



Article ZnMn₂O₄ Nanopyramids Fabrication by Hydrothermal Route: Effect of Reaction Time on the Structural, Morphological, and Electrochemical Properties

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Abstract: $ZnMn_2O_4$ spinels are prepared by a simple hydrothermal route with control of the reaction time, ranging from 6 h to 18 h. The evolution of the structural and morphological parameters under the effect of time was analyzed by XRD, ATR-FTIR, XPS, and SEM-EDS. The XRD results show that for longer reaction times (18 h), the $ZnMn_2O_4$ spinel samples present a tetragonal structure with high crystallinity and an average crystallite size of 32.3 ± 1.7 nm, larger than those obtained for 6 h and 12 h. The ATR-FTIR spectra confirm the structural results, with well-defined peaks related to stretching vibrations of M-O (M = Zn, Mn) functional groups. XPS reveals the co-existence of several metal oxides and hydroxides at the outermost surface. SEM analysis shows that the samples present a pyramid morphology, better defined at 18 h, with an average particle size of $6.2 \pm 1.5 \mu m$. EDS analysis of $ZnMn_2O_4$ (18 h) reveals atomic ratios of 0.45, 0.22, and 0.50 for Zn/Mn, Zn/O, and Mn/O, respectively, in good agreement with the expected values. Based on the CVs, the synthesized $ZnMn_2O_4$ samples formed at 18 h showed the most promising electrochemical properties, with a specific capacity of 102 F g⁻¹, offering great potential in supercapacitor applications.

Keywords: hydrothermal synthesis; ZnMn₂O₄ spinel; nanopyramids; electrochemical performances

1. Introduction

The ever-increasing fossil fuel consumption requires searching for new energy sources [1]. Energy storage is crucial in ensuring developments in using these energies [2]. Supercapacitors are essential electrochemical energy conversion and storage devices thanks to their high power density, fast charge/discharge rate, and excellent cycling stability [3,4]. Due to their attractive features, carbon, conductive polymers, and transition metal oxides are used as electrode materials in supercapacitors. Transition metal oxides are a form of pseudocapacitive materials based on pseudocapacitive redox charge storage [5]. They have attracted much attention in the last decade due to their unique physicochemical properties, high chemical activity, and interactive behavior [6]. In addition to energy storage in electrostatic carbon material, they exhibit electrochemical faradaic reactions between ion electrodes and material at a suitable potential [7]. Among them is the ternary metal oxide zinc manganite, ZnMn₂O₄, which has a tetragonal spinel structure with space group I41/amd. In the typical spinel structure, the Zn and Mn atoms are, respectively, located on the tetrahedral and octahedral sites of a unit cell [8]. It provides an attractive opportunity



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). to substitute cations in its crystal lattice tetrahedral and octahedral sites. They have good safety, are inexpensive, and are environmentally friendly [9]. Thanks to these properties, they have been investigated in various other applications, such as in photocatalysis [10], gas sensors [11], and electrode materials for batteries [12]. Multiple methods for the preparation of ZnMn₂O₄ have been reported in the literature, such as solid-state reaction [13], co-precipitation [14], sol-gel [15], thermal decomposition [16], hydrothermal route [17], solvothermal [18], the ultrasonic spray pyrolysis method [19], and the polyol-assisted pyrosynthesis method [20]. The hydrothermal method is a simple one-step process with high efficiency and low cost in terms of instrumentation and precursor materials. In this process, the reaction system is an aqueous solution containing the precursors. Crystal growth is carried out under high temperature and pressure in a closed steel pressure vessel called an autoclave [21]. As reported in the literature, the synthesis method and used conditions affect the material's structure. Barkhordari et al. presented the synthesis of ZnMn₂O₄ nanosheets by cathodic electrodeposition [22]. Mani et al. synthesized $ZnMn_2O_4$ spinel by the hydrothermal method with a double-hydroxide (NaOH:KOH, 1:1) treatment and utilizing zinc nitrate and manganese nitrate as precursors. The hydrothermal process was run for 24 h at 200 °C, producing a cubic-like morphology [23]. Senthilkumar et al. obtained hetarolite nanostructures using a similar method, with a 1:2 double-hydroxide treatment (NaOH:KOH) and employing zinc chloride and manganese chloride as precursors for hydrothermal treatment for 24 h at 180 °C. [8]. The present work used a hydrothermal process with a hydroxide treatment (NaOH) for up to 18 h at 180 °C with acetate precursors to prepare ZnMn₂O₄ micro/nanopyramid electrodes for supercapacitor applications. To the authors' best knowledge, this is the first time the production of these pyramid-like structures over stainless steel mesh has been reported.

