Development of a Cu-MOF Based Pseudocapacitor Diode with Enhanced Rectification and Charge Storage Performance

M.Tech. Thesis

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Submitted in partial fulfillment of the
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DEPARTMENT OF METALLURGICAL
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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DEVELOPMENT OF A CU-MOF BASED PSEUDOCAPACITOR DIODE WITH ENHANCED RECTIFICATION AND CHARGE STORAGE PERFORMANCE** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2023 to May 2025 under the supervision of **Dr. Dhirendra Kumar Rai, Associate Professor, IIT Indore.**

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Goswami
23/5/25

Signature of the student with date
(SOURABH GOSWAMI)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of the Supervisor of
M.Tech. thesis (with date)
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SOURABH GOSWAMI has successfully given his M.Tech. Oral Examination held on **May 22, 2025.**

Signature of Supervisor of M.Tech. thesis
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Abstract

This work explores the potential of a two-dimensional Copper(II) metal-organic framework (Cu-MOF), synthesized from 2,5-pyridinedicarboxylic acid and cupric nitrate trihydrate, as a pseudocapacitor diode (CAPode) for iontronic logic applications. Three-electrode measurements of the MOF showed stable rectification performance over 1000 cycles despite a drop in overall capacity to 52% of its original value, thus providing the robustness of its ion-selective mechanism. For device evaluation, the Cu-MOF with its redox-active copper sites, was used as the working electrode alongside activated carbon (AC) as the counter electrode in an aqueous 3 M KOH electrolyte. Under forward bias, the device showed strong Faradaic charge storage due to the oxidation of Cu^0 to Cu^{2+} and intercalation of OH^- ions on the Cu-MOF, while reverse bias was effectively inhibited because of ion-sieving ability and electrostatic repulsion of K^+ ions, showing strong rectification behavior. Electrochemical measurements indicated a specific capacity of 15 C/g and rectification ratios (RR_I: 3.99-4.29; RR_{II} 1.62-1.69) comparable to or better than those reported in previously available carbon- and transition-metal-oxide-based CAPodes. Further, the device was successfully operated as an ionic diode in logic circuits by demonstrating Boolean logic in AND and OR gate functions with clear voltage differentiation, though minor capacitive coupling phenomena was observed. These findings show the potential of coordination polymers like MOFs in facilitating the integration of energy storage with iontronics systems, and show a promising platform for future ionic computing and multifunctional applications.

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Table 2 Boolean logic of AND Gate

NOMENCLATURE

Cu	Copper
K^+	Potassium ion
OH^-	Hydroxide ion
M	Molar
C/g	Coulomb per gram
I	Current
t	Time
m	Mass
V	Volt
υ	Scan Rate
C	Specific Capacity

ACRONYMS

CAPode	Pseudocapacitor Diode
MOF	Metal Organic Framework
PDC	Pyridinedicarboxylic acid
RR	Rectification Ratio
EDLC	Electric Double Layer Capacitor
2D	Two Dimensional
XRD	X-Ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
CV	Cyclic Voltammetry
GCD	Galvanostatic Charge Discharge
AC	Activated Carbon

Chapter 1

Introduction

1.1. Introduction

Supercapacitors are advanced energy storage device that store energy either by physically adsorbing electrolyte ions on the porous surface of its electrodes (known as electrical double-layer capacitors) or through reversible redox reactions on its electrode-electrolyte interface (known as pseudo-capacitors). Supercapacitors typically have lower energy density compared to batteries, but they are excellent at delivering power quickly and supports rapid charge-discharge cycles [1]. They are widely studied and find significant importance in applications requiring instant charge transfer and long cycle life, such as power supply for electronic devices, regenerative braking in electric vehicles, start-up assist for engines and so on [2].

To broaden the scope of supercapacitor applications, researchers are not only working on boosting their energy density, which remains their main drawback, but are also developing multifunctional supercapacitors. These advanced devices are designed to combine energy storage with added functionalities such as logic operations, brain-machine interfaces, energy storage chips etc [3]. By merging multiple features into a single device, researchers aim to create efficient solutions for next generation electronic devices.

Supercapacitor-diode (CAPode), a new concept first proposed by Kaskel et. al. in 2019, combines the properties of an ionic diode into an electric double-layer capacitor (EDLC) [4]. A new asymmetric capacitor concept is proposed providing high energy storage capacity for only one charging direction. Size-selective microporous carbons ($w < 0.9$ nm) with narrow pore size distribution are demonstrated to exclusively electrosorb small anions (BF_4^-) but size-exclude larger cations (TBA+ or TPA+), while the counter electrode, an ordered mesoporous carbon (w > 2 nm), gives access to both ions. This architecture exclusively charges in one direction with high rectification ratios (RR = 12), representing a novel capacitive analogue of semiconductor-based diodes (“CAPode”). By precise pore size control of microporous carbons (0.6 nm, 0.8 nm and 1.0 nm) combined with an ordered mesoporous counter electrode (CMK-3, 4.8 nm) electrolyte cation sieving and unidirectional charging is demonstrated by analyzing the device charge-discharge response and monitoring individual electrodes of the device via in situ NMR spectroscopy. By pore-size engineering of carbon electrodes and ion-sieving effects of electrolyte, the CAPode achieved high energy storage capacity with unidirectional charging behaviour. Further investigation was carried out by Yan et. al. in which two types of CAPodes with tunable bias directions was successfully developed by utilizing polyanionic and polycationic electrolyte, where the polymeric ions are large and the counter ions are small [5]. The same group later reported a redox-based CAPode using spinel ZnCo2O4 in aqueous electrolyte, that stores charge through Faradaic reaction at the electrode/electrolyte interface and unidirectional charging is realized through ion-selective surface redox effect of spinel ZnCo2O4 in aqueous KOH electrolyte [6]. Recently, Kaskel et. al. in 2024, presented a new hybrid CAPode based on ion-selective surface redox response. The device employs nickel bismuth sulfide ($Ni_3Bi_2S_2$), grown directly on a nickel substrate as a battery-like working electrode, while activated carbon (AC) serves as the EDLC-like counter electrode in an aqueous KOH electrolyte [7]. The new structure has remarkably improved rectification ratios and greater cycling stability compared to earlier redox-type CAPodes. The device leverages ion-selective transport processes and redox chemistry to facilitate high-level energy storage and conversion, thereby enabling seamless integration with various energy electronics technologies. Operando electrochemical analysis clarifies the working mechanisms, and the effective blocking characteristic of the device facilitate successful integration into logic circuits (AND, OR), signifying its viability for ionologic applications.

Alongside these advancements, the field has also seen increased diversification. For example, CAPodes based on commercial nickel foam offer and inexpensive and readily producible alternatives with excellent rectification and long-duration charge storage, again through selective redox reactions of OH^- ions in alkaline environments [8]. Another significant development is the supercapattery-diode, where battery-type layered double hydroxide (LDH) nanosheets are coupled with AC to offer high energy density and excellent rectification, further expanding the concept of CAPode to new material platforms and applications [9].

Together, these developments capture the rapidity of evolution of ionic diodes technology- ranging from pore-size engineering and ion-sieving in carbon electrodes to redox-active and battery-like electrodes with tunable directionality and logic functionality- positioning CAPodes on a versatile platform for next-generation energy storage, rectification and iontronics logic devices.

In this work, we explore the potential of coordination polymers as ion-selective electrodes for CAPodes by synthesizing a 2D Cu(II) coordination polymer (2D-CuPDC) derived from pyridinedicarboxylic acid [10]. Leveraging its unique structural features- including a distorted square pyramidal geometry at Cu centres, layered plane propagation, and thermally stable porous networks, we employed 2D-CuPDC as the working electrode alongside activated carbon (AC) in an aqueous 3M KOH electrolyte to construct a CAPode. The device demonstrated a specific capacity of 15 C/g and a rectification ratio (RR_I) of 3.99-4.29 and (RR_{II}) 1.62-1.69 at various scan rates, demonstrating comparable results with earlier systems such as microporous carbon-based ($RR_I \approx 9$ and $RR_{II} \approx 0.9$) [4] and $ZnCo_2O_4$ pseudocapacitive diodes ($RR_I \approx 7.3$-14.6 and $RR_{II} \approx 0.71$-0.89) [6]. The rectification arises from 2D-CuPDC's ion-sieving effects of charge-selective anion and cation (K^+) intercalation via its Cu-center during redox processes. This work highlights the promise of coordination polymers in bridging the ionic and electronic functionalities of CAPodes while achieving simultaneous energy storage and rectification, paving the way for ionic diodes in MOF-based systems.

1.2. Literature Review

The emergence of pseudocapacitor diodes (CAPodes) is a significant advancement in the field of energy storage technology because it combines the rectification properties of ionic diodes with the high-power density of supercapacitors. This literature reviews significant advances in CAPode research, with emphasis on basic design concepts, novel materials, performance parameters, and potential applications.

