

Influence of water on the electrochemical properties of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ and WO_3 sol-gel coatings and electrochromic devices

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Abstract

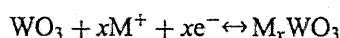
The paper focuses on a systematic study of the influence of water on the electrochemical and optical properties of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ and WO_3 sol-gel coatings as well as devices made with these layers. The coatings were studied electrochemically in 1 M LiClO_4 in propylene carbonate (PC) electrolyte with water content up to 3 wt.% by cyclic voltammetry (CV) and chronoamperometry (CA) up to 7000 cycles. For $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ the exchanged charge was found to increase from 3 mC/cm^2 (dry electrolyte) up to 11 mC/cm^2 (3 wt.% water) so that the capacity of this counter electrode is greatly improved. For WO_3 coatings, the transmittance change ($T_{\text{colored}} - T_{\text{bleached}}$) is higher in wet electrolyte (1 wt.% water) than in dry electrolyte and remains constant (74%) under extended CV or CA cyclings. The electro-optical behavior of solid state electrochromic (EC) devices made with these layers with incorporation of water in the solid electrolyte is also drastically improved. They color and bleach reversibly with a constant and higher contrast and higher coloration efficiency (about 36 cm^2/C) from the first cycle up to more than 50000 CA cycles using safe applied voltages.

Keywords: $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$; WO_3 ; Electrochromism; Device; Water content in electrolyte; Long-term behavior

1. Introduction

Electrochromic (EC) materials change their optical properties (transmittance or reflection) in a reversible manner when a current flows through them [1,2]. Large EC glazings can be used for architectural and automotive applications in order to control the solar radiation entrance. The typical configuration of EC

devices made with the sol-gel process (and used in this report) is glass/fluorine doped tin oxide (FTO, $\text{SnO}_2\text{:F}$)/ WO_3 (EC layer)/solid composite electrolyte/ $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ (ion-storage layer)/FTO/glass. Since the counter electrode remains transparent during cycling, the reversible coloration and bleaching reactions are given only by:



where M is a monovalent cation (H^+ or Li^+).

Tungsten oxide layers are the best studied EC layers and were prepared by sputtering, evaporation

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and sol–gel processes [1,3,4]. Sol–gel $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layers are transparent ion-storage layers which do not change their transmittance during lithium-intercalation and were first prepared by Baudry et al. [5]. Different sol–gel preparation methods [3,5–7] and sputter deposition methods [8] for $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ films were published.

The preparation of the WO_3 sol–gel layer, of a similar sol–gel $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layer and of the EC device with the inorganic–organic composite electrolyte used in this paper and their electrooptical characterization under dry conditions have been published elsewhere [9–18]. But the influence of water on the EC properties of these layers and devices was not yet studied.

It is, however, already known that water plays an important role in the lithium intercalation and coloration behavior of some electrochromic materials [19–23]. Judeinstein et al. [19,20] studied amorphous and crystalline sol–gel $\text{WO}_3 \cdot n\text{H}_2\text{O}$ layers ($n=0$ to 2) in propylene carbonate (PC) with 1 M LiClO_4 and found that the Li^+ diffusion into the oxide layer becomes easier when the water content of the layer increases. For a given crystallinity, the response time for optical switching becomes faster as the water content increases, but the drawbacks are a shorter memory time and a faster degradation of the layers. The reversibility during the first CV cycles increased with the hydration state of the $\text{WO}_3 \cdot n\text{H}_2\text{O}$ layer. A high reversibility is observed for hydrated oxides such as amorphous $\text{WO}_3 \cdot 1.8\text{H}_2\text{O}$, but the amount of injected charge decreases when the number of cycles increases. In less hydrated samples (amorphous $\text{WO}_3 \cdot 0.6\text{H}_2\text{O}$) the intercalated charge is smaller, but the injected charge increases and the reversibility improves upon cycling. Similar results were obtained by Bohnke et al. [21] by the examination of evaporated WO_3 thin films in organic electrolyte (1 M LiClO_4 in PC) containing different amounts of water (0.1% to 10%). They observed that the higher the water content in the electrolyte is, the faster the electrochromic response is. In other words, the coloration kinetics which is very slow in anhydrous Li^+ -electrolyte can be increased considerably by adding water to the electrolyte to become even faster than in H^+ electrolyte. Water in the electrolyte was also found important to obtain a reversible process. Knowles et al. [22] also showed that some water must be incor-

