TWO-DIMENSIONAL LAYERED COBALT-BASED COORDINATION POLYMER FOR SUPERCAPACITIVE PERFORMANCE

M.Sc. Thesis

by SHASHANK RATHI



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TWO-DIMENSIONAL LAYERED COBALT-BASED COORDINATION POLYMER FOR SUPERCAPACITIVE PERFORMANCE

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Submitted in partial fulfillment of the requirements for the award of the degree

of Master of Science

by SHASHANK RATHI



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CANDIDATE'S DECLARATION

I hereby certify that the work presented in the thesis TWO-DIMENSIONAL LAYERED COBALT-BASED COORDINATION POLYMER FOR SUPERCAPACITIVE PERFORMANCE, which was submitted to the DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work completed during the time period from July 2022 to May 2023. This thesis is being submitted in partial fulfillment of the requirement for the award of the degree of MASTER OF SCIENCE, under the supervision of Prof. Shaikh M. Mobin, Department of Chemistry, IIT Indore.

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Abstract

Coordination Polymers (CPs) are an intriguing choice and have lately been acknowledged as attractive materials to be utilized for supercapacitor application. In this report, we prepared a layered Co-CP by utilizing a slow diffusion technique. Further, Co-CP was well characterized using SC-XRD, displayed excellent pseudocapacitor behavior with excellent specific capacitance (Cs) around 1092 F g⁻¹ at 1.5 A g⁻¹, and sustained its cyclic retention at 98% over 6500 GCD cycles. The electrolytic study was performed utilizing three different electrolytes (NaOH, KOH, LiOH), and further evaluated the electrochemical performance of the Co-CP in different electrolytic concentrations (3M, 5M, 7M of NaOH).

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NOMENCLATURE

°C	Degrees Celsius
gm	Gram
i _{ih}	Hydrated ionic radii
i _{ion}	Ionic radii
mL	Milliliter
mmol	Millimole
ν	Nu
%	Percentage
θ	Theta
Cs	Specific Capacitance

ACRONYMS

DABCO	1,4-diazabicyclo [2.2.2]octane
Al	Aluminium
CNT	Carbon nanotube
Co	Cobalt
DMF	Dimethylformamide
Au	Gold
Li	Lithium
Ν	Nitrogen
0	Oxygen
Pt	Platinum
К	Potassium
Na	Sodium

Chapter 1 Introduction

The search for renewable energy sources has become increasingly important as the need for sustainable energy sources rises as a result of massive CO₂ emissions and the rapid decline in the availability of non-renewable fuel sources.¹ But there are a number of challenges with renewable energy, energy storage being the major one. The utilization of renewable sources is challenging due to their intermittent nature and reliance on the weather, which doesn't affect non-renewable energy.² Therefore, developing more efficient and adaptable energy storage technology is necessary. This encouraged the researchers to elevate the effectiveness of pollution-free energy storage systems.³ Because of this, there has been an increase in interest in storage systems with high power and energy densities.⁴ Consequently, encouraging the applied science of energy storage has broadly developed as an intriguing future.^{5,6}

1.1 Supercapacitors

Being a prominent candidate for energy storage, the supercapacitor is progressively spreading and one can predict that soon they will be the biggest slice of the cake.⁷ Contrary to batteries, they do not offer high energy density but possess high capacitance and low internal resistance, which batteries don't offer.⁸ Compared to batteries, they provide a thousand times power over a volume and can be charged and discharged in split seconds.³ Their reversible process of charge storage provides them high cyclic stability, where they can hold out against millions of cycles, unlike batteries which are only capable of a few thousand.⁹ Along with these characteristics, they also show an extensive thermal range that can reach up to -40 °C.¹⁰ Intriguing applications for supercapacitors include fuel cells and low-emission electric vehicles, but they are also widely employed in

consumer electronics and medical technology.^{11–13}

1.1.1 Types of Supercapacitors

Supercapacitors have been classified on the basis of physiochemical processes accountable for the energy storage mechanism^{10,14,15} as:

- 1) Electric double-layer capacitance (EDLC)
- 2) Pseudocapacitors
- 3) Hybrid capacitors

In EDLC charge storage occurs electrostatically, like conventional one. Here channel for the charge storage is the accumulation of charge on the electrode/electrolyte junction and no transfer of charge occurs between them.¹⁶ Due to the double layer, which results in reducing the separation between the electrodes while increasing the surface area, EDLCs attain more energy density.^{17,18} It also shows high reversibility in charge storage owing to the non-Faradaic process and therefore materials like graphene¹⁹, carbon nanotubes²⁰, and activated carbon²¹ are used due to their non-Faradaic charge storage mechanism.²² However, in the case of pseudocapacitors, reversible redox reaction occurred through the Faradaic process at the electrode/electrolyte junction for storage, where transfer of charge takes place.²² Metal oxides/hydroxides(e.g. Co₃O₄, Ni(OH)₂)^{23,24} because of their high specific capacitance and lower resistance, often used for the pseudocapacitors.²⁵ Conducting polymers (e.g. polypyrrole)²⁶ also offer appealing choices due to their redox process of charging and discharging. But in the case of hybrid capacitors, both EDLC and pseudocapacitor type materials are used to assemble.²⁷ Consequently, it benefitted from both materials and therefore offers higher energy density without any decrease in cyclic stability in comparison to other supercapacitors. Based on the electrode configuration used, hybrid capacitors are further categorized into composites, asymmetric, and battery-type. ²⁸

Still, EDLCs show inferior performance when one talks of energy density and specific capacitance and on the other hand pseudocapacitor owing to their rapid oxidation-reduction process exhibit poor rate performance and power density. Therefore, it becomes crucial to develop new alternatives for electrode material to ameliorate the electrolytic performance. Electrode material must have characteristics like elevated conductivity, steadiness over a wide range of temperatures, and inertness towards chemicals and corrosion. It should provide a large specific surface area and should be inexpensive and environmentally safe.^{29–32}

1.2 2D Coordination Polymers for Supercapacitor Application

Over the past few years, encouraging research on two-dimensional (2D) materials, which includes MXene,³³ Covalent organic frameworks (COFs),³⁴ B₄C,³⁴ C₃N₄,³⁵ Coordination Polymers (CPs),³⁶ and layered metal oxides/hydroxides^{28,37} are competently explored. Among these 2D CPs is an intriguing choice and have lately been acknowledged as attractive materials to be utilized for supercapacitor application on account of their tunable porosity, extensive surface area, and their flexibility to host a number of guest molecule. It is comprised of metal clusters and organic linkers and thus provides distinguished physical and chemical properties and shows tunable characteristics that include magnetism, luminescence, and conductivity. Also, their synthetic procedure also involves straightforward reaction pathways. Its properties can be tailored for a specific application by squarely controlling the size, shape, and composition of the synthesized CP. An attractive feature of constructing CPs with mixed linkers to produce 2D layered or 3D scaffolds is there due to their extensive use in the fields of energy or gas storage, sensing, and catalysis.38-40

1.3 Electrolytic Effect on Supercapacitor Application

The performance of CPs for supercapacitor applications can be enhanced using several strategies and the most intriguing among them is the selection of the electrolyte since cations possessing high charge density can render increment in the capacitance while the working window of voltage depends on the electrolyte taken where higher the cations' redox potential, more will be the potential window.^{41,42} So, the choice of electrolyte becomes vital for the supercapacitor application. Many elements need to be examined including conductivity, stability under the working circumstances, mobility of the ions, and viscosity, etc.⁴³

