

Research Article

RGO/ZnCo₂O₄ Composites as an Electrode Material for High-Performance Supercapacitor Application

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Abstract: Recently, composite material-based supercapacitors have attracted a lot of attention due to their enhanced performance. In this work, we present a facile synthesis of RGO/ZnCo₂O₄ direct solution-based composites through a hydrothermal route anchored on nickel foam. ZnCo₂O₄ nanospheres wrapped under ribbon-like RGO nanosheets combine the synergistic properties of both in the form of hybrid electrode material. As a result, the RGO/ZnCo₂O₄ electrode exhibits a specific capacitance of 755.38 F/g at a scan rate of 5 mV/s with improved cyclic stability up to 2000 cycles. In addition to this, the hybrid electrode material also shows a good value for energy density and power density as 10.75 Wh/kg and 1500 W/kg at a current density of 1 A/g with 93.47% efficiency. This study thus signifies that the synergistic effect of both the electrodes in combination as a hybrid gives a better performance than the individual ones.

Keywords: reduced graphene oxide; ZnCo₂O₄; composite; electrochemical; supercapacitor

1. Introduction

There is a major energy crisis going out in all areas of society. It's the need of the hour to preserve energy as well as search for reliable and eco-friendly energy production and storage technologies¹. Electrochemical energy storage is one of the most researched options within these decades. One of the major reasons which captures the attention towards electrochemical energy production is that it is among the environmentally friendly and sustainable forms of energy storage techniques². Supercapacitors are a class of energy storage devices that have been explored for their improved and exceptional electrochemical properties as compared to other devices³. Among various parameters governing the performance of a supercapacitor, electrode material is one of the most crucial parameters to be optimized. Currently, a good amount of literature is available on studies of supercapacitive properties of binary & ternary metal oxides, polymers, sulphides, and carbon & its derivatives as electrode material for supercapacitor applications^{4,5}. Metal oxides generally exhibit multiple oxidation states along with fast redox activity and good rate capability but still have some drawbacks such as agglomeration of nanosized particles, poor rate capability, and low capacitance during the surface redox reaction and ion diffusion⁶. To improve the performance of transition metal oxides they can be combined with carbon-based materials such as graphene and its derivatives^{1,7}. These carbon-based derivatives provide a conducting backbone along with improved energy storage due to their exceptional. physical and chemical properties⁸.

Given the above discussion, in the present work, we are reporting the results obtained on a combination of RGO with ZnCo_2O_4 deposited on nickel foam via the hydrothermal route as a direct solution-based composite^{1,9}. Hydrothermal method is among one of the facile, low-cost, eco-friendly, cost-effective and conventional methods of synthesis. In addition, it also provides cleaner and more efficient products with less use of catalysts and precursors. The integrated electrode material synthesized via the hydrothermal route shows improved electrochemical performance as compared to their counterparts. This study is expected to provide new opportunities for better asymmetric electrode materials for their application in energy storage devices^{10,11}. Table 1 presents a comparative literature survey of the presented work.

Table 1. Literature survey & comparative analysis of presented results.

Sr.No	Method Used	Substrate	Morphology	Electrolyte	Specific Capacitance	Ref.
1	Hydrothermal	Nickel foil	Nanorods	2M KOH	704.2 F/g @ 0.75 A/g	7
2	Hydrothermal	Nickel foam	Nanowires arrays	3M KOH	1256 F/g @ 3 A/g	12
3	Hydrothermal	Nickel foam	Nanosheets	2M KOH	860 F/g @ 20 A/g	4
4	Hydrothermal	Nickel foam	Spherical	3M KOH	546 F/g @ 2 mA/g	13
5	Microwave-assisted	Glassy carbon electrode	Nanosheets	0.1M KOH	562 F/g @ 20 mV	14
6	Hydrothermal	Nickel plate	Nanoflakes	2M KOH	599 F/g @ 1 A/g	1
7	Hydrothermal	Nickel foam	Nanospheres	3M KOH	755.38 F/g @ 5 mV/s	Present work

2. Experimental Procedure

All the reagents used for the experiment are of AR grade. Distilled water was used throughout the process. Nickel foam used as a substrate was purchased from MTI Korea. Double Distilled Water was used as a solvent throughout the process. Before deposition, nickel foam substrate of dimension 2 cm × 4 cm was cleaned subsequently through ultrasonication in 1M dil. HCl, ethanol, acetone, and distilled water for 15 min each and dried overnight at 60 °C.