porated into the WO_3 film to obtain a coloration. In contrast to these results, Janke et al. [23] showed that the intercalated charge density of sputtered WO_3 and $\text{CeO}_2-x\text{-TiO}_2$ thin films decrease with increasing water content in the electrolyte (0.5% to 9–10% water in 1 M LiClO_4 in PC) and with increasing cycle number, whereby the degradation of $\text{CeO}_2-x\text{-TiO}_2$ is similar to that of WO_3 up to 4–5% water content and slightly smaller with higher water content (up to 8–10%). The degradation processes of evaporated WO_3 thin films in aqueous media were studied by Arnoldussen [24]. Pyper et al. [25] investigated by in situ Raman spectroscopy the electrochemical reduction of sol–gel WO_3 thin films in dry lithium electrolyte (PC with lithium salt, 7 ppm water) and after addition of 500 ppm of water. They did not observe a change of the peak pattern of the lithium bronzes to that of the hydrogen bronzes and concluded that no hydrogen intercalation takes place in these mixed electrolytes, but suggested that water may play a catalytic role for the Li^+ -intercalation.

The published results show that the influence of water on the electrochromic properties of EC layers is very important, particularly for the long-term behavior, but depends strongly on the preparation of the layers (sputtering or sol–gel techniques) and the heat treatment of the layers. No reports are available yet for the influence of water on the ion storage behavior of sol–gel $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layers and on the electrooptical behaviour of the sol–gel WO_3 layer used here as well as for EC devices built with these layers and a solid inorganic–organic composite electrolyte.

This paper therefore fills this gap and presents some preliminary data on the influence of water added into the electrolytes on the EC properties of sol–gel $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ and WO_3 layers as well as devices built with these layers.

2. Experimental

2.1. Sols and coatings

The $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol ($x=0.45$) was prepared by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.056 mol) and $\text{Ti}(\text{O}^i\text{prop})_4$ (0.069 mol) in 250 ml ethanol followed by stirring the sol at 30 °C for 4 days. The tungsten oxide (WO_3) sol was produced using a

modified synthesis based on the reaction of tungsten metal powder with an excess of hydrogen peroxide (30% solution), to give the peroxotungstic acid, in the presence of ethanol and glacial acetic acid and is described elsewhere [9–13]. The solid ionic conductor is based on glycidoxypopyltrimethoxysilane (GPTS), LiClO_4 , $\text{Zr}(\text{O}^n\text{Pr})_4$ and tetraethylene glycol (TEG) and its preparation was described elsewhere [9–13].

The K-glass substrates (glass coated with FTO, Pilkington, $17 \Omega_{\square}$) were washed, dried and heat treated at 450°C for 15 min. The $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layers were deposited on these substrates by the dip-coating technique with a withdrawal rate of 4 mm/s at 20°C with 38% air humidity. The single layers were then heated in air from room temperature up to 450°C with a heating rate of 2.5 K/min, kept for 15 min at 450°C and then cooled down to room temperature in the oven within 5 h.

The WO_3 layers were deposited in a single coating step on K-glass by the same technique under the same experimental conditions and then heat treated at 240°C for 1 h. This temperature was chosen, because the layers obtained at this temperature are still X-ray amorphous and show a better long-term stability lower change of optical density $\Delta\text{OD} = \log_{10} (T_{\text{bleached}}/T_{\text{colored}})$ than layers heat treated at lower temperatures [10,11].

The fabrication of the EC devices (size $5 \times 10 \text{ cm}^2$) of the form K-glass/ WO_3 /inorganic–organic composite electrolyte/ $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ /K-glass was performed by mounting in air a double sided adhesive tape (thickness 1 mm, 3 M) at the edges of one of the functional coatings and then assembling the two coated substrates. The mounted cells were then filled with the liquid inorganic–organic composite electrolyte through a small hole, heated at 105°C for 12 h to solidify the electrolyte and then extra sealed using butyl rubber (3 M) and adhesive tape. Devices were made with dry electrolyte and by adding 1 to 3 wt.% water to the electrolyte before filling the cells.

2.2. Characterization of coatings and devices

The layer thickness was determined either by scratching the layer before the heat treatment ($(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ coatings) or by etching with 1 M KOH solution (WO_3 layers) and subsequently mea-

suring the step height with a TENCOR P-10 surface profiler.

The coatings were studied electrochemically in a three-electrode cell using a platinum sheet as counter electrode, a Ag/AgClO_4 reference electrode (0.01 M AgClO_4 in 1 M LiClO_4 in propylene carbonate (PC)) and a liquid electrolyte consisting of 1 M LiClO_4 in propylene carbonate without or with added water (up to 3 wt.%). The water content was determined by Karl–Fisher titration. The working electrode (size $4 \times 9 \text{ cm}^2$) was pressed against a silicone O-ring on one side of the three electrode cell. The electrochemical area was 7 cm^2 .

