# Influence of Water on the Electrochromic Properties of $Nb_2O_5$:Mo, $WO_3$ and $(CeO_2)_x(TiO_2)_{1-x}$ Sol-Gel Coatings and Electrochromic Devices

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Water plays an important role in the intercalation and coloration behavior of some electrochromic (EC) materials. This paper focuses on a systematic study of its influence on the electrochemical and optical properties of $Nb_2O_5$:Mo and $WO_3$ electrochromic sol-gel coatings and a $(CeO_2)_x(TiO_2)_{1-x}$ ion storage layer, as well as devices made with these layers. The thickness of the coatings were 200 nm for $WO_3$, 120 nm for $Nb_2O_5$:Mo and 200 nm for $(CeO_2)_x(TiO_2)_{1-x}$. The coatings were studied electrochemically in 1 M $LiClO_4$ in propylene carbonate electrolyte with water content up to 3 wt% by Cyclic Voltammetry (CV) and Chronoamperometry (CA). The potential ranges were -2 V to 1 V, -1.5 V to +2 V and –2.2 V to +1 V vs $Ag/AgClO_4$ for $(CeO_2)_x(TiO_2)_{1-x}$, $WO_3$ and $Nb_2O_5$:Mo layers respectively and the CV scan rate was 50 mV/s.

For $(CeO_2)_x(TiO_2)_{1-x}$ the exchanged charge, which was practically constant from the 50$^{th}$ CV-cycle, was found to increase from 3 mC/cm² (dry electrolyte) up to 11 mC/cm² (3 wt% water in electrolyte). This improvement is important for the coloration of EC-devices built with this counter electrode because its charge capacity is known to be a limiting factor for the transmission change of the devices.

For $WO_3$-sol-gel coatings the exchanged charge and therefore the change of the optical density ($\Delta OD=\log(T_{bleached}/T_{colored})$) measured at 550 nm was also higher in wet electrolyte (1 % water) than in dry electrolyte. Moreover it remained rather constant (0.8 – 0.7) from the first cycle up to 7000 cycles, while without water, the ΔOD decreases continuously from 0.76 (1$^{st}$ cycle) down to 0.43 (7000$^{th}$ cycle). For both layers these improvements are partly due to an increase of the kinetics of the intercalation and deintercalation of $Li^+$ ions with the water content, but a combined intercalation of $H^+$ and $Li^+$ ions cannot be ruled out.

The behavior of sol-gel $Nb_2O_5$:Mo coatings is opposite: The ΔOD decreased only slightly from 1.0 (1$^{st}$ cycle) to 0.85 (3500$^{th}$ cycle) in dry electrolyte while it strongly decreased from 0.92 to 0.25 in electrolyte with 3 wt% water. The exchanged charges behaved in a similar way.

In spite of the different electrooptical behavior of the $WO_3$ and $Nb_2O_5$:Mo EC-layers, 5 x 10 cm$^2$ EC-devices prepared with them with the configuration glass/ FTO/ EC-layer/ inorganic-organic composite electrolyte/ $(CeO_2)_x(TiO_2)_{1-x}$/ FTO/ glass exhibited a definitely improvement with the incorporation of water in the composite electrolyte.

With 3 % water in the composite electrolyte the change of the optical density ΔOD at 550 nm remained practically constant from the first cycles: 0.4 for the $WO_3$/ $(CeO_2)_x(TiO_2)_{1-x}$ cell and 0.3 for the $Nb_2O_5$:Mo/ $(CeO_2)_x(TiO_2)_{1-x}$ cell (figures 1a, b). The devices were successfully switched up to 50000 cycles and 14000 cycles respectively and the devices built with a dry electrolyte presented a lower value of the ΔOD and a definitely shorter lifetime. The better properties exhibited of the EC-devices built with a wet electrolyte are therefore essentially due to the better behavior of the counter electrode, namely a higher charge capacity and a higher reversibility of the intercalation/ deintercalation process.

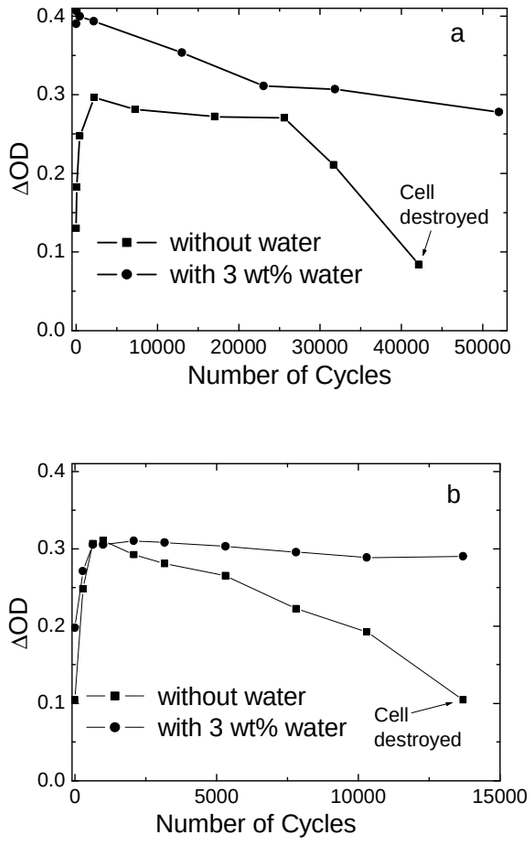


Figure 1a,b: Change of the optical density ΔOD at 550 nm of EC-devices with the configuration glass/ FTO/ EC-layer/ composite electrolyte/ $(CeO_2)_x(TiO_2)_{1-x}$/ FTO/ glass without and with 3 wt% water in the electrolyte as function of the CA cycle number, whereby the EC-layer is a) $WO_3$ and b) $Nb_2O_5$:Mo and the switching properties are a) (-2 V, 120 / +2 V, 120 s) and b) (-2,5 V, 120 s/ +1 V, 120 s).