



Short communication

Electrochemically synthesized nanocrystalline spinel thin film for high performance supercapacitor

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ABSTRACT

Spinel is not known for their supercapacitive nature. Here, we have explored electrochemically synthesized nanostructured NiCo_2O_4 spinel thin-film electrode for electrochemical supercapacitors. The nanostructured NiCo_2O_4 spinel thin film exhibited a high specific capacitance value of 580 F g^{-1} and an energy density of 32 Wh kg^{-1} at the power density of 4 kW kg^{-1} , accompanying with good cyclic stability.

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1. Introduction

In recent years, supercapacitors have emerged as a potential power source for future electrical vehicles (EVs) and mobile devices. Modern batteries are generally incapable of producing the required peak currents without degradation of their long-term performance [1–3]. Supercapacitors can be rapidly charged and discharged to provide peak power during acceleration and climbing of EVs and thus they are ideally suited for the load-leveling required in EVs. Therefore a lot of research works have been done in the past few years to improve the performances of supercapacitors [4–11]. In a supercapacitor, energy is derived from the stored charge in the active electrode material. This charge is stored either in the form of an electrical double layer capacitance (EDLC) or in a form associated with a Faradaic process involving redox reactions (redox capacitance). EDLCs have low specific capacitances, because their charge storage is mainly limited by the available active surface area. In this regard, activated carbons are known to have very high specific surface area (up to $\sim 2500 \text{ m}^2 \text{ g}^{-1}$) but low specific capacitances (up to $\sim 280 \text{ F g}^{-1}$) [6]. Redox capacitors usually show higher capacitances compared with EDLCs. This is due to redox

reactions involving the exchange of protons, with less emphasis on surface area, which results in higher utilization of electrode material. Conducting polymers and metal oxides come under this category. However, conducting polymer-based materials also have some disadvantages such as lower density and low stability at high discharge rates which may be an issue for many repeated redox processes.

Among the promising oxide materials (e.g., oxides of Mn, Fe, Co, Ni, Cr, In, Sn, Mo, V, etc.) [12–22] for supercapacitors, ruthenium oxide is noteworthy because of its superior electrochemical response [13,14]. Unfortunately, its expensive and some-what toxic nature are the main drawbacks. However, most of these supercapacitor electrode materials do not have high rate charge–discharge capability. Here, a supercapacitor electrode based on nanocrystalline spinel NiCo_2O_4 is reported, which was found to give a high specific capacitance of 570 F g^{-1} even at a high charge–discharge rate at 50 A g^{-1} .

In this work, we have examined a novel low-temperature route for synthesizing NiCo_2O_4 using a two-step process involving potentiostatic deposition followed by heat treatment, was used to synthesize NiCo_2O_4 . The electrochemical behavior of NiCo_2O_4 was compared to the best-known supercapacitor materials

2. Experimental

Analytical grade chemicals ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 M KOH) and research grade stainless-steel (SS, grade 304,

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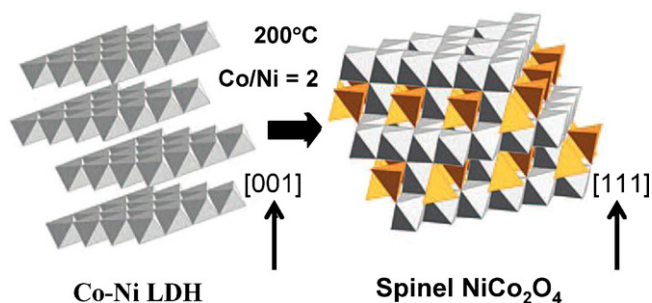


Fig. 1. Schematic illustration for formation process of NiCo₂O₄.

