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Electrochromic $Ni_{1-x}O$ pigment coatings and plastic film-based $Ni_{1-x}O/TiO_2$ device with transmissive light modulation

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ABSTRACT

Novel nickel oxide coatings (100–600 nm in thickness) with low surface roughness (<20 nm) and haze levels down to 6% were deposited at a temperature not higher than 150 °C on FTO glass and conducting plastic films. The coatings were deposited on the substrates from water dispersions made of $Ni_{1-x}O$ pigment synthesized via the peroxo route by reaction of a H_2O_2/urea mixture with Ni-acetate precursor. The bunsenite $Ni_{1-x}O$ pigment was obtained after thermal treatment of xerogels at 400 °C for 24 h. Processing common for paint manufacturing was applied for the preparation of water dispersions of the $Ni_{1-x}O$ pigment, i.e., intensive milling of the pigment with dispersant. Dispersant (NiO_xH_y) was prepared by colloidal precipitation technique from Ni-sulfate precipitated with sodium hypochlorite.

The materials ($Ni_{1-x}O$ pigment, NiO_xH_y precipitate, coatings) were investigated using various analytical techniques (TG, DSC, SEM, TEM, IR and optical spectroscopy), while the electrochromic properties were determined by means of in situ spectroelectrochemical measurements, applying standard electrochemical techniques (cyclic voltammetry, chronocoulometry). The results revealed a convenient, simple, and robust technique for making "electrochromic paint" coatings from pre-prepared $Ni_{1-x}O$ pigment. They demonstrate the potential of the described electrochromic coatings for manufacturing plastic film based electrochromic devices providing transmissive light modulation.

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1. Introduction

Monolithic "smart" windows and electrochromic (EC) sunroofs made on glass substrates (glass-based EC) have great potential for glare/heat control systems for architectural and automotive applications. As glass-based EC devices appear on the market, there is an inevitable need for cost reduction by high-throughput manufacturing. One possibility for reducing the price of solar control products is their mass production [1] by roll-to-roll (R2R) [2] coating techniques (www.coatema.de) on flexible polymer films. A wide choice of highly transparent plastic films exists but all products known [3] (i.e., crystalline, amorphous and solution castable amorphous) have in common that they do not withstand processing temperatures higher than 160 °C. This rules out the possibility of depositing most inorganic electrochromics, which require post-deposition heat-treatment at elevated temperatures (>300 °C).

To the best of our knowledge, the only inorganic electrochromic dispersion coatings on flexible substrates produced so far are those of the Chameleon Optics coating company (www.chameleon.com), disclosed in patents [4]. The casting solution comprises a dispersion of water-insoluble iron (III) ferrocyanide particles with an average particle size of less than 1 μm and polyvinyl alcohol acting as the polymer binder. Dispersion of EC particles is produced in-situ and further mechanical treatment, common to the production of paints is not required. The main focus of this study was the preparation of an "electrochromic paint" that could be applied on plastic film via a mass production wet deposition technique such as coil coating. The development of such paint obviously makes sense, due to the wide choice of electrochromic materials and the possibility of using them for manufacturing plastic film-based EC devices. Such devices have great potential for EC sunroofs, sight control EC appliance doors and aircraft cabin EC windows being developed within the framework of the INNOSHADE EU project. Another interesting application is the use of anodic electrochromics, such as Prussian Blue or nickel oxide, in combination with cathodic organic electrochromics, such as poly(3,4-ethylenedioxythiophene) (PEDOT), potentially enabling the production of plastic film-based EC devices with blue, blue–violet or even neutral coloration (www.innoshade.eu). Nickel oxide was selected as a candidate for the "electrochromic paint" because,

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in thin film form, NiO exhibits high coloring and fast transmittance variation between dark brown Ni^{+3} and transparent Ni^{+2} oxidation states. In addition, the low cost and ease of fabrication are advantages [5,6].

We recently succeeded in making substoichiometric $Ni_{1-x}O$ films by wet processing based on the peroxo route and nickel acetate precursor, which exhibit a strong electrochromic effect when directly (no pre-cycling) cycled in 1 M $LiClO_4$/PC electrolyte [6]. The bleaching and colouring resulted in an optical modulation $\Delta T \sim 60\%$ attained after the intercalation of about -20 mC/cm^2 and providing an electrochromic efficiency of about 40 cm^2/C. This was attributed to the presence of Ni^{2+}/Ni^{3+} couples, established from XPS studies. The grey $Ni_{1-x}O$ as-deposited films obtained after heat treatment at 350 °C are electrically conductive and the determined E_{gap} was about 3.60 eV, enabling their *p*-type semi-conductivity to be inferred. XRD revealed the formation of a single nano-crystalline phase of bunsenite NiO with a crystallite size below 10 nm. The films have also been tested in complementary EC devices. In combination with WO_3 films, tested up to 1000 cycles, they showed good EC colouring/bleaching changes. However, our attempts to deposit electrochromic $Ni_{1-x}O$ films on plastic foils failed due to the too high heat treatment temperatures (i.e., 350 °C). This led us to the development of dispersions of $Ni_{1-x}O$ pigment particles and their deposition on plastic foils at 150 °C. The starting material was $Ni_{1-x}O$ pigment obtained by following the same synthesis route as used for the preparation of the corresponding $Ni_{1-x}O$ thin films [6] but instead of heat treatment at 350 °C, the corresponding xerogel was heat treated at 400 °C for 24 h. The as-prepared $Ni_{1-x}O$ pigment was then used for making electrochromic paint, which served in the final stage for the deposition of electrochromic $Ni_{1-x}O$ pigment coatings on plastic foils.

