

A Flexible Supercapacitor Made of Ni-doped ZnMn₂O₄ with a High Specific Surface Area

Pengwen Wu^{1,a,*}

¹Department of Materials Science and Engineering, Hefei University of Technology, Hefei, China

a. 2030353834@qq.com

*corresponding author

Abstract: Flexible supercapacitors with excellent electrochemical performance and flexible portability have a wide range of application scenarios and development potential. The electrochemical performance of asymmetric supercapacitors is more excellent and stable than that of conventional supercapacitors. A quasi-solid Zn-MnO₂ flexible supercapacitor is reported in this paper. High surface area spinel ZnMn₂O₄ (ZMO) was prepared by rapid reaction of ternary deep eutectic solvent and potassium permanganate, and then ZMO with different Ni doping ratio was prepared by hydrothermal reaction. ZMO/CC is prepared by growing ZMO on carbon cloth by hydrothermal reaction, which is used as the cathode of supercapacitor. Zn/CC was prepared by electrodeposition as anode. The electrochemical properties of flexible supercapacitors and electrode materials were characterized. It is found that the specific capacitance of Zn/CC at 10mA cm⁻² is 1.5mF cm⁻², and that of ZMO/CC at 5mA cm⁻² is 11mF cm⁻². The cathode and anode materials have typical faradaic pseudocapacitive behavior, the anode materials have good coulomb efficiency, ZMO/CC has good electrochemical reversibility, and the charge transport resistance is only 7 Ω.

Keywords: Supercapacitors, portable energy storage devices, high surface area spinel

1. Introduction

In recent years, human beings have begun to pursue sustainable development, and traditional fossil energy has gradually been eliminated because it is difficult to regenerate and will bring many environmental problems [1-3]. Renewable energy and clean energy such as solar energy, water energy, tidal energy and wind energy are gradually receiving people's attention [4, 5]. However, there is an inevitable time and space gap between renewable energy generation and use.

The operational principle of batteries and supercapacitors is predicated on paired electrodes in ionic contact through an electrolyte, where energy conversion mechanisms are governed by interfacial phenomena at the electrode/electrolyte boundary. [6, 7]. The difference between them is that the energy conversion of the battery is achieved by converting chemical energy into electrical energy through the redox reaction of the anode and cathode [8], the energy conversion of supercapacitors does not necessarily go through redox reactions[6], and the voltage always increases linearly when it is charged and discharged at constant current. Batteries now dominate the market, with high energy density. However, there are problems with electrolyte leakage, and thermal runaway occurs when the battery is overcharged and discharged. Moreover, working at high power will aggravate the side reaction between the electrode and the electrolyte, produce lithium dendrites that cannot be eliminated,

and lead to a battery explosion, which is serious safety hazards [9-11]. Supercapacitors have high power and cycle life, fast charging and discharging speed, and are more secure. However, low energy density and high production costs have become the main difficulties of supercapacitors[12-16].

Supercapacitors are categorized into three primary classes according to their underlying charge storage mechanisms: electric double-layer capacitors (EDLCs) relying on electrostatic charge separation, pseudocapacitors involving faradaic redox reactions, and hybrid asymmetric supercapacitors combining both charge storage approaches. [6, 9, 14, 17]. EDLCs operate through electrostatic charge storage mechanisms involving reversible ion adsorption/desorption at the electrode-electrolyte interface. To increase the surface area of the electrode and improve its performance, the electrode material is usually porous conductive material (activated carbon/carbon nanotubes/graphene / 3D carbon nano allotrope, etc.), and the electrolyte is liquid or solid material with high ionic conductivity and low conductivity. In contrast, pseudocapacitive energy storage originates from fast surface-confined Faradaic reactions, utilizing electrode materials such as transition metal oxides, conductive polymers, or heteroatom-doped carbon structures containing O and N functional groups. Since the EDLC does not undergo redox reactions, the reaction rate is fast, and the cycle life is long. At the same time, the pseudocapacitor has higher energy and power densities [14, 18-22].

