**The cathode in sodium-ion batteries**

MOFs are being used as a precursor for synthesizing electrodes. The following are the advantages of using MOF as a template or precursor as a cathode. MOFs offer nanoporous structures that can control geometry and pore size as a result helps in improving cyclic stability. Controlling the morphology of MOF is easy so, helps in improving the movement of ions and electrons. Ligands can be modified by doping to improve characteristics. However, the energy density and cyclic stability of SIBs are insufficient for practical use, mainly limited by the unsatisfactory electrochemical performance of the cathode, caused by the huge volume change and sluggish kinetics due to the large ion radius. <https://doi.org/10.1002/celc.201900843>

In literature mostly the MOFs are being used in composite forms for the cathode in sodium ion batteries. Here two categories of cathodes’ materials are being discussed. 1) MOFs’ composite as cathode 2) Pristine MOF as cathode.

**A. Pristine MOFs**

1. **Aluminum coordinated poly (tetrahydroxy benzoquinone)**

Quinone derivatives like anthraquinone, benzoquinone, phenanthraquinone, and naphthoquinone are attractive cathode material because of high redox potential and high theoretical capacity almost 600 mAg-1. However, it has low cyclic stability as it gets dissolved in electrolyte and also has low thermal stability. Metal-organic coordination polymers and porous coordination polymers are easy to synthesize and are thermally as well as structurally stable. Aluminum tetrahydroxy benzoquinone is one of the coordination polymers.

For synthesis of P(THBQ-Al), coordination reaction between benzoquinonedihydroxydiolate (C6O6H2)2- as a ligand and aluminum cation as a complex metal ion was done. For comparison THBQ was also synthesized.

The sample was amorphous in nature due to Al-O bond. It decomposed at 350 ℃ so, it was thermally stable as compared to another sample. SEM confirmed that the sample agglomerates at nanometer size. It was highly insoluble electrolyte maintaining the structural integrity during cycling.

P(THBQ-Al) showed high reversible capacity of 113 mAh/g. It showed stable electrochemical reaction mechanism. It showed excellent cyclic stability with minimum capacity fading over 100 cycles. It was stable even at high rate of 100 mA/g due to its insolubility and structural robustness in the electrolyte. XPS and IR confirmed the reversible sodiation and desodiation of carbonyl to sodium phenoxide and also indicated that Al3+ did not participated directly in redox reaction.

P(THBQ-Al) showed excellent electrochemical performance such as high reversible capacity of 113 mA/g and less capacity fading. Electrochemically inert Al3+ made the structure stable. It prevented from loss of active material. <https://doi.org/10.1021/acsami.7b13911>

1. **Co-HAB**

In rechargeable batteries organic materials which are redox active are gaining attention but they are structurally unstable and have less electrical conductivity. Co-HAB (Cobalt hexaaminobenzene) is a 2D conductive MOF having accessible and stable active site due to conjugated coordination bond between metal and linker. So, it can be used as a high-power energy storage material.

Different samples of Co-HAB were prepared on the basis of synthetic method. One series was made by varying the NH4OH amount and one sample was made by using mixed solvent method symbolized as Co-HAB-D. Co-HAB-D was found to be the best among all samples. Cobalt nitrate hexahydrate as a metal source and hexaaminobenzene as a linker source was used.

TEM confirmed hexagonal pores less than 1nm with a honeycomb arrangement. SEM revealed rod-like crystals. Enhanced crystallinity increased electrical conductivity. Co-HAB-D showed best morphology, conductivity and crystallinity among all samples. It was also structurally stable under harsh conditions.

Co-HAB-D showed a reversible specific capacity of 291 mAh g-1. It had theoretical capacitance of 312 mAh g-1. Three ions of sodium could intercalate per unit of HAB. It showed capacity retention of 226 mAh g-1 at 500 mA g-1 with 100% coulombic efficiency after 50 cycles. Due to ideal sodium diffusion pathway and intrinsic conductivity, it showed high-rate performance. Its real capacity was 2.6 mAh g-1. CV indicated pseudocapacitive charge-storage mechanism. It maintained 80% capacity retention in a completely charged state even after 10 days.

Co-HAB-D was found to have features of ideal electrode like porosity, redox active site, stability and high intrinsic conductivity. <https://doi.org/10.1021/jacs.8b06020>

1. **Fe (III) dihydroxy benzoquinone-based metal organic framework**

For the synthesis of MOF, solution of Fe(NO3)3.9H2O and solution of 2,5-dihydroxybenzoquinone (dhbq) as a was mixed. Precipitates were collected after centrifugation.

