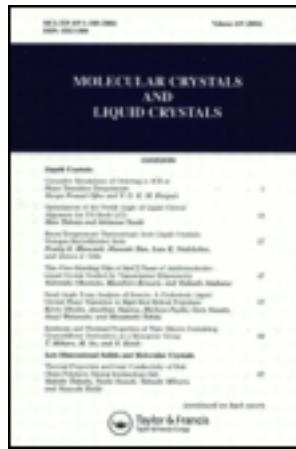


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Effects of Charge Asymmetry in a Nematic Liquid Crystal in Contact with an Amorphous Tungsten Trioxide Layer

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Abstract A new kind of a LC cell has been made, by using a standard sandwich configuration with one of the ITO electrodes covered by a thin layer of WO_3 . In this LC cell the electro-optical response become polarity sensitive. The inhibiting switching configuration corresponds to the anodic polarization of WO_3 film. Here we present the time behavior of the charge and discharge both for the anodic and the cathodic currents. A model based on the charge carriers exchange between both the ITO- WO_3 and WO_3 -LC interfaces is reported. Our model is also capable to explain the electric and the electro-optic asymmetric responses of the cell.

Keywords Electro-optic; Electrochromic Materials; Liquid Crystals; Charge Asymmetry

INTRODUCTION

An interesting polarity dependent electro-optic response has been recently observed in asymmetric cells filled with nematic liquid crystals [1,2]. The cells were obtained by inserting a thin layer of tungsten trioxide (WO_3) onto one of the conductive indium tin oxide (ITO) deposited glass plates.

It is known that in usual nematic liquid crystal cells the electro-optic response does not depend on the sign of an applied external field. In the asymmetric cells the optical switching can be seen only for one direction of the applied electric field. Such an asymmetric cell has been prepared by mixing with the nematic liquid crystal a small amount of UV photopolarizable monomer. Irradiating the cell from one face a polymer network of decreasing density appears within the liquid crystal which also produces a gradient of fixed charges. This gradient, in turn, causes a non-symmetric injection of current into the cell [3].

In this paper we focus our analysis on the nematic liquid crystal cells with a WO_3 layer. Tungsten trioxide (WO_3) is among the most studied materials for active electrochromic electrodes, because of its properties of good ionic conductivity for small cations (H^+ , Li^+ , Na^+) coupled with a reasonable electronic conductivity [4-10] and a remarkable change in the electronic band structure and consequently in the optical transmission spectrum, when cations are intercalated. Many applications have been studied, like hydrogen sensors [11], energy and light control system in buildings and vehicles, information display panels and others [10,12]. In principle, the reversible intercalation-deintercalation processes of small ions occur in WO_3 bulk crystals. It shows a very

complex polymorphism [13-17], strongly dependent also on electronic impurities, grain size distribution, thermal and mechanical history [18], but all the various phases can be considered as successive deformations, associated to phonon condensation [19], of a simple cubic structure of ReO₃ type, based on corner-sharing octahedral units WO₆; the guest cations can enter in available interstitial sites between such octahedra.

On the other hand, the high efficiency of intercalation for small ions, needed for practical applications, has been achieved in thin films [20,21] deposited by using several different techniques [22-26] like r.f. magnetron sputtering, evaporation, sol-gel synthesis. In these films the basic units are still the WO₆ octahedra, but they can be arranged in disordered configurations of three-, four- and six-membered rings, leaving many empty spaces [27-28], appreciably larger than the interstitial sites in the bulk crystal. A refined study [29], aimed to model the radial distribution function (RDF) given by X-ray measurements, suggests a dominant six-membered rings configuration, making these "amorphous" films quite similar to the crystals with hexagonal symmetry. Obviously the real symmetry is expected to depend on the deposition technique and on the specific parameters used during the film preparation, but a preferred hexagonal distribution seems to be frequent in the tungsten trioxide films. Another ubiquitous character of these films is the presence of water in remarkable amount. In fact, the open disordered structure allows for the intercalation of water molecules during the process of film deposition, and this fact seems to be correlated to the high values of proton conductivity [28,30-32] and even to Li⁺ ion conductivity [33].