Compared with traditional supercapacitors, asymmetric supercapacitors have wider operating voltage and higher energy density with stable voltage windows. It is usually composed of two electrodes with different electrochemical properties, one having , a high specific capacity, and rapid charge and discharge capability, usually an EDLC material, and the other has a high Faraday capacitance, usually a pseudocapacitive material, such as a metal oxide or conductive polymer. A hybrid supercapacitor represents an electrochemical energy storage device with an asymmetric configuration, where the charge storage mechanism involves distinct processes at each electrode: the positive electrode primarily relies on faradaic redox reactions characteristic of batteries, while the negative electrode operates through an EDLC mechanism[9, 23-25]. Both electrodes of the asymmetric supercapacitor show capacitive characteristics, so its CV curve presents an ideal rectangle, and the GCD curve is a triangle. In contrast, the hybrid supercapacitor shows obvious cathode and anode peaks due to a battery electrode. As a representative study, Fan et al. fabricated an asymmetric supercapacitor employing graphene/MnO₂ composite as the cathode and activated carbon as the anode, with neutral Na₂SO₄ aqueous electrolyte. This energy storage device exhibited a stable operational voltage window of 0-1.8 V, achieving a peak energy density of 51.1 Wh kg⁻¹ while demonstrating remarkable cyclic stability. Notably, the system retained 97% of its initial specific capacitance after 1000 charge-discharge cycles, indicating superior electrochemical durability[26]. A water-based hybrid supercapacitor with NiCo₂S₄@Ni(OH)₂ composite and activated carbon as cathode and anode, respectively, designed by Yang et al., has a high energy density of 53.3Wh kg⁻¹, a high power density of 6420Wh kg⁻¹, and a specific capacitance of 98.8% after 2000 cycles[27].

Among the pseudocapacitive electrode materials, ZnMn₂O₄ has attracted much attention due to its low cost, abundant reserves, and environmental protection[28]. Many research teams have prepared ZnMn₂O₄ by various means, hoping to improve its shortcomings, such as easy powdering, low Coulomb efficiency, and poor electronic conductivity in the reaction process[29]. Zou et al. prepared the ZnMn₂O₄ by a simple one-step surfactant-assisted solvothermal method; the discharge capacity reached 812 mAh g⁻¹ after 200 cycles under a current density of 0.1 A g⁻¹[30]. Moreover, the composite of ZnMn₂O₄ with carbonaceous material can also improve its electronic conductivity, and introducing oxygen ion defects can promote electrochemical activity[31-34].

As a promising electrode material, Zn demonstrates notable merits including cost-effectiveness, eco-friendliness, and exceptional stability in aqueous electrolyte systems. Particularly noteworthy are its superior electrochemical characteristics, exhibiting a high theoretical capacity of 820 mAh g⁻¹

coupled with a favorable standard reduction potential of -0.76 V versus the standard hydrogen electrode (SHE)[35, 36]. Therefore, Zn is suitable for hybrid supercapacitor anode material. It is reported that using $\text{Zn}(\text{SO}_4)_2$ neutral electrolyte effectively solves the problem of low Zn stripping/plating efficiency and improves the cycle life[37-39].

Flexible supercapacitors have become a hot topic. It not only inherits the excellent chemical properties of traditional supercapacitors, such as fast charge and discharge and high output power, but also has the advantages of portability, lightweight, and the ability to maintain its mechanical integrity when bent or folded[40-42]. At present, it has been practiced in the fields of curved or folding screen smartphones, flexible displays, and flexible touch screens[43]. Therefore, exploring new flexible electrode materials and assembling them into flexible supercapacitors will be a trend, widely used in many fields, such as wearable performance source devices, soft robots, motion detection, etc.

In this work, we prepared high-surface-area spinel ZnMn_2O_4 with different Ni doping levels and grew it on carbon cloth by the hydrothermal reaction to produce $\text{ZnMn}_2\text{O}_4/\text{CC}$ (ZMO/CC). We used ZMO/CC as a flexible supercapacitor cathode, Zn/CC as the anode. LiCl, ZnCl_2 and MnSO_4 were dissolved in pure water of polyvinyl alcohol to prepare the polymer electrolyte. We assembled a quasi-solid Zn-MnO_2 flexible supercapacitor. This work will provide new ideas for developing flexible supercapacitors and contribute to developing wearable performance source devices and other fields.