2. Materials and Methods

2.1. Materials Synthesis

Nanopyramid ZnMn₂O₄ spinel samples were deposited directly on a stainless steel mesh (SSM, Bolin Metal Wire Mesh Co., Ltd., Hengshui, China) by hydrothermal processes. These SSM substrates (with a wire diameter of 35 μ m and a screen opening of 45 μ m) were cut into a rectangular shape (2 cm \times 5 cm), immersed in 10⁻³ M hydrochloric acid (HCl, \geq 37 wt.%) for a few seconds, then successively cleaned with acetone and ethanol for 10 min using an ultrasonic cleaner, and finally rinsed with distilled water. In this experiment, an aqueous solution containing 0.075 M of zinc acetate dihydrate (Zn(CH₃COO)₂.2H₂O, \geq 98 wt.%) and 0.15 M manganese acetate tetrahydrate (Mn(CH₃COO)₂.4H₂O, \geq 99 wt.%) was prepared by dissolving these chemicals (in a 1:2 molar ratio) in 20 mL distilled water under magnetic stirring at 800 rpm for 30 min. Then, 5 M sodium hydroxide (NaOH, \geq 98 wt.%) was added dropwise to the previous solution until reaching pH = 10. The reaction system was transferred to a Teflon-coated stainless steel autoclave. Depending on the experiment, a piece of SSM was placed in the autoclave and held at 180 °C for 6 h, 12 h, or 18 h. The coated mesh was carefully removed from the container and washed with distilled water. After drying, the mesh was annealed at 400 °C for 2 h and used as a supercapacitor electrode. Unless otherwise stated, all used chemicals were acquired from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Materials Characterization

X-ray diffraction (XRD) was carried out using a BrukerD8 advance X-ray diffractometer (Bruker Inc., Billerica, MA, USA) with CuK α (k = 1.541 Å) radiation. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis was performed in Spectrum Two from Perkin Elmer equipped with a UATR Two accessory (Perkin Elmer Inc., Waltham, MA, USA). The spectra were obtained through 32 scans of data accumulation at a resolution of 4 cm⁻¹ in the transmission mode at room temperature and treated in Perkin Elmer Spectrum IR software. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were recorded using a Hitachi model S2400 (Hitachi Inc., Tokyo,

Japan) with Bruker light elements EDS detector (Bruker Inc., Billerica, MA, USA). A beam of highly energetic electrons (25 keV) was focused on the sample's surface and secondary electron images were acquired. X-ray photoelectron spectroscopy (XPS) was performed using an XSAM800 spectrometer from Kratos (Kratos Analytical Ltd., Manchester, UK). X-rays from the Al K α source were used to irradiate the samples, which were fixed to the XPS holder with a metal spring. Additional operational conditions, spectra acquisition, and further data treatment details are reported elsewhere [24]. The binding energy (BE) of aliphatic carbon atoms, set at 285 eV, was used as a reference to correct the charge shifts. The quantification factors of Mn $2p_{3/2}$ and Zn $2p_{3/2}$ were weighted, taking into account the multiplicity of states. Other quantification factors were those of the software library.

