**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, which helps improve cyclic stability. Controlling the morphology of MOF is easy so, it 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>Wang, Z., Tao, H., & Yue, Y. (2019). Metal‐organic‐framework‐based cathodes for enhancing the electrochemical performances of batteries: a review. *ChemElectroChem*, *6*(21), 5358-5374.

In literature mostly the MOFs are used in composite forms for the cathode in sodium ion batteries. Here three categories of cathodes’ materials are being discussed. A) Pristine MOF as cathode B) MOFs’ composite as cathode C) MOF-derived cathode

**A. Pristine MOFs**

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

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

For the synthesis of P(THBQ-Al), a 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 due to the 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 a highly insoluble electrolyte that maintained the structural integrity during cycling.

For the electrochemical performance test, a coin cell was made with sodium metal as an anode and NaClO4 in TEGDME as an electrolyte. The current density was 20 mA/g.

P(THBQ-Al) showed high reversible capacity of 113 mAh/g. It showed a stable electrochemical reaction mechanism. It showed excellent cyclic stability with minimum capacity fading over 100 cycles. It was stable even at a 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 participate directly in a 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> Kim, H. J., Kim, Y., Shim, J., Jung, K. H., Jung, M. S., Kim, H., ... & Lee, K. T. (2018). Environmentally sustainable aluminum-coordinated poly (tetrahydroxybenzoquinone) as a promising cathode for sodium ion batteries. *ACS applied materials & interfaces*, *10*(4), 3479-3486.

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 an accessible and stable active site due to the 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 based on the synthetic method. One series was made by varying the NH4OH amount and one sample was made by using a 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 were used.

For an electrochemical performance check coin cell was made having sodium metal as an anode and 1M NaPF6 in diethylene glycol diethyl ether as an electrolyte.

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 the 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 a 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 the ideal sodium diffusion pathway and intrinsic conductivity, it showed high-rate performance. Its real capacity was 2.6 mAh g-1. CV indicated a 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 electrodes like porosity, redox-active site, stability, and high intrinsic conductivity. <https://doi.org/10.1021/jacs.8b06020> Park, J., Lee, M., Feng, D., Huang, Z., Hinckley, A. C., Yakovenko, A., ... & Bao, Z. (2018). Stabilization of hexaaminobenzene in a 2D conductive metal–organic framework for high power sodium storage. *Journal of the American Chemical Society*, *140*(32), 10315-10323.

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

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

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

For the electrochemical test, a coin cell was made with sodium metal as a counter electrode and NaPF6 in dry diglyme as an electrolyte.

The material had a high reversible capacity of 180mAh g-1, and excellent cyclic performance over a 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 have 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> Kapaev, R. R., Baghishov, I., Ryazantsev, S. V., Novichkov, D., Presniakov, I. A., Orlova, E. D., ... & Stevenson, K. J. (2024). Fe (III) dihydroxybenzoquinone-based metal organic framework for sodium battery cathodes: Properties, charge-discharge kinetics and redox reaction mechanisms. *Journal of Power Sources*, *609*, 234679.

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

Nowadays 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. et al.* introduced Cu-TBA (TBA = octahydroxytetrabenzoanthracene) and reduced the energy gap between organic linkers which enhanced its electrochemical performance. It had a rhombus topology, and metallic band structure with big conjugating units. It had a high specific surface area of 613 m2 g-1 and, a reversible capacity of 153.6 mAh g-1 at 50 mA g-1. <https://doi.org/10.1002/adma.202401878> Qi, M., Cheng, L., Wang, H. G., Cui, F., Yang, Q., & Chen, L. (2024). A Rhombic 2D Conjugated Metal–Organic Framework as Cathode for High‐Performance Sodium‐Ion Battery. *Advanced Materials*, 2401878.

