Properties of electrochromic devices made with Nb_2O_5 and Nb_2O_5:X (X=Li, Ti or Mo) as coloring electrode

M. Schmitt, M. A. Aegerter *
Institut für Neue Materialien gem. GmbH, Department for Coating Technology, Im Stadtwald 43
D-66123 Saarbrücken

ABSTRACT

Electrochromic windows using Nb_2O_5, Nb_2O_5-Li_2O, Nb_2O_5-TiO_2 and Nb_2O_5-MoO_3 sol-gel layers as cathodic coloring electrodes and CeO_2-TiO_2 as anodic ion-storage electrode have been assembled and tested. In agreement with a theoretical estimation, the switching behavior of these devices is strongly dependent on the difference between the internal potential of the electrochromic and the ion-storage electrodes. Only the configuration using a Nb_2O_5-MoO_3 layer enters in consideration for long-time switching within the safe voltage range -2.5 V < V < +2.5 V. All other cells require larger negative potentials. The 8x4 cm^2 devices built with Nb_2O_5:Mo are transparent with a slightly yellow color in the bleached state (+2.5 V) and dark gray in the colored state (-2.5 V). For a fixed thickness of the EC electrode (180 nm) the photopic transmittance increases with the thickness of the ion storage layer d_{IS} in agreement with the model prediction. It reaches a maximum of ca. 0.3, corresponding to a Li^+ intercalated charge density of 18 mC/cm^2. For $d_{IS} \cong 950$ nm., such devices are stable up to at least 12,000 cycles under potentiostatic cycling between ±2.5 V, 120 s.

Keywords: electrochromism, device, niobia, doped niobia, sol-gel

1. INTRODUCTION

An electrochromic device consists of an electrochemical cell which changes its color on application of a voltage. For transmissive systems a sandwich geometry is usually used with two half-cells combined by an electrolyte (liquid or solid). The first half cell consists of glass / transparent conductive layer / electrochromic layer and the second one of glass / transparent conductive layer / ion storage layer. Such devices can be used as windows in cars and buildings. Many devices have been built with WO_3 as coloring electrode [1-6] but only one is reported with Nb_2O_5 [1]. It was assembled by Orel et al. using a sol-gel Nb_2O_5-Li_2O film deposited by dip-coating technique on FTO (SnO_2:F) glass with molar ratio Li/Nb=0,1 and sintered at 500 °C. The cell was assembled in the sandwich configuration using SnO_2:Sb:Mo as ion storage layer and a Li-containing ormolyte as ion conductive layer. The device exhibited a gray color in the colored state, a transmission change of 45 % and a good reversibility. Its lifetime was short because the voltage used to cycle the cell was relatively high.

This paper discusses first the electrochemical properties of six EC cells made with either pure or doped Nb_2O_5 materials as EC electrodes and CeO_2-TiO_2 layers as ion-storage electrode calculated according to the graphical model of Bullock and Branz [11]. The theoretical predictions are then compared to the experimental results.

2. EXPERIMENTAL

All electrochemical measurements (films and devices) were realized using an EG&G 270 A potentiostat / galvanostat (Princeton Applied Research). The determination of the electrochromic properties of the films were performed using a special three electrode cell. The counter electrode was a platinum foil and the reference electrode was a 0,01 M solution of $AgClO_4$ dissolved in the used electrolyte in contact with a silver wire. The electrolyte was a 1 M solution of $LiClO_4$ dissolved in propylene carbonate (PC). The potentiostatic insertion of the lithium ions was realized at -2.2 V vs. $Ag/AgClO_4$ for 120 s and the bleaching at +1.0 V vs. $Ag/AgClO_4$ for 120 s. Amperometric measurements were carried out at -2.5 V and +1.0 V and the coloring-bleaching cycles with -2.5 V and +2.5 V each during 120 s. Coulometric titrations were performed with a constant current of -2.5 $\mu A/cm^2$. Cyclic voltammograms were obtained at a scan rate of 50 mV/s.

The determination of the density of the layer was realized using a Siemens D 5000 x-ray reflectometer and software.

The optical spectra in the ultraviolet-visible-near infrared (UV-Vis-NIR) range were recorded in situ with a CARY 5E spectrophotometer (Varian). The transmission spectra were measured before ($T_{bleached}$, bleached state) and after ($T_{colored}$, colored state) the insertion of Li^+-cations. The change of the optical density was calculated from these measurements according to $\Delta OD = \log(T_{bleached}/T_{colored})$ [7]. The light transmittance was calculated according to DIN EN 410 (eq. 1) where D_λ is the relative radiation function of the light D_{65}, $\tau(\lambda)$ is the measured spectral transmission, $V(\lambda)$ is the spectral ratio for the sensibility of the human eye for day-light and $\Delta\lambda$ is the spectral bandwidth [8].

$$\tau = \frac{\sum_{\lambda=380nm}^{\lambda=780nm} D_\lambda \tau(\lambda) V(\lambda) \Delta\lambda}{\sum_{\lambda=380nm}^{\lambda=780nm} D_\lambda V(\lambda) \Delta\lambda} \quad (1)$$

The configuration of the cells were: glass / FTO / Nb_2O_5 based electrode / liquid electrolyte / CeO_2-TiO_2 / FTO / glass. The sheet resistance of the commercial FTO-glass (Libbey Owens Ford) was 17 $\Omega_\square$. The liquid electrolyte was a 1 M solution of $LiClO_4$ in propylene carbonate (PC). The distance between working (Nb_2O_5) and counter (CeO_2-TiO_2) electrode was 1 mm. The devices had a size of 8x4 cm^2. Working [12] and counter electrode [5] were prepared by the sol-gel process and deposited by dip-coating technique.

