Electrochemical deposition of $ZnCo_2O_4$ nanosheets on Ni foam for supercapacitor applications

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ABSTRACT: This study describe the method of electrochemical deposition to create $ZnCo_2O_4$ supported on nickel foam for capacitor applications. Using scanning electron microscopy (SEM) and other electrochemical methods to of sample materials demonstrates the nanostructure and chemical performance of substances grown on Ni foam. The as-prepared samples are directly applied in supercapacitors to improve charge-discharge performance and the ability of save electric energy.

KEYWORD: Electrochemical deposition, $ZnCo_2O_4$ nanosheets, supercapacitor

1 INTRODUCTION

With the deterioration of the environment and the depletion of conventional energy source, development of clean and high-efficiency energy storage systems (lithium ion batteries, electrochemical supercapacitors, Ni-H batteries, etc.) has been put forward. Recently, supercapacitors (or electrochemical capacitors) have attracted great attention due to their higher power densities, faster charge–discharge rates, longer cycle lifetimes and lower costs than conventional rechargeable batteries, and have shown great promise in the fields of uninterruptible power supplies, hybrid electric vehicle systems, aerospace, emergency lighting, and renewable energies. Although there are some advanced methods such as typical coprecipitation, hydrothermal synthesis, high-temperature calcinations of hydroxide or carbonate precursor mixtures and electrochemical deposition in the development of SCs, the practical applications of SCs are still largely inhibited because of the shortage of suitable electrode materials. Therefore, the most critical task for improving SCs is to explore electrode materials with high capacity, long cycle life, friendly to environment and low costs unlike RuO2 based materials.

Recent studies have shown that binary metal oxides such can exhibit better electrochemical performances than single-component metal oxides due to their higher electron conductivities and richer redox reactions. A typical example is ZnCo2O4 (that is Zn-ions occupy the tetrahedral sites in the cubic spinel and the trivalent Co-ions occupy the octahedral sites) with a spinel structure, which has been investigated for application in the areas of Li-ion batteries, electrocatalysts, gas sensors, etc. Nevertheless, reports on ZnCo2O4 materials as electrodes for supercapacitors are yet limited. Very recently, Shen et al. first reported the fabrication of ZnCo2O4 porous nanorods/nickel foam architectures through a polyol refluxing process followed by thermal treatment, which with good capacitive behavior. Zhou et al. prepared ZnCo2O4 porous nanotubes using an electrospinning technique followed by calcination and obtained a specific capacitance of 770 F/g at 10 A/g and good cycle stability. The particle size of ZnCo2O4 usually range from $0.1–1cm^2$ with high surface area. However, the electrode materials were mostly synthesized using hard templates, surfactants or long-chain polymers, making the synthesis process complicated. To the best of our knowledge, studies on the ZnCo2O4 nanosheets electrode materials for SCs are limited.

Also, the electrochemical deposition technique can be considered as an alternative, which tailoring a thin layer of electrode architecture on the current collector for electrical capacitor (EC) application. It has wide range of advantages such as easy to set up, available for large area deposition and requires low operation temperature, which uses less energy and has high execution. Therefore, we use electrochemical deposition technique to fabricate ZnCo2O4 nanosheets. Plus, the solution of Zn(NO3)2·6H2O (0.005 mol), Co(NO3)2·6H2O (0.01 mol) and KCl (0.005 mol) is easy to obtain and we can alternate the structure of ZCO nanosheets by controlling the contents of solute without complex operations and toxic substances.

Herein, we report a cost-effective and simple route for direct growth of ZnCo2O4 composite nano-sheets materials by an electrochemical deposition process on a porous Ni foam (with approximately 1×1cm2), and their application as a binder-free electrode for high-

performance supercapacitors. The unique shell nanostructure is expected to deliver exceptional electrochemical performance.

