Potato Chip-Like 0D Interconnected ZnCo$_2$O$_4$ Nanoparticles for High-Performance Supercapacitors

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Abstract: Zinc cobaltite (ZnCo$_2$O$_4$) is an emerging electrode material for supercapacitors due to its rich redox reactions involving multiple oxidation states and different ions. In the present work, potato chip-like 0D interconnected ZnCo$_2$O$_4$ nanoparticles (PIZCON) were prepared using a solvothermal approach. The prepared material was characterized using various analytical methods, including X-ray powder diffraction and scanning electron microscopy. The possible formation mechanism of PIZCON was proposed. The PIZCON electrode material was systematically characterized for supercapacitor application. The areal capacitance of PIZCON was 14.52 mF cm$^{-2}$ at 10 µA cm$^{-2}$ of current density, and retention of initial capacitance was 95% at 250 µA cm$^{-2}$ following 3000 continuous charge/discharge cycles. The attained measures of electrochemical performance indicate that PIZCON is an excellent supercapacitor electrode material.

Keywords: ZnCo$_2$O$_4$; electrode material; areal capacitance; supercapacitors

1. Introduction

Accumulation and energy storage are significant challenges for the further development of various modern devices, such as hand-held devices, hybrid electric vehicles, solar panels, memory backup systems, and defibrillators [1–3]. To overcome this energy problem, scientists have designed and developed novel energy storage devices (batteries and supercapacitors) [4]. Currently, supercapacitors are the most popular energy storage device due to their exceptional electrochemical characteristics, such as high-power density, fast charge–discharge process, low cost, long life cycle, and low environmental impact [5–7]. Supercapacitors store energy based on two operating mechanisms: electric double-layer capacitors (EDLCs) and pseudocapacitors [8–10]. In the former, the charge is stored electrostatically at the electrode–electrolyte interface, and in the latter, the redox reaction is responsible for charge storage [11]. Carbon with various dimensions (0D, 1D, 2D, and 3D) is used as the electrode material for EDLCs. The lower capacitance of carbon-based materials hinders practical applications [12–14]. Transition metal oxides/sulfides/hydroxides and conducting polymers are used as electrode materials for pseudocapacitors [15–17]. In particular, transition metal oxides with spinel structure (TMOSS) (ternary form) exhibit excellent electrochemical characteristics as an electrode material for supercapacitors [18]. Among the TMOSS, zinc cobaltite (ZnCo$_2$O$_4$) is a potential electrode material for pseudocapacitors due to its high theoretical capacitance, multiple oxidation states, and excellent electrochemical properties [19–22].
The morphology of the electrode material is a crucial aspect of the electrochemical performance of supercapacitors, notably, tuning the electrode material’s morphology by changing the reaction parameters, such as precursor concentration, type of surfactant and solvent, reaction time and temperature [23–25]. To date, research groups have reported diverse morphologies of ZnCo$_2$O$_4$ nano/microstructures, exposing different physicochemical and electrochemical properties [26–28].

In this study, potato chip-like interconnected ZnCo$_2$O$_4$ nanoparticles were prepared using solvothermal synthesis, and we investigated the physicochemical properties of the as-prepared material via various analytical tools. When exposed as an electrode material for supercapacitors, the PIZCON exhibited a high areal capacitance of 14.52 mF cm$^{-2}$ at current density 10 $\mu$A cm$^{-2}$, rate capability, and excellent cyclic stability. Based on the above results, the authors suggested that the PIZCON is a potential electrode material for high-performance supercapacitors.