The concept of CAPodes was initially demonstrated in 2019 using porous carbon electrodes with carefully controlled pore sizes to enable ion-selective transport. Kaskel et al. synthesized a CAPode mimicking an electric double-layer capacitor (EDLC) by using microporous carbon (pore size 0.87 nm) and mesoporous carbon (pore size 4.8 nm) with a tetrabutylammonium tetrafluoroborate ($TBABF_4$) electrolyte solution [4]. The pore size asymmetry enabled one-way ion transport, leading to a rectification ratio (RRI) of 12 and specific capacitance of 70 F/g. The process, however, required pore size engineering and the use of organic electrolytes, thus preventing scalability. Subsequent works by Yan's group introduced pseudocapacitive CAPodes from transition metal oxides like $ZnCo_2O_4$ that harnessed ion-selective redox reactions with an aqueous KOH solution [6]. This architecture provided a high RRI of 3.75 and specific capacity of 50.2 C/g, suggesting the potential for using redox-active materials to simplify device fabrication. A breakthrough was achieved when battery-type materials, like layered double hydroxides (LDHs), were incorporated into CAPodes. Murugesan et al. (2024) fabricated a "supercapattery-diode" by incorporating NiCoLDH nanosheets and activated carbon (AC) with KOH electrolyte. Redox reactions of the LDH (Ni^{2+}/Ni^{3+} and Co^{2+}/Co^{3+} reversals) and interlayer distance (8.1–9.2 Å) enabled high energy storage (162 C/g at 1 A/g, 34 Wh/kg) and rectification (RRI = 23, RRII = 0.98) [9]. The hybrid approach surpassed previous EDLC and pseudocapacitive CAPodes, exhibiting the synergism of battery-like redox reactions and supercapacitor kinetics.

More recent research highlights the importance of materials structure in the optimization of CAPode performance. For example, orthorhombic MoO_3 had two-fold ion-sieving activities: its layered structure (interlayer distance of 6.9 Å) allowed intercalation of H^+/Na^+ and repelled larger ClO_4^- anions [11]. This gave a 10x higher rectification ratio than those carbon-based systems ($RR_I = 35$) and biocompatibility for potential bioelectronic devices. Likewise, polyionic liquid electrolytes (e.g., PVBImTFSI) allowed the synthesis of p-type and n-type CAPodes by leveraging the immobility of polymerized ions, with tunable rectification directions without pore engineering [5].

LDH-type systems also highlighted the significance of lattice engineering. Through metal cation tuninig (Ni, Co, Zn, Mn), researchers regulated d-spacing and redox ability. NiCoLDH had higher specific capacity (312 C/g) because of multiple redox sites, while NiMnLDH had higher RR_I (61) because of lower surface area and tight stacking [9]. These results highlight the balance needed between energy storage and rectification: higher d-spacing facilitates better ion accessibility at the cost of reduced rectification efficiency.

Aqueous electrolytes have become increasingly popular because of their safety and compatibility with redox-active materials. Murugesan et. al. showed that KOH outperformed NaOH and LIOH in LDH-based CAPodes because of the smaller hydrated radius of K^+, improving mobility and minimizing polarization [9]. Still, organic electrolytes are pertinent for high-voltage applications. For instance, super concentrated $HClO_4$/$NaClO_4$ allowed MoO_3-based CAPodes to function at 1.6 V with 100% retention of capacitance after 10,000 cycles, highlighting the significance of electrolyte concentration in stabilizing interfacial kinetics [11].

CAPodes were incorporated into logic gates with high success, representing a major breakthrough in ionic computing. Tang et. al. (2022) fabricated AND/OR gates from $ZnCo_2O_4$-based CAPodes, which were shown to have rectification ratios ($RR_I = 3.4$, $RR_{II} = 0.79$) for binary signal processing [6]. Similarly, MoO_3-based devices were shown to have uniform performance in alternating voltage tests with a maintained current ratio of 5:1 in forward and reverse biases in 0.1 s pulses [11]. Such achievements solidify the potential of CAPodes in the development of neuromorphic circuits for low-power devices.

A major recent advancement in this field is the fabrication of 3D-printed ultamicroporous CAPodes, as demonstrated by Gellrich et. al [12]. Their approach is based on a liquid precursor combined with CO_2 etching to form high-precision sub-nanometric pores for selective ion-sieving and high rectification ratios. Through the use of inkjet and extrusion printing, miniaturized in-plane CAPodes were fabricated and integrated into logic gate circuits and high pass filter devices which is a major step towards scalable, microstructured iontronic devices.

Despite progress, there are challenges that persists in this field. Firstly, the interconnection between energy storage and rectification process is not yet understood. For instance, cycling-induced exfoliation of LDH increased capacitance but altered d-spacing, suggesting dynamic structural effects. Secondly, more miniaturization is needed for wearable or implantable electronics integration. Thirdly, biocompatibility assessments are in their infancy; while MoO_3 showed over 90% cell viability, longer-term in vivo studies are needed.

Further research should prioritize:

a) Material design: Exploring 2D materials (MXenes, Graphene) and MOFs/COFs for selective ion sieving.

b) Hybrid electrolytes: The blending of polyionic liquids with redox mediators to widen voltage windows.

c) Mechanistic investigations: Employing in-situ spectroscopy and modeling to deconvolute capacitive/rectification contribution.

d) System integration: Building arrays of CAPodes with transistors and memristors for future logic circuits.

Briefly, CAPodes are a key intersection of iontronic principles and energy storage technologies. Building on advances in materials science and the developments of electrolytes, they have great potential for novel and neuromorphic computing structures.

1.3. Thesis Objective and Scope

The general aim of this thesis is to explore the possibilities of a 2D Cu-MOF as an ion-selective electrode material for CAPodes in next-generation iontronic devices. By leveraging the redox functionality of Cu-MOFs, the project aims to provide multifunctional devices that store energy and rectify ions in parallel. The project addresses the requirements for high performance materials that bridge supercapacitors and logic gates, with the specific aims of maintaining high-stability in aqueous electrolyte.

Scope of the thesis is the synthesis of the 2D Cu-MOF from 2,5-PDC and Cupric nitrate trihydrate and comprehensive electrochemical characterization in three- and two-electrode configurations for CAPode application. The study is analyzed by rectification ratio measurements at various scan rates and current densities and investigation of charge storage mechanism by Dunn’s method. Practical demonstration include the logic operation in AND and OR gate function from Cu-MOF||AC asymmetric cell in 3 M KOH.

This work provides insights into the multifunctional application of coordination polymers in energy storage and ionic signal processing and provides guidelines for ionic applications. Through the illustration o structure-property relationships in Cu-MOF-based CAPodes, the thesis enables the design of hybrid electronic-ionic systems to integrate into neuromorphic computing platforms and energy storage.

1.4. Organization of the Thesis

The thesis is organized to provide a logical and comprehensive flow from the initial background of CAPodes to experimental use and application of 2D MOF as ion-selective electrode for logic operation.

The thesis is introduced by providing context for the evolution of multifunctional supercapacitors and CAPodes. It provides a concise overview of the limitations of conventional supercapacitors and the necessity of incorporating extra functions such as rectification and logic functions and the history of CAPode development- highlighting the developments from pore-size control, redox-active materials to hybrid device architectures. The introduction also provides context for discussion of coordination polymers, specifically Cu-MOF, as next generation CAPode candidates. The Experimental Section consists mostly of material synthesis procedure and characterization of the prepared material using various techniques such as XRD, FESEM, EDX, FTIR and TGA. The Results and Discussion section is subsequently broken down into various subsections corresponding to the working mechanism of the MOF based CAPode, ion-sieving and capacitive effects in the forward and reverse bias conditions. The thesis then proceeds to thorough electrochemical analysis, first in a three-electrode setup for intrinsic material properties and secondly in a two-electrode full-cell device. Quantitative techniques such as CV, GCD and Dunn's method are utilized to dissect the kinetic and rectification performance. Discussion is then taken to device behavior, such as chronoamperometry and logic-gate operation, to illustrate the practical implementation of the CAPode in AND and OR logic circuits.

The conclusion section highlights the dual nature of Cu-MOF CAPode's performance in ionic rectification and energy storage. The section also recognizes the limitation of the current work, such as capacity decay and moderate energy density, and suggests directions for future work, such as material optimization and device miniaturization.

Chapter 2

Experimental Section

2.1. Synthesis of Cu-MOF

A copper-containing metal-organic framework (Cu-MOF) was prepared based on a method derived from earlier reported research on 2D CuPDC [10]. The synthesis was carried out through the reaction of cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) (241 mg, 1.19 mmol) with 2,5-pyridinedicarboxylic acid (2,5-PDC) (100 mg, 0.59 mmol) in a 2:1 molar ratio using a mixed solvent system of water and dimethylformamide (DMF) (30 ml, 1:1 v/v). The reaction was carried out at a reflux for six hours at 140°C, resulting in a blue crystalline material. The synthesis yielded a material with a two-dimensional layered network, consistent with the behaviour of the earlier reported 2D CuPDC framework. A schematic illustration of the synthesis is shown in (Fig. 1).

