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Enhancing Electrochemical Properties of Super Capacitor Using Bimetallic Zn-Fe MOF Derived Composite as an Electrode Material.

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ABSTRACT

Energy crises due to different factors causes the need of Energy storage devices. Among different ESS supercapacitors are widely used to passage the gap between traditional capacitors and batteries. For the development of the electrode material of supercapacitors different materials have been widely used. MOFs are known for their highest electrochemical performance. So, this study is based on the synthesis of bimetallic Zn-Fe MOF adding from the combined effect of both metals. The sample shows the superior S_C of 11586 F/g at 0.1 A/g making it helpful to be used as an electrode material in supercapacitors.

Introduction

Owing to overpopulation, industrial development and fast expansion of the global economy, the need for energy is becoming the need of hour [1]. Utilization of non-renewable energy resources can cause energy crises which brings alarming situation in the near future [2]. So, there is a need for renewable energy resources. Towards this objective, ESS are used which commonly include super capacitor and batteries. Batteries are known for their high U but have low P_m, while supercapacitors have low energy density while high P_m which makes them attractive candidates while using them in many applications where there is a need of burst of power [3]. Super capacitors based on their charge storage procedure are divided into two categories, EDLC (electrostatically double layer capacitor) and pseudo capacitor. Charge is stored by physical adsorption of ions in EDLCs on the electrode surface forming electric double layer there is no faradic reactions. While in pseudo capacitor charge is stored faradically in which active material undergo redox reactions to store and release charge [4].

The important factors contributing performance of supercapacitors are active materials and electrolytes both play crucial roles in determining the electrochemical output of supercapacitors. Many electrode materials are used in this context for both EDLCs or pseudo capacitors. Commonly used electrode material for EDLC is activated carbon, graphene, CNTs these materials have good cyclic stability but low capacitance due to absence of redox reactions [5]. While the electrode material for pseudo capacitor includes transition metal oxides such as Fe_3O_4, ZnO, MnO_2,NiO, Co_3O_4 , metal sulfides including FeS, MoS_2, Cu_2S ,metal nitrides as TiN, Fe_4N, Cr_2N and conducting polymers such as PANI and PPY these materials participate in redox reactions and results in good capacitance while they have low cycle life due to degradation after some time [6, 7] . So in order to overcome the intrinsic draw backs of these materials research have been focused towards novel and hybrid materials combining both EDLC and pseudo capacitors such as Mxenes and MOFs [8]. MOFs are a type of crystalline materials having 3D structures comprising of metal atoms and organic linker. They have high surface area, porosity and pore volume [9]. MOFs are crystalline in nature so due to their arrangement of atoms in regular manner they have low conductivity [10], so to overcome this draw back heat treatment of in the presence of inert environment are commonly used treatment [11].

Researchers have been working on synthesis of MOFs using different routes . seyoon shin et al. synthesized Ni monometallic MOF derived Ni@C composite and achieved specific capacitance of 742 F/g at 1 A/g [12]. Many monometallic MOFs have been synthesized until now, but as monometallic MOF has only one metal node, so scientists proposed the integration of second metal node to the framework which can enhance distribution of ions and have synergistic effect of both metals used. Mengde Li et al. synthesized bimetallic Co/Ni MOF with the highest capacitance of 1493 F/g [13].

In this work we synthesized bimetallic MOF containing Zn-Fe as metals to boost the electro-chemical traits of supercapacitor using simple method. The GCD was performed at different current densities and results show specific capacitance of 11856 F/g at 0.1 A/g.

Synthesis of Zn-Fe/C MOF

The synthesis of Zn-Fe MOF has been done through simple co-precipitation method in metallic solution were solved in solution of organic linker. Then the solution was left for aging for some time after the precipitates were settled the solution was washed and dried to get bimetallic MOF. This MOF further underwent pyrolysis in an inert environment to achieve MOF derived product .

Results and discussion

As these materials have been used due to their good electrochemical performance so to check their electrochemical performance cyclic voltammetry and galvanostatic charge discharge technique was performed. EIS (electrostatic impedance spectroscopy) was performed to check the charge transfer resistance or solution resistance of material. Also, Raman spectroscopy is conducted for structural analysis.

