CrossMark

The role of thermal analysis in optimization of electrochromic effect of nickel oxide thin films, prepared by the sol-gel method: Part III

R. Cerc Korošec[a,*], M. Felicijan[a], B. Žener[a], M. Pompe[a], G. Dražić[b], J. Padežnik Gomilšek[c], B. Pihlar[a], P. Bukovec[a]

[a] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia
[b] National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia
[c] Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia

ABSTRACT

Electrochromic thin films were prepared from nickel chloride NiCl$_2$ precursor by the sol-gel method. To obtain reversibility of the colouring/bleaching process and maximal change in transmittance during potential switching, thin films should be thermally treated to an optimal degree. From dynamic TG measurements of the sol-gel prepared thin films, deposited on a substrate, a temperature was determined at which makes it essential to prepare several films thermally treated to a different extent by changing the duration of the treatment at this temperature. Electrochromic response of such prepared films was additionally tested by spectroelectrochemical measurements.

From the comparison of dynamic TG measurement of thin film and the corresponding xerogel it is evident that xerogel starts to decompose at considerably higher temperature. Therefore the results obtained for xerogel samples could not be used for optimization of the thermal treatment of thin films. The described optimization was done for the originally prepared films and also for films in which the content of the counter ions (chloride, lithium) was lower. From the results of spectroelectrochemical measurements, optimized thermal treatment for both thin films is reported together with the change in transmittance between the bleached and the coloured state (at λ = 480 nm) and their coloration efficiency. TEM of cross-sections revealed the structure and thicknesses of both films.

1. Introduction

Non-stoichiometric nanostructured or polycrystalline nickel oxide possesses several excellent properties. It is a p-type semiconductor with a wide band gap (3.6–4.0 eV) [1] and also anodic electrochromic material which colours from transparent (Ni^{2+}) to deep brown (Ni^{3+}) upon oxidation, exhibiting high electrochromic efficiency [2]. In a form of thin film it offers promising candidature for many applications such as functional sensing layers for gas sensors [3,4], antiferromagnetic layers [5], p-type transparent semiconducting films [1], electrochromic or ion storage layer in smart windows [6] and optical recording material [7]. Recently fast developing research area of NiO application is in new types of photo-electrochemical devices for the conversion of solar energy into electricity and for fuel production, based on p-type dye-sensitized solar cells [8,9].

Chemical methods of deposition (spray pyrolysis and sol-gel) enable preparation of large-area samples; they are also less technically demanding as physical ones with regard to the equipment needed for thin films preparation/deposition. Nanostructured films, prepared from colloidal solutions, are highly porous and comprised of small nanoparticles, resulting in a large surface area [1].

For the preparation of NiO films from NiCl$_2$ precursor salt, spray pyrolysis technique was mainly used [10–15], while the sol-gel method rarely [1,16]. In these articles the dependence of thin film structure on the preparation conditions and consequently on band-gap energy or electrochromic properties is reported. In most cases the substrate temperature was 350 °C, leading to formation of cubic NiO films [10,11,14]. The dependence of the substrate temperature on the formation of nickel oxide phase was followed in a temperature range from 225 to 425 °C [12]. Authors reported that at a substrate temperature less than 225 °C nickel oxide was not yet formed. In a region between 225–275 °C, pyrolytic reaction begins and leads to formation of NiO, which starts to crystallize at temperatures higher than 275 °C. Properties of the prepared films depend strongly also on precursor

concentration [13]. When concentration of $NiCl_2$ solution was less than 0.2 M, cubic NiO was formed on a heated substrate (350 °C). At a higher solution concentration, chloride concentration increases, while that of oxygen decreases, leading to decrease in crystallinity and to porous structure. Besides, at concentrations between 0.2 and 0.3 M, carriers type changes from the expected p-type to n-type. Different precursor solutions were also sprayed on substrate, heated at 350 °C [15]. Out of four different solutions, pure NiO was obtained from $NiCl_2$ and Ni $(NO_3)_2$ solutions, while from $Ni(OH)_2$ and $NiSO_4$ not. Highly transparent bunsenite NiO films with a thickness ranging from 300 to 1500 nm were prepared by sol-gel method from $NiCl_2$ precursor [1]; the resulting sol was applied on substrates, heated from 300 to 320 °C for 15 min. In obtained films NiO crystallite size was around 4.5 nm. Electrochemical oxidation was highly reversible; change in transmittance at 500 nm was around 60%. Sol-gel prepared films from nickel chloride, citric acid and butanol or ethanol quickly reach electrochromic stability [16]; the transmittance modulating was from 80% to 30%. Film thickness is not mentioned, but we assume they are probably thick.

In our previous work we have shown that degree of the thermal treatment required to obtain electrochromic nickel-oxide thin films with maximal electrochromic (EC) response depended strongly on the precursor used and on the chosen chemical route for their preparation [17–20]. From the past investigations it is well known that too high processing temperature significantly lowers electrochromic effect, the layer could even become inactive [21]. On the other hand, in insufficient thermally treated films optical modulations decrease soon after beginning of the cycling [22]. There is no explicit rule for the extent of treatment needed to obtain optimum properties. Counter-ions (sulfates, acetates etc.) play an active role in the formation of the nickel-oxide structure.

