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Research Article

Investigation of Flower-like $ZnCo_2O_4$ Nanowire Arrays Growth on 3D-Ni Foam as Supercapacitor Electrode Material

Fatma Nur TUZLUCA YEŞİLBAĞ[1*]

[1] Department of Physics, Erzincan Binali Yıldırım University, Erzincan 24100, Turkey

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Abstract

As a supercapacitor electrode material, flower-like $ZnCo_2O_4$ nanowire (NW) arrays were directly grown on 3D-Ni foam using the hydrothermal method. Structural and morphological analysis of the electrode material was characterized by XRD, FE-SEM, and EDS, while its electrochemical analysis was characterized by CV, GCD, and EIS. The electrode material demonstrated excellent electrochemical performance with a maximum areal capacitance of 1.01 F cm^{-2} at a current density of 0.5 mA cm^{-2}. After 2.000 charge-discharge cycles, the electrode showed excellent cycle stability, having 72% of the initial areal capacitance.

Keywords: $ZnCo_2O_4$ nanowire, supercapacitor, Ni foam and hydrothermal method.

Süperkapasitör Elektrot Malzemesi Olarak 3D-Ni Köpük Üzerinde Büyüyen Çiçek-Benzeri $ZnCo_2O_4$ Nanotel Dizilerinin Araştırılması

Öz

Bir süperkapasitör elektrot malzemesi olarak, çiçek benzeri $ZnCo_2O_4$ nanotel (NW) dizileri hidrotermal yöntem kullanılarak doğrudan 3D-Ni köpük üzerinde büyütülmüştür. Elektrot malzemesinin yapısal ve morfolojik analizi XRD, FE-SEM ve EDS ile karakterize edilirken elektrokimyasal analizi ise CV, GCD ve EIS ile karakterize edilmiştir. Elektrot malzemesi, 0,5 mA cm^{-2} akım yoğunluğunda maksimum 1,01 F cm^{-2} 'lik alansal kapasitans ile mükemmel bir elektrokimyasal performans göstermiştir. 2,000 şarj-deşarj döngüsünden sonra elektrot, başlangıçtaki alansal kapasitansın % 72'sine sahip olarak mükemmel bir döngü kararlılığı sergilemiştir.

Anahtar Kelimeler: $ZnCo_2O_4$ nanotel, süperkapasitör, Ni köpük ve hidrotermal metot.

1. Introduction

Supercapacitors (Ultracapacitors or electrochemical capacitors), which have high power density, long cycle life, high reversibility and fast charge-discharge ratio compared to batteries, are the focus of researchers for new generation electrochemical energy storage applications. Supercapacitors are investigated in two different ways, based on energy storage mechanisms: electrical double layer capacitors (EDLC) and pseudocapacitors. In EDLCs, energy is stored by ionic charge separation from the electrode and electrolyte interface, while in pseudocapacitors energy is stored by a reversible redox reaction between the electrolyte and electroactive sites on the electrode surface (Lv et al., 2017; Huang et al., 2015; Wang et al., 2014; Zhao et al., 2017). Since the electrode materials largely determine the performance of the supercapacitors, the improvements made with these materials also affect the performance positively. For example, the nanostructures of the electrode surface increase both the surface area and the electrochemically active states, as well as shorten ionic diffusion pathways (Lin et al., 2016; Zhao et al., 2020). Furthermore, the electrode material being in a composite structure not only improves conductivity but also increases the stability of the structure (Chen et al., 2014; Xie et al, 2018). Three-dimensional (3D) structures such as reduced graphene oxides, carbon nanotubes, carbon-based materials, conductive polymers and various metal oxides are investigated for new generation energy storage devices (Moon et al., 2017).

Recently, both theoretical specific capacitance and electrochemical performance of AB_2O_4 type binary transition metal oxides such as $ZnCo_2O_4$ are found to be much better than single component transition metal oxides such as Co_3O_4 (Rajesh et al. 2017; Wang et al., 2019; Wu et al., 2015). These binary transition metal oxides, which are rich in electrochemical activity and redox reactions due to their chemical composition, have been found to have good electrical conductivity as well as low activation energy for electron transfer between multiple cations (Mohamed et al., 2013; Liu et al., 2012; Rajesh et al. 2017; Wu et al., 2015).