The preparation of any optically clear (no haze) EC coatings from pigment dispersions is not easy and the type of binder and dispersant must be properly selected. Various dispersants are known and have already been employed for the stabilization of pigment particle dispersions: macromolecules are the most popular in the paint industry [7]; beta-diketone and alkyltitanates [8] have been used for making titania coatings at low temperatures. Various alkyltrialkoxysilanes [9,10] have been used for making a variety of functional coatings [11–15], while the corresponding fully condensed polyhedral oligomeric silsesquioxanes (POSS) have recently been applied for the fabrication of solar spectrally selective paint coatings [9,10]. However, none of the aforementioned dispersants, including trisilanol POSS, have been found to be effective for making electrochromic paints that could be made of $Ni_{1-x}O$ pigment dispersions, either leading to poor homogeneity and high haziness of coatings or their EC effect was small.

Another challenge for the preparation of electrochromic $Ni_{1-x}O$ paints and the deposition of electrochromic coatings is the selection of the binder. Simple organic polymers obviously do not work since they hinder the direct particle-to-particle contacts needed for facilitating electron transport within the $Ni_{1-x}O$ pigment particles. Accordingly, the idea of having a dispersant that would allow de-agglomerated $Ni_{1-x}O$ particle dispersion and would also assure good particle-to-particle contacts was borrowed from the colloidal precipitation technique [5], used for providing various nickel hydroxides at low temperatures. Nickel hydroxides are weakly crystalline [16,17] materials, electrochemically active and can be prepared with nickel in various valence states. Nickel hydroxides have been extensively studied in the past due to their remarkable electrochemical stability during charging–discharging processes in alkaline cells, which has been interpreted [18] on the assumption of highly reversible redox transfer between well-defined phases described by Bode et al. [19]. The electrochromic [20,21] and structural properties of various nickel hydroxides (β(II)-$Ni(OH)_2$, β(III)-NiOOH, γ-NiOOH and α-$Ni(OH)_2$, the latter two phases containing also water molecules) [16,18] have been determined by various techniques, providing a suitable platform for their further applications. They are easy to prepare from simple inorganic salt precursors precipitated with a base. We deliberately chose Ni-sulphate because the corresponding α(II)-$Ni(OH)_2$ and β(II)-$Ni(OH)_2$ phases can be easily prepared and chemically oxidized with NaOCl, thus enabling the making of β(III)-NiOOH, a mixture of β(II) and β(III) phases or even γ-$NiOOH_{1-x}$ phase with Ni in 3+, a mixture of 2+ and 3+ or 3.5+states, respectively [16].

The so-prepared NiO_xH_y precipitate, which had a double role as binder and dispersant, was the key material for the preparation of the pigment dispersions. A standard process usually used for making paints was employed. In the first stage, during milling, the as-prepared $Ni_{1-x}O$ particles were continuously wrapped with NiO_xH_y precipitate, resulting in the final stage of the dispersion process in the water/$Ni_{1-x}O$ pigment/NiO_xH_y precipitate dispersion, i.e. paint.

Due to the importance of the NiO_xH_y precipitate, its composition was studied by means of IR, XPS and XRD spectra, in order to reveal the valence states of the Ni ions, the coordination of the sulfate counter anions that could remain within the precipitate, the presence of the hydroxyl groups and the structure of the precipitate. TEM microscopy was employed for assessment of the particle size of the $Ni_{1-x}O$ pigment particles and NiO_xH_y dispersant, enabling an insight to be gained into their distribution in the corresponding pigment dispersions.

The remainder of this work is constructed as follows. The thickness of the $Ni_{1-x}O$ pigment coatings was determined using AFM measurements, which also provided information about their surface morphology and surface roughness. The optical properties were determined from their UV–vis spectra, giving information about the haze level of the coatings. The electrochromic properties of the $Ni_{1-x}O$ pigment coatings were studied using standard electrochemical techniques (cyclic voltammetry, chronocoulometric measurements) and the EC properties of the coatings were determined from in-situ spectroelectrochemical measurements performed in 1 M $LiClO_4$/PC electrolytes. Finally, the plastic film-based NiO and anatase pigment coatings [22] were laminated in order to make a flexible EC device to demonstrate the electrochromic effect of the corresponding EC cell.

2. Experimental

2.1. Materials and synthesis

2.1.1. $Ni_{1-x}O$ pigment

The preparation of $Ni_{1-x}O$ thin films from peroxo sols has already been reported [6] and will be only briefly repeated here. Equal weights of nickel(II) acetate powder ($Ni(CH_3COO)_2 \cdot 4H_2O$, Sigma Aldrich; ~5.0 g) and hydrogen peroxide-urea powder (Sigma Aldrich; ~5.0 g) were mixed in a glass beaker (500 ml) at room temperature. After homogenization, the powder mixture was heated to ~80 °C while being stirred. In about 2 min, a strong exothermal reaction took place, with the release of bubbles, leading to a deep green viscous ionic solution, which was diluted with absolute ethanol. After stirring the solution for about 15 min, the mixture was digested at ~80 °C for 2 h and then dried at 150 °C for 2 h. The dried xerogel was further heat-treated at 400 °C for 24 h, leading to the formation of $Ni_{1-x}O$ pigment. Prolonged heating imparted a metallic luster to the powder (Fig. 1). SEM micrographs of the $Ni_{1-x}O$ pigment are presented in Fig. 2. The pigment exhibited a spongy structure, without showing any specific particle morphology.

2.1.2. Preparation of dispersant/precipitate

Dispersant was prepared in the form of a precipitate obtained after mixing Ni-sulfate with sodium hypochlorite, which was used by Faure et al. [16] for chemical oxidation of α(II)-$Ni(OH)_2$

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