Each electrolyte has its own strength and weakness. Among liquid electrolytes, which are most often used for energy storage applications, organic and ionic electrolytes possess a wide working potential window which results in a high value of energy density. But their low conductivity and high viscous nature result in capacitors that show moderate capacitance and exhibit poor power rates.⁴⁴ In contrast, aqueous electrolytes, which are inexpensive and environmentally safe, exhibit good charge propagation and power rates, high ionic conductivity, and low viscosity, therefore exhibiting high capacitance and better power rates.^{45,46} Aqueous electrolytes are further divided among acidic, basic, and neutral electrolytes. Each of these is widely explored for the supercapacitor application.⁴⁷

Chapter 2

Review of Past Work

Recently Cobalt-based CPs have intrigued researchers owing to their distinctive structural and electrical properties. Shao et al.48 prepared nanorod-like Co-MOF via solvothermal synthesis and displayed Cs around 414.5 F g⁻¹ applying 0.5 A g⁻¹ using a 3M KOH electrolyte and displayed a retention rate of 113% over 30000 cycles. The prepared device provided 12.0 Wh Kg⁻¹ energy density and 258.1 W Kg⁻¹ power density. Kang et al.⁴⁹ reported C_s of 726 F g⁻¹ using a Ni-MOF which exhibited 94.6% cyclic stability over 1000 cycles and displayed 16.5 Wh Kg⁻¹ energy density. Ma et al.⁵⁰ reported a Ni/Co-based nanoscale CP with a Cs of 1160.2 F g⁻¹ and a retention rate of 66% over 7000 cycles. Dian-Durzan et al.⁵¹ synthesized mesoporous carbon from Co-MOF and Cobalt-based CP which exhibits 330 F $g^{-1}C_s$ at 1 A g^{-1} using a 6M KOH electrolyte and 98% capacitance retention after 3000 cycles. The device displays 9.1 Wh Kg⁻¹ energy density and 700 W Kg⁻¹ power density. Hong et al.⁵² via a one-pot solvothermal reaction synthesized Ni-Co/Graphene oxide composite with a retention rate of 99.6% after 300 cycles and a C_s of 447.2 F g⁻¹. Moreover, various studies utilize electrolytic cation's effect on supercapacitor application to escalate the performance of the material. In this regard, Houpt et al.⁵³ utilizing composites of MoS₂ Nanosheets, CNTs, and ZIF-8, prepared an electrode material and explored its electrochemical kinetics using LiCl, NaOH, KCl, and KOH where the composite exhibited best charge storage with KOH. Kumar et al.54 synthesized CNS0.15 and explored its efficacy in distinct electrolytes where sulfide displayed better efficacy NaOH. In our recent work, involving Ni-CP55, an analogous trend was reported.

In this report, we have synthesized Co-CP employing a slow diffusion method. Synthesized Co-CP when utilized for supercapacitors application laid out excellent performance. It displayed C_s of 1092 F g⁻¹ at 1.5 A g⁻¹ where it maintained a retention rate of 98% after 6500 GCD cycles. Further for the optimization of the prepared CP to disclose the electrochemical effects, we utilized aqueous electrolytes, where NaOH, KOH, and LiOH were used. Our research, when compared to the earlier, is found to be more acceptable since the synthesis was carried out at room temperature with safe and sound conditions. Further, its unordered appearance allowed improved interaction and more sites for the electrochemical reaction. Also, using the single material approach for the electrode material not only offers a cut in the production cost but provides a handy fabrication of the device.

Chapter 3

Experimental Section

2.1 Materials

Every single one of the reagents was purchased commercially and put to use without being purified. The following items were acquired from Finar and Merck Chemicals: Co(NO₃)_{2.}6H₂O, DABCO (1,4diazabicyclo[2.2.2]octane), 5-Hydroxyisophthalic acid, NaOH, KOH, LiOH, N,N-dimethylformamide (DMF), and methanol. Additionally, deionized water was used in order to prepare the electrolyte for the application.

2.2 Synthesis of Co-CP

In a typical procedure, 5 mL of DMF solution (solution 1) was utilized to dissolve 54.63 mg (0.3 mmol) of 5-Hydroxyisophthalic acid and 33.65 mg (0.3 mmol) of DABCO. The obtained solution was then gently poured (1 mL) into a tiny crystallization tube with a micropipette. Co(NO₃)_{2.6}H₂O (0.3 mmol, 87.30 mg) was further dissolved within 5 mL of pure methanol in a different tube (solution 2). Besides, a buffer was prepared taking equal amounts of DMF and methanol and followed solution 1 in the crystallization tube. Then solution 2 was cautiously placed over the buffer. The tube was made airtight using parafilm and subsequently placed in normal conditions. After a week, rose-pink-colored Co-CP crystals began to appear on the tube wall. The obtained crystals were separated and left to dry out naturally.



Figure 1. Schematic Representation of Co-CP

2.3 Electrochemical Measurement

The primary techniques applied for assessing the Co-CP as an electrode material were potentiostatic cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). At room temperature, a standard three-electrode system was used to conduct the electrochemical study where Pt-wire counter electrode, silver chloride reference electrode, and for working electrode, carbon cloth (CC) was utilized. To continue further analysis and serve as the working electrode, 400 μ g of Co-CP was dissolved in 1 mL of ethanol, then sonicated for an hour before it was drop-casted on carbon cloth and air-dried at room temperature.

For the calculation of C_S (F g⁻¹) of our coordination polymer, we utilized the GCD technique where we used the following relationship;⁵⁶

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \tag{1}$$

Where I/m, Δt , and ΔV are depicting the current density, time during the discharge cycle of GCD, and potential window of the GCD respectively.

Chapter 4

Characterization

The slow diffusion technique was employed in this work to synthesize the rose pink crystals of Co-CP by reacting Co(NO₃)_{2.6}H₂O with the mixed ligands 5-Hydroxyisophthalic acid and DABCO (1,4-diazabicyclo[2.2.2]octane) at room temperature. This reaction is depicted in Figure 1.

4.1 PXRD Analysis: The 2θ range of 5-80° opted for the XRD probe in order to establish the crystalline nature and purity of the synthesized Co-CP (Figure 2a). It was discovered that synthesized Co-CP was displaying similar characteristics peaks in XRD that correspond to the simulated one. The XRD analysis confirms the synthesized Co-CP's crystalline nature by revealing no impurity peaks. The synthesized Co-CP's organized molecular structure promotes electrochemical performance by increasing the rate of



Figure 2. (a) PXRD Spectra and (b) TGA Curve of Co-CP

electron transport.57

4.2 TGA Analysis: To ascertain Co-CP's thermal stability, thermogravimetric analysis was performed in the N_2 atmosphere where the weight loss at the initial stage (Figure 2b) can be attributed to the

evaporation of non-coordinated water and DMF molecules that reside in the cavity of the coordination polymer. Further weight loss between 150- 250° C was observed due to residual solvent. We observe a ~25 wt.% loss around 300 due to the breakdown of the organic ligands and decomposition of the framework between 400-450° C which concludes that our CP possesses excellent thermal stability.^{58,59}

