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Spray Deposited Transition Metal Ferrite Thin Films for Li-Ion Batteries

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Abstract : Iron based compounds have drawn much attention for their potential as counter electrode in Li-ion batteries because of their low cost and low toxicity. Nanocrystalline transition metal $CuFe_2O_4$ thin film was deposited using an automated homemade spray pyrolysis unit over Antimony doped Tin Oxide (ATO) substrate. The ATO layer was deposited over the quartz substrate prior to deposition of ferrite film. X-ray diffraction (XRD) measurement shows that the film is of single phase, with tetragonal structure for $CuFe_2O_4$. Magnetization studies reveal that the film is ferrimagnetic in nature. Electrochemical measurement indicates porous $CuFe_2O_4$ film as promising electrodes for Li-ion batteries.
Keywords: Spray Deposited Transition Metal Ferrite Thin Films for Li-Ion Batteries.

Introduction

Ferrites having the general formula MFe_2O_4 (M= Transition metal ion, e.g. Ni, Co, Cu, etc.) are one of the most attracting class of materials, for their intriguing properties such as various redox states, electrochemical stability, pseudocapacitive behavior, etc.,[1,2,3]. Nowadays, they are used in supercapacitors and in Li-ion batteries[4]. Compared to other oxide ferrites, $CuFe_2O_4$ in powder form is best suitable active anode material in Li-ion batteries[5-7]. But the drop in the reversible capacitance and poor cycleability are major drawbacks. Recently, reported that this material deposited over a conducting substrate gives better electrochemical performance compared to powder[4]. In the present work, a novel approach of Antimony doped Tin Oxide (ATO) over quartz substrate was prepared by spray pyrolysis method with the conductivity value of ~ 20 Ω. Thin film of $CuFe_2O_4$ have been deposited by spray pyrolysis over conducting ATO substrate, which was previously coated over quartz substrate, to serve as back contact for use in Li-ion battery. The structural, morphological and magnetic properties of ferrite layer deposited over ATO are analyzed and the electrochemical studies are performed using cyclic voltammeter (potentiostat response mode) to understand their response and suitability for use in Li-ion batteries.

Experimental procedure

Deposition of Conducting ATO Electrode over Quartz Substrate

0.1 molar ratio of tin chloride and antimony chloride (93:7) were dissolved in a solvent of 350 ml ethylene glycol, 150 ml of water and 5 ml of HCl is added to maintain the pH acidic. Double sided polished quartz (2.5 cm × 2.5 cm × 1 mm) was used as substrate after cleaning ultrasonically in acid and de-ionized water. The substrate was maintained at 400 ˚C as measured by a K-type thermocouple. Compressed and moisture filtered air was used as the carrier gas and the substrate to nozzle distance is fixed at 35 cm. The precursor solution was sprayed onto the pre-heated substrate at a pressure of 40 Kg/cm^2 through a spray gun of inner nozzle diameter 0.3 mm. When the precursor solution was sprayed (500 spray) onto the hot substrate for 0.5 s, the temperature reduced to 320 ˚C. Therefore, a time interval of 30 s between the sprays was given so that the substrate regains its temperature to 400 ˚C. The deposition parameters were optimized by performing a number of trials. The aerosol on reaching the hot substrate undergoes a pyrolytic decomposition to form clusters which then develops into a continuous film in the presence of water as follows,

$SnCl_2.\ 2H_2O + nH_2O \rightarrow SnO_2 + 2HCl\uparrow + (n+1)\ H_2O\uparrow + H_2\uparrow$ (1)
$SnCl_2.\ 2H_2O + SbCl_3 + H_2O \rightarrow Sn_{1-x}\ Sb_x\ O_2 + 4HCl\uparrow + 1/2\ Cl_2\uparrow + H_2O\uparrow$ (2)

The prepared ATO substrate shows a resistance value less than 40 Ohm (5mm X 5mm) and is comparable with that of the commercially available ITO substrate (~ 20 Ohm). Optimized parameters for deposition of ATO substrate is given in table 1.

Deposition of $CuFe_2O_4$ Film over ATO Layer

Table 1: Optimized parameters for deposition of ATO substrate

Parameters	Specification
Starting materials	Tin Chloride and Antimony Chloride
Solvent	350 mL of Ethylene Glycol, 150 mL of double distilled Water and 5 mL of HCL
Substrate	Quartz
Substrate temperature	400 ˚C
Carrier Gas	Moisture filtered air
Pressure of Carrier Gas	40 kg/cm^2
Duration of single spray	0.5 sec
Nozzle to substrate distance	35 cm
No. of spray	500 spray

The optimal deposition parameters of $CuFe_2O_4$ film is given in table 2. The solution containing the metal ions were sprayed onto the preheated ATO substrate in a similar manner as mentioned above. The solution decomposes pyrolytically to form the required film and the chemical reactions involved in the formation of the film can be written as,