2. Materials and Methods

2.1. Solvothermal Synthesis of PIZCON

All chemicals were of the highest purity available and used directly without further purification. The synthesis of potato chip-like interconnected ZnCo$_2$O$_4$ nanoparticles (PIZCON) was performed using the solvothermal method. In a typical synthesis procedure, 1 mM of zinc acetate dihydrate, 2 mM of cobalt acetate tetrahydrate, and 3 mM of urea were dispersed in 70 mL of ethylene glycol with constant magnetic stirring at room temperature (RT) for 20 min, thus forming a clear pink colored solution. The solution was then transferred into a 100 mL Teflon lined stainless steel autoclave and the hydrothermal temperature was set to 180 $^\circ$C/12 h. After cooling to room temperature, the obtained precipitate was collected and washed with DI water and ethanol several times. The rinsed precipitate was dried at 80 $^\circ$C/12 h. Finally, the dried powder was annealed at 400 $^\circ$C/6 h at a ramping rate of 5 $^\circ$C/min. Scheme 1a shows the schematic diagram of the overall solvothermal synthesis method of potato chip-like ZnCo$_2$O$_4$ nanoparticles.

2.2. Characterization

Phase confirmation/crystalline nature and morphology of the as-prepared sample was investigated with X-ray diffraction (XRD) using a diffractometer (D8 Advances, Bruker, Germany) with a Cu Kα radiation source ($\lambda = 1.5406$, an accelerating voltage of 40 kV, and cathode current of 30 mA) and field emission scanning electron microscopy (FE-SEM) using an S-4800 instrument (Hitachi, Japan), respectively. The cyclic voltammetry (CV), galvanostatic charge–discharge (CD), and electrochemical impedance spectroscopy (EIS) of the PIZCON was tested at RT to assess the electrochemical performance using a three-electrode electrochemical work-
station (CHI 660 D CH Instruments Inc., USA). In contrast, the prepared active material served as a working electrode. The electrode was fabricated for the electrochemical analysis using a casting of the active material on a glassy carbon electrode (GCE). Firstly, the GCE was gently polished with alumina powder with a 0.05 mm size using a CH Instrument (CHI) polishing kit, followed by rinsing with DI water and drying at room temperature. Secondly, 5 mg of active material was dissolved in 0.1 wt% of 1 mL ethanol solution containing Nafion and sonicated for 15 min to form a slurry. Then, 5 mL of this slurry was drop cast onto the GCE surface and dried at room temperature. Finally, the GCE was rinsed with DI water to remove the loosely attached sample on the GCE surface. The electrode had a planer structure over a working area of about 0.07 cm$^2$. Furthermore, an Ag/AgCl and a Pt wire were used as a reference and a counter electrode, respectively. For all electrochemical experiments, 6 M KOH solution was used. The EIS spectrum was fitted using the Randles equivalent circuit model.

The average crystallite size ($D$) of the sample was estimated from the Debye–Scherer equation: $D = K \lambda / \beta \cos \theta$, where $K$ is a constant related to the shape of the crystal (0.89), $\lambda$ is the wavelength of the radiation employed, $\beta$ is full width at half maximum (FWHM) of the obtained characteristic peak in radians, and $\theta$ is the Bragg diffraction angle.

From GCD curves, areal capacitance was calculated according to the following equation: $C = 2 \times I \times t / (V \times S)$, where $C$ is areal capacitance (F/cm$^2$), $I$ is the discharge current, $t$ is the discharge time (s), $V$ represents the potential window (V), and $S$ is the active material surface area of the single electrodes (cm$^2$).

3. Results and Discussion

The crystallographic structures of the PIZCON were first characterized by X-ray powder diffraction (XRD). Figure 1 shows the XRD spectrum of PIZCON, and all of the recognized diffraction peaks can be matched well to the standard ZnCo$_2$O$_4$ phase (JCPDS card no. 23-1390) and previous reports [3]. No additional diffraction peaks regarding possible impurities were observed in the XRD spectrum, demonstrating our synthesis approach produced PIZCON material with high purity. The characteristic peaks were identified at 21.2, 31.1, 36.8, 38.5, 44.7, 55.6, 59.3, 65.1 and 77.2$^\circ$, which correspond to the respective peaks (111), (220), (311), (222), (400), (422), (511), (440) and (553) of the cubic spinel structure of ZnCo$_2$O$_4$ [8]. The average crystallite size ($D$) of the sample was estimated from the Debye–Scherer equation [29] and the $D$ of the PIZCON was about 15 nm.

