. For the hybrid supercapacitor of **1**, CV was run at different scan rates of 10, 20, 30, 40, 50 mVs^{-1} (Fig. 8A). From the CV, the specific capacity was computed as 99.3 Cg^{-1} with KFCN. However, for the assembly of **1**//AC alone, it was 73.3 Cg^{-1} at scan rate of 10 mVs^{-1} . Fig. 8B represents the current-potential graph at a scan rate of 50 mVs^{-1} with and without KFCN. A comparison for Q_s with and without KFCN is shown in Fig. 8C.

GCD was performed at various current densities ranging from 1 to 4 Ag^{-1} (Fig. 8D), which showed enhancement in the capacitive nature due to KFCN in KOH electrolyte. The EIS spectra of cobalt crystal (**1**) electrode with and without KFCN (Fig. 8E) indicated the “charge transfer mechanism” and that the charge transfer resistance (R_{ct}) falls across all the potential values. With the addition of additive KFCN, the value of peak current became higher. This is due to fact that the time for discharge remains the same or slightly shorter than the charge time. But when the KFCN is added in the 1 M KOH electrolyte solution, the peak current abruptly increased. Being associated with Warburg impedance, as KFCN was introduced to the electrolyte, the conductivity of ions somewhat increases leading to a rapid mass transfer. The solution resistance (R_s) decreased to 1.83Ω with KFCN as compared to 2.343Ω without KFCN. Moreover, the charge transfer resistance (R_{ct}) improved to 2.73Ω from 18.23Ω . In simpler terms, the addition of KFCN alters the electrolyte's conducting mechanism. **Table 2** shows the values of different parameters of EIS. The experimental and fitting curves with circuit diagram, percent error and chi-squared value are also provided in **Fig. S3** and **Table S5**. The stability of the device was determined by 5000 GCD cycles, which showed cyclic stability of 97% (Fig. 8F). The energy and power densities were calculated as 35.3 Whkg^{-1} and 1280 Wkg^{-1} respectively. A comparison of different values of Energy Density, Power Density and Specific Capacity of cluster **1** in the absence and in the presence of KFCN is provided in **Table 3**. The enhanced performance of cluster **1** may be attributed to the presence of multi-components (metal centers) with in the product.

