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Synthesis of Co_3O_4 Electrode Material for Supercapacitor Applications

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Abstract : Nanocrystalline cobalt oxide material has been successfully synthesized via ultrasonication-precipitation method. The obtained material shows the cubic phase and spherical size agglomerated morphology as confirmed by the powder X-ray diffraction and scanning electron microscopy measurement. The electrochemical performance of the modified electrode has been analyzed systematically. The electrode material exhibits higher specific capacitance of 530 F/g at 1 A/g current density in 1M KOH electrolyte, which is a potential electrode material for charge storage (pseudocapacitor) applications.

Key words: Metal oxide; structural; cyclic voltammetry.

Introduction

Electrochemical capacitors (ECs) have been attractive because of their potential applications in energy storage devices such as digital cameras, mobile phones, electric hybrid vehicles, electric tools[1]. Supercapacitors can be classified into two types based on the energy storage mechanism. i.e electrochemical double layer capacitors (EDLC) and Pseudocapacitors. The capacitance of EDLCs is based on charge separation at the electrode/electrolyte interface and the capacitance of pseudocapacitors (PCs) storage arises from fast and reversible faradic redox reactions that can occur within the electro-active materials[2]. Electrode materials for supercapacitor have been classified into three types such as carbon, metal oxides and polymers. Among them, the metal oxide based electrode materials are attractive for pseudocapacitor due to higher charge storage. Based on the redox metal oxide electrodes, the RuO_2 is a suitable electrode material for pseudocapacitor because of their high specific capacitance, good electronic conductivity and high electrochemical stability. However, due to its high cost and toxicity, the researchers are aiming at developing alternative electrode materials for pseudocapacitors[3]. In recent years, researchers identified metal oxide based electrode materials such as nickel oxide, manganese oxide, and cobalt oxide owing to its low cost, non-toxic and environment friendly in nature as compared to RuO_2 electrode material[4,5]. The cobalt oxide (Co_3O_4) seemed to be a perfect electro-active electrode material for pseudocapacitor. In this present work, Co_3O_4 nanoparticles have been synthesized and their structural and electrochemical properties have been investigated.

Experimental

For the material preparation, $0.1\text{MCo}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL ethanol under vigorous stirring at room temperature. The pH value was adjusted by adding ammonia solution with continuous stirring for 2h at room temperature and stirring was continued further 3h in 60°C . The obtained final product was

filtered, washed with several times to remove the impurities. The sample was dried at 100°C in air and calcined at 400°C for 5 h to obtain Co₃O₄ nanoparticles.

Result and Discussion

Powder X-ray diffraction Analysis

The crystalline structure of the cobalt oxide material was studied by powder XRD as shown in Fig.1. The formation of Co₃O₄ nanoparticles with cubic structure and was compared with the standard data file (JCPDS No.65-3103). No impurities peaks of cobalt oxide phases were detected, which indicates the high purity phase formation. The average crystallite size was calculated by using the Scherrer formula,

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

D is the crystallite size, β is the full width half maximum, λ is the wave length of X- ray and θ is the diffraction angle. The average crystallite size of the nanoparticles was found to be 19.5nm.

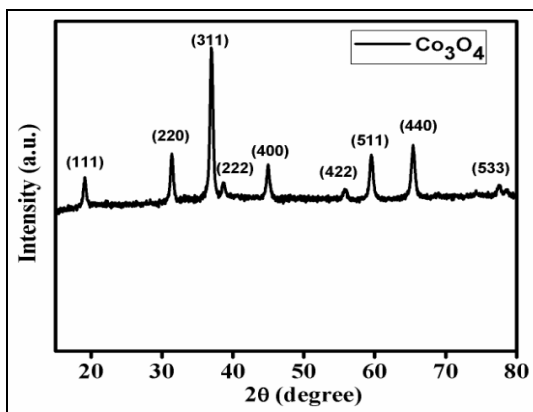


Fig.1. XRD pattern of Co₃O₄ nanoparticles.

