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Electrochromic TiO_2, ZrO_2 and TiO_2-ZrO_2 thin films by dip-coating method

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ABSTRACT

Sol-gel processing of TiO_2, ZrO_2 and mixed Ti/Zr oxide thin films has been studied as application of these coatings in electrochromic devices. Their structural transformations as a function of annealing temperatures were analyzed by XRD and FTIR techniques. Electrochromic behavior of the three kind materials was investigated by cyclic voltammetry and the basic electrochromic characteristics were determined.

Keywords : Sol-gel deposition ; Thin films ; XRD ; Electrochromic ; Cyclic voltammetry

1. Introduction

Electrochromism is defined as effect of the color change caused by applied electric field or voltage. The induced change in the optical absorption retains even when the excitation source is removed [1]. Electrochromic (EC) materials are exclusive interesting due to the variety of potential applications, including elements for information displays, antiglare rear-view mirrors, sunroofs and smart windows [2,3].

Nanostructured thin films with their porous structure facilitate increased mobility of the injected ions, and therefore are promising candidates for the enhancement of electrochromic properties. These films can be manufactured by sol-gel technology, which allows nanoscale morphology, porosity, smoothness and uniform surfaces of the resulting films [4,5]. The other advantage of sol-gel deposition is its ability to produce a wide range of materials including mixed oxide films with easy controlling their properties, thickness [6].

Titanium dioxide possesses high refractive index, chemical stability and high dielectric constant. The anatase TiO_2 exhibits a promising behavior as electrochromic material [7]. The anatase phase possesses tetragonal symmetry and is consisted from TiO6 octahedras with two adjacent and shared edges, forming "zigzag" double chains. Vacant sites also form such rows, which are large enough to accommodate ions such as H^+ and Li^+.

Counter electrode is a very essential part of EC device. It must satisfy the following requirements such as reversible storage of a proper charge under the form of injected ions; to be transparent in the spectral range of the device application; upon ion intercalation and deintercalation to act as optically passive or to exhibit electrochromic effect in a sense opposite to that of working EC electrode and to be stable during long term cycling [8]. Optically passive counter electrodes can be ion storage materials with a large charge capacity and a high transparency. So far, these favorable properties have never been approached by a single stoichiometric compound. For example, CeO_2 is highly transparent, but possesses very low charge capacity. The mixed oxides based on cerium oxide reveal excellent transparency in the visible spectrum and during the intercalation/deintercalation cycles these oxide films are not influenced by the alkali ions and do not change their optical transmittance. Recently, the thin films of ZrO_2-TiO_2-CeO_2 [9] and $CeTi_2O_6$ [10] are investigated as counter electrodes in EC cells.

In this work, the sol-gel deposited TiO_2, ZrO_2 and mixed coatings are studied with respect to their application as electrochromic materials. The obtained thin films were structurally analyzed by XRD and FTIR spectroscopy. The electrochromic properties were monitored by the means of cyclic voltammetry and their electrochromic characteristics were determined.

2. Experimental

The formation of titanium dioxide [11] and zirconium dioxide sols were performed by using titanium ethoxide and zirconium propoxide as precursors at room temperature. Anhydrous ethanol was used as solvent. The introduction of acetic acid caused an exothermic reaction. Gelation was obtained by adding a small amount of water. Acetylacetone was used as a peptizing agent.

Mixed oxide system was obtained by mixing equal molar parts of the two solutions and aged for a week. During this week, the mixed solution was treated at temperature of 40°C in ultrasonic bath. The three solutions possessed clear and transparent appearances. They were found to be with the high stability up to 2 year without changing of their film forming properties.

Uniform coatings of TiO_2, ZrO_2 and TiO_2-ZrO_2 have been obtained by dipping in the colloidal solutions (with the withdrawal speed around l0cm min^{-1}) on Si, glass and conductive glass substrates. After drying at 80 °C, the films were annealed at different temperatures in the range of 300-600°C in air. The temperature was increased with the rate of 10°C min^{-1} and cooling rate of 20-25°C min^{-1}, respectively.