In this study, due to the contribution of Co cations to high capacity, Zn cations to electron transport and advantages of variable oxidation states, flower-like $ZnCo_2O_4$ nanowire arrays on 3D-Ni foam were successfully synthesized and structural and electrochemical analyzes were performed.

2. Material and Methods

First of all, to remove the native oxide layer on the surface the Ni foam, it was cleaned in ultrasonic cleaner for 1 M HCl (50 ml) ultra-pure water, ethanol 15 min respectively (Figure 1).

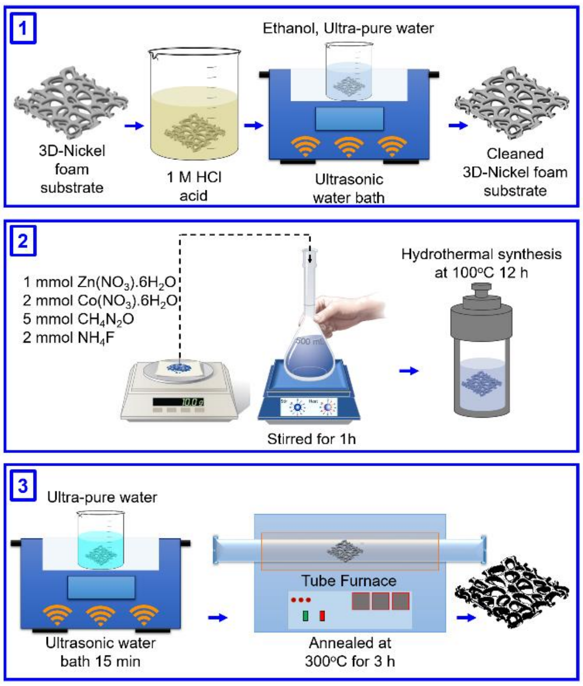

Figure 1. Schematic illustration synthesis of flower-like $ZnCo_2O_4$ NW arrays on 3D-Ni foam substrate.

A stainless steel autoclave with Teflon-lined was used for hydrothermal synthesis. 3D-Ni foam was also placed in this autoclave together with the solution consisting of $Zn(NO_3).6H_2O$, $Co(NO_3).6H_2O$, CH_4N_2O, and NH_4F such that 1, 2, 5 and 2 mmol were respectively. The autoclave, which was heated at 100°C for 12 h, was allowed to cool down to room temperature. After growth, the sample was placed in ultra-pure water for 15 min to remove the excess material that is not in contact with the sample surface and subjected to ultrasonic bath treatment. Then the sample was annealed in tube furnace for 3 h in a 300°C air environment (Figure 1). So that, large-scale vertically aligned flower-like $ZnCo_2O_4$ NW arrays were successfully synthesized on the 3D-Ni foam hydrothermal method.

3. Resarch Findings

The crystal structures and morphologies of the $ZnCo_2O_4$ NW arrays were characterized by using the PANalytical Empyrean X-ray Diffraction device with Cu-Kα, λ = 1.54060 Å, Field Emission Scanning Electron Microscope with FEI Quanta 450 FEG, and EDAX energy Dispersion X-ray Spectroscopy. Gamry Reference 1010E potentiostat device was used to determine the electrochemical performance analysis by Cyclic Voltammetry, Galvanostatic Charge-Discharge and Electrochemical Impedance Spectroscopy.

All electrochemical measurements were tested in a three-electrode electrochemical test cell, 1 M potassium hydroxide aqueous electrolyte solution and at room temperature. During these measurements, 2×1 cm^2 platinum foil was used as the counter electrode, Ag/AgCl as the reference electrode and 2×1 cm^2 flower-like 3D-Ni@ $ZnCo_2O_4$ NW arrays as the working electrode.

Equation (1) was used to calculate the areal capacitance (C):

$$C = \frac{Ixt}{AxV} \quad (1)$$

The symbols in this equation were expressed as; *I*: Constant discharge current, *t*: Discharge time, *V*: Potential window, *A*: Electrode area

In Figure 2, XRD diffraction pattern of flower-like 3D-Ni@ $ZnCo_2O_4$ NW arrays measured at 10° - 80° range were illustrated. Diffraction peaks can be indexed as spinel structured $ZnCo_2O_4$ (JCPDS card No. 23-1390) (Ratha et al., 2015; Zhang et al., 2016).

