Hydrothermally synthesized highly stable binary manganese magnesium sulfide (MnMgS) composite with carbon nanotubes for high-performance supercapattery applications

M. A. Sadi ^{a,*}, A. Mahmood ^b, W. Al-Masry ^b, C. W. Dunnill ^c, N. Mahmood ^d ^a Department of Electrical Engineering, Muhammad Nawaz Sharif University of Engineering and Technology, Multan Pakistan

^b Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia

^c Energy Safety Institute (ESRI), Swansea University Bay Campus, Swansea, SA1 8EN, UK

^d Department of Physics, The University of Lahore, Lahore, 54000, Pakistan

The device which combines the outcomes supercapacitor (SC) and battery is known as supercapattery. Due to their high conductivity, sensitivity, and storage capacity, carbon nanotubes have drawn attention in energy storage (EES) applications. To achieve high-performance supercapattery, this study used an electrode based on carbon nanotubes (CNTs) and manganese magnesium sulfide (MnMgS). It showed 963 C/g specific capacity which is significantly greater than the reference sample's value of 1 A/g. The supercapattery is engineered using the CNT-doped MnMgS electrode (MnMgS/CNT//AC), which has a specific capacity (C_s) of 268 Cg⁻¹ at 1 Ag⁻¹ current density. A significantly higher power and energy densities of 2230 WKg⁻¹ and 35.6 Wh/Kg than the previously published graphs is proposed. Moreover, electrochemical impedance spectroscopy (EIS) and Brunauer-Emmett-Teller (BET) tests and verify an increase in surface area and conductivity. The device goes through 5000 GCD cycles as part of a reliability test to investigate stability, and it is found that 95% of the claimed capacity is maintained. Our research offers a great foundation for creating high-performing energy storage devices similar to supercapattery.

(Received September 3, 2024; Accepted December 2, 2024)

Keywords: Mn-based Suphide; Doping; Capacitance; Battery; super-capacitor; Energy Storage devices

1. Introduction

The growing need for energy, a lack of fossil fuels, and the changing climate have all raised attention in energy storage systems. Accordingly, effective as well as high-performing energy harvesting systems that possess special qualities like stability, high power (P) energy densities (E), and sustainability have become essential for current technology [1, 2]. Supercapacitors and batteries are the two most significant options for storage of energy. The batteries exhibit low P and increased E with low stability. Conversely, the supercapacitors feature low energy density and power higher density power.

Three classes of supercapacitors are distinguished by the way in which they store charge. While the pseudocapacitor (PCs) under oxidation-reduction reactions stores charge by transferring electrons from the electrode and electrolyte, the electric double layer capacitors (EDLCs), stores charge at the electrolyte / electrode surface. With more energy and power density as compared to the other two, hybrid supercapacitors combine the advantages of both EDLCs and PCs. The researcher is inspired to develop a novel type of energy harvesting device by the shortcomings of the two energy storage systems [3, 4].

The energy density (E) and Power density (P), two fundamental characteristics of both battery and SC, are combined in the newly developed supercapattery energy harvesting device. The

^{*} Corresponding author: m.abdullahsadi92@gmail.com https://doi.org/10.15251/CL.2024.2112.965

qualities of a supercapattery device are measured using two distinct electrodes: a capacitor and a battery grade. [5-9]. In fueled batteries, metal hydroxides, oxides, phosphates, sulfides, and phosphides have often been utilized as anode components.[10-12]. Their poor power charges limit their range of motion, even as the batteries' remarkable energy thickness makes them a great match and a doorway to more efficient energy use. Moreover, the efficiency and implementation of their cycle security mechanisms are compromised by the quick Faradic reaction attributed to their charge limit structures.[13-17]. Supercapacitors integrating EDLCs and PCs regarding the distribution of charge storage science (I). The EDLCs include carbon nanotubes as well as carbon-improved materials for the design, such as graphene, graphite, incited carbon, and carbon black. The electric double layer capacitor's charge-storing pattern consists of the actual desorption and adsorption of electrolyte particles, whereas the energy-storing mechanism of pseudocapacitors is defined by different redox reactions inside a limited potential zone. [5, 18, 19]. Together, these half-breed energy-storing devices have outstanding cyclic security potential, more noteworthy superiority thickness, and high energy densities. The cathode material that is used determines the electrochemical appearance that an energy-storing device conveys. Better electrochemical execution is conveyed by the material's increased electrochemically active locations, solid precious stone design, and high porosity [20, 21].

