

Transparent storage layers for H⁺ and Li⁺ ions
prepared by sol-gel technique

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ABSTRACT

Thin layers of mixed oxides CeO₂ - TiO₂ and CeO₂ - ZrO₂ with molar ratio 1:1 have been prepared by sol-gel process using the dip-coating technique. The precursor sols consist of a mixture of nitrate ammonium cerium salt (Ce(NH₄)₂(NO₃)₆), zirconium propoxide or tetraisopropyl orthotitanate and ethanol. The thickness of the multilayer films is typically 300nm after densification at 450°C. Their use as transparent H⁺ and Li⁺ ions storage electrode (counter electrode) for electrochromic devices is studied by electrochemical voltammetry, impedance and optical spectroscopies. They have typically an optical transmission of 80% in the visible range, do not color after ions insertion and show good electrochemical stability. These layers have been also tested in complete all solid state cell having the configuration /glass/ITO/EC/electrolyte/CeO₂ - TiO₂/ITO/glass/. The electrochromic layer (EC) was either WO₃ or polytoluidine. The protonic electrolyte was a cellulose-polyacetate polymer and the lithium electrolyte was PEO-LiN(SO₂CF₃)₂. Their electrochemical, optical and lifetime performances are reported.

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INTRODUCTION

The development of all solid state electrochromic devices such as smart windows and reflective mirrors is of utmost importance¹. A typical system working in transmission is made of five layers sandwiched between two glass substrates (Figure 1). There are two transparent electrical conductors which are required for setting up a distributed electric field, an electrochromic layer, an ionic conductor (electrolyte) and an ion storage layer (counter electrode) for H⁺ or Li⁺ ions.

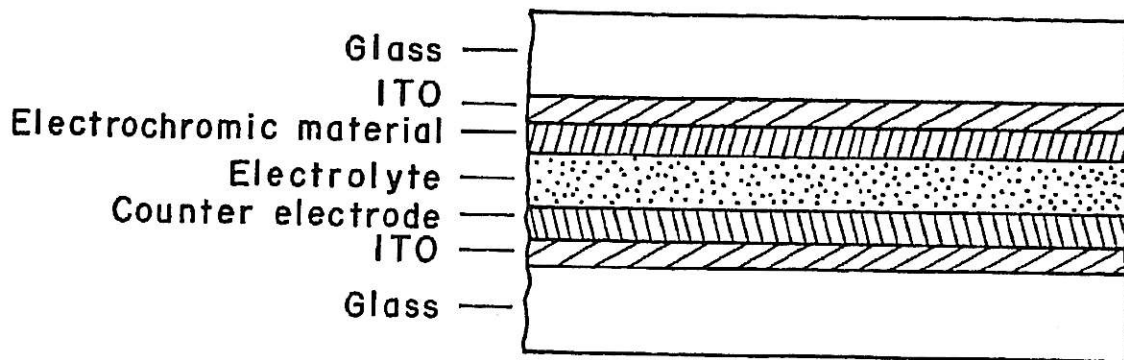
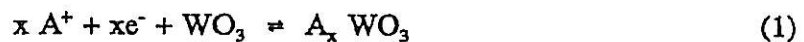


Figure 1 - Schematic cross-section of a typical solid state electrochromic device working in transmission

When a small current is passed through the cell the ions stored in the counter electrode diffuse toward the electrochromic layer and change its transmittance continuously over a wide spectral range and consequently alter the overall optical transmission of the device. These devices have a time response which varies from seconds to less than a minute and most of them can maintain their optical properties when the power is turned off for several hours (memory effect). When the process is reversible, the original bleached state is obtained by reversing the applied voltage.

The current collecting layers are usually made of a mixed oxide In₂O₃ - SnO₂ (ITO) of low electrical resistivity. Nowadays the preferred electrochromic layer is WO₃ which structure and color are modified by electrochemical insertion of ions following the reaction.



where A⁺ can be H⁺, Li⁺, Na⁺, etc..

The net result of the insertion reaction is the reduction of the transparent WO_3 host material and its transformation into a blue colored tungsten bronze $\text{W}^{6+}_{1-x} \text{O}_{3-x} \text{W}^{5+}_x (\text{OA})_x$. Its coloration is due to the presence of a large absorption band in the visible and near infrared region ($E_{\text{max}} \approx 1.4\text{eV}$) attributed to electronic transitions from the reduced tungsten ions states W^{5+} toward the conduction band^{2,3}. Although the chemical diffusion of Li^+ ions is smaller than that of H^+ , those ions are preferred for the realization of devices as hydrogen usually present degassing phenomenon and the acid media of the electrolyte limits the lifetime of the protonic based devices⁴.

Many electrolytes have been proposed and tested. The advantages of polymeric ion conductors over liquid ones is now recognized^{4,5} as they provide good electrolyte/electrode contact and present less problems of leakage. Among them polyethylene oxide (PEO) complexed with alkali salts such as LiClO_4 , LiCF_3SO_3 or $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ exhibits good Li^+ conductivity in the range $10^{-5} - 10^{-7} \text{Scm}^{-1}$ at room temperature. The use of PEO with the first two salts is somewhat limited because of the crystallization of these compounds at room temperature. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is preferred since its vitreous transition temperature is much lower.

