International Journal of Technical Research and Applications e-ISSN: 2320-8163,
www.ijtra.com Special Issue 37 (February, 2016), PP. 12-15

PREPARATION AND STRUCTURAL, MORPHOLOGICAL AND ELECTROCHEMICAL CHARACTERISTICS OF SPINEL $FeCo_2O_4$ NANOSTRUCTURES WITH ENHANCED SUPERCAPACITANCE ACTIVITY

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Abstract— **We report a facile synthesis and characterization of a less investigated Mixed Transition Metal Oxide (MTMO)- $FeCo_2O_4$ nanostructures on its utilization as electrode material for energy related applications by co-precipitation method. The as-synthesized nanostructures were characterized by thermogravimetery analysis (TG),X-ray diffraction(XRD),Fourier transform infrared spectroscopy(FTIR),Scanning electron microscopy(SEM) and EDAX. Electrochemical properties of the $FeCo_2O_4$ electrode performance were characterized by cyclic voltammetry(CV) and galvanostatic charge-discharge measurements in 1 M KOH electrolyte using a three electrode system. The asymmetric supercapacitor gave a high specific capacitance of 355 F/g at a discharge current density of 10 A/g. Moreover, they showed an excellent cycle stability and better capacity retention of 89% after 2000 continuous charge-discharge cycles. Thus a beneficial attempt have been exerted towards partly displacing the cobalt in somewhat expensive and toxic cobalt based oxide (Co_3O_4) with cheaper and more environmentally friendly alternate elements without losing its high electrochemical effectiveness.**

Index terms- **$FeCo_2O_4$ nanostructures, co-precipitation, cyclic voltammetry, galvanostatic charge-discharge and asymmetric supercapacitor.**

I. INTRODUCTION

With the depletion of fossil fuels and considerable concern about the global environmental impact of conventional energy technologies, there is an urgent need for the development of new energy sources and new technologies associated with energy conversion and storage.[1,2] .In this context, electrochemical supercapacitors which act as a special and novel storage device can meet the ever growing consumption demands and alleviate the energy crisis due to their high power density, long cycle life and rapid recharge capability. Electrode materials have become the core component for supercapacitors and can be divided into three types including carbon materials, conducting polymers and transition metal oxides. Carbon materials with low cost, good electrical conductivity and chemical stability seem to be ideal materials for electrical double layer capacitors but they suffer from low specific capacitance (lower than 400F/g)[3] .While conducting polymers have higher specific capacitance their cycle life is extremely poor because of its substantial expansion and contraction during the charging- discharging process[4]. Compared with the two types, transition metal oxides possess multiple oxidation states that are in favour of a fast redox reaction ,resulting in a much higher specific capacitance[5]. Among the transition metal oxides RuO_2 exhibits the best electrochemical performance (as high as 1580 F/g) but its toxic nature and high cost limits its application[6] .The application of other metal oxides are mainly restricted by their poor electrical conductivity and low energy density. Therefore it is imperative to develop alternative electrode materials that are inexpensive, environmentally friendly and with superior electrochemical performance. Aside from simple binary metal oxides, mixed transition metal oxides (MTMO) have drawn growing attention for electrochemical energy storage in recent years. They show unique properties that originate from the coexistence of two different cations in a single crystal structure as well as partial replacement of M in spinel M_3O_4 with other 3-d metals (Mn,Fe,Co,Ni) that can enhance their properties[7]. For example,$MnCo_2O_4$, $NiCo_2O_4$, $CuCo_2O_4$, $ZnCo_2O_4$ have been widely reviewed as promising electrodes for supercapacitors because of their higher electrical conductivity and electrochemical activities in comparison with corresponding M_xO_y and Co_3O_4 [8]. Saad Gomaa Mohamed et al. investigated the application of $FeCo_2O_4$ nano flakes as an electrode for supercapacitors[9]. No study regarding the application of $FeCo_2O_4$ nanoparticles as an electrode for supercapacitors has been reported. We report a facile synthesis and characterization of FeCo2 O_4 nanostructures on its utilization as electrode material for energy related applications by co-precipitation method.

II. 2.EXPERIMENTAL

A. Materials used

All the chemicals are of extra pure and used without any further purification. Cobalt(II)chloride hexahydrate($CoCl_2 .6H_2 O$), Iron (III) Chloride anhydrous ($FeCl_3$),sodium hydroxide were obtained from Merck, Black Pearl Carbon -15nm,1475m^2g^{-1} (Cabot Corporation), Polyvinylideneflouride(PVdF)(Aldrich),

N-methyl-2-pyrrolidone(NMP)(Merck).Deionised water was used throughout the process.