Moreover, the study of the stoichiometry of the deposited tungsten trioxide films reveals an uptake of the water molecules during storage after film production [34]:



Ion beam analysis was used to investigate the presence of hydrogen contained in the tungsten oxide films at different times after production, obtaining significantly different profiles [34]. This increase indicates that the film takes up hydrogen-containing species during storage with a ratio H/W = 0.3 three hours after production.

Dehydration reactions and structural transformations of the films, strongly affecting the ionic conductivity, can be obtained by thermal annealing [35,36]. In general, high temperature annealing of the WO_3 samples lead to a crystalline structure belonging to the standard sequence [16] derived from cubic ReO_3 structure. The temperature value necessary to this transition depends in some amount on the bulk or thin film character of the sample and on the deposition technique; its variations are reported between 300 °C for evaporated films [35] and 500 °C for films prepared by the sol-gel process [25]. For lower temperatures intermediate steps are observed on the way toward crystallization and structural collapse, in particular the elimination of water molecules trapped in the film structure [35]. This process occurs over a wide range of temperature, reflecting the different trapping potential for such molecules; in principle, the deposition methods and the thermal history are relevant. For this reason, specific structural, spectroscopic (IR and Raman) and electrochemical measurements are quite useful for any set of film samples.

RESULTS

As it is shown in Fig.1, a nematic liquid crystal cell consists of two glass plates deposited with a thin layer of conductive indium tin oxide (*ITO*); on one of the plates it was deposited by radio-frequency sputtering a tungsten trioxide (WO_3) layer which is amorphous and extremely porous [1,2,9,10,32]. The sample plates are fixed at a distance of $8\mu m$ apart by using Mylar spacers. On the two *ITO* surfaces two ohmic contacts (with indium-tin alloy) are soldered. The cell was filled with a nematic liquid crystal called *E7* (*BL001* produced by Merck) with initial planar alignment and oriented in such a way to have maximum transmitted light on a microscope stage between crossed polarizers.

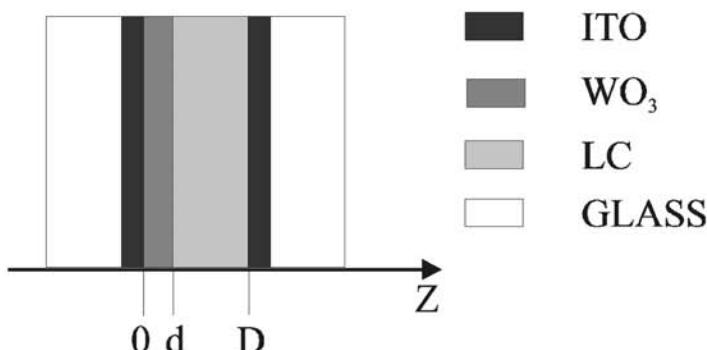


FIGURE 1 A cross section of the cell. The thickness of WO_3 layer is around 600\AA and the thickness of liquid crystal is $8\mu m$

When a DC voltage is applied a transition from planar to homeotropic alignment is expected. This indeed happens, but only in the case of cathodic polarization (from now on we will consider the polarization with respect to the WO_3 side of the cell), and the

transmitted light goes practically to zero. In the case of anodic polarization, although for a very short time one can see a blackening of the optical field, a decrease of the electric field in the bulk below the threshold and strong diffusion and turbulence force the image to become bright again.

The idea is that only in the case of anodic polarization there are currents injected into the cell and a building up of surface charges. These charges produce an internal electric counter field, which will inhibit the switching to the homeotropic state (Fig.2).