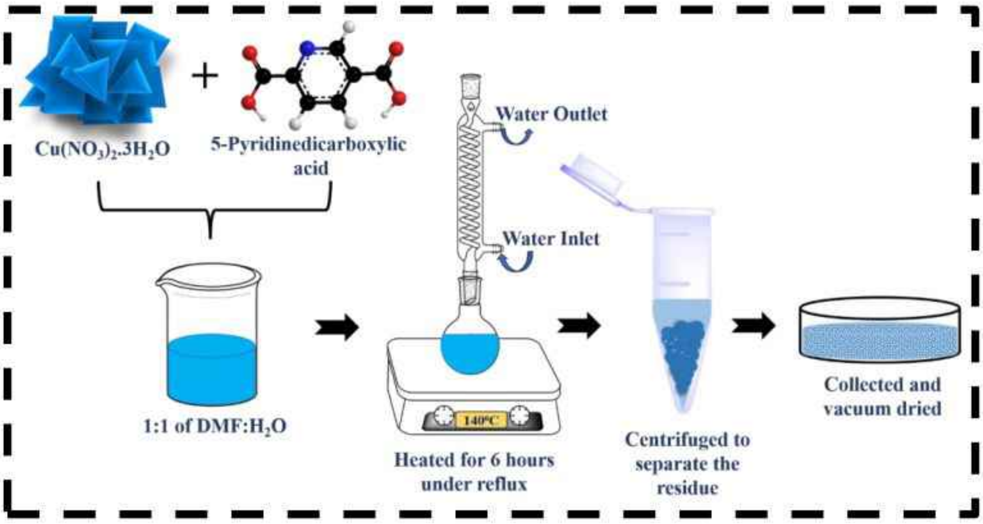

Fig. 1- Synthesis of Cu-PDC using $Cu(NO_3)_2.3H_2O$ as Cu source and 2,5-PDC as ligand.

2.2. Characterization of Material

The X-ray diffraction (XRD) analysis of the synthesized material confirms both its structural properties and phase purity. All the observed diffraction peaks are in complete agreement with the reported peaks of the two-dimensional Cu(II) coordination polymer in literature, as indexed by the CIF file of the original publication [10]. The occurrence of sharp and well-defined peaks indicates a high crystallinity, with no visible impurity phases or other crystallographic orientations, thereby confirming the successful reproduction of the target structure (Fig. 2).

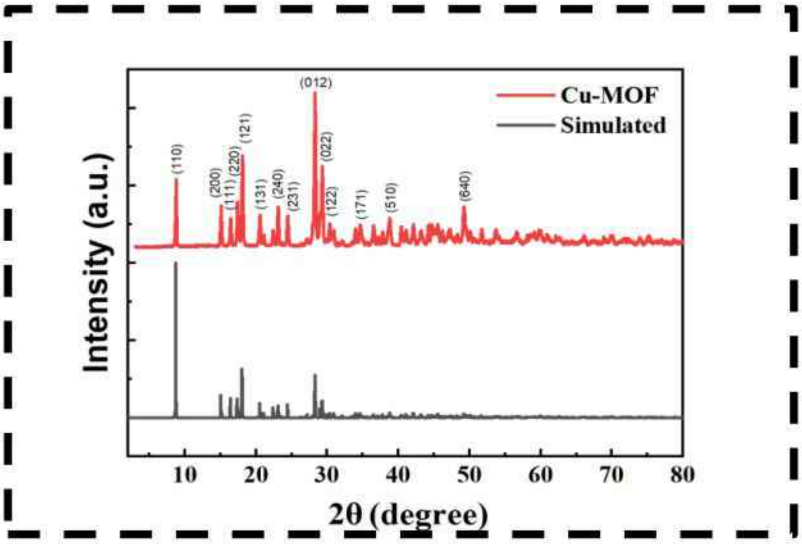

Fig. 2- PXRD pattern of as-synthesized and simulated Cu-MOF **[R8]**.

Field emission scanning electron microscopy (FESEM) and EDX analysis reveals that the material has a well ordered two-dimensional layered morphology. Moreover, energy dispersive X-ray (EDX) spectroscopy confirms the elemental composition, where the presence of the anticipated elements in the compound is confirmed (Fig. 3 (a), (b)).

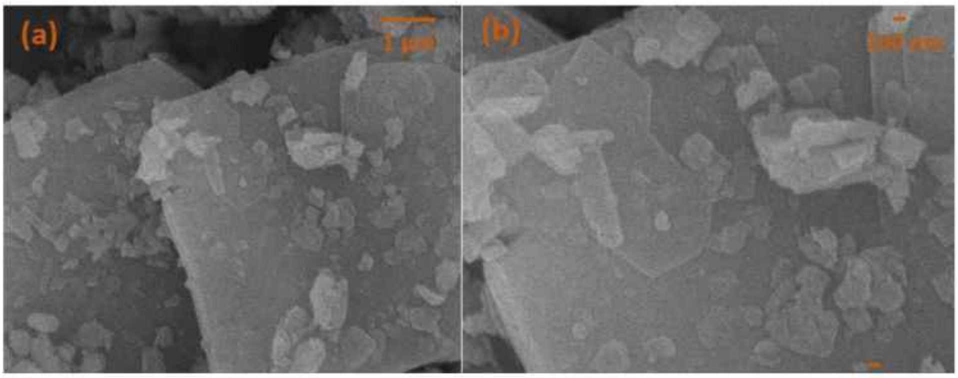

Fig. 3 (a) SEM of Cu-MOF

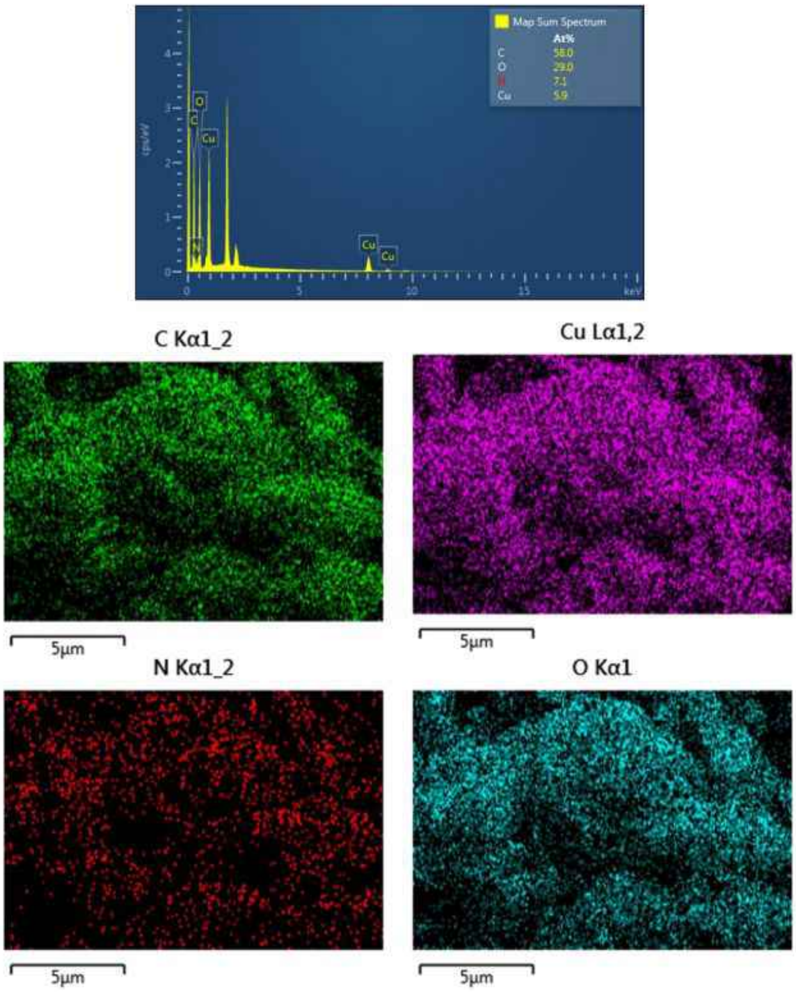

Fig. 3 (b)- EDX analysis of Cu-MOF

Fourier Transform Infrared (FTIR) spectroscopy was performed to identify the characteristic functional groups inherent in the synthesized MOF structure. The obtained spectral analysis identifies clear vibrational bands that affirms the presence of essential coordination bonds as well as characteristics of the original ligands (Fig. 4 (a)). The spectrum indicates Cu-N stretching at 456 cm^{-1}, Cu-O coordination bands at 521 and 575 cm^{-1}, and =C-H bending vibrations in the 763-936 cm^{-1} range. The fingerprint region comprises C-O stretching modes (1045-1258 cm^{-1}), C=C stretching (1419 cm^{-1}), heteroatomic C=N stretching (1540 cm^{-1}), and carbonyl C=O stretching (1683 cm^{-1}). Moreover, the spectrum indicates =C-H stretching vibrations in the higher wavenumber region in the range of 2836-3069 cm^{-1}. Collectively, these spectroscopic features confirm the successful synthesis of the anticipated Cu-MOF structure, with intact organic linker moieties.

Further, Thermogravimetric Analysis (TGA) indicates that 2D-CuPDC is stable up to 260.5° C and undergoes a four-step decomposition (Fig. 4 (b)). The weight loss observed (9.3 %) can be designated to the dehydration of adsorbed water and solvents. Beyond that point, weight loss of 40.4 % is observed due to decarboxylation. Subsequent weight loss is observed in a two-step disintegration of the aromatic group of the linkers.

