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Cobalt–Zinc MOF-Derived Phosphorus-Doped Carbon Composites on Nickel Foam as High-Performance Supercapacitor Electrodes

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ABSTRACT:

Co/Zn MOF is an all-metal-organic framework made up of cobalt and zinc in equal measures (2-methylimidazole served as the organic bond and methanol was used as a solvent). The precursor was carbonized at 900°C under an argon atmosphere as a source of phosphorus. The result of this process was a product of a phosphorus-doped carbon-metal phosphide compound bonded to nickel foam. Based on the X-ray diffraction tests, new crystalline phases CoP and Zn_3P_2 were produced. The electrochemical performance of battery was to be tested in cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) with the help of a three-electrode system, in which 6 M KOH is the electrolyte. The electrode displayed nearly rectangular CV curves and well-defined redox peaks and nearly symmetrical GCD curves with good reversibility and pseudocapacitive features. It was made of a material of maximum specific capacitance of 1194 F/g and current of 1.5 A/g. This proves that phosphorus-doped Co/Zn MOF-based carbon composites are potential materials that can be used as electrodes in supercapacitors with high power performance.

Introduction:

Increasing world demand of a good store of energy has encouraged numerous researches of the supercapacitors that fills the gap between battery mechanism and the normal capacitors mechanism. Supercapacitors are widely used due to high power density, rapid charging, rapid discharging, and long life. They have however very low energy density and that is a big drawback to batteries [1].

Zinc phosphide and cobalt phosphide are said to be the most promising electrode materials to work with because they possess a high electrical transportation rate, rich redox activity and high electrochemical stability [2]. Researchers have applied metal-organic frameworks as temporary models to push their performances to even greater heights, because they possess superior surface area, the pore size can be tuned, and centers of metal are evenly dispersed to form nanostructured TMP-carbon composites [3].

Above all, bimetallic MOF gives an opportunity to the two types of metals to cooperate with each other in a manner that improves their performance. Cobalt is a nice example of redox and Zinc enhances electrical stability and conductivity. A good current collector is porous, conductive, three-dimensional nickel foam, which also allows an electrode to be prepared binder-free with the support material. [4].

Synthesis of Co/Zn MOF-Derived Phosphorus-Doped Carbon Composites:

Co/Zn MOF precursor has been prepared by following co-precipitation procedure in which the salts of the co-precipitated cobalt and zinc were dissolved in methanol in the presence of 2-methylimidazole. The reaction was carried out at room temperature and the purplish product was an MOF precipitate. Washing and drying of the product so obtained followed. In another attempt to prepare the same into porous carbon structure, the dry precursor was burned in high temperature (900 C) in the presence of argon.

Results and Discussions:

XRD Analysis:

Sample 1, with a Co to Zn ratio of 1:1, exhibits many diffraction peaks indicating the CoP and Zn3P2 phases with a broad peak at approximately 25 degrees that perhaps represents amorphous carbon [2]. The sharp peaks indicate that the material was indeed crystallized by means of carbonization and phosphorus doping. The presence of metal phosphide and carbon in this composite suggests that the precursor in the form of MOF was successfully transferred to a bimetallic phosphide carbon structure. The CoP step imparts the material with redox activeness and Zn3P2 should enhance electrical conductivity and stability [4]. The amorphous carbon is broad, indicating the amorphous has to be graphitized to some extent, and could contribute to the movement of electrons. On the whole, XRD results indicate that Sample 1 has a very promising structure that can be used in electrochemical energy storage [5].

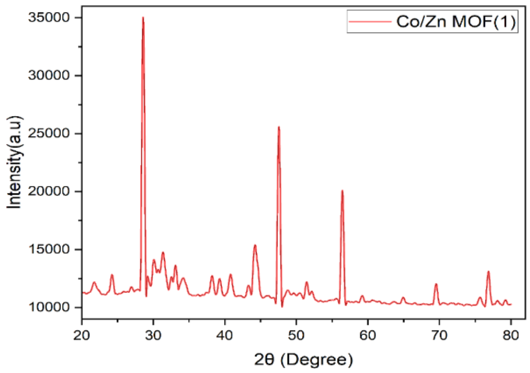

Fig.1: XRD of Co/Zn MOF

Cyclic Voltammetry (CV):

Sample 1 CV curves were recorded at varying scan rate between 10 and 100 mV/s and voltage varied between -0.8 and 1.0 V. The curves were nearly rectangular in shape with obvious oxidation and reduction peaks. These peaks imply that the charge storage principle is not of the electric double-layer capacitance (EDLC) but that of the pseudocapacitance. [4, 6]. When the scan rate was raised to 100 mV/s, the electrode exhibited a large area in the CV curve, indicating that the electroactive sites are readily available as well as the ions can travel within the material at a high rate. This implies that the charge transfer reaction is rapid and faradaic reactions are reversible. The fact that the CV curves have the same shape when measured with varying scan rates indicates that the material used as an electrode is structurally stable. This is due to the stability of the material that is composed of cobalt and zinc mixed with conductive carbon. [1, 7].

