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A MONOLITHIC THIN FILM ELECTROCHROMIC WINDOW

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ABSTRACT

Three closely related thin film solid state ionic devices that are potentially important for applications are: electrochromic smart windows, high energy density thin film rechargeable batteries, and thin film electrochemical sensors. Each usually has at least one mixed ion/electron conductor, an electron-blocking ion conductor, and an ion-blocking electron conductor, and many of the technical issues associated with thin film solid state ionics are common to all three devices. Since the electrochromic window has the added technical requirement of electrically-controlled optical modulation, (over the solar spectrum), and since research at the authors' institution has focused primarily on the window structure, this paper will address the electrochromic window, and particularly a monolithic variable reflectivity electrochromic window, as an illustrative example of some of the challenges and opportunities that are confronting the thin film solid state ionics community.

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A MONOLITHIC THIN FILM ELECTROCHROMIC WINDOW

1. INTRODUCTION

The objective of this paper is to present a unified, though personal, view of some of the materials science and engineering challenges and opportunities associated with producing practical thin film solid state ionic devices. This has been done by focusing primarily on one example that has been the subject of research at the Electro-Optics Technology Center at Tufts University: a monolithic variable reflectivity electrochromic (EC) window. An attempt will be made to answer three questions: (1) What are some of the important questions that have been answered as a result of the EC window research to date?; (2) What are some of the remaining unanswered questions and likely answers?; and (3) What is the prognosis for the future, especially for EC windows, and can we extrapolate to other applications of thin film solid state ionics?

Before specifically discussing the EC window, it should be noted that the monolithic, variable reflectivity EC window incorporates almost all of the principles of thin film solid state ionics and of other thin film solid state ionics applications - especially rechargeable batteries and electrochemical microsensors. All three applications usually employ two mixed electron/ion conductors, an electron-blocking ion conductor, and two ion-blocking electron conductors. Because the a priori desired optical and charging/discharging power properties are different for the window and the battery, these two devices have different materials requirements for their two mixed conducting electrodes, (i.e., two electrochromic layers, EC_1 and EC_2 , for the window and, correspondingly, an anode and cathode, respectively, for the battery). In particular, in the window it is highly desirable to have a low density of states, low effective mass, charge transport band, for at least one of the two electrodes. This allows one to obtain a large change in the plasma energy, E_p , for a small change of inserted/extracted electrons in the band, or very efficient optical modulation. On the other hand, the battery requires a cathode and anode which have relatively high density of states energy bands so as to maximize the amount of charge that can be transported and to minimize the change of battery voltage as charge is transported. However, for both these applications, as well as for sensor applications, it is highly desirable that charge transport in the two electrodes be relatively rapid, to minimize the time to change charge states.

The EC window that we shall review in this paper is a monolithic variable reflectivity EC window which has been discussed in previous papers^{1,2,3}. The primary motivation for research on this window has been to reduce energy use in buildings which, in the United States, accounts for approximately 36-40% of the annual national energy consumption⁴. Of this energy consumption, approximately one-third is wasted through windows (literally, "thrown out of the window"), and approximately a half of that wasted energy is by radiation transfer.

Three major issues have influenced the focus of our research on the EC window. They are: (i) Obtain an electrically-tunable, spectrally-selective, optical transmission modulation over the solar spectrum (approximately 0.4-2.0 μm wavelength); (ii) Develop a structure which can be fabricated economically on large-area amorphous substrates (e.g., glass, plastic); and (iii) Develop a window which will be durable for many years of use (>20 years).

To satisfy issues (i) and (iii), it was decided to develop a window that was based on variable reflectivity as compared to variable absorption, and to use lithium ions to charge compensate for electron insertion/extraction in the electrochromic layers. To satisfy issues (ii) as well as (iii) it was decided to

develop a completely inorganic, thin solid film, monolithic structure which could be fabricated by a reactive sputter deposition process, as well as by related deposition processes.