In seeking for optimal temperature and duration of thermal treatment, thermal analysis plays an important role. From dynamic TG measurements temperature of heat treatment could be determined, while from isothermal ones possible durations of treatment. Measurements of electrochromic response of several films thermally treated to a different degree are also essential [19]. Thermal decomposition of thin films begins at lower temperature with regard to corresponding xerogels due to higher surface area of small particles. For sol-gel prepared film we observe a difference of around 30 ° [17,18] while for precipitated films formed by alternately dipping deposition the difference was more than 100 ° [20]. Therefore, it is important to perform measurements on thin films rather than on the corresponding xerogels.

The starting solution contains precursor salt and different additives, complexing agents or templates which enable tailoring of the desired properties of the final material. During thermal treatment of the starting amorphous layer, dehydration, combustion of organic phases and decomposition of the initial precursor take place in several temperature regions, specific for the separate system. For the majority of the mentioned applications the final temperature of the heat treatment is chosen with the aim to achieve polycrystalline or nanosized NiO which still contains lattice defects, impurities or oxygen excess. The reason is that stoichiometric NiO is not a semiconductor any more, but becomes an insulator.

The present work is a continuation of our studies on sol-gel derived nickel oxide films prepared from a $NiSO_4$ and $Ni(CH_3COO)_2$ precursors. In this work, we took $NiCl_2$ as a precursor salt. The procedure for the optimization was carried out in the same manner as described in Part I [17]. Isothermal temperature, at which makes it essential to thermally treat thin films for electrochromic applications, was chosen on the basis of dynamic TG measurements of films, supported on a substrate. Our previous investigations showed that results obtained for the corresponding xerogels could not be used because higher decomposition temperature was determined in the latter case. Electrochromic behaviour was tested using *in-situ* VIS-spectroelectrochemical

measurements. From the part of the sol chloride ions were removed by washing (see Experimental), therefore a remark is made also on differences in behaviour of thin films with different chloride and lithium concentration. Transmission Electron Microscopy analysis (TEM) shows the structure of both optimized films.

2. Experimental

2.0 M LiOH (p.a., Kemika, Zagreb, Croatia) solution was added dropwise to 0.6 M solution of nickel(II) chloride (p.a., Kemika) to pH 9.0. For one series of samples, the green precipitate was washed four times with water (washed sample). The slurry was peptised with glacial acetic acid to pH 4.5, some water was added to adjust the viscosity. For unwashed samples the green precipitate was only centrifuged so that a high amount of chloride and lithium ions was retained. Xerogels were obtained by air-drying of the starting sols.

Chloride content in the samples was determined for the corresponding xerogles by ion chromatography (IC) using AS4A separation and AG4A guard column (Dionex, USA). The Dionex DX500 chromatograph was used. The lithium concentration was determined by flame atomic absorption technique (AAS) using Varian AA240 atomic absorption spectrometer.

Thin films were prepared on different substrates using the dip-coating technique. For TG measurements the microscope cover glasses were used while for *in-situ* spectroelectrochemical measurements $SnO_2/$ F conducting glass (square resistivity 25 Ω/▢; 1 × 3 cm²). Before deposition a wetting agent was dispersed on substrates using a dip-coating technique. For microscope cover glasses a solution of 1 wt.% of Etolat TD-60 (TEOL Factory, Ljubljana, Slovenia) in distilled water was prepared, while for conducting glasses a solution of 1 wt.% of Teloxide (TEOL Factory, Ljubljana, Slovenia) in ethanol was used. After the wetting solution had dried, the thin film was deposited with a pulling velocity of 5 cm min⁻¹. The samples for spectroelectrochemical measurements were heat treated in muffle furnace (Bosio, Slovenia) allowing the temperature accuracy of ± 1 °C.

Detailed Instrumental parameters of thermogravimetric measurements are described in Part II [18] and of spectroelectrochemical measurements in Part I [17].

Simultaneous TG-MS measurements were performed on a Mettler Toledo TGA/DSC1 instrument, coupled to a Pfeiffer Vacuum ThermoStar mass spectrometer. Around 5 mg of the xerogel was placed in a 150 µL alumina crucible and heated with a heating rate of 5 K min⁻¹ from 25 to 1000 °C. The furnace was purged with air (flow rate of 50 mL min⁻¹). Blank curve was subtracted. Evolved gases were introduced into mass spectrometer via 75-cm long heated capillary.

For the TEM study a cross section of the sample on a < Si > substrate was prepared using an adapted Gatan cross-sectional TEM specimen preparation kit. After mechanical thinning and dimpling, ion milling using 3.8 keV argon ions at a 10° incident angle was used. Samples were examined by a JEOL 2010 F transmission electron microscope, operated at 200 kV. The chemical composition of the phases was determined using a Link ISIS-300 energy dispersive X-ray spectroscopy (EDXS) system from Oxford Instruments with an ultra-thin window Si(Li) detector.

3. Results

Comparison of dynamic thermogravimetric curves of a thin film, deposited on a substrate and the corresponding xerogel shows that thermal decomposition processes occurred at a lower temperatures in a thin film sample (Fig. 1a). After dehydration, completed at around 150 °C, thermal decomposition of acetate groups occurred and simultaneously nickel oxide began to form [10,11,17]. Onset temperature of the described decomposition was ∼200 °C for thin film sample and ∼330 °C for xerogel. From the shape of the TG curve of thin film it is evident that at least two step process took place in the temperature