



Elaboration, characterisation and electrochemical properties of calcium doped iron oxide thin films prepared by spray pyrolysis

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Abstract

Fe₂O₃ and Fe₂O₃:Ca thin films were deposited by reactive chemical pulverization spray pyrolysis technique on heated glass substrates at 500 °C to study their crystalline structure, composition and electrochemical properties as a function of Ca concentration (0, 2 at.%, 5 at.%, 10 at.%). The films were characterized by X-ray diffractometry (XRD), EDAX 9100 analyser and scanning electron microscopy (SEM). The cyclic voltammetry study showed that the 5 at.% Ca doped Fe₂O₃ thin films exhibit a good capacity to insert and extract the Li⁺ ions.

Keywords: Spray pyrolysis, iron oxide, Calcium, Structure; Electrochemical properties

1. Introduction

The iron oxide material is one of the most important materials for a wide range of applications such as a gas sensors [1,2], electrochromic material [3,4], photoelectrochemical solar cell for solar energy conversion [5,6] and negative electrode in rechargeable batteries. Fe₂O₃ thin films have been prepared using many techniques such as r.f. sputtering [7], electrodeposition [8], metal-organic deposition (MOD) [9], sol-gel process [10], spray pyrolysis [11,12], etc.

Our previous study indicated that a Fe₂O₃ film prepared by spray pyrolysis shows a good voltammetric response indicating its ability to insert/extract large charge densities of small ions such as Li⁺. This makes it a potential material to be used as electrode in lithium-ion batteries [13].

Iron oxide thin films doped with Ca prepared by a liquid-phase deposition method (LPD) have been investigated as potential ethanol gas sensors [14]. The aim of this work is to obtain the elaboration optimal conditions for a negative electrode with a good stability and a capacity to insert/extract the Li⁺ ions in order to use in rechargeable batteries.

2. Materials and methods

Undoped and Ca doped Fe₂O₃ thin films were obtained by spray pyrolysis in air atmosphere, The solution was prepared from anhydrous iron chloride (FeCl₃) in deionized water using a precursor concentration of 0.05 M. The prepared solution was sprayed at spray rates of 6 ml/min onto the clean glass substrates heated at 500 °C using compressed air as carrier gas. The deposition time was 6 min. The nozzle to substrate distance was about 40 cm. The structural characterizations are performed using X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1054\text{\AA}$). The surface morphology was examined by scanning electron microscopy (SEM). For electrochemical investigations, thin films of undoped and calcium doped iron oxide are deposited on glass substrates pre-coated with transparent and conducting layers of ITO. The sprayed Fe₂O₃/ITO thin films are immersed in propylene carbonate (PC) with 0.5 M LiClO₄. They are studied by cyclic voltammetry in a three-electrode cell configuration, using a platinum sheet as counter electrode, saturated calomel as the reference electrode (SCE) and thin films of Fe₂O₃/ITO as the working electrode. The ions insertion/extraction is performed by using the Voltalab PGZ100 Potentiostat.

3. Results and discussion

3.1 X-ray diffraction (XRD)

Figure 1 reports XRD spectra of the undoped and calcium doped Fe₂O₃ thin films deposited on glass substrates grown at 500 °C with an atomic concentration of 2 at.%, 5 at.% and 10 at.%. The films crystallized in the rhombohedral (hexagonal hematite α -Fe₂O₃, the PDF numbers 72-0469 and 24-0072) structure with a preferred orientation along the (104) direction, while peaks associated to Ca are not observed.