3. THEORETICAL MODEL

An important parameter for the realization of an electrochromic device is the internal chemical potential difference (emf) of the electrochromic electrode (EC) and the ion storage (IS). This parameter, introduced by Rauh and Cogan [9], plays an important role in the reaction voltage. The current needed to color a cell can be expressed as [10]:

$$I = \frac{V_e}{R_t} = \frac{V_a - (\Phi_{IS} - \Phi_{EC}) - V_b}{R_t} \quad (2)$$

where V_e is the effective coloring voltage, R_t is the sum of the resistances to electronic and ionic currents in the various layers, V_a is the applied voltage, V_b is the sum of all interface barriers and Φ_{IS} and Φ_{EC} are the internal potential differences (emf) of the IS and EC layers. Bullock and Branz [11] have also reported a graphical method to determine a useful cell configuration and to predict their performance. While the method is fully described in their paper it is worthwhile to summarize the procedure in our particular case. From the coulometric titrations of the IS and EC layers, equipotential curves have been drawn in the x-y plane of Li_xMeO (EC layers) and $Li_yMe'O$ (IS layer). These lines have been then superimposed with the Li-conservation lines determined by:

$$y = y_0 + rx \quad (3)$$

with

$$y_0 = \frac{Q_0}{q\rho_{IS}d_{IS}} \quad (4)$$

and

$$r = \frac{\rho_{EC}d_{EC}}{\rho_{IS}d_{IS}} \quad (5)$$

where Q_0 is the total charge of mobile ions, q the electron charge, ρ_{EC} and ρ_{IS} are the molar densities of the EC and IS films and d_{EC} and d_{IS} the respective film thicknesses. The intersections of the Li^+-conservation lines with the applied voltage contours give the relations x(V) and y(V). With this model different device geometries and material candidates were compared. It should be noted that the calculated voltages are only approximate as in this calculation the resistances of the films are not taken in consideration.

4. RESULTS AND DISCUSSION

The above procedure has been applied to six electrodes: two Nb_2O_5 coatings sintered at 450 °C and at 600 °C, a Nb_2O_5*0.1Li_2O, coating sintered at 500 °C, a Nb_2O_5*0.6TiO_2 coating sintered at 600 °C and a Nb_2O_5*0.4MoO_3 coating sintered at 500 °C and to a CeO_2-TiO_2 ion storage electrode. The structural and electrochromic properties of the niobia based coatings are reported in another paper of these proceedings [12]. Figure 1 shows the Fermi potential of the layers calculated from the coulometric titration curves. For pure Nb_2O_5 one observed that the Fermi potential increases with the sintering temperature. It does not change significantly for Nb_2O_5:Li and Nb_2O_5:Ti but a large decrease is observed for Nb_2O_5:Mo. Within the safe applied voltage to be used (±2.5 V), all electrochromic layers can incorporate a large amount of Li ions up to x≅1. For the ion storage layer, Ceo_2-TiO_2, only a small amount of Li up to ca. $y_0 = 0,14$ can be intercalated.