2. Experiments

2.1. Preparation of ZnMn_2O_4

DES was prepared by mixing choline chloride ($\text{C}_5\text{H}_{14}\text{ClNO}$), glycerol ($\text{C}_3\text{H}_8\text{O}_3$) and zinc chloride (ZnCl_2) at a molar ratio of 1:2:0.6 and stirring at 70°C for 2 hours. After stirring 5mL DES with 5mL aqueous solution of 0.5 M KMnO_4 for 10 minutes, the resulting precipitate was centrifuged and filtered. A triple-cleaning procedure was performed with distilled water and anhydrous ethanol, after which the materials were subjected to thermal drying at 80°C for 12 hours to obtain ZMO with high surface area. The Ni-doped ZMO with various doping levels was prepared by adding $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to the hydrothermal reaction. The ratios of $\text{C}_5\text{H}_{14}\text{ClNO} : \text{C}_3\text{H}_8\text{O}_3 : \text{ZnCl}_2 : \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were 1:2:0.5:0.1, 1:2:0.4:0.2, 1:2:0.3:0.3.

2.2. Assembly of Flexible Supercapacitors

The fabrication of Zn/CC composite anodes was achieved using a constant-current electrodeposition method, utilizing an aqueous solution containing 0.5 M zinc sulfate heptahydrate, 1 M sodium sulfate, and 0.3 M boric acid. This electroplating procedure was carried out at room temperature ($25 \pm 2^\circ\text{C}$) with a consistent current density of 40 mA cm^{-2} for 10 minutes. The mass of deposited zinc (8.3 mg cm^{-2}) was measured using a precision balance (BT25S, $\pm 0.01 \text{ mg}$ accuracy). In parallel, ZMO/CC composite cathodes were prepared via a hydrothermal synthesis approach, where 1 cm^2 carbon fabric substrates experienced regulated crystal formation in pressurized reaction vessels.

A quasi-solid-state Zn- MnO_2 energy storage unit was assembled by carefully arranging three key elements: ZMO/CC positive electrode, Zn/CC negative electrode, and a NKK separator membrane (Nippon Kodoshi Corporation), all infused with a custom-designed PVA-derived gel electrolyte. This polymer electrolyte was prepared by sequentially dissolving 3 M lithium chloride (2.54 g), 2 M zinc chloride (5.45 g), and 0.4 M manganese sulfate (5.45 g) in 20 mL of purified water containing 2 g of polyvinyl alcohol, followed by thorough mixing at 85°C for one hour with constant agitation. Before device construction, all electrode components and separators underwent electrolyte immersion treatment and subsequent air-drying to remove excess moisture. The final device was created through

sequential layering and electrolyte solidification, producing robust energy storage units with uniform specifications of 0.5 cm² electrode area and 0.8 mm total thickness.

2.3. Materials and electrochemical characterization

CV, GCD, and EIS tested the electrochemical properties of ZMO/CC and Zn/CC samples and supercapacitors. The electrochemical characterization included CV analysis at a sweep rate of 0.2 mV s⁻¹ and EIS testing with a 5 mV AC signal over a frequency span of 1000 kHz to 10 MHz. Furthermore, the device's operational parameters, such as its current density and capacity per unit mass, were quantified.