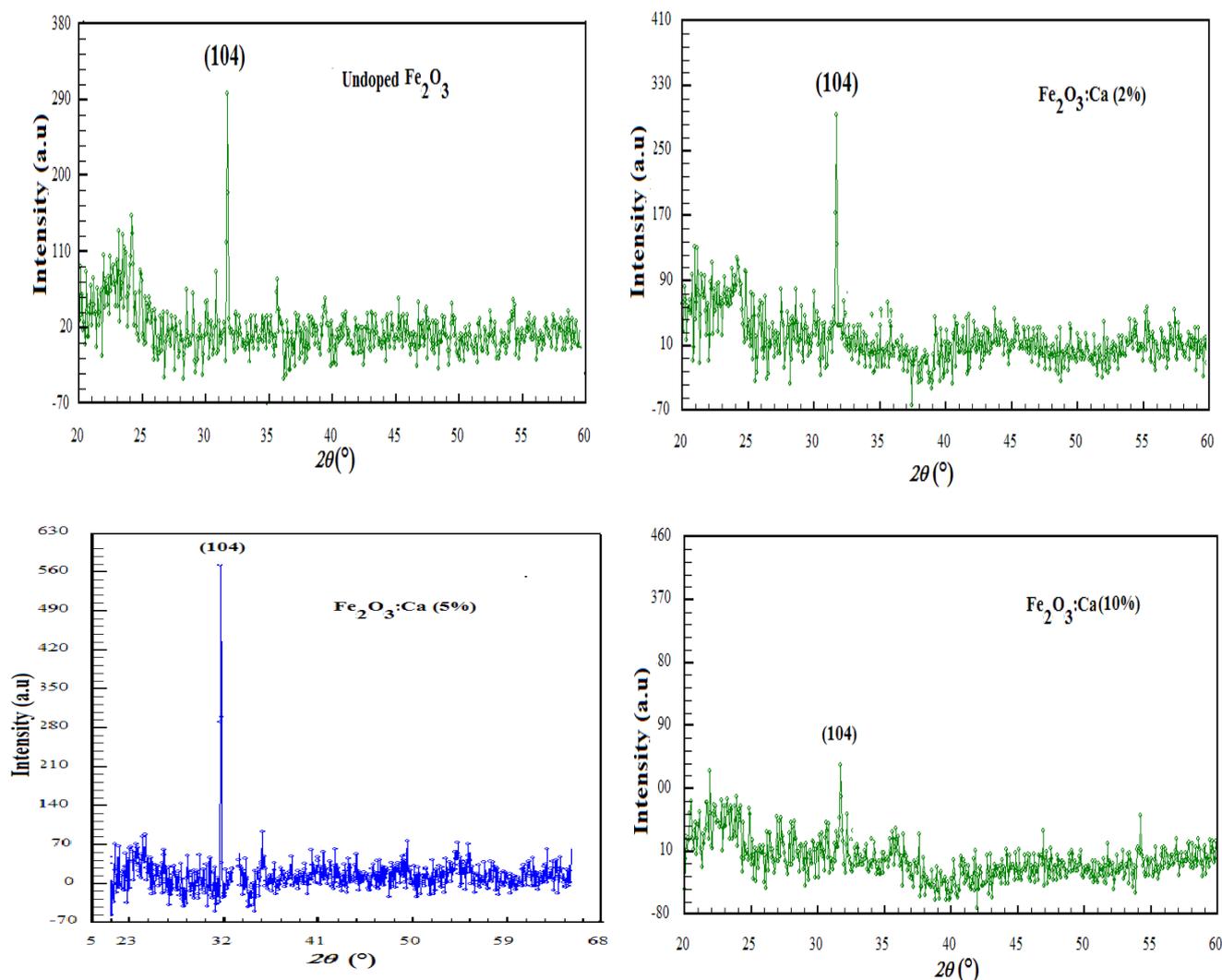


Figure 1: X-ray diffraction spectra of undoped and Ca doped Fe₂O₃ thin films

3.2 Composition and Surface morphology

Composite of the undoped and calcium doped Fe₂O₃ thin films were measured by EDAX analysis. Figure 2 shows the energy dispersive X-ray spectra of thin films doped with 5% Ca. As we can see, the spectrum reveals the existence of all expected elements, Fe, O and Ca atoms and some impurity as silica originated from the substrate.

Figure 3: shows SEM micrographs of Ca doped Fe₂O₃ films. All films show morphology with crystallites in the spherical form. We can see that 5 at.% Ca doped films are distinguished by a uniform grain size.

3.3 Electrochemical characterisation

The electrochemical characteristics of Fe₂O₃ and Ca doped Fe₂O₃ deposited on thin films of ITO are studied by recording the cyclic – voltammogrames (CV) in a propylene carbonate (PC) solution with 0.5 M of the lithium perchlorate trihydrate (LiClO₄).