B. Synthesis of $FeCo_2 O_4$ nanoparticles

The co-precipitation process was performed as follows: a solution containing 0.01M of $FeCl_3$ and 0.02M of $CoCl_2 .6H_2 O$ was added drop wise to a solution of sodium hydroxide having a concentration of 0.5M and pH 9 with continuous stirring for 2 hours at 90^o C. The precipitate was formed immediately and remained in the mother solution which was placed in a water bath for 4 hours. After cooling, the precipitate was filtered and washed repeatedly with distilled water until traces of sodium chloride formed during the reaction was removed. The precipitate was dried in a hot air oven for 2 hours and then it was ground well and was calcined at 350^oC for 4 hours to get $FeCo_2 O_4$ nanoparticles.

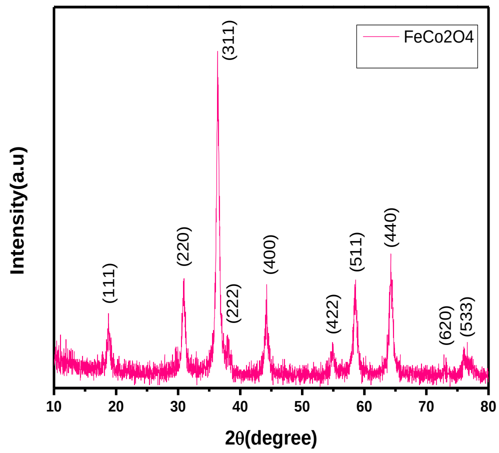
C. Characterization

Thermogravimetric analysis of the precursor was carried out at a heating rate of $10^o Cmin^{-1}$ under air atmosphere to find out the phase formation and/or complete crystallization temperature of the precursor using TGA analyser(Model Q600 SDT,TA instruments),the powder X-ray diffractometer (Ultimate Rukagu IV) recorded from 5 to 80^o using Cu-kα radiation (λ = 0.15408nm) at room temperature. FTIR spectra was recorded by FTIR spectrometer(SHIMADZU) in the range 4000-400 cm^{-1} .The surface morphology was analyzed by Scanning Electron Microscope(Hitachi,Model:S-3000N).Electrochemical measurements were carried out using an electrochemical analyzer(VSP,Bio-Logic,France).

III. RESULTS AND DISCUSSION

A. XRD analysis

X-ray diffractrogram of $FeCo_2 O_4$ is shown in figure-1.The XRD pattern agrees with the JCPDS no. 04-0850 and without any collateral peaks, indicating high purity of the prepared sample. All the diffraction peaks attribute to an ordered spinel structure with a pure single phase cubic spinel structure. A space group of Fd-3m was confirmed with a lattice constant of a= 8.24215 Å.[10] The average crystallite size of about 14.2 nm was calculated using Debye-Scherer equation.



B. FTIR spectral studies

The FTIR spectra of $FeCo_2 O_4$ in figure-2 shows two strong absorption peaks at 640 cm^{-1} and 541 cm^{-1} corresponding to the stretching bond of metals in the octahedral system and the stretching vibration of metal-oxygen bond in the tetrahedral system of the spinel structure i.e., Fe-O respectively.[11] The peak at 3434 cm^{-1} relates to stretching vibration of the interlayer water molecule and the peak at 1623 cm^{-1} relates to the bending vibration of the interlayer water molecule. No other peaks were found in the FTIR spectrum indicating that the purity of FeCo2 O_4 is good without the presence of other phases in the sample.