$Cu(NO_3)_2.3H_2O + 2Fe(NO_3)_2.9H_2O + nH_2O \rightarrow$

$CuFe_2O_4 + (23+n)\ H_2O\uparrow + 6NO_2\uparrow + O_2\uparrow$ (3)

The deposited sample was annealed at 500 ˚C and at 600 ˚C for 2 h in air. Sample annealed at 600 ˚C show better crystallinity and hence used for further characterization. The phase of the deposited film was confirmed by X-Ray Diffraction (INEL PSD MODEL) using Co-K_α (λ= 1.789 Å) radiation. The surface morphology was studied using a Scanning Electron Microscope (SEM) (JEOL – Japan JSM 840-A) and Atomic Force Microscope (AFM) in dynamic mode (SPI 3800 N). Magnetic measurements were done in a Vibrating Sample Magnetometer. The film thickness was estimated using a XP-1 Surface Profiler, Ambios technology Inc. Electro chemical performance of film was carried out using CHI Instrument (Model: CHI1100A).

Table 2: Precursors and substrate temperature to deposit $CuFe_2O_4$ film

Parameters	**Optimized deposition condition for $CuFe_2O_4$**
Starting materials	Copper Nitrate and Iron Nitrate
Solvent	300 mL of Water and 1mL of HCl
Substrate	ATO
Substrate temperature	350 ˚C
Carrier Gas	Moisture filtered air
Pressure of Carrier Gas	40 kg/cm^2
Duration of single spray	0.5 sec
Nozzle to substrate distance	35 cm

Results and discussion

Fig. 1 shows the XRD pattern of spray deposited $CuFe_2O_4$ film on ATO substrate sintered at 600 ˚C for 2h. It is observed that, In Fig. 1, apart from the ATO peaks, the other peaks indexed with the (h k l) value indicates the formation of tetragonal $CuFe_2O_4$ phase with the lattice parameter value of a=b= 5.842(5) Å and c= 8.682(1) Å[8].

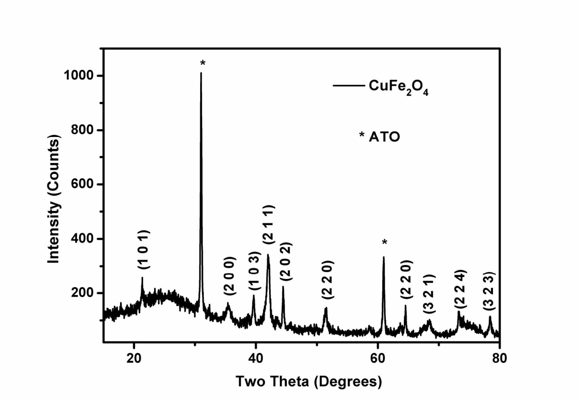

Figure 1: XRD pattern of spray deposited and annealed (600 ˚C/2h in air) $CuFe_2O_4$ film on ATO substrate.

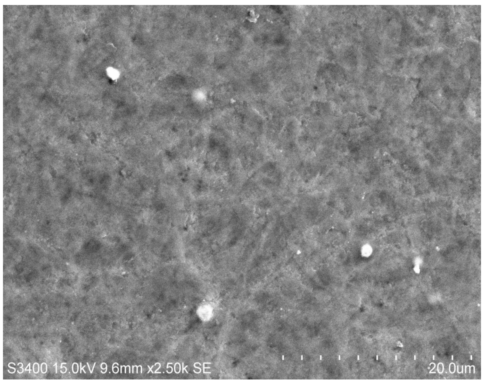

Figure 2: SEM image of $CuFe_2O_4$ thin film.

The average crystallite size in the deposited film, calculated using Scherrer's formula, was found to be 18 nm. The morphology of the prepared thin film was analysed using scanning electron microscopy (SEM) technique and is shown in Fig. 2.