The electrochemical measurements were performed using an EG&G 273A potentiostat. The samples were studied by cyclic voltammetry (CV) with a scan rate of 50 mV/s and a potential range of -2 to $+1$ V for $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layers, a range of -1.5 to $+2$ V for WO_3 layers and a range of -2 to $+2$ V for the EC windows. Chronoamperometric (CA) measurements were performed by applying the same potentials respectively for 120 s. The CV cycle scan rate (50 mV/s) and the lapse of time of CA cycles (2 min) were chosen to obtain data in a reasonable experimental time (typically 10000 cycles in 30 days). As will be shown below, the lapse of time for each cycle does not always allow for full intercalation of the layers but is sufficient for a full deintercalation. It is nevertheless convenient for comparison purposes. For chronopotentiometric (CP) measurements a constant current of $-/+5 \mu\text{A}/\text{cm}^2$ was applied up to 7000 s. The measurements were stopped when the potential exceeded -2 or $+1$ V, respectively. Impedance spectroscopy was performed with a Zahner IM6 impedance spectrum analyzer using an AC modulation amplitude of 10 mV with a frequency range of 0.1 Hz–100 kHz.

In situ transmittance measurements were carried out with a CARY 5E UV/VIS/NIR spectrophotometer. The transmittance of the WO_3 coatings was measured in the electrochemical cell against a reference cell having a quartz glass and a float glass window. The transmittance of the EC devices was measured against air as a reference.

Structural characterization of the coatings were performed using an X-ray diffractometer (Siemens D500) and a high resolution transmission electron microscope HR-TEM (Philips CM200-FEG).

3. Results and discussion

3.1. Material characterization

The thickness of the WO_3 single layers and of the $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ single layers was 200 nm. The water content of the “dry” liquid electrolyte was 0.03 wt.%. X-ray diffraction spectra indicate that both layers are almost X-ray amorphous. TEM micrographs show also that the $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layer is amorphous, and that the WO_3 layer, however, contains nanocrystalline regions 2 to 3 nm in size [13].

3.2. Electrochemical characterization

3.2.1. $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol-gel coatings

The cyclic voltammetry (CV) curves of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layers (thickness 200 nm) measured up to 500 cycles in liquid electrolyte without and with addition of water are shown in Figs. 1 and 2. Without water the cathodic and anodic currents decrease strongly and continuously with the number of cycles, whereby with 3 wt.% added water, the CV-cycles are more reversible and the currents decrease much more slowly. They reach practically stable values after 500 cycles.

Fig. 3 shows the intercalated charge calculated by integration of the current. It decreases strongly without added water from 17 mC/cm^2 (first cycle)

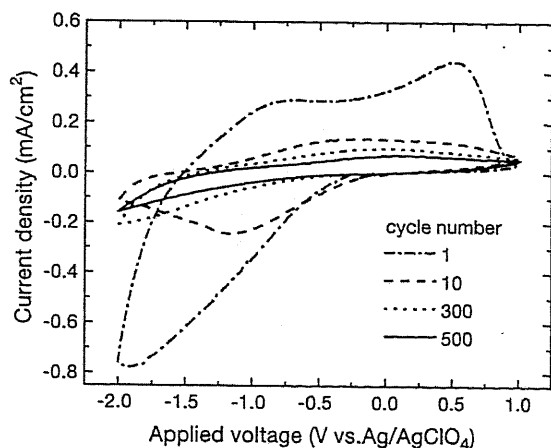


Fig. 1. Cyclic voltammetry of a $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol-gel single layer (200 nm thick) in 1 M LiClO_4 in PC with no water added (0.03% water content, scan rate 50 mV/s).

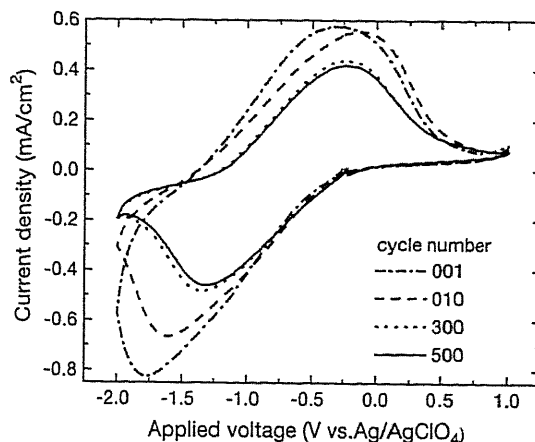


Fig. 2. Cyclic voltammetry of a $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol-gel single layer (200 nm thick) in 1 M LiClO_4 in PC with 3% water added to the electrolyte (scan rate 50 mV/s).