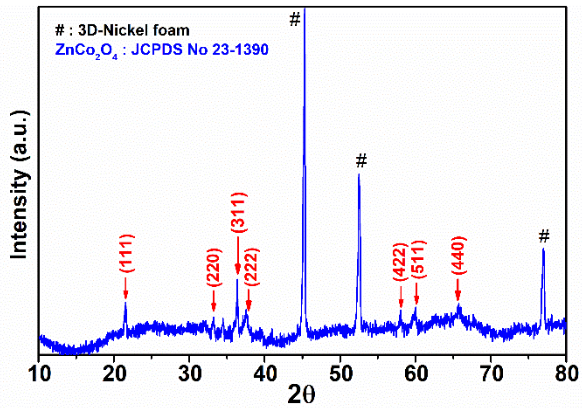

Figure 2. XRD pattern of flower-like 3D-Ni@ $ZnCo_2O_4$ NW arrays.

Figure 3 shows the FE-SEM images and EDS analysis of the morphology of flower-like $ZnCo_2O_4$ NW arrays. As seen in figure, flower-like $ZnCo_2O_4$ NW arrays have grown onto the 3D-Ni foam surface densely and uniformly. The purity and composition of the flower-like $ZnCo_2O_4$ NW arrays was further confirmed by EDS analysis. As seen in the EDS spectrum, there are no impurities other than the presence of Zn, Co, O and Ni elements.