0.2 mm thick) sheet were used for preparation of electrode. The area of SS for deposition was 3 cm × 4 cm. NiCo₂O₄ spinel was synthesized by a two-step process. In the first step, potentiostatic deposition of Co–Ni double layer hydroxide was carried out onto SS by using aqueous mixed electrolyte of Co(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O (0.55:0.45 in molar ratio) at –1.0 V vs. Ag/AgCl in a three-electrode cell in which the counter electrode was platinum (Pt), the reference electrode was Ag/AgCl (with saturated KCl solution) and the working electrode was SS. In the second step, the heat treatment of the deposit on SS was carried out at 200, 300 and 600 °C. The chemical composition of deposits was determined by means of energy dispersive X-ray (EDX) spectroscopy (using EDAX, Horiba EX-220SE attached to Hitachi, SEM S3000-N). The microstructure of the electrode materials was observed by means of a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-6340F). X-ray diffraction patterns of the deposits were obtained by an X-ray diffractometer (XRD, RIGAKU, R1NT2100). Thermo-gravimetric analysis (TGA) curves were measured by using a TG analyzer (SII Model 3200). All capacitive measurements were performed by the use of a potentiostat (AUTOLAB®, Eco Chemie, PGSTAT 30) in 1 M KOH electrolyte.

3. Results and discussion

Fig. 1 shows the schematic illustration of the NiCo₂O₄ formation process at 200 °C. The EDX analysis shows that the deposit obtained

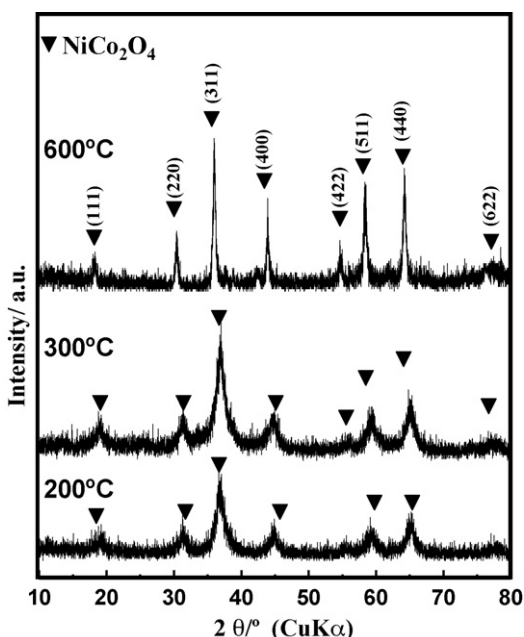


Fig. 2. XRD patterns of NiCo₂O₄ synthesized at various temperatures.

