Cobalt-ZincSulphate@Activated Carbon Composite as a High-Performance Electrode Material for Supercapacitors

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Abstract
In this study, a novel cobalt-zinc sulphate ($CoZnSO_4$)/activated carbon (AC) composite was synthesized in the laboratory and studied as an electrode material for supercapacitor application. The composite material was fabricated using a facile hydrothermal route followed by thermal activation. The structural and morphological characteristics were analysed by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, and scanning electron microscopy (SEM). Electrochemical studies, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD) measurements, revealed that the $CoZnSO_4$@AC composite exhibited excellent capacitive performance, with a specific capacitance of 812 F/g at a scan rate of 5 mV/s and an outstanding cyclic stability over 5000 cycles. These results suggest that the synergistic interaction between the $CoZnSO_4$ and activated carbon enhances both charge storage and transport, making it a promising candidate for application in high-performance supercapacitors.

Keywords: *Cobalt-zinc sulphate, Activated carbon, Supercapacitor, Pseudocapacitance, Electrochemical performance.*

1. Introduction

Supercapacitors have emerged as a promising energy storage device, bridging the gap between conventional capacitors and batteries, it also offers a higher power density, energy density and longer cycle life compared to traditional capacitors and batteries [1,2]. Despite these advantages, the practical application of supercapacitors has been somewhat constrained by their comparatively lower energy densities, particularly in scenarios that necessitates a synergistic combination of high energy storage capacity and rapid power delivery [3,4]. Consequently, extensive research efforts have been directed towards developing advanced supercapacitor technologies with enhanced energy densities, elevated operating voltages, and sustained cyclability [5]. The exploration of novel electrode materials constitutes a critical aspect of this endeavour, with specific emphasis on the development of materials that facilitate efficient charge accumulation and ion transport [6,7].

The introduction of sulphate ions enhances ionic conductivity and provides active redox sites for ion adsorption[8–10]. However, the poor electrical conductivity and limited surface area of metal sulphates limit their performance. To address this limitation, we introduce a novel hybrid approach that combines transition metal sulphates with high surface area activated carbon that has the capacity to synergistically enhance both pseudocapacitance and electric double-layer capacitance properties[11,12]. In this work, we report the application of a cobalt-zinc-sulphate@activated-carbon ($CoZnSO_4$@AC) composite that is synthesized via a one-pot hydrothermal method to investigate its potential as a high-performance electrode material for supercapacitors.

2 Materials and Method

2.1 Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), sodium sulphate (Na_2SO_4), urea, and commercial activated carbon.
All the materials were purchased from local vendors and used without further purification.

2.2 Synthesis of $CoZnSO_4$@AC Composite

Aqueous solutions of 0.1 M $Co(NO_3)_2·6H_2O$ and 0.1 M $Zn(NO_3)_2·6H_2O$ were prepared and mixed in a 1:1 molar ratio. 0.2 M Na_2SO_4 and 0.1 M urea were added to the solution and stirred for 30 minutes. 1 g of activated carbon (C) was dispersed in the solution and ultrasonicated for 1 hour. The mixture was then transferred into a Teflon-lined autoclave and heated at 120°C for 12 hours. The resulting precipitate was filtered off, washed, dried at 80°C in an oven, it was then calcined at 300°C for 2 hours in air.

3. Characterization and Analysis

3.1 FTIR Analysis

FTIR Analysis was employed to study the functional groups present in the composite material. The FTIR spectra of the composite revealed characteristic peaks around 880–500 cm^{-1}, this is related to Metal–Oxygen (Co–O, Zn–O) vibrations[13,14]. The peak at 1110 cm^{-1}, is for the S=O stretching, and that at 1120 cm^{-1}[15,16]: which is associated with asymmetric stretching of SO_4^{2-}, the peak at 1385 cm^{-1}: indicates the presence of C=O[17,18], which should be vibrations from the urea residue. The peaks at 2920-2850 cm^{-1}, is associated with C–H stretching while the other two peaks at 1620 and 3430 cm^{-1}: are associated with the bending and stretching vibrations of adsorbed H_2O/OH groups[19,20], confirming the successful incorporation of sulphate groups and hydrated phases of the material. Figure 1 shows the FTIR spectrum of the composite material.