Initially, graphene oxide was synthesized using a modified Hummer method. For the synthesis of direct solution-based nanocomposites, a graphite oxide suspension was prepared by exfoliating 0.2 mg/mL graphite oxide powder as obtained from the method in the above-mentioned process in 80 mL distilled water for 2 h to form graphene oxide. To this solution then respective metal oxide nitrates were added in a 1:2 ratio along with urea and ammonium fluoride. The complete solution was then stirred for 30 min and then transferred to a Teflon-lined 100 mL autoclave along with the clean piece of nickel foam for 180 °C /6 h. The autoclave was allowed to cool at room temperature and nickel foam substrate with a pinkish-grey color material was washed thoroughly and allowed to cool at 60 °C for 12 h followed by calcination at 300 °C/2 h. The mass deposited on the nickel foam was weighed to be about 1 mg. This nickel foam deposited with a greyish-pink layer is a composite electrode material of RGO/ ZnCo_2O_4 .

3. Results and Discussion

The morphological properties were examined using the JEOL JSM IT-300 Scanning Electron Microscope (SEM) at an accelerating voltage of 20 kV.

The electrochemical/supercapacitive properties of the electrode materials such as Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) were studied using CHI (660C) electrochemical workstation in a three-electrode system in 3M KOH as an electrolyte.

3.1 Structural Characterization of RGO- ZnCo_2O_4 Composite Electrode

The morphology of the electrode material has been greatly influenced by the combination of the two electrode materials. The morphologies have been presented at three different scales 100 μm, 2 μm, and 100 nm for all the electrode

materials. Figure 1 illustrates an SEM micrograph of the composite structure, it can be observed from the micrograph that branches of nickel foam are completely covered with the electrode material¹⁵. ZnCo₂O₄ nanospheres are wrapped around ribbon-like RGO nanosheets, forming a close-spaced porous nanoarchitecture that facilitates the transportation of ions¹⁶. Structural studies also confirm the proper formation of composites as both the individual morphologies are intertwined into each other resulting in a synergistic effect.

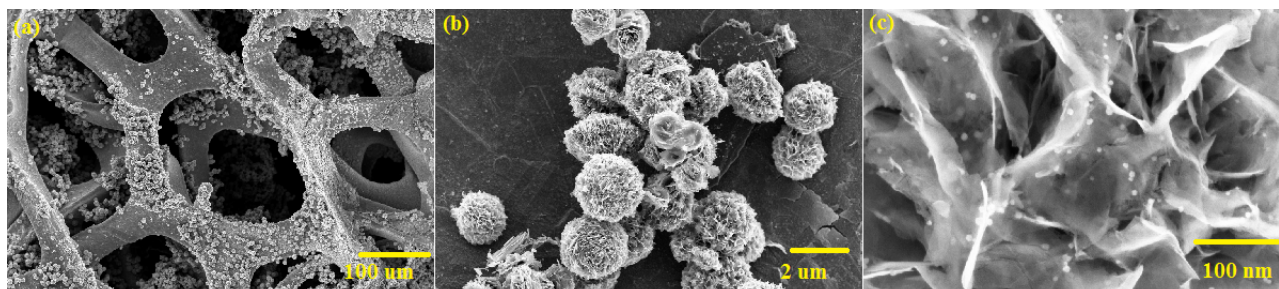


Figure 1. (a–c) SEM micrographs of RGO-ZnCo₂O₄ composites at three different magnifications.

