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Color neutral nanocomposite nickel-tantalum oxide for electrochromic windows

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Abstract. Electrochromic windows can darken on demand to limit the solar gains entering a building to reduce the risk of overheating, while preserving the view towards the exterior. Yet, the switching speed and contrast as well as the durability of commercial products still need to be improved. Novel materials are investigated to address these shortcomings. Since gel or polymer electrolytes limit the durability of electrochromic glazing, all-solid state, inorganic devices are considered. The optical properties of doped nickel oxides were studied in order to obtain a color neutral anodic electrochromic oxide. The addition of tantalum was shown to increase the light transmittance and to provide a coating with better color neutrality compared to nickel vanadium oxides. The study of the crystalline structure by X-ray diffraction suggests that a nickel oxide-tantalum pentoxide nanocomposite is formed. These results are encouraging to use nickel tantalum oxide as an anodic electrochromic oxide.

1. Introduction

Highly glazed buildings require a method to control the solar gains in order to prevent overheating. Mechanical shadings are sensitive to strong winds, block the view when they are closed and might disturb the user when they are actuated. Electrochromic windows are able to modulate the solar gains entering a building by varying their spectral transmittance in the solar range [1]. They preserve the view toward the exterior, their switching is silent and no mechanical parts are required. However, they still suffer from limitations in terms of durability, switching speed and color neutrality. These drawbacks could be overcome using novel nanocomposite and inorganic solid-state materials. An electrochromic device usually comprises two transparent conductors, an ion conductor and two electrochromic coatings. Tungsten trioxide is commonly used as a cathodic electrochromic oxide, varying from transparent to dark blue, and nickel oxides are commonly used as an anodic electrochromic oxide, varying from brown to yellow. In the clear state, both the anodic and cathodic electrochromic material should have a high solar and light transmittance to reach color neutrality. Tungsten trioxide is highly transparent in the clear state and the residual tint is usually due to the nickel oxides used as counter electrode (or anodic layer). Avendaño et al. [2] have shown that magnesium doping could improve the light transmittance of nickel oxides. Nickel-vanadium oxides are often used for coatings deposited by magnetron sputtering due to the non-magnetic nature of the Ni-V target. However, they often exhibit a strong yellow color and this has an impact on the color neutrality of the electrochromic window in the clear state. Tantalum pentoxide can be used as a solid ion conductor for electrochromic devices [3]. In order to facilitate the transport of lithium between the anodic electrochromic oxide and the ion conductor, nickel-tantalum nanocomposite oxides are envisaged. The addition of tantalum is expected to improve the color neutrality of the anodic electrochromic oxide.

2. Methods

In this study, nickel-vanadium and nickel-tantalum oxides are deposited by magnetron sputtering on glass substrates. The following alloy targets were used: industrial nickel-vanadium, which is standard in the industry, Ni-V (92-8 at. %, Testbourne) and a custom-made Ni-Ta target (91-9 at. %, AJA int.). Unlike pure nickel targets, both of these alloy targets are non-magnetic which is advantageous to obtain a better control of deposition parameters at industrial scale. Lithium was added to the nickel-vanadium and nickel-tantalum oxides using a dry lithiation method developed in our laboratory [4]. The optical properties of the samples were studied by spectrophotometry in the range 350-2100 nm in the "as-deposited" and lithiated states using a Zeiss diode array spectrometer [5].

The spectral properties of materials or devices are used to determine the coefficients of solar direct transmittance τ_e and light transmittance τ_v according to equation (1) and (2) respectively [6]. The color coordinates can be obtained using the calculations described in the same standard [6].

$$\tau_e = \frac{\sum\limits_{\lambda=350nm}^{2100nm} S_\lambda \tau(\lambda)\Delta\lambda}{\sum\limits_{\lambda=350nm}^{2100nm} S_\lambda \Delta\lambda} \tag{1}$$

where S_λ is the relative spectral distribution of the solar radiation, $\tau(\lambda)$ is the spectral transmittance of the glazing and $\Delta\lambda$ is the wavelength interval (in nm).

$$\tau_v = \frac{\sum\limits_{\lambda=380nm}^{780nm} D_\lambda \tau(\lambda)V(\lambda)\Delta\lambda}{\sum\limits_{\lambda=380nm}^{780nm} D_\lambda V(\lambda)\Delta\lambda} \tag{2}$$

where D_λ is the relative spectral distribution of illuminant D65, $\tau(\lambda)$ is the spectral transmittance of the glazing, $V(\lambda)$ is the spectral luminous efficiency for photopic vision defining the standard observer for photometry and $\Delta\lambda$ is the wavelength interval (in nm).