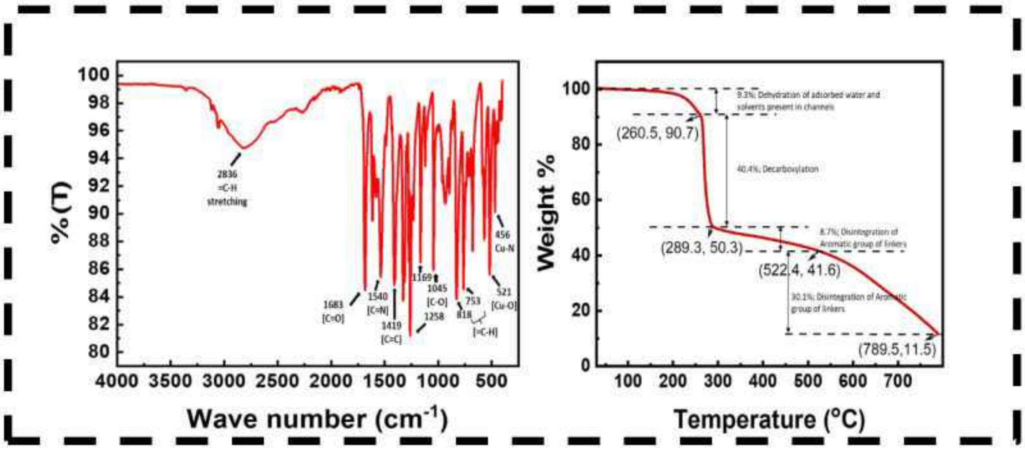

Fig. 4 (a) FTIR spectrum and (b) TGA of the Cu-MOF

2.3. Preparation of Electrode Material

The electrode slurry was prepared through homogenous mixing of active material (Cu-MOF), conductive carbon black and PVDF binder in a mass ratio of 7:2:1. Carbon black is used to improve electrical conductivity and PVDF is a polymeric binder employed to provide mechanical strength. 1000 ml N-methyl-2-pyrrolidone (NMP) was employed as a solvent to break PVDF and allow slurry formation. The mixture was magnetically stirred for 12 hours to form a viscous, homogenous dispersion, which would allow uniform coating of Nickel foam as current collectors on electrode fabrication.

2.4. Preparation of Electrolyte

A 3 M aqueous KOH electrolyte was prepared by dissolving KOH pellets in deionized water while accounting for the exothermic dissolution process. 8.415 g of KOH (molar mass = 56.11 g/mol) is weighed and gradually added in a beaker containing 50 mL of deionized water. The solution is then put in sonication for 15 minutes, so that KOH pellets get completely dissolved in the solvent.

Chapter 3

Results and Discussion

3.1. Working Mechanism of the Cu-MOF based Pseudocapacitor Diode

The working mechanism of the Cu-MOF based pseudocapacitor diode is comprehensible by an interplay among redox activity, ion-sieving behaviour and capacitive characteristics. The Cu-MOF, with its porous structure and redox active Cu^0 centres, plays a crucial role as the working electrode. Under forward-bias (positive potential, Fig. 5 (a)), the Cu^0 is oxidized to Cu^{2+} ($Cu^0 \rightarrow Cu^{2+} + 2e^-$), a reaction promoted by hydroxide ions (OH^-) in the 3M KOH electrolyte. This Faradaic reaction is responsible for the anodic current peak in cyclic voltammetry (CV). Simultaneously, charge neutrality is maintained by the intercalation of OH^- ions into the pores of the MOF and the adsorption of K^+ ions on the activated carbon counter electrode by the electric double-layer capacitance (EDLC). Hence, a notable current response during oxidation is the result of the interplay of these processes at the two electrode surfaces.

Under reverse bias conditions (negative potential, Fig. 5 (b)), the system shows a blocking behavior. Cu-MOF's pore architecture and charge distribution prevent the participation of K^+ ions in reduction reactions on the basis of electrostatic repulsion due to the negatively charged framework. This behavior stops the regeneration of Cu^{2+} to Cu^0 and consequently the response is with a negligible Faradaic current. While a minor residual electric double-layer capacitance (EDLC) current might result due to surface adsorption of K^+ on the MOF, it is negligible compared to the response under forward bias conditions. The encountered asymmetric current response is analogous to the rectification behavior encountered in semiconductor diodes, and therefore the "CAPode" nomenclature. Unlike conventional PN junction diodes, which results in energy dissipation in the form of heat when operated in the forward bias mode- hence leading to higher power consumption in normal logic circuits- CAPodes utilize energy-efficient capacitive logic architecture. These devices benefit from the tenets of adiabatic computing [13], wherein stored charge is retrieved during the discharge phase and not irrecoverably lost.

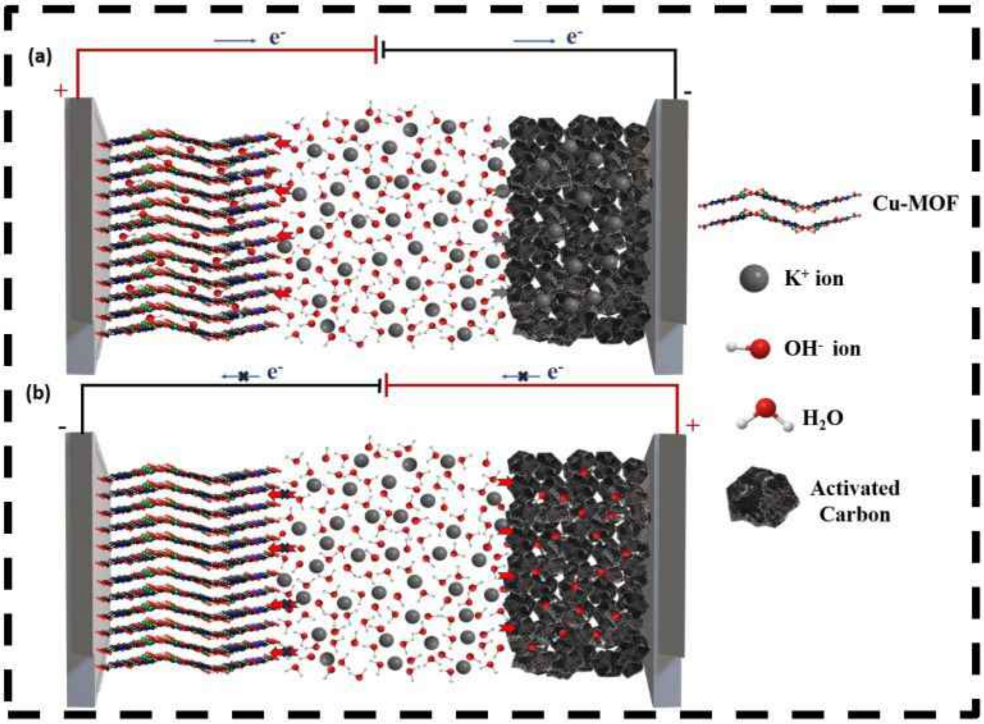

Fig. 5- Working scheme of the CAPode containing Cu-MOF as the working and activated carbon as the counter electrode in (a) positive polarization and (b) negative polarization

The rectification mechanism observed in this CAPode is a result of ion-sieving effects: charge-selective blocking of K^+ ions upon negative polarization of the working electrode. This one-way ion transport is complemented by the potential dependent activity of the Cu^{2+}/Cu^0 redox couple. The CV asymmetry is consistent with the reported CAPode systems such as MoO_3 and $ZnCo_2O_4$, and the Cu-MOF's Faradaic contribution demonstrates comparable energy density and rectifications, consistent with devices based solely on EDLC. This mechanism demonstrates the untapped potential of MOFs in designing advanced CAPodes by integrating charge-selective ion transport with tunable redox activity.

3.2. Electrochemical Performance of the Cu-MOF Electrode in a Three-Electrode Configuration

Electrochemical measurements were conducted on the Cu-MOF electrode in a three-electrode configuration, with a potential window of -0.5 to 0.5 V vs. Ag/AgCl as the reference electrode, to study its CAPode-like behavior and rectification characteristics. The CV curves, recorded at different scan rates in aq. 3 M KOH electrolyte, show intense redox peaks, indicating that the charge storage mechanism of Cu-PDC is largely governed by redox (pseudocapacitive) reactions (Fig. 6). Interestingly, when the scan rate is increased, the response current in the positive polarization area is also increased, while the response current in the negatively polarization area is extremely low. This intense asymmetry if response polarization in indicative of rectification behavior and suggests that Cu-PDC electrode charges in one direction preferentially, in line with the governing working mechanism of CAPode. The specific capacities of the Cu-PDC electrode at various scan rates were determined from the CV profiles through the equation-

$$\mathbf{C} = \frac{absolute\ area}{active\ mass * scan\ rate}$$

With the increase of scan rate from 10 to 100 mV/s, there was a corresponding reduction in specific capacity from 83.21 to 64.09 C/g. This is typical of pseudocapacitive materials, where high scan rates limit the time for complete redox reactions and hence reduce the capacity available [14].