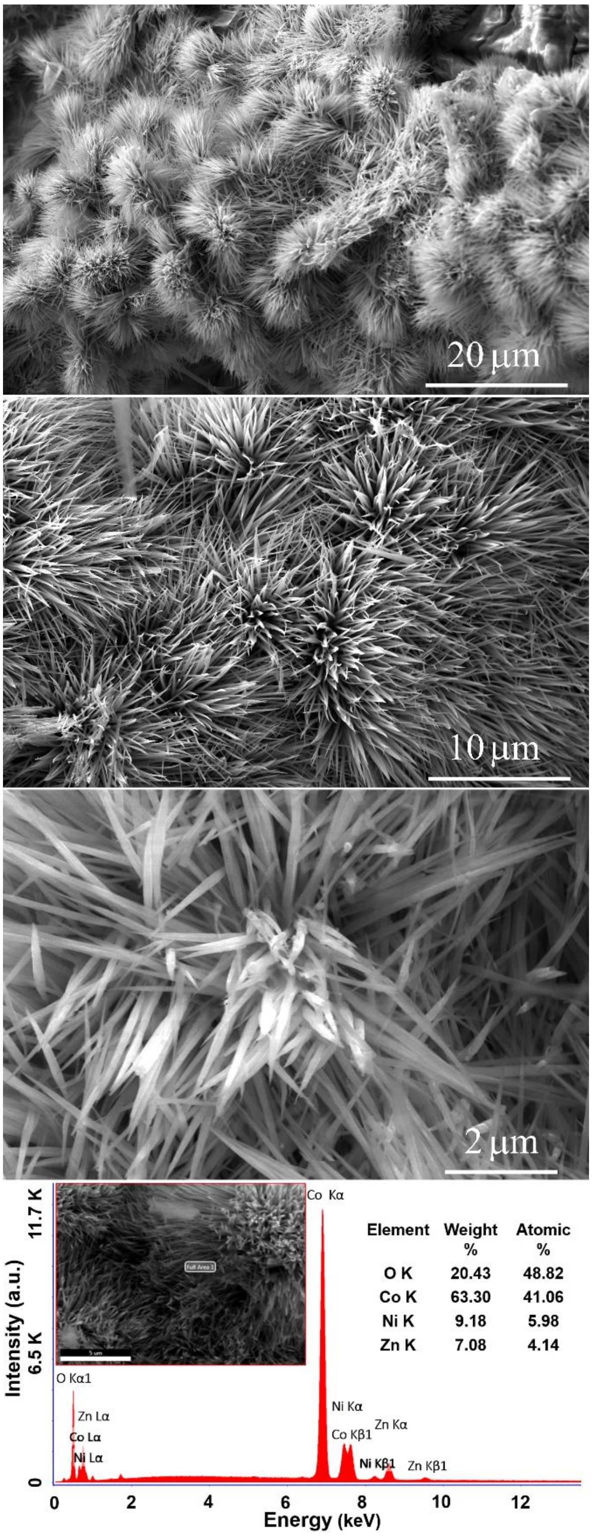

Figure 3. FE-SEM images and EDS analysis of flower-like 3D-Ni@ $ZnCo_2O_4$ NW arrays.

According to EDS analysis, the atomic contents of Zn, Co, O and Ni are 4.14% and 41.06%, 48.82% and 5.98% respectively.

Electrochemical properties of the flower-like 3D-Ni@ $ZnCo_2O_4$ NW arrays are given in Figure 4-8. In Figure 4, the CV curves of the electrode measured at various scan rates ranging from 5 to 100 mV s^{-1}. It can be seen that the CV curves of the electrode have two redox peaks, which reveal that capacitive characteristics of this electrode.

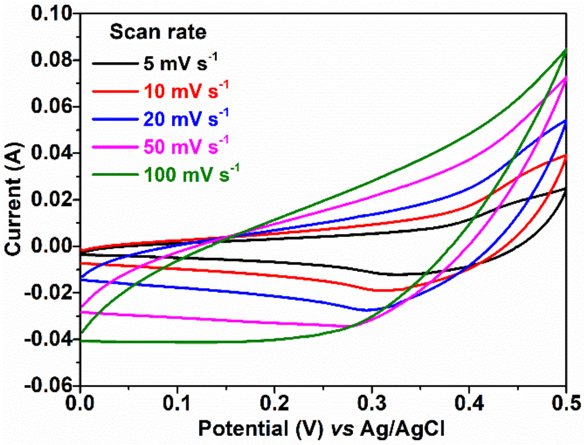

Figure 4. The CV curves at different scan rates.

GCD measurement data for calculating the areal capacitance of the 3D-Ni@ $ZnCo_2O_4$ NW arrays electrode is given in Figure 5. Measurements for these GCD curves were carried out in the potential range of 0 to 0.4 V, suitable for the electrolyte at various current densities from 0.5 to 10 mA cm^{-2}.

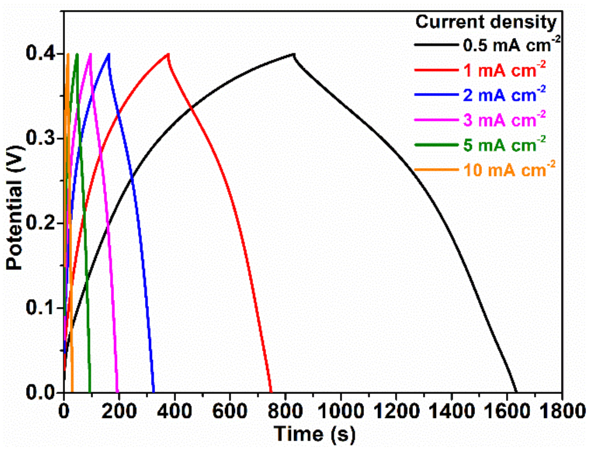

Figure 5. The GCD curves at different current densities.

According to equation (1), the areal specific capacitances of the electrode have been calculated to be 1.01, 0.94, 0.83,0.75, 0.63 and, 0.43 F cm^{-2} at current densities of 0.5, 1, 2, 3, 5 and, 10 mA cm^{-2} respectively (Figure 6). As can be seen Figure 6, as current density increases, areal capacitance decreases. This indicates the loss of efficiency of the active material at the electrode at high current densities.

