Fe₂O₃ sol-gel derived optical coatings for electrochromic device

Fe,O, filmi pripravljeni po sol-gel postopku

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Thin iron oxide films (69 nm-1500 nm) were deposited by dip-coating method from iron ion containing sols which have been made from a FeCl₃ 6H₂O precursor precipitated with ammonium hydroxide. Homogeneous sols were obtained after peptization of precipitates with addition of glacial acetic acid (60 mol %) and no organics (ethylenglycol, glycerol ethyl acetylacetate etc.) were added in order to adjust sol viscosity for depositing the xerogel film. In situ UV-VIS spectro-electrochemical measurements revealed that films heat-treated in the temperature range 200°C- 350° C exhibited intensive bleaching in 0.001M LiOH, KOH and NaOH electrolytes at cathodic potential (-1.45 V) and became coloured again at anodic potential (0.6V). Electrochromism has not been observed for films heat-treated at 500° C when α -Fe₂O₃ (hematite) is formed.

Key words: Iron (III) okside, electrochromism, infrared spectra, in situ spectroelectrochemistry

Filme železovega (III) oksida smo pripravili po sol-gel postopku. Kot izhodno spojino (precursor) za pripravo sola smo uporabili FeCl₃ 6H₂O, ki smo ga raztopili v vodi. Pri dodajanju (NH₃)_{aq} (25%) tej raztopini je prišlo do tvorbe oborine, ki smo jo po večkratnem spiranju (10X) peptizirali z led ocetno kislino (60 mol%). Tako pripravljenemu solu nismo dodali organskih snovi (etilenglikol, glicerol, etil acetilacetat...) za spreminjanje viskoznosti . In situ UV-VIS spektroelektrokemijske meritve kažejo, da se filmi žgani v temperaturnem območju 200°C-350°C razbarvajo v 0.001M LiOH, NaOH, KOH pri potencialu -1.45V in postanejo ponovno obarvani pri potencialu 0.6V. Filmi žgani na 500°C niso elektrokromni. Pri tej temperaturi namreč že pride do tvorbe hematita α -Fe₂O₃.

Ključne besede: Železov (III) oksid, elektrokromizem, infrardeči spektri, in situ spektroelektrokemija

1 Introduction

Iron oxide belongs to the transition metal oxides and is considered as a promising electrochromic material¹. Burke and Lyons² first reported that the thick oxide layer grown on iron substrate by potential cycling in alkaline medium exhibits an electrochromic transition. The colour of the layer changes from transparent at negative potential to yellow-green at positive potential. With the help of potential modulated reflectance spectroscopic measurements they found that passivative layer is composed of a mixture of α -FeOOH, γ -Fe₂O₃ (maghemite) and α -Fe₂O₅ (hematite).

Iron hydrous oxides FeOOH, γ -Fe₂O₃ and α -Fe₂O₃³ have been the subject of countless studies. Conventional preparation methods lack the concept of designing the metal oxide structure at atomic or molecular level. The solgel route ⁴ has recently attracted considerable attention because it has the potential to design the structure of the

final compound at the very beginning of the process, i. e. in initial solution.

When the substrate (usually glass) is slowly pulled out of the sol the meniscus is formed at the substrate/sol interface. Due to the evaporation of the solvent, the species which are present in the sol start to react. Condensation reactions between sol particles produce the formation of gel. During a final stage of drying, as the liquid-vapour meniscus recedes into the film interior, the film collapses and a compact xerogel film is formed. Further heat treatment of the xerogel films (200°C-500°C) produces oxide films with different degree of crystallinity and chemical composition.

2 Experimental

Instrumental

FT-IR spectroscopic measurements were performed in the spectral range on Digilab FTS-80 FT-IR spectrometer M. Maček: Fe₃O₃ sol-gel derived optical coatings for electrochromic device

equipped with near-normal and variable angle reflection cells (Barnes) for obtaining reflection-absorption spectra (IR RAS) and near-grazing incidence angle FT-IR spectra. VIS and NIR spectra of films were recorded on Perkin Elmer LAMBDA9 spectrophotometer with resolution 2 nm. Thickness measurements were performed on a Surface Profiler Alfa Step 200.

Cyclic voltammetric and chronocoulometric experiments were performed with an EG and GPAR model 273 computer controlled potentiostat-galvanostat, driven by a model 270 Electrochemical Analysis software. Single-scan or multiscan cycling and chronocoulometric measurements were performed within and at potentials +0.6 V and -1.45 V, respectively.

In situ UV-VIS spectroelectrochemical measurements were performed on a HP 8451A diode array spectrophotometer with EG and G PAR model 2644A polarographic analyser.

The coatings were made on the dip coating unit with pulling speed of 1 cm/min.

Preparation of Sols, Gels and Coatings

Iron oxide was prepared from a FeCl₃ \cdot 6H₂O precursor which was dissolved in deionised water (2x) (10 g of FeCl₃ \cdot 6H₂O in 100 g H₂O). 11 ml ($\rho = 0.91$ g/cm³) of 25 % (NH₃)_{ag} was added dropwise into the solution until pH ~ 9 was reached. Peptization was attained by glacial acetic acid (up to 60 mol.%). After filtering and sonification, the viscous sols as formed, were used immediately for making films by dip-coating procedure.

The corresponding oxides and films were obtained by heat-treatment of xerogels and xerogel films at 300°C and 500°C, respectively.