2 EXPERIMENTAL

2.1 *Material preparation and synthesis of ZnCo2O4 nanosheets arrays on Ni foam.*

All the reagents for synthesis and preparation were of analytic grade and used as received without further purification. Nickel foam (NF) (approximately 1×1cm2) is cleaned with acetone solution every 15 min for three times to remove the oil layer, then rinsed with deionised water in an ultrasound bath every 5 min for three times which need to change deionised water every time, and cleaned with concentrated HCl solution for 15 min in order to remove the NiO layer and the acetone on the surface. After that, rinsed with deionised water and anhydrous alcohol again, and then dried at 80℃ for 12 h. The electrochemical deposition is performed in a standard three-electrode glass cell consisting of the Ni foam as working electrode, a platinum plate as counter electrode, and a saturated calomel reference electrode (SCE). In a typical process, Zn(NO3)2·6H2O (0.005mol), Co(NO3)2·6H2O (0.01mol) and KCl (0.005mol) are first dissolved in 50ml of DI water and the solution is mixed well at room temperature. And then the working electrode is dipped into the solution and a potential of −1.1 V (vs SCE) is applied for 200 s, 400 s and 600 s to achieve different thicknesses of ZCO. Every two pieces of Ni foam are as for a group, and a similar experimental procedure was followed to grow ZCO nanosheets on Ni foam for 400 s and 600 s using other groups. After electrochemical deposition, the Ni foam coated the bimetallic (Zn, Co) hydroxide precursor was then dried in an oven at 80℃ overnight to remove the residue water and ethanol and then followed by sintering at 300°C for 12 h in a muffle furnace. After 12 h of sintering, the green colored thin film samples were converted to a black colored film. A diagram of the database are shown in table 1.

Table 1 Mass of the sediment at different time.

t/s	200	400	600
Mass/mg (1)	0.6	1.0	0.95
Mass/mg (2)	0.7	0.8	1.7
Specific capacitance (F/g)	243	488	354

2.2 *Material characterization.*

In order to examine the characteristics of the materials, the morphology and elemental composition of the as-prepared ZCO sample was confirmed by a powder X-ray diffractometer (Bruker D8 Advance X-ray diffractometer) under Cu K_α radiation (λ=1.54184 Å) and scanning electron microscope (SEM, JEOL, JSM-7800F) with an energy dispersive spectrometer (EDS).

2.3 *Electrochemical measurements.*

The samples with sediment on Ni foam should be performed in a three-electrode electrochemical cell in 2.0M aqueous KOH solution where platinum electrode served as the counter electrode and calomel normal electrode as the reference electrode using electrochemical station. The nominal area of the ZnCo2O4-Ni foam immersed into the electrolyte is controlled to be around 1×1 cm2. The mass loading of the ZnCo2O4 mesoporous nanosheets on Ni foam is around 0.7~1.2 mg/cm2. Amperometric curve (It), cyclic voltammetry (CV), charge–discharge (CD), electrochemical impedance spectrum (ZK) and are conducted to measure the electrochemical performance of these two electrodes. The specific capacitance (C), energy density(E), and power density (P) are calculated by these formulas offered next.

$$C = \frac{\int i \times d\Delta u}{v \times \Delta u \times m}$$

$$C = \frac{i \times t}{\Delta u \times m}$$

$$E = \frac{1}{2} \times C \times \Delta u$$

$$P = \frac{E}{t}$$

in which, Δu , v , i, m, t are the potential difference (V), the voltage sweep rates (mV/s), the discharge current density (A/g), quality of materials (g), and discharge time (s), representatively.

For CV and CD measurements, all the electrodes were dipped in 2.0M aqueous KOH solution and carried out at different scan rates and different current densities to keep the potential window 0.8 V is selected to observe the oxidation and reduction peak positions at room temperature. For cycle stability test, the as-prepared electrode is tested under current density of 5 A/g in 2000 charge/discharge cycles to measure the capacitive characteristics of the sample. Furthermore, plotting the EIS spectrum of samples.