3.2 Electrochemical Characterization of RGO-ZnCo₂O₄ Composite Electrode

The electrochemical properties of all the electrodes were studied and compared using a CHI (660C) electrochemical workstation. The electrolyte used here was 3M KOH in a three-electrode system with a calomel electrode as a reference electrode, graphite as a counter electrode, and nickel foam deposited with active material as a working electrode. The mass deposition of active material is 0.1 mg. A brief analysis of all the electrochemical parameters has been added in Table 2.

The electrochemical charge storage behaviour of the electrode material as obtained from CV analysis is represented in Figure 2. The analysis is carried out in the potential range of 0 V to 0.4 V at the scan rates ranging from 5 mV to 100 mV. Being a direct composite with a combination of RGO and metal oxide, RGO shows more dominance of EDLC-type behaviour as compared to pseudocapacitive, and hence the curves are broad and rectangular^{17–19}. Also, it can be observed that redox peaks that were visible at lower scan rates slowly vanish with the increase in scan rate as graphene sheets start interacting with ZnCo₂O₄, and the overall behaviour is non-faradic^{20,21}. The specific capacitance is obtained as 755.38 F/g at a scan rate of 5 mV/s.

Table 2. Comparative analysis of electrochemical parameters for RGO-ZnCo₂O₄ composite Vs. RGO/ZnCo₂O₄.

Electrode Material	Method	Morphology	Specific Capacitance (F/g)	Energy Density (Wh/kg)	Power Density (kW/kg)	Coulombic Efficiency (%)	Equivalent Series Resistance (Ω)	Rate Capability (%)
RGO	Hydrothermal	Microspheres	578.56	194.24	1.066	90	0.76	95
ZnCo ₂ O ₄	Hydrothermal	Microspheres	702.40	78.85	2.85	96.50	3.69	89.56
(ZnCo ₂ O ₄ + RGO)	Hydrothermal	Nanospheres wrapped in ribbon-like sheets	755.38	10.75	1500	93.47	2.1	85

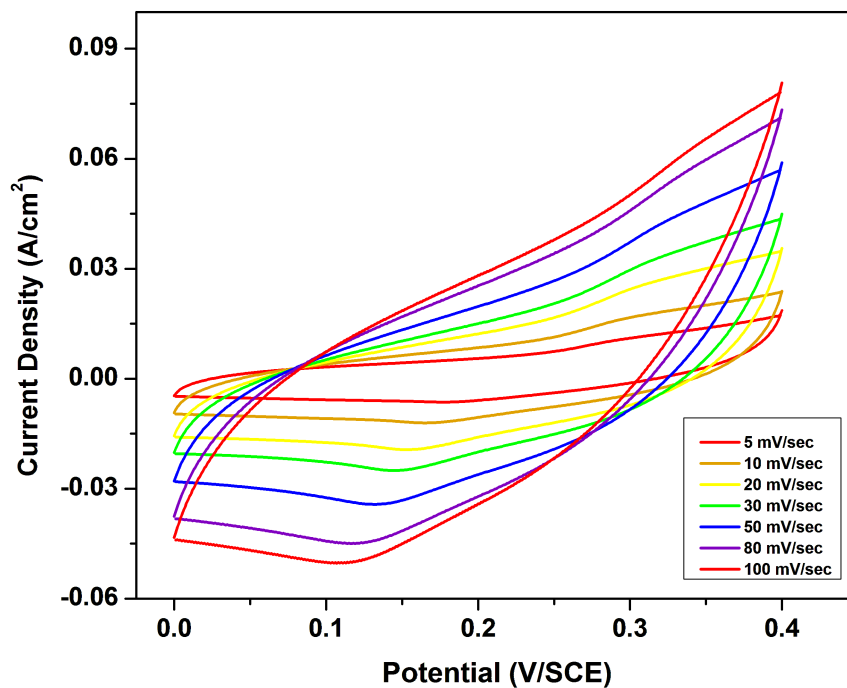


Figure 2. CV profile of RGO-ZnCo₂O₄ composite electrode material.

