Synergetic effect of electron irradiation on the supercapacitive properties of electrodeposited iron oxide thin films

U. M. Chougale, M. C. Rath, V. J. Fulari

Abstract— The present work aims to investigate the effect of electron irradiation on the supercapacitive properties of iron oxide thin films. A supercapacitor electrode with promising features has been developed by modifying iron oxide thin films. High surface area porous iron oxide thin films are deposited by electrodeposition method. As deposited iron oxide thin films were irradiated with electron beam with different doses (10, 30 and 50 kGy). The structural and morphological modification of iron oxide electrodes have been analyzed by XRD, FTIR and SEM and found the change in structure as well as surface morphology of the electron irradiated maghemite electrodes. The electrochemical properties of the proposed electrodes were studied in 0.5 M Na2SO3 electrolyte with cyclic voltammetry, galvanostatic charge discharge and EIS techniques. Specific capacitance of maghemite thin film electrodes has been enhanced from 616 to 678 F/g after electron. Furthermore the samples show long term cycling performance with 16% enhancement in stability after irradiation. Subsequently electrochemical impedance spectroscopy indicates the suitability of the maghemite electrodes for supercapacitor application with decrease in electrode resistance after electron irradiation. The proposed electrodes are easy to prepare, economic, environmentally benign with enhanced stability.

Index Terms— electrodeposition, electron irradiation, maghemite, microspheres, supercapacitors

1 INTRODUCTION

Most of the researchers have been forced to design the simple electrochemical capacitors as excellent system for energy storage due to growing energy demands of modern society [1],[2],[3]. The specific power and specific energy of supercapacitors are the key factors for development of supercapacitors [4]. Due to their high power, fast charge discharge rate, long cycle life and low cost, supercapacitors have gained more attention of worldwide researchers [5]. Supercapacitors based on carbon, polymer and metal oxides materials are well reported. Among the metal oxides, iron oxides are being used on large scale for energy storage because of high theoretical capacity, affordable cost, favorable stability, and eco friendliness [7]. Also high electronic conductivity of Fe2O3 made it suitable for current collector in supercapacitor devices [8, 9]. However, low rate of power capability, short cycling capability may hinder use of iron oxides for supercapacitor application. Sufficient efforts have been made to overcome these problems. Moreover, electron beam irradiation of the electrodes can improve its capacitance. Considerable research work has been devoted to improve the power capability of supercapacitors, for high energy needs.

In the present work, our objective was to develop low cost efficient supercapacitor by tailoring the crystal structure and morphology of iron oxide electrodes by electron beam irradiation. In present study we demonstrate that, electron irradiation of iron oxide electrodes generates greater specific capacitance.

2 EXPERIMENTAL WORK

2.1 Deposition of thin films

The iron oxide thin films were deposited on well polished stainless steel substrates by potentiostatic mode of electrodeposition with standard three electrode system. The typical electrodeposition bath contain Fe2(SO4)3 and NaOH as starting materials.

2.2 Irradiation experiment

The good quality films deposited with optimized parameters were exposed to 10 MeV electron beam in Industrial Electron Accelerator at BARC Mumbai with different doses (10, 30 and 50 kGy). The irradiation experiment was carried out using electron beam with average beam power of 1 kW and 1 kGy dose per pass, 33 mA current and 10 μs pulse width at conveyor speed of 1 m/min.

2.3 Characterization of samples

All the films were characterized for its structural analysis by Bruker D2-Phaser X-ray powder diffractometer with Cu kα (λ=1.5418 Å) radiation and Perkin-Elmer FT-IR Spectrum-One was used to record FT-IR spectrum. The surface morphological modifications of samples were investigated by scanning electron microscopy (JEOL-6360). The electrochemical analyzer CHI608E with standard three electrode cell comprising counter electrode (platinum) and reference electrode (SCE) was used for electrochemical measurements. The electrochemical properties of the electron irradiated iron oxide electrodes were evaluated in 0.5M Na2SO3 electrolyte with cyclic voltammetry, galvanostatic charge discharge and EIS techniques within potential window -0.6 V to 0.1 V. The pristine, 10 kGy, 30 kGy and 50 kGy irradiated samples were named viz A, B, C, and D respectively.

3 Results and Discussion

3.1 Structural analysis

Figure 1 shows the X-ray diffraction pattern of electron beam irradiated iron oxide samples with different doses. All the samples show the cubic crystal structure of deposited iron oxide thin films confirmed by matching of calculated 'd' values with JCPDS card No. 39-1346. Thus XRD confirm cubic crystal structure of γ-Fe2O3 i.e. Fe3+ in octahedral position and O in close packed cubic arrangement as reported earlier in the formation of γ-Fe2O3 at room temperature from FeCl3 and Fe2(SO4)3 solutions [7, 10]. The crystal growth of sample A observed in (311), (410), (421) and (630) direction. For the samples B, C and D change in atomic plane orientation was not observed. Only intensity of prominent (410) peak increases after electron irradiation indicating the growth of crystal in particular (410) direction. The crystallite size of 28, 34, 56 and 64 nm was estimated using Scherrer formula [11] for samples A, B, C and D respectively. The increase in crystallinity and crystallite size affect electrochemical performance as the intercalation and deintercalation of ions takes place at atomic planes contribute charge storage in crystalline material [12].