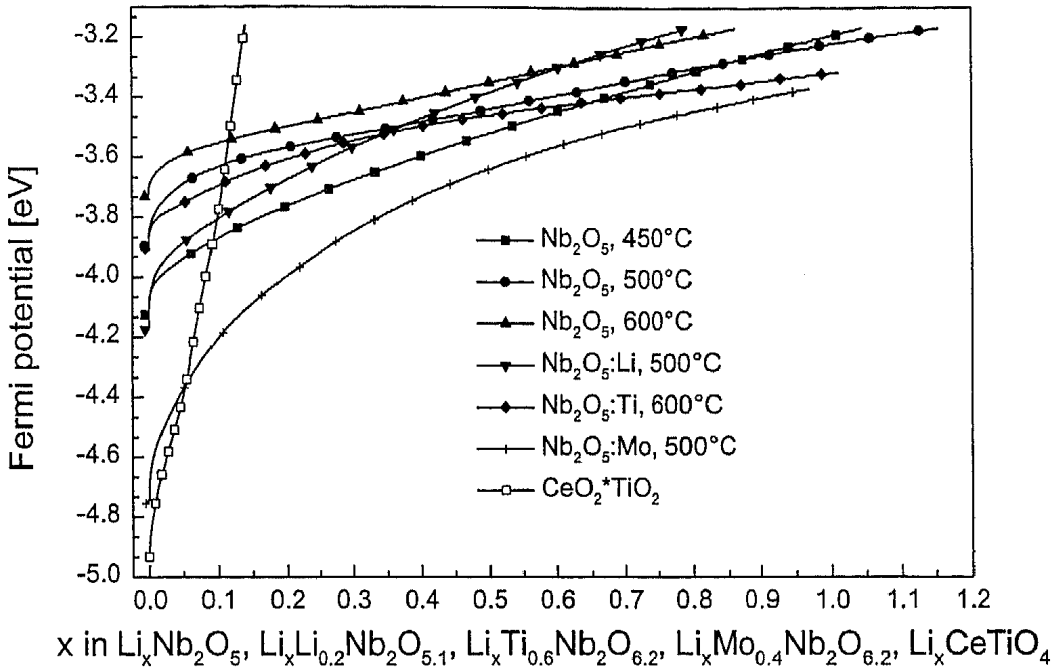

Figure 1: Fermi potential curves of the different electrochromic niobium oxide films and the CeO_2-TiO_2 film (IS electrode).

Figure 2 shows, as an example, the equipotential curves obtained in the x-y plane of $Li_xNb_2O_5$•0,4MoO_3 and Li_yCeO_2•TiO_2. For this determination it was assumed a maximum value $y_0 = 0,14$ (eq. 4) for the ion storage electrode. In the figure it is also superimposed the straight lines corresponding to the values of r ranging from 0,05 to 1 (eq. 5). From the intersection of the set of curves the cell voltage can be obtained for this particular layer configuration. They are reported in figure 3. The results show that the amount of Li ions (x) which can be intercalated and consequently the change in the transmittance of such a cell should considerably increase when the value of r decreases. In other words for such a configuration of materials the thickness of the IS electrode should be made larger than the thickness of the EC electrode.

Figure 4 shows the calculated voltages obtained for r = 1 for devices built with the IS layer (CeO_2-TiO_2) and all EC layers. Although the value r = 1 probably not the best value to be chosen to build a cell (too low x-value) the results indicate that niobia doped with molybdenum will color with the lowest applied voltage, that within the safe range of voltage only a small amount of Li ions (x ≅ 0.12 - 0.15) can be incorporated in any of the EC layers and that finally a small amount of Li (x ≅ 0.02) will always remain in the layer in the bleached state. Remembering that the predictions of this graphical determination are only qualitative, as the electric resistance of the layers are not taken into consideration, the prediction has been experimentally qualitatively verified.

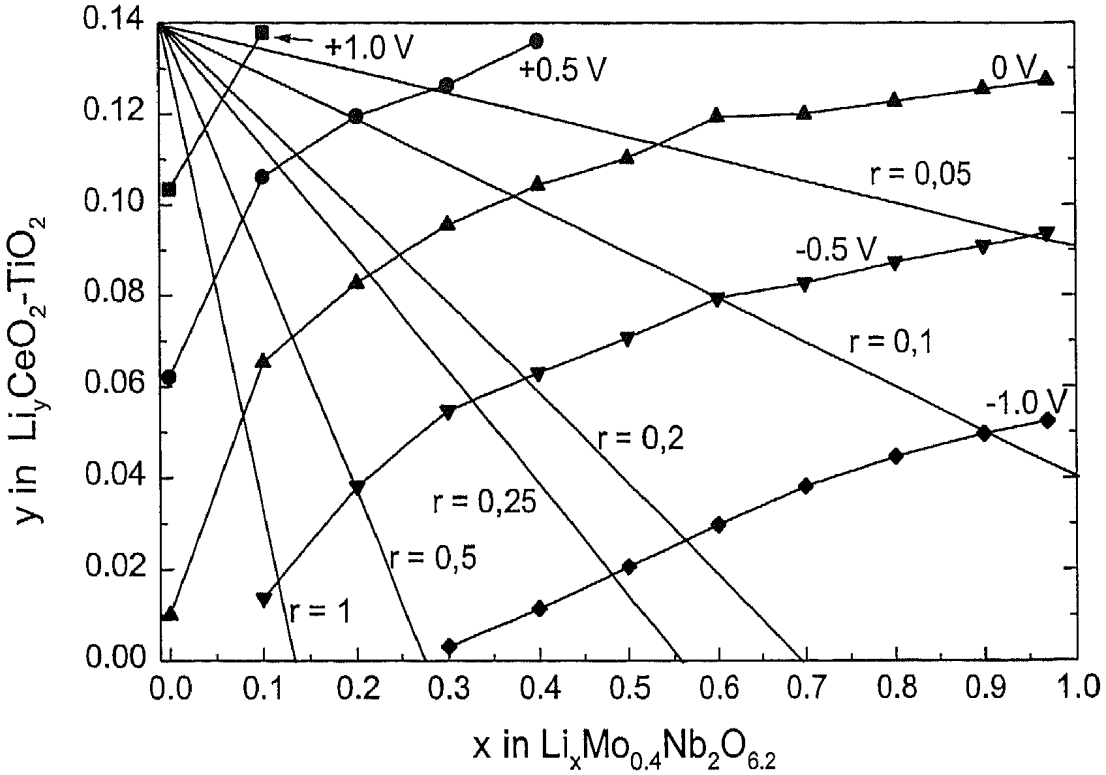

Figure 2: Equipotential curves of $Li_xNb_2O_5$•0,4MoO_3 and Li_yCeO_2•TiO_2 superimposed with the straight lines corresponding to r (eq. 5). y_0=0.14.