1. **Tricycloquinazoline based 2D cMOF**

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

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

For evaluation of electrochemical performance, a coin-type half battery was made. For it, sodium metal was used as a counter electrode and Ni3(HATQ)2 as a cathode with a voltage range of 1.0V-3.6V. CV was done at a voltage range of 1 -3.6 V. CV indicated a good reversible specific capacity of 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 showing cyclic stability.

Ni3(HATQ)2 was bipolar due to the presence of an n-type coordination core i.e. NiN4 and a p-type ligand i.e. TQ. This increased the cyclic stability and capacitance. It provided a new pathway to increase the performance of batteries 10.1039/d4sc00932k Chen, D., Cheng, L., Chen, W., Wang, H. G., Cui, F., & Chen, L. (2024). Tricycloquinazoline Based 2D Conjugated Metal-Organic Framework for Robust Sodium-Ion Batteries with Ion Co-Storage of Both Cations and Anions. *Chemical Science*.**(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 fade with 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. A 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. *et al.* used an iron-based metal organic framework. The Fe-MOF was prepared by using 1,4-benzene dicarboxylic acid (H2bdc) as a ligand and iron chloride hexahydrate (FeCl2.6H2O) as a metal source via solvothermal method. The resulting MOF was calcinated at 700℃ forming Fe3O4/ C nanocomposites. The Composite was fluoridated by using HF.

FeF3/C nanocomposite exhibited a branch-like morphology due to which electrochemical performance was enhanced. High-resolution transmission electron microscopy confirmed the encapsulation of FeF3 nanoparticles within a highly graphitized carbon framework. Graphitized carbon improved its electrochemical performance. A branch-like framework prevents volume expansion and a highly porous carbon framework improves electrolyte permeation. Some nanoparticles of FeF3 formed nanoclusters while others dispersed in a carbon framework.

CV showed the occurrence of side reactions on the surface of the electrode and interface. At low current density, it had low columbic efficiency but capacitance was high. During the initial discharging sample showed a high capacity of sodium storage of about 280 mA g-1 during a current density of 75 mA g-1, Abnormal columbic efficiency was due to side reactions and formation of SEI. FeF3/C nanocomposite had a 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 have 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 ions 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.* *et al*. 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 the solvothermal method. Na2FePO4F/C and NFPF-Al/MC were prepared by solid-state method. For the 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 more active sites for electrochemical reactions. It also confirmed the uniform mesoporous structure of the carbon network with 6% doping improving the absorption of electrolytes. 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. Sodium metal foil as anode and NaClO4 in EC:DC was used as electrolyte. NFPF-Al/C showed the 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> Li, H., Wang, T., Wang, X., Li, G., Shen, J., & Chai, J. (2021). MOF-derived Al-doped Na2FePO4F/mesoporous carbon nanonetwork composites as high-performance cathode material for sodium-ion batteries. *Electrochimica Acta*, *373*, 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 the 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 the carbon matrix is very important. Here the author used MIL-101(V) as a source of carbon matrix.

MIL-101(V) was synthesized via solvothermal method by taking 1,4-benzene dicarboxylic acid as a ligand source and VCl3 as a metal source. Calcination was done to produce a composite using Na2CO3, NH4H2PO4, and MIL-101(V) as reagents. For carbon framework and metal source, MOF was used and labeled 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 an average diameter of 500 nm. HR-TEM also showed some external defects.

To check electrochemical performance, a coin cell was made having sodium as an anode and fluoroethylene carbonate, PC, and NaClO4 as an electrolyte. The potential range was 2.5 – 3.8.

GCD confirmed higher capacity retention in M-NVP/C after 100 cycles. Long-term cycling at 5C and 10C retained a capacity of 84.17% and 84.5% after 1000 cycles. EIS showed a 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 a 3D carbon framework allowed higher surface area, and electrical conductivity and it also stabilized the structure over long-term cycling. M-NVP/C has great potential in increasing high capacity and long-life cathode material in sodium-ion batteries. <https://doi.org/10.1016/j.jallcom.2019.03.346> Cao, X., Sun, Q., Zhu, L., & Xie, L. (2019). Na3V2 (PO4) 3 nanoparticles confined in functional carbon framework towards high-rate and ultralong-life sodium storage. *Journal of Alloys and Compounds*, *791*, 296-306.**(paid)**

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

Iron oxyfluoride (FeOF) was found to be a 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 were synthesized as it offer 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 were synthesized.