2.3. Electrochemical Measurements

The electrochemical properties of the samples were assessed using a conventional three-electrode system connected to Squidstat Plus electrochemical workstation (Admiral Instruments, Tempe, AZ, USA). The ZnMn₂O₄ samples treated at reaction times of 6, 12, and 18 h were used as the working electrode. A platinum mesh was used as the counter electrode, whereas HANNA Instruments' saturated calomel electrode (SCE), model HI5412, served as the reference electrode. Sodium sulfate (1 M) (Na₂SO₄, \geq 99 wt.%, Sigma-Aldrich, St. Louis, MO, USA) aqueous solution was employed as the electrolyte.

3. Results and Discussion

3.1. Materials Characterization

Figure 1 shows the XRD patterns obtained at different reaction times in the angular range of $2\theta = 20-90^{\circ}$. The peaks of ZnMn₂O₄ (6 h and 12 h) from the XRD studies correspond to the tetragonal ZnMn₂O₄ (JCPDS 00-028-1468, a = b = 9.64 Å, c = 9.91 Å) and (JCPDS 00-03-1483, a = b = 10.3218 Å, c = 7.5521 Å). ZnMn₂O₄ (18 h) agrees with (JCPDS 00-032-1472, a = b = 5.71 Å, c = 10.8699 Å), indicating the presence of zinc manganese nanoparticles. Based on the obtained XRD data, a schematic illustration of the different crystal structures of the prepared materials was created using VESTA software (Figure 2).



Figure 1. XRD patterns of ZnMn₂O₄ obtained at different times, 6 h (brown), 12 h (red), and 18 h (green).



Figure 2. Schematic crystal structure of ZnMn₂O₄ spinel produced for (a) 6 h, (b) 12 h, and (c) 18 h.

As can be seen, a small content of $ZnMn_2O_4$ is present at the lowest time (6 h). At 12 h, the intensity of the peaks increases, although there is still one more additional peak at 27.26°. No impurities are detected at the highest time (18 h). Compared to the seed layer and samples prepared with a reaction time of 12 and 6 h, the XRD peaks of the samples prepared for 18 h increased and shifted to higher angles, from 29.22° to 29.29°, 32.85° to 32.96°, and 36.33° to 36.43°, for the (112), (103), and (211) crystal planes, respectively. By changing the hydrothermal reaction time, the lattice parameters of the samples change, as illustrated in Figure 2 and attested in Table 1, resulting in a shift of the peaks in the XRD patterns. These changes in the lattice parameters are related to the defects, stress, and composition. An ideal tetragonal spinel structure with space group I41/amd was achieved for the samples produced at 18 h (Figure 2c). In the XRD spectra, a right- or left-shift diffraction can be seen. The left-side shift (lower 2-Theta) reveals the lattice relaxation, and the right-side shift (higher 2-Theta) reveals the lattice strain [25]. In this work, the strain generated in the material during synthesis caused the peak shift, showing improved crystal properties.

Time (h)	6	12	18
	29.22	29.33	29.29
2θ (radians)	32.85	33.12	32.96
	36.33	36.37	36.43
	0.42	0.45	0.28
β (radians)	0.47	0.46	0.26
	0.79	0.32	0.24
	19.30	18.38	29.56
D (nm)	17.69	17.84	31.89
	10.64	25.94	35.29
Average crystallite size (nm)	15.87	20.72	32.25
Microstrain	-0.054	-0.022	-0.017
Dislocation $\times 10^{15}$ (m ⁻²)	3.969	2.329	0.962

Table 1. Calculated lattice parameters for ZnMn₂O₄ spinel samples.