to 2.8 mC/cm^2 (500th cycle). The addition of 1 wt.% water to the electrolyte improves only slightly the intercalated charge density, but by adding 2 to 3 wt.% water, the decrease is smaller from about 18 mC/cm^2 (first cycle) down to 11 mC/cm^2 (500th cycle). Fig. 4 shows that the ratio $Q_{\text{out}}/Q_{\text{in}}$ of the deintercalated to the intercalated charge increases with the water content of the electrolyte from 0.90 (without water) to 0.99 (3% water, after 500 CV cycles). This indicates a better reversibility of the ionic charge exchange with the wet electrolyte.

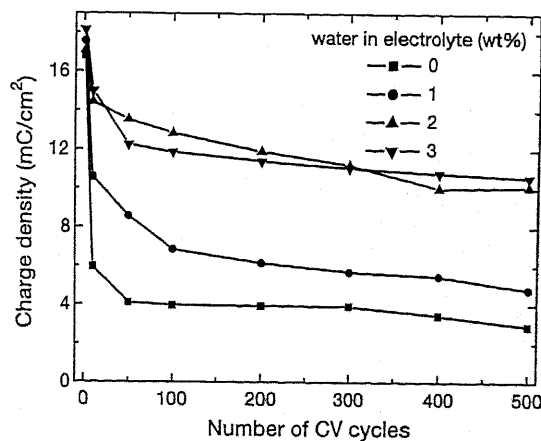


Fig. 3. Intercalated charge density (Q_{in}) in $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol-gel single layers (200 nm thick) in 1 M LiClO_4 in PC without and with added water as a function of the CV-cycle number.

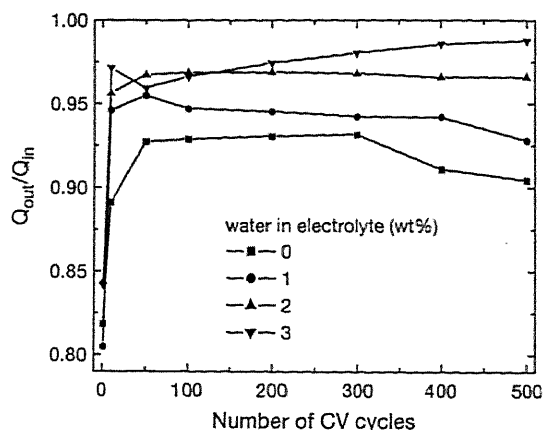


Fig. 4. Ratio of deintercalated (Q_{out}) to intercalated charge density (Q_{in}) during CV-cycle of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol-gel single layers (200 nm thick) in 1 M LiClO_4 in PC without and with added water as function of the CV-cycle number.

The kinetics of the exchange of charges have been determined by measuring CA cycles. Fig. 5 shows typical results obtained during the 360th cycle for various amounts of water in the electrolyte. The results confirm that the amount of charge exchanged during 2 min in wet electrolytes is higher and is essentially due to the drastic increase of the kinetics. However, the charge values also slightly decrease with the number of cycles (not shown) in agreement with the results obtained with CV cycles (Fig. 3). As already observed for CV-cycling (Fig. 3), the intercalated charge during CA cycling (Fig. 3), the intercalated charge during CA cycling is also very similar for

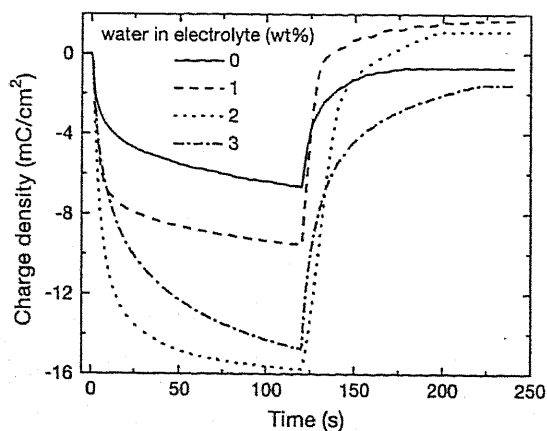


Fig. 5. Evolution of the charge density of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ single layers during the 360th CA cycle (-2 V, 2 min/ $+1$ V, 2 min) with different water contents in the electrolyte (1 M LiClO_4 in PC).

2 and 3 wt.% added water. As remarked above, the reversible incorporation of Li^+ is not finished after a lapse of time of 2 min but it is sufficient for a full deintercalation. This improvement in the kinetics may be due to a combined insertion of Li^+ and H^+ ions and an increasing H^+ -intercalation with increasing water content because the intercalation of H^+ is known to be faster than the intercalation of Li^+ -ions.

