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ZIF Derived Composite for Enhancing Electrochemical Properties

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ABSTRACT

The demand of energy is increasing, which results in energy crises. In this regard supercapacitors have gained a lot more importance and have bridge the performance gap between conventional capacitors and batteries. Different materials have been explored as an electrode material to enhance the supercapacitance of supercapacitors. MOFs have earned a lot more importance in this regard as they have high potential in delivering electrochemical performance. This study focuses on the synthesis of bimetallic ZIF Ce-Ni/C, combining the synergistic effects of both metals. The sample shows the supercapacitance of 2369 F g^{-1} at 0.3 A g^{-1}, showing it is helpful to be used as an electrode material.

Introduction

The increase in the application of energy sources and the demand of energy is rapidly increasing. The fossil fuels are finite and are diminishing with time. The renewable energy sources, such as solar and wind energy have gained importance but there are certain drawbacks associated with them such as variation in the production of energy and so does it cannot cope with the demand of energy. Supercapacitors have gained a lot more importance because of their rapid charging and discharging capabilities [1].

There are basically two types of supercapacitors, electric double layer capacitors (EDLC) and pseudo-capacitors. The classification of supercapacitors is based on their charge storage mechanism. The EDLC stores charge because of formation of electric double layer at the electrode-electrolyte interface. In pseudo-capacitors the storage, mechanism is faradic in nature. In hybrid supercapacitors charge storage takes place because of both electrostatically and electrochemically [2-4].

The electrode material plays a crucial role in the functioning of supercapacitors and in this regard MOFs play a crucial role. MOFs are porous in nature made up of metal ions and organic linkers arranged in the form of clusters. They have high electrochemical characteristics because of large surface area. Bimetallic MOFs have gained high applications then monometallic MOFs. Different metal ions have different properties and have revolutionized the energy storage phenomenon because of introduction of functions of different metal ions. [5, 6].

After thermal treatment MOFs because of decomposition of organic linkers are converted into metal oxides .The metal oxides because of porous in nature have enhanced electrochemical properties. [7]. Metal oxides have enhanced electrical conductivity than original MOFs, have fast charging process. Metal oxides have high specific capacitance and efficient energy storage capacity because of additional redox sites.[8, 9].

Huge amount of work is being done in orde to combine the characteristic features of MOFs and metal oxides offering large storage capacity for energy, fast charge-discharge process and excellent cyclic stability. MOFs comprising of imidazole type linkers are characterized as ZIFs, because of structural resemblance with zeolites [10-12].

Researchers are working to synthesize MOFs by using different methods. Seyoon shin et al. synthesized Ni monometallic MOF derived Ni@C composite and seized specific capacitance of 742 F/g at 1 A/g [13].In addition to monometallic MOFs, bimetallic MOFs have gained a lot more importance because of their advanced electrical properties Zhou et al. prepared $NiCo_2O_4$byannealing Ni/CO-MOF which is synthesized using the hydrothermal method. The electrode material displayed a high specific capacitance of 1214 F g^{-1} at a current density of 1 A g^{-1} [14].

In this work, we have synthesized bimetallic ZIF consisting of cerium and nickel by simple method to increase the electrochemical performance.

Synthesis of Ce-Ni/C ZIF

The synthesis of Ce-Ni ZIF was done by using simple co-precipitation method through mixing of metallic solution to organic linker. After mixing the sample is left for aging to form precipitates. After the formation of precipitate the sample is washed and dried and then followed by pyrolysis in an inert environment to form ZIF-derived products.

Results and discussions

The synthesized sample was then analyzed through cyclic voltammetry (CV) and galvanic charge-discharge (GCD) to check the electrochemical performance of the sample. In order to check the charge transfer resistance and solution resistance the electrostatic impedance spectroscopy (EIS) of the sample is done.