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

For the electrochemical performance test, a coin cell was made using sodium metal as a counter electrode and NaClO4 in EDC/PC as an electrolyte.

The electrochemical performance of FeOF-H2SiF6/C was better than FeOF. CV showed two cathodic peaks at approximately 1.7V and 1.2V during the 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.

The graphitic carbon layer reduces aggregation and particle growth which improves conductivity and redox performance making it a promising cathode material for cathode in SIBs. <https://doi.org/10.1016/j.carbon.2019.04.081>Yanuar, M. A., & Kim, J. (2019). FeOF nanoparticles wrapped by graphitic carbon layers prepared from Fe-MIL-88B as a cathode material for sodium-ion batteries. *Carbon*, *149*, 483-491. **(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 have high theoretical capacities. FeS2 is a conversion-type material. It is environment-friendly, cheap, and 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 cucumbers were constructed by growing nanoflakes of FeS2@C nanoflakes on FeS2@C nanorods. The 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 a 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.

For the electrochemical test, the coin cell was made with sodium metal foil as a counter electrode and NaCF3SO3 in DEG/DME as an electrolyte.

CV showed a discharge capacity of 422 mAh/g during the 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 a 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. The 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> Lu, Z., Wang, N., Zhang, Y., Xue, P., Guo, M., Tang, B., ... & Dou, S. (2018). Metal–organic framework-derived sea-cucumber-like FeS2@ C nanorods with outstanding pseudocapacitive Na-ion storage properties. *ACS Applied Energy Materials*, *1*(11), 6234-6241.**(no option)**

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

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

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 a source of carbon metrics and 2-methylimidazole as a nitrogen source.

The morphology of PI@NC resembles 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 a uniform distribution of oxygen indication homogenous distribution of PI.

For the electrochemical performance test, a 2025 coin-type battery was made. with Na foil as an anode and NaPF6 in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) with fluoroethylene carbonate. The potential range for charge/discharge was 1.5 – 3.,5 V

It showed capacity retention of approximately 72.2% and delivered a 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 showed 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>Chu, R., Song, H., Ullah, Z., Guan, Z., Zhang, Y., Zhao, L., ... & Liu, L. (2020). ZIF-8 derived nitrogen-doped carbon composites boost the rate performance of organic cathodes for sodium ion batteries. *Electrochimica Acta*, *362*, 137115. **(paid)**

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

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

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 electrolytes and thus improved the electrochemical performance. Moreover, pore size was also responsible for reducing the 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.

For the electrochemical performance test, a coin cell was made with sodium metal as an anode and NaClO4 in EC/DEC as an electrolyte. The potential range for charge/discharge was 2.7 – 4.0 V.

CV showed excellent reversibility and structural stability. The capacity retention was 88.6% and 93.6% over 100 cycles. 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 a discharge capacity of 118 mAh/g, corresponding to 100% theoretical capacity at a small current density. 10.1002/chem.201300005 Shen, W., Wang, C., Liu, H., & Yang, W. (2013). Towards highly stable storage of sodium ions: a porous Na3V2 (PO4) 3/C cathode material for sodium‐ion batteries. *Chemistry–A European Journal*, *19*(43), 14712-14718.**(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, and electrolyte permeation, accommodate volume expansion (by providing three-dimensional space), and shorten the diffusion path of ions and electrons. So, *Chen H. et al.* 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 a 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 sizes by using different concentrations of ethanol. After the synthesis of MOF, it was calcinated and then mixed with NaH2PO4, citric acid, and 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 a glove box.