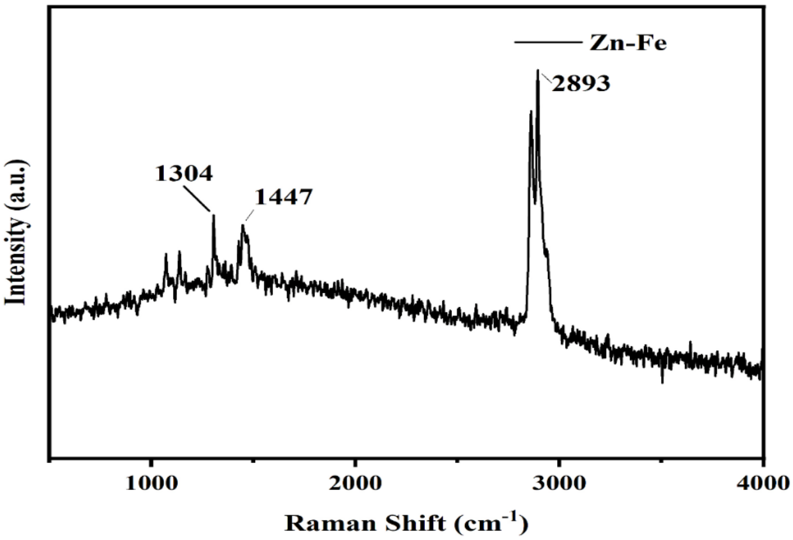

Figure.1. Raman spectroscopy of Sample Zn-Fe

Raman spectroscopy was employed to gather macroscopic insights into the characteristics of defects and dopants. The Raman spectra of sample Zn-Fe is shown in Fig.1. The G and D bands are located at 1300cm^{-1} and 1450 cm^{-1}. The G band is generally associated with the carbon structure and D band with the structural defects and disorder [14]. The intensity of peaks of D and G band is used to analyze the degree of disorder in carbon structure [15]. The intensity of D band was higher than G band in Zn-Fe and is associated with the dominancy of sp^3 hybridization and defects present in carbon structure due to heteroatom doping. The ratio of I_D/I_G was calculated to be 1.06. The ratio of I_D/I_G for S1 shows more disordered nature and more active sites which is preferred for supercapacitor applications [16, 17]. The red shift in D and blue shift in G band is due to heteroatom doping which causes the introduction of sp^3 hybridization in carbon atom [15, 18].

Chronopotentiometry is a widely used method to investigate the Sc and energy density of material. GCD curves were employed at various current densities of 0.1, 0.2, 0.5, 1 and 3 A/g and achieve the specific capacitance of as shown in table 1. Fig.2. shows nonlinear behavior between potential and time at constant current as the curve is not purely triangular and shows humps which is evident for the pseudo capacitor behavior of the material.

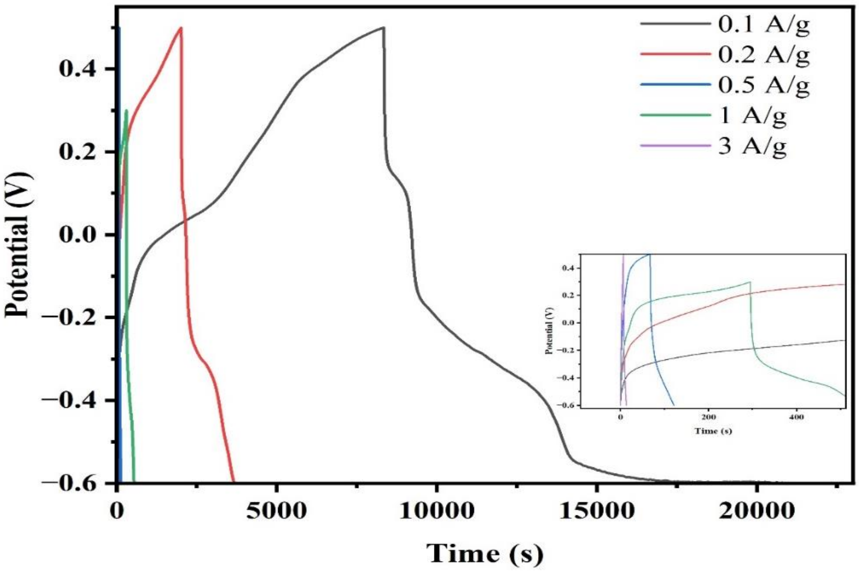

Figure 2 GCD profiles of sample Zn-Fe at different current densities.

The highest Sc of 11856 F/g is accomplished at 0.1 A/g because of ion diffusion process at this current density. This highest capacitance is due to the combined effect of both metals. GCD profiles are also used to calculate the *U* and P_m. Hence calculated values of *U*=552 and P_m=10922 at 0.2 A/g. Table.1 shows the Capacitance of sample Zn-Fe at different current densities.