To determine the average crystallite size (*D*) of the as-fabricated samples along the main diffraction peaks (112), (103), and (211), the Debye-Scherrer formula is employed (Equation (1)) [26]:

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where *K* is a dimensionless shape factor with a typical value of 0.9, λ is the X-ray wavelength (0.15406 nm), β (FWHM) is the line broadening at half the maximum, and θ is the Bragg angle. The average microstrain, ε , and the dislocation density, δ , were calculated from Williamson–Hall (Equation (2)) and Williamson–Smallman (Equation (3)) formulas [27]:

$$\beta cos\theta = \frac{K\lambda}{D} + 4\varepsilon sin\theta \tag{2}$$

$$\delta = \frac{1}{D^2} \tag{3}$$

According to Table 1, the average crystallite sizes of the nanostructures grow as the reaction time increases, from 15.9 ± 2.7 nm to 32.3 ± 2.6 nm, indicating improved crystallinity for a longer hydrothermal reaction time (18 h). Moreover, the type of strain generated in the materials changes from compressive to tensile, with a significant reduction in the dislocation density as the growth time changes, revealing that the lattice defect decreases as the particle sizes increase. Furthermore, the decrease in the lattice defect can be attributed to changes in the microstructure, shape, and deficiencies.

ATR-FTIR spectroscopy characterization was performed at wavelengths between 400 and 4000 cm⁻¹ to confirm the structural results. No significant differences can be noted by comparing all the gathered spectra (Figure 3). However, the growth time seems to affect only the intensity of the organic bands, which are less intense for the hydrothermal reaction time of 18 h, proving the water escaped from the sample [22]. In the region from 900 cm⁻¹ to 350 cm⁻¹, three peaks are observed at 722 cm⁻¹, 573 cm⁻¹, and 432 cm⁻¹, respectively, ascribed to stretching vibrations of tetrahedral group (Mn-O) and stretching vibrational mode of tetrahedral and octahedral group (M-O-M), where M=Mn, Zn [17,28,29]. Above 900 cm⁻¹, all bands are related to functional groups of organic compounds (Table 2).



Figure 3. ATR-FTIR spectra of ZnMn₂O₄ obtained at different times, 6 h (brown), 12 h (red), and 18 h (green).

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Table 2. Characteristic	absorption peaks	of FTIK spectra.

Wavenumber (cm ⁻¹)	Functional Groups	Source
1113.66	Mn–O–OH ethanol molecules on the surface	[30]
1212.22	C-O stretching	[31]
1595.01	C=O stretching	[32]
2144.12	CO_2 from atmosphere	[33]
2945.78	Aliphatic C-H stretching	[34]
3427.13	Associated O-H stretching	[31]

The samples were analyzed by XPS, with expected spinel compound stoichiometry $ZnMn_2O_4$. Figure 4 shows the wide spectra of all samples. Carbon, oxygen, zinc, and manganese were clearly detected. Table 3 shows the overall quantification. The experimental atomic ratios Mn/Zn included in Table 3 differ from the predicted ratios (equal to 2) for the spinel compounds stoichiometry: $ZnMn_2O_4$. Such differences result from the co-existence of several metal oxides and hydroxides identified by XPS at the surface of the coatings (as described below). The quantified oxygen includes oxygen from different sources, namely metal oxides and hydroxides, oxygen from carbonaceous moieties, and oxygen from the support. Besides the expected elements, iron from the SSM used as support is also detected in some samples. Iron is mainly in the form of Fe(III) oxide.



Figure 4. Wide spectra of $ZnMn_2O_4$ samples obtained at different times, 6 h (brown), 12 h (red), and 18 h (green).

at.%	6 h	12 h	18 h
С	36.5	40.4	18.6
О	43.7	45.4	46.1
Zn	8.1	3.6	17.2
Mn	11.6	10.5	18.1
atomic ratios			
Mn/Zn	1.4	2.9	1.1
O/Zn	5.4	12.5	2.7

Table 3. Atomic concentrations (at.%) and atomic ratios.