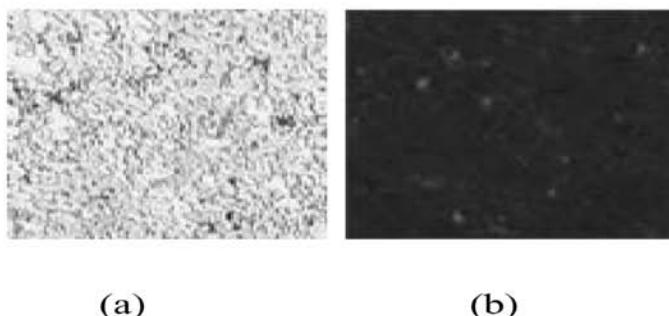


FIGURE 2 Images of the cell observed in a microscope between crossed polarizers: a) Light-on configuration, voltage corresponding to anodic polarization of the WO_3 layer. b) Dark configuration, cathodic polarization of the WO_3 layer.

In order to understand better why these phenomena happen we have analyzed the electric properties of the cells. Already [1,2], the impedance behavior has shown a linear tail at small frequencies indicating a rather high conductivity. Using a sequence of positive, zero, and negative voltage pulses for 110s each, 200 current measurements were done (with a pace of 0.55s) for each voltage pulse. In Fig.3 we have plotted the values of current for the sequence: +4V, 0

V , $-4 V$, $0 V$, and the plots reveal some facts: a) the time dependence of currents is typical for charging or discharging condensers; b) the anodic charging current is greater than the cathodic charging current; c) the discharge current following the anodic polarization is larger (in absolute value) than the discharge current which follows the cathodic polarization; d) also an ohmic current is quite visible in the case of the anodic polarization; d) in the case of the anodic charging current the time dependence of this current is not a simple exponential function.

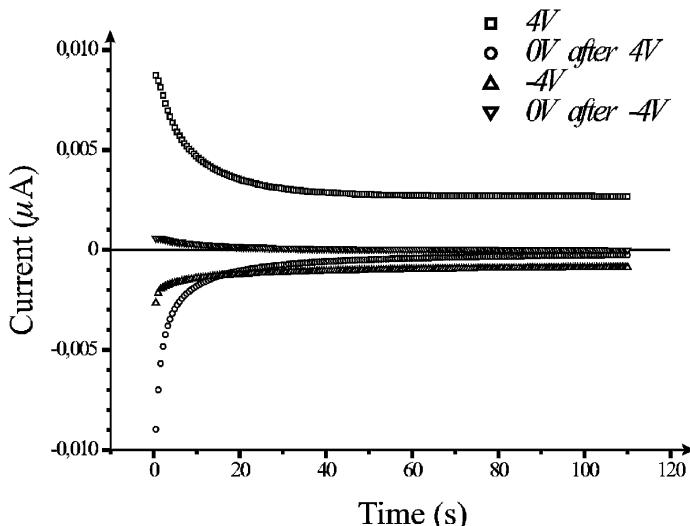


FIGURE 3 Charging and discharging currents in the cell with WO_3 layer and E7 for a sequence of $+4V$, $0V$, $-4V$, $0V$.

Integrating the currents one gets the charges that are stored in the cell. In order to minimize the influence of the ohmic currents when doing the integration we considered as the base that line which corresponds to the value of the current at the latest time instant. In Fig.4 the stored charge densities are plotted versus the amplitudes (ΔV) of the voltage steps.

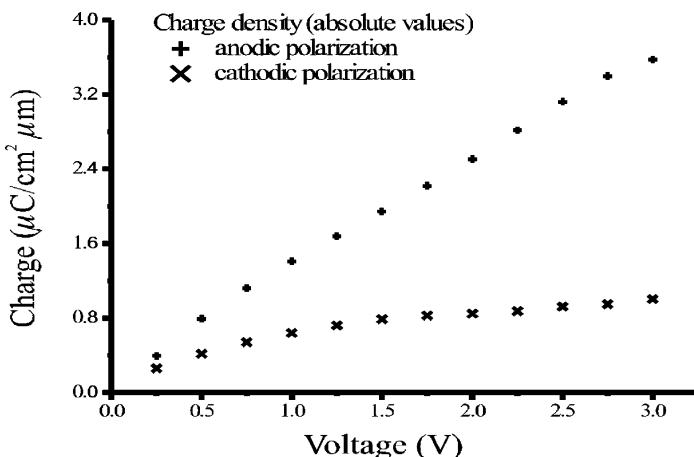


FIGURE 4 Stored charge density as a function of the voltage amplitude. Notice the difference between anodic and cathodic polarization.