FTIR measurements were performed in the spectral region 350-1600 cm^{-1} by Shimadzu FTIR Spectrophotometer IRPrestige-21 .XRD spectra of sol-gel thin films were recorded by means of XRD diffractometer Bruker D8, at the grazing angle 2° and step time 8 s and step 0.1°.

Electrochromic behavior was examined by cyclic voltammetry technique, performed in a standard three-electrode cell arrangement. The cell was consisted of Pt as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode. The electrodes were immersed in electrolyte of 1 mol/l $LiClO_4$ in propylene carbonate (PC). The color change was detected by optical system chopped light source and lock-in amplifier, attached to the cyclic voltammetry equipment. The current, the passed charge and the light transmittance were measured as a function of applied voltage at different wavelengths. Current density vs. voltage voltammograms were registered between -1.5 V and +1 V at different scanning rates ranging from 5 to l00mV/s. Simultaneously the values of current (*I*) and charge (Q) are measured in dependence on applied voltage.

Color efficiency (CE) experimentally qualifies the modulation of the optical properties of electrochromic materials. It must be pointed out that color efficiency is spectrally dependent, and comparison is possible only for CE values obtained for one and same wavelength.

3. Results and discussions

Fig. 1 presents the recorded XRD patterns of sol-gel obtained zirconia treated at different temperatures. XRD spectra of ZrO_2thin films revealed that the crystallization began at the lowest annealing temperature of 400°C. Increasing of temperature leads to sharpen the XRD peaks and appearance of some new weaker lines (located at 2θ = 38.5, 45, 59). All detected XRD lines are assigned to tetragonal ZrO_2 crystal modification [12].

Fig. 1. *XRD spectra of sol-gel ZrO_2 films, treated at different temperatures.*

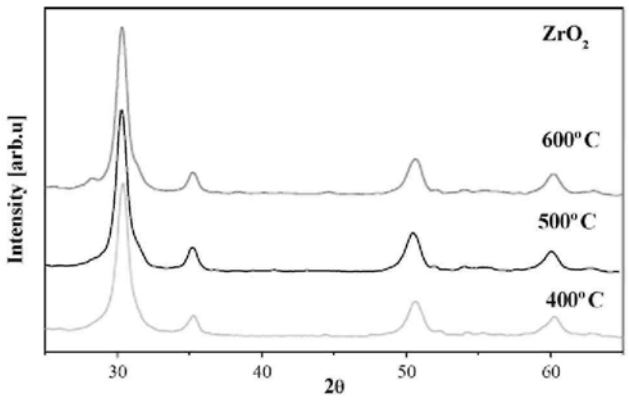
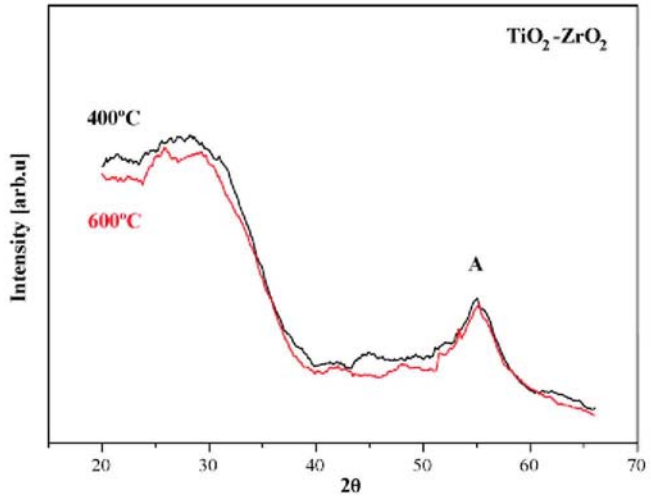