3 RESULT AND DISCUSSION

3.1 *TEM study.*

The SEM images of Ni foam coated with ZCO electrode material, which deposit in 10 min is shown in Fig. 1. The inset image revealed the presence of a porous region in the deposited ZnCo2O4 layer on the Ni foam. The porous structure has a tendency to enhance the cation pathway into the electrode matrix and result in high capacitive performance.
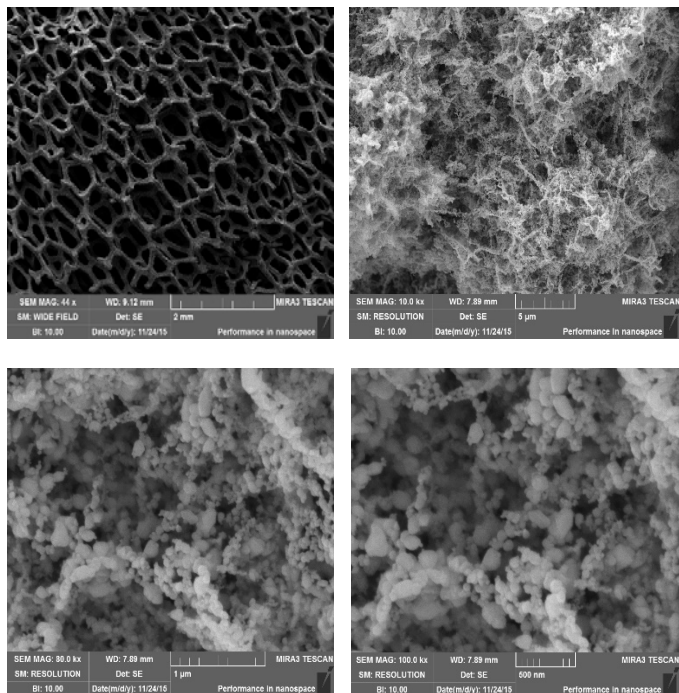
Fig.1.SEM images of deposited films from deposition solution of Zn(NO3)2·6H2O (0.005mol), Co(NO3)2·6H2O (0.01mol) and KCl (0.005mol) during 200s on nickel foam.

3.2 *Electrochemical study.*

The electrochemical studies were performed by cyclic voltammetry and charge–discharge measurements in 2 M aqueous KOH solution with the help of a three electrode configuration. From the cyclic voltammetry (CV) curves, the capacitance was calculated implementing the following formula (for a three electrode configuration):

$$C_{sp}^{CV} = \frac{\oint I(V)dV}{mr^2(V_f - V_i)} \qquad (1)$$

where C_{sp}^{CV} are the specific capacitances from the cyclic voltammetry measurements respectively, *I(V)dV* is the area under the cyclic voltammetry curve, m is the mass of the sample drop-cast on the GCE surface, r is the scan rate, s is the slope of the discharge curve and $V_f - V_i$ is the working potential window. Similarly, the energy density (E_d and power density (P_d) were calculated using the following equations (eqn (2) and (3)):

$$E_d = \frac{1}{2}C_{sp}^{CV}(V_f - V_i)^2 \qquad (2)$$

$$P_d = \frac{1}{2}C_{sp}^{CV}(V_f - V_i)r \qquad (3)$$

According these formulations, we can see that we the sample of 200's has low capacity of charge and discharge, which is 243F/g lower than 500 F/g at current density 0.005 mV/s. Sample of 400s' is 488 F/g lower than 1000 F/g at current density 0.005 mV/s.

