

A comparison of the electrochromic properties of WO₃ films intercalated with H⁺, Li⁺ and Na⁺

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The electrochromic response of WO₃ thin films under electrochemical insertion from nonaqueous electrolytes of one of the three different ions: protons, lithium and sodium cations is reported. In spite of the common belief that the nature of the ion does not change the electrochromic effect, we show that the sample colouring and bleaching are dependent on the intercalant ion and on the insertion rate. The facile insertion of protons is responsible for the highest optical contrast and the quickest response time of this intercalation electrode. Lithium and sodium-intercalated electrodes do not show large optical difference from the proton-intercalated tungsten trioxide unless large charging currents are used. Subtle changes in electrochromic efficiency and in the optical contrast in the red part of the spectrum can be detected; these are larger for the sodium than for the lithium intercalant. According to our analysis, the slow insertion kinetics of Na⁺ and the formation of a new M_xWO₃ (M=Li, Na) compound is responsible for most of the observed differences.

1. Introduction

WO₃ is the most commonly studied electrochromic material [1]. Other transition metal oxides in the form of thin films (such as TiO₂ and V₂O₅ [2]) have been recently investigated in view of its utility in smart windows [3–8] and antidazzle mirrors [9], as well as for large area nonemissive displays [10, 11]. The electrochromic effect [10] in the above thin films (i.e., the colour change induced electrochemically and observable by the naked eye) has been attributed to the simultaneous injection of an electron and of a charge-compensating cation [12] (mainly H⁺, Li⁺, Na⁺ or Ag⁺), this being interpreted as due to a polaron absorption or to a free carrier absorption. In theoretical explanations of the optical absorption in the intercalated material, the nature of the charge compensating cation has usually been disregarded. To build practical devices, however, the differences resulting from the use of one or another ion are considerable and they must be taken into account.

With this concept in mind, we report a comparison of the optical properties between the M_xWO₃ bronzes obtained with M = H, Li and Na, with the aim of discussing, not only the steady-state situation of an intercalated thin film, but also the kinetics of the coloration process. The electrochemical intercalation of the three cations has been carried out from nonaqueous and aprotic electrolytes to avoid the complications due to water in the electrochemical behaviour of the WO₃ electrodes. Such a procedure, although established for alkali cations, has not yet

been applied for protons, in spite of the fact that WO₃ thin films are soluble in water [13]. Another reason for not using water as a solvent is that the small solvent molecules are co-intercalated during the cation insertion, as shown for lithium ions by Bohnke *et al.* [14]. In the case, it is also possible that protons and lithium ions are both deintercalated during the bleaching process, and, consequently, that the coloration kinetics and the electrochromic efficiency vary with the water content of the electrolyte. It is also recognized that some water molecules are introduced to the sample during the film deposition process and during its storage in humid air, and thus play a fundamental role in the electrochromic phenomena [15–17]. The incorporated water [18] may change the diffusion process in the film by means of an ion exchange reaction between protons and Li⁺. In fact, this effect has been claimed to be responsible for the high diffusion coefficient of lithium ions observed at low concentration in the WO₃ thin film [19]. If this is the case, we expect a similar ion exchange reaction to take place both with lithium and with sodium ions. The aim here is to study to what extent this reaction controls the electrochromic properties of WO₃ and the coloration-bleaching kinetics at low and high cation concentration.

2. Experimental details

WO₃ thin films were prepared onto ITO-coated glass substrates by evaporation from a tungsten oxide source (samples A and B, 290 nm and 130 nm thick, respectively). A few sputtered samples were also

prepared for comparison with the evaporated ones (sample C, 120 nm thick, obtained by reactive magnetron sputtering from a tungsten target in an Ar/O₂ gas atmosphere. The electrochemical insertion of the different ions was performed in a three-electrode cell having as electrolyte either CF₃CO₂H 0.1 M + N[(CH)₂CH₃]₄ClO₄ 0.4 M in propylene carbonate (PC), for the experiments with protons, or LiClO₄ 1 M in PC (or NaClO₄ 0.7 M in PC) for the experiments with the alkali cations. The reference electrodes were Pt or Ag/AgCl (in the case of H⁺), Li or Na metal for the alkali cation electrolytes.

The stoichiometry of the tungsten bronzes M_xWO₃ was calculated from the inserted charge by the Faraday's law, taking the thin film density equal to 6.5 g cm⁻³ [20]. The water content of the reagents was < 0.1% for all the perchlorate salts, < 0.05% for CF₃CO₂H and < 0.005% for the PC solvent. The cell and the electrodes were always assembled in a dry box with low humidity content (< 10 ppm), to keep water contamination of the electrolyte as low as possible, and all the reagents had a purity > 99%. Potentiostats from AMEL (models 551, 553, 565) or EG&G (model 362), and the transmittance spectra were recorded *in situ* with an HP (model 8452A) diode-array spectrophotometer connected to an IBM-compatible computer.

