



High-performance carbon-coated ZnMn₂O₄ nanocrystallite supercapacitors with tailored microstructures enabled by a novel solution combustion method



Mozaffar Abdollahifar^a, Sheng-Siang Huang^a, Yu-Hsiang Lin^a, Yan-Cheng Lin^a, Bing-Yi Shih^a, Hwo-Shuenn Sheu^b, Yen-Fa Liao^c, Nae-Lih Wu^{a,*}

^a Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

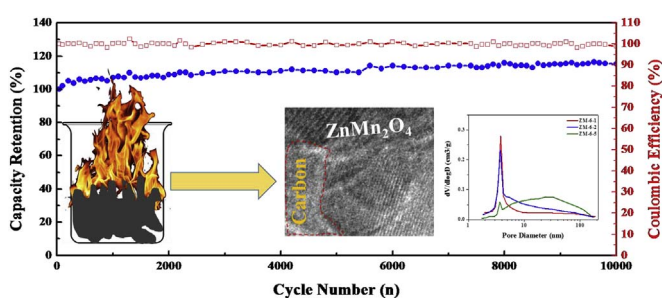
^b National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

^c Taiwan Beamline Office at SPring-8, 1-1-1 Kouto, Mikazuki, Sayo, Hyogo 679-5198, Japan

HIGHLIGHTS

- ZnMn₂O₄ neutral-electrolyte pseudocapacitor is for the first time demonstrated.
- C@ZnMn₂O₄ nanocrystallites are synthesised by modified solution combustion.
- C@ZnMn₂O₄ electrode exhibits ideal capacitor behavior with capacitance of 150 F g⁻¹.
- C@ZnMn₂O₄ electrode shows no capacitance fade after 10,000 cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

ZnMn₂O₄ nanocrystallite
Spinel
Pseudocapacitor
Neutral electrolyte
Solution combustion

ABSTRACT

Although ZnMn₂O₄ is widely studied as Li-ion battery anodes, it remains a challenge to tailor suitable microstructures of the oxide for supercapacitor applications. Carbon-coated ZnMn₂O₄ (C@ZMO) nanocrystallites showing high-performance pseudocapacitor behaviours in neutral aqueous electrolyte are for the first time successfully synthesised via a novel solution combustion process using polyethylene glycol as a multifunctional microstructure-directing agent. Controlling the molecular weight and amount of the polymer in the combustion solution enables the formation of highly-crystalline C@ZMO having substantially higher, by more than 5 folds, specific surface areas with mesoporous structures and conformal carbon coating via the one-pot synthesis process. The resulting C@ZMO supercapacitor electrodes in Na₂SO_{4(aq)} electrolyte exhibit ideal capacitive behaviours with specific capacitances up to 150 F g⁻¹ and cycle stability showing no capacitance fade after 10,000 cycles at 60% of full capacity and > 99% Coulombic efficiency. This study not only illustrates a new powerful synthesis route capable of producing conductive mesoporous crystalline oxide-based nanomaterials for energy storage applications but also reveals a new class of high-performance pseudocapacitive materials for neutral aqueous electrolytes.

* Corresponding author.

E-mail address: nlw001@ntu.edu.tw (N.-L. Wu).

1. Introduction

Supercapacitors (SCs) are currently being developed as high-efficiency and high-power electrochemical energy storage devices for future portable-electronics and electric-vehicle applications. SCs require rapid charge-discharge rates, a long cycle life (> 10,000 cycles), excellent reversibility, low maintenance requirements and high operational safety [1–4]. The electrochemical performance of SCs is strongly related to their electrode-materials' composition, surface area, and porosity [5]. The use of binary metal oxides [6] -particularly spinel structures, represented by AB_2O_4 (containing two transition metals A and B)- as pseudocapacitive electrode materials in SCs has been gaining increasing attention because of their potential superior electrochemical performance as compared with single component oxides because of their multiple available oxidation states and richer redox processes [6].

$ZnMn_2O_4$, having a spinel structure, has been widely investigated for its potential applications as Li-battery anode [7–12] but with only limited investigation for SC [13–16]. Previous studies used strong alkaline electrolytes, and the reported oxide electrodes mostly did not exhibit capacitor, but battery, behaviours. A recent paper by Brousse et al. [17] has clearly pointed out the fundamental differences in capacity-versus-voltage relation between pseudocapacitive materials and battery-like nanocrystallite electrodes. Furthermore, the use of the strong alkaline electrolytes may pose safety concern for practical applications. Being an energy storage electrode material, $ZnMn_2O_4$ has the advantage of nontoxicity, low cost (Table S1, Supporting Information) and high abundance of its raw materials as compared with other spinel (battery-like) electrode materials such as $NiCo_2O_4$ [18,19]. If development of this potential material is to continue, further research will be needed to improve its performance by tailoring its microstructures, such as crystal structure and dimension, surface area, pore structure, and morphology.