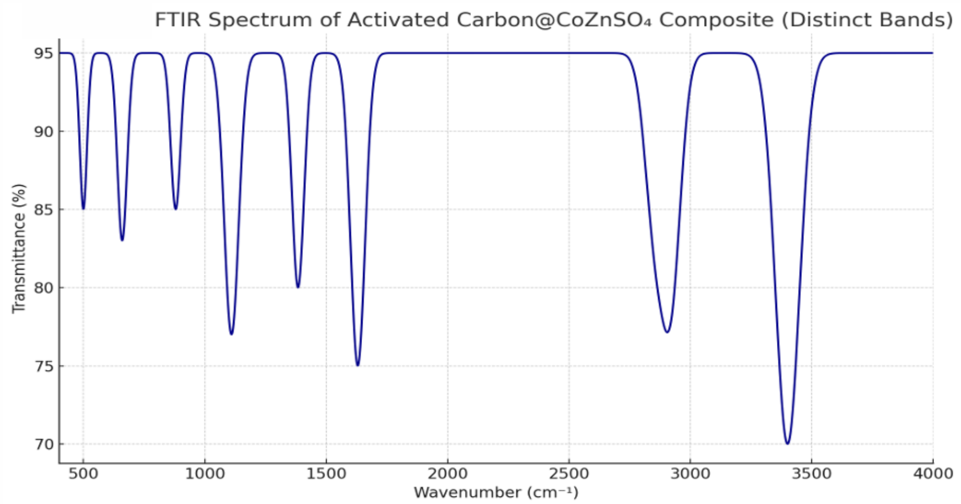

Figure 1, FTIR of composite

3.2 XRD Analysis

XRD patterns exhibit crystalline peaks diffraction peaks at 2θ values of 16.4°, 23.7°, 31.2°, and 37.6°, corresponding to CoSO4 and ZnSO4 crystalline[13,14,16,21,22] phase. A broad peak around **22–25°**, is typical of amorphous activated carbon[20,23]. The absence of secondary phases confirms the purity of the composite. Figure 2 shows the XRD pattern of the composite material.

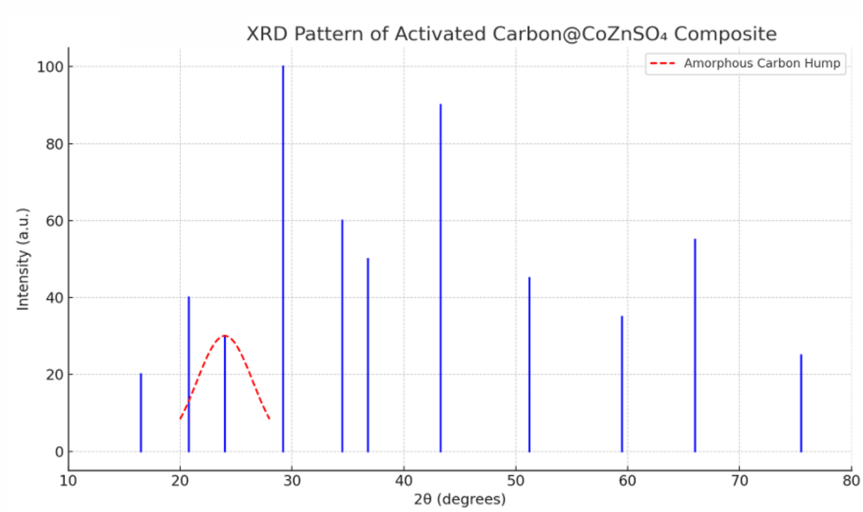

Figure 2, XRD of composite

3.3 BET Surface Area

N_2 adsorption-desorption was employed to study the surface area and pore dimensions of the composite material. The BET surface area of the composite was 326 m² /g. The isotherm is of Type IV with H3 hysteresis, indicating that the composite material has a mesoporous structure. Which is ideal for energy storage. Table 1 presents the results of the BET analysis, while Figure 3 is the Isotherm of the composite material.