4.3 FT-IR Analysis: To investigate the bonding and composition of the Co-CP, IR spectra were taken. In Figure 3a, the broad peak around 3200 cm⁻¹ corresponds to the v(O-H) stretching vibrations and confirms the presence of a deprotonated hydroxyl group of carboxyl.⁶⁰ The strong peaks at 1660.5 cm⁻¹ and 1373.5 cm⁻¹ are due to the symmetric $v_s(COO^-)$ and asymmetric $v_{as}(COO^-)$ modes of coordinated carboxylate while the strong peak at 1546.2 cm⁻¹ represent the characteristic $v_{as}(COO^-)$ stretching modes of carboxylate group.⁶¹ The observed peaks at 2963.7 cm⁻¹, 1279.1 cm⁻¹, 1101.8 cm⁻¹, and 1050.5 cm⁻¹ correlates to the v(C-H), v(C-N), v(C-C), and v(C-N) stretching vibrations respectively.³⁹ The peak around 780.4 cm⁻¹ is attributed to the stretching vibration of Co–O–H in the Co-CP.⁶² Further in the fingerprint region, the in-plane vibrations of the benzene ring were observed at 713.7 cm⁻¹ respectively.⁶³



Figure 3. (a) FT-IR Spectra and (b) EDS of Co-CP

4.4 Energy dispersive spectroscopy (EDS) Analysis: (EDS) was also exploited to determine the elemental composition of the produced Co-CP in order to establish the authenticity of the XRD results. (Figure 3b) For C, O, N, and Co, the wt.% were determined to be 46.8, 34.8, 9.4, 9.6, and 0.6 along with Al and Au peaks which were used for the analysis.

4.5 BET Analysis: The N₂ adsorption/desorption technique was employed for the Co-CP (Figure 4) to determine surface area and pore size using the BET method where BET surface area and pore diameter were found to be 169.8 m² g⁻¹ and 3.829 nm, respectively. Aggregates of plate-like particles produce slit-shaped pores responsible for the type III hysteresis.⁶⁴ These findings support the use of plate-like CP in providing a substantial area to improve comprehensive performance.⁶⁵



Figure 4. (a) BET Isotherm and (b) Pore Size Distribution of Co-CP.

4.6 FE-SEM Analysis: For supercapacitor applications, surface morphology is an important variable. Thus, SEM images were obtained to better visualize the surface morphology of Co-CP where aluminum (Al) was used as substrate and for coating, gold (Au) was utilized. The observed SEM images (Figure 5) exhibit characteristic layered or plate-like surface appearance. For electrochemical processes, a disordered framework might create substantial sites and improved interactions.⁶⁶ 1:d suggests the possibility of more accessible sites for the flow of ions toward

the electrode surface, thereby providing a more efficient route for the reaction.



Figure 5. (a-c) FE-SEM Images of Co-CP

Chapter 5

Structural Description of Co-CP



Figure 6. (a-b) Structure of Co-CP, (c) Ball and stick model, (d) View along the c-axis.

As shown in Figure 6a, the Co-CP unit is composed of Co(II) ion, 5-Hydroxyisophthalic acid molecule, and DABCO molecule. It is clear from Figure 6b that in a molecular unit of Co-CP, the Co(II) ion is coordinated by four O-atoms, among which 3 were part of two 5-Hydroxyisophthalic acid units and the remaining one contributed through water molecules, and 2 N-atoms coordinated were part of two DABCO units.

The 1D layer is formed when adjacent Co(II) ions are connected by monodentate and bidentate 5-Hydroxyisophthalic acid, respectively (Figure 6c). In Figure 6c, the one-dimensional network is linked through DABCO and thus provides a 2D framework.

In order to connect the resulting 2D frameworks, the oxygen atom of the carboxyl group in one framework and the coordinated water molecule in the other generate hydrogen bonding. Therefore, a 2D layered model is formed, as seen in Figure 6d, emphasizing Co-CP's porosity.

Crystal Name	Со-СР
Space group	P _{21/m}
a	10.3390(4)
b	7.18111(3)
с	13.8946(6)
α	90
β	91.287(3)
γ	90
volume	1031.35
Z, Z'	4, 0
R-factor	5.29

 Table 1 Crystallographic Information of Co-CP

Chapter 6

Electrochemical Performance

6.1 Electrolytic Effect on Co-CP Performance

By using the three-electrode method predominantly for cyclic voltammetry (CV) charge-discharge and galvanostatic (GCD), the energy storage properties of the Co-CP as an electrode material for the supercapacitor application were investigated (Figure 7-9). The potential window was taken between 0 to 0.54 V for 1M of NaOH, KOH, and LiOH, where CV was recorded at various scan rates (5,10, 20, 30, 40, 50, 70, 100 mV s⁻¹) and GCD at distinct current density (1.5, 2, 3, 4, 5, 6, 7, 8, 9, and 10 A g⁻¹).



Figure 7. (a) CV Curve at different Scan Rates (b) GCD Curve at different Current Densities (c) Variation of Specific Capacitance vs Current Density for Co-CP at **1M NaOH**



Figure 8. CV Curve at different Scan Rates (b) GCD Curve at different Current Densities (c) Variation of Specific Capacitance vs Current Density for Co-CP at **1M KOH**

LiOH, KOH, and NaOH exhibit greater electrochemical performance as demonstrated by the CV plot, and on comparing the area under the curve, the performance order was found to be NaOH > KOH > LiOH. The ionic radii (r_{ion}) and hydrated ionic radii (r_{ih}) of the ions give a firm footing for understanding the trend displayed by Co-CP in all three electrolytes. The r_{ih} follows the trend, Li^+ > Na > K.⁵⁴ Since solution resistance is proportional to the r_{ih} , Li^+ experience it the most, therefore, exhibits low specific capacitance and a moderate rate of charging. However, the ionic radii have a greater impact than hydrated ionic radii when we talk of K⁺ and Na⁺ ions.⁵⁴ Respective r_{ion} for K⁺ and Na⁺ ions is 0.138 nm and 0.102 nm where a larger r_{ion} of K⁺ ions lead to a lower circulation over the electrode surface, compared to Na⁺ ions. Since the capacitance amount and rate of charging and discharging predominantly rest upon both the factors, i.e., r_{ih} , rih

and r_{ion} , therefore the order of the specific capacitance for the electrolytes comes out as 1M NaOH (706 F g⁻¹) > 1M KOH (625 F g⁻¹) > 1M LiOH (405 F g⁻¹). Further, for 1M NaOH, from the CV plot, the obtained redox peaks confirm the pseudocapacitive behavior of the synthesized material.⁶⁷

The effect of scan rate was also noted where the area enclosed by the CV plot increased as we increased the scan rate. This behavior was observed due to the decline in the size of diffusion layer⁶⁸ which results in the increase of peak current.⁵⁵



Figure 9. CV Curve at different Scan Rates (b) GCD Curve at different Current Densities (c) Variation of Specific Capacitance vs Current Density for Co-CP at **1M LiOH**

To determine the charge storage capacity of the Co-CP electrode, we exploited the GCD technique where the pseudocapacitive behavior of our Co-CP was confirmed with the nonlinear curve obtained in the GCD and the superior Coulombic efficiency of the active material is apparent to the GCD's symmetrical charging/discharging time. The discharge curve displays a quick decrease in the potential corresponding to the solution's internal resistance, and another smaller potential decline that occurs due to the capacitive nature of our pseudocapacitive material.⁶⁹ The ohmic drop enables better performance at lower current densities, while at higher current densities, the performance declines to owe to slow reaction kinetics, since high current density prevents the material from ardently participating in the reaction.