XRD confirmed the formation of porous three-dimensional framework having intertwined layers. Three ligands chelated with one iron metal in octahedral environment (slightly distorted). Electron microscopy confirmed the particle size range from 20 nm to 80 nm.

The material had high reversible capacity of 180mAh g-1, excellent cyclic performance over thousand cycles. Its average discharge potential increased with higher current density indicating rapid ion diffusion. Density functional theory suggested that one unit of dhbq can accommodate 2 ions of sodium with a theoretical capacity of 305.8 mAhg-1.

Cheap and abundant materials had been used for the synthesis of MOF. It was thermally stable, showed fast ion diffusion and most importantly it was electrically conductive so less quantity of conductive fillers was needed. <https://doi.org/10.1016/j.jpowsour.2024.234679>

1. **Rhombic 2D Conjugated Metal–Organic Framework**

Now a days 2D conjugated MOFs are getting attention as energy storage materials. However, less utilization of active sites, low capacity, less life cycles are the hurdles in its utilization. *Qi M. etal.* introduce Cu-TBA (TBA = octahydroxytetrabenzoanthracene) and reduced the energy gap between organic linker that enhanced its electrochemical performance. It had rhombus topology, metallic band structure with big conjugating units. It had high specific surface area of 613 m2 g-1, reversible capacity of 153.6 mAh g-1 at 50 mA g-1. <https://doi.org/10.1002/adma.202401878>

1. **Tricycloquinazoline based 2D cMOF**

Two dimensional conjugated MOFs are constructed by formation of coordination bond between planar conjugated ligand and transition metal ion. Its square planar linkage helps in delocalization charge carriers. Tricycloquinazoline (TQ) is nitrogen rich and has electron deficient heteroatomic conjugated ligand thus act as electron donor with intercalation of anions and increase the acidity of coordination group. Integrated p-type TQ can act as bipolar material (i.e. it will store both cation and anion). *Chen D. etal.* 2D conjugated MOF Ni3(HATQ)2 based on hexaaminotricycloquinazoline (HAQT).

The surface area of sample was found to be 513 m2g-1 and pore size was 2.24 nm.

For evaluation of electrochemical performance coin type half battery was made. For it sodium metal was used as counter electrode and Ni3(HATQ)2 as a cathode. CV was done at a voltage range of 1 -3.6 V. CV indicated good reversible specific capacity 115.1 mA h g-1 after 150 cycles. It showed good capacity retention of 97%. Its coulombic efficiency was 100% at a current density of 1 A g-1 after 1000 cycles showed cyclic stability.

Ni3(HATQ)2 was bipolar due to presence of n-type coordination core i.e. NiN4 and p-type ligand i.e. TQ. This increased the cyclic stability, capacitance. It provided a new pathway to increase the performance of batteries 10.1039/d4sc00932k **(open access)**

1. **MOFs’ composite**
2. **FeF3/C nanocomposite:**

FeF3 is being used as a cathode material for SIBs and LIBs due to its high operational voltage and theoretical specific capacity. However, its electronic conductivity and capacity fades with passage of time because of volume expansion upon discharging. To overcome this problem composites of FeF3 nanostructures with carbonaceous materials are being formed as it decreases the distance of electron and iron diffusion. Series of samples were synthesized for comparison under different carbonization conditions out of which FeF3C/-700-3h was found to be the best.

For the synthesis of FeF3/C nanocomposite Zhang, L. *etal.* used iron-based metal organic framework. The Fe-MOF was prepared by using 1,4-benzenedicarboxylic acid (H2bdc) as a ligand and iron chloride hexahydrate (FeCl2.6H2O) as a metal source via solvothermal method. The resulted MOF was calcinated at 700℃ forming Fe3O4/ C nanocomposites. Composite was fluoridated by using HF.

FeF3/C nanocomposite exhibited a branch like morphology due to which electrochemical performance enhanced. High resolution transmission electron microscopy confirmed the encapsulation of FeF3 nanoparticles within highly graphitized carbon framework. Graphitized carbon improved its electrochemical performance. Branch like framework prevent from volume expansion and highly porous carbon framework improved electrolyte permeation. Some nanoparticles of FeF3 formed nano clusters while other dispersed in carbon framework.