In the galvanostatic intermittent titration technique (GITT) [13] the duration of the 1 mA cathodic current pulse was 0.5 s, and the relaxation time before the next current pulse was 120 s. The electrode potential drifted less than 20 mV during the last minute of the relaxation time. The frequency response analysis (FRA), already employed by Ho *et al.* [21] for similar tungsten oxide films, was applied to the data taken with the Solartron (model 1250) analyser in the range 1 mHz–65 kHz. In such experiments the electrode charge was varied, stepping the electrode potential each time by 0.5 V in the cathodic direction, and applying an a.c. signal to the electrochemical cell only after the residual current was less than 0.1 μA. In a similar potential-step experiment (–0.5 V of step height) the optical density variation at three different wavelengths and the current decay were recorded as a function of time for 25 min, for the three ions. Finally, constant current (i.e., galvanostatic) experiments were performed to measure the slow changes of the optical density at five different wavelengths, taking a step of current density of 10 μA cm⁻². Complete spectra from 300 to 820 nm were also taken each 1 mC cm⁻² of charge passed during similar galvanostatic experiments.

3. Results

The diffusion coefficient data from the GITT measurements are shown in Fig. 1. The values of D for the two ions, derived from the formula [19, 22]:

$$D = \frac{4L^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right) \quad (1)$$

follow almost the same curve for small amounts of the inserted charge (below 1.4 mC cm⁻²). For larger charges, D_{Li^+} was always laying above D_{Na^+} and approached a lower limit value of 1.3×10^{-10} cm² s⁻¹ for an inserted charge of 3.5 mC cm⁻² and larger. The lower limit of D_{Na^+} from GITT was 3.9×10^{-11} cm² s⁻¹ at an inserted charge of 5 mC cm⁻². A similar drop as a function of the inserted charge was observed for the M_xWO₃ electrode potential as well (M = Li, Na, see Fig. 2). The electrode intercalated with Na showed a larger potential drop than that intercalated with Li. In the impedance spectra in Fig. 3 the frequency response of the same two intercalation electrodes are shown. Their typical response was a loop at higher frequencies followed by a tilted straight line at lower frequencies, which can be viewed as the response of an equivalent circuit of the Randles type. The diameter of the loop was better defined for the Li_xWO₃ electrode, giving an intercept at 0.9 kΩ on the real axis, and was clearly smaller than for the Na_xWO₃ electrode, for which the line started at $Z' = 3.2$ kΩ. In its lower frequency part, the spectrum for Li_xWO₃ became steeper as the frequency reached its smallest value (1 mHz). Considering this feature as due to the finite thickness of the film, it is possible to find a value of D_{Li} of 3.9×10^{-12} cm² s⁻¹, deduced from the formula in [21]:

$$D = \frac{X2\pi\nu L^2}{3R_L} \quad (2)$$

In the above equation, X represents the value of Z'' at a frequency ν , at any point in the steeper part of the spectrum (capacitive behaviour), whereas L is the film thickness and R_L is the corresponding value of Z' ('limit' resistance). In spite of the fact that we worked with the same type of samples and with simi-

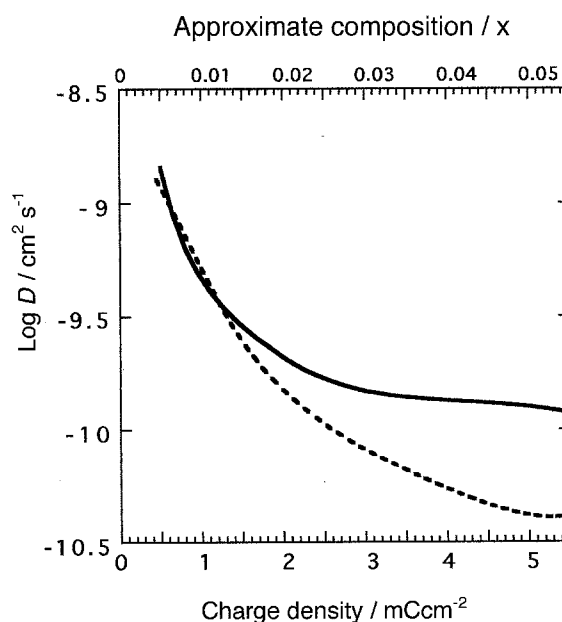


Fig. 1. Log D_{Li} (solid line) and log D_{Na} (dashed line) diffusion coefficients in WO₃ at room temperature as a function of the inserted charge. These values result from GITT measurements of sample A, with current density impulses of amplitudes 1 and 0.8 mA cm⁻² (for Li and Na, respectively) and duration 0.5 s, and with a relaxation time of 120 s.