The specific capacitance of an electrode material decreases with an increase in scan rate. Figure 3 displays the decreasing trend of capacitance, this happens because of the variation in the interaction of electrolyte from the surface to the matrix of the active electrode material^{21,22}. The minimum value of specific capacitance is obtained to be in the range of 250 F/g to 200 F/g at a scan rate of 100 mV/s.

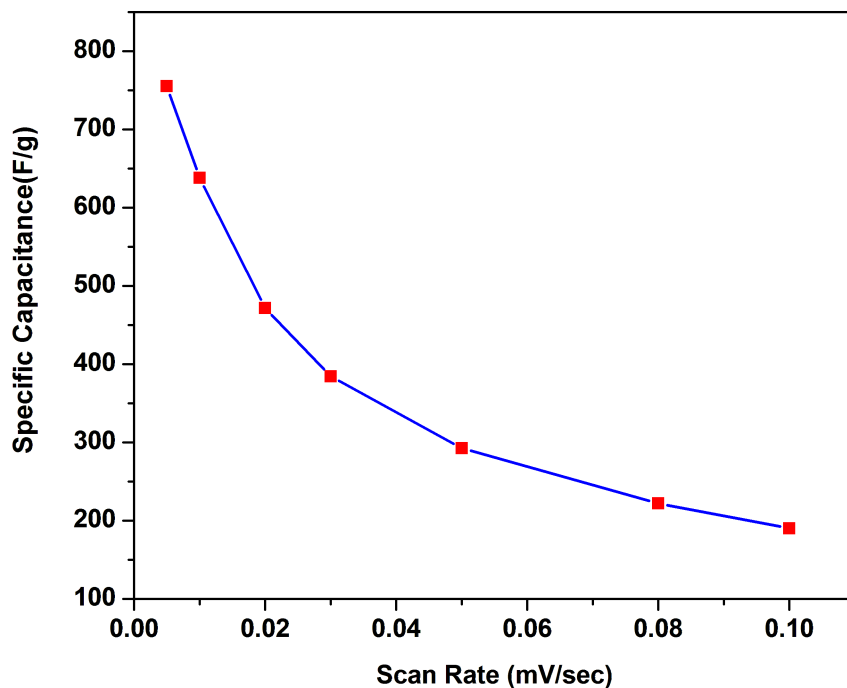


Figure 3. Specific capacitance vs. Scan rate profile for RGO-ZnCo₂O₄ composite electrode material.

The electrochemical ability of these electrodes was further characterized by Galvanostatic charge-discharge tests. Figure 4 illustrates the GCD curves ranging from 2 mA/cm² to 8 mA/cm² within the potential range 0–0.3 V. It can be observed that composites show a plateau-like behaviour which indicates non-faradic nature with easy desorption and adsorption of ions^{23,24}. The electrochemical behaviour is more shifted towards RGO. The area under the curve decreases as the current density increases. With higher current density the curve shifts towards higher voltages due to the polarization effect^{25,26}. The specific capacitance, energy density, and power density are obtained to be 650 F/g, 10.75 Wh/kg, and 1500 kW/kg respectively.