CV showed occurrence of side reaction on the surface of electrode and interface. At low current density it had low columbic efficiency but capacitance was high. During initial discharging sample showed high capacity of sodium storage of about 280 mA g-1 during current density of 75 mA g-1, Abnormal columbic efficiency was due to side reactions and formation of SEI. FeF3/C nanocomposite had discharge capacity of 163 mA h/g after 50 cycles. It has a capacity of 126.7 mA h/g after 100 cycles. It showed that intercalation and extraction of sodium ion was reversible. The nanocomposite achieved a high initial discharge capacity of 302.2 mA h g⁻¹ at a current density of 15 mA g⁻¹. However, at a higher current density of 1500 mA g⁻¹, it maintained a capacity of 73.2 mA h g⁻¹ and exhibited nearly 100% coulombic efficiency.

The FeF3 nanocomposites showed amazing electrochemical performance and has high sodium storage capacity at low density of current. It showed excellent rate performance at 1500 mA g-1 and has good capacity retention even after 100 cycles. <https://doi.org/10.1039/C7RA03592F> **(open acsess)**

1. **Al-doped Na2FePO4F/mesoporous carbon nanonetwork composites:**

Na2FePO4F gives a facile pathway to sodium ion for transportation due to its 2D layered structure. It is chemically and thermally stable. It has minimum structural changes upon redox reaction when being used as a cathode. It has high theoretical capacity and redox potential. The problem is with its low electrochemical conductivity which leads to less cyclic stability, storage performance and rate capability. To overcome this problem *Li H.* *etal*. substituted Al3+ at some Fe sites in Na2FePO4F and coated it with Al-MOF derived carbon nanonetwork.

MIL-53(Al) having formula Al(OH)(O2C-C6H4-CO2) was prepared by using Al(NO3)2.9H2O as a metal source and terephthalic acid as a ligand via solvothermal method. Na2FePO4F/C and NFPF-Al/MC were prepared by solid state method. For synthesis of Na2FePO4F/C; FeC2O4, NaCH3COO, NaF, NH4H2PO4 and glucose were used while for NFPF -Al/MC same raw materials were used except for glucose. MIL-53 (Al) was used in place of glucose. NFPF-Al/MC (Na1.9Fe0.94Al0.06PO4/MOF-C) was found to be the best among the series of Na2FePO4F synthesized.

SEM showed that the size of NFPF-Al/MC reduced to 50-80 nm. It improved rate capability as small particle size decreases the diffusion distance for sodium ions creating mor active sites for electrochemical reactions. It also confirmed uniform mesoporous structure of carbon network with 6% doping improving the absorption of electrolyte. TEM confirmed carbon coating and EDX confirmed Al doping.

To know about electrochemical performance coin type half cells were used with a 2-4 V voltage. NFPF-Al/C showed highest initial discharge capacity. At 5 C it maintained the discharge capacity of 62.3 mAhg-1. After 100 and 500 cycles it maintained 88.5% and 70.3% of capacitance respectively.

NFPF-Al/MC was proved to be the promising cathode material for sodium ion batteries due to improved capacity, rate capability and long-term stability as a result of Al doping as well as carbon coating. <https://doi.org/10.1016/j.electacta.2021.137905> **(paid)**

1. **Na3V2(PO4)3 nanoparticles confined in functional carbon framework**

Phosphates mixed with sodium and transition metals are considered as a good cathode material for sodium ion batteries among which Na3V2(PO4)3 is a best cathode material due to high ion transfer and structural stability. It lacks less electrochemical active sites low electronic conductivity, capacity and energy density. To overcome this NVP can be incorporated in carbon matrix. Source of carbon matrix is very important. Here the author used MIL-101(V) as a source of carbon matrix.

For MIL-101(V) was synthesized via solvothermal method by taking 1,4-benzenedicarboxylic acid as a ligand source and VCl3 as metal source. Calcination was done to produce composite using Na2CO3, NH4H2PO4 and MIL-101(V) as reagents. For carbon framework and metal source MOF was used labelled as M-NVP/C and for comparison two more samples were made one with citric acid and V2O5 instead of MOF and the other one without carbon framework.

XRD showed better crystallinity. SEM and TEM confirmed uniform coating of carbon which increased electrical conductivity and electrochemical performance. M-NVP/C has average diameter of 500 nm. HR-TEM also showed some external defects.

GCD confirmed higher capacity retention in M-NVP/C after 100 cycles. Long term cycling at 5C and 10C retained capacity of 84.17% and 84.5% after 1000 cycles. EIS showed the charge transfer resistance of 425.1 ohm after 15 cycles less than other samples. 3D carbon framework enhanced conductivity and reduced internal resistance.