The choice of a good counter electrode is more problematic. Various oxides such as V_2O_5 ^{6,7}, Ir_2O_3 ^{8,9}, CeO_2 ¹⁰ have been proposed recently but none of them exhibits ideal properties of transparency, reversibility and high kinetics for the electrochemical reaction with Li^+ ions. Recently we have proposed the use of $\text{TiO}_2 - \text{CeO}_2$ layers and have shown that this new compound allows a better Li^+ insertion kinetics than pure CeO_2 ^{7,11,12}.

In this paper we present the optical and electrochromic characterization of a new ion storage layer of composition $\text{ZrO}_2 - \text{CeO}_2$: it is prepared by the sol-gel process and shows very promising properties for the realization of electrochromic devices working either with H^+ or Li^+ ions. The $\text{TiO}_2 - \text{CeO}_2$ coating already described^{11,12} has been used to realize complete transmissive cell having the following configurations:

- a) /glass/ITO/ Li_xWO_3 /PEO- $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ / $\text{Li}_y(\text{TiO}_2 - \text{CeO}_2)$ /ITO/glass/
- b) /glass/ITO/ H_xWO_3 /cellulose-polyacetate polymer/ $\text{H}_y(\text{TiO}_2 - \text{CeO}_2)$ /ITO/ /glass/
- c) /glass/ITO/polytoluidine/PEO- $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ / $\text{Li}_y(\text{TiO}_2 - \text{CeO}_2)$ /ITO/glass/
- d) /glass/ITO/polytoluidine/cellulose-polyacetate polymer/ $\text{H}_y(\text{TiO}_2 - \text{CeO}_2)$ /

We present their optical and electrochemical properties and lifetime behavior and discuss their possible use for commercial devices.

2. MATERIALS AND PROCEDURES

We describe in this section the materials and procedures used to prepare the different coatings.

2.1. Electronic conductor

We used Baltracon Z 20 (Balzers) ITO thin films deposited on glass plates 1.5 mm thick; the layers have an electrical resistivity of $200 \Omega/\square$.

2.2 Electrochromic coating

The WO_3 layers were deposited from the corresponding oxide powder by vacuum evaporation onto ITO/glass substrates. The WO_3 films were amorphous to X-ray diffraction and their thickness measured with a Talystep was of the order of 200 - 300 nm. The films have been characterized electrochemically and the chemical diffusion coefficient for Li^+ ions $\bar{D} = 2,5 \cdot 10^{-11} \text{ cm}^2/\text{s}$ at 25°C has been determined by analysing the low frequency response of the impedance data⁷.

The polytoluidine coatings have been polymerized potentiodynamically directly on the ITO/glass substrate in deoxygenated 0.1 mol/l H_2SO_4 solutions containing 0,1 mol/l of aniline. The potential was cycled between 0.0 and 1.4 V vs HESS with a scan rate of 0.1 V/s. The polytoluidine film was obtained after 23 cycles.

2.3. Electrolyte

For the all solid state cell using Li^+ ions we used a polymer electrolyte complex prepared by dissolving polyethylene oxide (PEO) powder (M.W. = $9 \cdot 10^6$) and $\text{Li N}(\text{SO}_2\text{CF}_3)_2$ salt in acetonitrile with an O:Li atomic ratio of 10:1; this preparation corresponds to the highest conductivity of this system. The viscous liquid prepared in glove box in absence of humidity was poured on the glass /ITO/ WO_3 substrate. The solvent was evaporated at 50°C during 48h. The substrates were then kept in the dry box for further processing. The films are typically 50 to 200 nm thick.

For the all solid state cell using H^+ ions a cellulose polyacetate protonic gel was prepared with the following process: 0.5g of cellulose monoacetate (Rhodialite-Rhodia-Brazil) was diluted in 2 ml of acetone.

After dissolution 2 ml of an 80 vol% glacial acetic acid in water was added. The gel obtained was poured on one of the substrate.

2.4. Sol-gel storage coatings (counter electrode)

TiO₂ - CeO₂ thin films have been prepared by the sol-gel process using the dip coating technique. The precursor sol was prepared by dissolving Ce(NH₄)₂(NO₃)₆ salt in ethanol to which was added tetraisopropyl orthotitanate Ti(O-iso-C₃H₇)₄ with an atomic ratio Ti:Ce=1:1. The concentration of the cerium salt in ethanol was 0,25M (limit of solubility). No special care was taken to limit the presence of water in the solution as the cerium salt acts as an acid which reduces the pH and prevents the Ti(OPr)₄ precipitation. The layers were deposited by dip coating on carefully cleaned and dried ITO coated glasses (Baltracon Z 20) at a withdrawal speed of 10cm/min. After drying the films at room temperature for 15 minutes, they have been partially densified by heat treatment in air at 450°C during 15 min. Their thickness is typically 60 to 80 nm. The whole procedure was repeated 3 to 4 times to obtain thicker films.

The same method was applied to prepare ZrO₂ - CeO₂ thin films using however a precursor sol prepared by mixing zirconium propoxide (Zr(OPr)₃)₄, Ce(NH₄)₂(NO₃)₆ salt with atomic ratio Zr:Ce = 1:1 and ethanol.

3. TRANSMISSIVE DEVICES USING CeO₂ - TiO₂ STORAGE IONS ELECTRODE

In this section we present the optical and electrochemical behaviors of various all solid state cells working in transmission, all using the CeO₂ - TiO₂ sol-gel coating as counter electrode.