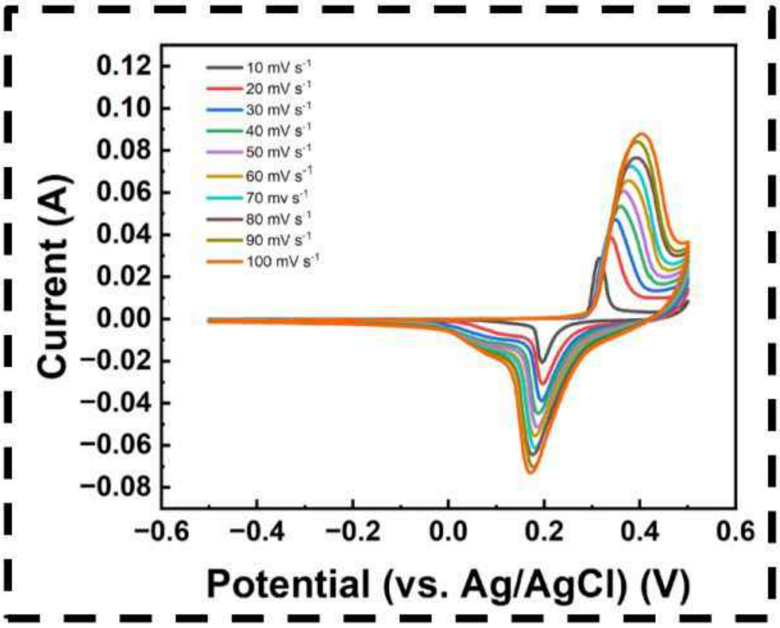

Fig. 6- Cyclic Voltammetry of Cu-MOF in a three-electrode setup

Two quantitatively analyze the rectification performance, two important parameters were utilized: rectification ratio I (RR_I) and rectification ratio II (RR_{II}) [4]. The two parameters are defined as-

$$\mathbf{RR_I} = \frac{Current\ value\ at\ the\ positive\ voltage\ cutoff\ point}{Current\ value\ at\ the\ negative\ voltage\ cutoff\ point}$$

$$\mathbf{RR_{II}} = \frac{Capacitance\ at\ the\ positive\ voltage\ range}{Capacitance\ over\ the\ entire\ voltage\ range}$$

The data shows that RR_I decreases from 60.23 at a scan rate of 10 mV/s to 25.54 at 100 mV/s while RR_{II} decreases from 1.95 to 1.87 (Fig. 7 (a) and (b)). These are comparable to, if not higher than, those for carbon-based CAPodes, thus establishing that the Cu-PDC electrode has strong rectification properties and enables efficient unidirectional ion transport.

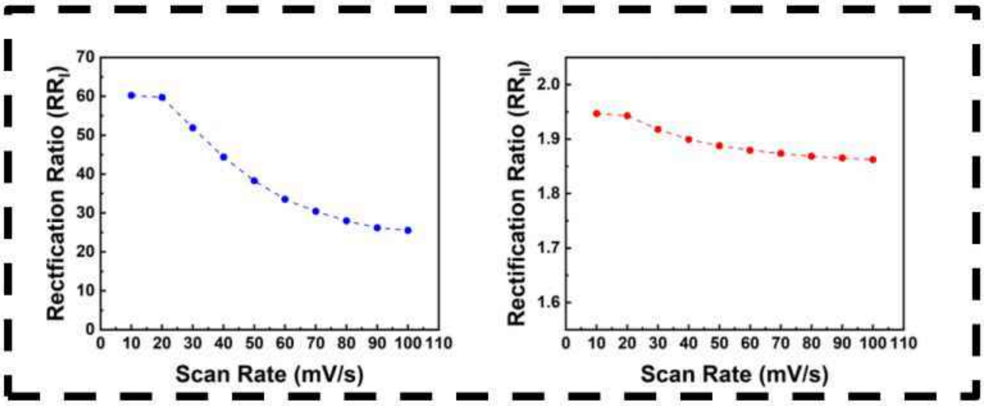

Fig. 7 (a) RR_I and (b) RR_{II} calculated for Cu-MOF from CV data

Galvanostatic charge-discharge (GCD) measurements were performed with the Cu-MOF coated Nickel foam electrode in a similar three-electrode configuration, with various current densities between 1 and 5 A/g (Fig. 8). The data showed a specific capacity of 78.9 C/g at a current density of 1 A/g, reflecting the effective pseudocapacitive charge storage. The high capacity is due to the porous nature of the Cu-MOF, which facilitates rapid ion diffusion and allows for the optimal use of the redox-active sites present in the material. Further optimization of the pore structure of the MOF, the electrolyte composition, or the electrode architecture may even enhance both the specific capacity and rate capability, making the materials even more attractive for practical CAPode devices.

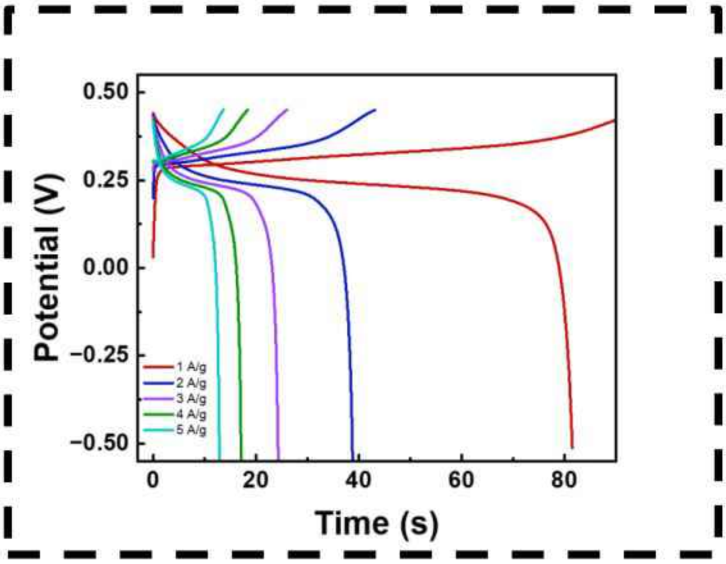

Fig 8- GCD of Cu-MOF in a three-electrode setup

Furthermore, the cyclic stability of the Cu-MOF electrode was probed for 1000 consecutive charge-discharge cycles to examine its long-term performance (Fig. 9). After cycling, the specific capacity of the electrode was reduced to 52.18% of the original capacity. The capacity loss is a result of degradation of the structure of the MOF framework, potential dissolution of active copper entities in the electrolyte, and/or mechanical strain due to repeated ion insertion and extraction during the redox reaction. Such capacity loss is a common feature of pseudocapacitive materials under long-term cycling condition [15].

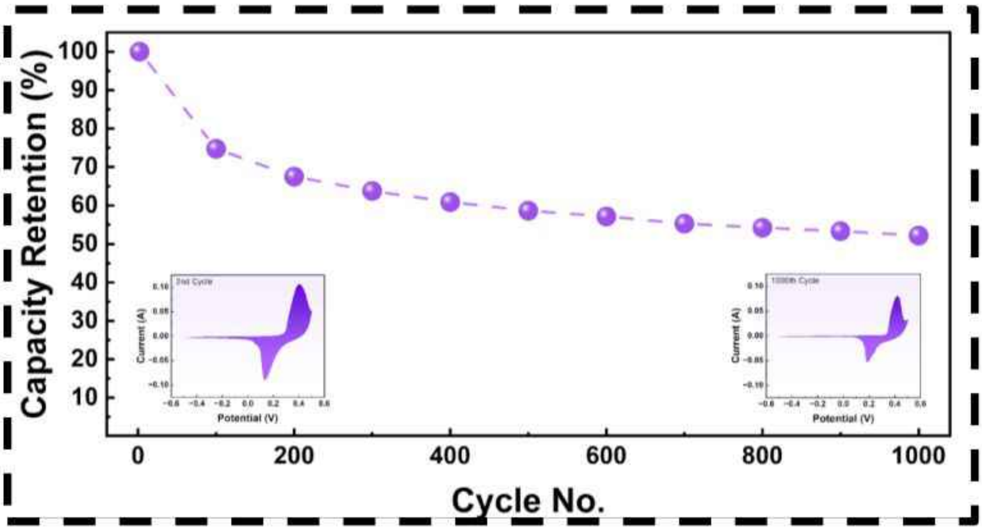

Fig. 9- Cyclic stability measurement for 1000 cycles of Cu-MOF in three-electrode setup

Although there was a reduction in specific capacity, the rectification performance of the Cu-MOF electrode was stable in the cycling test. The RR_{II} was always preserved at around 1.86, demonstrating that the capability of the electrode to preferentially allow charge storage in one direction was not adversely affected by cycling-induced degradation (Fig. 10). The consistent RR_{II} indicates that the ion-sieving ability and charge selective interfaces integral to the MOF structure are still intact, despite some reduction in electrochemical activity.