Chronopotentiometry is a widely used technique which is used to investigate the Sc and energy density of a material. GCD curves of the sample were achieved at various current densities 0.3, 0.5, 0.7, 1, 2 and 3 A g^{-1} and the respective specific capacitance is shown in table 1. The GCD curves obtained at various current densities is shown in figure 1, the curves are nearly triangular and have perfect symmetry in nature which shows the pseudocapacitive behavior.

The highest specific capacitance of 2369 F g^{-1} is shown by the sample at 0.3 current density, showing faradic charge-discharge process promoting pseudocapacitive nature. The energy density and power density respective to different current densities were also calculated. The sample Ce-Ni MOF shows energy density of 82.25 Wh Kg^{-1} and power density of 75 kw Kg^{-1} at 0.3 A g^{-1}.

Table 1 Capacitance of sample Ce-Ni/C MOF

J (A g^{-1})	Discharge time (s)	Sc (F g^{-1})
0.3	3948	2369
0.5	1870	1870
0.7	664	929.6
1	75	150
2	5.3	21
3	2	12

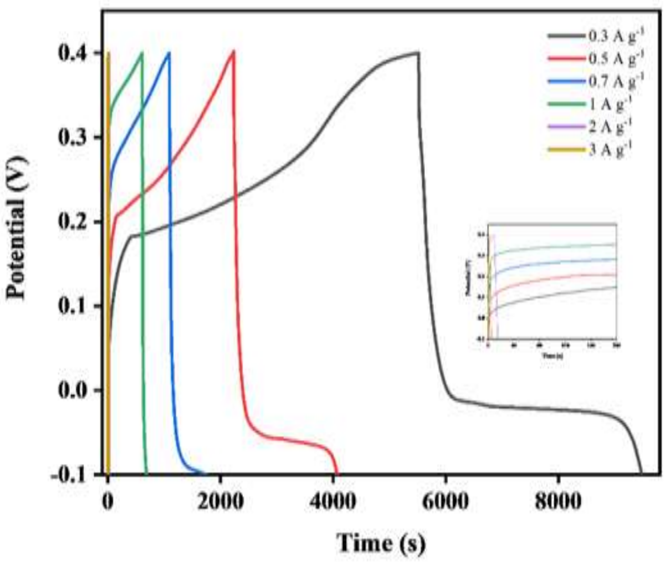

Figure 1 GCD curves of Ce-Ni/ZIF obtained at various current densities

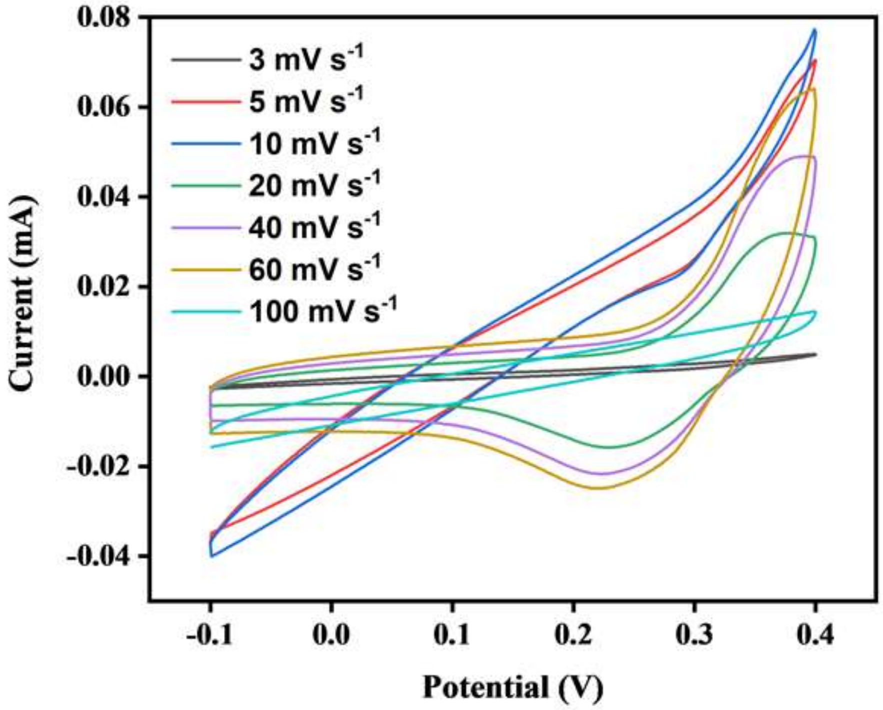

Figure 2 CV profile of sample Ce-Ni/ZIF taken at various current densities

In order to understand the charge storage mechanism, the cyclic voltammetry is done for sample Ce-Ni/MOF at various sweep rates. It gives information about the potential window and capacitance through area under the curve or redox behavior of prepared sample. The CV plot of sample Ce-Ni/ZIF at V of 3, 5, 10, 20, 40, 60 and 100 mV s^{-1}.