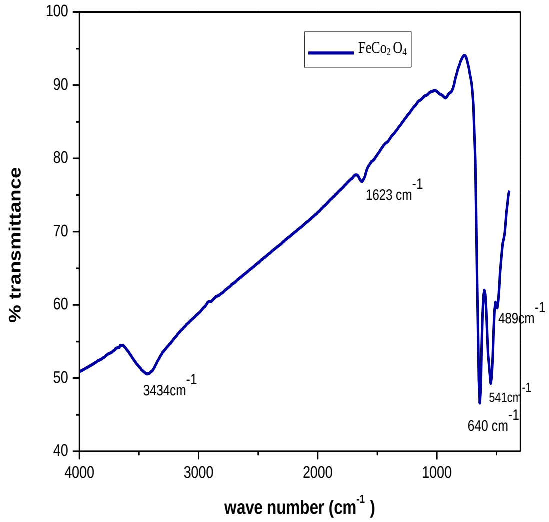


Fig-2

C. Thermal Analysis

The choice of suitable calcination temperature is highly dependent on the result of Thermogravimetric analysis (TGA).The TG curve of the Fe-Co hydroxide precipitate in figure-3 shows a net weight loss of 4% in the temperature range between 80^0 C and 350^0 C. This suggests that the precursor decomposed completely at 350^0 C. Hence a calcination temperature of 350^0 C was chosen to ensure the complete decomposition of the precursor to form $FeCo_2\ O_4$ .About 6% weight loss has occurred in the temperature range from room temperature to 80^0 C due to the removal of water from the dried precursor sample. The weight loss in the temperature range between 100^0 C and 350^0 C is due to the decomposition of the precursor to form $FeCo_2\ O_4$ .The overall reaction is as follows:

$$2\ Co(OH)_2 + Fe(OH)_2 + \frac{1}{2}\ O_2 \rightarrow FeCo_2O_4 + 3H_2O$$

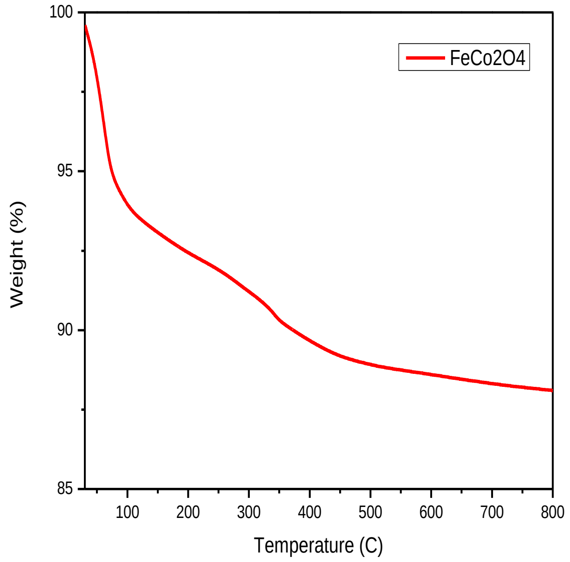


Fig-3

D. SEM Analysis

The FE-SEM image of the sample in figure-4 shows that the shape of the as-synthesized $FeCo2\ O_4$ is spherical, homogenous and agglomerated with average size of 8 nm. The calcination process has left behind pores which allow facile penetration of electrolyte during electrochemical reaction.

Element	Weight %	Atomic %
Oxygen	35.15	66.24
Iron	20.65	11.15
Cobalt	44.19	22.61
Total	100	100

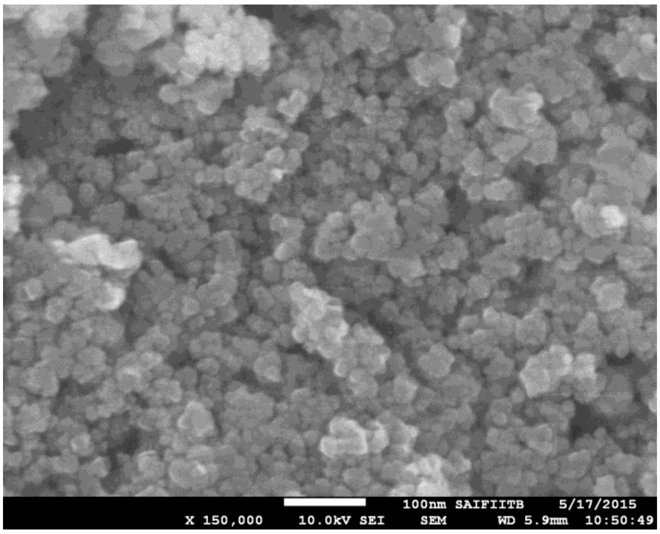


Fig-4

E. EDAX analysis

The EDAX pattern in figure-5 shows the presence of iron, cobalt and oxygen. The weight percentage and atomic percentage are given in the table below. EDAX confirmed that the sample contains iron, cobalt and oxygen in the ratio 1:2:4 with no trace of any other element.