With a variable reflectivity EC window it should be possible to achieve electrically-adjustable, spectrally-selective, optical transmission modulation over the solar spectrum and well into the thermal and far infrared^{1,2,3}. With such spectral selectivity it should therefore be possible to: (a) reduce the heating load in a building during a cold, but sunny, winter day by transmitting the solar spectrum into the building but reflect back into the building the thermal infrared; (b) reduce the heating load in a building on a cold winter night by reflecting back into the building all radiant energy generated within the building; (c) reduce the cooling and artificial lighting loads in a building on a hot, sunny, summer day by reflecting away the near infrared portion of the solar spectrum but allowing the visible portion (the luminous spectrum - a wavelength range of approximately 400 to 650 nm) to enter the building; and (d) reduce the cooling load in a building on a hot, but cloudless, summer night by transmitting all the radiant energy generated within the building (radiation cooling) to the "cold" night sky (especially in the 8-12 micrometer wavelength region). In addition to these spectrally-selective benefits, variable reflectivity: (i) very importantly reduces the amount of heating-caused strain due to optical absorption in the coatings as well as in the substrate (usually a glass pane); (ii) improves the thermal transfer efficiency of the window by reducing optical absorption (since 50% of what is absorbed is reradiated in each direction - i.e., into and out of the interior of the building); and (iii) allows one to use thinner films with consequent savings in manufacturing costs and in operating costs. Another motivation for the variable reflectivity window research is to reduce cooling loads in (stationary or moving) vehicles exposed to undesirable solar gains; and recent experiments indicate that a variable reflectivity window can significantly reduce cooling loads in automobiles⁵.

To achieve electrically-adjustable, spectrally-selective, optical modulation, the variable reflectivity window utilizes two electrochromic layers, in which the population of free electrons (or holes) can be reversibly varied. This, in turn, allows for the plasma energy to be adjusted, which results in an adjustable step-like spectral reflectivity function. The step-like reflectivity function has a relatively low reflectivity at photon energies above the "screened" (by the bound electrons) plasma energy, $E_p^* (= E_p/\sqrt{\epsilon_b})$, where ϵ_b is the real part of the bound electron contribution to the dielectric response function, and a relatively high reflectivity at photon energies below E_p^* . (This is illustrated in Figure 3 of reference 6.) Note that $E_p = \sqrt{(n)/m^*}$, where $[n]$ = density of free electrons (or holes) and m^* is their effective mass⁶.

Shown in Figure 1 is a cross-section of a five-layer configuration for the window. The inner 3 layers are comprised of two mixed electron/ion-conducting electrodes, EC_1 and EC_2 , which are separated by an ion-conducting layer, IC. These three layers are sandwiched between two electronically-conducting transparent conductors, TC_1 and TC_2 . Although we will review what has been learned about the entire window structure, in this paper we wish to discuss primarily what has been learned regarding the inner three layers.

2. RECENT PROGRESS

2.1. EC₁ Layer (cathodically-coloring, polycrystalline WO₃):

Polycrystalline (pc) tungsten oxide (nominally WO₃) films properly prepared by rf diode sputtering, (see discussion below), can exhibit a lithiated state near infrared reflectivity greater than 80%. However, both because of limits on the maximum concentration of lithium (and therefore of free electrons), and defects-caused scattering of free electrons, there is an upper photon energy limit, (namely

the maximum screened plasma energy), on both the spectral range and the amount of reflection modulation that one can obtain with polycrystalline films of lithiated tungsten oxide, pc-Li_xWO₃. Currently, the practical limits appear to be approximately 2.5-2.75 eV, (500-450 nm in wavelength), for E_p^{*}, and a near infrared (at approximately 2 μm wavelength) reflectance of approximately 80%, for a lithium molar concentration, x, of ≈ 0.5⁷. The height and transition width of the reflectance step is determined by the electron scattering which, in the simplified Drude model⁸, is described by a photon-energy-independent loss, or damping parameter, E_T. The smallest value of E_T that has been obtained for Li_xWO₃ films has been approximately 0.4 eV for an x value of approximately 0.5⁸.

One important question that our research has attempted to answer is, "What determines the limits to the spectrally-selective reflectivity modulation in a variable reflectivity EC window?" Employing the concepts of a simplified Drude free electron model, we have determined that, for EC₁ = pc-Li_xWO₃:

(a) The plasma energy, E_p, is limited by the maximum lithium molar concentration, x_{Li}, which, disallowing for any further structural transformation beyond the reported cubic phase for single crystals of Li_xWO₃^{9,10}, is 0.75, because for that phase all available lithium sites become occupied; however, it should be noted, for single crystals of cubic Na_xWO₃, the maximum molar sodium concentration, x_{Na} → 1, with a correspondingly higher E_p¹¹.

