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A Novel Bimetallic MOF for Energy Storage Application

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ABSTRACT:

Nowadays, extensive research work is being done in exploring the high performing electrode materials for supercapacitors to cope up with the energy crisis rising due to the immense use of energy consuming devices. Apart from materials based on carbon, TMOs and conducting polymers , MOFs are considered as a good choice for the electrode of SC due to its phenomenal electrochemical properties. The performance of SC electrode based on MOFs majorly depends on the synthesis method, its morphology, elemental and surface composition. Herein, a bimetallic Fe-Ce MOF is synthesized to use as electrode material of SC, results in enhancing the electrochemical properties mainly specific capacitance. The synthesized MOF exhibits the specific capacitance $4342Fg^{-1}$ at current density of $0.2Ag^{-1}$.

Introduction:

With the passage of time, energy needs are increasing day by day. The energy from the non-renewable energy sources is not sufficient to fulfill the needs. The non-renewable energy sources are also limited in amount and causing some serious pollution in the atmosphere as well [1]. Along with the power production, it is equally important to look at the aspect of energy storage. For the purpose of storing energy , batteries are excellent choice because of high energy density but the low power density of batteries, low charge- discharge rate and poor stability limits its use In various applications [2]. Contrarily, SCs are considered as an excellent choice for the applications where power bursts are required. The high P_d, high rate of charge and discharge, and good stability of SC makes it a suitable candidate among the energy storage devices [3, 4]. SC is categorized into EDLC (electrostatic double layer capacitor) and pseudo capacitors based on charge storage mechanism. EDLC based on carbon materials store charge electrostatically between the double layer forming at the electrode-electrolyte boundary. Whereas, the pseudo capacitors based on TMOs and conducting polymers store charge faradaically involving a redox reaction [5]

EDLC is more stable as compared to batteries but the limited energy density of EDLC makes it less useful [6]. On the other hand, pseudo capacitors involves a redox reaction and possess high E_d than EDLC but still have similarity in terms of low power density and low stability [7, 8]. The drawbacks of both EDLCs and pseudo capacitors cannot be neglected despite their features. So to overcome these drawbacks, the approachable solution is to fabricate a hybrid SC by combining one electrode from pseudo capacitors and the other electrode from EDLC [9]. Research is being done to explore the other electrode materials apart from the traditional electrodes. MOFs are used for the electrodes of SC owing to significant properties including high surface area, tunable porous structure, large pore volume. MOFs comprises of an organic linker along with metal atoms[10]. In this aspect, several monometallic MOFs were considered to specific capacitance and electrochemical properties of SC. Contribution of monometallic MOFs is insufficient in enhancing the electrochemical properties of SC because it involves only the contribution of metal ions from one metal. However, bimetallic MOFs are preferable over monometallic MOFs due to the reason of the incorporation of metal ions from two metals results in providing more active sites for charge deposition [11].

In this study, a bimetallic Fe-Ce MOF is synthesized to improve the electrochemical properties of SC. The synthesis is done by co precipitation method . The GCD performance of the synthesized sample at different current densities is analyzed.

Synthesis of Fe-Ce MOF:

The synthesis of sample involves simple co precipitation method. Metal salts were dissolved in the solvent followed by mixing with organic linker. Later, the solution was aged for few hours and then washed and dried at high temperature to get the powder form.

Results and Discussion:

GCD was performed by varying the densities of current to analyze the electrochemical performance of sample. The C_s with respect to current density is shown in table 1. Figure 1 shows the non- triangular curves that depicts the non-linear behavior between the potential and time. Moreover, the plateaus appearing at the curves corresponds to the pseudocapacitive behavior of sample.

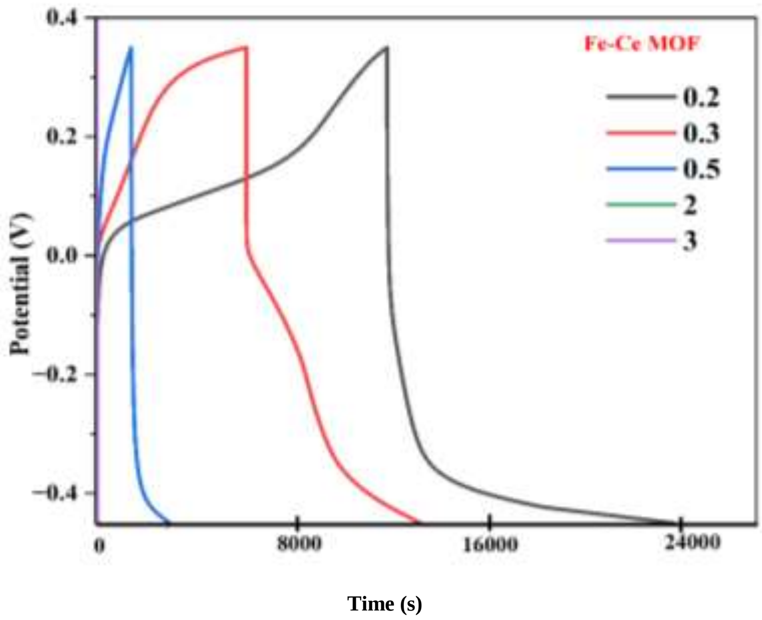

Figure 1, GCD curves of Fe-Ce MOF at different current densities

C_s of 4342 Ag^{-1} is observed at $0.2Ag^{-1}$ under the potential window of -0.45 to 0.35 V . This is due to the high rate of diffusion at this current density due to the metal ions of both metals. The C_s at different J_d is shown in table 1.