Because of their higher capacitance and respectable electrochemical stability, MnS and Ag₂S, two different metal phosphates along with sulfides, be viable options for electrode materials in energy harvesting systems.[22-25]. For example, using a solvothermal method, Bhushan *et al.* synthesized multiple dimensions nanostructures of MnS that confirmed an energy density of 22.75 Wh/Kg and a specific capacity of 159.12 Cg⁻¹ [23]. After 1000 cycles, it turned out that the capacitance retention of the MnS-based electrode was 72.27% [26].

The energy storage devices' high specific capacity, increased power and energy density (E) with improved cyclic-stability were derived from the doping-enhanced nature of the materials. To improve these qualities, more than one unique nanomaterial can be combined to make a nanocomposite that is made by combining various metal sulfides using nanostructured metal sulfides. [22, 27, 28]. Additionally, they put together a supercapacitor with a ZnS/MgS composite. The device demonstrated an astounding 91 Wh k/g energy as well as 7.78 kW k/g power density, along with an exceptional 99% cyclic stability after 5000 charging/discharging cycles.

Thus, the particular capacitance of an electrode can be increased by doping with carbon nanotubes (CNTs). Furthermore, due to their superior flexibility, chemical stability, and reduced cost, carbon nanotubes (CNTs) hold great promise for energy storage uses [29, 30]. The charge accumulation in the area accessible for the electrode-electrolyte interactions has a major impact on the charge accumulation in EDLC. Greater surface area results in more active sites that are available for interacting with electrolyte ions, which raises capacitance. A good electrode material and astounding energy storing devices are needed to encounter the demands of modern world on energy [31].

Currently, hydrothermal technique was utilized to synthesize the composite of magnesium sulfide, manganese sulfide, and manganese magnesium sulfide. In order to improve the material's electrochemical qualities, CNTs were also added (MnMgS). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are employed to examine the materials' morphology, content, and structural characteristics. The surface area and conductivity of the active substance doped with CNTs are improved. Measurements are made using Brunauer-Emmett-Teller (BET) and electrochemical impedance spectroscopy (EIS). The electrochemical properties are estimated using 2 and 3-electrode combinations. In addition, we have built a supercapattery and measured its Cs according to power density as well as energy density. It is tested for stability for a maximum of 5000 cycles as well as its charging/discharging times are recorded. Doping sulfide-based materials with carbon nanotubes (CNTs) create novel pathways for proposing high-performance energy storage devices.

2. Experimental section

2.1. Materials

We purchased activated carbon, carbon nanotubes, and KOH pellets Moreover carbon black, hydrochloric acid (HCl), magnesium chloride (MgCl₂), N-methyl 2-pyrrolidone (NMP), N-polyvinylidene-fluoride (PVDF), manganese nitrate (Mn(NO₃)₂) and sodium sulfide hydrate (Na₂S.nH₂O) from Sigma Aldrich. The Ni-foam was acquired through Urich Tech Malaysia. Without any purification, every chemical used was bought commercially. Purchased from ALS Co. LTD. in Japan, the platinum (Pt) wire and Hg/HgO were utilized as reference and counter electrodes, correspondingly.

2.2. Synthesis of manganese sulfide, manganese sulfide, and manganese sulfide nanocomposites

We synthesized the material using the easy hydrothermal process since it was more suited and convenient than other ways. To begin the process of making manganese sulfide, a 0.6 M primary solution consisting with manganese nitrate ($MnS(NO_3)_2$) and sodium sulfide hydrate ($Na_2S \cdot nH_2O$) was made. In order to make the solution, 3.5 g of $MnS(NO_3)_2$, was dissolved in DI water (30 ml).

By combining 1.3915 g of Na₂S·nH₂O in DI water (30 ml), an additional solution was produced. To produce uniform solutions, the two solutions were put on the magnetic stirrer individually and constantly swirled for 45 minutes. Subsequently, the $MnS(NO_3)_2$ solution was constantly stirred though the Na₂S·nH₂O and added drop by drop. The obtained solution was further stirred for an hour after the Na₂S·nH₂O solution had completely mixed with the Mn (NO₃)₂ solution. The final product was then placed in a teflon, sealed inside an autoclave, then calcinated at 120 °C for eight hours. The material was then gradually cooled down at room temperature. To eliminate the impurities while preserving the pH level, then the final solution was thoroughly cleaned using ethanol and enough of deionized water. For three to five hours, the yield mixture dried in an oven set to 50 °C.