Current Density (A g ⁻¹)	Specific Capacitance (F g ⁻¹)				
	1M NaOH	1М КОН	1M LiOH		
1.5	706	625	420		
2	585	509	315		
3	471	388	207		
4	417	333	148		
5	349	286	120		
6	306	244	99		
7	278	219	91		
8	246	192	89		
9	222	182	83		
10	183	165	74		

Table 1. C_s of Co-CP in various electrolytes.



Figure 10. (a) Nyquist Plots and (b) Cyclic Stability Curves of Co-CP

To evaluate the impedance, diffusion kinetics, and charge transfer phenomenon of our Co-CP,⁷⁰ electrochemical impedance spectroscopy (Figure 10a) was recorded for 1M NaOH, KOH, and LiOH. EIS was carried out in the frequency range between 0.1 Hz-100,000 Hz, where obtained semi-circular curve at the high-frequency region corresponds to the impedance offered by the solution and the diffusion kinetics. The intercept of the semicircle along the real axis attributes to the resistance offered by the solution (R_s) while charge transfer impedance (R_{ct}) can be calculated by evaluating the slope over the imaginary axis by the straight line.⁷¹ The low-frequency region where the straight line is observed corresponds to the Warburg impedance (Z_w) which often provides us with the resistance between the electrode and electrolyte interfaces.⁷² Here, due to the combined effects of the r_i and r_{ih}, similarity in the nature of the Nyquist plot of different electrolytes was observed⁷³ and the low value of R_s for the NaOH is in favor of the better performance displayed by Co-CP in the NaOH.

The capacitance retention rate (Figure 10b) of the electrode material was determined using GCD, where over 6500 cycles were conducted to determine the practical application of Co-CP. It exhibited an impressive rate of retention and persisted at 98%.

6.2 Concentration Effect on Co-CP Performance

To study the effect of electrolyte concentration of Co-CP, CV and GCD were again performed and compared at various concentrations of NaOH (1M, 3M, 5M, and 7M) (Figure 11-13) where CV was recorded at various scan rates (5,10, 20, 30, 40, 50, 70, 100 mV s⁻¹) and GCD at distinct current density (1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10 A g⁻¹)



Figure 11. CV Curve at different Scan Rates (b) GCD Curve at different Current Densities (c) Variation of Specific Capacitance vs Current Density for Co-CP at **3M NaOH**

Figure 11a, 12a, and 13a, displays the CV curves for the various concentrations, where, it is evident that as we increase the NaOH electrolyte concentration, the area under the CV plot also climbs. The CV curve that failed to display clear redox peaks at low NaOH concentration (1M) appears to be defining the redox peaks clearly as the NaOH electrolyte concentration was increased, while the gap between the redox peak declined. The behavior is attributed to the adsorption of almost

all of the ions of the electrolyte at high-area junction, which results in the starvation of the free electrolyte and also increases the internal resistance.⁷⁴ A shift in the oxidation and reduction peak was observed as we increased the scan rate in the voltammogram where the oxidation peaks shift to a higher potential while the reduction peaks to a lower potential. This phenomenon can be contributed to the Faradaic redox processes taking place at the electrode/electrolyte interface.⁷⁵



Figure 12. CV Curve at different Scan Rates (b) GCD Curve at different Current Densities (c) Variation of Specific Capacitance vs Current Density for Co-CP at **5M NaOH**

Figures 11b, 12b, and 13b display the GCD profile of the Co-CP at various concentrations. Since specific conductivity plays a vital role in determining the electrochemical performance as specific capacitance is directly proportional to the conductivity. Since an increase in the concentration of the electrolyte results in improved conductivity, therefore the increase in the specific capacitance can be attributed to the increase in the

conductivity.⁷⁶ Hence, our trend of specific capacitance follows 7M NaOH (1092 F g⁻¹) > 5M NaOH (947 F g⁻¹) > 3M NaOH (817 F g⁻¹) > 1M NaOH (706 F g⁻¹), which can be seen in Table 2. In the GCD profile, it was observed that the discharge time decreases with increasing current density. This behavior can be attributed to the decrease in ion diffusion as we increase current flow.⁷⁷



Figure 13. CV Curve at different Scan Rates (b) GCD Curve at different Current Densities (c) Variation of Specific Capacitance vs Current Density for Co-CP at **7M NaOH**

Current Density	Specific Capacitance (F g ⁻¹)				
(A g ⁻¹)	1M NaOH	3M NaOH	5M NaOH	7M NaOH	
1.5	706	817	947	1092	
2	585	772	830	1030	
3	471	685	712	912	
4	417	625	673	854	
5	349	583	629	809	
6	306	547	584	766	
7	278	518	556	727	
8	246	487	529	698	
9	222	463	496	652	
10	183	441	481	633	

Table 2. Cs of Co-CP various Concentrations of NaOH.

Table 3. Recent Work on Supercapacitors Application using CP or MOF-based Electrodes

Sr No.	Material	Electrolyt e	Curre nt	Specific capacita	Cyclic Stability	Energy density	Power density	Ref.
			densit y (A g ⁻¹)	nce (F g ⁻¹)		(kWh g ⁻¹)	(kW g ⁻¹)	
1	Co, N-doped CP	6М КОН	1	330	98%, 3000 cycles	9.1	700	59
2	Ni- MOF/rGO	6М КОН	1	954	80.25%, 4000 cycles	17.13	750	78
3	Ni-MOF nanosheets	1М КОН	1	1024.4	49%, 5000 cycles	13	-	79
4	Ni-Co-MOF	ЗМ КОН	1	827.9	-	29.1	800	80
5	Zn(tbip) derived porous C	6М КОН	0.5	369	96%, 2000 cycles	12.5	7200	81
6	rGO/ZIF-8	1М КОН	1	336	96%, 10000 cycles	11.7	500	82
7	Ni- BPDC/GO-3	6М КОН	1	630	95.7%, 10000 cycles	16.5	250	83
8	Ni-MOF	1М КОН	1	1024	49.1%, 5000 cycles	14.6	400	78
9	Ni-C/Ni- BDC	6М КОН	2	672	57%	17.8	350	84
10	Со-СР	7M	1.5	1092	98% over 6500 cycles			THIS WORK

Chapter 7 Conclusion

In conclusion, we prepared a layered Co-CP at room temperature and characterized it with SC-XRD and other analytical techniques. 1092 F g⁻¹ of specific capacitance at 1.5 A g⁻¹ was delivered by Co-CP in a 7M NaOH and sustained cyclic retention of 98% over 6500 cycles. The electrode/electrolyte junction's quick ion transport channels allowed this electrochemical behavior. The outcomes are then contrasted using three different electrolytes where, owing to the integrated consequences of r_{ion} and r_{ih}, Co-CP demonstrated superior results in NaOH. A further effect of concentration was determined using 3M, 5M, and 7M NaOH where with an increase in the concentration resulted in the increase of C_s value. As a result, this work offers a handy room temperature synthesis of a non-additive material for the electrochemical study of supercapacitor application.