To better understand the surface composition, XPS regions were studied in detail. Zn 2p is a doublet peak with a large spin-orbit split of 23.0 ± 0.2 eV. Figure 5 shows the main component, Zn $2p_{3/2}$, fitted with a single peak centered at 1020.9 ± 0.2 eV. This BE has been attributed either to Zn(0) or Zn(II) [35]. However, based on the Auger parameter (AP)— $2p_{3/2}$, L₃M₄₅M₄₅, equal to 2010.5 ± 0.3 eV—the oxidation state of zinc is +2 [35,36]. In this case, the AP is useful to distinguish between the possible oxidation states, since an AP energy shift of ca. 3.5 eV from the metallic form Zn(0) to Zn(II) is observed. Mn 2p is also a doublet peak with a spin-orbit separation of 11.5 ± 0.2 eV. In many examples reported in the literature, the doublet peak is shown, but with a deficient step-like baseline definition, which is over- or underestimated due to the difficulty in defining a Shirley-type curve limiting the real peak area. As for the Zn 2p region, to avoid an erroneous background



definition, only the main component of the doublet, $Mn 2p_{3/2}$ (Figure 5), was considered for qualitative analysis and quantification purposes.

Figure 5. XPS regions of (**a**) Zn $2p_{3/2}$, (**b**) Mn $2p_{3/2}$, (**c**) O 1 s, and (**d**) C 1s of ZnMn₂O₄ obtained at different times, 6 h (brown), 12 h (red), and 18 h (green).

The analysis of the Mn $2p_{1/2}$ component is not included, but yields the same information as the Mn $2p_{3/2}$, but with poorer statistics, given the lower intensity. Mn $2p_{3/2}$ was fitted with a minimum of three peaks centered at 641.1 ± 0.1 eV, 642.6 ± 0.1 eV, and 644.6 ± 0.1 eV. Identifying these components is not a straightforward task, mainly due to the large dispersion of values reported for each manganese oxidation state, with ranges of BE overlapping each other [35]. However, the Mn $2p_{3/2}$ profiles shown in Figure 5 are similar to that of Mn(III) species studied by Biesinger et al. [37]. Mn(III) is the oxidation state predicted for ZnMn₂O₄ structures, being the relative intensity of the satellite peak, centered at higher BE, a relevant feature to distinguish Mn(II) from Mn(III). Therefore, the fitted peaks in Mn $2p_{3/2}$ spectra are assigned to (for increasing BE): Mn(III), Mn(IV) mixed

with higher oxidation states [24,37], and a satellite peak. Yet, O 1 s fitted regions include two important peaks that confirm the presence of metal oxides and hydroxides, with peaks centered at 529.8 \pm 0.1 eV and 531.2 \pm 0.1 eV, respectively. These peaks include lattice oxygen (O²⁻) and hydroxyl groups in manganese, zinc oxides, and/or hydroxides. Peaks centered at higher BE in O 1 s are attributed to oxidized carbonaceous moieties, as also attested from C 1 s regions analysis. C 1 s regions were fitted with three peaks, centered at 285 \pm 0.1 eV, 286.7 \pm 0.1 eV, and 288.6 \pm 0.1 eV, assigned to C-C and/or C-H aliphatic carbon atoms, carbon singly bonded to oxygen, and carbon in carboxylate groups (O-C=O).

The morphology of the samples was investigated using SEM. As can be seen at lower magnification (Figure 6a,b,e,f,i,j), all the particles present a homogeneous surface coverage. The nanocrystals show a pyramid-like morphology, more distinct at higher magnifications, especially for $ZnMn_2O_4$ (12 h) and (18 h) (Figure 6g,h,k,l).



Figure 6. SEM micrographs of ZnMn₂O₄ prepared for (**a**–**d**) 6 h, (**e**–**h**) 12 h, and (**i**–**l**) 18 h at different magnifications of (**a**,**e**,**i**) ×450, (**b**,**f**,**j**) ×1000, (**c**,**g**,**k**) ×5000, and (**d**,**h**,**l**) ×10,000.