3.1. Device based on WO₃/electrolyte/CeO₂ - TiO₂

Two cells have been mounted. The first one, working with Li⁺ ions, has the following configuration:



The mounting of the cell was done in a glove box. The polymer electrolyte was poured onto the substrate /glass/ITO/Li_xWO₃/ and the other side of the window CeO₂ - TiO₂/ITO/glass was then pressed firmly against the first substrate. The cell was then sealed with Torr seal glue. Figures 2 and 3 summarize its optical (at λ = 750 nm) and electrical properties. The response to a potentiostatic signal is shown in figure 2. The curve of the current presents a rapid change of its curvature for a cathodic polarization (-2,5 V) around t = 20s, i.e. when the Li⁺ ions are transferred from the electrochromic WO₃ layer toward the storage coating. Similar behavior has also been observed with CeO₂-TiO₂ electrochemical study in a PC-0,1M LiClO₄ electrolyte¹¹. This indicates that the determining step of the process is the insertion of Li⁺ into CeO₂ - TiO₂. We believe that this rapid variation is due to a decrease of the diffusion coefficient of the lithium ion (\tilde{D}) when the concentration of Li⁺ reaches a certain value.

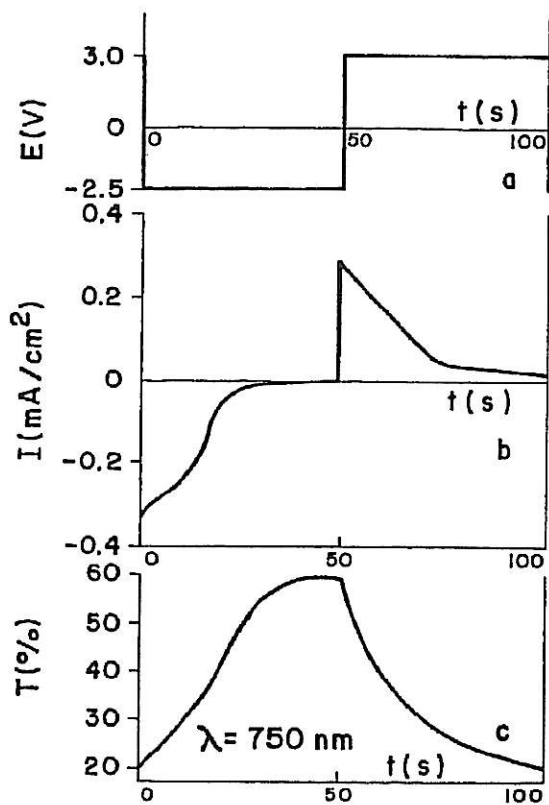


Fig. 2 Potentiostatic response of a $\text{WO}_3/\text{PEO} - \text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{CeO}_2\text{-TiO}_2/\text{window}$
 a) applied voltage (vs WO_3)
 b) current I
 c) optical transmission at $\lambda = 750 \text{ nm}$ (see also fig. 6)

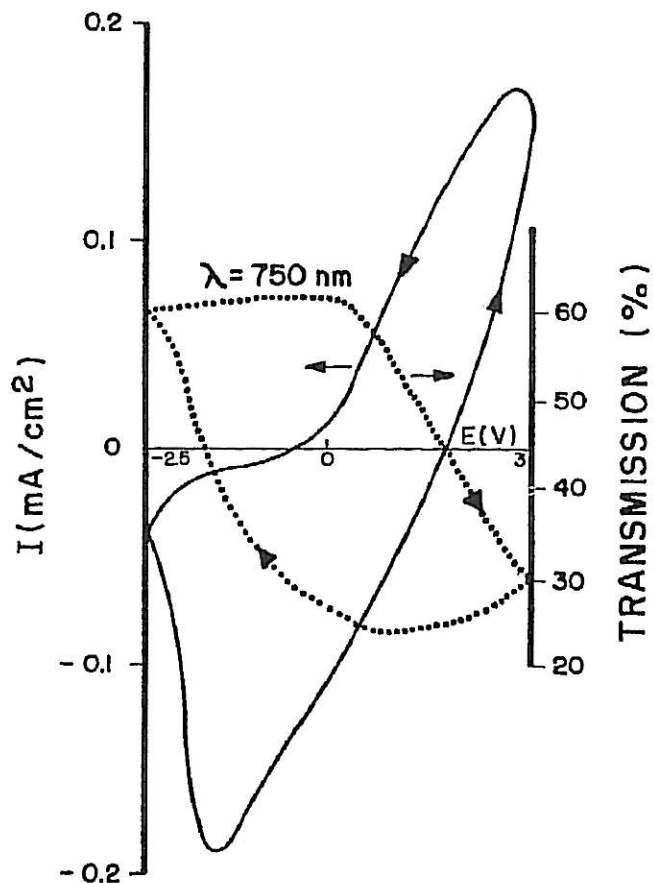


Fig. 3 Voltammetry of a $\text{WO}_3/\text{PEO} - \text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{CeO}_2\text{-TiO}_2/\text{window}$
 $v = 50 \text{ mV/s}$. E vs WO_3
 — current (left scale)
 - - - - optical transmission at $\lambda = 750 \text{ nm}$ (right scale)

In order to confirm this assumption, the current variation was studied varying the potential limits. By this way we change the residual charge (y) which stays inserted into the counter electrode, and thus, modify the initial charge before each new insertion. Figure 4 shows the observed response of the window. We can clearly observe the two steps variation of the current and see that the fall of the current is delayed when (y) is large (high negative limit of the potential step).