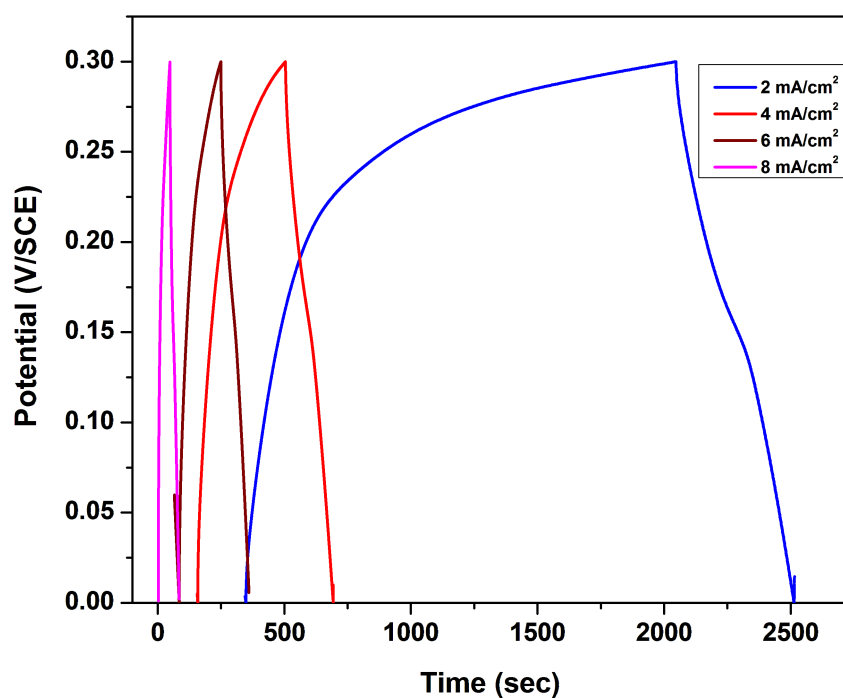


Figure 4. GCD curves of RGO-ZnCo₂O₄ composite electrode material.

Electrochemical impedance spectroscopy analysis was conducted for the electrodes (Figure 5). Nyquist plot shows the plot for various electrodes in the frequency range 0.1 Hz to 100 KHz. RGO-ZnCo₂O₄ composites show a small kink at the higher frequency region which is not a proper semicircle, a kind-off pseudo semicircle followed by a straight line²⁷. The analysis demonstrates that electrodes have low resistance and offer better conductivity. The plots were fitted using Z-view software to obtain an equivalent circuit diagram and calculate all the associated parameters such as ESR and R_s²⁸. The values of ESR are obtained as 2.1 Ω. The lower values of electrochemical resistance for these composite electrodes recommend fast ion transport within the system, which adds to its enhanced capacitance and electrochemical kinetics leading to its low electrochemical resistance^{7,29}.

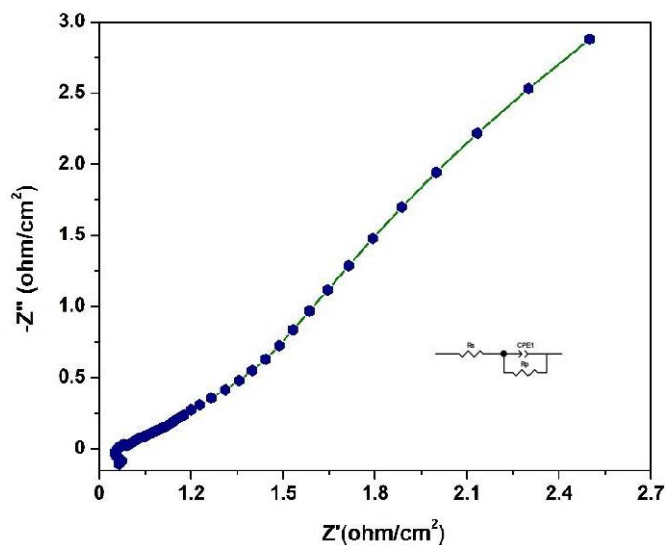


Figure 5. Nyquist plot for RGO-ZnCo₂O₄ composite electrode material.

Cyclic Stability tests were conducted to analyse the cyclic ability of these composite electrodes up to 2000 cycles. The capacitance goes down slowly due to prolonged charging-discharging; Figure 6 illustrates the plot of specific capacitance vs. no. of cycles, the values for capacitance retention rate are obtained as 85%. The Constant phase element (CPE) was evaluated by curve fitting the Nyquist plot in Z view, and the values of both ESR and CPE for the HZCo-NF electrode are obtained as $R_s = 2.1 \Omega$ and $CPE = 0.62$.