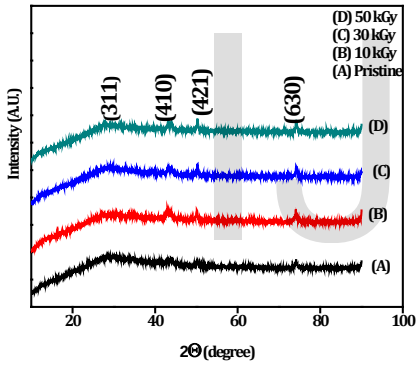

Fig. 1. X-ray diffraction pattern of electron beam irradiated iron oxide thin films

3.2 FT-IR analysis

The changes in the molecular bonding of maghemite thin films after electron irradiation were determined using FT-IR spectroscopy. Fig.(2) show the FT-IR spectra of as deposited (A) sample (A) and irradiated samples (B-D) (inset figure). All sample show the absorption peak around 466, 580, 873 and 1016 cm-1. The typical absorption peaks for γ-Fe2O3 due to Fe-O bending and stretching are observed at 466 and 580 cm-1 respectively. [7,13]. Shift in the absorption peaks towards high energy end observed for samples B, C and D indicating the change in bond length after electron irradiation. Thus FT-IR spectroscopy confirms the no change in the molecular arrangement of γ-Fe2O3 after electron irradiation.

3.3 Surface morphology

The scanning electron micrographs of the maghemite thin films are depicted in figure 3 (a), (b), (c) and (d) for samples A,

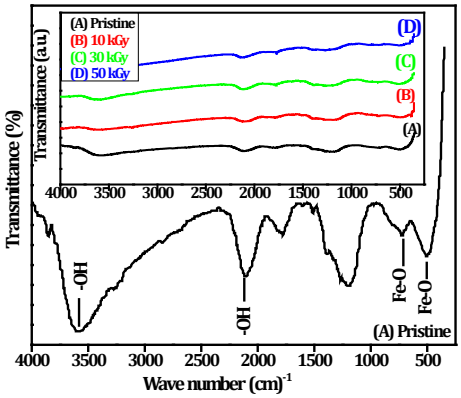

Fig.2. FT-IR spectra of electron beam irradiated maghemite thin films showing absorption bands.

B, C and D respectively. From SEM images it is clear that electron irradiation alters the surface morphology. Transformation of maghemite nanoflakes (sample A) into solid spheres like structure for sample B is observed. The heat generated during irradiation may coagulate the nanoflakes to form solid sphere like morphology. Further irradiation with higher dose of electron beam convert the solid spheres into nanoflakes microspheres for sample C. Still high dose electron irradiation lead to destruct the maghemite microspheres. Modification in maghemite morphology after electron irradiation is feasible for the supercapacitor application as the electroactive area for each sample will be modified.

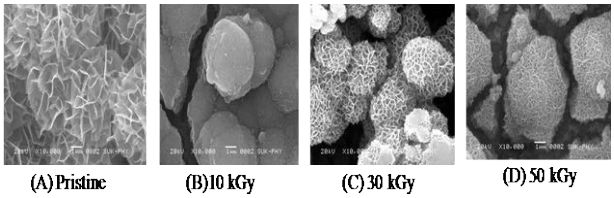

Fig. 3. Scanning electron micrographs of electron beam irradiated maghemite thin films (A) Pristine, (B) 10 kGy, (C) 30 kGy and (D) 50 kGy.

3.4 Electrochemical Measurement

As the transition metal oxides show pseudocapacitance through the reversible adsorption of ions of the electrolyte; the electrolyte and surface area of thin film are crucial while generating high specific capacitance [14]. Cyclic voltammetry (CV) technique has been employed to study the high or pulse power characteristics due to redox transition in the electroactive transition metal oxides. In order to evaluate the supercapacitive behavior of electron irradiated maghemite thin films, electrochemical properties of samples were investigated in 0.5 M aq. Na2SO3 electrolyte. Specific capacitance (Cs) and capacitance retaintion were estimated from cyclic voltammetry (CV)

using the relations (1) and (2) [15],

$$C = I_{avg} / (dV / dt) \quad (1)$$

Where, I is the average current in ampere and dV/dt is the scanning rate in volt/sec.

$$C_s = C/W \quad (2)$$

Where, W be the weight of active material deposited onto substrate.

The typical cyclic voltammograms of the sample A-D at scan rate of 5 mV are shown in Fig. 4. Inner active sites of samples being inaccessible or due to resistance offered buy ionic depletion at higher scan rates, sample exhibits maximum capacitance at lower scan rate [16].