NVP particles uniformly distributed in 3D carbon framework allowed higher surface area, electrical conductivity and it also stabilized the structure over long term cycling. M-NVP/C has a great potential of in increasing high capacity and long-life cathode material in sodium ion batteries. <https://doi.org/10.1016/j.jallcom.2019.03.346> **(paid)**

1. **FeOF nanoparticles wrapped by graphitic carbon layers**

Iron oxyfluoride (FeOF) was found to be promising cathode material because of its high theoretical capacity as well as favorable redox reactions. However, it faces issues like volume changes during charge and discharge cycles as well as electrical conductivity. To overcome these issues FeOF/ graphite carbon hybrids derived from MOF was synthesized as it offers high porosity and thermal stability.

Fe-MIL-88B was synthesized via solvothermal analysis by using FeCl3 as a metal source and terephthalic acid as a ligand. Then FeOF-H2SiF6/GCL composite was synthesized. For comparison FeOF-HF/GCL, FeOF-N/GCL and FeOF was synthesized.

The XRD confirmed that particles of FeOF-H2SiF6/GCL are smaller than FeOF. It showed that carbon matrix played a positive role by prevention the aggregation of FeOF. SEM confirmed the formation of composite. TEM confirmed FeOF were of spherical shape.

The electrochemical performance of FeOF-H2SiF6/C were better than FeOF. CV showed two cathodic peaks at approximately 1.7V and 1.2V during first scan showing active conversion reactions. More consistent peak intensities showed good cyclability. After 100 cycles it maintained 338.2 mAh g-1 with a fading rate of 0.22% per cycle. It had improved reversible capacity. EIS confirmed its low resistance.

Graphitic carbon layer reduces aggregation and particle growth which improved conductivity and redox performance making it a promising cathode material for cathode in SIBs. <https://doi.org/10.1016/j.carbon.2019.04.081> **(paid)**

1. **FeS2@C nanorods**

Conversion type reaction materials are of great interest as they can intercalate more than one sodium ion in a metal core as a result they are having high theoretical capacities. FeS2 is a conversion type material. It is environment friendly, cheap and present abundant in nature. However, its electrochemical performance was not good due to fast decay during its use as it faced changes in volume.

Porous FeS2@C nanorods like sea cucumber were constructed by growing nanoflakes of FeS2@C nanoflakes on FeS2@C nanorods. Hydrothermal method was used to prepare F-MIL nanorods and then sulfidation was done. For F-MIL, benzene dicarboxylic acid was used as a ligand.

XRD showed high crystallinity of FeS2@C nanorods. BET showed the specific surface area of 102.7 m2/g. Pore size was found to be approximately 10 nm. SEM and TEM confirmed a sea cucumber like structure.

CV showed discharge capacity of 422 mAh/g during first cycle. After 50 cycles activation process improved performance. The electrode showed stable cycling. It had coulombic efficiencies above 98%. It achieved reversible capacities between 384 and 108 MAh/g at current densities ranging from 0.05-10 A/g. It delivered 160 mAh/g after 10,000 cycles at 20 A/g.

In carbon shell nano sized FeS2 particles speed up the transportation of sodium ions and electrons. Interspace between FeS2 particles not only improved the electrolyte permeation but also buffered the volume expansion. Carbon framework facilitated the conduction. Therefore, it exhibited comparable specific capacity, rate capacity, and excellent cyclic stability. <http://dx.doi.org/10.1021/acsaem.8b01239> **(no option)**

1. **ZIF-8 derived nitrogen-doped carbon composites:**

Organic materials are worthy of being used as electrode in batteries due to low cost, high specific capacity, structural diversity, and renewability. Poor electronic conductivity is the main obstacle for using them as electrode.

PI@NC was prepared by using 3,4,9,10-perylenentetracarboxylic dianhydride ethylene diamine (PI) and N-doped carbon matrix (NC) via in-situ polymerization. ZIF-8 was used as source of carbon metrics and 2-methylimidazole as a nitrogen source.

The morphology of PI@NC resembles to that of ZIF-8 nanocrystals i.e., polyhedron-like structure. SEM and TEM confirmed the uniform coating of PI on the surface of NC. EDX showed uniform distribution of oxygen indication homogenous distribution of PI.

It showed capacity retention of approximately 72.2% and delivered high reversible capacity of 126 mAh/g. EIS indicated fast charge transfer rates. After 200 cycles it maintained 100% coulombic efficiency and 96.2% of its capacity at 0.1A/g and showing excellent cyclic stability. The polymer matrix and NC covering helped in structural stability.