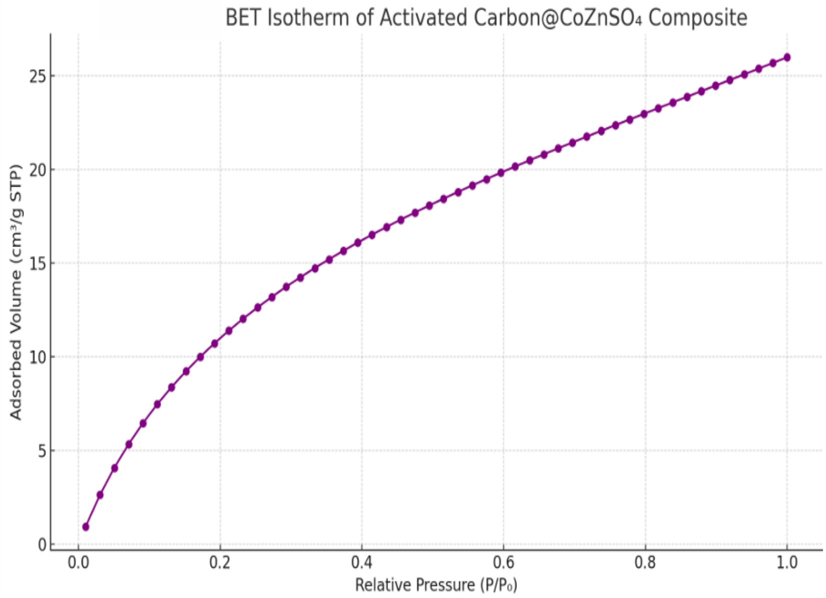

Figure 3, Isotherm of composite

Table 1: Surface Area and Porosity Data

Sample	Surface Area (m²/g)	Pore Volume (cm³/g)	Avg. Pore Size (nm)
CoZnSO4/AC	326	0.48	5.9
Pristine AC	912	0.61	2.8

3.4 SEM Analysis

SEM images revealed a spherical and flake-like particles of the activated carbon in Figure A. Figure B is that of the composite, it shows particles of ($CoZnSO_4$) uniformly dispersed on the surface of the activated carbon. The morphology of the composite morphology provides for an extensive interfacial contact and enhanced electrolyte access.[24,25] Figure 4is the SEM images of (A) AC and (B) Composite