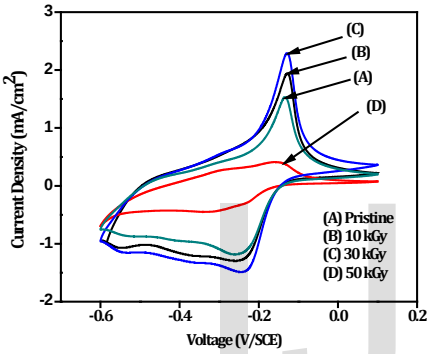

Fig. 4. Cyclic voltammograms of electron beam irradiated maghemite thin films in 0.5 M Na2SO3 solution at scan rate 5 mV/s.

Sample A bears maximum specific capacitance of 618 F/g d at scan rate of 5 mV/s. The maximum specific capacitance of 630, 678 and 478 F/g estimated for sample B, C and D respectively. The charge storage mechanism in transition metal oxides being a function of fast redox reactions on the surface, the enhancement in capacitance of sample B and C is attributed to electrode surface modification while decrease in capacitance for sample D due to increase in intrinsic resistance of the electrode material attributed to destruction of electrode surface structure [17]. The cyclic stability of different maghemite samples at scan rate of 100 mV/s were studied for 250 CV cycles. The Fig. 5 (a-d) show the cyclic voltagrams of maghemite samples for 1st and 250th cycle. It is observed that, after electron irradiation, capacitance retaintion increases from 78% for sample A to 85 % and 94% for sample B and C respectively whereas 80% capacitance retaintion observed for sample D. Since active material gets dissolved and /or detached exhibiting reversible oxidation /reduction in electrolyte decrease in the specific capacitance observed after cycling.

The nyquist plots for samples are shown in figure 6. The decrease in electrode resistance from is 14.43 Ω for sample A to 9.45 and 9.17 Ω for sample B and C respectively observed after electron irradiation. For sample D, it is 54.0 Ω. Thus after electron irradiation electrode resistance decreases initially and further increases for 50 kGy radiation dose. This change in resistance may attribute to surface modification of maghemite thin films after electron. Thus EIS supports the findings of cyclic voltammetry

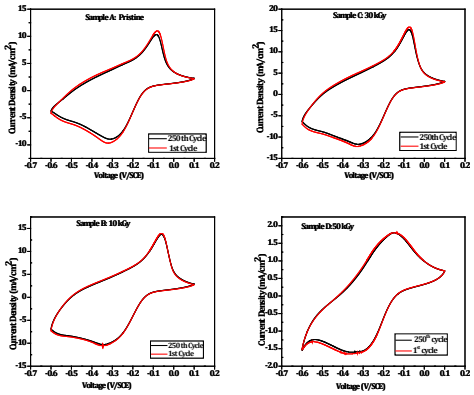

Fig. 5. Cyclic stability of electron irradiated maghemite thin films in 0.5 M Na_2SO_3 solution at scan rate 100 mV/s

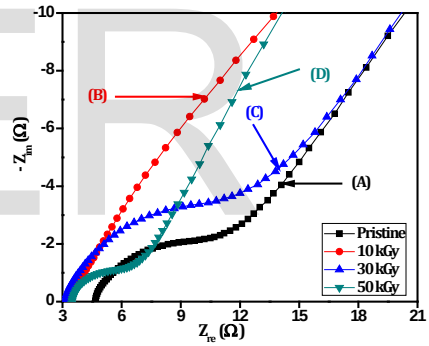

Fig. 6 The nyquist plots of electron beam irradiated thin films showing alteration in electrode resistance after irradiation

The typical charge discharge curves for pristine and electron irradiated maghemite thin films at current density 5 mA/cm2 are depicted in fig. 7. The charge-discharge curves reveal the suitability of maghemite electrode for supercapacitor application. The charging time of maghemite electrodes decreases after electron irradiation. The coulombic efficiency of the electrodes increases from93 to 95% for sample A to C and further it decreasesto 91% for sample D. Thus electron beam irradiation improves the charging discharging performance of elctrodeposited maghemite thin films which indictes the suitability of electron beam irradiated maghemite thin films as high performance supercapacitor electrodes.

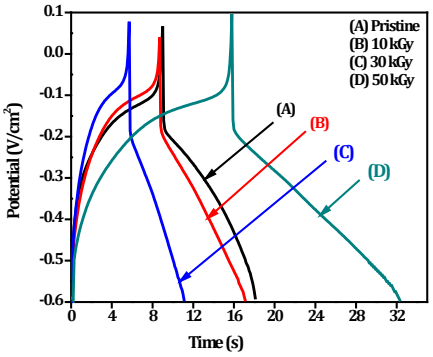

Fig. 7. Charge-discharge curves of electron beam irradiated maghemite thin films at current density 5 mA/cm2

4 Conclusion

Electron beam irradiation at lower doses affects the structural and morphological properties of elctrodeposited maghemite (γ-Fe2O3) thin films. Crystallinity of maghemite samples increases with electron irradiation for lower doses without change in atomic structure. Electron irradiation modifies surface morphology of maghemite samples non destructively. Electron irradiation at lower doses helps to improve the electrode surface hence to increase the capacitance. Cyclic stability of electrodeposited maghemite thin film electrodes increases after electron beam irradiation. Electron irradiation has synergetic effect on the supercapacitive properties of maghemite thin films.

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