REFERENCES

- Boorboor Ajdari, F.; Kowsari, E.; Niknam Shahrak, M.; Ehsani, A.; Kiaei, Z.; Torkzaban, H.; Ershadi, M.; Kholghi Eshkalak, S.; Haddadi-Asl, V.; Chinnappan, A.; Ramakrishna, S. A Review on the Field Patents and Recent Developments over the Application of Metal Organic Frameworks (MOFs) in Supercapacitors. *Coord. Chem. Rev.* **2020**, *422*, 213441. https://doi.org/10.1016/j.ccr.2020.213441.
- (2) Luo, X.; Wang, J.; Dooner, M.; Clarke, J. Overview of Current Development in Electrical Energy Storage Technologies and the Application Potential in Power System Operation. *Appl. Energy* 2015, 137, 511–536. https://doi.org/10.1016/j.apenergy.2014.09.081.
- González, A.; Goikolea, E.; Barrena, J. A.; Mysyk, R. Review on Supercapacitors: Technologies and Materials. *Renew. Sust. Energ. Rev.* 2016, 58, 1189–1206. https://doi.org/10.1016/j.rser.2015.12.249.
- (4) Meng, X.-X.; Li, J.-Y.; Yang, B.-L.; Li, Z.-X. MOF-Derived NiO Nanoparticles Prilled by Controllable Explosion of Perchlorate Ion: Practical Excellent Performances and Applications in Supercapacitors. Appl. Surf. 2020. 507. 145077. Sci. https://doi.org/10.1016/j.apsusc.2019.145077.
- (5) Song, J.; Yu, Z.; Xu, T.; Chen, S.; Sohn, H.; Regula, M.; Wang, D. Flexible Freestanding Sandwich-Structured Sulfur Cathode with Superior Performance for Lithium–Sulfur Batteries. *J. Mater. Chem. A.* 2014, 2 (23), 8623–8627. https://doi.org/10.1039/C4TA00742E.
- Peng, S.; Li, L.; Tan, H.; Cai, R.; Shi, W.; Li, C.; Mhaisalkar, S. G.; Srinivasan, M.; Ramakrishna, S.; Yan, Q. MS 2 (M = Co and Ni) Hollow Spheres with Tunable Interiors for High-Performance Supercapacitors and Photovoltaics. *Adv. Funct. Mater.* 2014, 24 (15), 2155–2162. https://doi.org/10.1002/adfm.201303273.
- (7) Libich, J.; Máca, J.; Vondrák, J.; Čech, O.; Sedlaříková, M. Supercapacitors: Properties and Applications. J. Energy Storage 2018, 17, 224–227. https://doi.org/10.1016/j.est.2018.03.012.

- Miller, J. R.; Simon, P. Electrochemical Capacitors for Energy Management. *Science* 2008, *321* (5889), 651–652. https://doi.org/10.1126/science.1158736.
- Li, X.; Xiao, X.; Li, Q.; Wei, J.; Xue, H.; Pang, H. Metal (M = Co, Ni) Phosphate Based Materials for High-Performance Supercapacitors. *Inorg. Chem. Front.* 2018, 5 (1), 11–28. https://doi.org/10.1039/C7QI00434F.
- Kötz, R.; Carlen, M. Principles and Applications of Electrochemical Capacitors. *Electrochim. Acta* 2000, 45 (15–16), 2483–2498. https://doi.org/10.1016/S0013-4686(00)00354-6.
- (11) Khaligh, A.; Zhihao Li. Battery, Ultracapacitor, Fuel Cell, and Hybrid Energy Storage Systems for Electric, Hybrid Electric, Fuel Cell, and Plug-In Hybrid Electric Vehicles: State of the Art. *IEEE Trans. Veh. Technol.* **2010**, *59* (6), 2806–2814. https://doi.org/10.1109/TVT.2010.2047877.
- (12) Tummuru, N. R.; Mishra, M. K.; Srinivas, S. Dynamic Energy Management of Renewable Grid Integrated Hybrid Energy Storage System. *IEEE Trans. Ind. Electron.* **2015**, *62* (12), 7728–7737. https://doi.org/10.1109/TIE.2015.2455063.
- (13) Zandi, M.; Payman, A.; Martin, J.-P.; Pierfederici, S.; Davat, B.; Meibody-Tabar, F. Energy Management of a Fuel Cell/Supercapacitor/Battery Power Source for Electric Vehicular Applications. *IEEE Trans. Veh. Technol.* **2011**, *60* (2), 433–443. https://doi.org/10.1109/TVT.2010.2091433.
- (14) Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical Energy Storage for Green Grid. *Chem. Rev.* 2011, *111* (5), 3577–3613. https://doi.org/10.1021/cr100290v.
- (15) Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* 2011, *334* (6058), 928–935. https://doi.org/10.1126/science.1212741.
- Kiamahalleh, M. V.; Zein, S. H. S.; Najafpour, G.; Sata, S. A.; Buniran, S. Multiwalled Carbon Nanotubes Based Nanocomposites For Supercapacitors: A Review Of Electrode Materials. *Nano.* 2012, 07 (02), 1230002. https://doi.org/10.1142/S1793292012300022.

- (17) S. Iro, Z. A Brief Review on Electrode Materials for Supercapacitor. *Int. J. Electrochem. Sci.* 2016, 10628–10643. https://doi.org/10.20964/2016.12.50.
- Wu, H. P.; He, D. W.; Wang, Y. S.; Fu, M.; Liu, Z. L.; Wang, J. G.; Wang, H. T. Graphene as the Electrode Material in Supercapacitors. In 2010 8th International Vacuum Electron Sources Conference and Nanocarbon; IEEE, 2010, pp 465–466. https://doi.org/10.1109/IVESC.2010.5644267.
- (19) An, C.; Wang, Y.; Jiao, L.; Yuan, H. Mesoporous Ni@C Hybrids for a High Energy Aqueous Asymmetric Supercapacitor Device. J. Mater. Chem. A. Mater. 2016, 4 (24), 9670–9676. https://doi.org/10.1039/C6TA02339H.
- (20) Wu, T.; Chen, B. Synthesis of Multiwalled Carbon Nanotube-Reinforced Polyborosiloxane Nanocomposites with Mechanically Adaptive and Self-Healing Capabilities for Flexible Conductors. *ACS Appl. Mater. Interfaces* **2016**, 8 (36), 24071–24078. https://doi.org/10.1021/acsami.6b06137.
- (21) Tian, W.; Gao, Q.; Zhang, L.; Yang, C.; Li, Z.; Tan, Y.; Qian, W.; Zhang, H. Renewable Graphene-like Nitrogen-Doped Carbon Nanosheets as Supercapacitor Electrodes with Integrated High Energy–Power Properties. J. Mater. Chem. A. Mater. 2016, 4 (22), 8690–8699. https://doi.org/10.1039/C6TA02828D.
- (22) Chmiola, J.; Largeot, C.; Taberna, P.-L.; Simon, P.; Gogotsi, Y. Monolithic Carbide-Derived Carbon Films for Micro-Supercapacitors. *Science* 2010, 328 (5977), 480–483. https://doi.org/10.1126/science.1184126.
- (23) Parveen, N.; Cho, M. H. Self-Assembled 3D Flower-Like Nickel Hydroxide Nanostructures and Their Supercapacitor Applications. *Sci. Rep.* 2016, 6 (1), 27318. https://doi.org/10.1038/srep27318.
- (24) Meher, S. K.; Rao, G. R. Ultralayered Co ₃ O₄ for High-Performance Supercapacitor Applications. J. Phys. Chem. C. 2011, 115 (31), 15646–15654. https://doi.org/10.1021/jp201200e.
- (25) Chen, H.; Zhou, J.; Li, Q.; Tao, K.; Yu, X.; Zhao, S.; Hu, Y.; Zhao, W.; Han, L. Core–Shell Assembly of Co ₃ O ₄ @NiO-ZnO Nanoarrays as Battery-Type Electrodes for High-Performance

Supercapatteries. *Inorg. Chem. Front.* **2019**, *6* (9), 2481–2487. https://doi.org/10.1039/C9QI00607A.