These results are even more interesting if we compare them to similar measurements made with a cell filled with the same nematogen liquid crystal *E7* but with symmetric *ITO* deposited glass plates. In this case there is, of course, a complete symmetry of the current with respect to the polarity of the voltage steps but the charges stored into the cell are about 3 times smaller than in the case of the cell with an insertion of a WO_3 film.

Then we wanted to see what would happen when instead of *E7* liquid crystal we insert a non-polar, organic oil *cis*, *trans*-decahydronaphthalene ($C_{10}H_{18}$) (*DHN* for short). In this case the charging and discharging currents are orders of magnitude less than in the case of *E7* filled cells. The now poorer signal to noise ratio prevents one to tell a difference between the anodic and cathodic polarization. In the case of *DHN* the estimated dielectric constant is ≈ 2 which is

consistent to the value 2.1733 obtained by squaring up its refraction index $n=1.4742$.

As far as $E7$ between ITO plates is concerned the estimated stored charge density is $\approx 1.2 \mu C/cm^2 \mu m$ and in the case of cells with WO_3 its value is $\approx 1.3 \mu C/cm^2 \mu m$ for cathodic polarization and $\approx 4 \mu C/cm^2 \mu m$ for anodic polarization which is equivalent to a dielectric constant in the range 10^4 - 10^5 . Such a tremendous difference between $E7$ and DHN cannot be explained only by the fact that $E7$ (a mixture of cyano-biphenyls) is polar, but mainly to the fact that within $E7$ there are dissolved positive and negative ions [37]. Even more, if in a cell with a WO_3 layer at cathodic polarization the charge density is slightly large than in the case of symmetric $ITO/E7/ITO$ cell, when applying an anodic polarization the overall charge density triples. The fact that the stored charge density is so different when the two polarizations are concerned indicates that a process of charge compensation takes place in the layer of WO_3 during the cathodic polarization on one hand, and a liberation of new charge (protons) takes place during the anodic polarization on the other hand. We will use these facts in the following model.

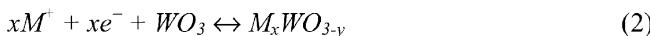
Furthermore the cells have undergone to cyclability tests, during which the applied voltage was swept for about thirty hours between $-2.5V$ and $2.5V$, and the measured currents were found perfectly reproducible [38].

DISCUSSION AND CONCLUSIONS

As we have stressed from the very beginning, WO_3 is a highly porous material. Inside its channels and voids there are sites which favours the

reaction $H_2O \leftrightarrow H^+ + OH^-$, most probably because there are non saturated W bonds which can attract the oxygen side of OH^- . A certain concentration of H^+ appears which, eventually prevents the reaction to go from left to right [39].

Note that WO_3 is also an electrochromic material. It can accept a large amount of cations (H^+ , Li^+ , Na^+ , K^+) from a source to form nonstoichiometric tungsten bronze M_xWO_{3-y} according to



where M^+ are the cations and $0 \leq x \leq 0.5$ and $0 \leq y \leq 0.03$ [10]. When the value of x is large ($x > 0.1$ - 0.2) the tungsten bronze changes its color to blue. In our case the WO_3 film remains always transparent indicating that it is a dilute bronze. Also the fact that the stored charge density was about $1-4 \mu C/cm^2 \mu m$ for the whole cell compared to the maximum observed stored charge density of $100 nC/cm^2 \mu m$ only in WO_3 [40] tells us that we have a dilute bronze.