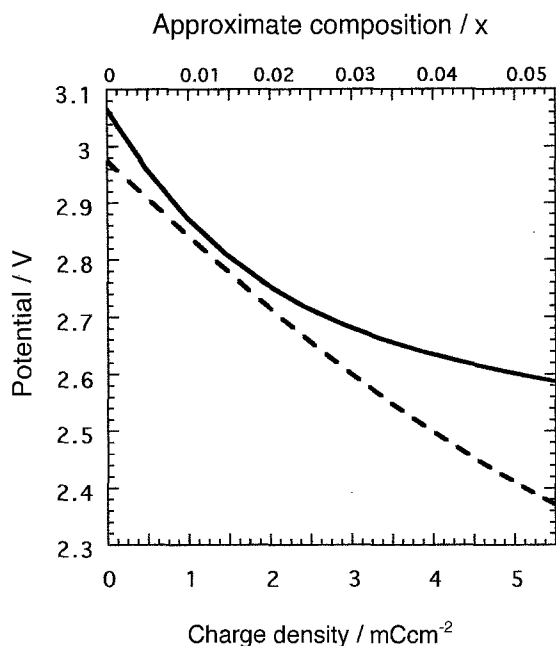


Fig. 2. Quasiequilibrium potentials of the WO₃ electrodes measured at the end of the relaxation time of 120 s during insertion of Li⁺ (solid line) and of Na⁺ (dashed line), against the corresponding metal, during the GITT experiments.

lar intercalant concentration in GITT and in the FRA (Frequency response analysis), the diffusion constant for Li⁺ found with the latter is considerably lower.

The transmittance spectra in the visible region (Fig. 4(a) and 4(b)) were observed to depend on the intercalant ion up to a certain extent, in particular in the red and near-infrared region. For example, the transmittance at a wavelength of 820 nm dropped 40% more with H⁺ than with Na⁺ with the same inserted charge of 5.5 mC cm⁻², and approached a saturation in a more transparent state for Na_xWO₃ and in a more absorbing state for H_xWO₃. In another galvanostatic insertion experiment, the electrochro-

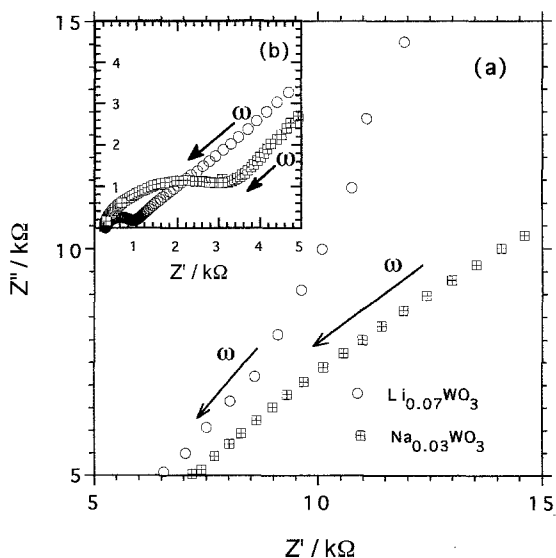


Fig. 3. (a) FRA spectra at low frequencies (from 1 mHz to 1 Hz) for M_xWO₃ electrodes (sample A) intercalated potentiostatically with -5.7 mC cm⁻² (open dots representing M = Li, x ≈ 0.07, equilibrium potential 2.45 V against Li) and with -2.1 mC cm⁻² (squares representing M = Na, x ≈ 0.03, equilibrium potential 2.35 V against Na). (b) FRA spectra at high frequencies (from 1 Hz to 65 kHz) for the same electrodes as in (a).