Similarly, a 0.6 M solution of $Na_2S \cdot nH_2O$ and magnesium (V) chloride (MgCl₂) was used to produce magnesium sulfide. 1.404 g of $Na_2S \cdot nH_2O$ and 4.86 g of MgCl₂ were individually dissolved in DI water and agitated for a maximum of two hours. The $Na_2S \cdot nH_2O$ solution was continuously stirred while the MgCl₅-based solution was added dropwise. The uniform solution was heated to 140 °C for eight hours in the oven. After one more wash, it was dried for three to five hours at 60 degrees Celsius. Three precursor mixtures were used to create a composite material: a 0.6 M solution of $Mn(NO_3)_2$ and (MgCl₂), combined with a 0.6 M solution of Na_2SH_2O in deionized water (30 ml).

After mixing 4.84 of MgCl₂, 3.512 g of Mn(NO₃)₂, and 1.3901 g of Na₂S·nH₂O to 30 ml of DIW individually and mixing to make a uniform mixture, the required solutions were obtained. After combining these solutions, the oven was set to 140 °C for eight hours. After then, the material was progressively cooled to ambient temperature as well as washed many times with DIW and ethanol to get remove of all leftover impurities. After that, the material was dried for three to five hours at 60 °C placed in a petri dish. Physical mixing of CNTs in MnMgS helped to produce the MnMgS/CNTs composite.

3. Results and discussion

To verify that the materials are crystalline, XRD is used. Figure 1 (a) displays the X-ray diffraction peaks of MnMgS and MnMgS doped with CNTs. The MnS contribution is represented by the XRD peaks detected at $2\theta = 28.3^{\circ}$, 31.5° , 38.3° , 50.4° , 60.8° , and 72.6° , which correspond to (200), (111), (200), (220), (222), and (400). On the other hand, the magnesium sulfide MgS is responsible for the remaining XRD peaks at $2\theta = 32.1^{\circ}$, 51.6° , and 74.3° , which correspond to (111), (220), and (400). The production of MnMgS is confirmed by these XRD peaks in composite situations. The peak in the CNT-doped sample was observed at $2\theta = 27.8^{\circ}$, which is equivalent to the MnMgS/CNT nanocomposite's (200). With SEM, the surface morphology of MnMgS/CNTs is analyzed. The SEM image of large pour size MnMgS nanostructures is displayed in Figure 1(b).

The MnMgS/CNT composite structure, which has a flower-like form and improves charge storage capacity, is shown in Figure 1(b).



Fig. 1 (a) XRD of MnMgS and MnMgS/CNT composite. (b) SEM image of MnMgS/CNT composite.

3.1. Measurement of CNT-doped MnMgS electrodes electrochemically

The electrochemical properties of MnMgS and CNT-doped MnMgS are investigated through the use of a potentiostat, galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV). The electrodes' electrochemical performance is first evaluated using a three-electrode arrangement; the same investigation is then conducted using a two-electrode arrangement. All three samples' CVs were evaluated at multiple scan rates ranging from 3 mV/s to 50 mV/s within a potential window of 0 - 0.7 V. The CV graphs for both MnMgS as well as MnMgS/CNT are shown in Figure 2(a–b). The redox peaks of graph shapes make it clear that MnMgS/CNT exhibit Faradaic performance, which is indicative of battery-quality materials. While the electrolyte's OH-ions react with the working electrode, the faradaic reaction happens. When the scan rate rises, oxidation/reduction peaks display increasing current values. The provided equation was used to calculate each electrode's specific capacity.

$$Qs = \frac{1}{mv} \int_{V_i}^{V_f} I \times V dV$$
(1)

The variable Q_s in the calculation given stands for specific capacity, $\int_{V_i}^{V_f} I \times V dV$ represents the CV curve's area, whereas the m stands for active mass and v stands for and scan rate, accordingly. This formula is divided by the 0.7 V potential range "V" to find the specific capacity (Cs).

For MnMgS and MnMgS/CNT, the specific capacities calculated from equation (1) are 785 C/g and 1105 C/g, correspondingly. The combined synergistic impact of both MgS and MnS resulted in a rise in specific capacity when MgS and MnS were joined to produce the MnMgS sample, which exhibited a specific capacity of via CV. The oxidation peaks demonstrated an extra increase after the MnMgS composite was doped with CNT. [32, 33].

The material MnMgS/CNT dominates the sample MnMgS, rendering certain beneficial surface regions unavailable for charge storage. One interesting finding from Figure 2(a-b) is that, although the MnMgS exhibits greater peaks than the sample MnMgS, the doped material's oxidation peaks move to a higher potential, demonstrating the poor rate capacity of CNT. Nonetheless, compared to other samples, the doped material's broad surface exhibits a greater current response. The CV performance of all the samples is compared in Figure 2(c), which indicates that the MnMgS sample worked better than others because of its larger surface area and high specific capacities were 785 C/g and 1105 C/g, accordingly.