PI@NC delivered significant cyclic stability, low solubility, high electronic conductivity and rate capability. <https://doi.org/10.1016/j.electacta.2020.137115> **(paid)**

1. **Na3V2(PO4)3/C**

A porous material Na3V2(PO4)3 (NVP) uniformly coated with carbon layer was synthesized via sol-gel and freeze-drying method.

SEM confirmed the size of particles within the range of 1-2 mm. The porous morphology was observed and pores were interconnected. This improved the penetration of electrolyte and thus improving the electrochemical performance. Moreover, pore size was also responsible for reducing path length of sodium ions diffusion thus increasing charge/discharge rates. TEM confirmed carbon coating of 5-10nm thickness. This improved ion and electron transport.

The capacity retention was 88.6% and 93.6% over 100 cycles. This indicated electrochemical reversibility and structural stability. After 100 cycles there were no side reactions, and no change in crystallinity.

Na3V2(PO4)3/C had good electrochemical performance like it had improved cyclic performance, rate performance, and specific capacity. It showed the discharge capacity of 118 mAh/g, corresponding 100% theoretical capacity at small current density. 10.1002/chem.201300005 **(option?)**

1. **Na3V2(PO4)3/C core shell**

Na3V2(PO)4 shows poor cyclic stability and low-rate performance due to sluggish ion transport, structural stress and low electron conductivity. Graphene-coated core-shell spheres enhance surface area, electrolyte permeation, accommodate volume expansion (by providing three dimensional space), and shortens the diffusion path of ions and electrons. So, *Chen H. etal.* synthesized Na3V2(PO4)3/C core shell. He used clusters of vanadium-oxygen of V-MOF as a source of V and organic ligands as source of core shell which will prevent the growth of Na3V2(PO4)3.

The V-MOF was synthesized via hydrothermal method by using V2O5 as a metal source and oxalic acid as a ligand. Three types of samples were made with different particle size by using different concentration of ethanol. After the synthesis of MOF, it was calcinated and then mixed with NaH2PO4, citric acid, water. The sample with 400 mL concentration of ethanol labeled as NVP-0.01M was found to be best in electrochemical performance.

For checking the electrochemical performance 2032 cell was made. For cathode formation active material, polyvinylidene fluoride, N-methyl pyrrolidinone was used to make slurry. The anode was made of sodium metal. The cell was assembled in glove box.

The SEM and TEM confirmed the core-shell structure of sample. It provided the three dimension al space which helped to accommodate the volume change as a result lifecycle of battery increased. NVP-0.01M had smallest particle size among other samples which decreased the transport distance of electrons and sodium ions. The amorphous nature of coating helped to overcome the challenges in structural deformation and electronic conductivity. It showed the diameter of 0.23µm. BET confirmed the pore size of 6.9nm of NVP-0.01M.

The discharge capacity decreased in NVP-0.01M but it showed best electrochemical performance. GCD showed low internal resistance. It showed capacity retention of 91.3% of its initial capacity after 500 cycles at 1C. It exhibited excellent rate performance of 109.0 mAh g-1. Its capacity remained high even at high rates comparatively (a capacity of 65.9 mAh g-1 at 50 C).

So, NVP-0.01M showed excellent electrochemical performance which is due to its ultra small size which improved electronic conductivity and lightened the bulk stress. Core-shell sphere increased the rate of electrochemical reactions hence, increasing the cycling. <https://doi.org/10.1016/j.est.2023.109932> **(PAID)**

1. **Selenium/ Carbon composite**

The ZIF-67 crystals were synthesized via solvothermal method using Co (CH3COO)2 and methylimidazole. After it composite was made by using Se powder.

Se-ZIF composite had dodecahedral shape and surface had cavities. EDX confirmed uniform distribution of Se, Co throughout the framework. Surface area decreased from 820 m2/g to 3 m2/g and pore volume from 0.44 to 0.014 cm3/g, indicating breakage of metal-organic bond and carbonization of organic part. The polyhedral shape was preserved even after extensive cycling due to stable solid electrolyte interface.

It had initial coulombic efficiency of 84%. It had high cyclic stability. After 700 cycles it showed minimal decay in capacity. It showed retention capacity of 78% when current was increased from 0.1-2 A/g. CV showed fast kinetics.