Furthermore in order to better understand the nature of the films, the crystal structure is studied using X-ray diffraction. A Empyrean system (Theta-Theta, 240mm) equipped with a PIXcel-1D detector, Bragg-Brentano beam optics and parallel beam optics was used. The Scherrer formula equation (3) can be used to determine the crystallite size.

$$B(2\theta) = \frac{K\lambda}{L\cos\theta} \tag{3}$$

with K the constant of proportionality (taken to 0.9 unless otherwise indicated), λ the wavelength of the X-ray radiation of the source (0.154056 nm for Cu Kα), L the crystallite size, θ the Bragg angle and B, the line broadening at half the maximum intensity.

3. Results and discussion

3.1. Sample preparation

Nickel oxide from the Ni-V and Ni-Ta targets were deposited on a glass substrate according to the parameters indicated in Table 1. They are named hereafter Ni-V-Ox and Ni-Ta-Ox, which does not indicate a stoichiometry.

Table 1 Deposition parameters.

	Ni-V-Ox	Ni-Ta-Ox
Target	Ni-V (92-8 at. %)	Ni-Ta (91-9 at. %)
Applied power	DC-p 200 W	DC-p 100 W
Substrate	glass	glass
Deposition time	30 min	30 min
Ar / sccm	41.7	62.6
O$_2$ / sccm	1.0	1.5
Ratio O$_2$/Ar	2.38 %	2.38 %
Working pressure	$1,8.10^{-2}$ mbar	$1,9.10^{-2}$ mbar

3.2. Optical properties

The spectral transmittance was recorded after deposition of the doped nickel oxide coatings; the samples were placed back in vacuum to undergo three lithiation steps. After each one, their transmittance was measured; the results are displayed in Figure 1.
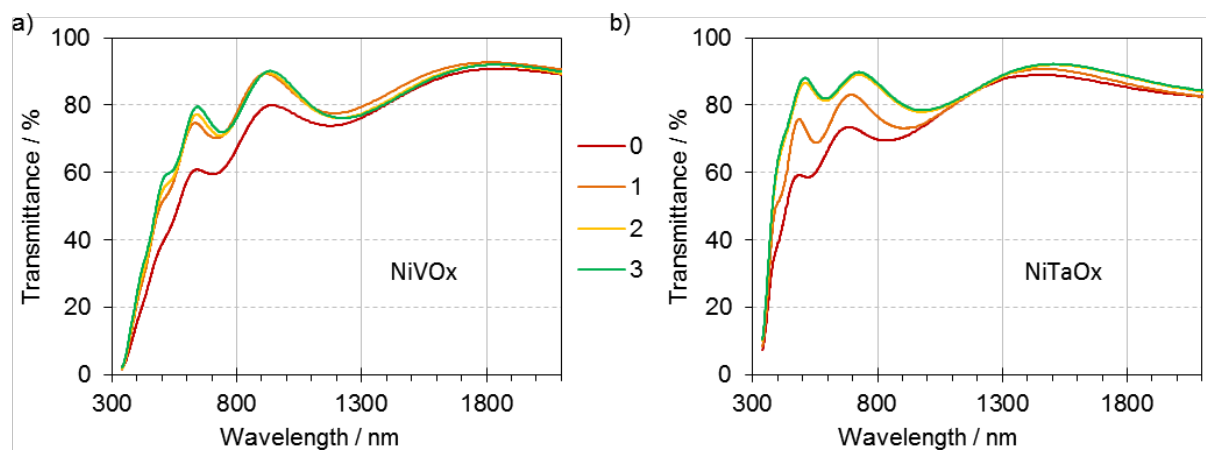

Figure 1   Spectral transmittance after successive lithiations, the legend indicates the number of lithiation steps applied on the a) Ni-V-Ox sample and b) Ni-Ta-Ox sample.