Figure 3 shows the obtained results from GCD's evaluation of the electrodes at current density ranges of 1 A/g to 2.6 A/g in potential ranges of 0 to 0.65 V. The material showed battery-

graded, as demonstrated through the non-linear behavior of galvanostatic charging/discharging shown in Figure 3.



Fig. 2. Cyclic voltammetry for (a) MnMgS (b) MnMgS/CNT (c) The cyclic voltammetry of MnMgS and MnMgS/CNT at 30 mV/s. (d) Specific capacity of MnMgS and MnMgS/CNT via CV.



Fig. 3. (a) Representation of galvanostatic charging/discharging for MnMgS. (b) Graph show GCD for doped material MnMgS/CNT. (c) GCD comparison of MnMgS and MnMgS/CNT at 1 A/g. (d) Specific capacity of MnMgS and MnMgS/CNT via GCD.

The graphs demonstrate that the discharge duration as well as, consequently, increasing current density lowers the specific capacity (C_s). The limited time allowed for the electrolyte ions electrode material interaction is what causes the decreased discharge time. The -ve relationship between current density and C_s is demonstrated by the fact that discharge time rises with lower current densities. Furthermore, the charge carrier interaction at higher current densities as a result of increased excitement leading to internal resistance is another cause of the drop-in discharge time. The below equation is used to determine the C_s of GCD electrodes.

$$Q_s = \frac{I \times t}{m}$$
(2)

where the current and discharge time are denoted by "I" and "t," respectively.

The MnMgS showed 601 C/g and MnMgS/CNT 963 Cg⁻¹ at 1 Åg⁻¹. Having the larger surface for electrode-electrolyte interaction and increased conductivity provided by CNT is responsible for this extraordinary increase in specific capacity [31]. The MnMgS/CNT has a higher specific capacity due to its faster ion diffusion path for electrolyte ion interaction with the material of the electrode [34, 35].

The BET was also used to measure its pore size, surface area, as well as pore volume. BET computes surface area by measuring the adsorption isotherm. Although this technique works best with materials that have isotherm curves, it is frequently applied to a variety of materials [36]. The BET isotherm for the MnMgS/CNT is shown in Figure 4(a). The MnMgS/CNT has a surface area of 19.92 m^2/g and a pore volume of 0.039 cm³/g. With a pore size of 16.62 nm, ions appear to move swiftly. These results suggest that the high surface area and large pore size of CNT-doped MnMgS can store an enormous quantity of charge rapidly. With cycle stability, the improved surface area improved the C_s. Greater surface area for higher charge accumulations, and faster ion movement is facilitated by a bigger volume of holes. The EIS measurement is displayed in Figure 4(b). The lowest impedance of the MnMgS/CNT makes it more advantageous for supercapattery design. Because the components' properties resemble that of a battery, the EIS form in this instance cannot be quite vertical. The doping of CNTs has led to this increased conductivity.



Fig. 4. (a) Nitrogen Adsorption-desorption isotherm of MnMgS and MnMgS/CNT. (b) EIS of MnMgS and MnMgS/CNT.

A supercapattery device is made using the sample MnMgS/CNT as the +ve electrode along with CB as the -ve electrode in order to do additional research on the performance of the sample. The best sample was used in conjunction using activated carbon to generate the actual device for use in real-world applications. Following the assembly of a two-electrode system, Figure 5 (a–c) illustrates the evaluation of GCD and CV performance at different scan speeds and current densities.



Fig. 5. (a) Tunable cyclic voltammetry of asymmetric device (3-50 mVs⁻¹). (c) Galvanostatic charging/discharging of asymmetric device. (c) The specific capacity vs scan rate for (MnMgS/CNT)//AC.
 (d) Specific capacity against different current densities for (MnMgS/CNT)//AC.

To create the actual device, activated carbon was used as cathode and the binary composite material sample MnMgS/CNT as the positive electrode. This device was electrochemically characterized in an electrolyte solution containing 1 M KOH. Equation (3) below indicates in clearly that the energy density depends on the potential range as well as Cs of the object.