(b) E_p^{*} = E_p/√ε_b is limited by E_p, (estimated maximum, for x_{Li} = 0.75, is 6.2 eV), and the intrinsic band gap (E_g) narrowing with lithium insertion¹², (i.e., the bound electron contribution to the dielectric response function, ε_b, increases to approximately 6 when E_g decreases as x_{Li} approaches its maximum of 0.75); and thus the maximum in E_p^{*} is estimated to be approximately [6.2/(√ε_b)]_{max} ≈ 2.5 eV. (It is tempting to speculate that one may be able to alter the microstructure and/or composition by altering the growth process of the films and thus exceed these extrapolated maximum values for E_p and E_p^{*}.)

(c) Experimentally, E_T is presently limited to a minimum value of approximately 0.4 eV in Li_xWO₃ films, primarily by growth-induced disorder and by extended defects (crystallographic shear planes^{6,13}) caused by oxygen nonstoichiometry; therefore, one might be able to grow films for which E_T could be reduced further, (for example, to values ≤ 0.2 eV, as has been observed for single crystals of Na_xWO₃¹¹), and attaining E_T ≤ 0.2 eV in pc-Li_xWO₃ films would have important benefits: e.g., near infrared reflectivities exceeding 90% could then be obtained, and with films thinner than 100 nm.

As mentioned above, we have reported recently that one can deposit cathodically-coloring, pc-WO₃ films which exhibit a lithiated state near infrared reflectivity > 80%⁷. These films were deposited on to a heated substrate (approximately 430 to 440°C) under the following conditions: 10 mTorr oxygen pressure, rf (13.6 MHz) power = 200 Watts, target (Cerac, reduced WO₃) diameter = 125 mm, and target-to-substrate distance = 75 mm. The resulting films were polycrystalline, as confirmed by TEM (transmission electron microscopy) and Xray diffraction studies. The crystallite sizes, as determined by TEM measurements, varied between 5 and 30 nm, with the crystallite size distribution peaking close to 30 nm. The unlithiated films have a monoclinic structure, but are highly oriented, with the c-axes of the crystallites being predominantly perpendicular to the plane of the substrate. For small amounts of lithium insertion, the Drude energy loss, or damping, parameter, E_T, is normally relatively high (≈ 1 eV). This results in a relatively high free carrier absorption or a relatively small reflectivity in the infrared - i.e., there results a "step-like" reflectivity function that is slowly changing with wavelength which only reaches a relatively low step height. On the other hand, upon additional lithium insertion, a symmetry change

(from monoclinic to cubic⁶) occurs, which we believe accounts for the observed decrease in E_T to ≈ 0.4 eV, (and a consequent sharpening of the transition and a raising of the step height of the reflectivity function), with increased lithium insertion. One may therefore infer that if the crystallite sizes were increased, E_T could be decreased, even when the amount of inserted lithium is relatively low; and with such a lowering of E_T there would be a corresponding increase in the height and sharpness of the reflectivity step-function, or an improved spectral-selectivity and a decrease in the optical absorption. It should be mentioned at this point that pc-WO₃ has been deposited at ambient temperature by an ion assisted process¹⁴, indicating that with the appropriate deposition process high temperatures should not be necessary to attain a high degree of crystallinity and associated high reflectivity modulation.

In addition, recent experiments indicate that there is a bandgap narrowing with increased lithium insertion (lithiation) of these films¹². This partially compensates for the optical bandgap widening accompanying the lithiation, due to the Burstein-Moss effect¹⁵ associated with increased conduction band filling, or increase in Fermi level. Note that the opposite happens with increased sodiation - i.e., there appears to be a bandgap widening as more sodium is added to WO₃¹¹. This amplifies the optical bandgap widening associated with the Burstein-Moss effect. Thus, lithiation of WO₃ has a beneficial effect for window applications - it insures that ultraviolet radiation is not readily transmitted through the window. (Very likely the difference between the lithium and sodium cases is associated with their different crystal structures, but further work is needed to clarify the model.)