***Fig. 2**. XRD spectra of sol-gel TiO_2-ZrO_2 films, treated at different temperatures.*



The lattice parameters are determined. The lattice parameters are a = 4.343 Å and b = 3.122 Å for sample, treated at annealing temperature of 400°C. After 600°C, the films are fully crystallized in tetragonal phase with lattice parameters a = 5.594Å and b = 2.98 Å. The sizes of crystallites are estimated by using the Scherer formula. It is observed that the crystallites become bigger after higher annealing treatment, but still their dimensions are nanosized. The crystallite size of 400 °C annealed film is 6 nm, increasing to 9 nm for 500°C and l0 nm for zirconium oxide film annealed at 600°C. The annealing procedure is accomplished in oxygen atmosphere, which induces additional oxidation of the film and respectively more stoichiometric oxide matrix.

Our previous study [11] of sol-gel TiO_2 films showed that their crystallization began at the temperature above 450°C in anatase phase. The anatase crystal modification is reported as suitable for electrochromic applications [7].

XRD spectra of TiO_2-ZrO_2 films are shown in Fig. 2. It can be seen that mixing the two oxides in a system (molar ratio 1:1) results in thin films that remain amorphous even after thermal treatment at 600°C as observed from XRD measurements (it must be noted that intensity axis is extended five times in comparison to Fig. 1). The broad peak at 2θ = 55 can be related to anatase titania [13]. A broad feature located in the range 2θ = 20-33 might be a overlapping of XRD lines, as there are cited the most intensive XRD lines (tetragonal ZrO_2 and anatase TiO_2). The line shapes clearly indicate predominantly amorphous films. This is an interesting result as it is known that amorphous structure favors intercalation and deintercalation of small ions into film structure [14].

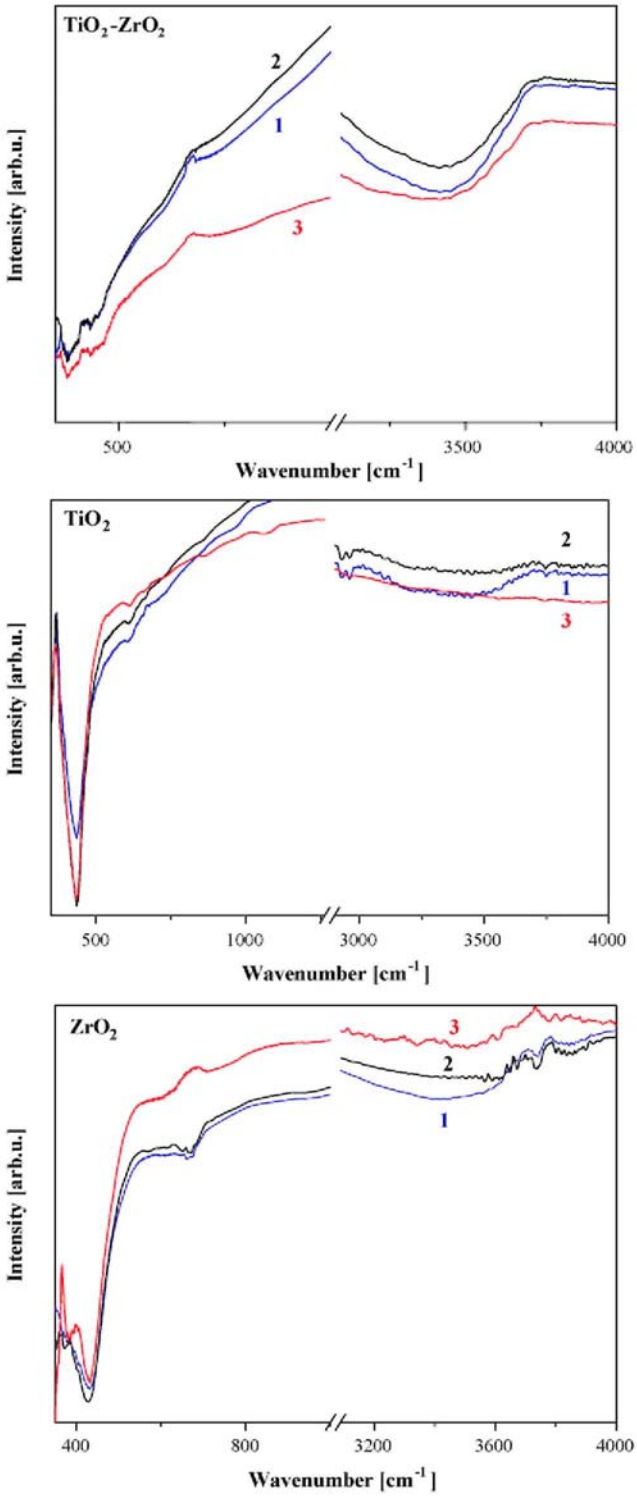
FTIR spectra of dip-coating films of ZrO_2 , TiO_2 and ZrO_2 -TiO_2 annealed at three temperatures of 400, 500 and 600 °C are given in Fig. 3.