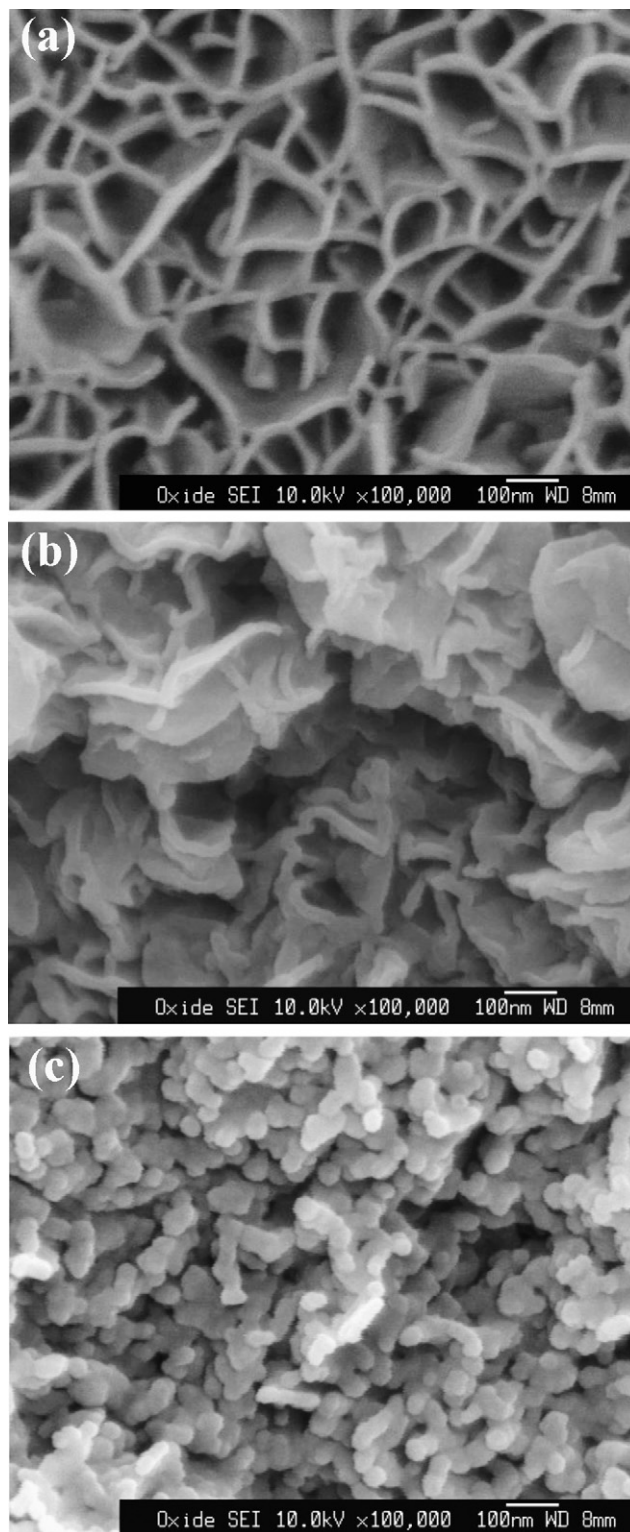


Fig. 3. SEM images of NiCo₂O₄ synthesized at (a) 200 °C, (b) 300 °C, and (c) 600 °C.

at 200 °C gives NiCo₂O₄ composition. Fig. 2 shows the XRD patterns of the NiCo₂O₄ samples heat-treated at 200 °C (3 h), 300 °C (3 h) and 600 °C (1 h). The formation of nanocrystalline cubic spinel NiCo₂O₄ structure (PDF#20-0781) was confirmed. The broad XRD patterns at 200 °C indicate that the size of the NiCo₂O₄ crystals is in the nanometer range. In addition, the XRD patterns do not show the presence of NiO. Fig. 3 shows the SEM images of the NiCo₂O₄ samples obtained at 200, 300 and 600 °C. At 200 °C, a network of