2.2. IC Layer (amorphous LiNbO₃):

Some of the charge transport properties of thin films of amorphous (a) LiNbO₃ have been previously reported¹⁶. Subsequent studies have been made on the effects of the processing conditions, (particularly the sputter gas composition and the rf power), on the effective electronic resistivity. The effective electronic resistivity, $\langle\rho_e\rangle_{eff}$, is defined as the product of the 2-terminal large-signal electronic resistance, R_e , and the 2-terminal film device (or cell) area, A , to thickness, d , ratio, (A/d) , (i.e., $\langle\rho_e\rangle_{eff} = R_e \cdot (A/d)$). The effective electronic resistivity is used because, for device purposes, it is the total series resistance (including the effects of potential barriers) that is of interest, not simply the resistance associated with the intrinsic resistivity of the film. (It should be noted that having high electronic potential barriers at both interfaces of the IC layer should lead not only to high $\langle\rho_e\rangle_{eff}$, but also to stable operation at relatively high voltages, an especially very desirable property for high voltage batteries.)

Although these studies are not yet completed, the results to date show that one can obtain films with effective electronic resistivities $\geq 10^{14}$ Ω -cm and lithium ion conductivities $\geq 5 \times 10^{-3}$ S/cm. Currently, primarily to decrease device fabrication time, non-optimum deposition process conditions have been used to fabricate window devices. For such devices one usually obtains an effective electronic resistivity $\geq 2 \times 10^{10}$ Ω -cm which, for cells of area ≤ 20 cm² is sufficiently high to carry out qualitative cell evaluation studies, (i.e., the electronic current "leak" is sufficiently small that the cells remain in their states for a long enough time to permit one to perform single switching cycle optical measurements, but the leakage is not low enough to quantitatively establish charge transfer and optical state reversibility after many switching cycles). It should be noted that we have obtained further evidence for a high $\langle\rho_e\rangle_{eff}$ for a-LiNbO₃ films in a metal (aluminum)/a-LiNbO₃/metal (aluminum) structure - such as-deposited structures occasionally exhibit an electret-like effect, in that there is a persistent open circuit voltage sometimes several hundred millivolts to several Volts. (This type of a phenomenon also has been observed and reported recently by at least one other group¹⁷ in a different inorganic electrolyte, e.g., Li₂O-SiO₂-P₂O₅.) These results indicate that the a-LiNbO₃ films have very low electron mobility, determined primarily by the microstructure of the films. However, at this time we shall not attempt to further model the electron

mobility nor the electret-like effect in these films of a-LiNbO₃.

There remains the interesting unanswered question as to what is the appropriate model for lithium ion conduction in a-LiNbO₃? Glass et al. have reported relatively high room temperature lithium ion conductivity ($\sigma_{Li} \geq 0.5 \times 10^{-5}$ S/cm) for rapidly quenched glassy LiNbO₃¹⁸; and they have pointed out that there are many orders of magnitude difference in the room temperature lithium ion conductivity between glassy, roller-quenched LiNbO₃ and crystalline LiNbO₃, with the glassy material having the much higher conductivity. Also, recently we have been observing an apparent mass density (ρ_m) dependence of σ_{Li} for low density (65%-80% of bulk density) a-LiNbO₃ films: σ_{Li} appears to decrease as ρ_m decreases. Also in our low mass density a-LiNbO₃ films σ_{Li} is approximately two orders of magnitude smaller than that found by Glass et al. for their higher mass density glassy LiNbO₃. On the basis of these observations, we suggest the following speculative qualitative model.

In highly ordered crystalline LiNbO₃, lithium ions are "captured" in oxygen "cages," similar to niobium in the centers of oxygen octahedra in Nb₂O₅ or in LiNbO₃, and are thereby relatively immobile. In highly disordered a-LiNbO₃, many of the oxygen cages are open and the lithium ions are only weakly bound to the oxygen of the octahedra surrounding the niobium. If the mass density of the disordered, but stoichiometric, a-LiNbO₃ is high, the concentration of loosely bound lithium ions is likewise high, and the sites for such ions are relatively close to each other. This leads to the possibility of a relatively high lithium ion mobility. However, in low density a-LiNbO₃, in addition to a lower concentration of lithium, very likely there are a large number of voids. The voids open further the oxygen network, which probably leads to considerably longer, tortuous pathways for lithium ion diffusion; and the combination of reduced lithium concentration and longer path lengths could account for a lower σ_{Li} in lower ρ_m material, as well as why σ_{Li} is lower in lower density a-LiNbO₃ thin films than in higher density, glassy, roller-quenched LiNbO₃. Additional research is expected to clarify the model.