Pure zirconium oxide films show a strong absorption band around 432 cm^{-1} after annealing at 400 and 500 °C and it is shifting towards 454.7 cm^{-1} for annealed film at 600°C. These bands are indicative for tetragonal phase [15]. At the highest annealing temperature, an additional peak appears at 582.5 cm^{-1} assigned to tetragonal phase as well [15]. IRstudy suggests that ZrO_2 undergoes crystallization at relatively low temperatures (400 °C) in tetragonal crystal modification. Increasing the annealing temperature leads to better crystalline film structures. This conclusion confirms XRD analysis.

Titanium oxide films reveal IRlines related to anatase crystalline phase even after 400°C annealing. The IR spectrum for TiO_2 film, treated at 600 °C presents two absorption lines located at 430 and 863 cm^{-1}, attributed to anatase phase [16]. The spectra features show that TiO_2crystallized in favorable anatase modification.

The mixed Ti/Zr oxide system exhibits amorphous structure as it is deduced by XRD data. IR spectra possess weaker and broader absorption bands due to overlapping of Zr-O and Ti-O vibrations. New bands are detected at 380 cm^{-1}, 690 cm^{-1} (only for annealing film at 400 °C) assigned to amorphous ZrO_2 or to amorphous TiO_2 and a shifting towards 748 cm^{-1} associated to monoclinic zirconia.

Fig. 3. *FTIR spectra of TiO_2, ZrO_2 and Ti/Zr oxide films annealed at 400 °C (curve 1), 500°C (curve 2) and 600°C (curve 3).*



FTIR spectra of sol-gel deposited films reveal that water incorporation for ZrO_2 films vanishes slightly with annealing. IR bands at 3400-3800 cm^{-1} and 1647.3 cm^{-1} are detected and assigned to the structural vibrations of physically adsorbed -OH groups connected with Zr^{4+} and to a scissor bending mode of coordinated molecular water, respectively [17]. Similar absorption bands related to physically adsorbed water are observed for the mixed Ti/Zr oxide system regardless the annealing temperature as their intensities are significantly stronger than

those detected for pure components. The FTIR data for sol-gel TiO_2 show that the annealing at the highest temperature (600 °C) leads to a disappearance of OH groups. Some IR bands are referred to ν(C-H) bonds, due to the organic components. These lines are seen in all the spectra and resulted from the sol-gel processing.

The sol-gel films possess high initial transmittance. In visible spectral region the transparency reaches 60% when deposited on conductive glass and higher up to 80% on ordinary glass. The substrate reduces the optical transmittance due to the thin conductive layer of SnO_2:Sb. The color change of the films provoked by applying voltage is not as strong as it is reported for other electrochromic materials. The aim of this study is to determine if the sol-gel coatings are suitable for counter electrodes in electrochromic devices.

