Synthesis and Electrochemical Examination of Fe_2O_3/CeO_2 Nanocomposite for Supercapacitor Application

S. Arunpandiyan, A. Raja, Bilash Jyoti Gogoi, P. Soumya, P. Devendran, A. Arivarasan

Abstract**:** ***Fe_2O_3/CeO_2 nanocomposite was synthesized by a chemical precipitation method in room temperature. The prepared nanocomposite has been subjected to some characterization techniques such as XRD, SEM, FTIR, CV, etc., The presence of crystalline phases of CeO_2 and Fe_2O_3 were confirmed by the powder X–Ray diffraction analysis. Surface morphology of the prepared nanocomposite has been analyzed using SEM analysis. The functional group vibrations were analyzed by FTIR technique. The maximum specific capacitance achieved by using 1M KOH electrolyte solution is about 242 Fg^{-1} at 5 Ag^{-1} current density.***

Keywords**:** ***Fe_2O_3/CeO_2 nanocomposite, XRD, CV, GCD.***

I. INTRODUCTION

The increasing energy demand and growing global warming and environmental issues due to the consumption of commercial fuels have been stimulated the researchers throughout the globe to develop suitable energy storage devices. Supercapacitors (SPs) are one of the emerging energy storage technology with a longer life cycle, higher power density [1]. The main advantages of SPs are their cheap production cost and non-toxicity compared with other energy storage technologies. SPs are mostly used in the devices which requires the more durability, flexibility and power. They exhibit much more power than the electrolytic capacitors and batteries.

Electric double layer capacitors (EDLC) are the basic type of SP which is generally made up of carbon derived materials, they electrostatically store the energy. In recent years, metal oxide based pseudocapacitors are attracted more because of their higher specific capacitance values, longer life span, cheap cost, etc. They were store the energy by the form of faradaic reduction and oxidation reactions. The general metal oxides used in pseudocapacitor is NiO [2], MnO_2 [3], RuO_2 [4], Co_3O_4 [5], CeO_2 [6], Fe_2O_3 [7], CuO [8], TiO_2 [9], etc. Rather than single metal oxide, the mixed metal oxides or metal composites are providing the enhanced performance due to the enlarged potential window of different metal oxides in an electrochemical reaction.

In this research, we have synthesized Fe_2O_3/CeO_2 nanocomposite through the simple chemical precipitate technique and fabricated modified working electrode for high performance supercapacitor. The enlarged CV curve of the metal nanocomposite resulted in enhanced supercapacitor performance of the prepared modified working electrode.

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II. MATERIALS AND METHODS

A. Precursors

Cerium nitrate [$Ce(NO_3)_3.6H_2O$] was purchased from Himedia private limited, India. Ferrous chloride [$FeCl_2.XH_2O$] was procured from Molychem laboratory chemicals limited, India. And potassium hydroxide [KOH], sodium hydroxide [NaOH] were procured from SRL chemicals private limited, India. For all the synthesis procedures, D.I water was used as the solvent.

B. Synthesis of Fe_2O_3/CeO_2 Nanocomposite

Fe_2O_3/CeO_2 nanocomposite was synthesized by chemical precipitation method. In a typical synthesis, 0.05M Cerium nitrate and 0.05M Ferrous chloride solution were prepared in 100 of D.I water. 0.1 g of PVA was well dissolved in the above mixture and it was constantly stirred for 3 h. Then, 10 ml of absolute ethanol was dropped on to the above resultant solution and it was aged for 24 h to form the precipitates. The precipitates were separated by centrifugation and washed several times using DD water followed by ethanol. The attained reddish sample has been dried in an air oven at 80 °C and annealed at 500 °C.

C. Characterization Techniques

The prepared samples were characterized by X-Ray diffractometer (BRUKER-D8 Advance Eco XRCD) systems with SSD 160 1D Detector for structural confirmation. Surface morphology of the prepared sample was studied Scanning Electron Microscope
(EVO18 CARL ZEISS).

Functional groups present in the prepared sample were

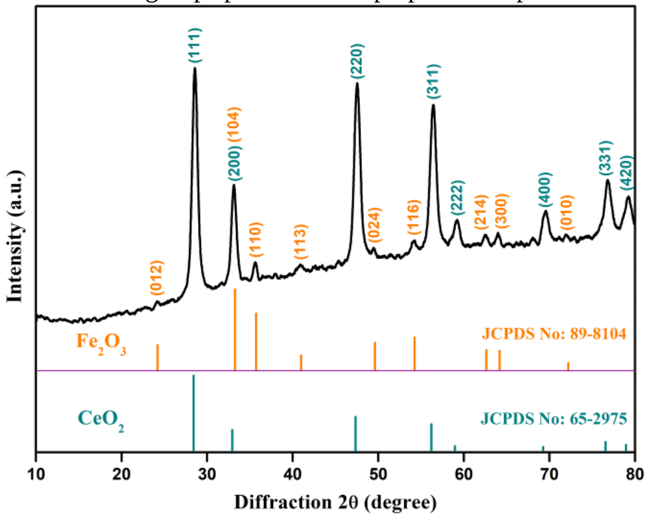

Fig. 1.Powder X-Ray diffraction pattern of Fe_2O_3/CeO_2 nanocomposite.

analyzed by Fourier Transform Infrared Spectrophotometer (IR Tracer 100) by applying the frequency from 400 to 4000 cm^{-1}. The supercapacitor performance was evaluated using electrochemical workstation (CH instrument CHI6008e, USA).