Let us first analyze the ITO - WO_3 interface alone. ITO has free electrons. They can diffuse into WO_3 pores where they force hydrogen to be bound by WO_3 , forming regions of H_xWO_3 bronze. The ITO side of the interface remains positively charged whereas the WO_3 side of it remains with unbalanced negative (localized) charge. The total (and local) concentration of H^+ has diminished so the reaction $H_2O \leftrightarrow H^+ + OH^-$ can proceed until the electric field from ITO toward WO_3 opposes any longer the diffusion of electrons. A contact potential is so set in. Connecting now electrically the two faces, a current will go, delivering electrons to the ITO side of WO_3 , until all the water and/or the catalyst sites are used. The system works like an electric battery.

If the *ITO* side is charged positively the protons in WO_3 are pushed to the right leaving to the left an increased negative charge. In the meantime a lack of electrons on the left side of WO_3 turns eq.1 to go from right to left, giving birth to an increased number of protons which are pushed to the right. Hence, the total positive charge on the right part of WO_3 is quite large. If we consider n the concentration of negative (fixed) charges which does not vary and $n(z)$ the concentration of positive ions, there is a net negative charge q when $n(z) < n$, and there is an equal positive charge of the same magnitude when $n(z) > n$. A plot of positive and negative carrier concentrations across the WO_3 layer is shown in Fig.5(a).

If now the *ITO* side is negatively charged, the protons are pulled to the left where they combine with a flow of *ITO* electrons. The stored charges are reversed but the new value q' is less than q due to hydrogen bronze formation (see Fig.5(b)). These two mechanisms, intercalation and deintercalation of protons to the left side of the WO_3 film, of which the latter seems to be more important, can explain quite easily why a discharge current following an anodic polarization was larger than in the case of the discharge current which followed the cathodic polarization.

Now, we have to take into account the role played by the liquid crystal. If the liquid crystal were a perfect dielectric, when applying an electric voltage across the cell the potential would vary linearly with distance and the electric field would be constant. On the contrary, if the liquid crystal contains a certain amount of free ions, there will be a build-up of negative charge to the anodic side of the cell and a similar build-up of positive charge on the other side. The electric potential will

no longer have a linear dependence and the electric field will not be constant. It will present a lower value in the bulk of the liquid crystal layer and higher values close to the surfaces. Fig.6 shows the above mentioned two cases. The larger are the boundary charges the higher are the values of the field near the surface and the lower is the field in the bulk. (One must not forget that the total area under the field plot is equal to the voltage across the liquid crystal.)

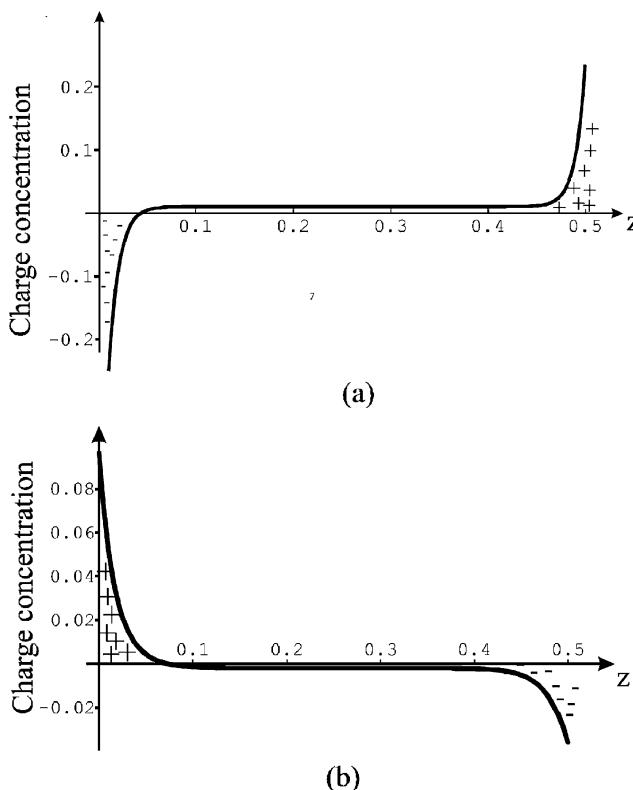


FIGURE 5 (a) Charge concentration inside the WO_3 layer in the case of anodic polarization. (b) Charge concentration in the case of cathodic polarization. Note the difference in scale with respect to anodic polarization.