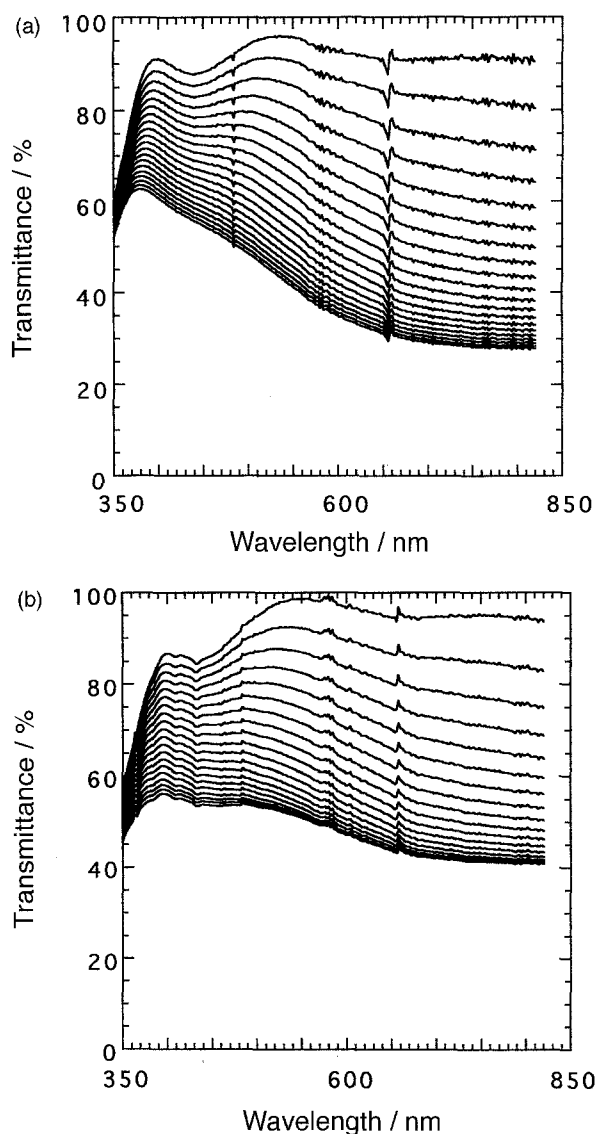


Fig. 4. (a) Transmittance spectra of H_xWO₃ (sample C) taken every 0.9 mC cm⁻² (Δx ≈ 0.03) of charge inserted at constant current (-3 μA cm⁻²); (b) transmittance spectra of Na_xWO₃ (sample C) taken every 1.1 mC cm⁻² of inserted charge (Δx ≈ 0.04) at -8.5 μA cm⁻². The first spectrum of each set is the highest one and refers to an unintercalated electrode.

mic efficiency, η (defined as the optical density (o.d.) change per unit charge inserted), was taken from the slope of the optical density against charge density curves (Fig. 5(a), (b) and (c)). This electrochromic efficiency was larger for H⁺ intercalated WO₃ films than for films intercalated with the other cations. In particular this was true for the red light (at 700 nm $\eta = 63 \text{ cm}^2 \text{ C}^{-1}$ for H⁺, $36 \text{ cm}^2 \text{ C}^{-1}$ for Li⁺ and $27 \text{ cm}^2 \text{ C}^{-1}$ for Na⁺), but this disparity diminished in the blue part of the spectrum where the polaron absorption is less and the fundamental absorption is more important.

A further difference between H_xWO₃ and the other tungsten bronzes is that the electrochromic effect in H_xWO₃ saturated already at a charge density of 16 mC cm⁻² (Fig. 5(d)) (corresponding to a stoichiometry x of 0.5), whereas the optical absorption first reached a maximum and then decreased with increasing charge of the other two cations. For high x values the back reaction of hydrogen evolution from the

H_xWO_3 electrode may become significant and reduce the value of the electrochromic efficiency. By comparing the charge needed to reach the maximum o.d. in two galvanostatic experiments with different currents (500 and $5 \mu A cm^{-2}$), the back reaction current has been estimated to be, on the average, $3 \mu A cm^{-2}$. This small back reaction current had a negligible effect on the electrochromic efficiency in H_xWO_3 and should not affect the results in Fig. 5(d), which describe the beginning of the insertion process with the three different cations. Despite the hydrogen evolution back reaction, the electrochromic efficiency in the experiments with H_xWO_3 shown in Fig. 5(d) was higher than that of the WO_3 intercalated with the other two ions, as shown by the larger slope of the o.d. against charge curve for the H_xWO_3 electrode. The hydrogen evolution back reaction can become

important, therefore, only at larger cationic charge inserted into the electrodes. The composition for which the maximum of the o.d. is reached in Na_xWO_3 was $x \approx 0.6$; for larger amounts of inserted cations the sodium-tungsten bronze switched from dark blue to pale yellow, and a similar behaviour was observed in the lithium-tungsten bronze.

With respect to the insertion kinetics, in the potential step experiments ($0.5 V$ in the cathodic direction) we observed that the coloration kinetics with Na^+ was not as fast as that with protons and with lithium ions (Fig. 6(a), (b) and (c)). The final value of the optical absorption at any wavelength in Fig. 6(c) was, in fact, similar to that reached with lithium ions (Fig. 6(b)), but the relaxation time was one order of magnitude slower. Moreover, if the electrode potential was stepped back to the initial value (Fig.