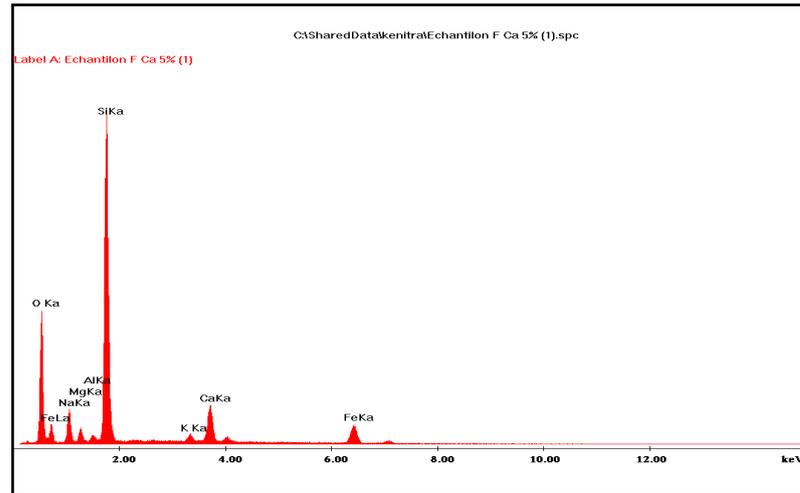


Figure 2: EDAX spectrum of Fe₂O₃:5 at.% Ca thin films

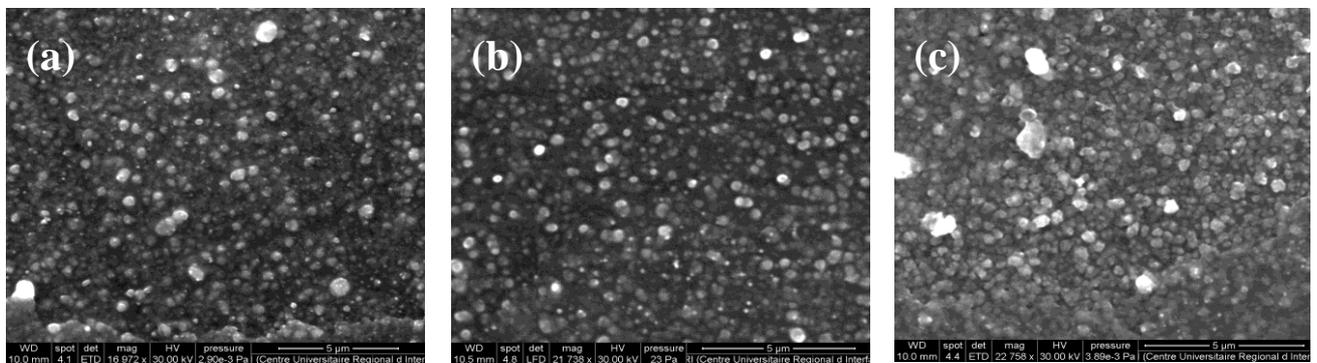


Figure 3: SEM micrographs of: (a) 2 at.%, (b) 5 at.%, and (c) 10 at.% Ca doped Fe₂O₃ thin films.

The cyclic voltammogram of undoped Fe₂O₃/ITO films with applied potential between -1.5 and 1.5V versus (SCE) are illustrated in figure 4. It can be seen that the films favours the Li⁺ intercalation/des-intercalation process, as we reported in our earlier work [13].

We are varied the concentration of the LiClO₄ propylene carbonate in order to investigate its effect on the insertion /extraction of the Li⁺ ions. Figure 5 shows the cyclic voltammograms of undoped Fe₂O₃/ITO films in a solution with 0.5 M and 1 M of the LiClO₄.

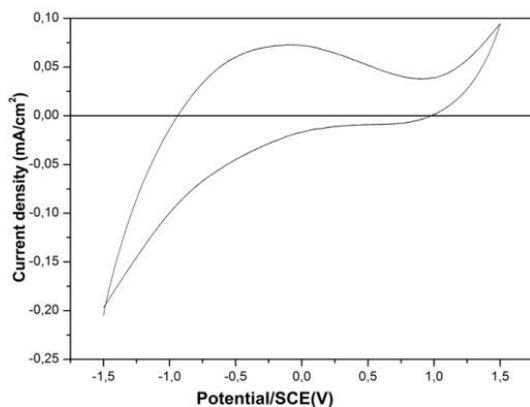


Figure 4: Cyclic voltammograms of undoped Fe₂O₃ thin film in 0.5 M of LiClO₄ propylene carbonate. The scan rate is 50 mv/s.