Table 1: Specific Capacitance of Fe- Ce MOF from GCD

$J(Ag^{-1})$	Discharge Time (s)	$C_s(Ag^{-1})$
0.2	10345	4342
0.3	8129	3226
0.5	1106	732
2	876	453
3	99	32

Cyclic voltammetry at different scan rates were performed to analyze the behavior of sample by examining the plot between current and potential under the same potential window. Figure 2 shows the CV profile of same for different scan rates. The CV profile of synthesized sample is analyzed in the window of potential -0.45 V to 0.35 V. specific capacitance is calculated from CV curve by measuring the area under the current-potential cruve.

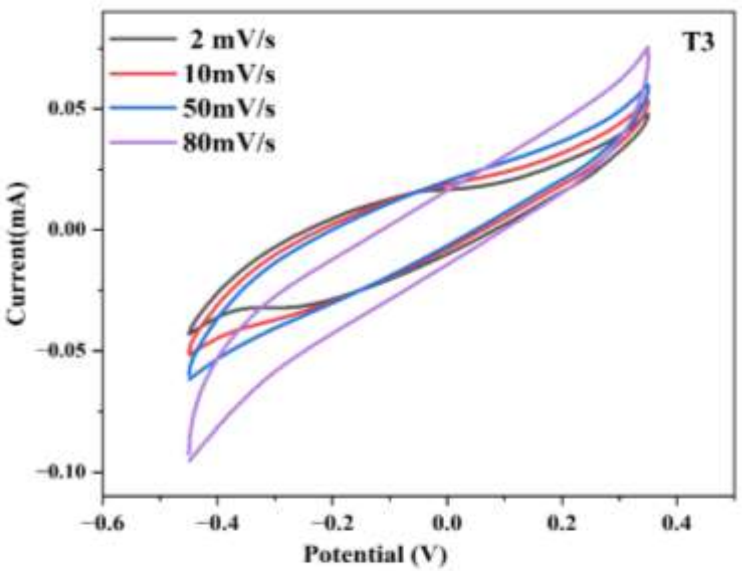

Figure 2: CV plots of sample

Table 2: Specific Capacitance of Fe-Ce MOF from CV

Scan Rate (mV/s)	$C_s (Ag^{-1})$
2	67
10	24
50	8
80	3

Increasing scan rate, decreases C_s due to decrease in area under the curve and redox activity. The highest C_s of 67 F/g is observed at the scan rate of 2 mV/s . The redox peaks at lower scan rates represents the pseudo capacitive nature of the sample. Table 2 shows C_s at different scan rates of CV.

Electrochemical impedance spectroscopy was performed to evaluate the resistance offered to the transfer of electron and the solution resistance. The capacitive behavior due to contribution of both metals Fe and Ce in comparison with resistance of the sample was analyzed by EIS As shown in figure 3, the Fe-Ce MOF shows R_{ct}=982 ohms and R_s= 8 ohms.

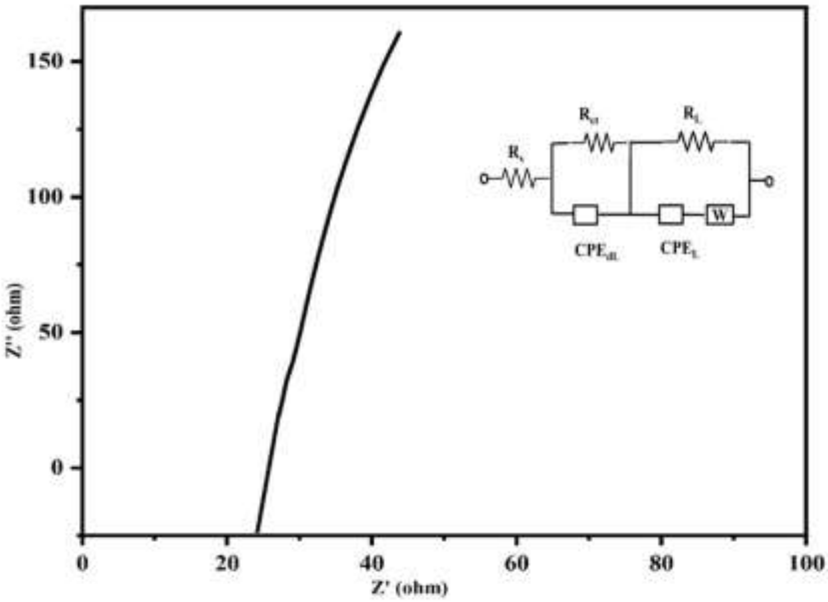

Figure 3, EIS of Fe-Ce MOF with fitted circuit

Conclusion:

Fe-Ce MOF was synthesized by simple co precipitation method. GCD and CV profiles confirms the pseudo capacitive behavior of sample. C_s of 4342 Ag^{-1} is observed at $J_d = 0.2\ Fg^{-1}$. Enhanced C_s of Fe Ce MOF depicts that this sample can be used as an electrode of supercapacitors.

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