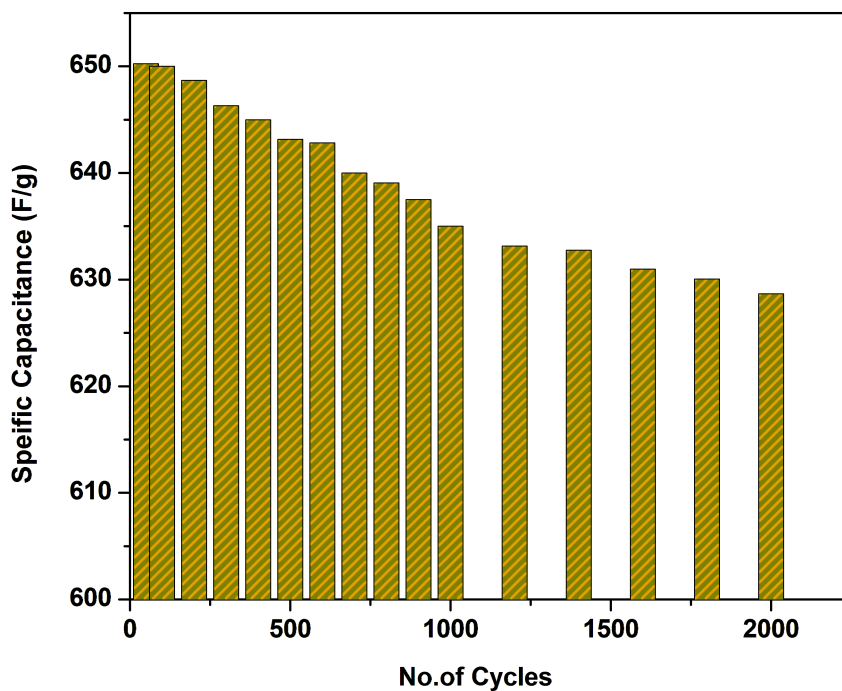


Figure 6. Cyclic stability plot up to 2000 cycles for RGO-ZnCo₂O₄ composite electrode material.

4. Conclusions

To conclude with, it can be said that RGO-ZnCo₂O₄ composite electrode material exhibits an improved electrochemical performance. Studies on surface morphology confirm the formation of composites as two distinct nanostructures are observed to be intertwined into one frame, RGO ribbon-like nanosheets have wrapped nanospheres of ZnCo₂O₄ resulting in concrete and strong nanoarchitecture. The electrochemical analysis also indicates that the synergistic effect of the combination has led to a higher specific capacitance of 755.38 F/g at a scan rate of 5 mV. Galvanostatic charge-discharge studies suggest that the electrode material is non-faradic with RGO dominance over ZnCo₂O₄. Energy density and power density are evaluated to be 10.75 Wh/kg and 1500 kW/kg with a coulombic efficiency of 93.47%. Also, the impedance spectroscopy results indicate a low internal resistance of 2.1 Ω with a higher value of capacitance. Cyclic stability tests up to 2000 cycles illustrate the rate capability of the electrode material in terms of charge-discharge cycles it can sustain without degradation of performance, which was obtained to be 85%. Overall, evaluation of this composite electrode material suggests that it has immense potential to be used as an electrode material for supercapacitive devices and exhibit better and improved performance as compared to their counterparts.

Author Contributions

Nidhi Tiwari: Experimentation, Conceptualization, Data collection and data analysis, Methodology, Formal analysis, Investigation, Writing-original draft. R.K. Kamat: Suggestions for improvement, Supervision and Editing Shrinivas Kulkarni: Supervision, Editing.

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Conflict of Interest

On the behalf of all authors, I declare no known conflict of interest about the present manuscript. The funding or financial support organization name as well as funding number have been mentioned and acknowledged in the manuscript. We confirm that the manuscript has been read and approved for submission by all named authors.

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