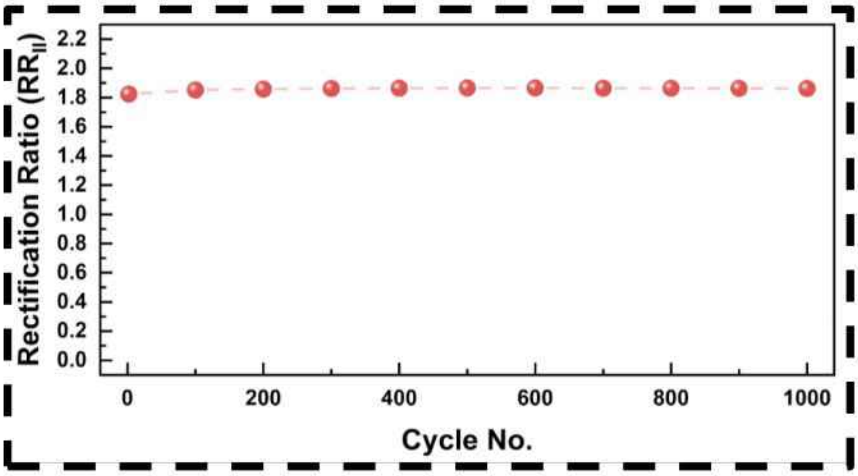

Fig. 10- Rectification Ratio (RR_{II}) of Cu-MOF for 1000 cycles

The results show one important advantage of the Cu-MOF electrode: although its overall capacity can be lost in the long term, its rectification function- essential for CAPode and iontronics applications- is retained for long-term use. This decoupling of capacity retention and rectification stability renders MOF's good candidature as stable device elements in applications where stable unidirectional ion conduction is essential, even if capacity loss is tolerable. Future work can explore means to improve structural stability and capacity retention, e.g. by incorporating conductive carbon moieties or protective layers, but preserving the excellent rectification function.

3.3. Electrochemical Performance of the Pseudocapacitor Diode (CAPode)

The CAPode was fabricated using the CU-MOF as the working and activated carbon (AC) as the counter electrode in an aqueous 3 M KOH electrolyte in a Swagelok cell setup. The electrochemical measurements were performed in a systematic manner with three different mass loading ratios of Cu-MOF to AC (1:1, 1:2 and 1:3) in an attempt to enhance charge storage as well as rectification performance. In a two-electrode setup, potential window is the difference of the cell voltage across both the working and counter electrodes. If we assume the MOF working electrode to be +0.5 V and the AC counter electrode to be -0.5 V, the difference is 1 V. Hence, in a potential window of 1 to

-1 V, cyclic voltammetry (CV) was conducted with varying scan rates, to investigate the CAPode like characteristics and rectification behavior of the device (Fig 11, 12 (a) and (b)).

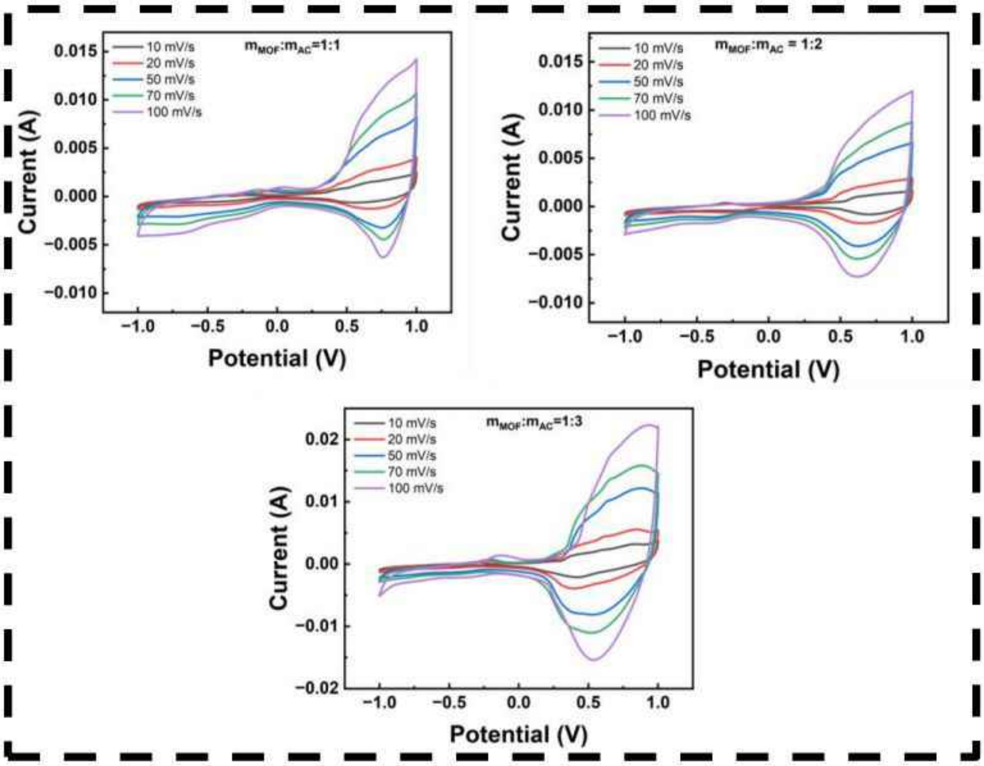

Fig. 11- CV of CAPode with different mass-loading ratios of working and counter electrode

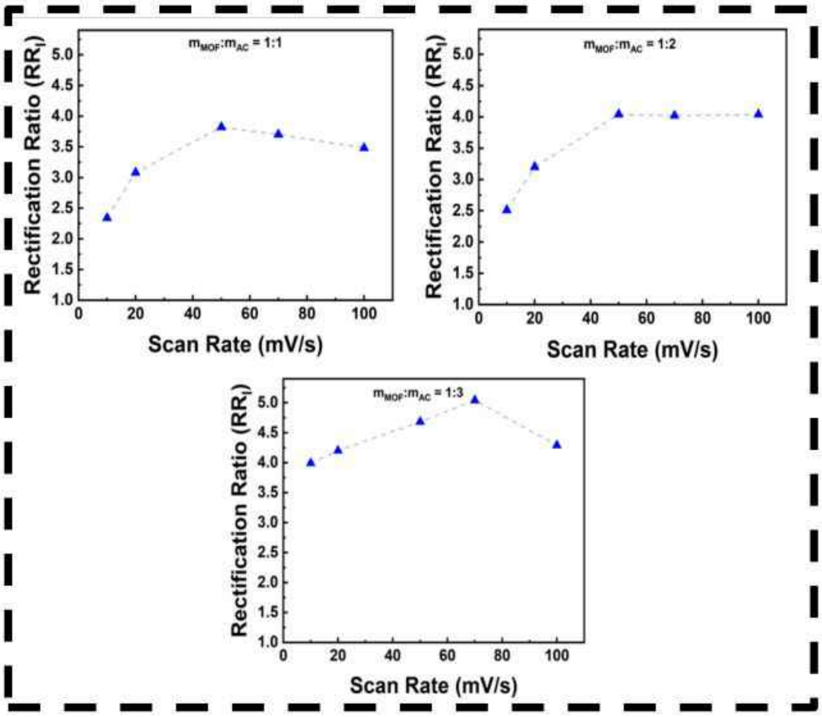

Fig. 12 (a)- RR_I of CAPode calculated from CV data

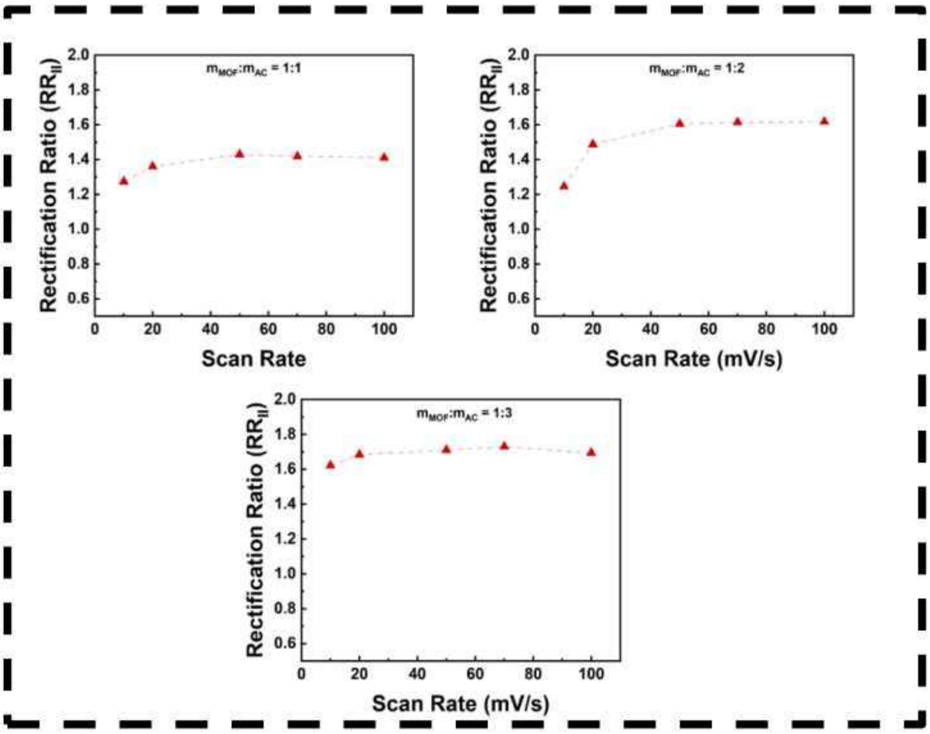

Fig. 12 (b)- RR_{II} of CAPode calculated from CV data

The CV curves showed an extremely strong asymmetry in the current response with significant charge storage under positive bias and much weaker current in the negative direction, which is evident by the area enclosed by the curves in both the positive and negative polarizations. This is due to the selective ion transport nature of the Cu-MOF which facilitates effective charge by both Faradaic and non-Faradaic reactions under positive bias and suppresses charge transfer under negative bias. The remaining small current in the negative direction is likely to be due to due to the electric double layer created by K^+ ions adsorbed on the Cu-MOF structure. This selective reaction is analogous to rectification in semiconductor diodes but with the added benefit of energy storage in the forward direction. Out of all the three different mass ratios, the 1:3 quantitatively shows better charge storage and rectification and hence considered the best mass optimization here after. To quantitatively analyze the rectification performance of the 1:3 mass ratio, RR_I was measured and found to increase with scan rate, from 3.99 at 10 mV/s to 4.29 at 100 mV/s. This suggests the enhancement of the migration of K^+ ions towards the Cu-MOF surface at elevated scan rates, reducing the electrode polarization and enhancing rectification. Similarly, RR_{II} also showed a slight increase with scan rate, from 1.62 to 1.69**.** These results imply that the device shows superior ion-selectivity and rectification performance even at higher charge-discharge rates.