The particle sizes were analyzed using the DigimizerTM image analysis software (Figure 7), which resulted in average sizes of $6.2 \pm 1.5 \,\mu\text{m}$, $6.9 \pm 2.1 \,\mu\text{m}$, and $369.3 \pm 50.7 \,\text{nm}$ at times of 18 h, 12 h, and 6 h for the hydrothermal process. The particle size measured from SEM is much larger than the dimension of the crystallites estimated by XRD analysis. This is expected, as each particle measured from SEM micrographs, shown in Figure 7, can include multiple crystallites characterized by a given crystal structure with a given orientation. These results show that the particles stop growing at 12 h; however, as shown in the previous analysis (Figure 2), the crystalline structure of the sample obtained at 12 h does not present the predicted tetragonal structure. EDS was performed in combination with SEM (Figure 8) to determine the elemental composition of the samples [38]. Figures 6–8 and Table 4 show that for 18 h, the atomic ratios agree with the expected. It is clear from SEM micrographs and EDS that the topography of the spinels, the mean particle diameter, and the atomic ratio are affected by the hydrothermal reaction time. The higher reaction time results in better regularity, homogeneity, compactness, and uniformity.

Table 4. Atomic ratios of Zn, Mn, and O in ZnMn₂O₄ spinel samples.

Atomic Ratios	6 h	12 h	18 h	Predicted Ratios
Mn/Zn	1.6	1.5	1.8	2
O/Zn	2.7	-	3.5	4



Figure 7. SEM micrographs and particle size distribution of ZnMn₂O₄ spinel prepared for (**a**,**d**) 6 h, (**b**,**e**) 12 h, and (**c**,**f**) 18 h.



Figure 8. SEM-EDS elemental mapping of Zn, Mn, and O in $ZnMn_2O_4$ samples prepared for (a,b) 6 h, (c,d) 12 h, and (e,f) 18 h.

3.2. Electrochemical Studies

The electrochemical characterization of the electrodes was assessed by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) cycling, and electrochemical impedance spectroscopy (EIS) at each reaction time (6 h, 12 h, and 18 h). Figure 9 displays the ZnMn₂O₄ nanopyramid CV curves for samples produced at different reaction times. For each sample, the scan rates range from 1 to 100 mV s⁻¹ in a stable voltage window from 0.15 V to 0.35 V. As can be seen, CV curves exhibit similar shapes for all produced electrodes with different current intensities [39]. They feature an electrical double-layer capacitive character and excellent electrochemical reversibility, based on the absence of redox peaks and an almost rectangular shape up to 25 mV s⁻¹, with symmetrical anodic and cathodic halves [40]. The voltammograms' shape deviates from the ideal rectangle at higher scan rates as a result of the Na⁺ ions reaching the samples' outer surface, resulting in a higher diffusion resistance and rapid polarization. The diffusion also explains the current intensity increase when the scan rate increases. More ions reach the electrode-electrolyte interface, whereas very few ions participate in the charge–transfer reaction [22]. Therefore, one can say that the charge–transfer reaction rate at higher scan rates is limited by the diffusion process [41,42].



Figure 9. Effect of scan rate $(1-100 \text{ mV s}^{-1})$ on the CV curves of ZnMn₂O₄ spinel prepared for (**a**) 6 h, (**b**) 12 h, and (**c**) 18 h.

Figure 10a compares the cyclic voltammograms of the produced materials and bare SSM substrate at a scan rate of 10 mV s⁻¹ [43]. The curve for the sample treated for 18 h presents the largest area. For lower time (12 h and 6 h), the CV area declined dramatically and was almost null for the bare substrate, revealing reduced charge–storage capacity. However, large areas demonstrate good contact between the electrode's surface and the electrolyte [34].

The specific capacitance, C_s , value is determined according to the inner area of the CV curves at various scan rates (Equation (4)) [44],

$$C_s = \frac{\int IdV}{2mv\Delta V} \tag{4}$$

where the numerator is the area of the CV curve (cathodic scan), v is the potential scan rate (mV s⁻¹), m is the active material mass (g), and ΔV is the potential window (V).

The corresponding values are presented in Figure 10b. The highest specific capacitances for each sample produced at 18, 12, and 6 h were obtained at a scan rate of 1 mV s⁻¹, with values of 102, 64.1, and 28.8 F g⁻¹, respectively.