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**Figure 1.** XRD spectrum of the PIZCON.
Figure 2a,b shows the SEM images of the PIZCON at different magnifications. The lower magnification of the SEM image (Figure 2a) is composed of zero-dimensional (0D) nanoparticles and displays a porous structure with enough space at a large scale. The higher magnification FE-SEM image (Figure 2b) shows that nanoparticles are interconnected to form a chip-like morphology. As reported in the previous literature [30,31], this feasible interconnected structure benefits electrochemical reactions in aqueous electrolytes because it can promote electrolyte diffusion and enhance electrons by providing a fast transmission pathway.

Figure 2. FE-SEM images of PIZCON at lower (a) and higher (b) magnification. (c) Photography of chip-like structure (not to scale).

Based on SEM observations, we propose a plausible formation mechanism of PIZCON, as shown in Scheme 1b. In the first step of the formation process, the urea (acting as growth director) was decomposed into two parts: Co$_3^{2-}$ and NH$_4^+$ in ethylene glycol solution. Furthermore, Zn$^{2+}$ and Co$^{2+}$ ions interact with both EG and Co$_3^{2-}$, leading to the formation of ZnCo glycolate through a strong chelating interaction. A large number of nanoparticles are formed and gather together during the nucleation and crystal growth step. In the last step, the nanoparticles grow further due to the Ostwald ripening process, and finally, potato chip-like zinc cobaltite nanoparticles form due to the self-assembly process. The decomposition of the organic species at 400 $^\circ$C for 6 h in air leads to an increase in the porosity of the final PIZCON [3,7].

A systematic electrochemical analysis was implemented at RT to explore the supercapacitor’s PIZCON electrode material. Figure 3 shows the CV curves of PIZCON obtained at different scan rates within the potential window of 0.0 to 0.6 V.

Figure 3. CV curves of PIZCON at different scan rates.
From the CV curves, a pair of redox peaks were identified that indicate that the PIZCON exhibits pseudocapacitive behavior. According to previous reports [7, 15], the corresponding oxidation and reduction reactions can be defined as the following equation:

$$\text{ZnCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{ZnOOH} + 2\text{CoOOH} + e^-$$  \hspace{1cm} (1)

We also observed the following points as the PIZCON scan rate increased from 5 to 250 mV s$^{-1}$: (i) the shape of the CV curves did not change, indicating excellent speed capability; (ii) the anode peaks moved towards the higher voltage region and the cathode peaks moved to the lower voltage area, demonstrating internal resistance and a polarization effect during the faradic process; (iii) the PIZCON exhibits better reversibility and fast charge/discharge capability because the anodic and cathodic peaks were small [3, 7].

Figure 4 displays the plot for an anodic peak current versus the square root of the scan rate of the PIZCON. This plot confirms that the redox reaction dominates the diffusion control process because peak anodic peak current increases linearly and proportional to the square root (a well-fitted linear relationship) [13].

![Figure 4. Anodic peak current ($x 10^{-5}$ A) versus square root of scan rate (mV s$^{-1}$)$^{1/2}$ plot of PIZCON.](image)

GCD is a complementary method for measuring the electrode’s areal capacitance at constant current density [20]. The GCD curves of PIZCON at different current densities within the potential window of 0 to 0.4 V are presented in Figure 5 and the corresponding discharge time was measured to be 277.3, 103.5, 51.6, 33.7, 24.2, 9.8, 4.5, 3.5, and 2.3 s.

![Figure 5. GCD curves of PIZCON at different current densities.](image)
Figure 6 shows the plot of areal capacitance and current density of the PIZCON electrode. The PIZCON exhibits areal capacitances of 14.52 and 13.62, 13.02, 12.84, 12.62, 11.87, 10.62, 9.93, and 9 mF cm$^{-2}$ at a current density of 10, 25, 50, 75, 250, 500, 750, and 1000 mA cm$^{-2}$, respectively. Table 1 shows the electrochemical performance of the previously reported ZnCo$_2$O$_4$ configurations. From the table, the areal capacitance of the PIZCON electrodes in this study is comparable to that of the ZnCo$_2$O$_4$ configurations electrodes with a range of morphologies reported elsewhere.