The SEM and TEM confirmed the core-shell structure of the sample. It provided the three-dimensional space which helped to accommodate the volume change as a result lifecycle of the battery increased. NVP-0.01M had the 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 a 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 the 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 an 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> Chen, H., Zhou, M., Zhang, X., Xu, S., & Zhou, H. (2024). V-MOFs derived Na3V2 (PO4) 3/C core-shell spheres toward ultrastable sodium-ion batteries. *Journal of Energy Storage*, *77*, 109932.**(PAID)**

1. **Selenium/ Carbon composite**

The ZIF-67 crystals were synthesized via the solvothermal method using Co (CH3COO)2 and methylimidazole after that, a composite was made by using Se powder.

Se-ZIF composite had a dodecahedral shape and the surface had cavities. EDX confirmed the 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 the organic part. The polyhedral shape was preserved even after extensive cycling due to a stable solid electrolyte interface.

For the electrochemical performance test, a coin-type cell was made with sodium metal foil as an anode and NaSO3CF3 in diethylene glycol dimethyl ether.

It had an initial coulombic efficiency of 84%. It had high cyclic stability. After 700 cycles it showed minimal decay in capacity. It showed a 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> Yang, X., Wang, S., Denis, Y. W., & Rogach, A. L. (2019). Direct conversion of metal-organic frameworks into selenium/selenide/carbon composites with high sodium storage capacity. *Nano Energy*, *58*, 392-398.**(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 drawbacks. In this composite, electrochemical properties can be enhanced due to the synergic effect between porous N-doped C materials and Co nanoparticles.

Co/Zn-ZIF was synthesized via the 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 temperatures. For comparison, Na3V2(PO4)2F3/N-PC was also synthesized.

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

SEM confirmed the hollow sphere structure of the sample having nano cube Co/N-PC that was attached to the interior as well as the surface. It increased the conductivity and specific surface area. It also prevented microstructural collapse while charging and discharging. BET confirmed a pore size of 7.170 nm. There was an 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 and polymerization occurred. It caused irreversible capacity loss as the ion deincarceration channels were 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-shaped 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 electrodes play a very important role in the electrochemical performance of fiber batteries. *Ma X. et al.* synthesized NVP-C composite nanoarrays on graphite fiber via V-MOF nanoarray as a template.

The V-MOF was synthesized via the 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 the uniform distribution of NVP in the carbon framework decreased the transport pathway of sodium ions, as a result, improved the rate capability. EDX confirmed the uniform distribution of C, V, P. Na, and O which improved the conductivity and fiber morphology and increased the electrochemical performance, especially Na+ insertion and extraction.

For checking electrochemical performance fiber-shaped SIBs were made with HC@GF as anode and NVPC@GF as cathode. It showed a working voltage of 3.3 V at 50 mA/g in predicted 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 a 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. Ma, X., Zhang, H., Liu, Y., Yan, W., Chen, C., & Zhang, K. (2024). MOF-derived Na3V2 (PO4) 3-carbon@ graphene fibers for flexible fiber-shaped sodium ion battery. *Journal of Electroanalytical Chemistry*, *975*, 118740.

1. **TiO2@V2O5**

Vanadium oxide is a low-cost cathode material with a layered and crystal structure. It can have different morphologies in terms of lattice pattern and crystal structure, which can modify its cyclic capabilities and capacity. *Mehek R. et al.* synthesized a composite having an inner core made of V2O5 nanoparticles on nanoporous carbon covered by titanium nanoparticles, which in turn is covered by a core-shell. The core-shell is made of Ti-doped V-MOF (V-MIL-101).

The MOF V-MIL-101 was synthesized via the hydrothermal method using vanadium chloride as a metal source and terephthalic acid as a ligand. The composite was synthesized by using MOF and tetrabutoxytitanate (TBT) via hydrolysis, air calcination, and pyrolysis. Four different samples having 1% wt., 2% wt., 3% wt., and 4% wt. were synthesized and labeled as x-TiO2@V2O5/C. For comparison only V2O5 on carbon substrate was also synthesized. The best results were obtained by 3% [-TiO2@V2O5/C](mailto:.-TiO2@V2O5/C).