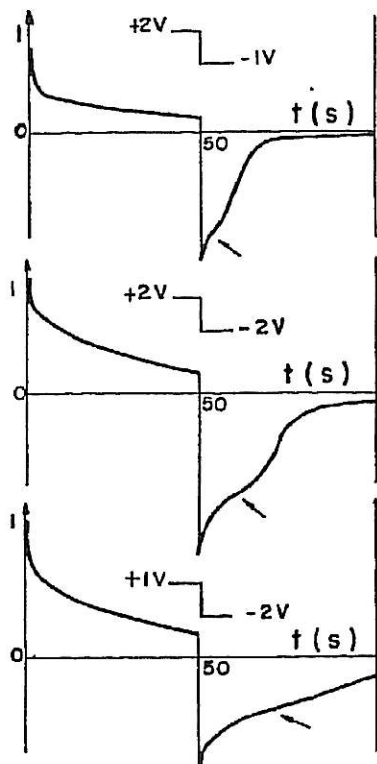


Figure 4 - Response of the $\text{Li}_x\text{WO}_3/\text{PEO-LiN}(\text{SO}_2\text{CF}_3)_2/\text{TiO}_2 - \text{CeO}_2$ to different voltage steps.

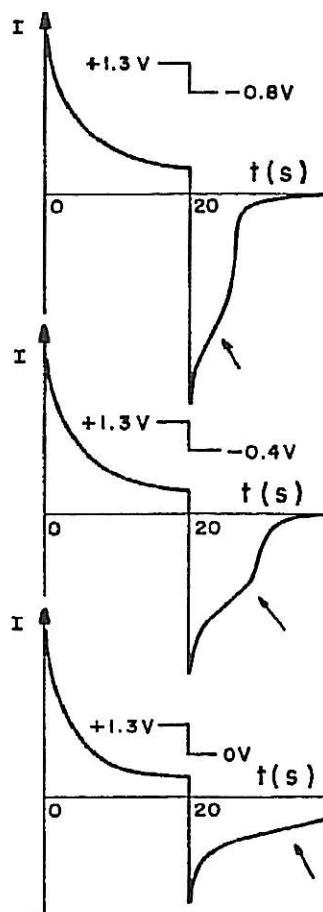


Figure 5 - Response of the $\text{H}_x\text{WO}_3/\text{cellulose-polyacetate}/\text{TiO}_2 - \text{CeO}_2$ to different voltage steps.

Figure 3 shows the dynamic behavior of the same window where a cyclic voltammetry and the variation of the optical transmission at $\lambda = 750 \text{ nm}$ are recorded simultaneously. This opto-voltammetry allows to follow both variations in real time.

The overall optical transmission of the window in the visible-near infrared range is shown in figure 6. In the bleached state the window presents an optical transmission of the order of 60% between 700 and 1000 nm. This value is reduced to 20% when the window polarization is inverted (colored state).

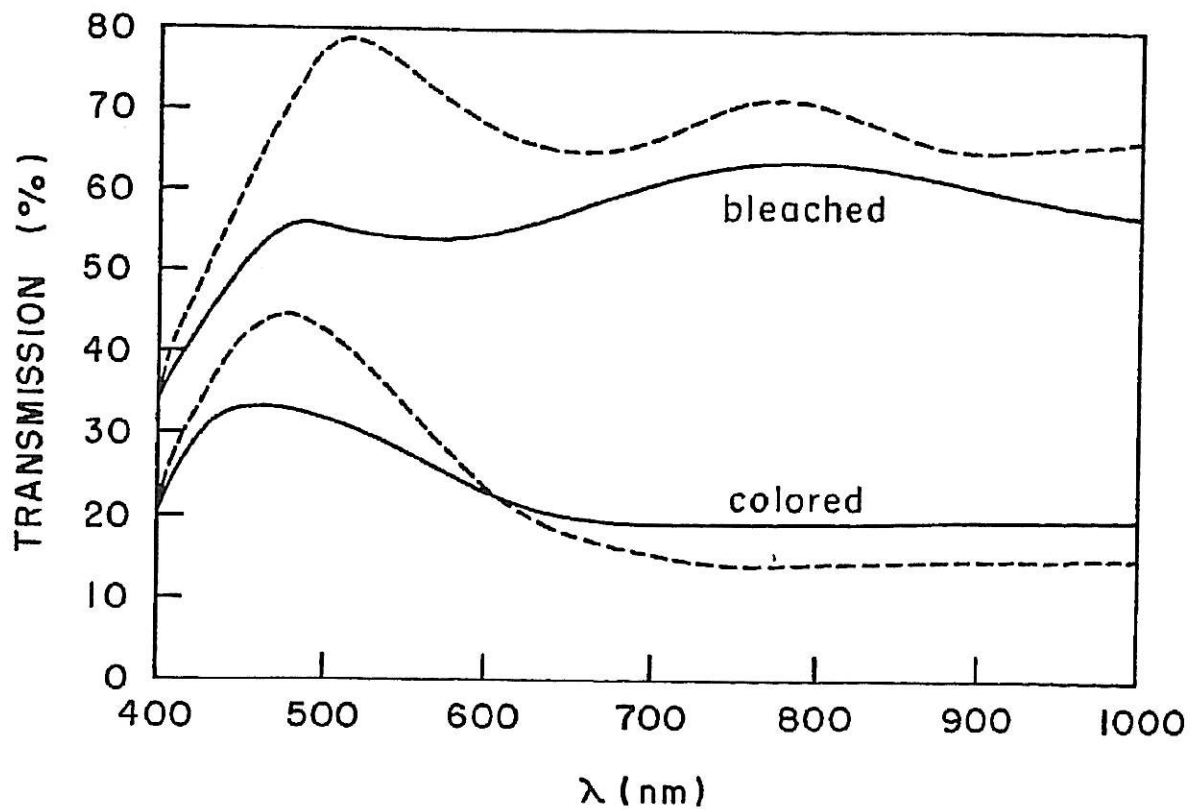


Figure 6 - Optical transmission of all solid state windows having the configuration:

— /glass/ITO/Li_xWO₃/PEO-LiN(CF₃SO₂)₂/CeO₂-TiO₂/ITO/glass/

----- /glass/ITO/H_xWO₃/cellulose-polyacetate/CeO₂-TiO₂/ITO/glass/

Respective polarization vs WO₃: -2.5V and -1.1V (bleached state); 3V and 1.4V (coloured state)

The second window which has been built up is working with H⁺ ions and has the following configuration:

/glass/ITO/H_xWO₃/cellulose-polyacetate/H_y(CeO₂-TiO₂)/ITO/glass/

The mounting of the cell was done in air using the same procedure as described above. Figures 5,6,7 and 8 show its optical and electrical properties.

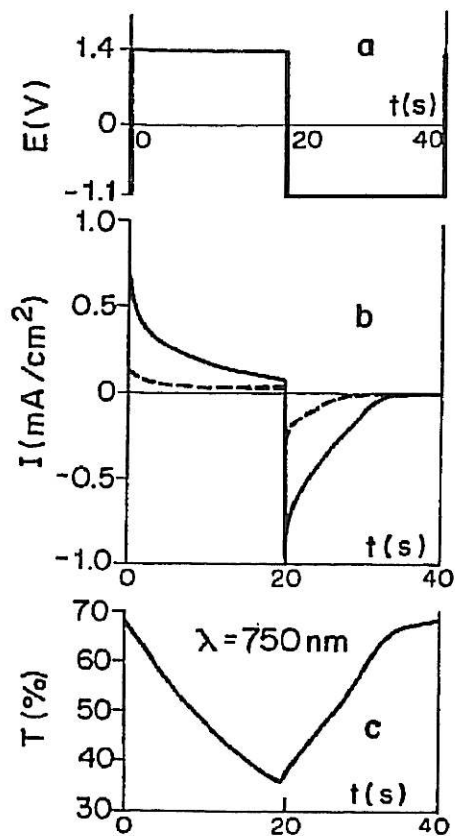


Fig. 7 - Potentiostatic response of a $/WO_3/cellulose$ polyacetate/ $TiO_2 - CeO_2/$ window
a) applied voltage (vs WO_3)
b) current I
— after 25 cycles
- - - after 400 cycles
c) optical transmission at $\lambda = 750$ nm (see also fig. 6)

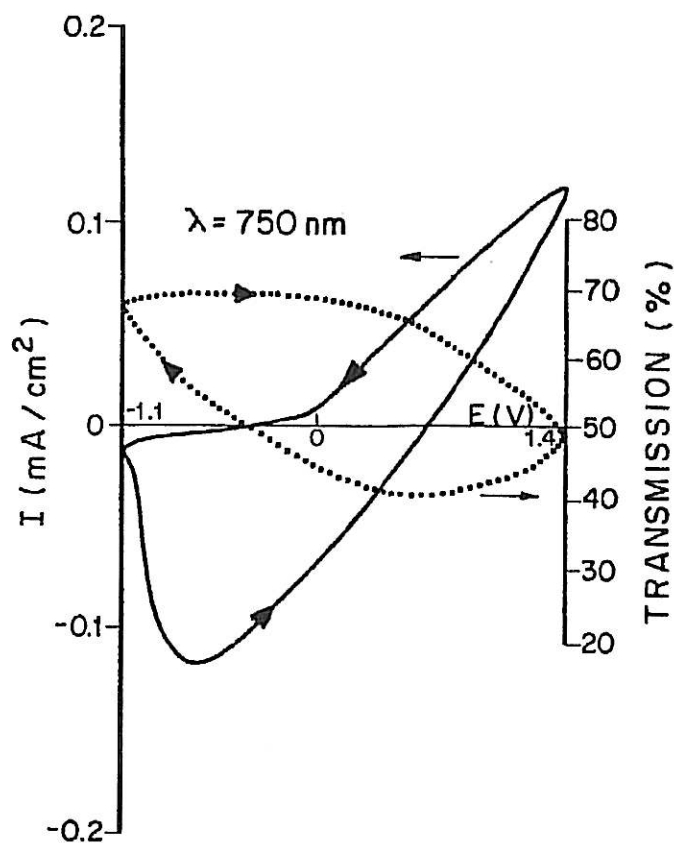


Fig. 8 - Voltammetry of a $/WO_3/cellulose$ polyacetate/ $TiO_2 - CeO_2/$ window
 $v = 50$ mV/s, E vs WO_3
— current (left scale)
- - - optical transmission at $\lambda = 750$ nm (right scale)

This window has basically the same properties as the first one which uses Li^+ ions. The optical variation is however faster (see for example figures 5,7 and 8) but its lifetime is considerably reduced because of

corrosion of the WO_3 and/or ITO layers by the acidic electrolyte (see fig. 5). The overall optical transmission variation is slightly larger for the aqueous electrolyte; this is due to the fact that after several cycles we have observed in the Li^+ conducting window the presence of small bubbles or holes in the PEO-Li complex polymer. These bubbles tend to coalesce and start to scatter the transmitting light reducing in this way the optical transmission in the bleached state. We believe that this phenomenon can be eliminated by using plasticizers in order to strengthen the polymeric structure.