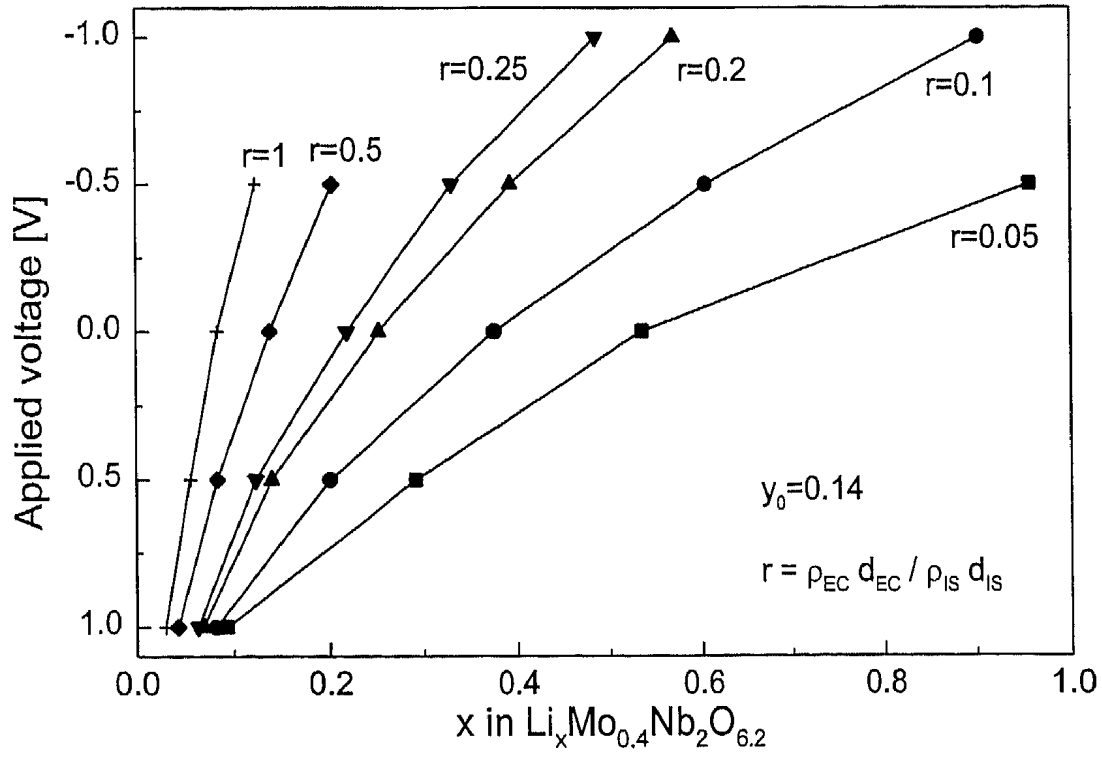

Figure 3: Calculated cell voltages of a device built with $Li_xNb_2O_5$•0,4MoO_3 and Li_yCeO_2•TiO_2 coatings.

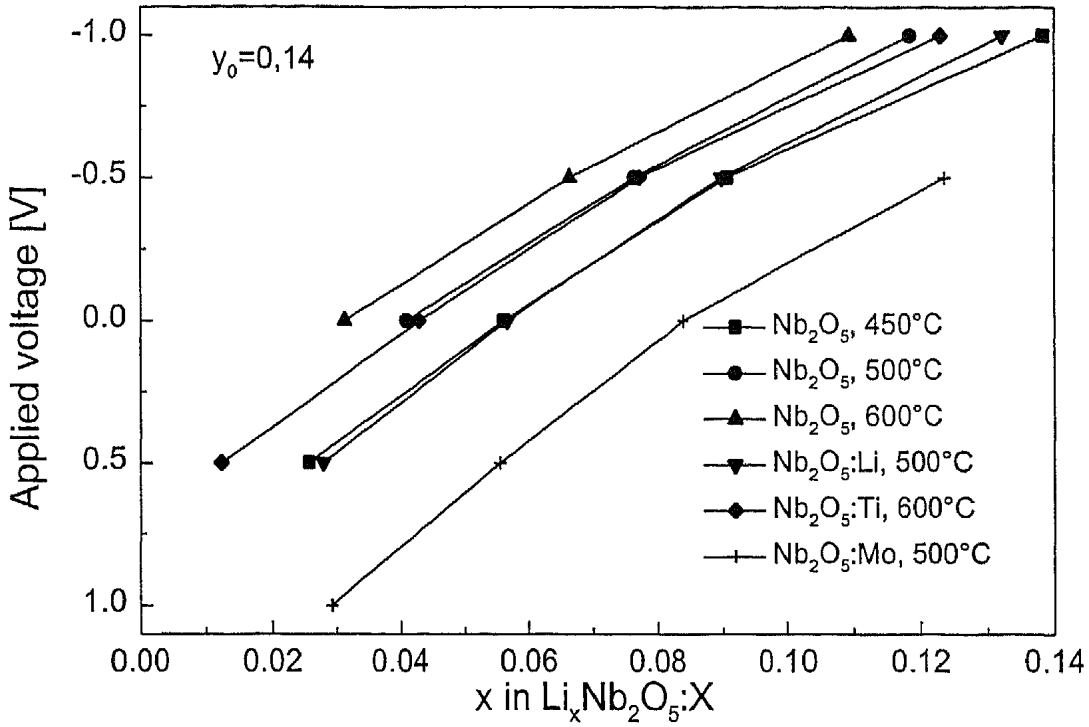

Figure 4: Calculated applied voltages of electrochromic cells with different electrochromic electrodes. The ratio r according to eq. 5 is r = 1.