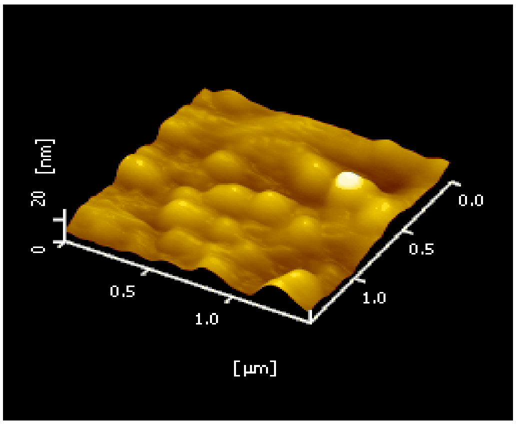

Figure 3: AFM image of $CuFe_2O_4$ thin film

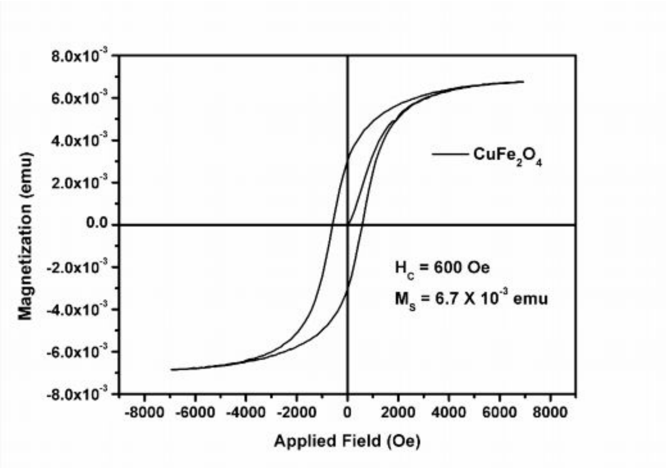

Figure 4: Magnetization curve of $CuFe_2O_4$ thin film at room temperature shows ferrimagnetic behaviour.

It can be seen that the spray deposited $CuFe_2O_4$ thin film had very good adherence[9] to the substrate and has relatively dense, compact and continuous morphology. The morphology of $CuFe_2O_4$ film consist of uniform spherical particles[4] with few larger sized particles. The topography of the prepared thin film was analysed using atomic force microscope (AFM). The AFM image of $CuFe_2O_4$ film is relatively smooth and the root mean square (RMS) roughness value is found to be 20 nm which is clearly depicted in the Fig. 3. This observation also substantiates with the SEM result. The thickness of the deposited film was found to be 1400 Å. Field dependent magnetization curve (M-H curve) at room temperature shows clear ferrimagnetic behaviour[10] with the saturation magnetization (M_S) value of 0.0066 emu and also explains the soft magnetic nature of the $CuFe_2O_4$ thin film with the Coercivity (H_C) value of 562 Oe which is shown in Fig. 4.

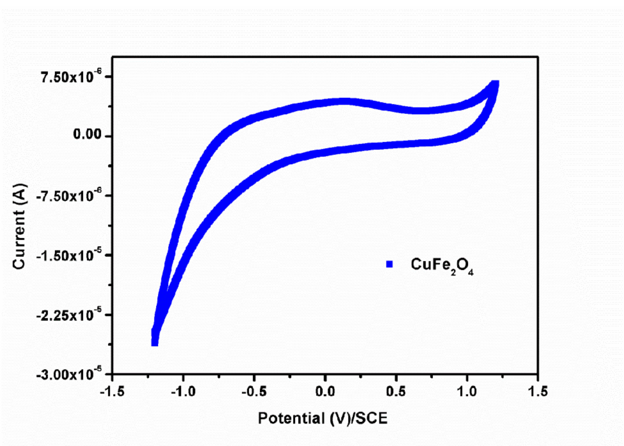

Figure 5: Cyclic voltammogram of $CuFe_2O_4$ thin film

$CuFe_2O_4$ thin film electrode potential response was performed in three electrode systems is shown in Fig. 5. The voltammogram is a display of current versus potential. The aim of this study is to test the electrochemical performance of the spray deposited $CuFe_2O_4$ thin film. The current response was recorded between the potential range -1.2 V to +1.2 V at a potential sweep rate of about 0.1 V/s in the 0.01 M $LiClO_4$ + propylene carbonate (Fig. 5) electrolyte. A platinum wire and saturated calomel electrode were used as counter and reference electrodes. During the anodic scan the Li^+ ions get intercalated into the film from the electrolyte causing an oxidation reaction (Colored state). In the voltammogram, the absence of anodic peaks at 0.1 V and 0.42 V corresponding to Copper and iron respectively, attributed to the non-oxidation state of both copper and iron which clearly indicates the stability of the material[4]. During the cathodic scan the ions gets deintercalated from the film which leads to reduction (bleaching) showing the reversible cyclic property. From the voltammogram, we observed that the anodic current response value of 2.7 μA and the cathodic current response of -7.7 μA. It is interesting to note that, the shape of the film is stable as observed from the electrochemical measurement during the 50^{th} cycle (not shown here) i.e., no peeling off of films is observed. Though the characterization concerning the battery applications has not been presented here the stability of the film is one of the major factors for the battery application during its charging and discharging cycles[11].

Conclusion

Nanocrystalline $CuFe_2O_4$ ferrite thin film was deposited over the ATO substrate by spray pyrolysis. The XRD result confirms the single phase nature without any evidence of secondary phase. The SEM and AFM studies reveal that the spray deposited $CuFe_2O_4$ is dense, compact and spherical particles with continuous morphology. The magnetization result clearly shows hysteresis behaviour due to ferrimagnetic nature. The electrochemical data implies that the $CuFe_2O_4$ ferrite thin film is more stable which can be used as a promising electrode in Li-ion batteries. The $CuFe_2O_4$ film spray deposited onto ATO substrate show good electrochemical behavior and hence further optimization may lead to development of low cost and high efficient ferrite layers for use in Li-ion batteries. The result concludes that, the newly deposited ATO over quartz (substrate) can be a better alternate for the commercially available ATO substrates for ferrite thin films to use in Li-ion batteries.

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