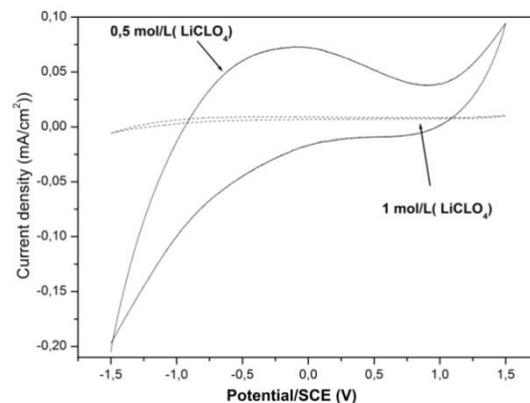


Figure 5: Cyclic voltammograms of undoped Fe₂O₃ thin film in 0.5 M and 1 M of LiClO₄ propylene carbonate. The scan rate is 50 mv/s.

It can be seen that the increase of the LiClO_4 concentration in the solution lead to narrowing the cyclic voltammogram of the films, indicating a decrease of the Li^+ intercalation/des-intercalation process. We can conclude that there may be a relationship between the concentration of Li^+ ions in the solution and their mobility which can be controlled by the scan rate. In order to investigate the doping effect by calcium, we recorded the cyclic voltammograms of the undoped and 2 at.%, 5 at.%, 10 at.% Ca doped films (figure 6). We can see that the insertion of calcium favours the capability to insert /extract the Li^+ ions.

films doped 5 at.% of Ca show an open cyclic than undoped films, and the curve shape illustrate the existence of two large anodic current peaks A and B corresponding to the oxidation states of thin films and the cathodic current peak C corresponding to the reduction state of thin films. It is concluded that the doping of the Fe_2O_3 by calcium illustrate a significantly reduction/oxydation phenomena for the optimal conditions, indicating a good voltammetric response.

The cyclic voltammograms stability of $\text{Fe}_2\text{O}_3:5$ at %Ca thin films has being studied by recording 5 cycles of the oxydo/reduction process (Figure 8), we can see that the cycles are reproducible.