As deposited, the Ni-V-Ox sample exhibits a strong brownish color: one lithiation make it brighter and the second and third lithiation have only a little effect of the optical properties. The Ni-Ta-Ox sample has, as deposited, a very slight brown tint. The successive lithiations increase the transmittance especially around 500 nm. The solar direct transmittance and light transmittance of both samples are indicated in Table 2.

Table 2 Evolution of solar direct transmittance τ_e and light transmittance τ_v as a function of the number of lithium dispenser used. The lithiated Ni-Ta-O sample reaches τ_v = 84 %.

lithiation steps	Ni-V-Ox		Ni-Ta-Ox	
	τ_e	τ_v	τ_e	τ_v
0	56.8%	48.5%	66.8%	62.1%
1	65.7%	60.8%	73.8%	71.5%
2	66.3%	62.3%	80.6%	83.3%
3	67.5%	64.3%	81.4%	84.3%

The samples produced from the Ni-Ta target exhibit higher transmittances, especially in the short wavelengths. It has a large influence on the solar direct transmittance which is 67 % for the Ni-V-Ox sample against 81 % for the Ni-Ta-Ox sample after three lithiations. Furthermore, it seems that the transmittance increase of the sample Ni-V-Ox is not very strong after the first lithiation and might imply

saturation. This low transmittance has also an impact on the hue and the light transmittance, as depicted in Figure 2.
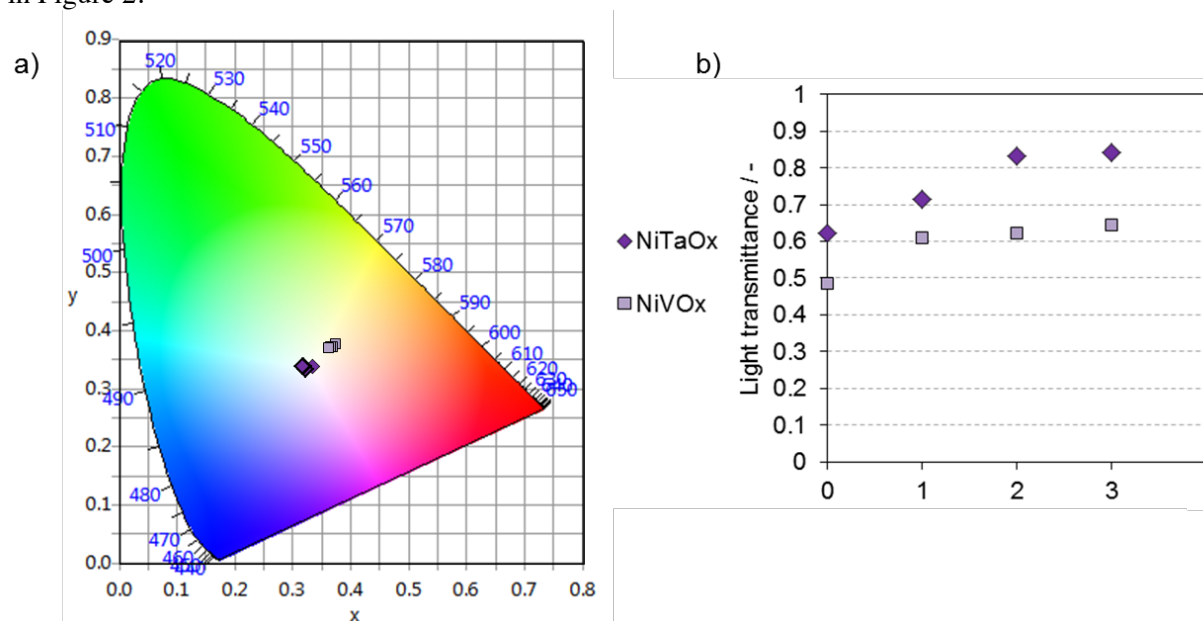

Figure 2 a) x, y color coordinates and b) light transmittance before after successive lithiations of the Ni-V-Ox sample (light squares) and the Ni-Ta-Ox sample (dark diamonds). The Ni-Ta-O sample is color neutral.