D. Electrode Fabrication

The prepared Fe_2O_3/CeO_2 nanocomposite was well mixed with activated carbon (for enhancing the conductivity) and Polyvinylidene fluoride or polyvinylidene difluoride PVDF (binder) in 85:10:5 weight ratio. Then, an appropriate amount of N-Methyl-2-pyrrolidone (NMP) was added to the above sample to form a slurry. The obtained slurry was painted on the Ni-foil (1 cm^2) and dried in the air oven at 60 °C for 12 h.

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction (XRD) Analysis

The XRD pattern of synthesized Fe_2O_3/CeO_2 nanocomposite was recorded between the 2θ angle of 10 to 80° as shown in fig 1. From the diffraction pattern, presence of Fe_2O_3 and CeO_2 crystalline phases was confirmed by matching with the standard JCPDS database. The diffraction peaks appeared at the 2θ angles 28.59, 33.09, 47.52, 56.42, 59.12, 69.59, 76.81, 79.29 with corresponding planes 111, 200, 220, 311, 222, 400, 331, 420 respectively, which is associated with the face-centered cubic crystalline structure of CeO_2. Remaining diffraction peaks appeared at 24.20, 33.09, 35.58, 40.88, 49.55, 54.16, 62.50, 63.96, 72.08 with corresponding planes 012, 104, 110, 113, 024, 116, 214, 300, 010 respectively are attributed to the rhombohedral crystalline structure of Fe_2O_3. The peak intensity of the Fe_2O_3 was dominated by CeO_2 because of its high crystallinity.

B. Scanning Electron Microscope (SEM) Analysis

Surface morphology and elemental analysis were done by SEM. The SEM images of the prepared sample at different magnifications was shown in fig 2 (a, b). SEM images reveal that the prepared samples have been in the Nano dimension, and they exhibit nanorods like surface morphology. Presence of Ce, Fe, O elements in the calcinated sample was confirmed by E-Dax spectrum as shown in fig 2 (c). The overall

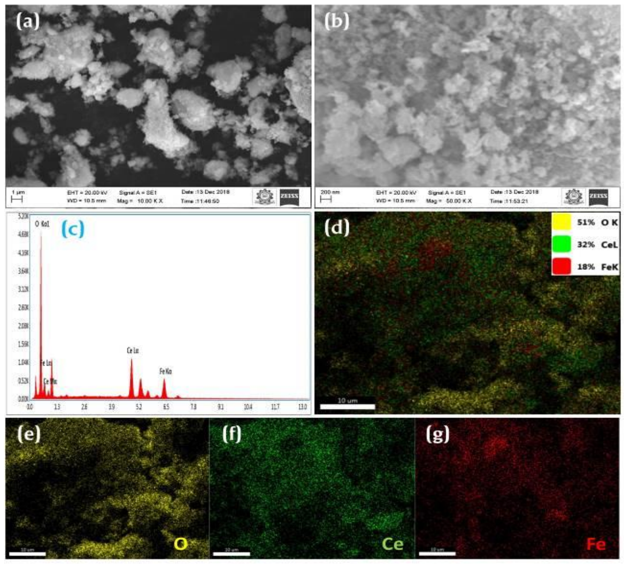

Fig. 2.SEM images of (a, b) Fe_2O_3/CeO_2 nanocomposite at different magnifications, (c) E-Dax spectrum, (d) overall mapping, (e-g) elemental mapping of O, Ce, Fe similarly.

elemental mapping shown in fig 2 (d) shows that all the elements were uniformly dispersed in the whole sample. The 51% of the oxygen element was observed in the surface of the material, which provides as the more effective to the redox reactions. The elemental mapping for O, Ce, Fe elements were displayed in fig 2 (e–g).

C. FT-IR analysis

The FT-IR was carried out to study the functional groups and vibrational properties. The FT–IR spectrum of the prepared sample was recorded in the range of 400–4000 cm^{-1} as shown in fig 3. The broad absorption peak appears at 3376 cm^{-1} is due to the OH stretch vibration. Absorption peaks appearing around 1432 cm^{-1} and 860 cm^{-1} are maybe the presence (NO^{3-}) groups available from the precursor materials [10]. The sharp absorption peaks appearing at 529, 454 cm^{-1} are attributed to the metal oxide vibrations, such as Ce–O and Fe–O.