Numerous techniques, such as solvothermal [20–23], precipitation [24–28] hydrothermal [7,23], electrospinning [8,29], molten salt [30], sol-gel [31], combustion [15], and other methods [32,33], have been developed for the synthesis of $ZnMn_2O_4$ materials with different microstructures. Among these synthesis methods, the one-pot solution combustion method appears the most favourable because it has an economical high yield with inexpensive precursors, is suitable for large-scale production, requires simple equipment, and allows for a fast reaction to complete crystallisation [34]. However, up to now this technique has been applied mainly to synthesize materials of micron-sized crystallites with low specific surface areas [15,35], and to our knowledge there has been no report on the attempt to control the pore structures of the resulting materials, which are critical for many applications such as catalysis [36], adsorption [37], and SCs [38]. Indeed, effective pore-structure tailoring remains a challenging task to the combustion synthesis because it typically completes within a substantially shorter high-temperature calcination time (a few minutes) than the conventional solid-state calcination processes (hours).

In this work, we demonstrated the success in applying polyethylene glycol (PEG) as an effective multi-functional microstructure modifier to the solution combustion synthesis of nanocrystalline $ZnMn_2O_4$. PEG serves not only as a pore-structure directing agent but also as a precursor for forming a carbon shell on the oxide grains, which in turn assists in inhibiting crystallite growth and enhances the electronic conductivity of the oxide powder. The resulting carbon-coated $ZnMn_2O_4$ (C@ZMO) composite powders containing highly crystallized nanocrystallites with conformal carbon coating and differently distributed pore structures and exhibiting outstanding pseudocapacitor performance in aqueous neutral electrolyte were obtained. Both the microstructures and electrochemical properties pertaining to the SC application were characterized in detail.

2. Materials and methods

2.1. Materials

Manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$), sodium sulphate (Na_2SO_4) and urea ($CO(NH_2)_2$) were obtained from Sigma-Aldrich. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and PEG polymers with two different molecular weights, including 200, designated as PEG-200, and 6000, as PEG-6000, were from Alfa-Aesar. All the chemical materials used in this study were analytical grade and used as received without further purification.

2.2. Solution combustion

The solution combustion process typically proceeded as follows. First, a selected amount of PEG was dissolved in 40 mL of distilled water at room temperature in a beaker and stirred to obtain a homogeneous solution (A). Then, a 60 mL aqueous solution of $Mn(NO_3)_2$ and $Zn(NO_3)_2$ with a Mn/Zn molar ratio of 2 was added to the solution (A) dropwise and the resulting solution was stirred to form a homogeneous solution (B) at room temperature. Next, a 40 mL aqueous solution of urea was added to solution B so that the urea/nitrate molar ratio was 1.2. Magnetic stirring (800 rpm) was performed throughout the entire process and for a further 10 min afterward. The mixed solution was transferred into a 500 mL beaker and placed on a preheated muffle furnace at $370 (\pm 10) ^\circ C$. At this temperature, evaporation of the solvent first produced a voluminous and fluffy gel, which was obtained within 20 min. The gel began to boil and in a few minutes ignited, with rapid evolution of a large amount of gas. The entire combustion (“burning”) process lasted for only a few minutes. The final brown–black product was collected and washed several times using distilled water. Finally, the samples were dried at $150 ^\circ C$ for 10 h in a vacuum oven.

2.3. Material characterization

Nitrogen adsorption–desorption isotherms were obtained using a Micromeritics ASAP-2020 after the samples were degassed at $200 ^\circ C$ for 12 h. The Brunauer–Emmett–Teller (BET) equation [39] and Barrett–Joyner–Halenda (BJH) method [40] were utilised to obtain the specific surface area and pore size distribution (PSD) of the synthesised samples. Scanning electron microscopy (SEM; JSM-7600F, JEOL) was employed to investigate the morphology of the samples. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed using the JEOL JEM- 1200EX II and FEI Tecnai TF20, Philips, respectively. Thermogravimetric analysis (TGA) was performed by heating the samples in an air flow at a rate of 100 mL min^{-1} using a Perkin-Elmer Diamond TGA-DTA thermal analyser with a heating rate of $10 ^\circ C \text{ min}^{-1}$. Raman spectroscopy was performed using the UniG2D, UniNano Tech. Operando XRD analysis was performed using Ti mesh as the current collector and by placing the electrode in an acrylic cell. The two sides of the cell were perforated and sealed using Kapton foils to allow the probing beam to pass through the cell. Measurements were carried out using beamline 01-C2 at the National Synchrotron Radiation Research Center in Taiwan and BL12B1 at the SPring-8 facility in Japan. Approximately 15 s of X-ray beam exposure time was necessary to acquire a single XRD pattern. The scan rate was 2 mV s^{-1} . For operando study, the XRD patterns were continuously acquired when the electrode was under cycling [41]. All XRD patterns shown were converted to a wavelength of 1.5405 \AA using Winplotr software.

2.4. Electrochemical characterizations

Electrodes were prepared from *N*-methyl-2-pyrrolidone (NMP) based slurries comprising 80 wt% active material (C@ZMO), 10 wt% conductive carbon additives, including 5 wt% Super P (Timcal) and

Download English Version:

<https://daneshyari.com/en/article/7726168>

Download Persian Version:

<https://daneshyari.com/article/7726168>

[Daneshyari.com](https://daneshyari.com)