

SYNTHESIS OF COBALT FERRITE NANOPARTICLES BY HYDROTHERMAL METHOD FOR SUPERCAPACITORS APPLICATION

H. KENNAZ^{1,*}, A. HARAT^{1,}, O. GUELLATI^{1,2}, N. MANYALA³ AND M. GUERIOUNE¹**

¹LEREC Laboratory, Physics Department, Badji Mokhtar-Annaba University, BP.12, Annaba 23000, Algeria

² Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, Algeria

³Department of Physics, Institute of Applied Materials, SARChI Chair in Carbon Technology and Materials,
University of Pretoria, Pretoria 0028, South Africa

(*) hibakennaz@yahoo.fr, (**) harat_aicha@univ-annaba.dz

ABSTRACT

Spinel cobalt ferrites CoFe_2O_4 nanoparticles (NPs) have been synthesized by hydrothermal method, with optimized growing conditions. The structural and morphological characterizations of the as-prepared material were investigated using X-ray diffraction (XRD), and field high resolution transmission electron microscopy (HRTEM). The obtained CoFe_2O_4 NPs are of single phase cubic spinel structure with nanoplatelet shape and an average particle size of 17 nm. The electrochemical performances were measured using three electrode configuration by cyclic voltammetry (CV) measures in 6M KOH electrolyte. CV tests have been performed for three different loading masses of the obtained CoFe_2O_4 as active material on a Ni foam current collector. These ferrites nanoparticles show high values of specific capacitance, the best result being obtained for the lowest loading mass, with 315 F/g.

Key words: Cobalt ferrite NPs, hydrothermal, supercapacitors, electrodes, specific capacitance.

Symbols :

C capacitance, F/g

i current, A

ΔV potential window, V

m mass, g

I current density, A/g

CV cyclic voltametric measures

Greek letters :

v potential scan rate, mV/s

Indices / Exponents :

s specific

1. INTRODUCTION

Since several decades, a large panel of materials have been investigated as electrodes for Supercapacitors (SCs) applications in energy storage field. The SCs have a high power density, superior chemical stability, long cycle life and rapid charge-discharge rates as compared to batteries... SCs can be classified in terms of their energy storage mechanism, as: electrochemical double layer capacitors (EDLCs), where the electrode material is mainly carbonaceous, with non-faradaic accumulation of charge, and pseudocapacitors electrodes such as metal oxides materials, which generate charge storage due to the fast reversible redox (faradaic) process.

Recently, the spinel ferrites metals oxides are widely studied, such as CuFe_2O_4 [1], CoFe_2O_4 [2], MnFe_2O_4 [3]. In particular, cobalt ferrite has received renewed attention due to its low-cost price, high permeability, strong

anisotropy, high Curie temperature, good electrical resistivity, and remarkable mechanical hardness and chemical stability.

To date, many methods have been developed to obtain CoFe_2O_4 NPs such as co-precipitation [4], thermal decomposition [5], hydrothermal [6], and sol-gel techniques [7]. However, hydrothermal method is preferable due to its higher yield and simplicity, low pollutant aspect associated to the use of water as reacting medium and higher degree of compositional control.

In this work, we synthesized CoFe_2O_4 NPs, using a hydrothermal technique. The electrochemical capacitance behavior of the obtained nanoparticles has been studied in 6M KOH using cyclic voltammetry (CV). The CoFe_2O_4 sample with different loading masses of active material show considerably higher specific capacitance value for the smallest mass.

2. EXPERIMENTAL METHOD

2.1 CoFe_2O_4 NPs SYNTHESIS:

Cobalt ferrite has been synthesized using hydrothermal method. Firstly, an aqueous solution is made by mixing 10 ml of 1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to 10 ml of 0.5 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (with atomic ratio Fe:Co = 2:1). Then, a solution of 10 ml of 6 M NaOH was added in the mixture. The final solution was kept under vigorous magnetic stirring for 30 minutes and was transferred into a Teflon-lined stainless steel autoclave which was introduced in a preheated oven at 200°C and 18 hours of times. The solution was filtered and washed several times with deionised water and the collected powder was dried at 80°C overnight.

2.2 ELECTROCHEMICAL MEASUREMENTS:

The working electrodes (WE) were composed with the synthesized electroactive material CoFe_2O_4 NPs, mixed with carbon black and polyvinylidene fluoride (PVDF) at the mass ratio of 80 : 10 : 10 %, respectively. A few drops of N-methylpyrrolidone (NMP) were added to the last mixture to form slurry which was pasted onto sheets of Ni foam current collectors (1.0 × 1.0 cm). The prepared electrodes were dried at 60°C in an electric oven overnight. The loading masses of the obtained active materials are (0.8, 1.7, 3.2 mg).