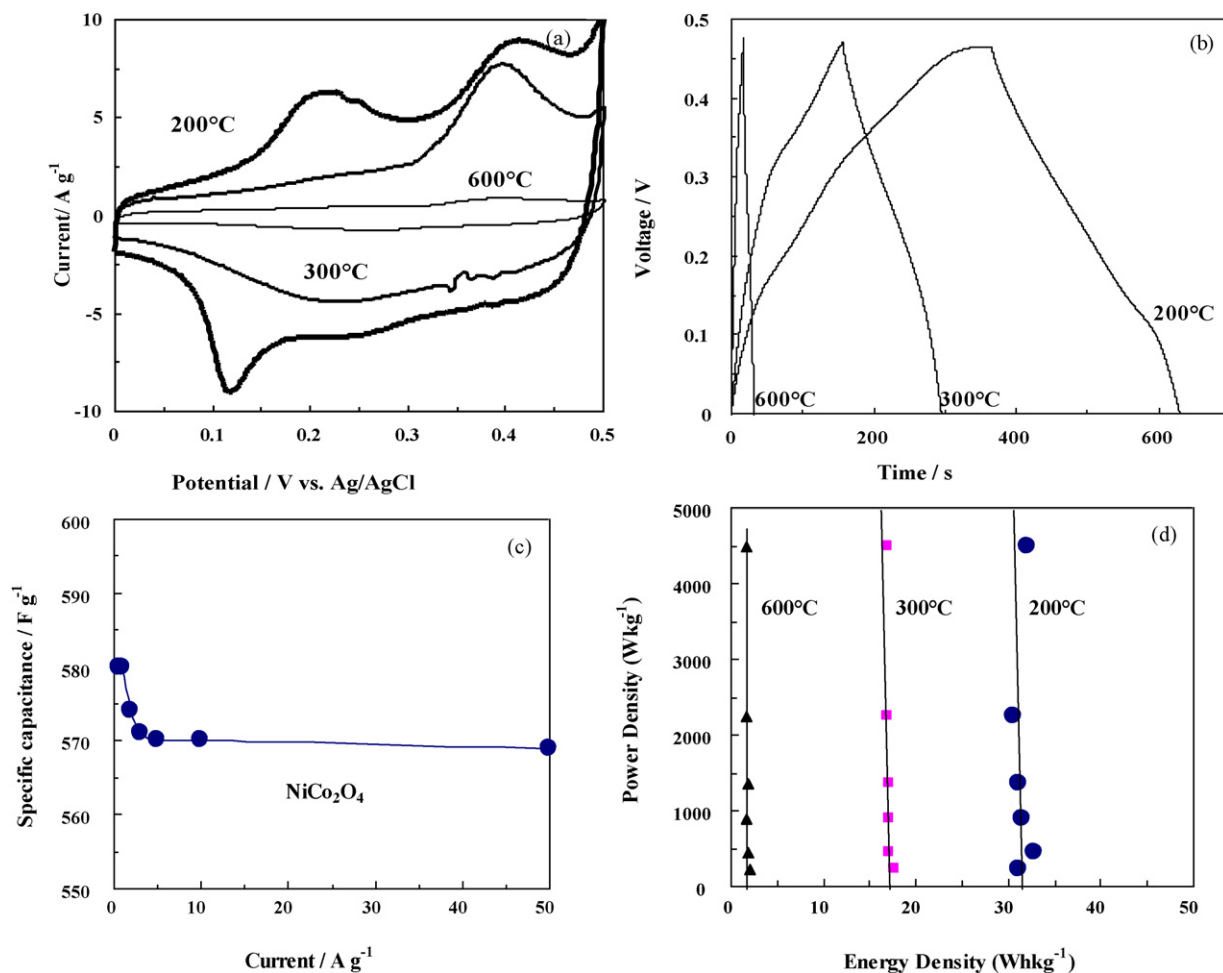
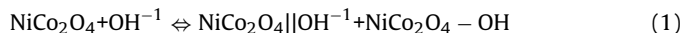


Fig. 4. (a) CV curves at 10 mV s⁻¹ sweep rate, (b) charge–discharge curves at 1 A g⁻¹, (c) dependence of specific capacitance on specific current, and (d) power density vs. energy density, for the NiCo₂O₄ samples obtained at different temperatures.

NiCo₂O₄ nanosheets spread over the entire surface was obtained (Fig. 3a). The average thickness of the nanosheets was ~10 nm. The morphology of NiCo₂O₄ obtained at 300 °C was quite different from that at 200 °C. The nanosized sheet-structures are residing on one another to form the heaps (Fig. 3b). On the other hand, uniform particle size of 30–40 nm was observed for the sample treated at 600 °C (Fig. 3c).

Fig. 4a compares the cyclic voltammetric (CV) behavior for the NiCo₂O₄ samples prepared at different temperatures, at sweep rate of 10 mV s⁻¹. The area of the CV curve for the NiCo₂O₄ sample obtained at 200 °C is large, whereas, the CV area has decreased significantly for the sample obtained at 300 °C and almost null at 600 °C, indicating the fading of charge-storage activity for crystalline NiCo₂O₄. This clearly suggests that the NiCo₂O₄ sample obtained at 200 °C gives much higher supercapacitive activity, compared to the sample obtained at higher temperatures. It is well known that the specific capacitance decreases with increasing crystallinity. The SEM images indicate that the spinel NiCo₂O₄ electrode obtained at 200 °C has porous morphology, high surface area and long-range interconnectivity, which are considered to be the prime reasons for its high supercapacitive activity. The unique feature shown in Fig. 4a is the presence of twin anodic peaks ca. 0.217 V and ca. 0.417 V, which can be assigned to Ni^{II}/Ni^{III} and Co^{II}/Co^{III} transitions, respectively. Such a feature was not reported previously for NiCo₂O₄, but mainly Co^{II}/Co^{III} transitions were observed [23]. In the case of NiCo₂O₄ sample obtained at 300 °C, Co^{II}/Co^{III} transitions were mainly observed. In this case, the electrochemical