Fig. 6 shows the 1st, 5th and 10th chronopotentiometric (CP) measurement performed with a fresh $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layer with an electrolyte containing 0 and 3 wt.% water. The slope of the potential-time behavior during the intercalation process is strongly reduced with the amount of water in the electrolyte indicating that the amount of charge, which can be inserted without exceeding the safe voltage of -2 V increases. In agreement with the long-term cycle behavior of the CV and CA measurements, the intercalated charge nevertheless decreases with the cycle number from 34 mC/cm² (first CP cycle) to 32 mC/cm² (10th CP cycle) for wet electrolyte (3 wt.% water) and from 22 mC/cm² (first cycle) to 17 mC/cm² (10th cycle) for dry electrolyte.

Fig. 7 shows also CP measurements performed after 500 CV cycles in electrolyte containing different amounts of water. The difference between the slopes of the potential-time behavior with and without water

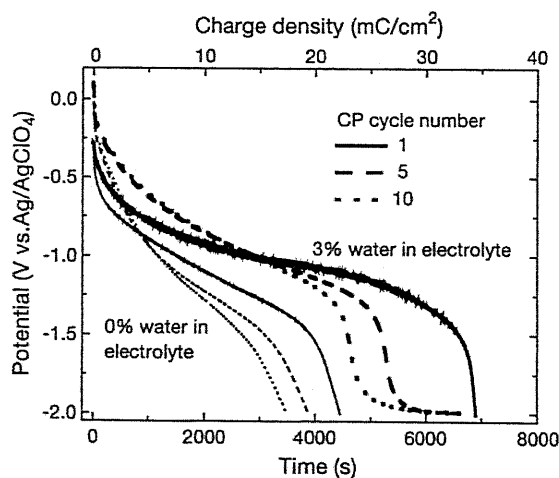


Fig. 6. 1st, 5th and 10th chronopotentiometric switching with constant current of $\pm 5 \mu\text{A}/\text{cm}^2$ of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol-gel single layers (200 nm thick) with 0 and 3 wt.% water in the electrolyte (1 M LiClO_4 in PC) measured with fresh layers (limiting voltages: -2 V, $+1$ V).

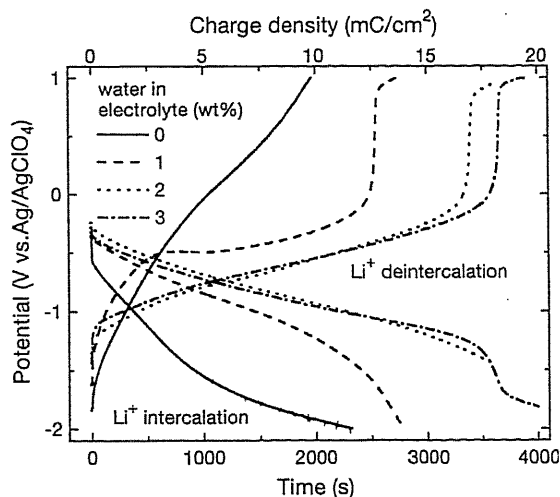


Fig. 7. Chronopotentiometric switching with constant current of $-/+5 \mu\text{A}/\text{cm}^2$ of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ sol-gel single layers (200 nm thick) with different amounts of water in the electrolyte (1 M LiClO_4 in PC) measured just after 500 CV cycles (limiting voltages: -2 V , $+1 \text{ V}$).

are now larger than those presented in Fig. 6. The amount of charge intercalated after 500 CV cycles with 3 wt.% water in the electrolyte, $Q_{\text{in}} \approx 20 \text{ mC}/\text{cm}^2$ (safe voltage -1.8 V), is not so different from that obtained after 10 CP cycles ($24 \text{ mC}/\text{cm}^2$, -1.8 V , Fig. 6) and was found to remain constant with further CP cycles. On the contrary, Q_{in} obtained with the dry electrolyte is reduced from $17 \text{ mC}/\text{cm}^2$ (10th CP cycle, Fig. 6) down to $12 \text{ mC}/\text{cm}^2$ (after 500 CV cycles) and was found to decrease continuously with further CP cycles. This shows again that the reversibility of the intercalation reaction is improved by addition of water to the electrolyte.

The electrolyte resistance, measured by impedance spectroscopy, decreases only slightly by addition of water from 70Ω (dry electrolyte) to 50Ω (3 wt.% water). Therefore the IR-drop, 2.5 mV for dry and 1.75 mV for wet electrolyte, can be neglected for the CP measurements and was also not taken into account for the CV and CA measurements.