3 Results and discussion

FT-IR Spectroscopy

Films. The FT-IR reflection-absorption (IR RAS) spectra of films prepared by heat-treatment of xerogel films at 300°C and 500°C are shown in Figure 1. Strong bands at 520 cm⁻¹ and 432 cm⁻¹ characterise the phonon spectra of films heat-treated at 300°C. Further heating of the same film to 500°C did not change the position of the bands at 520 cm⁻¹ and 432 cm⁻¹, except that the width of the 520 cm⁻¹ band is decreased.

Characteristic bands of films appear at frequencies which nearly coincide with the TO modes of bulk (monocrystalline) α -Fe₂O₃, i.e. 520 cm⁻¹ and 432 cm⁻¹, respectively. This means that in the case of films the polarisation charge effect does not influence the band position, thus confirming that they consist of particles which are too small to exhibit surface modes ⁶. Similar to the TO modes, it revealed that also LO modes at 675 cm⁻¹, 491 cm⁻¹ and 371 cm⁻¹ are only slightly shifted in relation to the LO modes of the bulk α -Fe₂O₃ (Figure 2).

Beside the position of LO and TO modes also their widths strongly support the assumption that films do not contain large agglomerated particles making the film heterogeneous. For this reason it is likely that TO phonon mode broadening in the spectra of films heat-treated at 300°C may be considered of the lower degree of order in the distribution of iron ions in the structure of the film. This feature is characteristic of the γ -Fe₂O₃ phase which is formed at 250°C-300°C with regard to the more ordered α -Fe₂O₃ phase obtained at 500°C. Further confirmation was obtained from the corresponding LO spectra (Figure 2) which even more clearly exhibited phonon mode broadening.



Figure 1: FT-IR reflection-absorption spectra (IR RAS) of Fe₂O₃
 film (TO modes) prepared at 300°C (a) and 500°C (b- α Fe₂O₃).
 Slika 1: FT-IR refleksijsko-absorbančna spectra (IR RAS) Fe₂O₃
 filma žganega na 300°C (a) in 500°C (b- α Fe₂O₃)



Figure 2: NGIA- FT-IR spectra of Fe₂O₃ films (LO modes) prepared at 500°C (a-α-Fe₂O₃), 300°C (b) and 200°C (c).
 *indicates LO modes of Al-O modes (c.f. -Al₂O₃) formed during the temperature- treatment.

Slika 2: NGIA-FT-IR spektri Fe₂O₃ filmov (longitudinalna optična nihanja) žganih na 500°C (a-α-Fe₂O₃), 300°C (b), 200 °C (c). * označuje longitudinalna optična nihanja Al-O vezi. (pri žganju nastane Al₂O₃)

Electrochemical Measurements

Chronocoulometric measurements showed that the corresponding Q were large, being in the range of 10-25 mC/ cm² and depend on film thickness. (Figure 3)

Finally, when Q was expressed per nm of film thickness it was found that maximal Q/d values were about 0.2 mC/cm²nm.

The results of the in situ UV-VIS spectro-electrochemical measurements are depicted in Figure4. The most salient feature was a decrease in the absorbance (Δ A) in the UV spectral range (<400 nm) which appeared at cathodic potential (U = -1.5 V). When voltage was changed in anodic direction, the films became coloured again.

The maximal absorption change appears in the spectral range 300 nm-390 nm (Figure 4). This corresponds well to the results obtained by Gutiérrez and Beden⁷. We are not able to confirm that our electrochromic films also consist of FeOOH because, in addition to OH groups, they also contain acetate groups. These groups considerably contribute to the electrochromism of the films, as was observed even for films heat- treated at quite low temperatures (135°C). The films retain their electrochromic properties until the temperature of heat-treatment exceeds 350° C, when α -Fe₂O₃ is formed.



Figure 3: Cathodic and anodic total charge density (Q) of
Fe₂O₃ films heat-treated at 300°C as function of film thickness:
(a) cathodic scan, (b) anodic scan, electrolyte 10⁻³ M LiOH, charging potential -1.45V (a) and 0.6V (b)

Slika 3: Katodna in anodna celotna gostota naboja (Q) Fe₂O₃ filmov (2ganih na 300°C) v odvisnosti od debeline filmov: (a) katodna smer, (b) anodna smer ; elektrolit: 0.001M LiOH ; potencial: -1.45V (a) in 0.6V (b)

At the present state of research we are not able to give an answer concerning the mechanism which is responsible for the electrochromism of the films. Nevertheless, it is likely that one of the mechanisms already proposed for the



Figure 4: Spectroelectrochemical response (cathodic scan-bleaching) of Fe₂O₃ film prepared at 300°C (thickness 69 nm) in 0.1 M LiOH.

Slika 4: Spekroelektrokemijski odziv (katodna smer-razbarvanje) Fe₂O₃ filma zažganega na 300°C (debelina 69nm) v 0.1M LiOH

colouring and bleaching of nickel oxide films may also be responsible for electrochromic properties of iron oxide films.

4 Conclusions

Thin iron oxide films were deposited by dip-coating technique from aqueous colloidal solutions made from a FeCl₃ · 6H₂O precursor and precipitated with ammonium hydroxide. The viscosity of the sol was adjusted by the addition of acetic acid which acts as a peptising agent.

The films were prepared by heating the xerogel films at various temperatures (135°C, 200°C, 300°C, 500°C). Films prepared at 500°C correspond to α -Fe₂O₃ and are not electrochromics. Films prepared by heat-treatment in the temperature range 135°C-350°C exhibit reversible electrochromism. They bleach at cathodic and colour at anodic potential. Electrocromic films very likely consist of mixed γ -Fe₂O₃ and ferrihydrite phases with OH– and acetate inclusions.

5 References

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