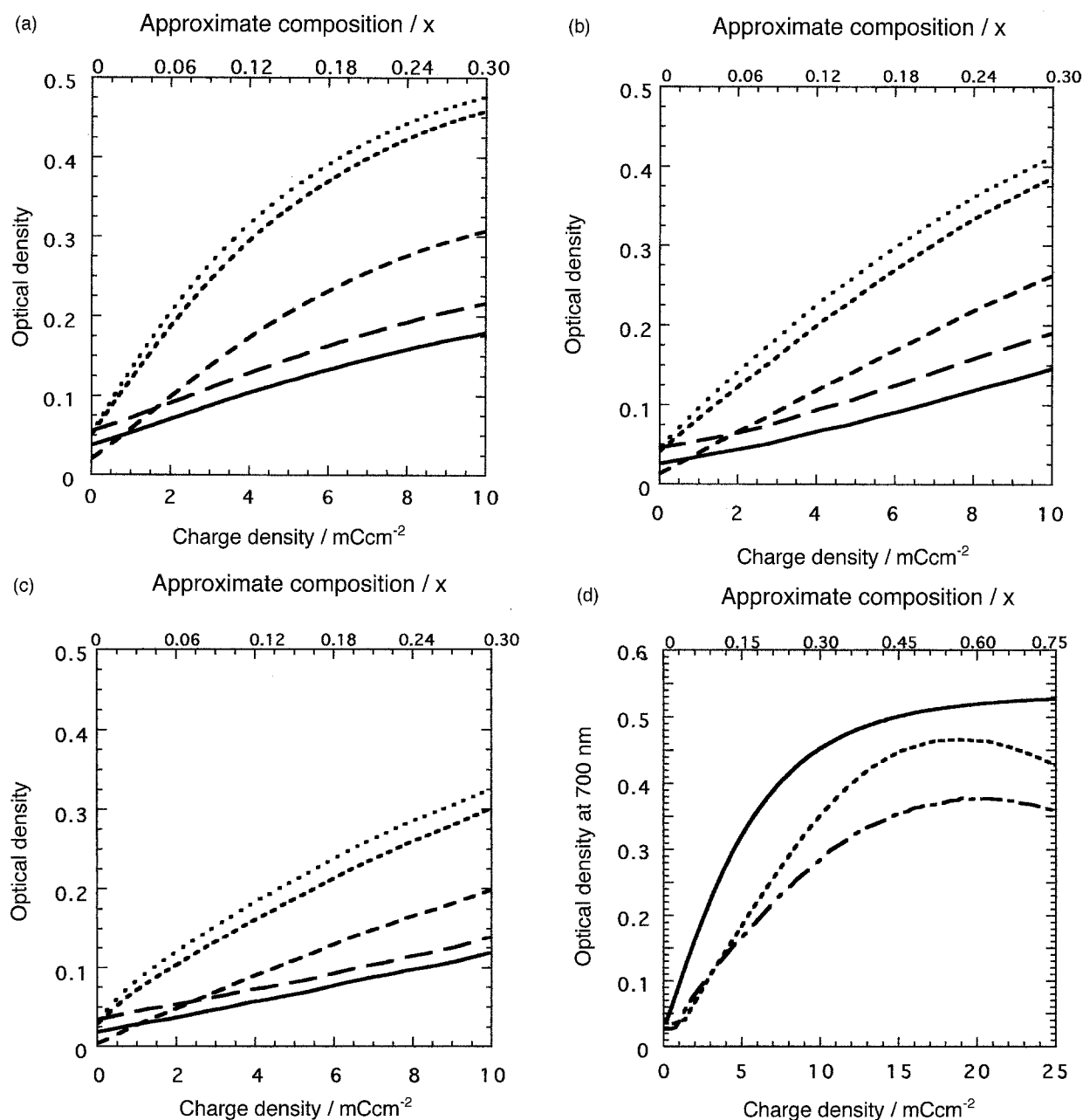
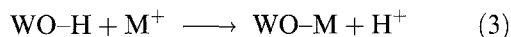


Fig. 5. Optical density (o.d.) variation of M_xWO_3 (sample C) at 5 wavelengths as a function of H^+ (a), Li^+ (b) and Na^+ (c) concentrations intercalated at about $-5 \mu A cm^{-2}$. (d) Comparison of the o.d. changes at 700 nm in M_xWO_3 electrodes intercalated at constant current ($-5 \mu A cm^{-2}$) with the three different ions up to $25 mC cm^{-2}$. Curves: (a) 760 (upper), 700, 530, 440, 400 (lower); (b) 820 (upper), 700, 550, 450, 400 (lower); (c) 820 (upper), 700, 530, 430, 400 (lower); (d) — o.d. of H_xWO_3 , - - - o.d. of Li_xWO_3 and - · - · o.d.

7 (a), (b) and (c)), the electrochromic reaction was not fully reversible. This can also be attributed to a self-discharge mechanism of the intercalated electrode or, alternatively, to a nonreversible electrochromic behaviour of the thin film electrode.

4. Discussion

The GITT experiments with lithium and sodium ions indicate that in a first stage of the intercalation process the ionic exchange reaction first proposed for lithium ions by Zang *et al.* [19]



takes place for both alkali cations used in the present work (i.e., with $\text{M} = \text{Li}, \text{Na}$). The validity of Equation 3 is in agreement with the ionic exchange reaction invoked by Schlotter and Pickelmann [23] to explain the i.r. reflectance spectra of the sodium tungsten bronzes. In the present case, the diffusion coefficient measured with GITT is that of the proton and not of the alkali cation, thus confirming the presence of a certain amount of protons or water in the samples prepared by thermal evaporation and left for sufficient time in contact with humid air. The average of this diffusion coefficient D_{H^+} , taken from the range in which the two curves in Fig. 1 coincide, is $5.6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, and agrees well with data reported for protons by other authors (see Table 1). The discrepancy between the Li^+ diffusion coefficients found here with two different techniques ($1.3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ with GITT and $3.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ with impedance) shows that the relaxation time between impulses chosen for GITT was not long enough to get an equilibrium concentration for the lithium ions in the thin film. For the same reason, the lower value of the diffusion coefficient calculated from GITT for sodium ($4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$), although smaller than that of lithium, is still much larger than other data [22, 27–29]. The decay of the diffusion coefficients in Fig. 1 with increasing charge density suggests not only the transition from the proton diffusion to an alkali diffusion mechanism, but also the increasing occupancy of the sites for ion diffusion. Such results suggest that since GITT requires an equilibrium concentration, and this may not be easily reached in the case of ions with very low mobility, quantitative results on the diffusion coefficients of such ions calculated with this technique should be taken with care.