The light transmittance of the Ni-Ta-Ox sample reached higher levels and this sample shows better color neutrality compared to the Ni-V-Ox sample. The color rendering index varies from 91.4 to 97.6 for the Ni-Ta-O sample while it ranges from 80.3 to 83.7 for the Ni-V-O sample. Ni-Ta-O is therefore a promising candidate towards electrochromic device with high color neutrality in the bleach state. Dong et al. [3] also investigated ways to increase the transmittance of electrochromic devices in the short wavelengths by adding Mg and Li to the nickel oxide; the transmittance reached at 400 nm is 62 % for their Ni-Mg-Li-O sample which is similar to the one achieved with our lithiated Ni-Ta-O sample. However, the transmittance at 600 nm of their Ni-Mg-Li-O sample is 66 % while it is above 80 % for our sample.

3.3. Crystal structure
The crystal structure of a nickel tantalum oxide and a nickel vanadium oxide deposited on glass was studied using X-ray diffraction (XRD). The samples were cut in two parts: one part was kept as-deposited and the second one was lithiated. The two parts were then measured by XRD, the resulting diffractograms are in Figure 3, along with results from an un-doped nickel oxide. The angles corresponding to diffraction peaks cubic NiO are indicated with dashed lines.

The studied Ni-Ta oxide exhibits the typical diffraction peaks of crystalline NiO (with a cubic structure, *bunsenite*) located at 37.044, 43.038 and 62.497 ° for the (111), (200) and (220) diffraction planes respectively. In the reference pattern (ICDD:04-005-9695), the strongest peak originates from the (200) orientation followed by the (111) and the (220) ones. In the diffractograms shown in Figure 3, the main orientation is (111) expect for the Ni-V oxide for which it is (220). This indicates a preferential orientation of the grains in the coatings. The crystallite size was determined from the peak position and the FWHM using the Scherrer formula, the calculated values are reported in Table 3.
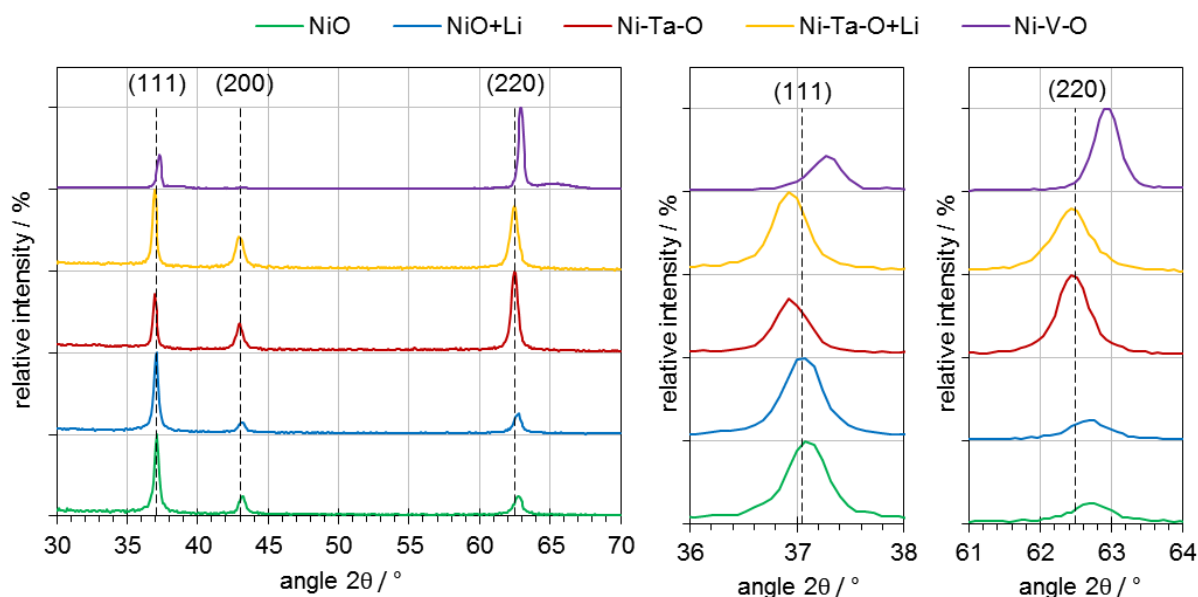
Figure 3 Diffraction pattern of a Ni-V, Ni-Ta and Ni oxide before and after lithiation obtained by XRD. The vertical dashed lines indicate the (111), (200) and (220) diffraction planes of cubic NiO (reference pattern ICDD:04-005-9695). The intensity was weighted relative to the most intense peak for each diffractograms.