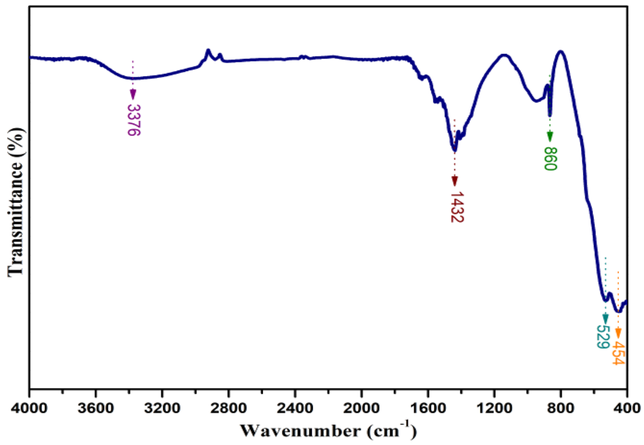

Fig. 3.The FT-IR spectrum of Fe_2O_3/CeO_2 nanocomposite.

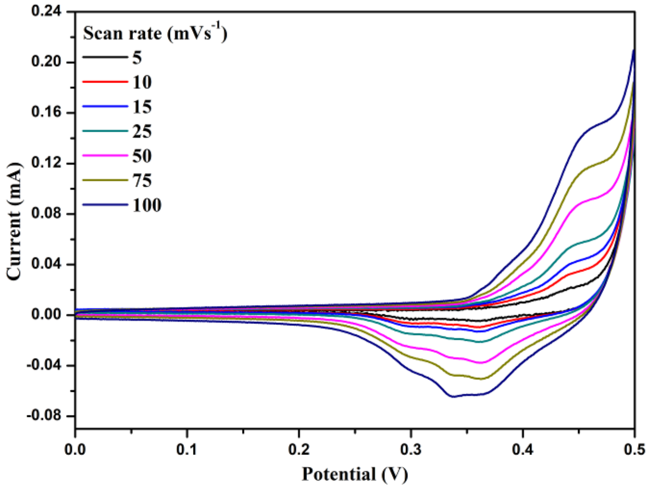

Fig. 4.Cyclic voltammogram of the Fe_2O_3/CeO_2 nanocomposite.

D. Electrochemical Studies

The electrochemical performance of the Fe_2O_3/CeO_2 nanocomposite modified working electrode was tested in three electrode systems. The 1 M KOH was used as an electrolyte for testing the supercapacitor performance. The cyclic voltammogram (CV) of the fabricated modified working electrode was shown in fig 4. The CV graph was performed at various scan rates from 5, 10, 15, 25, 50, 75, 100 mVs^{-1}. The potential window of the CV curve is optimized and set between 0 – 0.5V. The CV graphs possessed faradaic reduction and oxidation (Redox) peaks, which denotes that the Fe_2O_3/CeO_2 nanocomposite having the pseudocapacitive nature.

Galvanostatic charge-discharge (GCD) curve of the modified working electrode as shown in fig 5. The GCD were performed at various current densities starting from 5 to 9 Ag^{-1}. The discharge time was low compared with the charging time. The specific capacitance was calculated by using formula 1.

$$C_{sp} = I \times \Delta t / m \times \Delta V \quad (1)$$

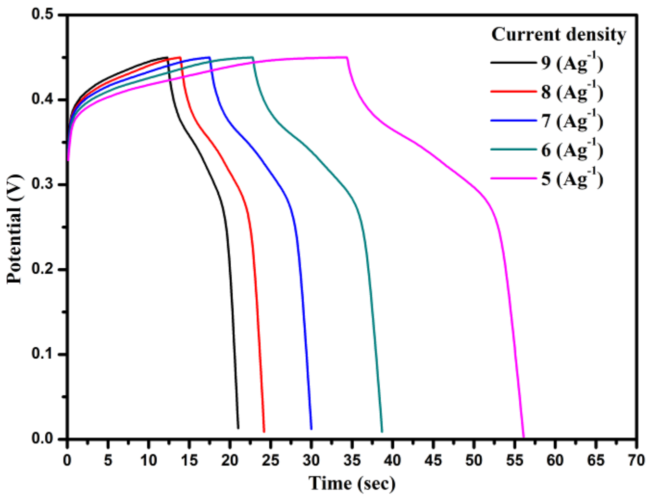

Fig. 5.Galvanostatic charge discharge of the Fe_2O_3/CeO_2 nanocomposite.

Here I is current (A), Δt is discharge time, m is active mass and ΔV is the potential window. The specific capacitance calculated from GCD curve is 242, 212, 194, 183, 174 Fg^{-1} at the current densities of 5, 6, 7, 8, 9 Ag^{-1} similarly.

IV. CONCLUSION

The Fe_2O_3/CeO_2 nanocomposite was successfully synthesized from simple chemical precipitation technique. The surface morphology was revealed by the SEM analysis. The presence and distribution of Fe, Ce, O elements were confirmed by the E-Dax and mapping. The crystalline phases of the Fe_2O_3/CeO_2 nanocomposite was studied by using X-Ray diffraction pattern. Supercapacitor performance has been calculated using GCD technique and achieved maximum specific capacitance of 242 Fg^{-1} at 5 Ag^{-1} of current density.

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