CV curves are recorded at different sweep rates-100-10mV/s. It is observed that with increasing scan rate, current rises significantly. The higher currents passing through film structure can cause a destruction of the electrochromic coatings, and they must be avoided. The shapes of the registered voltammograms and the peaks positions differ for the various rates. It can be also observed that CV curves of $ZrO_2$and Ti/Zr oxide system are very similar (see Fig. 4) and considerably different from the cyclic voltammogram of TiO_2 film. The electrochromic characteristics (color efficiency and optical modulation) show highest values for the samples annealed at lowest temperature of 300 °C as seen from Fig. 5. The optical modulation values are higher for TiO_2 films up to 27%, on the other hand $Zr0_2$ films possess ΔT below 17%. The lowest values were found out for the mixed films with maximum 13.5% (at λ = 650 nm). Meanwhile, the color efficiency reveals different tendency as ZrO_2 shows highest values of 45 cm^2/C (at λ = 450 nm) and 43 cm^2/C (at λ = 550 nm). Similar results are reported for more studied electrochromic materials such as MoO_3 [18,19], which is a little surprising as Zr oxide is not known to possess electrochromic effect and even to be intercalated material. Further investigations are needed to uncover if this behavior is due to the specific microstructure obtained by sol-gel deposition.

Fig. 4. *CV curves of ZrO_2 and TiO_2-ZrO_2 (a) and TiO_2 (b) films, treated at 300°C.*