Figure 5 shows the voltage of different cells measured by coulometric titrations of these devices. Each are made with two 65 to 90 nm thick layers of an EC Nb_2O_5-based composition and one 240 nm thick CeO_2-TiO_2 ion storage layer. To calculate the values of r for such systems a determination of the density of the layers have been made using x-ray reflectometry. The values of ρ and r are summarized in table 1. They typically lay around 1.0. It is clearly seen that the maximum amount of Li that can be intercalated is not larger than x=0.3 and that the voltage required to color the cells is smaller for Nb_2O_5 doped with Mo than for all other compositions. A cyclic voltammetry of the cells (fig. 6) also confirms the results. The cell with the molybdenum doped film exhibits an intercalation peak at -1.1 V. The peaks of the other cells appear at much more negative potentials and the current density and consequently the change in optical density are smaller. For example the peaks for the cell with Nb_2O_5 which was sintered at 600 °C appears at -1.9 V.

Table 1: Film thickness d, density ρ and ratio r (eq. 5). The density of the Nb_2O_5:X coatings were measured by reflectometry, the density of the CeO_2-TiO_2 layer was calculated assuming a porosity p = 18.5 %.

	Nb_2O_5 (450 °C)	Nb_2O_5 (600 °C)	Nb_2O_5:Li (500 °C)	Nb_2O_5:Ti (600 °C)	Nb_2O_5:Mo (500 °C)	CeO_2-TiO_2
d [nm]	125	125	160	150	180	140
ρ [g/cm³]	4.54	4.85	4.23	4.14	4.10	4.59
r	0.88	0.94	1.05	0.97	1.15	----

According to the model prediction (fig. 3) a decrease of r allows to insert a larger amount of Li and consequently a larger change in Δτ should be observed. Values as large as $x \cong 0.5$ should be obtained for applied potentials of about -1.0 V. The experimental results only partially confirm the results. First the potentials needed to reasonably color the devices are much more negative than those predicted. This was expected as the model does not take into account the resistance of the layers

and the interface barriers so that the effective coloring voltage V_e (eq. 2) is certainly much smaller than the applied voltage V_a. In what follows, the cells were all driven with V_a = -2.5 V.

The influence of the parameter r (eq. 5) on the cycling behavior and the prediction of the model (see fig. 3) has been tested with 4 cells. Each one was built with a 180 nm thick Nb_2O_5:Mo coating as EC electrode and the thickness of the ion storage electrode has been varied from 240 nm (1 layer) to ca. 950 nm (4 layers). In this way the values of r have been estimated to r = 0.67 (1 layer), 0.33 (2 layers), 0.22 (3 Layers) and 0.17 (4 layers).

Figure 7 shows the behavior of the intercalated charge density obtained up to 12,000 cycles while figure 8 shows the value of the change of the photopic transmittance $\Delta\tau$ (eq. 1) calculated from the variation of the transmission data. Both values increase rapidly with the number of cycles, pass by a maximum after a certain number of cycles and then rapidly decrease. The increase in charge (x) and $\Delta\tau$ predicted for an increase of the thickness of the IS layer is only partially observed. When comparing the largest amount of charge exchanged and the value of x the value grows from 8 mC/cm² for 1 layer to 15 mC/cm² for 2 layers and then tend to saturate to 18 mC/cm² for 3 layers and 16.5 mC/cm² for 4 layers. This non linear behavior is not yet understood. As these maximum values depend on the number of cycles realized and are followed by a drastic decrease, it seems that a corrosion is occuring at the electrolyte / IS interface. The values of r may therefore increase during the cycles in an unpredicted way and this may explain the failure of the model. Also for increasing thickness of the IS layer the electrical resistance of the layer increase accordingly and decrease considerably the effective coloring voltage. The largest amount of lithium ions exchanged (18 mC/cm²) is obtained with a 3-dip IS layer while half of the charge can be inserted with a 1-dip layer. The maximum change of light transmittance does not vary practically when 2, 3 or 4 IS layers are used. In each case the maximum lies at $\Delta\tau$ = 0.28.