3. Results & Discussion

The electrochemical characteristics of Zn/CC anode and ZMO/CC cathode were systematically investigated through cyclic voltammetry and galvanostatic charge-discharge analyses. **(Figure 1a and b)** presents the CV profiles recorded at scan rates spanning from 10 to 500 mV s⁻¹, with defined potential windows of -0.9-0 V (anode) and 0-1 V (cathode). Both electrodes demonstrate progressive current enhancement with increasing scan rates, consistent with faradaic charge storage mechanisms. Subsequent GCD measurements **(Fig. 2a and b)** were conducted under controlled current densities: 1-10 mA cm⁻² for the anode and 0.5-5 mA cm⁻² for the cathode. The Zn/CC anode exhibits near-symmetrical triangular profiles across all tested current densities, confirming its stable coulombic efficiency. In contrast, the ZMO/CC cathode displays minor potential plateaus in GCD curves, attributable to surface-mediated redox processes that maintain electrochemical reversibility. These measurements form the basis for the capacitance calculations summarized in **(Fig. 3a and b)**. **(Fig. 4 a and b)** shows the electrochemical impedance spectra (EIS) from 1000KHz to 0.01Hz for Zn/CC and ZMO/CC, respectively. Electrochemical impedance spectroscopy (EIS) is one of the fundamental techniques for obtaining information about ion diffusion and electron transfer at the electrode surface. The Nyquist plots of anode and cathode materials typically exhibit a semicircular shape. This semicircular pattern reveals the charge transfer and double-layer phenomena occurring at the interface between the electrolyte and the electrode. Electrochemical impedance spectra reveal charge transfer resistance through semicircle diameter measurements, which directly reflects the energy barrier for electrons traversing the electrode-electrolyte boundary. A smaller diameter indicates faster charge transfer kinetics, thereby enhancing the performance of supercapacitors. The charge transport resistance is 26 Ω for Zn/CC and 7 Ω for ZMO/CC.