Complex impedance, on the other side, is an alternative technique for measuring the diffusion coefficients of ions in a film of finite thickness. This has been shown to work in the present case only for the lithium ions. The fact that Li^+ can diffuse all the way through the film and become blocked at the ITO–WO₃ interface is shown by the increasing of the slope in the low frequency range of the complex impedance plot. The fact that the Na^+ ions cannot diffuse so far in the same time scale and that the intercalation kinetics is quite slow with Na^+ (i.e., the

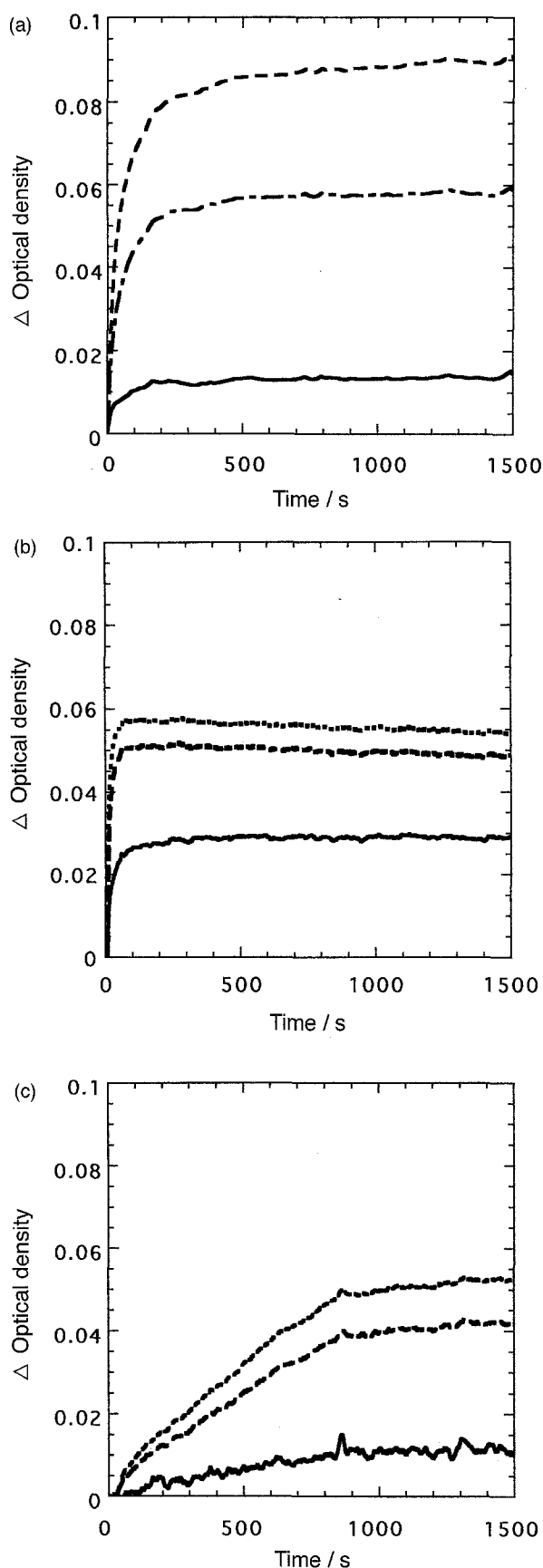


Fig. 6. Optical density variation (Δ o.d.), i.e., coloration time response of M_xWO_3 (sample B) as a function of time during a potential step of -0.5V with $\text{M} = \text{H}^+$ (a), Li^+ (b) and Na^+ (c). Curves: (—) 400, (---) 650 and (- - -) 800.

Table 1. Diffusion coefficients for the proton in WO_3 according to literature data

$D_{H^+}/cm^2 s^{-1}$	Method	Reference
4×10^{-10}	a.c. impedance	[24]
1.8×10^{-10}	chronoamperometry	[25]
$1 \times 10^{-9}/2 \times 10^{-10}$	current-potential curves calculated with a digital simulation model	[26]

charge transfer resistance is high) are shown in the impedance plot by the lower slope in the low frequency range and by the larger high frequency loop, respectively. The larger high frequency loop demonstrates, furthermore, that the intercalation of Li is a faster surface process than the intercalation of Na, ruling out the role of impurities in the electrolyte like water (usually more reactive with Na than with Li) in such surface reaction.