$$E = \frac{1}{2}CV^2 \tag{3}$$

where "V" stands for a prospective window and "C" for specified capacity. Consequently, the device needs to operate at a wider potential window to generate high energy density[37]. In a threeelectrodes assembly, the CV peaks for activated carbon (AC) and sample MnMgS/CNT are computed independently at 3 mV/s throughout potential ranges of -1 to 0 V and 0 to 0.6 V, respectively. The CV graph for the two electrodes, the sample MnMgS/CNT electrodes and activated carbon were done at a range of different scan rates, from 3 to 50 mVs⁻¹, in a 0 to 1.6 V potential range. For higher potentials, presence of redox-peaks along with non-rectangular shape of the CV curves suggest a non-capacitive and battery-graded nature. At lower potentials, the CV curves indicate capacitive behavior. The device's strong rate capability is explained by the form holding of CV at higher scan rates. Additionally, GCD was used to study the device's behavior in the 0 to 1.6 V potential range at current densities ranging 1 to 2.4 Ag⁻¹. The possibility of supercapattery development is increased by these findings. The remarkable stability of the device and storage capacity are demonstrated by the well-maintained form of GCD peak and its steady behavior at rising current density levels. The maximum Cs of 354 C/g for the device sample MnMgS/CNT/AC was obtained by CV @ 3 mVs⁻¹, whereas a maximum capacity of 268 Cg⁻¹ was determined using GCD calculation.

The supercapattery tested 5000 galvanostatic charging-discharging cycles at 5.4 Ag^{-1} (a constant current density) to investigate its endurance. The charging/discharging time calculated over 5000 cycles is shown in Figure 6(a). The capacity retention graph, which is displayed in Figure 6(b), was determined to be 88% after 5000 cycles. Figure 6(b) also displays the Coulombic efficiency (CE), which was determined to be 95% after 5000 GCD cycles with the above equation. The estimated b-values of the MnMgS/CNT//AC, that fall in the supercapattery b-value range, are shown in Figure 6(c). The b-value corroborate that formation of supercapattery has been done. For the battery, b-values are 0 to 0.5, the supercapattery 0.5 to 0.8, and the supercapacitor range from 0.8 to 1.0 as shown in Figure 6(d) [38]. These studies demonstrate that both a faradic and a capacitive mechanism contribute to the device's capacity for charge storage. The following formulas can be used to find the power and energy densities.

$$P(W kg^{-1}) = \frac{E \times 3600}{\Delta t}$$
(4)

$$E\left(Wh\,kg^{-1}\right) = \frac{Q_S \times \Delta V}{2 \times 3.6} \tag{5}$$



Fig. 6. (a) Cyclic stability up to 5000 cycles. (b) Specific capacity retention and columbic efficiency and after 5000 charging/discharging cycles. (c) Linear fitting for (MnMgS/CNT)//AC asymmetric device (d) Comparing with other works in terms of power and energy densities.

Compound Name	Energy Density (WhKg ⁻¹)	Power Density (Wkg ⁻¹)	Specific Capacity (Cg ⁻¹)	Ref.
Zinc sulfide/Manganese sulfide	91	7.78		[41]
Cobalt-Metal organic framework/polyaniline	23.2	1600	162.5	[42]
cobalt sulfide nanotubes	27.7	500		[43]
NiCo ₂ Se ₄ (Nanotubes)	25	490		[44]
Cu ₂ P ₂ O ₇ (Nanoflakes)	11.54	7060		[45]
MoS	5.42	128		[46]
MnMgS	35.6	2230	1105	This Work

Table 1. Highlights of the comparison of power density and energy density to previous studies.

The energy density (E), as shown in Figure 6(d), was determined to be 39.4 WhKg^{-1} at a power density of 2400 W k/g. This value is higher compared to earlier published values of un-doped sulfides, suggesting that CNT-doped MnMgS performs better in energy storage device uses [22, 39, 40]. The comparison of this work's energy and power density with previous works is shown in Figure 6(d). Because of improved results of MnMgS/CNT sample, it has been established that CNT doping improved the binary metal sulfide's performance, offering MnMgS/CNT a viable option for supercapattery applications.

4. Conclusion

In this study, MnS, MgS, and MnMgS were synthesized using the hydrothermal technique. Following the doping of the binary composite MnMgS with CNT, an electrochemical performance comparison is carried out for several samples. Because of the CNT's large surface area, which promotes stronger and a shorter ion diffusion path, the MnMgS/CNT showed better capacity. The specific capacity of 268 Cg⁻¹ at 1 Ag⁻¹ and 95% cyclic stability were achieved in a supercapattery device after 5000 GCD cycles. The device was found to have a power density of 2230 WKg⁻¹ and energy density of 35.6 WhKg⁻¹. These results imply that high-performance supercapattery devices can be designed using MnMgS/CNT.

Acknowledgments

Asif Mahmood would like to acknowledge the Researcher's Supporting Project Number (RSP2024R43), King Saud University, Riyadh, Saudi Arabia.

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