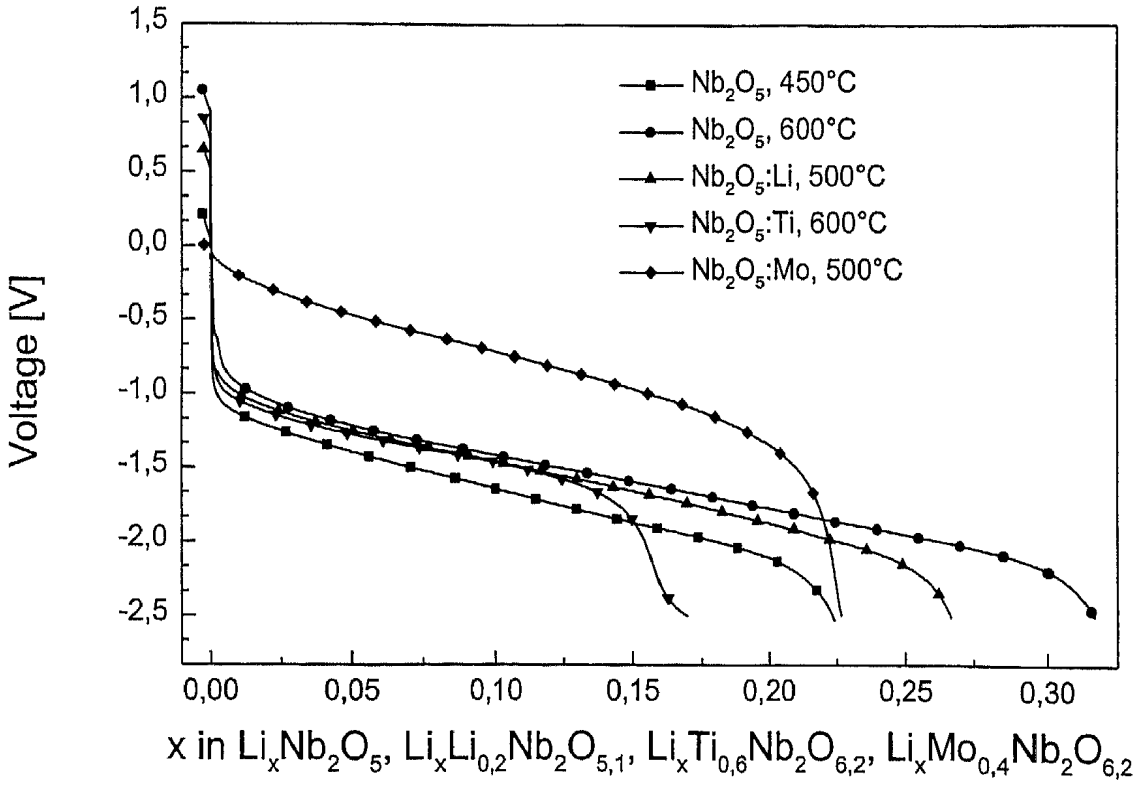

Figure 5: Coulometric titration curves of devices with the different working electrodes. I = -5 μA/cm². 0.88 < r < 1.15 (see table 1).

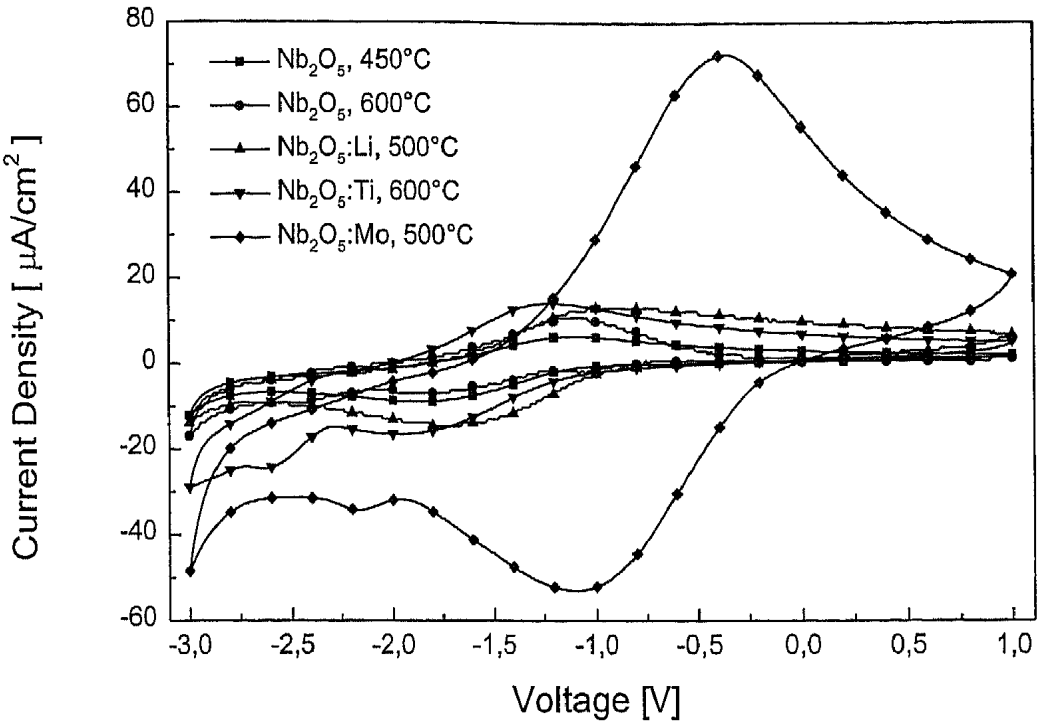

Figure 6: Cyclic voltammetries of electrochromic devices with different working electrodes. Scan rate: 50 mV/s.