The different optical properties of the various tungsten bronzes can be related to the diffusion properties of the ions in the oxide. The diffusion being related to the atomic mass of the ion (the larger the mass, the slower the diffusion), it seems that there is the same ionic bond between any intercalant alkali ion and the oxygen atoms of the host. The slower diffusion of the sodium ion is responsible for an accumulation of the intercalant close to the electrochemical interface and, consequently, for the formation of tungsten bronzes with a lower coloration efficiency (Fig. 4). Two explanations can be advanced for the low coloration of the electrode parts with a high concentration of the intercalant: one is simply the low absorption coefficient of the new Na_xWO_3 bronze phase. The second is that the accumulation of W^{5+} centres close to the surface makes the sample less absorbing, because the probability of the intervalence charge transfer $W^{6+} \longrightarrow W^{5+}$ (related to the optical transition) is inversely proportional to the density of the W^{5+} centres present in the intercalated regions. The much faster diffusion in the oxide of the protons than that of the alkali is responsible, in our opinion, for the fastest response time of the WO_3 with H^+ . The absence of irreversible phase transitions and colour changes of the H_xWO_3 thin film is probably due to the hydrogen discharge occurring with the back reaction. This means that the film is never truly saturated with protons, although it is optically highly absorbing due to a uniform distribution of the light absorbing centres, and that the insertion process can always be reversed. For lithium and for sodium ions, not only is the coloration efficiency lower, under the same experimental conditions as with protons, but a new, less absorbing, yellow compound is eventually formed when the intercalated charge density exceeds 20 mC cm^{-2} . When such a high charge of Li^+ or Na^+ is intercalated, a negative coloration efficiency has been seen at several wavelengths. Furthermore, it was observed that: (i) there is an irreversible optical change for Na ions (during bleaching after a potential step, the optical density variation is slower and

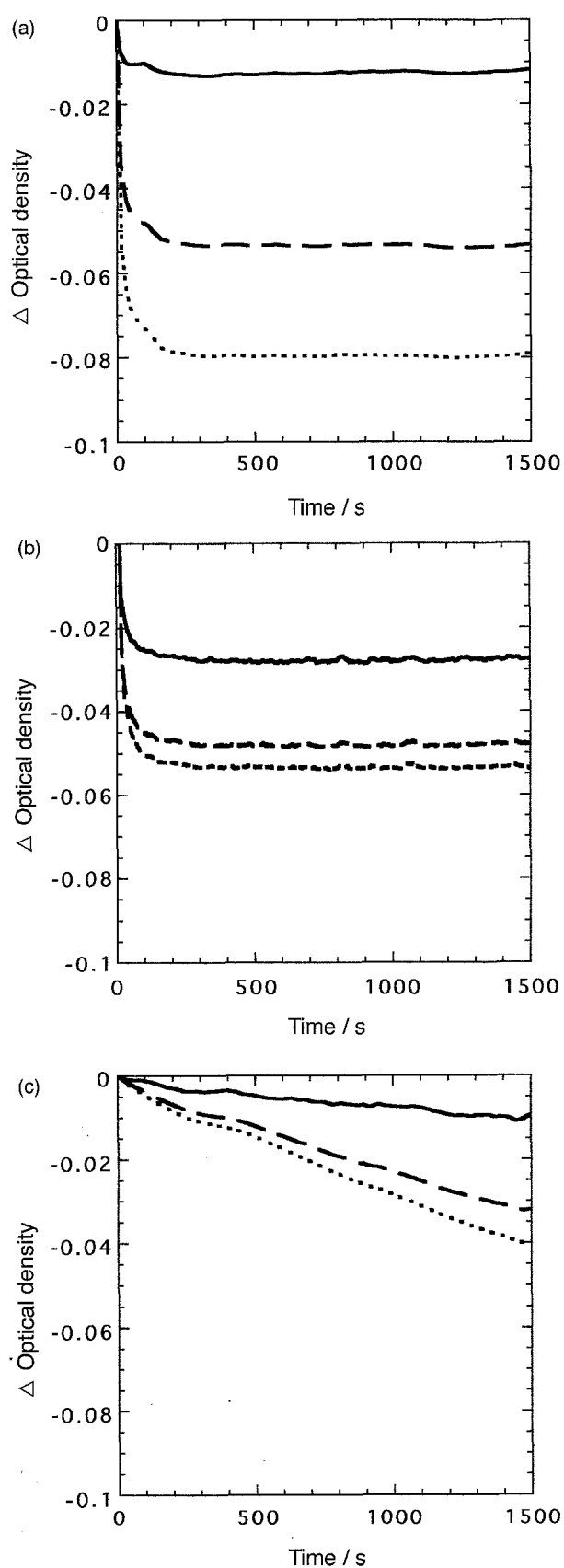


Fig. 7. Bleaching time responses of M_xWO_3 (sample B) during a potential step of +0.5V subsequent to the step described in fig. 6, after 1 h relaxation at open circuit, with H^+ in (a), Li^+ in (b) and Na^+ in (c). Curves: (—) 400, (---) 650 and (· · ·) 800.

smaller than during coloration, see Fig. 6); (ii) this also holds to a lesser extent for the lithium ions, although from the potential step, the coloration and bleaching kinetics of Li^+ are more similar to that of

the proton than to that of the sodium ions. The different time response and optical contrast upon bleaching after the coloration step, as seen in Fig. 7(c) compared with Fig. 6(c), is also a proof that there is a surface accumulation of the ions with the slowest diffusion coefficient, and that this accumulation modifies the electrode behaviour, preventing a further ion insertion and the deeper coloration of the electrochromic electrode.