The electrochemical performances of the samples were examined by CV tests in a conventional three-electrode configuration in 6 M KOH electrolyte. The CV tests were performed over the voltage range 0.0 to 0.4 V at 5mV/s of scan rate, using glassy carbon plate and Ag/AgCl (3 M KCl) as the counter and the reference electrode, respectively.

3. RESULTATS

3.1 STRUCTURAL AND MICROSTRUCTURAL ANALYSIS

Figure 1 shows the XRD pattern of the as-synthesized ferrite sample. The XRD spectra reveal that all the peaks correspond to the characteristic reflections of the single- phase cubic spinel type lattice of CoFe_2O_4 (space group Fd3m), which matches well with the standard XRD patterns (JCPDS. No: 22-1086). No additional phase was detected.

From the HRTEM micrograph (figure2) we observe that the powder consists of nanoplatelets (square shape) nanoparticles with an average particle size of about 17 nm.

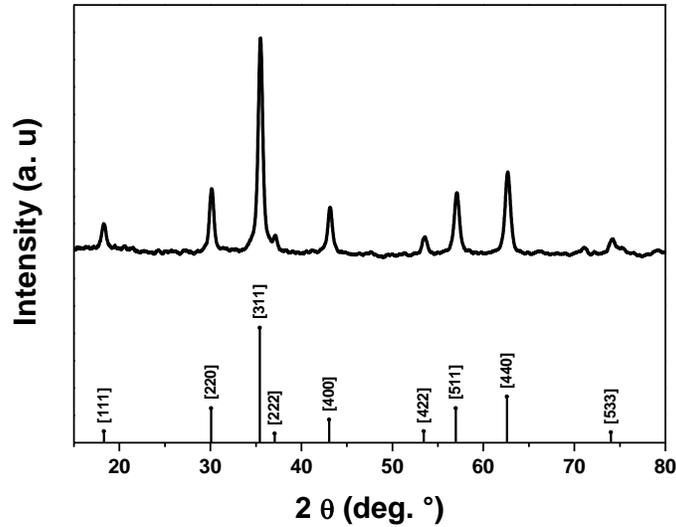


FIGURE 1. XRD patterns of CoFe₂O₄ NPs.

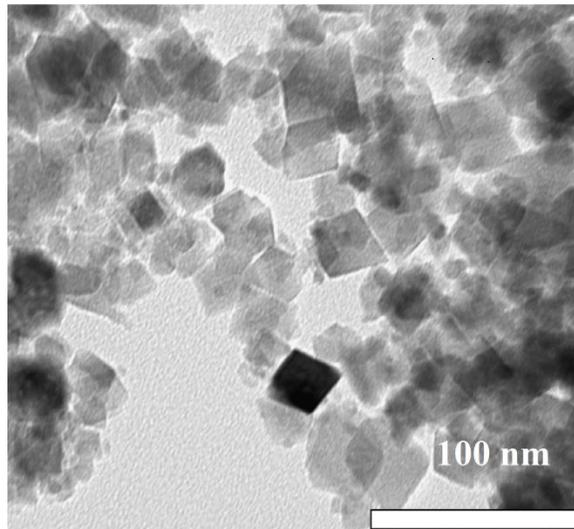


FIGURE 2. HRTEM micrograph of CoFe₂O₄ NPs.

3.2 ELECTROCHEMICAL ANALYSIS

Electrochemical measurements of the obtained CoFe₂O₄ NPs were performed by CV tests. Figure 3 shows the CV curves of NPs with three different loading masses recorded within the potential range of [0-0.4] V and at a scan rate of 5mV/s. One can notice the presence of typical peaks due to the faradaic redox reactions; and the increase of the integrated area and current density with the decrease of the loading mass, which indicates the good capacitance behaviour with lowest cost materials.

The specific capacitance (C_s) of our electrodes was calculated using the following equation:

$$C_s = \frac{\int i dV}{m \cdot v \cdot \Delta V}$$

Where i is the current (A), ΔV is the potential window (V), m is the loading mass of the active material (g) and v is the potential scan rate (mV/s). According to figure 4, which represents the variation of the specific capacitance with loading mass, C_s increases as the mass decreases, which can be attributed to the fast ion diffusion in the lowest loading mass electrode, where the low thickness vacillate electrolyte penetration into the electrode and alkali cations diffusion to inner pores of CoFe_2O_4 nanostructure [8, 9, 10].