EDX confirmed the core-shell structure having V in the core and Ti in the shell. XRD showed an orthorhombic crystal system. For electrochemical testing, a coin cell assembly and three electrode system was used. In three electrode system an Ag/AgCl in 3M KCl as a reference electrode, Pt wire as a counter electrode, and active material as cathode was used. A coin cell was made by using sodium foil as counter electrode and NaClO4 in EC:DC as electrolyte. The testing voltage range was 0.3V – 3.2V.

The composite 3% TiO2@V2O5/C showed the best electrochemical performance. CV indicated good stability and rate capability. Its GCD showed a discharge capacity of 276.2 mAh/g at 0.1 C outperforming all other composites and V2O5/C. Its energy density was 449 Wh/kg at 1.5 V. It showed capacity retention of 77.9% over 200 cycles with greater than 80% coulombic efficiency. EIS indicated a decrease in charge transfer and faster diffusion.

The Titania nanolayer as a shell is a good choice for cathodes made of metal oxide/carbon. Ti doping made structural changes that enhanced the performance of the composite as a cathode. Mehek, R., Iqbal, N., Javed, O., Noor, T., & Liu, W. (2024). Improved rate capability and long cycle life of metal-organic framework derived TiO2@ V2O5 composite as an efficient cathode for sodium-ion batteries. *Journal of Energy Storage*, *78*, 109921.

1. **Mn-BTC POM@MOF**

Polyoxometalates (POMs) are metal oxide cluster anions having exceptional structural and compositional properties. They are also called “electron sponges” due to their fast reversible charge transfer property and multielectron redox potential. Therefore, it is a potential candidate as an energy storage material. However, high solubility, low surface area, and aggregation in electrolytes are the main hurdles in its energy storage application. To stabilize it, various support materials like MOF and SiO2 are introduced. Polyoxivandates among POM are the most promising cathode material due to their high specific capacity. Various improvements are being made to improve specific capacity and stability. It could be done by proactive coating, active material, and electrolyte modification. Ullah I. et al. synthesized a composite NaDV@Mn-BTC where NaDV (sodium decavanadate Na6V10O28) in the scaffold of Mn-BTC (1,3,5 benzene tricarboxylic acid) based MOF. The Mn-BTC has a pore size distribution of 0.92 nm and can effectively accommodate NaDV.

For the electrochemical test, a three-electrode system was used with Pt wire as the counter electrode and Ag/AgCl as a reference electrode.

POM@MOF hybrid was synthesized via a facile solvothermal method by using Mn(OOCCH3)20.4H2O, PVP, BTC, and NaDV. For comparison pristine Mn-BTC and NaDV were also synthesized.

The Mn-BTC showed that 3D architecture provided a large surface area and interconnected network. Mn-BTC were assembled and interconnected with NaDV nanocrystals. It improved the electronic conduction at the interface of nanorods and nanocrystals. SEM and TEM revealed the interconnected nature of Mn-BTC and NaDV crystals.

The CV of NaDV@Mn-BTC material confirmed stable and reversible cycling indicating hydrolytic and structural stability. GCD showed a high discharge capacity of 137 mAh/g. After 100 cycles, it showed a high-rate capability and coulombic efficiency of 97.1% and capacity retention of 81%. After 1000 cycles it retained 62% capacity retention. EIS confirmed a decrease in charge transfer resistance indicating improved charge kinetics.

The composite showed high capacity due to V+5 reduction to V+4. The energy storage and stability were due to the synergic redox effect of V and Mn. Ullah, I., ul Haq, T., Khan, A. A., Inayat, A., Shoaib, M., Haider, A., ... & Hussain, I. (2023). Sodium decavanadate encapsulated Mn-BTC POM@ MOF as high-capacity cathode material for aqueous sodium-ion batteries. *Journal of Alloys and Compounds*, *932*, 167647.

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. et al.* have 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.

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

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

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.)

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