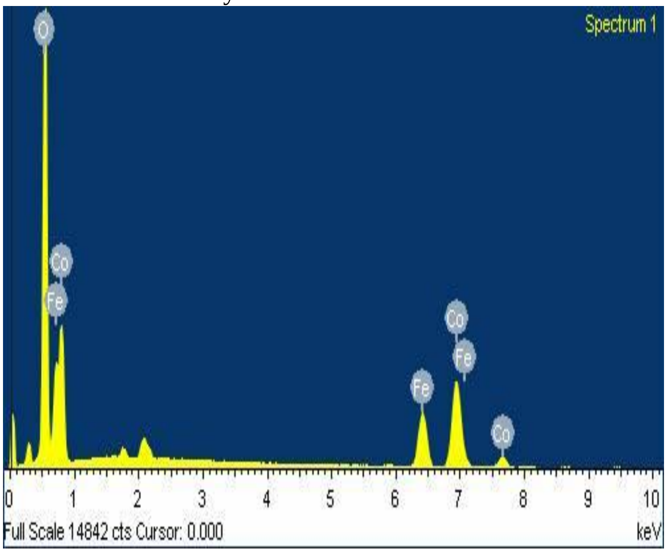


Fig-5

F. Cyclic Voltammetry Studies

The shape of the CV curves in figure-6 demonstrates that the capacitive behavior is characteristic of Faradaic pseudo capacitance process originating from reversible redox reaction. A pair of redox peak is observed with one anodic peak and one cathodic peak in each CV curve within the potential range from 0 to 0.5V Vs Ag/AgCl at 1M KOH at all sweep rates which is mainly associated with Faradaic redox reactions.

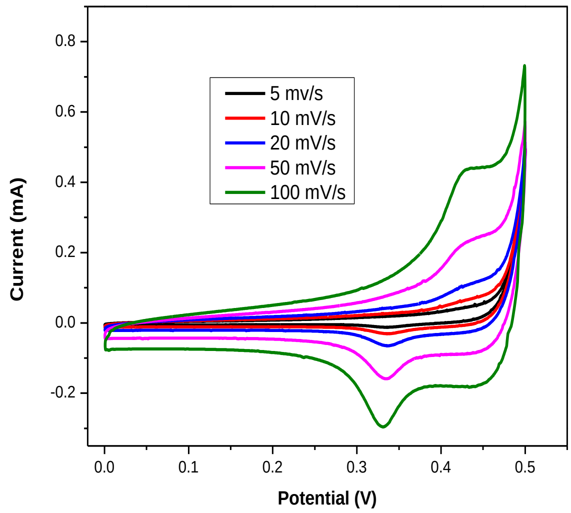


Fig-6

G. Charge-Discharge Studies

The non-linear shape of the charge-discharge curve in figure-7 indicates the pseudo capacitance behaviour of $FeCo_2O_4$. The discharge specific capacitance at 10A/g was 355 F/g. The specific capacitance gradually decreased to 317 F/g thus showing an excellent cycle stability and better capacity retention of 89 % after 2000 continuous charge-discharge cycles.

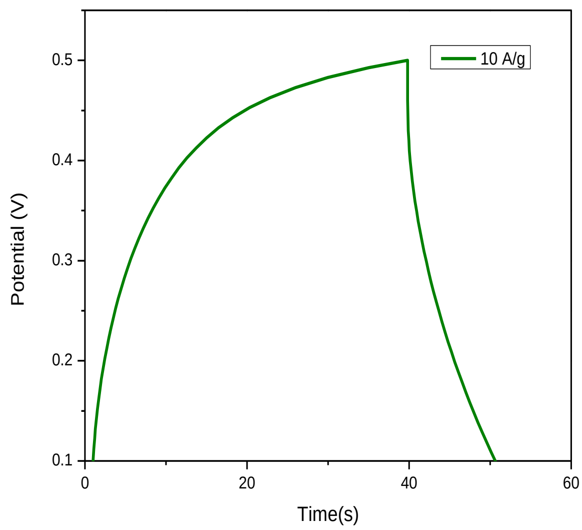


Fig-7

IV. Conclusion

The present work demonstrated the facile synthesis of $FeCo_2O_4$ with enhanced electrochemical performance.XRD studies confirmed the formation of the pure single phase cubic spinel structure. FTIR analysis showed two strong absorption peaks at 640 cm^{-1} and 541 cm^{-1} corresponding to the stretching bond of metals in the octahedral system and the stretching vibration of metal-oxygen bond in the tetrahedral system of the spinel structure respectively. Cyclic voltametric studies carried out using a three electrode system showed the pseudo capacitance behaviour of the sample. Galvanostatic charge-discharge studies revealed excellent cyclic performance, high specific capacitance and electrochemical stability of the as-synthesized sample thus demonstrating its high performance in supercapacitor applications

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