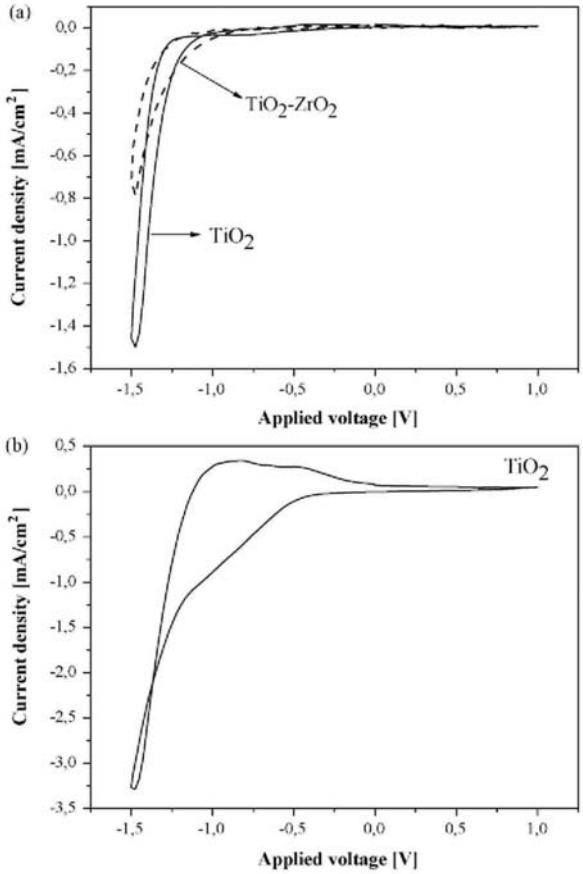


Fig. 5. *Electrochromic characteristics of sol-gel films, treated at 400°C.*

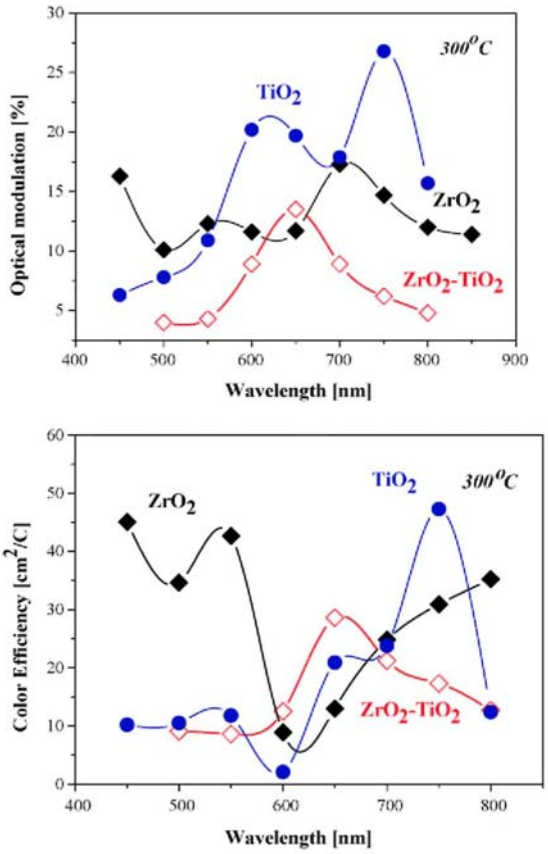
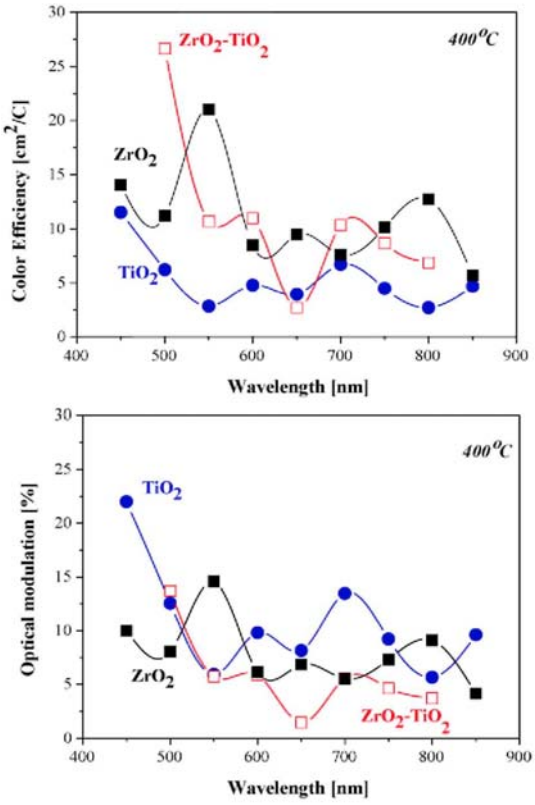


Fig. 6. *Electrochromic characteristics of sol-gel films, treated at 400°C.*



Increasing the annealing temperature, the values of electrochromic characteristics are considerable smaller (as seen from Fig. 6). For titania films, the optical modulation drops down to 6.7% (400 °C, λ = 700nm) and to 8.9% (500°C, λ = 600nm), zirconium oxide shows 14.6% at 550 nm after 400 °C annealing and 5.5% (700 nm) after 500 °C. The mixed oxide system also presents a decreasing of the electrochromic characteristics. Meanwhile, their values are comparable and sometimes higher than those of pure components.

The electrochromic measurements indicate that the sol-gel thin films are stable upon reversible intercalation/deintercalation cycles (up to 1000 cycles testing), showing low color efficiency and optical modulation. The obtained structural and electrochromic results can satisfy the requirements for counter electrode in electrochromic devices.

4. Conclusions

In conclusion, the study reveals that sol-gel method is very suitable for producing pure and mixed metal oxide films. It is determined that although pure oxides crystallized at relatively low temperature, the thin films of TiO_2-ZrO_2 retain their disordered and amorphous structure even after high temperature annealing at 600°C for 1 h. XRD study reveals that ZrO_2 films possess nanosized structure. TiO_2, ZrO_2 and TiO_2-ZrO_2 films show good reversible process of intercalation and deintercalation of Li ions. Electrochromic properties makes them good candidates for counter electrodes in electrochromic devices, especially mixed TiO_2-ZrO_2 thin films, that remain amorphous, and exhibits optically passive behavior upon cycling. Similar data for high electrochromic performance of mixed vanadium-titanium oxide are recently reported [20] as transparency and optical modulation values, which indicates that titanium-zirconium oxide films are also perspective as a counter electrode.

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