The highest capacitance of 156 F g^{-1} was shown by sample Ce-Ni/ZIF at current density of 3 mV s^{-1}, because of highest area enclosed by the polygon surface. The sample shows different redox peaks which emphasized the pseudocapacitive behavior of sample, incorporating because of combined effect of two metals. The specific capacitance calculated by using different scan rates is shown in table 2.

Table 2 Capacitance calculated by using CV at various scan rates

Scan rate (mV s^{-1})	**Capacitance (F g^{-1})**
3	156
5	30.8
10	19
20	11
40	8
60	7
100	1

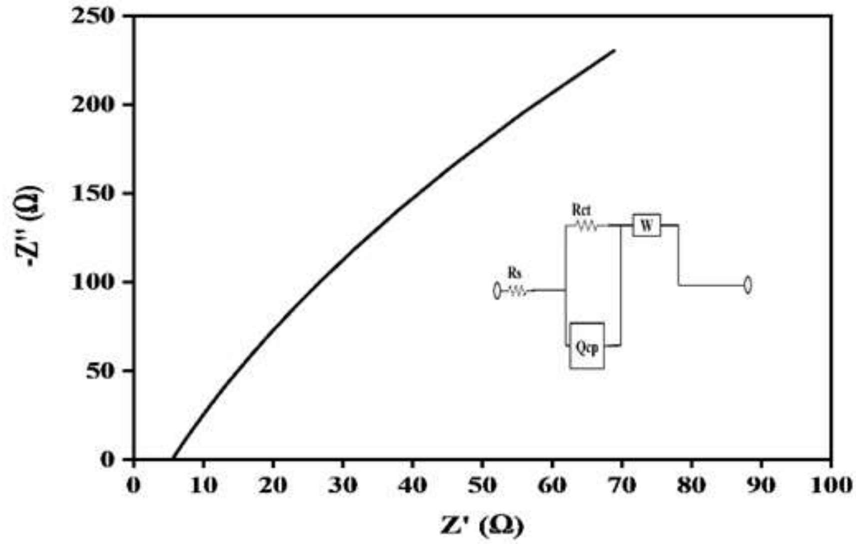

Figure 3 EIS and fitted circuit of sample Ce-Ni/ZIF

Electrochemical impedance spectroscopy (EIS) is done to find the electrochemical performance of the prepared sample and to dig out the electron transfer resistance and solution resistance through fitting data. Figure 3 shows the EIS graph of fitted data of Ce-Ni/ZIF, showing the Rs =5.488 Ω and Rct =2264 Ω.

Conclusion

In summary, the sample Ce-Ni/ZIF was prepared by following simple co-precipitation method and then carbonization is done. The electrochemical properties of sample are outstanding showing the capacitance of 2369 F g^{-1} at 0.3 A/g with energy density and power density of 82.25 Wh Kg^{-1} and 75 kw Kg^{-1} respectively. The pseudocapacitive behavior is confirmed by the CV results and resistance is shown in ohms. The electrochemical results of sample Ce-Ni/ZIF verified that it can be highly recommended as an electrode material for supercapacitors.

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