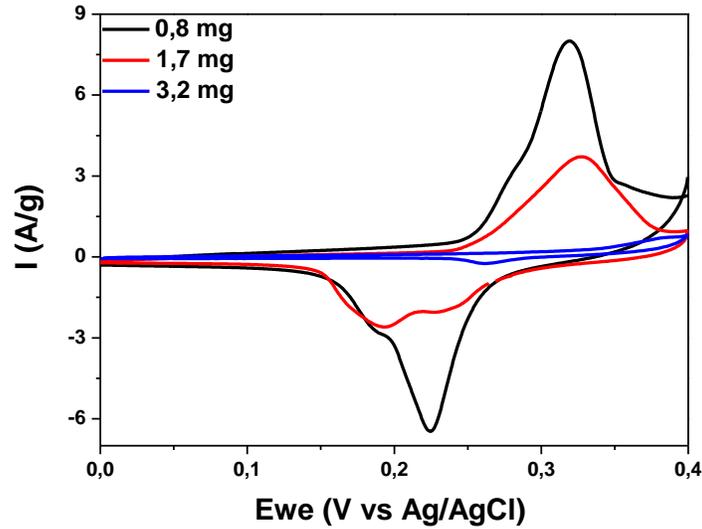


FIGURE 3. Cyclic Voltammetric curves of CoFe_2O_4 at different loading masses at scan rate of 5 mV/s.

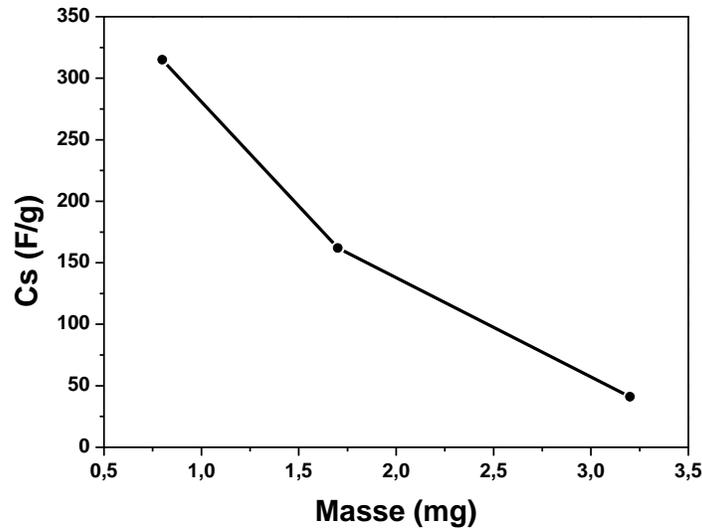


FIGURE 4. Variation of specific capacitance according to loading mass at 5 mV/s scan rate.

4. CONCLUSIONS

CoFe_2O_4 spinel ferrites NPs have been successively synthesized by hydrothermal method. Microstructural analysis (DRX) confirms the formation of the single-phase cubic spinel structure and the morphological studies (HRTEM) micrograph confirms the formation of nanoparticles with an average particle size of 17 nm. The

electrochemical properties of CoFe_2O_4 electrode material with 0.8 mg of mass evidence good faradaic type behaviour and higher specific capacitance value of 315 F/g at a scan rate of 5mV/s, which make it good candidate for supercapacitor application.

REFERENCES

-
- [1] M. Zhu, D. Meng, C. Wang, G. Diao, Facile fabrication of hierarchically porous CuFe_2O_4 nanospheres with enhanced capacitance property, *ACS Appl Mater Interfaces*, 5, 6030-7, 2013.
 - [2] V.S. Kumbhar, A.D. Jagadale, N.M. Shinde, C.D. Lokhande, Chemical synthesis of spinel cobalt ferrite (CoFe_2O_4) nanoflakes for supercapacitor application, *Appl Surf Sci*, 259, 39-43, 2012.
 - [3] S.L. Kuo, J.F. Lee, N.L. Wu, Study on pseudocapacitance mechanism of aqueous MnFe_2O_4 supercapacitor, *J. Electrochem Soc*, 154, 34-8, 2007.
 - [4] Y.I. Kim, D. Kim, C.S. Lee, *Physica*, 337, 42, 2003.
 - [5] S. Prasad, A. Vijayalakshimi, N.S. Gajbhiye, *J. Therm. Anal*, 52, 595, 1998.
 - [6] H. Wu, G. Liu, X. Wang, J. Zhang, Y. Chen, J. Shi, H. Yang, H. Hu, S. Yang, *Acta Biomaterialia*, 7, 3496, 2011.
 - [7] A. Hutlova, D. Niznansky, J.L. Rehspringer, C. Estournes, M. Kurmoo, *Adv. Mater*, 15, 1622, 2003.
 - [8] L. Z. Fan, J. Maier, High-performance polypyrrole electrode materials for redox supercapacitors, *Electrochemistry Communications*, 8, 937-940, 2006.
 - [9] K.R. Prasad, N. Miura, Electrochemical synthesis and characterization of nanostructured tin oxide for electrochemical redox supercapacitors, *Electrochemistry Communications*, 6, 849, 2004.
 - [10] C. Wan, L. Yuan, H. Shen, Effects of Electrode Mass-loading on the Electrochemical Properties of Porous MnO_2 for Electrochemical Supercapacitor, *Int. J. Electrochem.Sci*, 9, 4024- 4038, 2014.