Se/CoSe2/C composite outperformed other Se based materials due to its well-maintained polyhedral structure. It had remarkable stability and rate capability. <https://doi.org/10.1016/j.nanoen.2019.01.064> **(option?)**

1. **Na3V2(PO4)2F3/Co/N-PC**

The compound Na3V2(PO4)2F3 had less conductivity and diffusion rate of ions limiting its application as a cathode in batteries. The composite Na3V2(PO4)2F3/Co/N-PC was prepared from bimetallic Co/Zn-ZIF MOF to overcome these draw backs. In this composite, electrochemical properties can be enhanced due to synergic effect between porous N-doped C materials and Co nanoparticles.

Co/Zn-ZIF was synthesized via coprecipitation method by using cobalt nitrate, zinc nitrate, methyl imidazole and cetyltrimethylammonium bromide. The product was pyrolyzed at 900℃ followed by acid treatment to obtain Co/N-PC. The composite Na3V2(PO4)2F3/Co/N-PC was synthesized via spray drying and sintering at high temperature. For comparison Na3V2(PO4)2F3/N-PC was also synthesized.

For electrochemical properties half-cell assembly in argon-filled glove box was made. For making cathode; sample, acetylene black and CMC was used.

SEM confirmed hollow sphere structure of sample having nano cube Co/N-PC that were attached to interior as well as surface. It increased the conductivity, specific surface area. It also prevented from microstructural collapse while charging and discharging. BET confirmed pore size of 7.170 nm. There was increase in number of active sites. The morphology was also analyzed after 1, 50, and 100 cycles in electrode form. The hollow sphere disappeared and agglomeration, polymerization occurred. It caused irreversible capacity lose as the ion deincarceration channels blocked.

CV was done at 2.3-4.7 and showed reversible electrode reactions and displacement of three sodium ions. It showed excellent cyclic stability as its specific capacity increased by 15.65 compared to another sample. At 0.1C it showed a capacity of 126.66 mAh/g. EIS showed an increase in permeability across SEI. A further 3-electrode system was also used in which the positive electrode was a sample, the reference electrode was a sodium ring and the counter electrode was sodium metal. The assembly was closed in the glove box. The voltage was the same as that of CV. The carbon increased the electrode’s interface stability and reduced internal resistance.

The morphology of the composite increased the electrochemical performance. Co nanoparticles increased the rate of charge transfer, and nitrogen reduced sodium ions' deintercalation pathway, enhancing electrochemical performance. It showed 91.84% retention after 100 cycles. (Ma, J., Li, W., Lan, X., Liu, Z., Zhou, F., Lu, M., & Han, G. The Cathode Material of a Sodium Ion Battery, Na3v2 (Po4) 2f3, Undergoes Co/N-Doped Carbon Modification Using a Bimetallic Mofs Template. *Na3v2 (Po4) 2f3, Undergoes Co/N-Doped Carbon Modification Using a Bimetallic Mofs Template*.)

1. **Na3V2(PO4)3-carbon@graphene fiber**

Fiber-shape energy storage devices have high deformable flexibility. Mostly fiber electrodes are made by PBAs, transition metal sulfides, and oxides. They have low discharge voltage and less stability. Fiber electrode play very important role in electrochemical performance of fiber batteries. *Ma X. etal.* synthesized NVP-C composite nanoarrays on graphite fiber via V-MOF nanoarray as a template.

The V-MOF was synthesized via hydrothermal method by using VCl3, 2-ethyl methylimidazole, vanadyl acetylacetonate, and p-phthalic acid. The solution formed was mixed with GOF (graphene oxide fiber). The final product NVPC@GF was synthesized through to step calcination process and converting GOF to reduced graphene oxide labelled as GF. For comparison Na3V2(PO4)3 coated graphene fiber (NVP@GF) was synthesized. NVPC@GF was found to be better in terms of electrochemical performance.

MOF-derived carbon framework strongly combined with GF which made it cyclic stable. The voids between the nanorods and uniform distribution of NVP in carbon framework decreased the transport pathway of sodium ions as a result improved the rate capability. EDX confirmed the unform distribution of C, V, P. Na and O which improved the conductivity and fiber morphology increased the electrochemical performance especially Na+ insertion and extraction.

For checking electrochemical performance fiber-shaped SIBs was made with HC@GF as anode and NVPC@GF as cathode. It showed working voltage of 3.3 V at 50 mA/g in presodiated form.

NVPC@GF had three times more electron conductivity. CV showed fast diffusion kinetics. It retained 95.8% capacity retention after 200 cycles, with a capacity of 79.1 mAh/g. It showed excellent rate performance. After 1000 cycles at 2000 mA/g the discharge capacity remained 57.1 mAh/g maintaining coulombic efficiency almost 100%. The EIS showed less Rct of 352.4 Ω showing faster electron transport.