3.2.2. WO_3 sol-gel coatings

The transmittance of 200 nm thick WO_3 layers at the wavelength of 550 nm after potentiostatic switching (-1.5 V , 2 min/ 2 V , 2 min) in electrolyte with different water content is shown in Fig. 8 as a function of the CA-cycle number. The transmittance change

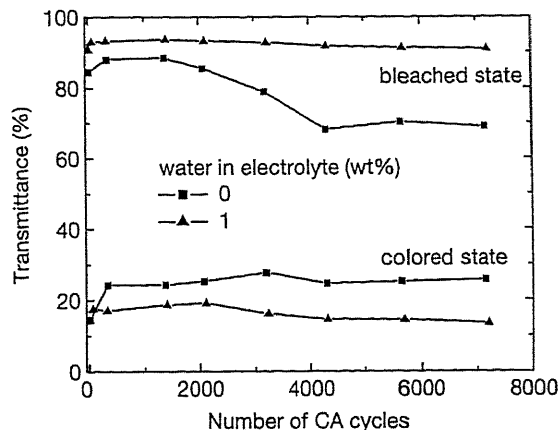


Fig. 8. Transmittance of WO_3 sol-gel single layers (200 nm thick) at $\lambda = 550 \text{ nm}$ as a function of the CA cycle number (-1.5 V , 2 min/ 2 V , 2 min) with no water and 1 wt.% water added to the electrolyte (1 M LiClO_4 in PC).

between the bleached and colored state is higher with 1 wt.% water content in the electrolyte than without water and remains constant ($\approx 74\%$) from the first cycle up to more than 7000 cycles. Without water, the transmittance change is smaller and decreases continuously down to 40% (7000th cycle).

The time variation of the normalized ratio T/T_{bleached} of WO_3 layers measured at 550 nm during the 7000th CA cycle is shown in Fig. 9. The coloration and bleaching kinetics are also much faster with 1% water in the electrolyte so that a 2-min lapse of time is

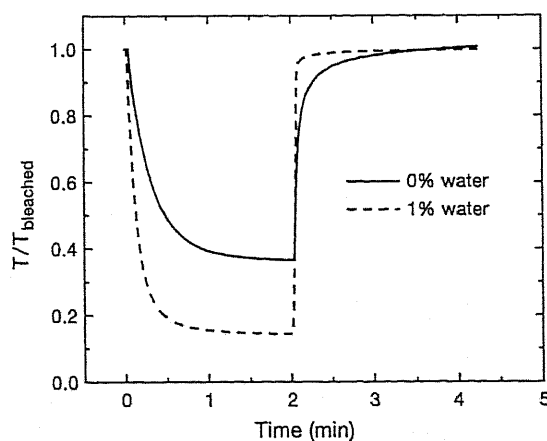


Fig. 9. Time evolution of the normalized transmittance T/T_{bleached} of WO_3 sol-gel single layers (200 nm thick) at $\lambda = 550 \text{ nm}$ during the 7000th CA cycle (-1.5 V , 2 min/ 2 V , 2 min) with 0 and 1 wt.% water in the electrolyte.

sufficient to color and bleach WO_3 with the wet electrolyte. As already postulated for the $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ layers, the faster kinetics observed with increasing water content might also be due to a combined intercalation of H^+ and Li^+ ions into the WO_3 layer and to an increase of the intercalation of H^+ with increasing water content.

The coloration efficiency CE, defined as the ratio $\Delta\text{OD}/Q_{\text{in}}$, has been calculated at 550 nm, using the results of the 2 min CA cycles. The value is only slightly higher with the electrolyte containing 1 wt.% water ($35.6 \text{ cm}^2/\text{C}$) than that obtained without water ($32.8 \text{ cm}^2/\text{C}$) (Fig. 10), which is in agreement with the results of Bohnke et al. [21]. This result shows that the coloring process of the WO_3 layer in dry and wet electrolyte is basically not different and that the darker coloration obtained during the application of -1.5 V during 2 min with the wet electrolyte (practically a value twice higher in optical density) is due to a kinetic effect and also to the smaller IR-drop. The results also confirm that the intercalated charge after 2 min using the wet electrolyte (ca. $26 \text{ mC}/\text{cm}^2$) is twice that obtained with the dry electrolyte (ca. $13 \text{ mC}/\text{cm}^2$).