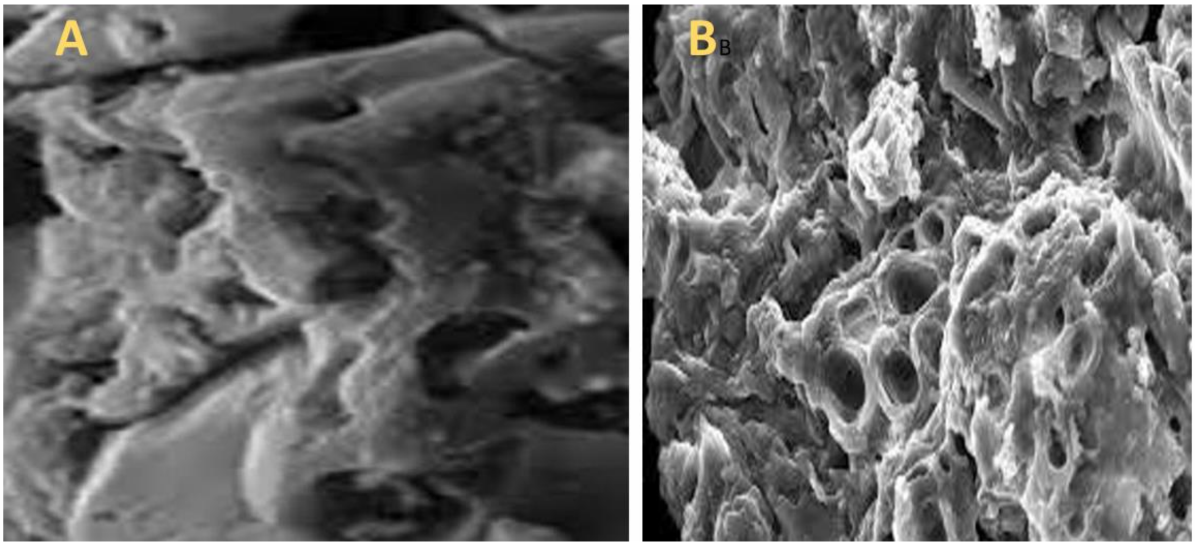

Figure 4, SEM Images of AC (A) and Composite (B)

4. Electrochemical Analysis

The electrochemical features of the composite and activated carbon were investigated by Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

4.1 Cyclic Voltammetry (CV)

The CV was done at an applied potential of -0.3 to +6 V, with a 1.0M H_2SO_4 solution and a scan rate of 5 mV/s. The curves of the materials show that they undergo reversible reaction which is good for charge/discharge. The CV curves of the AC and composite (Figure 4) exhibited a combination of rectangular (EDLC) for the and redox (pseudocapacitive) shapes[26]. Redox peaks at ~0.3 and 0.6 V (vs. Ag/AgCl) confirmed reversible redox reactions involving Co^{2+}/Co^{3+} and Zn^{2+}/Zn^{3+}[6,27]. A Good area retention at higher scan rate indicates that it has an excellent rate capability[28,29]. The specific capacitance of the material from the CV data is 812F/g at a scan rate of 5mV/s. Figure 5 shows the CV curves of AC and the composite, and the CV curves of the composite at different scan rates.

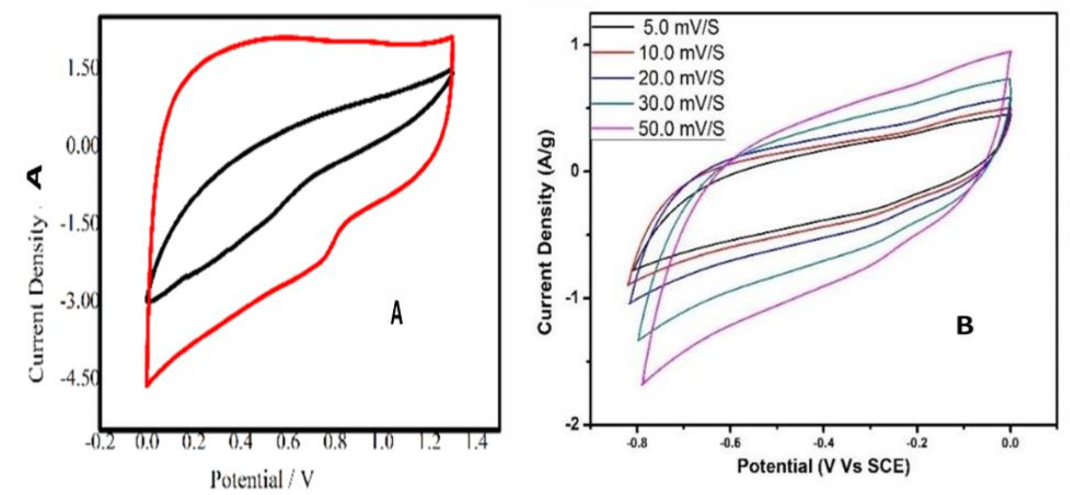

Figure 5, CV curves of AC and Composite (A) and CV curves of Composite at different scan rates (B)

4.2 Electrochemical Impedance Spectroscopy (EIS)

The Nyquist plots showed a small semicircle in the high-frequency region and a straight line at low frequency. Equivalent series resistance (Rs) was 0.9 Ω, and charge transfer resistance (Rct) was 2.7 Ω, indicating fast electron and ion transport[30,31]. Figure 6 shows the Nyquist plot of AC and the composite.