- (26) Chen, G.; Li, X.; Zhang, L.; Li, N.; Ma, T. Y.; Liu, Z. A Porous Perchlorate-Doped Polypyrrole Nanocoating on Nickel Nanotube Arrays for Stable Wide-Potential-Window Supercapacitors. *Adv. Mater.* 2016, 28 (35), 7680–7687. https://doi.org/10.1002/adma.201601781.
- (27) Li, Y.; van Zijll, M.; Chiang, S.; Pan, N. KOH Modified Graphene Nanosheets for Supercapacitor Electrodes. J. Power Sources 2011, 196 (14), 6003–6006. https://doi.org/10.1016/j.jpowsour.2011.02.092.
- (28) Zhao, B.; Chen, D.; Xiong, X.; Song, B.; Hu, R.; Zhang, Q.; Rainwater, B. H.; Waller, G. H.; Zhen, D.; Ding, Y.; Chen, Y.; Qu, C.; Dang, D.; Wong, C.-P.; Liu, M. A High-Energy, Long Cycle-Life Hybrid Supercapacitor Based on Graphene Composite Electrodes. *Energy Storage Mater.* 2017, 7, 32–39. https://doi.org/10.1016/j.ensm.2016.11.010.
- (29) Xie, L.; Sun, G.; Su, F.; Guo, X.; Kong, Q.; Li, X.; Huang, X.; Wan, L.; song, W.; Li, K.; Lv, C.; Chen, C.-M. Hierarchical Porous Carbon Microtubes Derived from Willow Catkins for Supercapacitor Applications. J. Mater. Chem. A. Mater. 2016, 4 (5), 1637–1646. https://doi.org/10.1039/C5TA09043A.
- (30) Frackowiak, E.; Béguin, F. Carbon Materials for the Electrochemical Storage of Energy in Capacitors. *Carbon. N. Y.* 2001, *39* (6), 937–950. https://doi.org/10.1016/S0008-6223(00)00183-4.
- (31) Kim, B. K.; Sy, S.; Yu, A.; Zhang, J. Electrochemical Supercapacitors for Energy Storage and Conversion. In *Handbook of Clean Energy Systems*; John Wiley & Sons, Ltd: Chichester, UK, 2015; pp 1–25. https://doi.org/10.1002/9781118991978.hces112.
- (32) Sevilla, M.; Mokaya, R. Energy Storage Applications of Activated Carbons: Supercapacitors and Hydrogen Storage. *Energy Environ. Sci.* 2014, 7 (4), 1250–1280. https://doi.org/10.1039/C3EE43525C.
- (33) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D Metal Carbides and Nitrides (MXenes) for Energy Storage. *Nat. Rev. Mater.* 2017, 2 (2), 16098. https://doi.org/10.1038/natrevmats.2016.98.

- (34) Chandra, S.; Roy Chowdhury, D.; Addicoat, M.; Heine, T.; Paul, A.; Banerjee, R. Molecular Level Control of the Capacitance of Two-Dimensional Covalent Organic Frameworks: Role of Hydrogen Bonding in Energy Storage Materials. *Chem. Mater.* 2017, 29 (5), 2074–2080. https://doi.org/10.1021/acs.chemmater.6b04178.
- (35) Wu, D.; Cao, K.; Wang, F.; Wang, H.; Gao, Z.; Xu, F.; Guo, Y.; Jiang, K. Two Dimensional Graphitic-Phase C3N4 as Multifunctional Protecting Layer for Enhanced Short-Circuit Photocurrent in ZnO Based Dye-Sensitized Solar Cells. J. Chem. Eng. 2015, 280, 441–447. https://doi.org/10.1016/j.cej.2015.06.006.
- (36) Li, W.; Sun, L.; Qi, J.; Jarillo-Herrero, P.; Dincă, M.; Li, J. High Temperature Ferromagnetism in π-Conjugated Two-Dimensional Metal–Organic Frameworks. *Chem. Sci.* 2017, 8 (4), 2859–2867. https://doi.org/10.1039/C6SC05080H.
- (37) Cai, X.; Shen, X.; Ma, L.; Ji, Z.; Xu, C.; Yuan, A. Solvothermal Synthesis of NiCo-Layered Double Hydroxide Nanosheets Decorated on RGO Sheets for High Performance Supercapacitor. *J. Chem. Eng.* 2015, 268, 251–259. https://doi.org/10.1016/j.cej.2015.01.072.
- (38) Yu, L.; Wang, X.; Cheng, M.; Rong, H.; Song, Y.; Liu, Q. A Three-Dimensional Copper Coordination Polymer Constructed by 3-Methyl-1 *H* -Pyrazole-4-Carboxylic Acid with Higher Capacitance for Supercapacitors. *Cryst. Growth. Des.* **2018**, *18* (1), 280–285. https://doi.org/10.1021/acs.cgd.7b01219.
- (39) Rajak, R.; Saraf, M.; Verma, S. K.; Kumar, R.; Mobin, S. M. Dy(III)-Based Metal–Organic Framework as a Fluorescent Probe for Highly Selective Detection of Picric Acid in Aqueous Medium. *Inorg. Chem.* 2019, 58 (23), 16065–16074. https://doi.org/10.1021/acs.inorgchem.9b02611.
- (40) Wang, H.-Y.; Su, J.; Ma, J.-P.; Yu, F.; Leong, C. F.; D'Alessandro, D. M.; Kurmoo, M.; Zuo, J.-L. Concomitant Use of Tetrathiafulvalene and 7,7,8,8-Tetracyanoquinodimethane within the Skeletons of Metal–Organic Frameworks: Structures, Magnetism, and Electrochemistry. *Inorg. Chem.* 2019, 58 (13), 8657–8664. https://doi.org/10.1021/acs.inorgchem.9b01000.