Sample of 600s' is 354 F/g lower than 500 F/g at current density 0.005 mV/s. Suggesting that the capability of such sample still need to be improved.
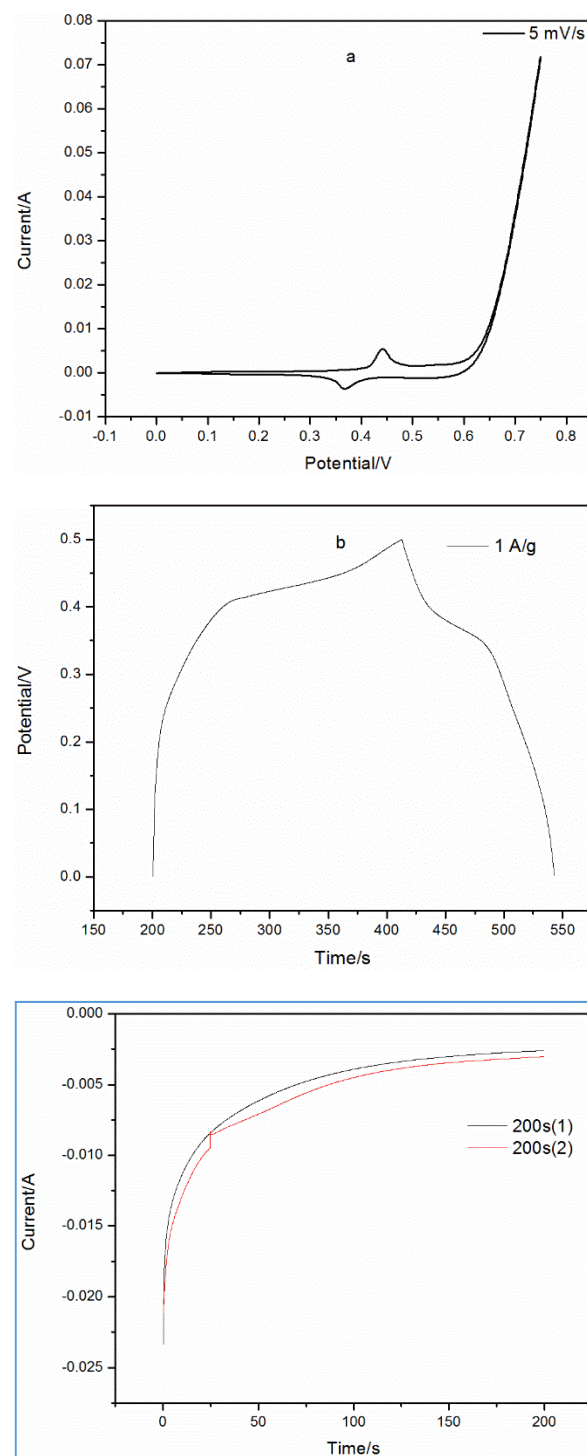

Fig.2.Sample of 200s'. (a)CV curves for composite electrodes at scan rate of 5 mV/s (inset: graph of specific capacitance calculated from Eq. versus concentration of cobalt ions), (b) CD (charge-discharge) profiles for composite electrodes at current density of 1 A g-1 (inset: graph of specific capacitance calculated from Eq. versus concentration of cobalt ions), (c) Amperometric curves (IT) for composite electrodes.

Although the CV curves of the ZnCo2O4 electrode obtained at different scan rates of 5–100 mV/s (Fig. 3a) were not perfectly symmetric, they were of nearly