The specific capacitance decreases as the scan rate increases, which can be explained by the fact that at low scan rates, the electrolyte ions have enough time to penetrate the pores of the electrode material [45]. Comparing the three samples, it is clear that the sample treated for 18 h resulted in a better response, possibly due to its purer crystalline structure. Kanakarj et al. [46] studied the use of $ZnMn_2O_4$ as a supercapacitor electrode. In their work, the material was synthesized by a one-step hydrothermal method, using nickel foil as substrate. The results show the formation of globular nanoparticles resulting in a C_s value of 87 F g⁻¹ for the calcinated ZnMn₂O₄ at 1 mV s⁻¹ in 1 M Na₂SO₄ electrolyte solution. The herein obtained value is higher than the one reported by Kanakarj et al. [46] and other previous studies working with the Na₂SO₄ electrolyte, as shown in Table 5.



Figure 10. (a) CV curves at 10 mV s⁻¹ of ZnMn₂O₄ samples prepared for 6 h, 12 h, and 18 h, and (b) variation of specific capacitance of ZnMn₂O₄ samples as a function of the potential scan rate.

However, there are several reports on $ZnMn_2O_4$ with higher specific capacitance values compared with the present work (Table 5). It is stated that the lower capacitance may be related to using an inert electrolyte, Na_2SO_4 , as opposed to using strongly alkaline electrolytes such as KOH [47]. Undoubtedly, the electrolyte can affect the charge–store mechanism. In light of this, transition metal oxides may exhibit different electrochemical properties, depending on the electrolyte and the nature of the CV.

Working Electrode	Substrate	Fabrication Method	Electrolyte	Scan Rate (mV s ⁻¹)	C_{s} (F g ⁻¹)	Source
ZnMn ₂ O ₄	SSM	hydrothermal	Na ₂ SO ₄ (1 M)	1	102	Present work
$ZnMn_2O_4$	nickel foil	hydrothermal	Na ₂ SO ₄ (1 M)	1	87	[46]
ZnMn ₂ O ₄	Ti	modified solution combustion	Na ₂ SO ₄ (1.75 M)	2	38	[48]
C-ZnMn ₂ O ₄	Ti	modified solution combustion	Na ₂ SO ₄ (1.75 M)	2	75	[48]
ZnMn ₂ O ₄	_	sol-gel auto-combustion	Na ₂ SO ₄ (2 M)	5	96	[49]
$ZnMn_2O_4$	nickel foil	hydrothermal	KOH (3 M)	5	492	[33]
ZnMn ₂ O ₄	nickel foil	hydrothermal	KOH (2 M)	5	776	[23]
Cd-ZnMn ₂ O ₄	nickel foam	hydrothermal	KOH (2 M)	2	364	[50]

Table 5. Comparison of the specific capacitance of ZnMn₂O₄ spinel (18 h) with previous studies.

Figure 11 shows the variation of galvanostatic charge–discharge (GCD) cycling of the spinel samples over the 0.2–0.6 V potential range at specific currents of 7, 5, 3, 2, and 1.5 mA g^{-1} . The ZnMn₂O₄ electrode treated for 18 h (Figure 11c) clearly shows a greater discharge time rate than the samples produced at 6 h and 12 h (Figure 11a,b, respectively). Due to the electrochemical double-layer capacitor feature, all the samples showed linear variation in the charge–discharge curves [33].



Figure 11. Effect of current density on the GCD curves of $ZnMn_2O_4$ spinel produced for (**a**) 6 h, (**b**) 12 h, and (**c**) 18 h.

The specific capacitance, C_s (mF g⁻¹), was measured according to Equation (5),

$$C_s = \frac{I\,\Delta t}{m\,\Delta V}\tag{5}$$

where *I* is the discharge current (mA), Δt is the discharge time (s), ΔV is the potential window (0.4 V), and *m* is the spinel material mass (g). A maximum specific capacitance of 754 mF g⁻¹ was measured for the ZnMn₂O₄ (18 h) at 1.5 mA g⁻¹ specific current, as shown in Table 6.