reaction can be given as follows:



Here, NiCo₂O₄ || OH⁻ represents the electric double layer formed by the hydroxyl ion, and NiCo₂O₄-OH represents the product formed by cathode reaction involving hydroxyl ion [22].

The supercapacitive performances of the NiCo₂O₄ samples obtained at different temperatures were evaluated by using the charge–discharge (CD) curves at measured at 1 A g⁻¹. The specific capacitance (SC) for the NiCo₂O₄ samples obtained at 200, 300 and 600 °C were 575, 324 and 31 F g⁻¹, respectively, calculated from CD curves in the range of 0.1–0.45 V. It is clear that the sample obtained at 200 °C gives exceptionally high SC value, compared with the sample dependence obtained at higher temperatures. Fig. 4c shows the dependence of the specific capacitance on specific current. After an initial decrease from 580 F g⁻¹ at 500 mA g⁻¹ to 570 F g⁻¹ at 2 A g⁻¹, the specific capacitance remains almost constant even at 50 A g⁻¹. Such a high performance can be compared with the best-known oxide materials. The relationship between power density and energy density was calculated from the charge–discharge curves. As shown in Fig. 4d, a maximum energy density of 32 Wh kg⁻¹ was obtained at power density of 4 kW kg⁻¹ for the NiCo₂O₄ sample formed at 200 °C, whereas those for the samples formed at 300 and 600 °C were much lower. The cyclic stability of the NiCo₂O₄ sample obtained at 200 °C was examined for 2000 cycles and the results are shown in Fig. 5. The 5% decrease in specific capacitance was seen in the initial 1000 cycles.

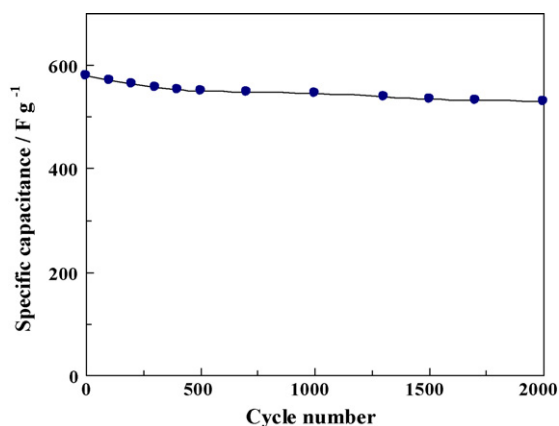


Fig. 5. Cyclic behavior at 0.5 A g^{-1} for the NiCo_2O_4 samples synthesized at 200°C .

Then, the charge–discharge profile becomes stable and a decrease in the specific capacitance of just 1% was observed for the next 1000 cycles.

4. Conclusion

In this communication, a new strategy for preparing spinel NiCo_2O_4 with unique microstructure was used and the obtained samples were applied as electrodes of supercapacitor. As a result, the specific capacitance of 580 F g^{-1} and a maximum energy density of 32 Wh kg^{-1} at power density of 4 kW kg^{-1} were obtained for the NiCo_2O_4 sample formed at 200°C . The spinel oxide prepared at 200°C was found to have porous nanostructure with long-range interconnectivity which creates electrochemical accessibility of OH^- ions electrolyte and a high diffusion rate through the bulk. These factors are crucial for supercapacitive characteristics. The strategy reported can be extendable to other spinel-type oxide and transition metal oxide systems.

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