If the cell is not symmetric, i.e. it has one thin layer of WO_3 , when anodically polarized the positive charge q in WO_3 close to the interface with the liquid crystal would attract a large quantity of negative free ions within the liquid crystal. The same amount of positive charge would be on the *ITO* side of the liquid crystal. When the cell is cathodically polarized the charge q' is smaller than q and the corresponding build-up charges in the liquid crystal are smaller.

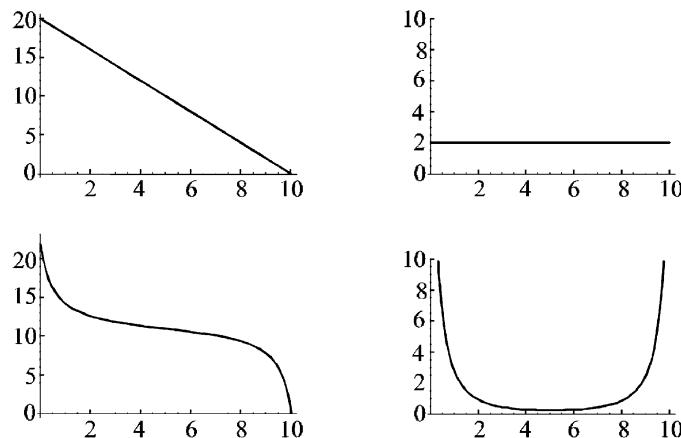


FIGURE 6 Electric potential (left) and electric field (right) inside the liquid crystal. The liquid crystal is a perfect dielectric (up) or contains free ions (down).

The important result is that for a convenient voltage range the electric field in the bulk of liquid crystal would be lower in the case of anodic polarization than in the case of cathodic polarization in such a way as to be below the transition threshold for anodic polarization but above the threshold for cathodic polarization. Even the strong electric field, which appears within a layer of around the Debye [37], cannot align homeotropically the liquid crystal molecules because of the strong

planar anchoring. Also there the injected currents are not negligible. In fact the asymmetry of the injected currents is due to the rectifying properties of the *ITO/ WO₃* junction which induces on the interface between *WO₃* and the liquid crystal a depletion layer of free charges when the cell is cathodic polarized with respect to the *WO₃* face. In the case of anodic polarization there is also an increase of the positive mobile carriers in a layer of around the Debye length at the *WO₃/nematic* interface which injects a current having the same sign with that injected by *ITO* at the other face. Both currents having the same direction give birth to a rather strong current, which inhibits the homogenous alignment. Without the *WO₃* layer, for each polarization, electrons can be injected on one *ITO* side whereas on the other *ITO* interface there is no injection. So the current is alternatively blocked on one or the other of the two interfaces. If we consider that the cell has two switches, these work in counterphase when the cell is symmetric but the *WO₃* layer reverses the phase of one switch so now they are in phase: on or off. Very recent measurements have shown that the same effect can be obtained with a thin layer of nickel hydroxide doped with *Li⁺* ions. The same process of creating a pair of depleted or enhanced layers of positive mobile ions is responsible for this effect.

One important task is to see which process is more important: the lowering of the electric field below the threshold or the asymmetry of the injected currents? To answer this question, at least qualitatively, we tried to see if a large capacitor inserted in series to the cell would modify the asymmetry of the electro-optic effect. The result was negative; i.e. the asymmetry still exists although the frequency limit for this asymmetry has been lowered a little. The capacitor was chosen

with such a value as to have the same voltage drop across the sample as it was in the case without the capacitor. The build-up of surface charges is the same only that now the injected currents are practically blocked. Of course, the much higher time constant of the system lowers the frequency limit. This experiment suggests that in this case, although one cannot overrule completely the influence of the injected currents, the lowering of the electric field in the bulk of the liquid crystal when the sample is anodically polarized plays the most important role.

Finally, both the question about lifetime of an electrochemical LC display and a control experiment with an ion-depleted NLC are under way.

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