3.2.3. EC devices

The time evolution of the normalized transmittance T/T_{bleached} of an EC device measured at 550 nm during

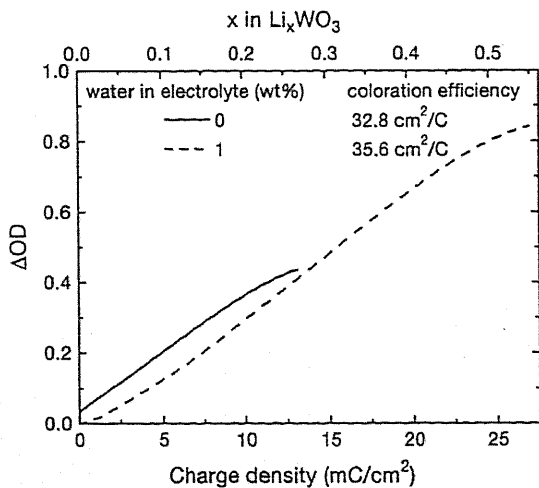


Fig. 10. Change of the optical density ($\Delta\text{OD} = \log(T_{\text{bleached}}/T_{\text{colored}})$) at $\lambda = 550 \text{ nm}$ of WO_3 sol-gel single layers (200 nm thick) as a function of the intercalated charge density (Q_{in}) with 0 and 1 wt.% of water in the electrolyte. The coloration efficiency CE is given by the slope of the graphs.

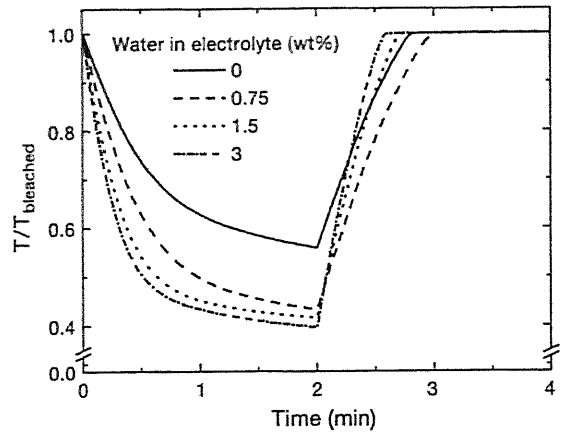


Fig. 11. Normalized transmittance, T/T_{bleached} , versus time of EC devices containing different amounts of water in the inorganic-organic composite electrolyte measured at $\lambda = 550 \text{ nm}$ during the 450th CA cycle ($-2 \text{ V}, 2 \text{ min}/+2 \text{ V}, 2 \text{ min}$).

the 450th CA cycle ($-2 \text{ V}, 2 \text{ min}/+2 \text{ V}, 2 \text{ min}$) is shown in Fig. 11 for different water contents in the inorganic-organic composite electrolyte. Similar results have been obtained up to 7000 CA cycles. The coloration and bleaching kinetics are faster with water in the electrolyte. Although the overall behavior of the transmittance spectra is not changed, an EC device made with water colors deeper than that built without water after a 2-min switching time.

Fig. 12 shows the evolution of the change of the optical density as a function of the CA cycle number.

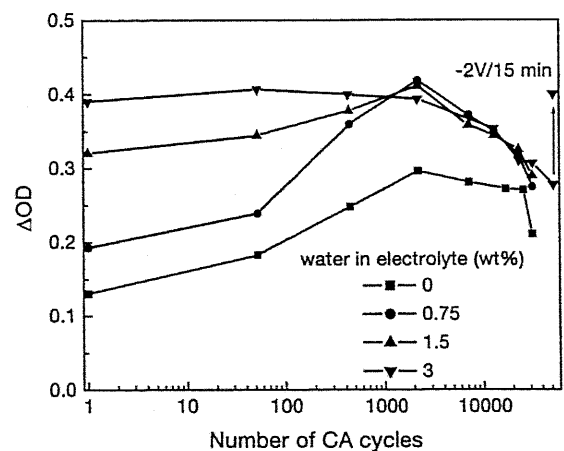


Fig. 12. Change of the optical density ΔOD at $\lambda = 550 \text{ nm}$ of EC devices containing different amounts of water in the composite electrolyte as a function of the number of CA cycle ($-2 \text{ V}, 120 \text{ s}/+2 \text{ V}, 120 \text{ s}$).

Drastic variations are observed without water. During initial cycling, ΔOD is small (about 0.15), increases continuously to about 0.3 up to 2000 cycles and then slightly decreases. This initial variation is considerably reduced by adding water in the electrolyte. For 3 wt.% water ΔOD is higher (about 0.4) and remains practically constant from the 1st up to the 2000th cycle where it starts to decrease. The decrease of the ΔOD values of the EC devices made with water from the 2000th up to the 50000th is due to a kinetic effect, because after 15 min -2 V applied voltage, the same value of the optical density ($\Delta OD = 0.4$) is reached (Fig. 12).