3.2 Device based on Polymer/electrolyte/ CeO_2 - TiO_2

The electrochemical and electrochromic response of an electro-polymerized polytoluidine film in either a 0.1M H_2SO_4 aqueous solution or a 0.1M LiClO_4 non aqueous acetonitrile (AN) solution have already been described¹³. A reversible insertion process was observed accompanied by a colour change ranging from yellow to blue. The electronic absorption spectrum of the polytoluidine film in the reduced and oxidized states are shown in fig. 9. The polyanisidine film shows similar optical properties.

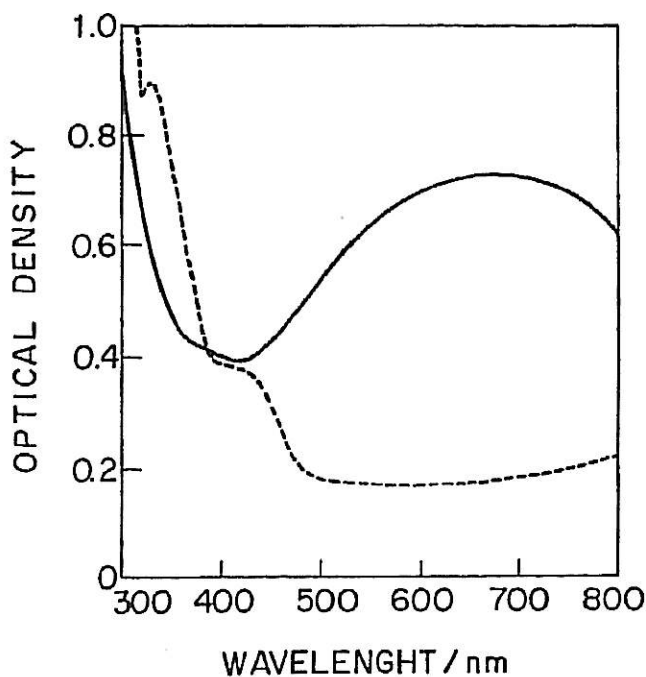


Fig. 9 - Optical density of a polytoluidine film in the reduced (bleached) state (—) and oxidized (colored) state (----).

Two electrochromic devices were built following the procedure described in section 2 using polytoluidine as electrochromic layer.

Fig. 10 shows the electrical and optical response (at $\lambda = 632.8\text{nm}$) of the device using a PEO-LiN(CF₃SO₃)₂ complex as polymer electrolyte.

We observe a smaller variation of the optical transmission compared to that seen in figure 9; this may be related to an interaction between the polytoluidine and the polymer electrolyte. The loss in charge between the 25th to the 2500th is smaller than 5% demonstrating a good reversibility of the electrochemical process.

The results are better using the protonic system made of cellulose polyacetate polymer electrolyte. Fig. 11 shows an optical transmission varying from 70% to 30% in 20s. The cyclic voltammetry does not show any sensible variation after more than 1000 cycles (fig. 12). Nevertheless small hydrogen bubbles appeared after the cycling.

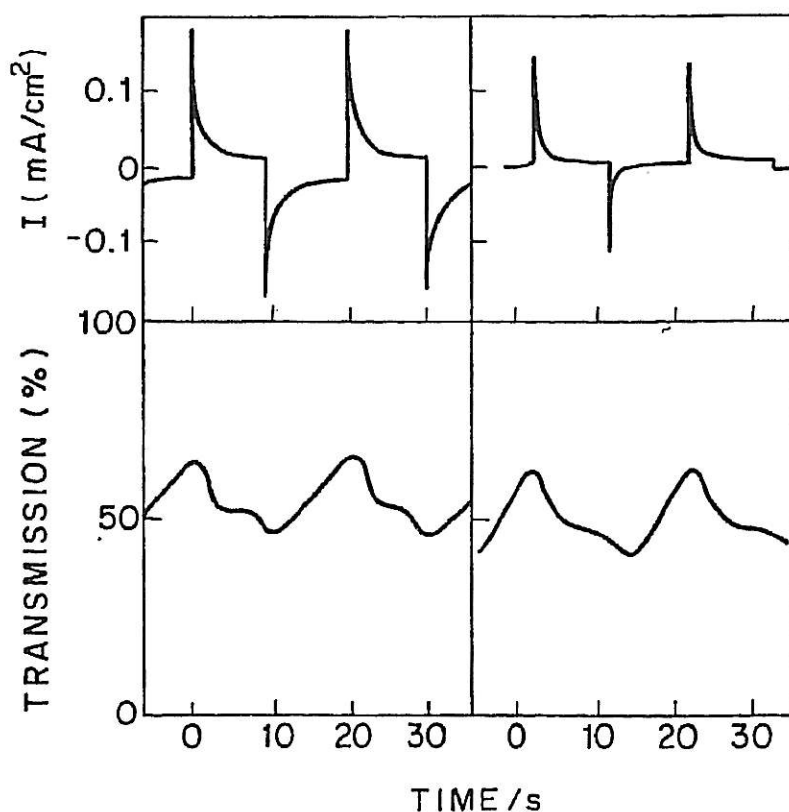


Fig. 10 - Potentiostatic response of a /polytoluidine/PEO-LiN(CF₃SO₂)₂/ CeO₂ -TiO₂/ window.

a) current I.

b) optical transmission($\lambda = 632,8 \text{ nm}$).