In order to probe the charge-discharge profile, GCD was performed at multiple current densities (1-5 A/g) and it demonstrated a clear asymmetric behavior for the CAPode system (Fig 13. (a))**.** The profiles present much longer discharge times between the positive potential window (1 to 0 V), reflecting privileged charge storage during forward bias operations. The specific capacity was calculated from the expression,

$$C = \frac{I\,\Delta t}{m}$$

and found to 15 C/g (at 1 A/g current density) from the discharge profile, which is significantly lower than what was obtained in the three-electrode setup for the Cu-MOF alone. This reduction in capacity can be attributed to a number of factors. In a two-electrode device, the overall capacity is determined by both electrodes connected in series where the less capacitive electrode defines the overall capability. Moreover, the internal resistance in the full cell is higher in a two-electrode system, with larger voltage drops and less available capacity. The same behavior has been reported for other CAPode systems, for example, the LDH-based devices reported by Murugesan et. al., [9] where the overall specific capacity in two-electrode setup (162 C/g for NiCoLDH-based device) was much smaller than that measured by three-electrodes.

The rectification property, expressed as the discharge capacity from 1 to 0 V (forward bias) divided by discharge capacity from -1 to 0 V (reverse bias), increases sharply with increasing current densities- from about 16 at 1 A/g to about 40 at 5 A/g (Fig. 13 (b)). This trend demonstrates improved rectification behavior at higher charge-discharge rates, in contrast to other CAPode systems reported to have diminishing rectification behavior at increasing rates. The rising rectification indicates that the diffusion-controlled processes that prevail at negative potentials are more significantly restricted at increased current densities than the redox processes at positive potentials.

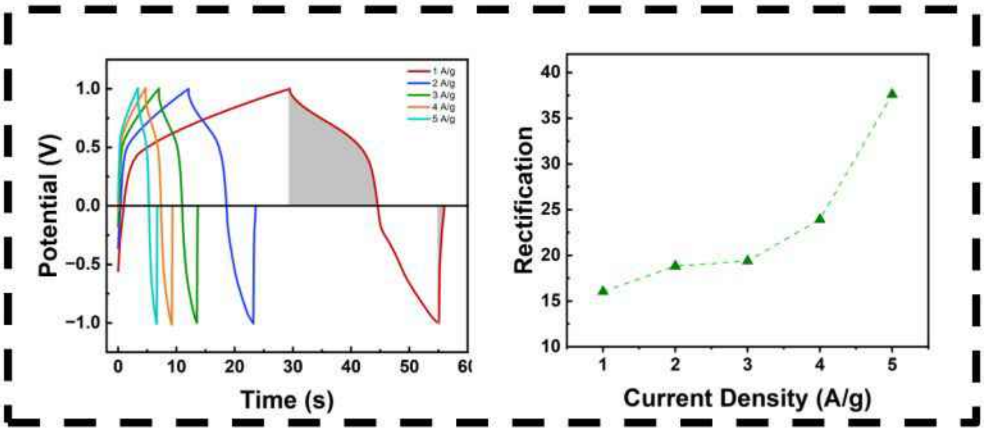

Fig. 13 (a) GCD of CAPode at 1-5 A/g and (b) Rectification calculated from discharge capacity of positive and negative polarization

To study the dynamic current response of the Cu-MOF/AC device with varying potential steps, chronoamperometry was performed and the current vs. time was plotted (Fig. 14). The current spikes to about 3 mA during the 1 V period as all Cu^0 ions in the working electrode oxidize to

Cu^{2+} marked as “Faradaic charging”, before slowly decreasing, which signifies redox reaction at the electrode surface. When connected to 0 V upon completion of the 1 V step, the plot exhibits a negative current flow designated as “Faradaic discharging” that describes the release of deposited charge from the previous redox reactions. The discharge current slowly reduces to zero as the system approaches equilibrium.

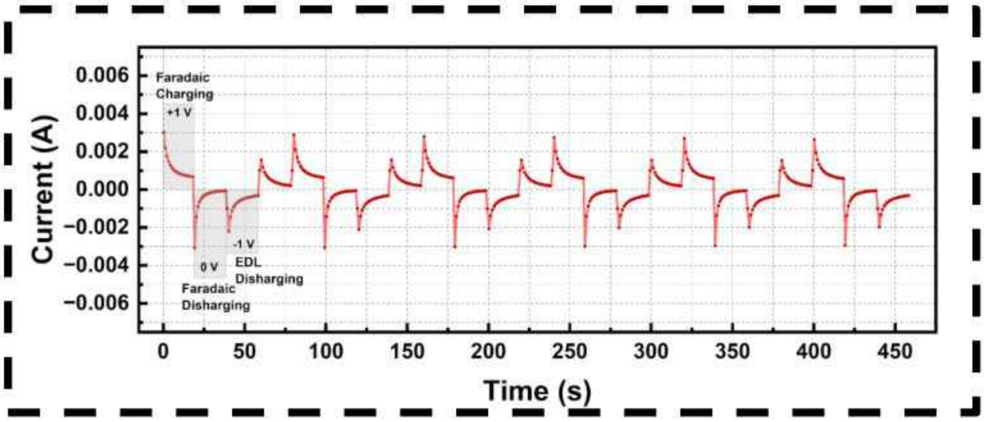

Fig. 14- Chronoamperometry at 1, 0 and -1 V applied for an interval of 20 seconds

During the -1 V interval, there is a negative current spike referred to as “EDL discharging”, indicating largely electric double layer formation and not highly efficient Faradaic processes. On being restored to 0 V from the -1 step, a positive flow of current is observed as the EDL charge is released, slowly coming back to equilibrium.

The rectification ratio, defined by the saturation current at +1 V to that at -1 V, somewhat reduces from 2.09 in the initial cycle to 1.85 in the sixth cycle (Fig. 15). The moderate reduction indicates small evolution of the electrode-electrolyte interface properties with cycling, although the repetitive values over 1.85 ensure steady ion-selective properties, validating efficient diode-like behavior. The asymmetry of current response between positive and negative bias conditions is the basis of the device’s functionality.

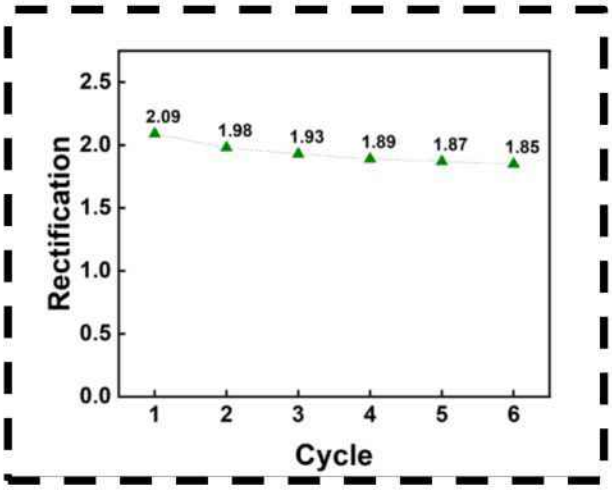

Fig. 15- Rectification of saturation current at 1 V and -1 V measured from chronoamperometry

3.4. Ionic Logic Operation

Ionic diodes have become the center of attraction for many researchers [16]. The ionic logic setup was constructed using two CAPodes wired in parallel and a 250 kΩ resistor, as per known circuit conventions. Signal generation was achieved with an SMG2082 waveform generator, which delivered pulse inputs of 5 seconds into the circuit. The output signals were detected and recorded with a RIGOL DS1064 oscilloscope, and measurements were taken across the resistor for monitoring the voltage response patterns. In this setup, a logical "1" was indicated by a 1 V signal and "0" by 0 V.

(i) OR Gate

The I/O behaviour of the CAPode-based OR gate showed excellent agreement with routine Boolean logic operation. As indicated from the voltage-time tracings, where the two inputs A and B were both at 0 (0,0), the output was still at 0 V, showing the intended low state. When input A or B was kept constant at 1 (1,0 or 0,1), the output went into a high state, as expected for correct OR gate functioning. When both inputs were kept at 1 (1,1), the output remained in the high state as well (Fig. 16). One of the striking aspects of the waveforms is the occurrence of small voltage spikes in the zero-state input signals, most evident in input B. The phenomena proves that CAPodes are not ideally isolated from channel to channel like conventional semiconductor devices. These spikes are presumably due to capacitive coupling phenomena, in which sudden voltage transitions in one channel can couple capacitively with neighboring circuit paths to produce the small voltage spikes seen in the measurement. These actions are consistent with earlier research on pseudocapacitor diodes and prove CAPodes can not only be used just as energy storage units but as operational components of iontronics computing systems.