5. Conclusions

Charge insertion in WO₃ films is an electrochemical reaction that depends strongly on the oxide film preparation and on the inserted ion diffusion. Among H⁺, Li⁺ and Na⁺, the first has the fastest diffusion, and the last the slowest. Moreover, the first shows the highest coloration efficiency at all wavelengths, and the last the lowest, this difference being larger the higher is the insertion current. In experiments with the three different ions all the oxide samples were equivalent and in the aprotic solvents the activity of ions to be intercalated was comparable. Nevertheless, the results with Li⁺, and particularly with Na⁺, show that there is a limiting concentration of the cation in the oxide films that, if exceeded, clearly induces optical and electrochemical irreversibility. Because the largest ions diffuse more slowly in the film, the local intercalant concentration after a potential step can be very high in the surface region, even when the average concentration is far below the above limit. Transient experiments, such as those described in this work, may help to choose the appropriate ion for each application depending of the time response and of the potential span required for the specific electrochromic device.

References

- [1] B. R. Faughnan, R. S. Crandall and P. M. Heyman, *RCA Rev.* **36** (1975) 177.
- [2] Y. Fujita, K. Miyazaki and C. Tatsuyama, *Jpn J. Appl. Phys.* **24** (1985) 1082.
- [3] J. S. E. M. Svensson and C. G. Granqvist, *Solar Energy Mater.* **12** (1985) 391.
- [4] R. D. Rauh and S. F. Cogan, *J. Electrochem. Soc.* **140** (1993) 378.
- [5] M. T. Nguyen and L. H. Dao, Fall Meeting of Electrochemical Society, Hollywood, FA, 15–20 Oct. (1989) abstr. 621.
- [6] S. Passerini, B. Scrosati, A. Gorenstein, A. M. Andersson and C. G. Granqvist, Fall Meeting of Electrochemical Society, Hollywood, FA, 15–20 Oct. (1989) abstr. 631.
- [7] D. K. Benson and C. E. Tracey, *Chemtech*, Nov. (1991) 677.
- [8] S. K. Deb, *Sol. Energy Mater.* **25** (1992) 327.
- [9] F. G. Baucke, Schott Information (Schott Glaswerke, Mainz, West Germany), **1** (1983) 11.
- [10] I. F. Chang, in 'Nonemissive "electrooptic displays"' (edited by A. R. Kmetz and F. K. von Willisen), Plenum, London (1976) p. 12; M. Green and D. Richman, *Thin Solid Films* **24** (1974) S45.
- [11] G. Beni and J. L. Shay, 'Advances in Image Pick-up and Displays' (edited by B. Kazan), Academic Press, New York (1982).
- [12] M. Green and B. Richman, *Thin Solid Films* **24** (1974) S45.
- [13] T. C. Arnoldussen, *J. Electrochem. Soc.* **128** (1981) 117.
- [14] O. Bohnke, C. Bohnke, G. Robert and B. Carquille, *Solid State Ionics* **6** (1982) 121.
- [15] R. Hurditch, *Electron. Lett.* **11** (1975) 142.
- [16] B. Reichman and A. J. Bard, *J. Electrochem. Soc.* **126** (1979) 583.
- [17] N. Yoshiike and S. Kondo, *ibid.* **130** (1983) 2283.
- [18] F. Rauch, W. Wagner and K. Bange, *Nucl. Instrum. Methods B* **42** (1982) 264.
- [19] J. Zhang, C. E. Tracy, D. K. Benson and S. K. Deb, *J. Mater. Res.* **8** (1993) 2649.
- [20] S. K. Deb, *Philos. Mag.* **27** (1973) 80.
- [21] C. Ho, I. D. Raistrick and R. A. Huggins, *J. Electrochem. Soc.* **127** (1980) 343.
- [22] W. Weppner and R. A. Huggins, *ibid.* **124** (1977) 1569.
- [23] P. Schlotter and L. Pickelmann, *J. Electron. Mat.* **4** (1982) 207.
- [24] J. P. Randin and R. Viennet, *J. Electrochem. Soc.* **129** (1982) 2349.
- [25] M. L. Hitchman, *Thin Solid Films* **61** (1979) 341.
- [26] B. Reichman, A. J. Bard and D. Laser, *J. Electrochem. Soc.* **127** (1980) 647.
- [27] L. Zhang and K. S. Goto, Fall Meeting of the Electrochemical Society 127, Hollywood, FA 15–20 Oct. (1989) abstr. 615.
- [28] M. Green, W. C. Smith and J. A. Weiner, *Thin Solid Films* **38** (1976) 89.
- [29] M. Green, *Thin Solid Films* **50** (1978) 145.