perfect mirror-image shapes, indicating that the electrode had an ideal pseudocapacitance behavior with a much enhanced high rate capability in comparison with the 200s', especially the curve at scan rate of 100 mV/s. (Fig. 3b) shows the CD curves of sample measured at different current densities from 1 to 10 A/g. According the curves, we can see two regions. (i) One region corresponds to the potential below almost 0.1 V where the potential curves vary almost parallel to the Y-axis, which suggests pure double-layer capacitance behavior from the charge separation on the electrode/electrolyte interface. (ii) The other one has sloped curves between 0.1 and 0.4 V, electrochemical adsorption/desorption or a redox reaction originating specific pseudocapacitance possibly on the electrode/electrolyte interface.
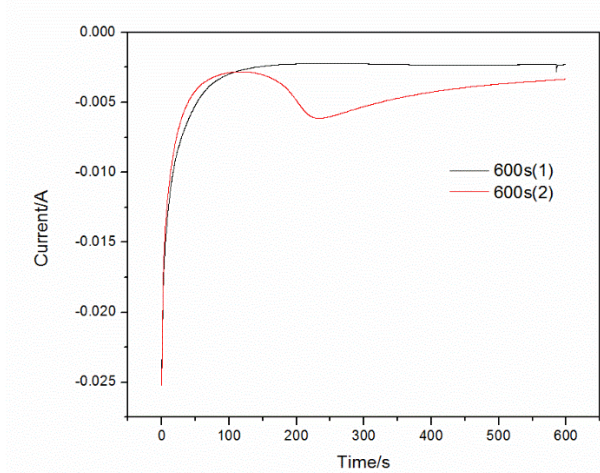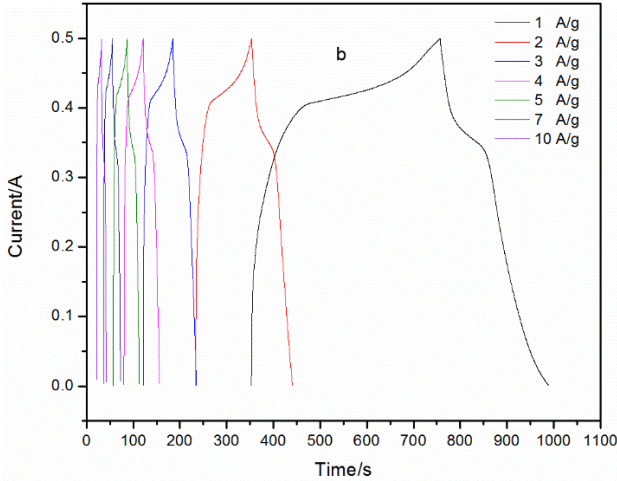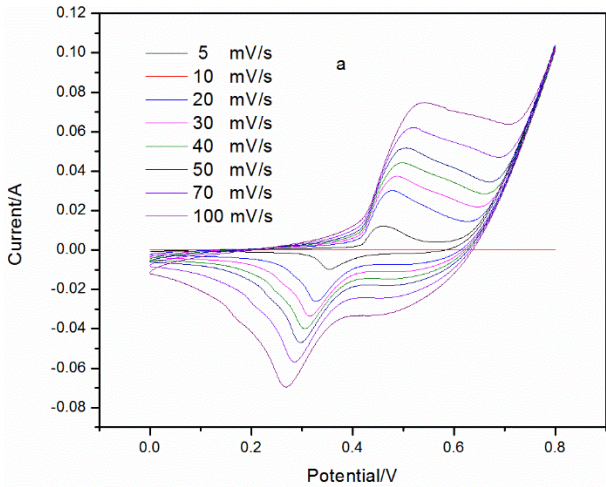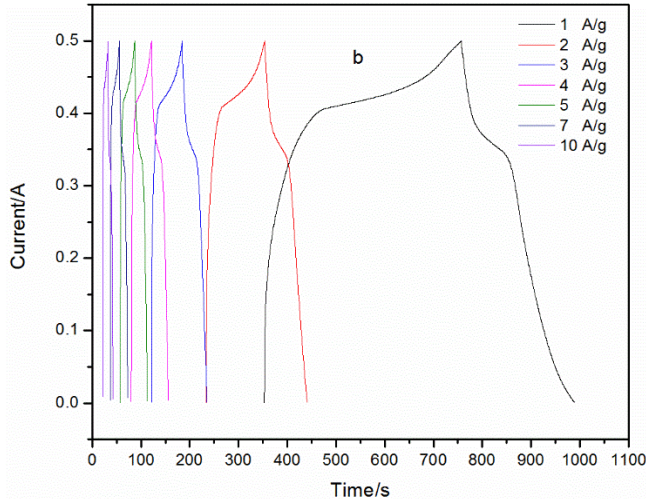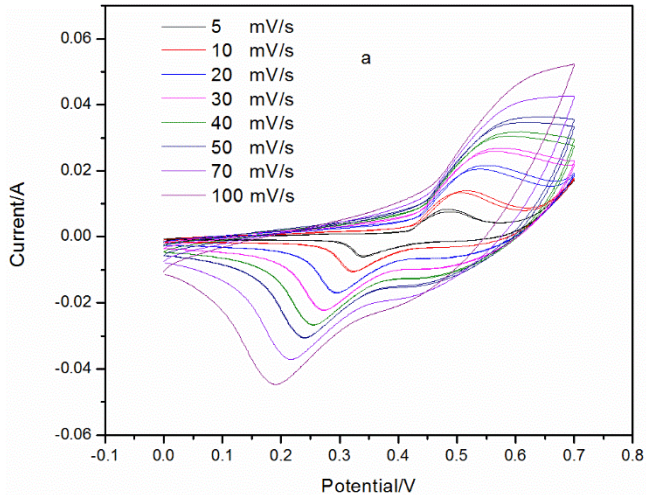

Fig.3.Sample of 400s'. (a)CV curves for composite electrodes at different scan rates of 5, 10, 20, 30, 40, 50, 70 and 100 mV/s (inset: graph of specific capacitance calculated from Eq. versus concentration of cobalt ions), (b) CD (charge-discharge) profiles for composite electrodes at current density of 1, 2, 3, 4, 5, 7 and 10 A/g(inset: graph of specific capacitance calculated from Eq. versus concentration of cobalt ions), (c) Amperometric curves (IT) for composite electrodes.