Surface Morphology

Fig. 2 shows the SEM images of the cobalt oxide nanoparticles. The image shows randomly distributed particles due to agglomeration. This type of morphology can provide greater surface area of the electrolyte, which is prime requirement for supercapacitor. The nanoparticles are greatly help the electrolyte ions penetrate into the inner region of the electrode material and makes Faradaic reactions on electrode surface.

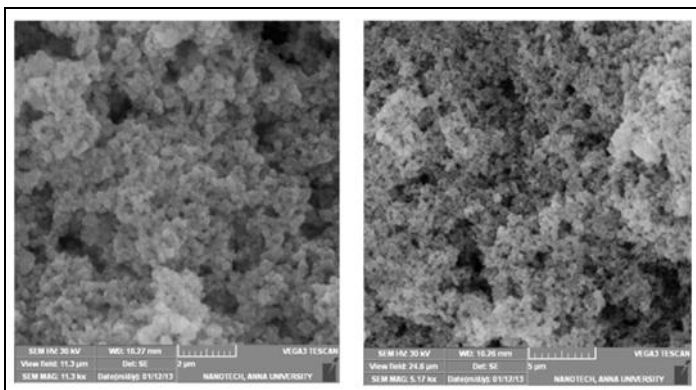


Fig.2. The SEM images of the Co₃O₄ nanoparticles.

Cyclic Voltammetry Analysis

CV curves obtained for different sweep rates in 1M KOH electrolyte at the broad potential range between 0.0 to 0.7V are shown in Fig.3.

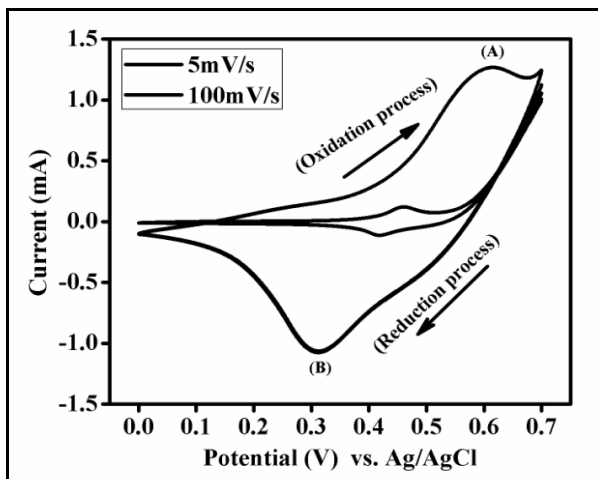
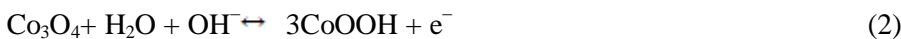


Fig.3. The CV curves of modified cobalt oxide electrode material.

The CV curves reveal the pseudocapacitive behavior, which is caused by the fast and reversible faradaic redox reactions of electro-active material. The redox peaks (A, B) correspond to the conversion between different cobalt oxidation states according to the following equations⁶⁻⁸



Cathodic peaks are shift towards negative potential range and anodic peaks are shift towards high potential range with the scan rate increased, which indicates the quasi-reversible feature of the redox couples. The capacitance 'C' was calculated from the following equation:

$$C = \frac{I}{\frac{dV}{dt}} \quad (4)$$

Where 'I' is the average current in amperes and dV/dt is the scan rate in mV/s. The specific capacitance (530 F/g at current density of 1 A/g) of the modified electrode is obtained by dividing the capacitance by the mass of the electrode material.

Conclusion

The pseudocapacitive behavior of cobalt oxide material prepared by ultrasonication -precipitation method has been studied. The average crystallite size and structure of cobalt oxide were analyzed by PXRD. The particles possess spherical morphologies as revealed by SEM studies. The modified electrode material exhibits the pseudocapacitive capacitance, which is promising electrode material for supercapacitor applications.

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