The MOF derived fiber possessed 3-D porous structure. It had improved conductivity, kinetics, life cycle and electrochemical performance. It was found to be a promising cathode material for SIBs.

**TiO2@V2O5**

The active material known as vanadium oxide (V2O5) exhibits considerable promise due to its distinctive crystal structure and layered architecture. V2O5 is verified to be a promising low-cost cathode for different rechargeable batteries. The presence of different polymorphs of V2O5 gives rise to variations in overall capacity and cycling capabilities, which can be attributed to differences in crystal structure and lattice patterns In this study, we designed a composite structure containing vana dium oxide nanoparticles on a nanoporous carbon substrate as inner core around which a shell of titanium nanoparticles is wrapped by Tidoping directly into the V-MOF (V-MIL-101) which was readily con verted into a core-shell structure [70] denoted as x-TiO2@V2O5/C where x represents the weight % loading of titania (x = 1 wt%, 2 wt%, 3 wt% and 4 wt%) around the vanadium octahedron core via carbonization under inert atmosphere. Interestingly, the Ti-doping not only induced the structural changes in the V-MIL-101, but also generated the oxygen vacancies in the x-TiO2@V2O5/C, which greatly enhanced the sodium storage performance of the electrode. This synthesis method is a sequential strategy which offers the tailoring of nanoarchitecture of materials for an unprecedented opportunity to utilize the functional properties

The vanadium based metal organic framework (V-MIL-101) [1,74] was synthesized by dissolving stoichiometric amounts (1:1 M rations) Terephthalic Acid (1.99 g) and Vanadium Chloride (VCl3) (1.88 g) in 60 mL of absolute ethanol. Synthesis of core-shell TiO2@V2O5/C composites0.20 g of as-synthesized V-MIL-101 particles were dispersed into 20 mL ethanol solvent followed by the addition of 0.3 mL of tetrabutox ytitanate (TBT) into the solution. hydrolysis, air-calcined pyrolyzed. The pyrolysis of bare V-MIL-101 without the loading of titania was also performed to achieve V2O5 structure on carbon substrate for the com parison purposes.

**HRTEM and FESEM Analysis**: High-resolution transmission electron microscopy (HRTEM) images reveal an octahedral core-shell structure with crystal edge lengths ranging from 10–50 nm. The surface of the core-shell structure is rough, with pores and a uniform attachment of titania nanoparticles. As titania loading increases from 1 wt% to 3 wt%, the octahedral shape is preserved, but deformation occurs at 4 wt%. The lattice fringes observed correspond to the TiO2 (110), (211), and (111) planes, showing a well-defined interface between α-V2O5 and TiO2.

 **Elemental Distribution**: Energy dispersive X-ray (EDX) spectrograms confirm the core-shell nature of the structure. The vanadium (V) is concentrated in the core, while titanium (Ti) is predominantly on the shell. Oxygen and carbon are distributed both in the shell and around the core. The elemental mapping supports the uniform distribution and successful formation of the TiO2@V2O5/C composite.

 **X-ray Diffraction (XRD)**: XRD patterns of the V2O5/C composite show peaks corresponding to the orthorhombic crystal system of α-V2O5 and rutile TiO2. Shifts in the peak positions are observed due to the incorporation of oxygen ions into the V2O5 crystal structure. Additional peaks indicate the presence of a non-stoichiometric VO0.9 phase.

 **Cyclic Voltammetry (CV) Analysis**:

* **Electrochemical Performance**: The CV tests show that the TiO2@V2O5/C composites exhibit superior electrochemical performance compared to the bare V2O5/C. The initial cathodic peak occurs at 1.5 V (V⁵⁺ to V⁴⁺ conversion), followed by another peak at 0.6 V (V⁴⁺ to V³⁺ conversion). Anodic peaks appear at 0.7 V and 1.6 V, representing the insertion and extraction of sodium ions.
* **Current Improvement**: The current values improve with the addition of titania. Specifically, for 3 wt% TiO2@V2O5/C, the current increases to 0.34 A, compared to 0.052 A for 1 wt% TiO2@V2O5/C. However, at 4 wt%, the current drops to 0.21 A. The 3 wt% TiO2@V2O5/C composite shows a favorable peak current growth with increasing scan rates, indicating good rate capability and stability.