Potential step from -0.8V to 1.5V (vs CeO₂ - TiO₂)

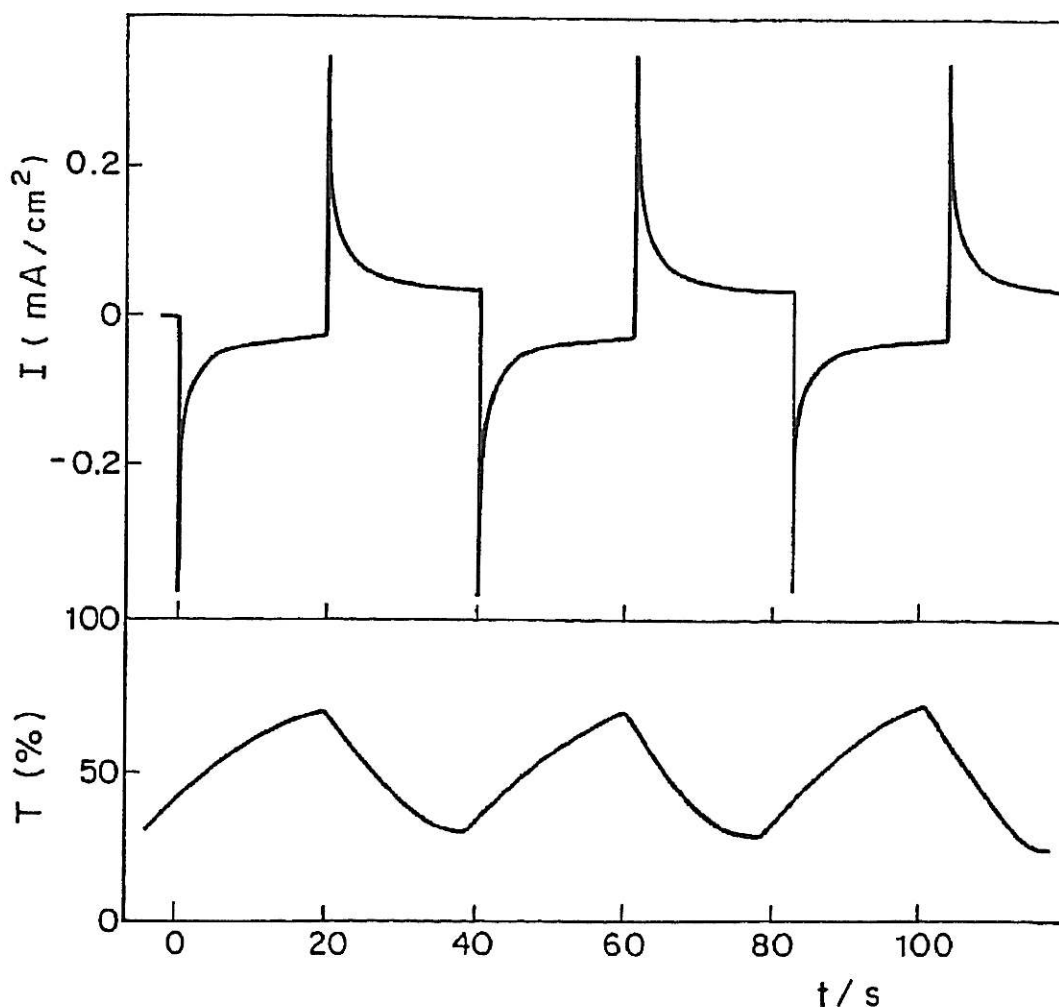


Fig. 11 - Optical transmission of the window /polytoluidine/cellulose-polyacetate/ TiO_2 - CeO_2 /. Potential step from -0.5V to +1.8 vs CeO_2 - TiO_2 .

4. A NEW COUNTER ELECTRODE

Films of ZrO_2 - CeO_2 were realized by the same process as that used for the CeO_2 - TiO_2 film (see section 2).

A voltammetry in a 0.1 M H_2SO_4 aqueous solution shows a reversible behavior and good H^+ insertion velocity (fig. 13). The X-ray spectrum is identical to the CeO_2 - TiO_2 one¹¹ and shows the characteristic CeO_2 crystallites peaks. Its behavior in organic electrolyte for Li^+ insertion and the realization of complete all solid state windows are under investigations.