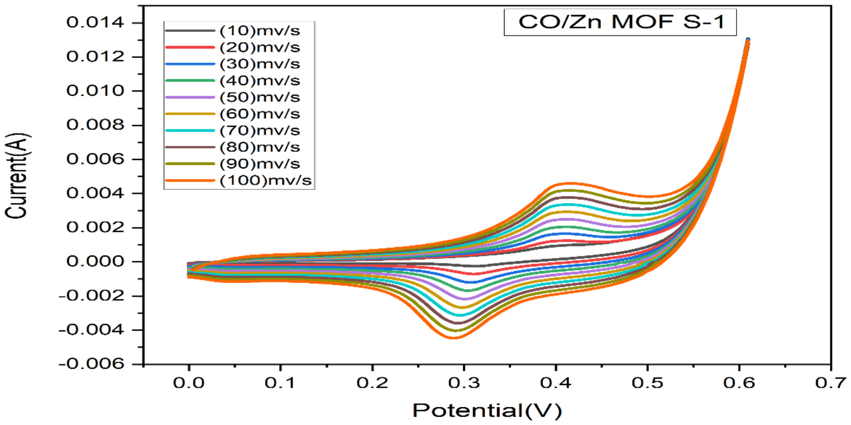

Fig.2:CV of Co/Zn MOF

Galvanostatic Charge–Discharge (GCD):

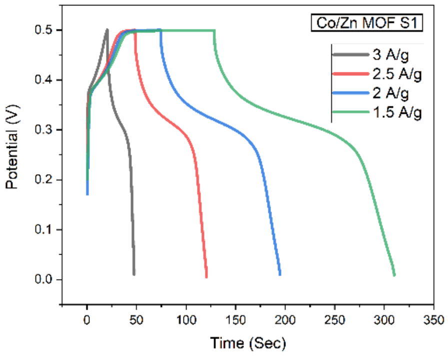

Fig.3: GCD of Co/Zn MOF

The GCD curves of Sample 1 at current densities of 1.5–3.0 A g^{-1} displayed nearly symmetric triangular shapes, which reflects high coulombic efficiency and reversibility. The electrode exhibited the following specific capacitances:

- 1194 F g^{-1} at 1.5 A g^{-1}
- 923 F g^{-1} at 2.0 A g^{-1}
- 634 F g^{-1} at 2.5 A g^{-1}
- 446 F g^{-1} at 3.0 A g^{-1}

The high capacitance at low current density is due to efficient electrolyte ion diffusion into the porous electrode, allowing maximum utilization of active sites. At higher current densities, the capacitance decreases because ions cannot fully penetrate the deeper pores within the limited discharge time. These results confirm that Sample demonstrates excellent capacitive behavior with high energy storage ability at low current densities and good rate capability at higher current densities. The synergistic effects of cobalt and zinc, combined with phosphorus doping and nickel foam conductivity, enhance both capacitance and reversibility [8].

Conclusion:

In this paper, the authors provide an account of how a carbon composite material (a blend of phosphorus and carbon) was successfully manufactured by introducing the nickel foam into a cobalt/zinc meta-organic framework (a 1:1 combination of cobalt and zinc). Carbonized high temperature, and then precipitated. XRD was used to prepare cobalt phosphide (CoP) and Zinc phosphide (Zn3P2) crystalline structure, which was randomly deposited onto a partially graphitized carbon structure. The redox effect of cobalt and the emergence of conductivity in zinc with the merits of electron transport by the amorphous carbon gives the spectacular performance of the obtained material. Numerous electrochemical studies showed that this material can be an incredibly useful electrode. The CV data revealed that cycle voltammetry was a pseudocapacitive technique and the familiar redox peaks were possibly giant signifiers of high reversibility and repeatability of the functionality at varying scan rates. GCD experiment yielded asymmetrical curves and sample specific capacitance was large at 1.5 A/g 1194 F/g. High current density electrode retained huge capacitance, as well as, huge rate ability and huge ion movement. Generally, phosphorus-doped material realized using Co/Zn MOF and cast on nickel foam is extremely ion and electron portable, one of the attributes of cobalt and zinc that can be prudently exploited, and does not fall apart. These properties make this material have a great future potential as supercapacitor electrode. Authors theories that ratios between cobalt and zinc, pore structure or material layout and flexible or asymmetric hardware may be optimized later so that the energy storage is usable in the real world.

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