- (41) Liu, T.; Pell, W. G.; Conway, B. E. Self-Discharge and Potential Recovery Phenomena at Thermally and Electrochemically Prepared RuO2 Supercapacitor Electrodes. *Electrochim. Acta* 1997, *42* (23– 24), 3541–3552. https://doi.org/10.1016/S0013-4686(97)81190-5.
- (42) Conway, B. E.; Pell, W. G.; Liu, T.-C. Diagnostic Analyses for Mechanisms of Self-Discharge of Electrochemical Capacitors and Batteries. J. Power Sources 1997, 65 (1–2), 53–59. https://doi.org/10.1016/S0378-7753(97)02468-3.
- (43) Wang, D.-W.; Li, F.; Liu, M.; Lu, G. Q.; Cheng, H.-M. 3D Aperiodic Hierarchical Porous Graphitic Carbon Material for High-Rate Electrochemical Capacitive Energy Storage. *Angew. Chem.* 2008, *120* (2), 379–382. https://doi.org/10.1002/ange.200702721.
- (44) Zhong, C.; Deng, Y.; Hu, W.; Qiao, J.; Zhang, L.; Zhang, J. A Review of Electrolyte Materials and Compositions for Electrochemical Supercapacitors. *Chem. Soc. Rev.* 2015, 44 (21), 7484–7539. https://doi.org/10.1039/C5CS00303B.
- (45) Lehtimäki, S.; Railanmaa, A.; Keskinen, J.; Kujala, M.; Tuukkanen, S.; Lupo, D. Performance, Stability and Operation Voltage Optimization of Screen-Printed Aqueous Supercapacitors. *Sci. Rep.* 2017, 7 (1), 46001. https://doi.org/10.1038/srep46001.
- (46) Peng, X.; Liu, H.; Yin, Q.; Wu, J.; Chen, P.; Zhang, G.; Liu, G.; Wu, C.; Xie, Y. A Zwitterionic Gel Electrolyte for Efficient Solid-State Supercapacitors. *Nat. Commun.* 2016, 7 (1), 11782. https://doi.org/10.1038/ncomms11782.
- (47) Iqbal, M. Z.; Zakar, S.; Haider, S. S. Role of Aqueous Electrolytes on the Performance of Electrochemical Energy Storage Device. *J. Electroanal. Chem.* 2020, 858, 113793. https://doi.org/10.1016/j.jelechem.2019.113793.
- (48) Shao, D.; Wang, L.; Lu, B.; Guo, J.; Zhang, S.; Lu, Y. A High N Content Cobalt-Based Metal Organic Framework with Nanorod Structure for Supercapacitor Electrode Material. *J. Electroanal. Chem.* 2019, 847, 113188. https://doi.org/10.1016/j.jelechem.2019.113188.
- (49) Kang, L.; Sun, S.-X.; Kong, L.-B.; Lang, J.-W.; Luo, Y.-C. Investigating Metal-Organic Framework as a New Pseudo-

Capacitive Material for Supercapacitors. *Chin. Chem. Lett.* **2014**, *25* (6), 957–961. https://doi.org/10.1016/j.cclet.2014.05.032.

- (50) Ma, Q.; Cui, F.; Zhang, J.; Yan, Y.; Cui, T. Facile Access to Ni/Co-Based Nanoscale Coordination Polymers for the Boosted Electrochemical Performance of Asymmetric Supercapacitors. *ACS Appl. Energy Mater.* 2022, 5 (10), 12165–12173. https://doi.org/10.1021/acsaem.2c01635.
- (51) Díaz-Duran, A. K.; Montiel, G.; Viva, F. A.; Roncaroli, F. Co,N-Doped Mesoporous Carbons Cobalt Derived from Coordination Polymer as Supercapacitors. *Electrochim. Acta* 2019, 299, 987–998. https://doi.org/10.1016/j.electacta.2019.01.023.
- (52) Hong, J.; Park, S.-J.; Kim, S. Synthesis and Electrochemical Characterization of Nanostructured Ni-Co-MOF/Graphene Oxide Composites as Capacitor Electrodes. *Electrochim. Acta* 2019, *311*, 62–71. https://doi.org/10.1016/j.electacta.2019.04.121.
- (53) Houpt, D.; Ji, J.; Yang, D.; Choi, J. H. High-Performance Supercapacitor Electrodes Based on Composites of MoS 2 Nanosheets, Carbon Nanotubes, and ZIF-8 Metal–Organic Framework Nanoparticles. ACS Appl. Nano. Mater. 2022, 5 (1), 1491–1499. https://doi.org/10.1021/acsanm.1c04065.
- (54) Kumar, V.; Panda, H. S. Miniaturization of Binary Metal Sulfides Electrode Materials in Water-Ethanol Solvent Medium: Remarkable Improvement in Specific Capacitance and Cyclic Stability. *Mater. Chem. Phys.* **2021**, 272, 125042. https://doi.org/10.1016/j.matchemphys.2021.125042.
- (55) Deka, R.; Kumar, V.; Rajak, R.; Mobin, S. M. Two-Dimensional Layered Nickel-Based Coordination Polymer for Supercapacitive Performance. *Sustain. Energy. Fuels.* **2022**, *6* (12), 3014–3024. https://doi.org/10.1039/D2SE00527A.
- (56) Ma, Q.; Cui, F.; Liu, M.; Zhang, J.; Cui, T. Facile Assembly of 2D Ni-Based Coordination Polymer Nanosheets as Battery-Type Electrodes for High-Performance Supercapacitors. *Nano.* 2021, *13* (25), 11112–11119. https://doi.org/10.1039/D1NR01102B.

- (57) Du, C.; Yeh, J.; Pan, N. Carbon Nanotube Thin Films with Ordered Structures. J. Mater. Chem. 2005, 15 (5), 548. https://doi.org/10.1039/b414682d.
- Jiang, W.-H.; Zhang, H.-Z.; Hou, G.-F.; Ma, D.-S.; Liu, B.; Yu, Y.-H. Five Co. Coordination Polymers with Different Counter Anions Based on [3,5-Di(4H-1,2,4-Triazol-4-Yl)Benzoato] Ligand: Directed Synthesis, Structures and Magnetic Properties. *RSC Adv.* 2017, 7 (72), 45641–45651. https://doi.org/10.1039/C7RA07089F.
- (59) Sargazi, G.; Afzali, D.; Ghafainazari, A.; Saravani, H. Rapid Synthesis of Cobalt Metal Organic Framework. J. Inorg. Organomet. Polym. Mater. 2014, 24 (4), 786–790. https://doi.org/10.1007/s10904-014-0042-z.
- (60) Wang, Y.; Ma, J.-X.; Zhang, Y.; Xu, N.; Wang, X.-L. A Series of Cobalt-Based Coordination Polymer Crystalline Materials as Highly Sensitive Electrochemical Sensors for Detecting Trace Cr(VI), Fe(III) Ions, and Ascorbic Acid. *Cryst. Growth. Des.* 2021, 21 (8), 4390–4397. https://doi.org/10.1021/acs.cgd.1c00311.
- (61) Meng, F.; Fang, Z.; Li, Z.; Xu, W.; Wang, M.; Liu, Y.; Zhang, J.; Wang, W.; Zhao, D.; Guo, X. Porous Co3O4 Materials Prepared by Solid-State Thermolysis of a Novel Co-MOF Crystal and Their Superior Energy Storage Performances for Supercapacitors. J. Mater. Chem. A. Mater. 2013, 1 (24), 7235. https://doi.org/10.1039/c3ta11054k.
- (62) Abedini, H.; Shariati, A.; Khosravi-Nikou, M. R. Adsorption of Propane and Propylene on M-MOF-74 (M = Cu, Co): Equilibrium and Kinetic Study. *Chem. Eng. Res. Des.* **2020**, *153*, 96–106. https://doi.org/10.1016/j.cherd.2019.10.014.
- (63) Hu, X.; Wang, H.; Qi, S.; Su, Z.; Wang, J.; Chen, K.; Li, S.; Huang, X.; Luo, S.; Xie, A. Co/C Nanomaterial Derived from Co Metal–Organic Framework for Oxygen Evolution Reaction. *Ionics (Kiel)* 2022, 28 (2), 813–821. https://doi.org/10.1007/s11581-021-04376-4.
- (64) Yurdakal, S.; Garlisi, C.; Özcan, L.; Bellardita, M.; Palmisano, G. (Photo)Catalyst Characterization Techniques. In *Heterogeneous Photocatalysis*; Elsevier, 2019; pp 87–152. https://doi.org/10.1016/B978-0-444-64015-4.00004-3.