Figure 6. Areal capacitance versus current density of the PIZCON electrode.

Table 1. Comparison of supercapacitor materials based on ZnCo$_2$O$_4$ configurations.

| Material     | Synthesis Method | Morphology     | Areal Capacitance @ Current Density | Ref    |
|--------------|------------------|----------------|------------------------------------|--------|
| ZnCo$_2$O$_4$ | Hydrothermal     | Flake-like     | 2.72 F cm$^{-2}$ @ 2.02 mA cm$^{-2}$ | [5]    |
| ZnCo$_2$O$_4$ | Hydrothermal     | Nanosheet array| 3.19 F cm$^{-2}$ @ 2 mA cm$^{-2}$   | [8]    |
| ZnCo$_2$O$_4$ | Hydrothermal     | Sheet-like     | 16.13 mF cm$^{-2}$ @ 10 µA cm$^{-2}$ | [9]    |
| ZnCo$_2$O$_4$ | Hydrothermal     | Hexagonal-like | 41.43 mF cm$^{-2}$ @ 10 µA cm$^{-2}$ | [18]   |
| ZnCo$_2$O$_4$ | Hydrothermal     | Rod-like       | 31 mF cm$^{-2}$ @ 10 µA cm$^{-2}$   |        |
| ZnCo$_2$O$_4$ (PIZCON) | Solvothermal | Potato chip-like | 14.52 mF cm$^{-2}$ @ 10 µA cm$^{-2}$ | Present work |

Another essential aspect of the evaluation of the supercapacitive performance is the electrode material’s cyclic performance [17]. Figure 7 shows the cyclic performance of the PIZCON electrode at a current density of 250 µm cm$^{-2}$ for 3000 cycles. Remarkably, 95% of capacitive retention after 3000 cycles indicates the PIZCON has excellent cyclic stability.
Figure 7. Cyclic performance of the PIZCON electrode.

The EIS measurement was performed to understand the kinetic properties of the PIZCON electrodes. Figure 8 shows the obtained Nyquist plot of the PIZCON electrode in the frequency range between 1 Hz and 0.1 MHz with a 5 mV of alternating current amplitude under open-circuit voltage ratings. The Nyquist plot of the PIZCON exhibited a perfect semicircle in the high-frequency section, which corresponds to the charge transfer resistance ($R_{ct}$) at the electrode–electrolyte interface [3,7]. The Nyquist plot showed a straight line in the lower frequency section, resembling the Warburg diffusion ($Z_w$) of the electrolyte [15,32]. The EIS constraints of the PIZCON electrode were estimated using the Randles electronic circuit model. For PIZCON, the solution resistance ($R_s$) and $R_{ct}$ were 3.27 and 24.02 $\Omega$, respectively. The obtained lower EIS fitted value for the PIZCON electrode indicates lower resistivity, which is consistent with the higher areal capacitance. These findings demonstrate that the PIZCON electrode material acts as a high-performance material and holds technological promise for electrodes of supercapacitors.

Figure 8. Nyquist plot of PIZCON electrode material (lower inset depicts the enlarged image at higher and mid-frequency regions, and the upper inset shows the equivalent Randles circuit model to fit the obtained PIZCON impedance data).

4. Conclusions

In conclusion, the authors effectively prepared chip-like 0D interconnected ZnCo$_2$O$_4$ nanoparticles (PIZCON) via the solvothermal method. The prepared PIZCON exhibits excellent structural properties. The areal capacitances of the PIZCON electrode were 14.52, 13.62, 13.02, 12.84, 12.62, 11.87, 10.62, 9.93, and 9 mF cm$^{-2}$ at different current densities
of 10, 25, 50, 75, 250, 500, 750, and 1000 mA cm$^{-2}$, respectively.

The areal capacitance retention was 95% over 3000 charge–discharge cycles at a current density of 250 µA cm$^{-2}$. The outstanding cyclic performance of the PIZCON highlights its exceptional performance as a superior electrode material in supercapacitor applications.

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