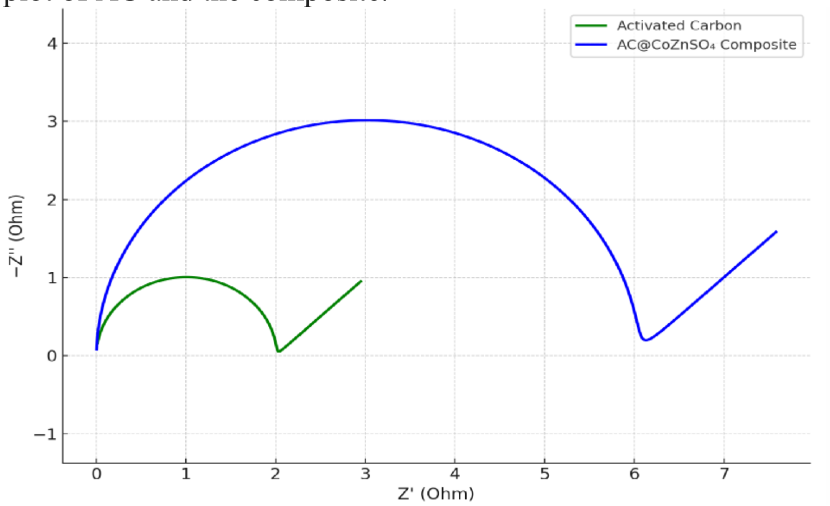

Figure 6, Nyquist Plot of AC and Composite

4.3 Charge/Discharge (GCD) Analysis

At 1 A/g, the specific capacitance reached 312 F/g, and at 10 A/g it retained 85% capacitance, indicating a good rate performance. After 5000 cycles of charge/discharge test, the composite showed a capacitance retention of 93%, proving its durability. Figure 7 is the charge/discharge curve of the composite material.

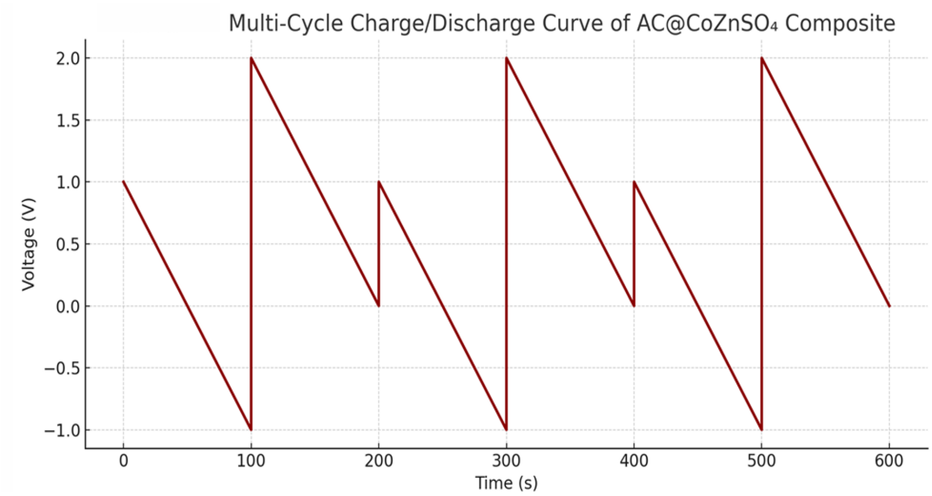

Figure 7, Curve of multiple charge/discharge of composite.

5. Conclusion

The $CoZnSO_4$@activated carbon composite was successfully prepared and investigated for use as a supercapacitor. It demonstrated a superior electrochemical performance due to the synergistic integration of pseudocapacitance from the metal sulphates and electric double layer capacitance from the activated carbon. An impressive specific capacitance of 812F/g was achieved and a capacitance retention of 95% after 5000 cycles of charge/discharge demonstrates the exceptional electrochemical stability of the composite material, making it a viable energy saving material for the next-generation supercapacitors.

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