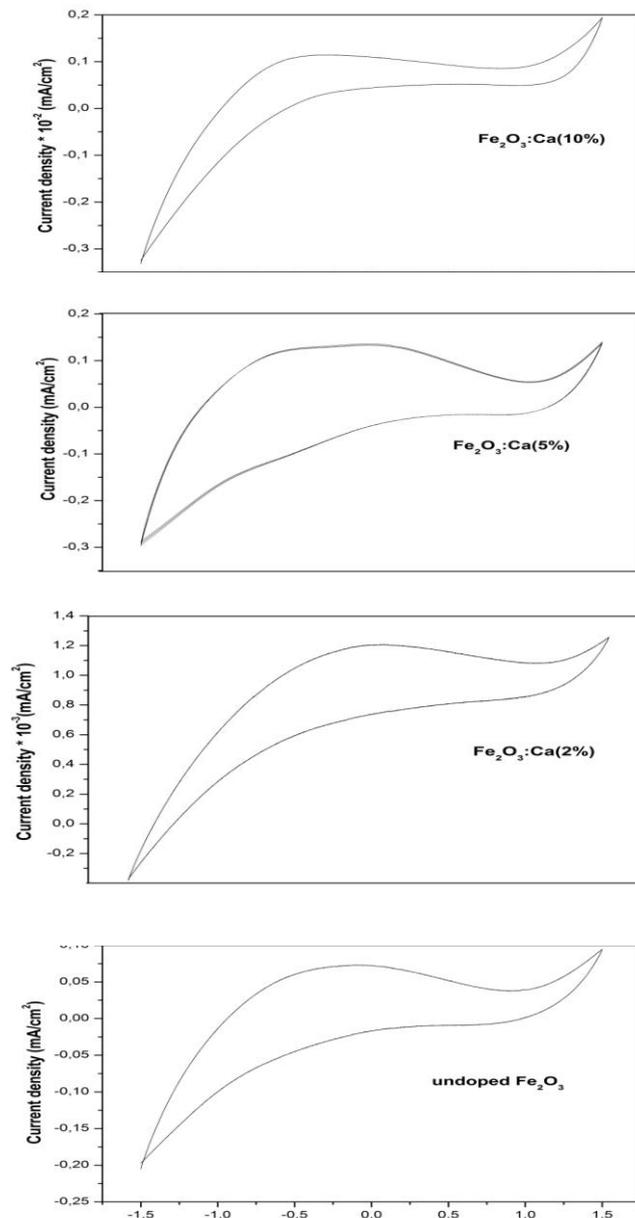


Figure 6: Cyclic voltammograms of undoped and Ca doped Fe_2O_3 thin film in 0.5 M of LiClO_4 propylene carbonate. The scan rate is 50 mv/s.

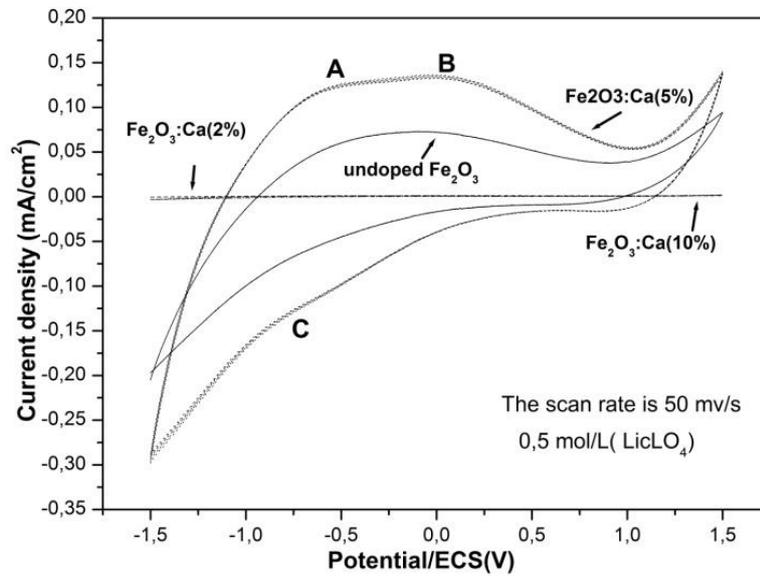


Figure 7: Comparisons of the cyclic voltammogrammes

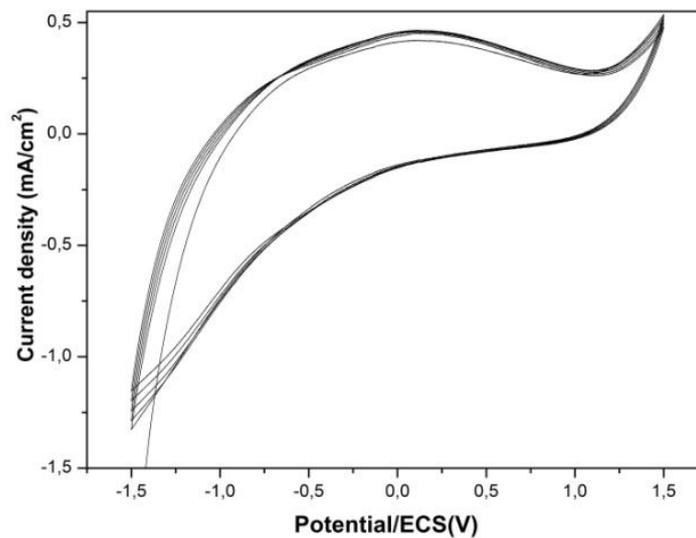


Figure 8: 5 cyclic voltammogrammes recorded for Fe₂O₃:5 at.%Ca thin films.

Conclusion

The highly oriented Fe₂O₃ thin films were deposited by the spray pyrolysis technique onto the glass substrates. XRD diffraction studies reveal the polycrystalline nature of the films. The electrochemical study shows that Ca doped Fe₂O₃ thin films have a good voltammetric response and a good stability especially at optimal conditions, indicating their ability to insert/extract a large charge densities of small ions such as Li. The obtained experimental data demonstrate that the deposited films can be used as electrode in lithium-ion batteries.

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