Table 3 Peak position (2θ), full-width at half maximum (determined by fitting the data with a Voigt profile) which accounts for the grain size broadening (B) and crystallite size (L) determined according to Scherrer Formula from the XRD spectra presented in Figure 3.

	(111)			(200)			(220)		
	2θ / °	B / °	L / nm	2θ / °	B / °	L / nm	2θ / °	B / °	L / nm
Ni-O	36.90	0.567	14.8	43	0.761	11.2	62.41	0.952	9.8
Ni-O+Li	36.97	0.423	19.8	43.04	0.577	14.8	62.59	0.62	15.0
Ni-Ta-O	36.95	0.361	23.2	42.98	0.526	16.2	62.46	0.526	17.7
Ni-Ta-O+Li	36.93	0.368	22.8	42.98	0.641	13.3	62.43	0.612	15.2
Ni-V-O	37.26	0.341	24.6	43.15	0.576	14.8	62.93	0.423	22.0

Upon insertion of lithium and/or tantalum, the peak position does not vary significantly indicating that Li and Ta are not distorting the NiO cubic structure. Furthermore, amorphization was not observed which confirm that the NiO structure is not altered. On the contrary, the diffraction peaks of the Ni-V oxide are shifted towards high angles compared to the NiO sample and reference pattern, this might indicates that vanadium atoms enters the crystal lattice and decreases the lattice parameters of NiO. It can also be observed that the crystallite size is larger for the (111) peak and smaller for the peaks (200) and (220) at higher angles suggesting vertical columns, in agreement with SEM observations (not shown).

The crystalline phase of β-Ta_2O_5 is usually observed when temperatures during deposition or calcination above 400°C are used. Here, the sample was deposited without substrate heating and this phase is not observed. The NiO cubic structure appears to be the only crystalline phase present in the sample and does not seem to be distorted by the tantalum: the NiO peaks are not shifted and the full-width at half-maximum is not broadened. Therefore, tantalum may be present as amorphous tantalum pentoxide suggesting a NiO:Ta_2O_5 nanocomposite layer.

Tungsten and tantalum oxides, when deposited at room temperature, are amorphous whereas all the nickel, nickel vanadium and nickel tantalum oxides studied were crystalline.

4. Conclusions

In this work, we report the spectral transmittance of nickel-vanadium and nickel-tantalum oxides at various lithiation levels. From the latter, the solar and the light transmittance as well as the color coordinates were calculated. It is shown that the presence of tantalum lead to films with a higher transmittance in the visible range and produces coatings with a better color neutrality. Furthermore, the addition of lithium has a stronger effect on nickel-tantalum oxides than nickel-vanadium oxides. The study of the diffraction pattern suggests that vanadium intercalates in the cubic NiO structure while the coating deposited from the Ni-Ta target seem to form a nanocomposite $NiO:Ta_2O_5$ film. This nanocomposite may be favorable to the transport of lithium ions if Ta_2O_5 is used as a solid ion conductor. These results are encouraging for the use of nickel-tantalum oxides as an anodic electrochromic film.

Acknowledgments

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