- (65) Rajak, R.; Saraf, M.; Mohammad, A.; Mobin, S. M. Design and Construction of a Ferrocene Based Inclined Polycatenated Co-MOF for Supercapacitor and Dye Adsorption Applications. *J. Mater. Chem. A. Mater.* 2017, *5* (34), 17998–18011. https://doi.org/10.1039/C7TA03773B.
- (66) Gao, S.; Sui, Y.; Wei, F.; Qi, J.; Meng, Q.; Ren, Y.; He, Y. Dandelion-like Nickel/Cobalt Metal-Organic Framework Based Electrode Materials for High Performance Supercapacitors. J. Colloid Interface Sci. 2018, 531, 83–90. https://doi.org/10.1016/j.jcis.2018.07.044.
- (67) Nishchith, B. S.; Ashoka, S.; Bhat, M. P.; Kurkuri, M. D.; Acharya, S.; Kumar, R.; Kalegowda, Y. Reversible Surface Reconstruction of Na3NiCO3PO4: A Battery Type Electrode for Pseudocapacitor Applications. *J. Power Sources* 2022, 520, 230903. https://doi.org/10.1016/j.jpowsour.2021.230903.
- (68) Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner's Guide to Cyclic Voltammetry. J. Chem. Educ. 2018, 95 (2), 197–206. https://doi.org/10.1021/acs.jchemed.7b00361.
- (69) Shokry, A.; Karim, M.; Khalil, M.; Ebrahim, S.; El Nady, J. Supercapacitor Based on Polymeric Binary Composite of Polythiophene and Single-Walled Carbon Nanotubes. *Sci. Rep.* 2022, *12* (1), 11278. https://doi.org/10.1038/s41598-022-15477-z.
- (70) Li, S.; Xu, X.; Yao, Z.; Jiang, X.; Huan, Y.; Hu, X.; Chen, W.; Wei, T. A Comparative Study on the Li ⁺ /Na ⁺ Transportation in NASICON-Type Electrolytes. J. Phys. Chem. C. 2018, 122 (36), 20565–20570. https://doi.org/10.1021/acs.jpcc.8b01987.
- (71) Vidhyadharan, B.; Misnon, I. I.; Aziz, R. A.; Padmasree, K. P.; Yusoff, M. M.; Jose, R. Superior Supercapacitive Performance in Electrospun Copper Oxide Nanowire Electrodes. *J. Mater. Chem. A* 2014, 2 (18), 6578–6588. https://doi.org/10.1039/C3TA15304E.
- (72) Tripathi, H. S.; Dutta, A.; Sinha, T. P. Tailoring Structural and Electrochemical Properties in Sr2+ Incorporated Nanostructured BiFeO3 for Enhanced Asymmetric Solidstate Supercapacitor. *Electrochim. Acta* 2022, 421, 140505. https://doi.org/10.1016/j.electacta.2022.140505.

- (73) Kumar, V.; Panda, H. S. Miniaturization of Binary Metal Sulfides Electrode Materials in Water-Ethanol Solvent Medium: Remarkable Improvement in Specific Capacitance and Cyclic Stability. *Mater. Chem. Phys.* **2021**, 272, 125042. https://doi.org/10.1016/j.matchemphys.2021.125042.
- (74) Hu, C.-C.; Tsou, T.-W. Ideal Capacitive Behavior of Hydrous Manganese Oxide Prepared by Anodic Deposition. *Electrochem. Commun.* 2002, 4 (2), 105–109. https://doi.org/10.1016/S1388-2481(01)00285-5.
- (75) Yu, L.; Yang, B.; Liu, Q.; Liu, J.; Wang, X.; Song, D.; Wang, J.; Jing, X. Interconnected NiS Nanosheets Supported by Nickel Foam: Soaking Fabrication and Supercapacitors Application. *J. Electroanal. Chem.* 2015, 739, 156–163. https://doi.org/10.1016/j.jelechem.2014.12.031.
- (76) Gilliam, R.; Graydon, J.; Kirk, D.; Thorpe, S. A Review of Specific Conductivities of Potassium Hydroxide Solutions for Various Concentrations and Temperatures. *Int J. Hydrogen Energy* 2007, *32* (3), 359–364. https://doi.org/10.1016/j.ijhydene.2006.10.062.
- (77) Wan, C.; Jiao, Y.; Bao, W.; Gao, H.; Wu, Y.; Li, J. Self-Stacked Multilayer FeOCl Supported on a Cellulose-Derived Carbon Aerogel: A New and High-Performance Anode Material for Supercapacitors. J. Mater. Chem. A. Mater. 2019, 7(16), 9556–9564. https://doi.org/10.1039/C8TA12261J.
- (78) Zhong, Y.; Cao, X.; Ying, L.; Cui, L.; Barrow, C.; Yang, W.; Liu, J. Homogeneous Nickel Metal-Organic Framework Microspheres on Reduced Graphene Oxide as Novel Electrode Material for Supercapacitors with Outstanding Performance. J. Colloid Interface Sci. 2020, 561, 265–274. https://doi.org/10.1016/j.jcis.2019.10.023.
- (79) Gu, M.; Wu, M.; Wang, S.-C.; Chen, C.; Xiong, D.; Yi, F.-Y. Morphology Control of Nanoscale Metal-Organic Frameworks for High-Performance Supercapacitors. *Electrochim. Acta* 2020, 343, 135617. https://doi.org/10.1016/j.electacta.2020.135617.
- (80) Quan, L.; Liu, T.; Yi, M.; Chen, Q.; Cai, D.; Zhan, H. Construction of Hierarchical Nickel Cobalt Selenide Complex Hollow Spheres for Pseudocapacitors with Enhanced Performance. *Electrochim. Acta* 2018, 281, 109–116. https://doi.org/10.1016/j.electacta.2018.05.100.

- (81) Cao, X.-M.; Sun, Z.-J.; Zhao, S.-Y.; Wang, B.; Han, Z.-B. MOF-Derived Sponge-like Hierarchical Porous Carbon for Flexible All-Solid-State Supercapacitors. *Mater. Chem. Front.* 2018, 2 (9), 1692– 1699. https://doi.org/10.1039/C8QM00284C.
- (82) Samuel, E.; Joshi, B.; Park, C.; Aldalbahi, A.; Rahaman, M.; Yoon, S. S. Supersonically Sprayed RGO/ZIF8 on Nickel Nanocone Substrate for Highly Stable Supercapacitor Electrodes. *Electrochim. Acta* 2020, 362, 137154. https://doi.org/10.1016/j.electacta.2020.137154.
- (83) He, F.; Yang, N.; Li, K.; Wang, X.; Cong, S.; Zhang, L.; Xiong, S.; Zhou, A. Hydrothermal Synthesis of Ni-Based Metal Organic Frameworks/Graphene Oxide Composites as Supercapacitor Electrode Materials. J. Mater. Res. 2020, 35 (11), 1439–1450. https://doi.org/10.1557/jmr.2020.93.
- (84) Bai, Z.; Liu, S.; Chen, P.; Cheng, G.; Wu, G.; Li, H.; Liu, Y. Nickel Nanoparticles Embedded in Porous Carbon Nanofibers and Its Electrochemical Properties. *Nanotechnology* 2020, *31* (30), 305705. https://doi.org/10.1088/1361-6528/ab8594.