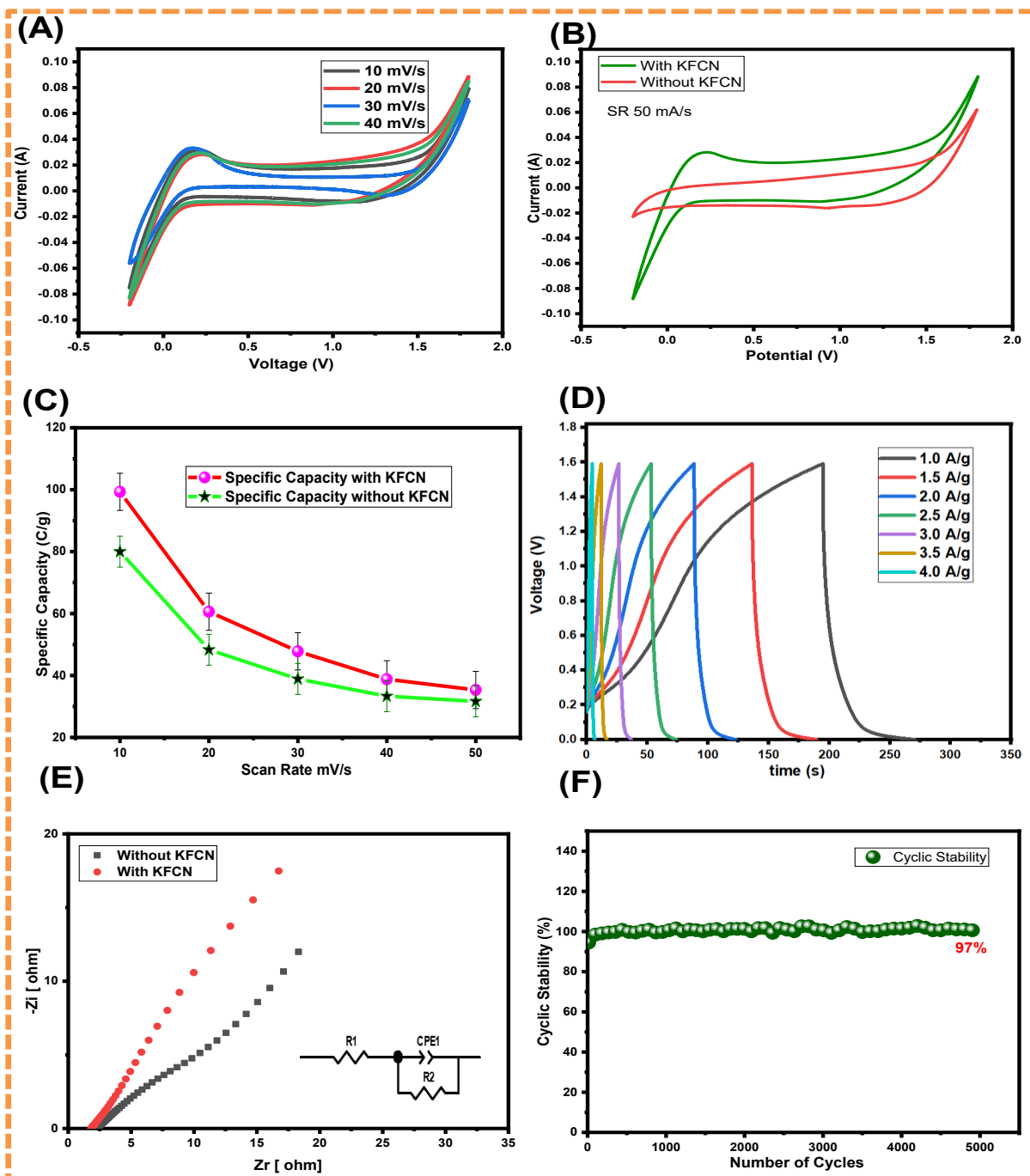


Fig. 8. (A) CV Graph of cluster 1 electrode in 1M KOH+0.2M KFCN (B) Graph of current-potential at scan rate 50 mAs^{-1} with and without KFCN (C) Specific capacity pattern at scan rate (10-50 mVs^{-1}) with and without KFCN (D) GCD plot of electrode at range of current density (1-4 Ag^{-1}) (E) Nyquist impedance plot of the electrode in KOH electrolyte with and without KFCN (F) Cyclic performance of electrode with 5000 range of cycles.

Table 2. Impedance parameters for three electrodes and two electrodes system.

Electrode	Electrode System	R ₁ (R _s) Solution Resistance (Ω)	R ₂ (R _{ct}) Charge Transfer (Ω)
Co7 (1)	3-Electrode System	4.271	4.462
Co7//AC	2-Electrode System	2.343	18.238
Co7//KFCN	2-Electrode System	1.832	2.734

Table 3. A comparison of Energy Density, Power Density and Specific Capacity of Co Cluster (1) in the absence and presence of KFCN

Material	Energy Density Wh/kg	Power Density W/kg	Specific Capacity Cg ⁻¹
Co-Cluster (1) without KFCN	20.4	825	89.0
Co-Cluster (1) with KFCN	35.3	1280	99.3

4. Conclusions

In the current work, we have reported the synthesis and X-ray structure of a unique multicomponent cobalt(II) cocrystal based on pyridine-2,6-dicarboxylic acid (PydcH₂). With the overall composition of [Co₁₃(Pydc)₁₀(PydcH)₆(H₂O)₂₄].14H₂O (**1**), the cluster comprises of seven Co(II) complexes: 2{[Co(Pydc)(Pydc-H)]⁻} (**1a**), 2[Co₂(Pydc)₂(H₂O)₅] (**1b**), 2{[Co₂(Pydc-H)₂(H₂O)₅]²⁺} (**1c**) and {[Co₃(Pydc)₄(H₂O)₄]²⁻} (**1d**). The electrochemical characteristics of cluster **1** were explored with the help of potentiostat, CV, GCD as well as EIS techniques, employing the three electrode and two electrode assemblies in 1M KOH electrolyte. The GCD data of **1**//AC exhibited the specific capacity of 89 Cg⁻¹, energy density of 20.4 WhKg⁻¹ and power density of 825 Wkg⁻¹ at the current density of 1 Ag⁻¹. In the presence of KFCN as an electroactive additive, the electrochemical activity was found to increase leading to the improvement in specific capacity (99.3 Cg⁻¹), energy density (35.3 Whkg⁻¹) and power density (1280 Wkg⁻¹) with extraordinary cyclic stability of 97% even after 5000GCD cycles. Upon analyzing the electrochemical attributes, like power density and

energy density in the absence and presence of KFCN, it is concluded that the electroactive additive played a vital role in enhancing the electrochemical properties of the hybrid device. This prospective study demonstrates the significant promise for creating a battery type supercapacitor having high power density and energy density with stable cycling over time. As a whole, this study offers implications for employing the additional redox-active materials to increase the power density of the hybrid supercapacitors.

List of abbreviation

Cyclic Voltammetry (CV), Galvanostatic charge-discharge (GCD), Electrochemical Impedance Spectroscopy (EIS), pyridine-2,6-dicarboxylic acid (PydcH₂), Supercapacitors (SCs), Electric vehicles (EVs), Methanol (MeOH), Electrode Double Layer Capacitor (EDLC), Nickel Foam (NF).

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2225000. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>

Supplementary information

Supplementary file contains single-crystal data and other information.

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