Table 6.	Specific ca	pacitance	of ZnMn ₂ (\mathcal{D}_4	measured at	different s	pecific	currents
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	Specific Capacitance (mF g ⁻¹)			
Specific Current (mA g ⁻¹)	6 h	12 h	18 h	
7	147	186	157	
5	195	238	253	
3	197	278	358	
2	416	443	742	
1.5	407	398	754	

To further explore the electrochemical performance, the energy density, E (Wh kg⁻¹), and the power density, P (W kg⁻¹), were obtained from the GCD curves at different specific currents using Equations (6) and (7) [51],

$$E = \frac{C_s \,\Delta V^2}{2} \tag{6}$$

$$P = \frac{E \times 3600}{\Delta t} \tag{7}$$

where ΔV refers to the potential difference in the charging and discharging processes (V) and Δt is the time of discharging process (s). As presented in the Ragone plots (Figure 13), ZnMn₂O₄ produced at 18 h delivers the highest energy density of 60.3 Wh kg⁻¹ at a power density of 300 W kg⁻¹.

To study the frequency response, EIS analysis was carried out in a wide range of frequencies, from 100 kHz to 1 Hz, at 5 mV of maximum amplitude of the AC signal. Usually, the impedance plots consist of a semicircle component at high frequency preceding a linear component at low frequency [52]. From Figure 12a,b, one can see that the Nyquist plots of all samples have similar behavior. However, a very low-diameter semicircle is only visible on the sample treated at 12 h. The semicircle is almost absent for the other samples, suggesting improved kinetics due to fast electron transfer rates and improved electrical contact between the stainless steel current collector and the active electrode material [52]. Furthermore, the electrolyte resistances are displayed as the intercept of the semicircle on the real axis [53]. The R_s values are 17.7 Ω , 12.7 Ω , and 13.6 Ω for 6 h, 12 h, and 18

h, respectively. As the reaction time increases, the straight line deviates to the left with an angle between 45° and 90° , indicating a lower Warburg impedance for the highest reaction time. An equivalent circuit model was drawn based on the experimental results (Figure 12c). The model includes the solution resistance (R_s), the charge transfer resistance (R_{ct}), the Warburg diffusion resistance (W), and the double-layer capacitance (C_{d1}). The C_{d1} was calculated by Equation (8),

$$C_{d1} = \frac{1}{2\pi f Z_{img} m} \tag{8}$$

where *f* is the frequency (Hz) and Z_{img} is the imaginary impedance (Ω). The results for each sample are presented in Figure 12d. The reaction time affects the C_{d1} , with the highest capacitance value exhibited for 18 h.



Figure 12. (a) Electrochemical impedance spectroscopy of $ZnMn_2O_4$ samples prepared for 6 h, 12 h, and 18 h with (b) the zoom on the Nyquist plots for the high-frequency region and (c) the equivalent circuit model. (d) Variation of the specific double-layer capacitance of $ZnMn_2O_4$ samples as a function of frequency.



Figure 13. Ragone plots (*E* vs. *P*) of ZnMn₂O₄ spinel produced for 6 h (brown), 12 h (red), and 18 h (green).

4. Conclusions

ZnMn₂O₄ spinels with pyramid-like morphology were synthesized using a hydrothermal method over stainless steel mesh substrates. The effect of the reaction time (6–18 h) was studied. XRD, ATR-FTIR, XPS, SEM-EDS, and electrochemical measurements were used to characterize the ZnMn₂O₄ nano/micropyramid samples. It has been found that the samples prepared using a reaction time of 18 h yield the best results in the present work. These samples had good crystallinity, morphology with improved uniformity, and interesting electrochemical results, with a specific capacitance of 102 F g⁻¹. The excellent properties of the nanostructured material are promising for supercapacitor applications.

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