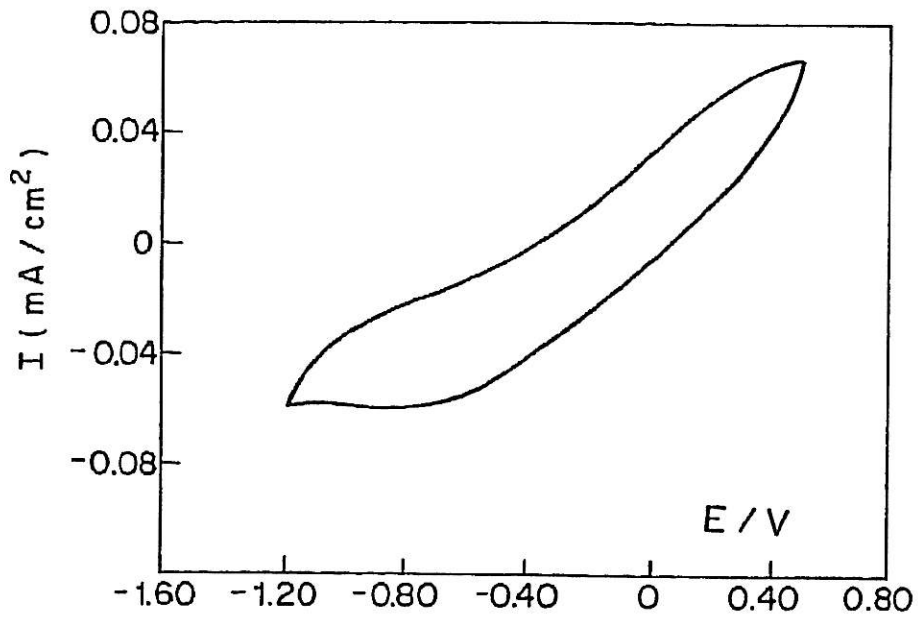


Fig. 12 - Cyclic voltammetry of the window /polytoluidine/cellulose-polyacetate/ TiO_2 - CeO_2 (E vs polytoluidine).

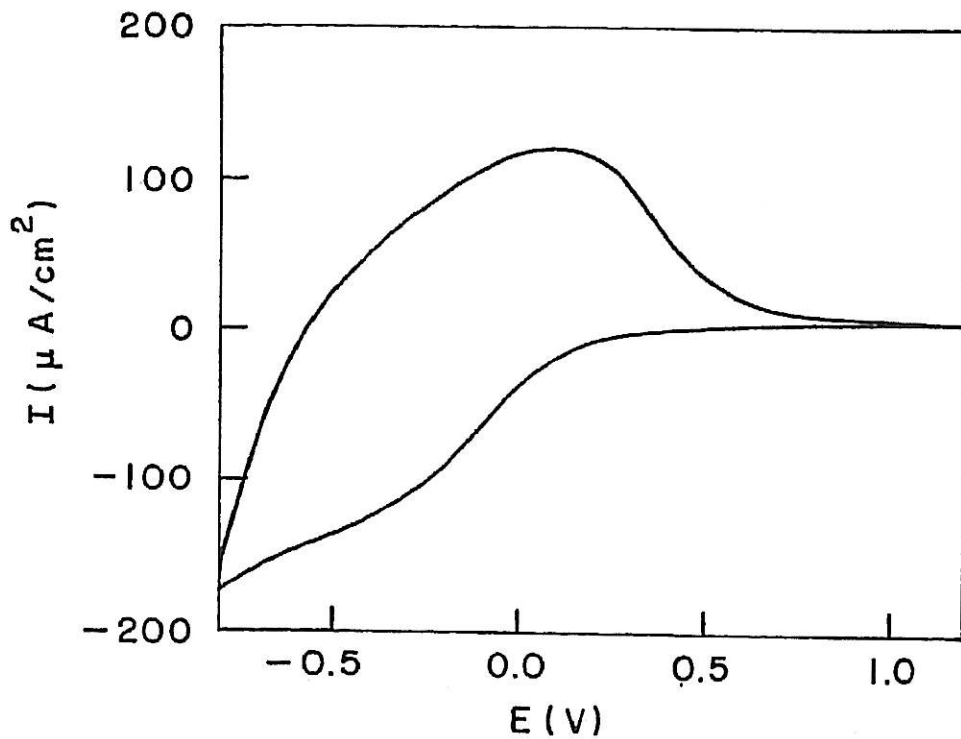


Fig. 13 - Voltammetry of a glass/ ITO/ZrO_2 - CeO_2 / in $0.1\text{M H}_2\text{SO}_4$ aqueous solution. $V = 50\text{mV/s}$, E vs HESS

5. CONCLUSION

Several all solid state electrochromic windows have been realized using as a counter electrode (ion storage) a $\text{CeO}_2 - \text{TiO}_2$ coating prepared by the sol-gel process. This compound can store either H^+ or Li^+ ions. The best optical and lifetime behavior is obtained using WO_3 as an electrochromic layer and $\text{PEO} - \text{LiN}(\text{CF}_3\text{SO}_2)_2$ as an electrolyte. The optical transmission change varies from 60% to 20% and the time response from the bleached state to the coloured state is of the order of 50 s. The speed limitation of the response is due to the insertion process of the Li^+ ion into the $\text{CeO}_2 - \text{TiO}_2$ layer as demonstrated by the rapid decrease of the potentiostatic response. The Li^+ chemical diffusion coefficient appears to decrease when a certain value of y is reached in the $\text{Li}_y(\text{CeO} - \text{TiO}_2)$ compound.

The H^+ conducting window shows a similar behavior. Its time response is however faster but its lifetime is drastically reduced because of corrosion phenomena due to the acid electrolyte.

The substitution of WO_3 by polymeric layers such as polytoluidine shows that the oxidation/reduction process are reversible; the layers present a good electrochemical response in either aqueous, non aqueous or polymer electrolyte. In the present state of the art the optical response is however less attractive for the Li^+ ion device; nevertheless a good stability of the film was observed in acid polymer electrolyte accompanied by a good optical response. This opens a new opportunity for protonic electrochromic devices.

6. ACKNOWLEDGMENTS

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