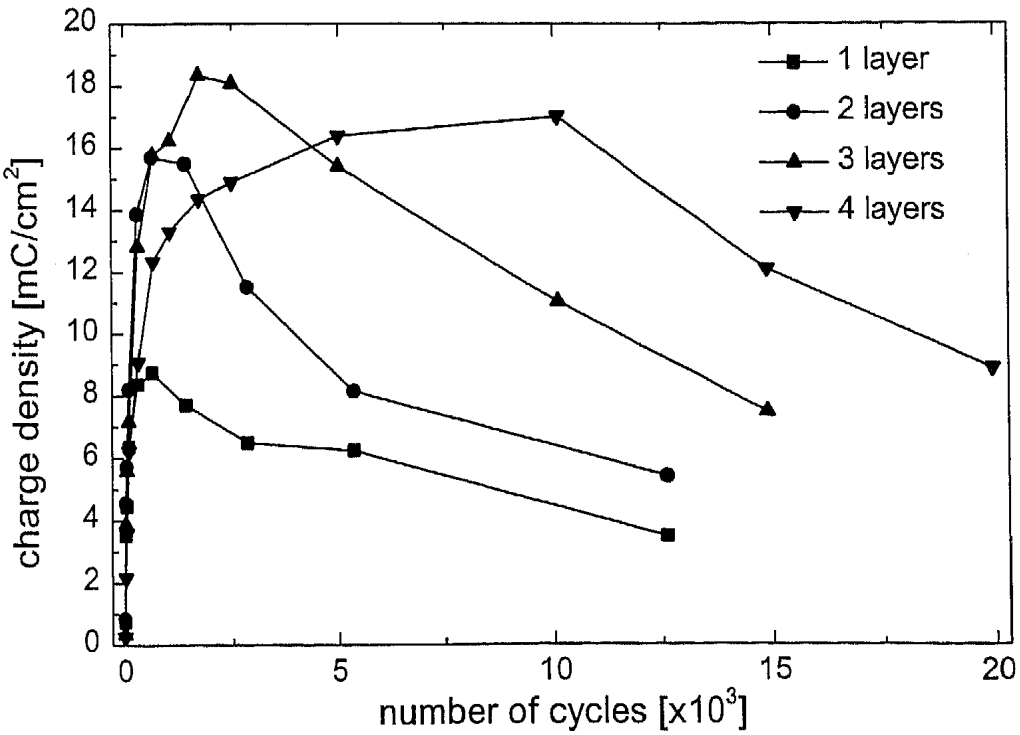

Figure 7: Intercalated charge density versus number of cycles of devices with a 180 nm thick Nb_2O_5:Mo coating as working electrode and various thicknesses of the CeO_2-TiO_2 IS electrode. Applied voltage: -2.5 V for 120 s.