Inputs		OR
Input A	Input B	Output
0	0	0
0	1	1
1	0	1
1	1	1

Table 1: Boolean logic of OR Gate

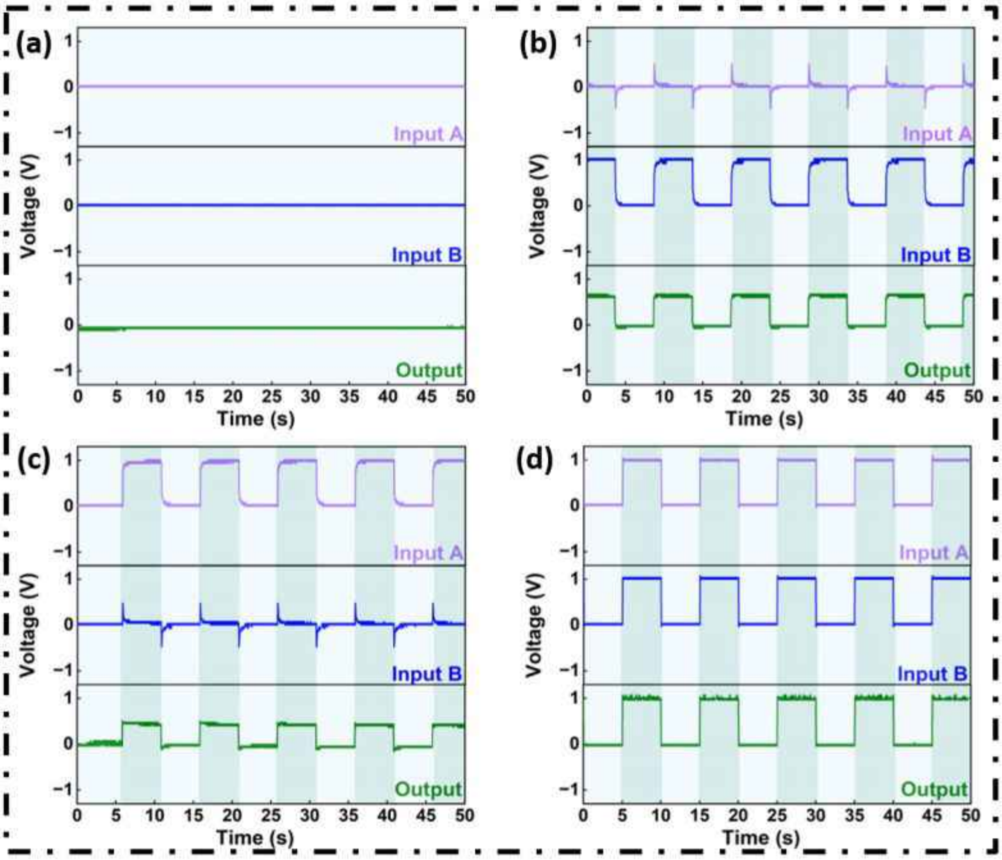

Fig. 16- Ionic logic operation for OR gate consisting of (a) 0 (0,0), (b) 1 (0,1), (c) 1 (1,0) and (d) 1 (1,1) Boolean logic

(ii) AND Gate

The operation of AND gate circuits was also successfully illustrated with the use of CAPodes. The circuit was configured according to conventional logic gate architecture, where inputs A and B were connected to the cathodes of the two CAPodes. As shown in the oscilloscope traces, the circuit exhibited impeccable Boolean logic operation strictly followed by the defined AND gate truth table. When both inputs were configured to high simultaneously (1 V), the circuit generated a high output voltage of around 1 V. When one or both inputs were configured to low (0 V), the output voltage was still about 0.3 V, clearly defining as a logic low state (Fig. 17). This performance verifies that CAPodes function well as ionic diodes in logic operations, promising that they can serve as building blocks for more intricated ionic computing circuits.

Inputs		AND
Input A	Input B	Output
0	0	0
0	1	0
1	0	0
1	1	1

Table 2: Boolean logic of AND Gate

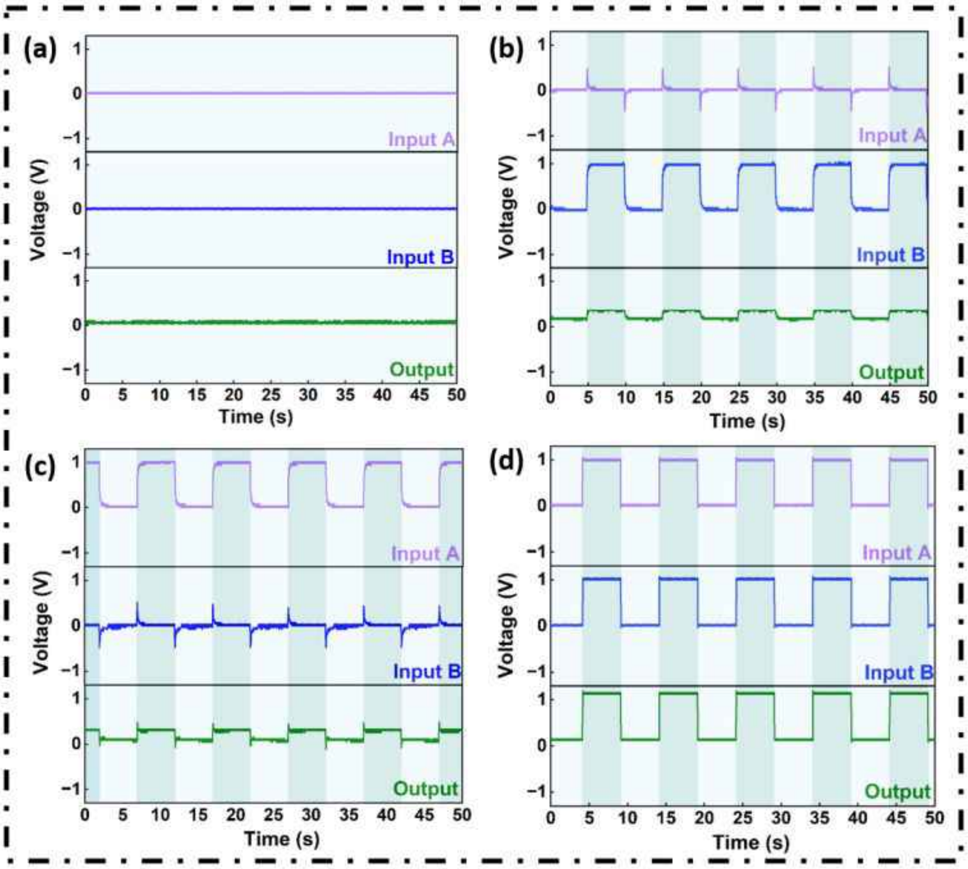

Fig. 17- Ionic logic operation for AND gate consisting of (a) 0 (0,0), (b) 0 (0,1), (c) 0 (1,0) and (d) 1 (1,1) Boolean logic

Chapter 4

Conclusion and Future Scope

The development of a Cu-MOF pseudocapacitor diode (CAPode) illustrates major advancements in conjoining energy storage and ionic rectification functions. The 2D Cu-MOF, prepared through solvothermal synthesis, showed a layered structure having redox-active Cu centers, allowing for ion-selective charge storage mechanisms within a 3 M KOH electrolyte. Under forward bias, the Cu-MOF supported Faradaic oxidation ($Cu^0 \rightarrow Cu^{2+}$) with simultaneous OH^- intercalation, whereas reverse bias prompted electrostatic repulsion of K^+ ions and thus effectively blocked redox processes and restricted charge storage to small electric double-layer capacitance. Such asymmetry provided rectification ratios (RR_I: 3.99-4.29; RR_{II}: 1.62-1.69) similar to previous carbon and transition-metal-oxide-based CAPodes, confirming that the material could be used for one-way ion transport.

Electrochemical characterization indicated that the capacity retention of the Cu-MOF was reduced to 52% after 1000 cycles under structural fatigue and Cu dissolution. Rectification stability, however, held, highlighting the resilience of this ion-sieving mechanism. In full-cell configuration, with activated carbon as the counter electrode, the specific capacity was found to be 15 C/g at 1 A/g current density. The CAPode functionality was also confirmed in ionic logic circuits, effectively mimicking OR and AND gates with clear voltage distinction, though accompanied by small capacitive coupling artifacts between channels.

Though the Cu-MOF CAPode demonstrates excellent dual functionality, capacity fade and moderate energy density are concerns for further scrutiny. Improving structural stability by employing composite designs (e.g. blending conductive carbon matrices) or exploiting new MOF architectures with maximized pore geometries and redox-active centers is one area of future research. Downsizing device size and incorporating hybrid iontronics-electronic systems is also a potential direction for advancing neuromorphic computing and bio-interfacing applications. This work highlights the potential of coordination polymers to serve as multifaceted platforms for future-generation iontronics devices, combining energy storage with logic functions in one architecture.

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