Table 1 Capacitance of sample Zn-Fe using GCD

***J* (A/g)**	**Discharge time (s)**	**Sc (F/g)**
0.1	13042	11856
0.2	1679	3052
0.5	238	108
1	63	58
3	8	21

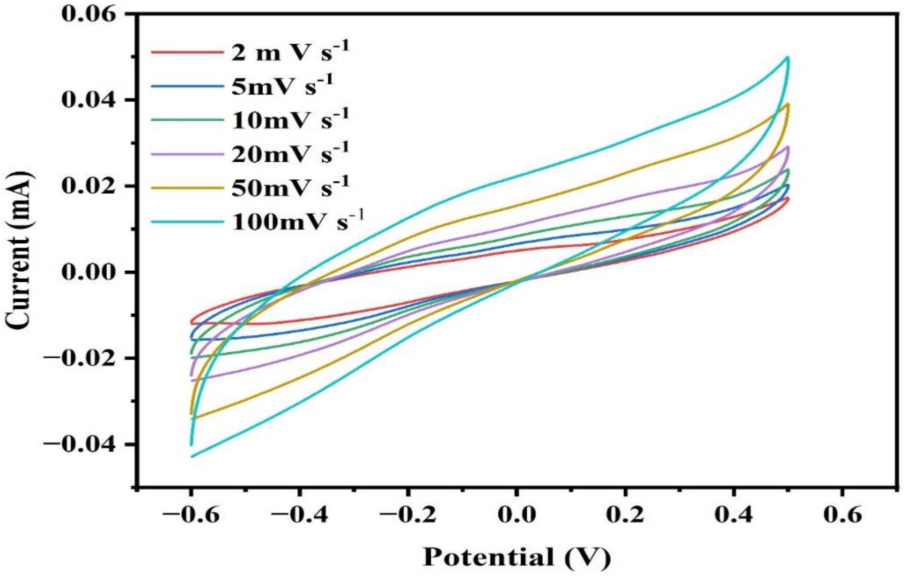

Figure 3 CV profiles of sample Zn-Fe at various scan rates.

Furthermore, CV was performed at various sweep rates and the plot between current and potential is obtained in the cyclic manner. The resulting plot provides information about the charge storage mechanism, potential window, Capacitance through area under the curve or the redox behavior of the material. Fig.3 shows the CV plot of Zn-Fe at different V of 1,2 ,5 ,10,20, 50 and 100 mV s^{-1}.

Scan rate (mV s^{-1})	**Capacitance (F/g)**
2	50
5	26
10	17
20	11
50	6
100	4

At 1mV s^{-1} sample have highest capacitance of 50 F/g due to larger area enclosed. Also, the graphs at lower sweep rates show pseudo-capacitor behavior of samples due to redox peaks occurring. The redox peaks are due to both metals which undergo redox reactions.Table.3 shows the capacitance calculated through CV at different sweep rates.

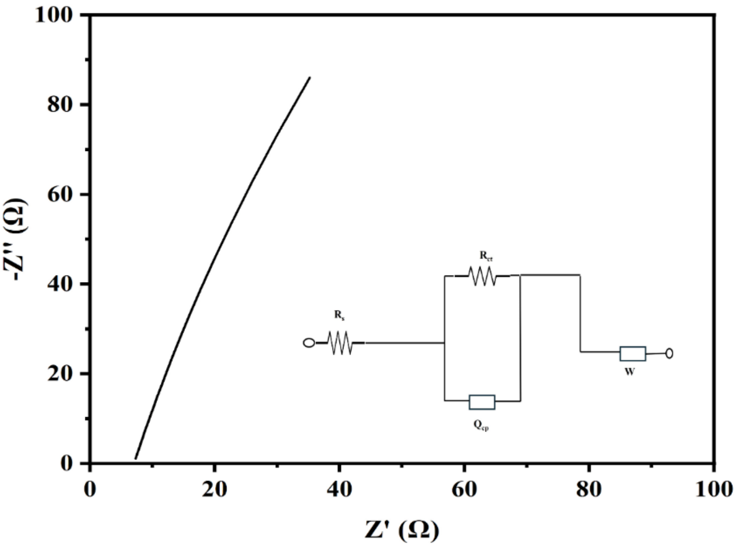

Figure 4 EIS and fitted circuit of sample Zn-Fe/C

EIS technique was performed to gain insight into the electron transfer resistance and solution resistance through fitted circuit. Like seen in Fig.4 the sample Zn-Fe/C shows Rct= 1019 and Rs=7.01 Ω.

Conclusion

In summary, the sample Zn-Fe was synthesized using simple process co-precipitation followed by carbonization. Raman spectra confirm the structural analysis in the sample. Further the sample shows outstanding electrochemical performance with the capacitance of 11586 F/g at 0.1 A/g with the energy density of and power density of . The CV profiles show the pseudocapacitive behavior of the prepared sample and the resistance value of ohms. The above-mentioned results show that the Zn-Fe with highest Sc can be used as an electrode material for super capacitors.

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