However, for windows made with a “dry” electrolyte a strong decrease of the coloration efficiency is observed from the 25000th cycle (Fig. 13) while for EC devices made with wet electrolyte, the CE remains constant up to 50000 cycles ($CE \approx 35 \text{ cm}^2/\text{C}$). Therefore, the decrease of the coloring of the EC devices without water from the 2000th up to the 40000th is not due to a kinetic effect, but to the decrease of the coloration efficiency (cell breakdown).

For a $5 \times 10 \text{ cm}^2$ EC device a preliminary study shows that the memory effect (EC device keeps the adjusted transmittance without applying a voltage) is not drastically altered by the presence of water in the solid electrolyte. A transmittance variation from 18% up to 33% at a wavelength of 550 nm was observed after 24 h for an EC device with 3 wt.% water after 7000 CA cycles.

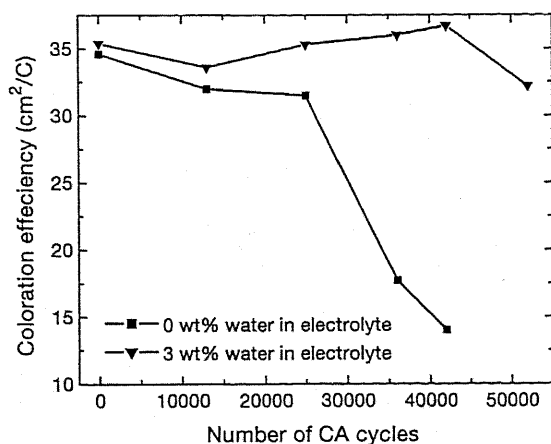


Fig. 13. Coloration efficiency CE of EC devices with 0 and 3 wt.% water in the composite electrolyte as a function of the CA cycle number.

4. Conclusion

The results presented in this paper show that the addition of small amounts of water (up to 3 wt.%) to a liquid and solid state Li^+ based electrolyte has an important benefit on the electrochemical and optical properties of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ and WO_3 sol-gel layers as well as solid state devices made with them.

A large increase in the “ Li^+ ” charge capacity was observed for the sol-gel $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ counter electrode in contrast to Janke et al. [23], who observed an opposite behavior with sputtered $\text{CeO}_{2-x}-\text{TiO}_2$ layers. A similar effect was observed for WO_3 layers leading to higher transmittance change but with the coloration efficiency remaining practically constant, about $35 \text{ cm}^2/\text{C}$, in agreement with Bohnke et al. [21]. The reversibility of the intercalation and deintercalation processes was also considerably improved. The faster kinetics observed with wet electrolytes also led to a higher degree of coloration for the WO_3 coatings. Drastic changes have been also observed in CP measurements. All these effects may be due to a combined intercalation of protons and lithium ions as already proposed for sputtered $\text{CeO}_{2-x}-\text{TiO}_2$ coatings and WO_3 layers in current literature [21,23] or to a catalytic role of water for the intercalation of lithium [21,25], as suggested by in situ Raman spectroscopy of WO_3 sol-gel films [25]. Bohnke et al. [21] discussed both possibilities for the improvement of the kinetics of evaporated WO_3 layers with increasing water content in the electrolyte. The water molecules in the electrolyte may hydrate the oxide layer through the channels present at its surface improving the kinetics of the Li^+ intercalation, as observed by Judeinstein et al. [19,20] for $\text{WO}_3 \cdot n \text{ H}_2\text{O}$ sol-gel layers.

The addition of water to the electrolyte used for an EC device of the form glass/FTO/ WO_3 /solid composite electrolyte/ $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ /FTO/glass has also important benefits as larger transmittance changes, faster kinetics and higher number of switching cycles (tested up to 50000) can be instituted while maintaining the contrast ratio. This is due to the higher intercalated charge and the improved reversibility of the intercalation reaction of $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ and WO_3 sol-gel layers with increasing water content of the electrolyte. On the contrary, with a dry electrolyte,

a drastic decrease of the coloration efficiency was observed after about 25 000 cycles leading to a breakdown of the devices.

It is finally believed that many published reports on EC properties of layers and devices measured or built with Li⁺ based electrolytes should be reconsidered in view of their water content. It was found that the water content of a PC-Li electrolyte prepared under dry condition and left in air with 70% RH (30 °C) for 5 days easily reaches a value of 3 wt.%! Water content may also play an important role for coatings obtained by other methods such as PVD or CVD.

Further studies to better understand these important results are underway.

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