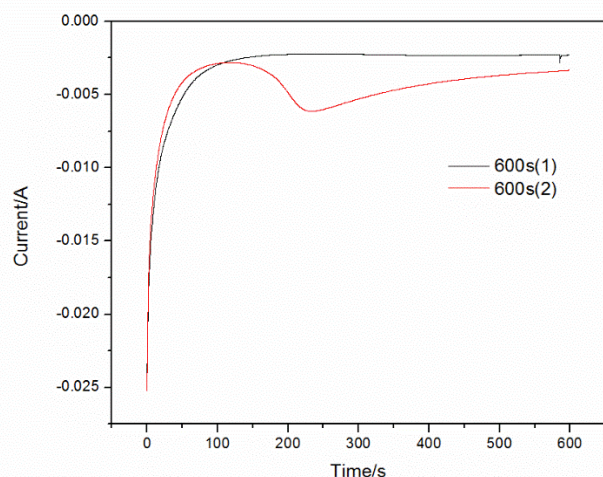Fig.4. shows a similar situation with Fig.3.

Fig.4. Sample of 400s'. (a)CV curves for composite electrodes at different scan rates of 5, 10, 20, 30, 40, 50, 70 and 100 mV/s (inset: graph of specific capacitance calculated from Eq. versus concentration of cobalt ions), (b) CD (charge-discharge) profiles for composite electrodes at current density of 1, 2, 3, 4, 5, 7 and 10 A/g (inset: graph of specific capacitance calculated from Eq. versus concentration of cobalt ions), (c) Amperometric curves (IT) for composite electrodes.

Fig.5. shows the stability of samples, which shows it dose not have high stability. It is obvious that the slot changes after 100 cycles and it ends ant 40s instead of almost 100s, which far outweigh our expectation.
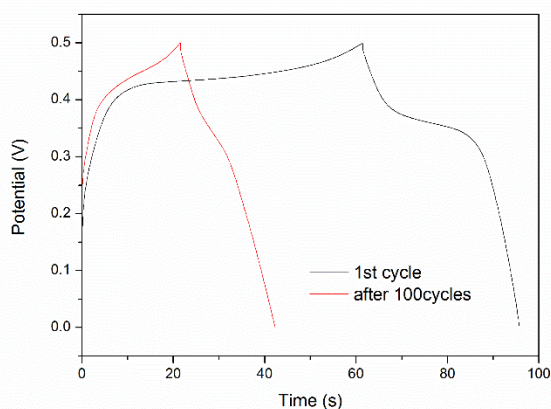

Fig.5. Cyclic stable tests of 1st cycle versus after 100 cycles.

4 CONCLUSION

In summary, we try to demonstrate the rational design and fabrication of meso/macroporous $ZnCo2O4$ nanosheets on a 3D Ni foam substrate using an electrochemical approach. From references, the supercapacitor electrode made from the $ZnCo_2O_4$ exhibited exceptional electrochemical performance in terms of specific capacity, cyclic stability and rate performance, which are much better than conventional electrodes. However, the samples from our tests have limited performance in specific capacity, cyclic stability and rate performance. We find three reasons. (i) We cannot prove the samples we made are pure ZCO. It is probable mix some impurities when testing or creating some unknown substances when reacting. We still need next steps to prove the speculation. (ii) The time of electrochemical reaction is inappropriate, which lead the mass of ZCO are not suitable for the supercapacitors. (iii) The raw materials are inappropriate for this approach, which lead to the low efficiency of tests. To prove these problems and produce a kind of materials of ZCO to improve the capability of supercapacitor applications still need a number of efforts.

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