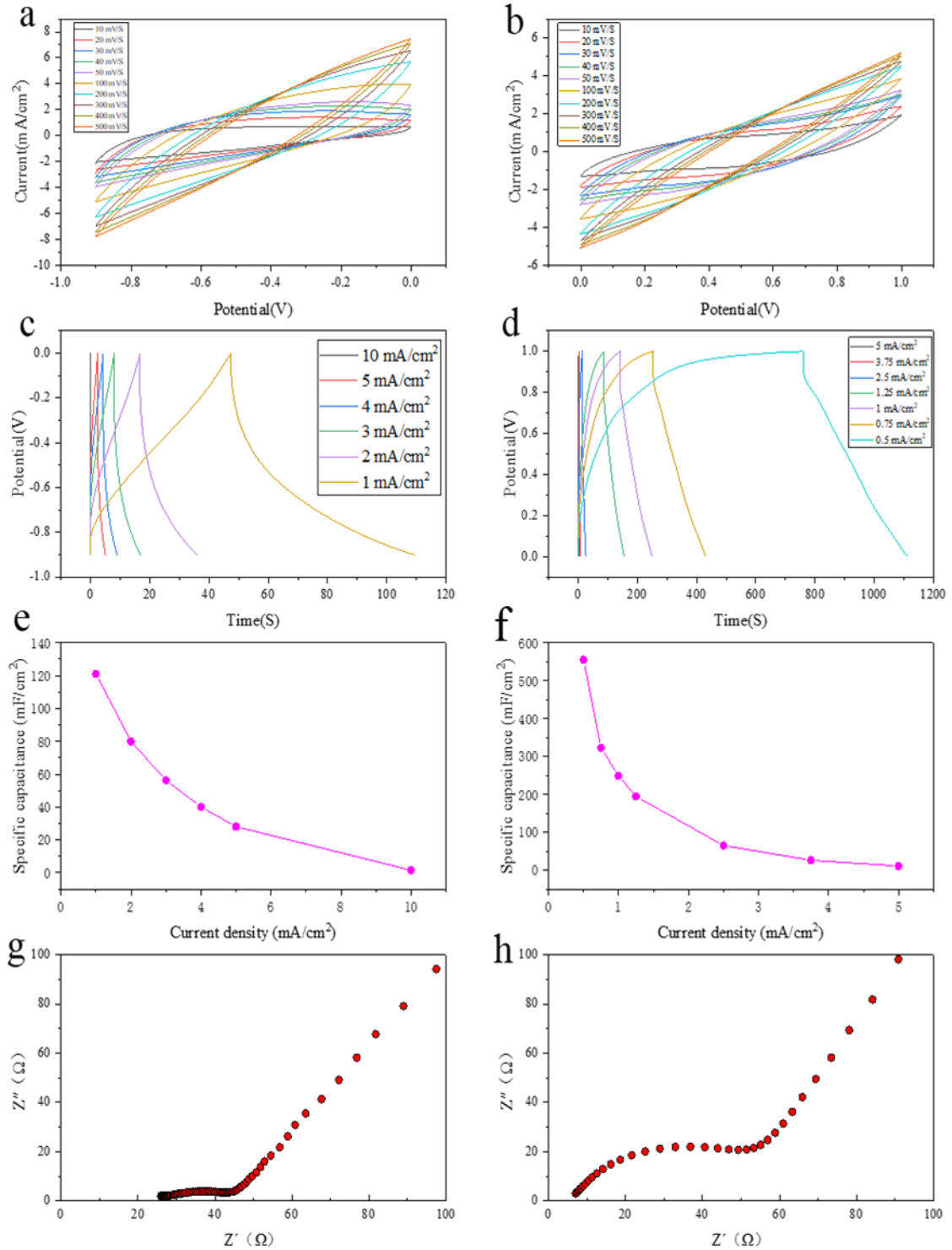


Figure 1: Electrochemical properties of Zn/CC anode and ZMO/CC cathode. (a, b) CV curves at different scan rates ranging from 10 to 500 mV/S. (c, d) GCD curves of the anode and cathode at different current densities and potential windows. (e, f) The areal capacitance with various currents derived from GCD curves. (g, h) Nyquist impedance plot of Zn/CC and ZMO/CC.

4. Conclusion

In conclusion, we have successfully fabricated nickel-doped ZMO spinels with high surface area and demonstrated the application of ZMO/CC composites in flexible non-solid supercapacitors. In our final supercapacitor, the surface area of anode Zn/CC is only 1cm^2 , and the surface area of cathode ZMO/CC is only 4cm^2 , which confirms the portability. The specific capacitance of Zn/CC is 1.5mF cm^{-2} at 10mA cm^{-2} , and that of ZMO/CC is 11mF cm^{-2} at 5mA cm^{-2} . The cathode and anode materials have typical faradaic pseudocapacitive behavior, the anode materials have good coulomb efficiency, ZMO/CC has good electrochemical reversibility, and the charge transport resistance is only $7\ \Omega$. This study shows that ZMO spinel can be used as a Zinc-based supercapacitor with portability and excellent electrochemical performance, which provides a reference for future research of flexible supercapacitors.

In contrast to lithium-ion battery systems, supercapacitors demonstrate compelling advantages in next-generation energy storage applications, primarily due to their unique electrochemical characteristics. The most prominent feature lies in their significantly higher charge/discharge rates (typically 10-100 times faster than lithium batteries), making these devices particularly suitable for scenarios demanding instantaneous energy transfer. This fundamental advantage has driven their successful implementation in automotive regenerative braking systems and IoT-enabled distributed energy networks. Furthermore, SCs exhibit exceptional cycle stability, maintaining over 90% of initial capacitance after 10^6 charge-discharge cycles, a performance metric that surpasses conventional battery technologies by three orders of magnitude. Therefore, although the initial cost of supercapacitors is high, their long life and low maintenance cost can bring long-term economic benefits. Supercapacitors have higher safety and environmental friendliness without thermal runaway. And the supercapacitor can perform well in a wide range of temperatures, which is different from the temperature-sensitive lithium-ion battery. Lithium-ion batteries are now the mainstream market, but now face serious recycling problems, such as complex recycling processes and pollution, compared with supercapacitors, which have a long life and less toxic materials and are easier to recycle.

All in all, supercapacitors have many advantages over Li-ion batteries, the most valuable of which are undoubtedly high power density, long cycle life, and wide temperature range. This makes the supercapacitor more useful in most cases and has more application scenarios. Whether in industry, military, or daily life, it can meet people's needs for high power and long life, such as servers, Bluetooth devices, refrigeration equipment, and so on. The wide temperature range illustrates the low failure rate of the supercapacitor, and even if a failure occurs, it is non-catastrophic and does not produce thermal runaway. Therefore, in the future, supercapacitor is bound to occupy the mainstream position of the market.

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