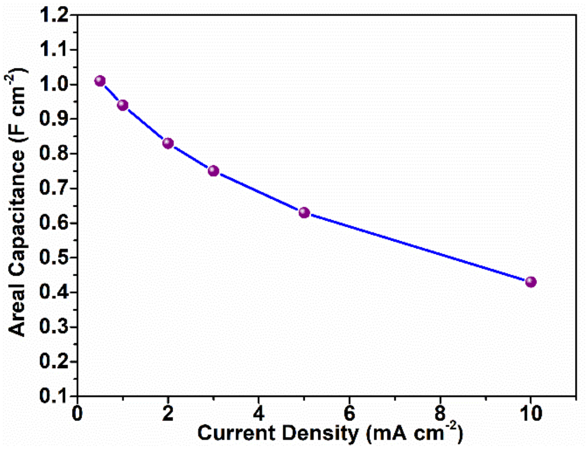

Figure 6. The areal capacitance vs. different current density.

Nyquist plots and equivalent circuit for EIS measurement of the electrode are given in Figure 7. In Figure 7, where the values of the parameters in the circuit are included, it is seen that the equivalent circuit is compatible with the experimental data. The value where the curve crosses the Z' axis at high frequency indicates the R_s series resistance, that is approximately 1 Ω, resulting from the solution resistance in the electrolyte. The slope of the low frequency curve shows the constant phase element (CPE), which indicates that electrolyte ions are diffused to the surface of the electrode. The charge transfer resistance value obtained from the equivalent circuit was found to be 1.22 Ω.

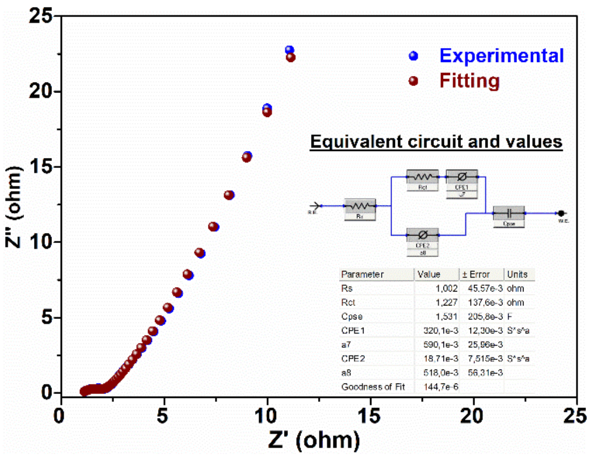

Figure 7. The EIS spectrum, equivalent circuit, and values.

In addition, in Figure 8, the cycle stability of the flower-like 3D-Ni @ $ZnCo_2O_4$ NW arrays electrode at a current density of 10 mA cm^{-2} is given. As seen, the electrode has 72% of the initial areal capacitance after 2.000 charge-discharge cycles.

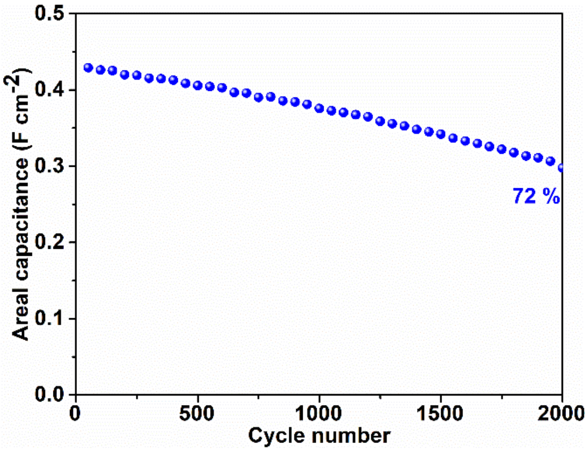

Figure 8. Cycle stability of electrode at a current density of 10 mA cm^{-2}.

4. Results

As a result, the areal capacitance of 3D-Ni@flower-like $ZnCo_2O_4$ NW arrays electrode, which was synthesized quite efficiently and successfully by hydrothermal method and subsequent annealing, was found to be 1.01 F cm^{-2} at 0.5 mA cm^{-2} current density. It was also determined that this electrode exhibited a good cycle stability, maintaining 72% after 2000 cycles. The capacitive performance of the 3D-Ni@flower-like $ZnCo_2O_4$ NW arrays supercapacitor electrode has significantly improved as the direct growth of the electrode material on the conductive 3D-Ni current collector without binders improves contact between the current collector and the electrode material as well as facilitates ion transport.

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