 **Galvanostatic Charge-Discharge (GCD) Curves**:

* **Discharge Capacity**: The 3 wt% TiO2@V2O5/C composite achieves the highest discharge capacity of 276.2 mAh/g at 0.1C, outperforming other composites and the bare V2O5/C (241.4 mAh/g). The GCD curve exhibits two plateaus corresponding to the two-step sodium ion insertion process. The energy density for the 3 wt% TiO2@V2O5/C is approximately 449 Wh/kg at an average potential of 1.5 V.
* **Rate Capability**: The 3 wt% TiO2@V2O5/C material also demonstrates excellent rate capability, retaining 262.5 mAh/g after cycling at a high current rate of 10C, and retains a significant capacity even at high current rates.

 **Cyclic Stability**:

* **Capacity Retention**: Over 200 cycles, the 3 wt% TiO2@V2O5/C composite maintains 77.9% capacity retention (215.18 mAh/g), demonstrating excellent cyclic stability with a high coulombic efficiency (>98%).

 **Electrochemical Impedance Spectroscopy (EIS)**:

* **Charge Transfer Resistance**: EIS analysis reveals that the charge transfer resistance decreases with the addition of titania. The semicircle in the high-frequency region becomes smaller, indicating improved charge transfer and conductivity for the TiO2-coated composites. The 3 wt% TiO2@V2O5/C composite shows the smallest charge transfer resistance and minimal impedance, which is beneficial for efficient sodium ion intercalation and deintercalation.
* **Sodium Diffusion**: The sodium ion diffusion rate, characterized by the Warburg coefficient, indicates faster diffusion in the 3 wt% TiO2@V2O5/C composite, which is supported by the smaller impedance in the EIS spectra

The composite with 3 wt% of TiO2 loading over V2O5 based shell exhibited an excellent discharge capacity of 276.2 mAh/g at 0.1C and maintained it up 250.1 mAh/g for 100 charge-discharge cycles. The proposed synthetic strategy and choice of titania nano-layer as the shell is a promising pathway towards con structing efficient metal oxide/C-based cathode materials for sodiumion batteries for applications involving long-term cycling. Rimsha Mehek

1. **MOF derived cathodes**
2. **Layered Transition-Metal Oxide (NaxMnO2)**

The layered sodium manganese oxides have gained attention among various cathode materials due to their high theoretical capacities. The main hurdle in their use is the complex phase transition while charging and discharging leading to low cycling stability. Layered cathode (NaxMnO2) can be of P2 or O3 type depending on the stacking pattern of oxygen layers and the sites of sodium ions. P2 has better cyclic and rate performance while O3 has higher Na content thus having high theoretical capacity. *Li C. etal.* has synthesized P’2-NaxMnO2 by using MOF Na[Mn(HCOO)3] (NM-MOF). The sodium and manganese in the MOF are uniformly incorporated accelerating the phase transition process.

The MOF Na[Mn(HCOO)3] was synthesized via mild solution chemistry by using MnCl2.4H2O as a metal source and HCOOH as a ligand source. Two samples of layered metal oxide were synthesized using Na[Mn-(HCOO)3]. One sample was synthesized via ultrafast calcination at 950℃ denoted as NMO-F (Na0.56MnO2) and the other was synthesized through a traditional calcination process at a temperature of 400℃ and 850℃ denoted as NMO-S (Na0.72MnO2). NMO-F was better in terms of stability and electrochemical performance.

To check the electrochemical performance coin cell was made. Sodium metal was used as anode.

The sample was crystalline. The SEM and HRTEM confirmed the particle size of less than 5um.

The redox peak in CV showed Mn3+/Mn4+ transition. NMO-F showed a higher voltage peak. In GCD it showed a higher discharge capacity of 202 mAh/g and better cyclic stability of 146 mAh/g after 100 cycles at 100 mA/g (84% retention) showing better structural stability. At a wide voltage window (1.5-4.3 V) it showed a higher specific capacity of 212.5 mAh/g showing reversible phase transition. XPS and in situ XRD confirmed reversible phase transition. NMO-F showed better cyclic performance.

NMO-F was proved to be a promising cathode material as it showed good cyclic stability and high specific capacity. (Li, C., Li, A., Li, M., Xiong, P., Liu, Y., Cheng, M., ... & Xu, Y. (2022). Ultrafast synthesis of layered transition-metal oxide cathodes from metal–organic frameworks for high-capacity sodium-ion batteries. *ACS Applied Materials & Interfaces*, *14*(21), 24462-24468.)