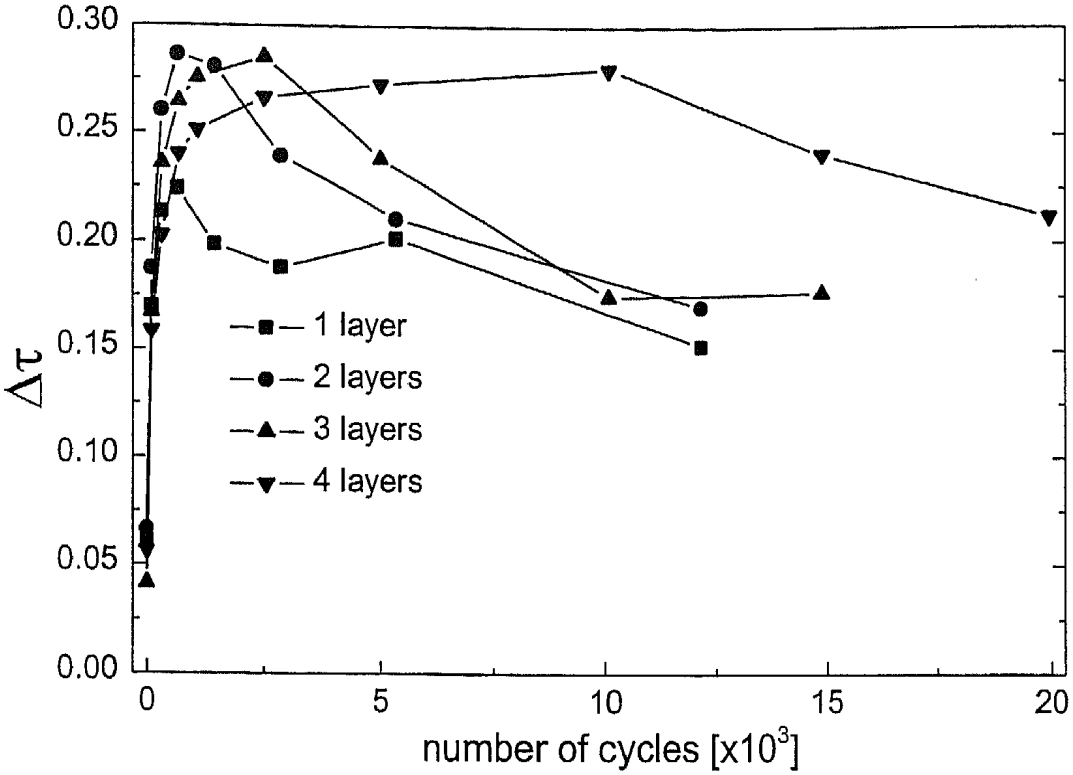

Figure 8: Change of light transmittance $\Delta\tau$ (eq. 1) versus number of cycles of devices with a 180 nm thick Nb_2O_5:Mo coating as working electrode and various thicknesses of the CeO_2-TiO_2 IS electrode. Applied voltages: -2.5 V and +2.5 V, each for 120 s.

5. CONCLUSION

The electrochromic properties of the cells made with Nb_2O_5 and Nb_2O_5 doped with Li, Ti, Mo as EC electrodes and CeO_2-TiO_2 as Li ion storage electrode have been determined using the graphical method of Bullock and Branz [11]. The experimental results have been compared with the prediction of the model. The composition and sintering temperature of the EC electrodes and the thickness ratio of both electrodes have a strong influence on the performance of the devices. Nb_2O_5:Mo layers sintered at 500 °C present the smaller emf difference with respect to the CeO_2-TiO_2 IS electrode. Such a cell can be switched safely for about 12,000 cycles in the voltage range of -2.5 V / +2.5 V. In agreement with the model charge and change of light transmission could be increased by increasing the film thickness of CeO_2-TiO_2. A maximum change of light transmission of 0.28 was obtained. With a 950 nm thick layer a lifetime of 12,000 cycles was achieved. The degradation of the cell at higher cycles number is attributed to a corrosion effect at the IS / liquid electrolyte interface.

ACKNOWLEDGEMENTS

The research has been financed in part by the Federal Ministry for Education, Research and Technology of Germany and the State of Saarland(Germany).

REFERENCES

1. Orel, B., Opara Krasovec,U., Macek,M., Svegl,F., Lavrencic Stangar,U., *Comparative studies of "all sol-gel" electrochromic devices with optically passive counter-electrode films, ormolyte Li+ ion-conductor and WO_3 or Nb_2O_5 electrochromic films.* Solar Energy Materials & Solar Cells, 1999. **56**: p. 343-373.
2. Sbar, N., Badding,M., Budziak,R., Cortez,K., Laby,L. Michalski,L., Ngo,T., Schulz,S., Urbanik,K., *Progress toward durable, cost effektive electrochromic window glazings.* Solar Energy Materials & Solar Cells, 1999. **56**: p. 321-341.
3. Daneo, A., Macrelli,G., Polato,P., Poli,E., *Photometric characterization of an all solid state inorganic electrochromic large area device.* Solar Energy Materials & Solar Cells, 1999. **56**: p. 237-248.

4. Bell, J.M., Skryabin,I.L., *Failure modes of sol-gel deposited electrochromic devices.* Solar Energy Materials & Solar Cells, 1999. **56**: p. 437-448.
5. Munro, B., Conrad,P., Krämer,S., Schmidt,H., Zapp,P., *Development of electrochromic cells by the sol-gel process.* Solar Energy Materials and Solar Cells, 1998. **54**: p. 131-137.
6. Nagai, J., McMeeking, G.D., Saitoh,Y., *Durability of electrochromic glazing.* Solar Energy Materials & Solar Cells, 1999. **56**: p. 309-319.
7. Cabanel, R., Chaussy,J. , Mazuer,J., Delabouglise,G. ,Joubert,J.C., Barral,G., Montella,C., *Electrochemichromism of Nb_2O_5 Thin Films Obtained by Oxidation of Magnetron-Sputtered NbNx.* J. Electrochem. Soc., 1990. **137 (5)**: p. 1444 - 1451.
8. 410, D.E., *Glas im Bauwesen; Bestimmung des Lichttransmissionsgrades, direkter Sonnenenergietransmissionsgrad, Gesamtenergiedurchlaßgrad, UV-Transmissionsgrad und damit zusammenhängende Glasdaten; Deutsche Fassung.* 1991: Beuth Verlag GmbH.
9. Rauh, R.D., Cogan,S.F., *Design Model for Electrochromic Windows and Application to the WO_3/IrO_2 System.* J. Electrochem. Soc., 1993. **140**(2): p. 378 - 386.
10. Bechinger, C., Bullock,J.N., Zhang,J.-G., Tracy,C.E., Benson,D.K., Deb,S.K., Branz,H.M., *Low-voltage electrochromic device for photovoltaic powered smart windows.* J. Appl. Phys., 1996. **80**(2): p. 1226 - 1232.
11. Bullock, J.N., Branz,H.M. *Application of a rapid graphical method for the design of electrochromic devices.* 1995: SPIE/ Vol. 2531.
12. Schmitt,M., Aegerter,M.A., *Electrochromic properties of Nb_2O_5 and Nb_2O_5:X (X=Sn, Zr, Li, Ti, Mo) sol-gel coatings, these proceedings.*