Therefore, it is anticipated that, with improved understanding of the relationships between the transport properties and deposition conditions, even higher electronic resistivity ($\geq 10^{14}$ Ω -cm) and higher lithium ion conductivity ($\sigma_{Li} \rightarrow 0.5 \times 10^{-5}$ S/cm) amorphous lithium niobate films will be able to be practically incorporated into window structures.

2.3. EC₂ Layer (In₂O₃, Nb₂O₅, or LiCoO₂):

2.3.1. In₂O₃ and Nb₂O₅ Films - Bi-layers of In₂O₃ over ITO (indium-tin oxide) or Al (aluminum), and of Nb₂O₅ over ITO or Al have been deposited by rf diode sputtering. The deposition conditions for the films were: T_{substrate} = ambient temperature or 200°C; rf (13.6 MHz) power = 100 Watts; deposition time, t_{deposition} = 120 minutes; target (Cerac) diameter = 125 mm; sputter atmosphere for In₂O₃ deposition = argon (partial pressure = 7 Mtorr) + oxygen (partial pressure = 15 Mtorr); atmosphere for Nb₂O₅ deposition = argon (pressure = 13 mTorr); thickness = 400 nm (In₂O₃) and 250 - 300 nm (Nb₂O₅); target-to-substrate distance = 55 and 70 mm for the In₂O₃ depositions and 70 mm for the Nb₂O₅ depositions.

Electrochemical studies have been made on the bi-layers^{19,20}. Cyclic voltammetry and coulometric titration studies indicated good reversibility for more than 1000 cycles; but, in the case of In₂O₃, for which we were able to directly measure the lithium concentration, (by atomic absorption spectroscopy), an unusually large quantity of Li, ([Li]/[In]) ~ 0.24, was retained. On the other hand, from a TEM diffraction analysis, there was no indication of a lattice constant change for a relative lithium insertion ([Li]/[In]) ~ 0.22 (as determined from an integration of the electrical current). Thus, it is not clear where the excess lithium is residing (e.g., within the native vacant sites²¹ and/or within the grain boundaries).

Lithium ion diffusion constant measurements, (by the galvanostatic intermittent titration method²², yielded values of approximately 10^{-11} cm²/sec for the In₂O₃ films, and approximately 10^{-12} cm²/sec for the Nb₂O₅ films. Optical transmission studies of the Nb₂O₅ films indicated that for lithiated films of Nb₂O₅ (200 nm thick), if [Li]/[Nb] was less than 0.15, there was less than a 10% transmission loss in the visible spectrum. For In₂O₃ films there was little optical modulation for lithiation insertions as high as [Li]/[In] = 0.24. These results suggested that both materials should be good candidates for the EC₂ layer.

In window devices, however, EC₂ layers composed of either In₂O₃ or Nb₂O₅ exhibited excessive electronic depletion when the TC₂ layer was biased positively. This resulted in series resistances which were too high for satisfactory device operation (i.e., the switching times for relatively safe and low applied voltages were too long to be practical). Because this had not been observed for window devices with EC₂ = LiCoO₂ films, and because LiCoO₂ is a hole conductor as well as an anodically-coloring material, we decided to focus on using LiCoO₂ as the EC₂ layer.

2.3.2. LiCoO₂ Films - Previously, we reported on some of the properties of films of anodically-coloring LiCoO₂ that had been prepared by rf diode sputtering from stoichiometric targets, and had been deposited on to heated (300°C) substrates^{23,24,25}. Because the as-deposited films, (polycrystalline - as determined by Xray measurements), were lithium deficient, their lower (t_{2g}) conduction band was not completely filled, (some of the cobalt was in a +4 oxidation state). This led to significant optical absorption in the visible part of the spectrum (especially for wavelengths shorter than 600 nm). Also, the amount of lithium that could be electrochemically inserted either before or after extraction, was such that the lithium concentration could not exceed the original, as-deposited concentration. Thus, one could not decrease the optical absorption in the visible part of the spectrum by further inserting more lithium. The reason, we suggested²⁴, was that the as-deposited films had a defect structure whereby there were immobile cobalt atoms occupying lithium sites in the lithium plane, (crystalline LiCoO₂ has a layered structure with alternating planes of oxygen/lithium/oxygen/cobalt/.....). This was proven by determining the oxidation state of the cobalt²⁴. The resulting lithium deficiency is accompanied by a reduction in the t_{2g} band electron population, (or an increase in the t_{2g} band hole population), which leads to increased band-to-band optical absorption in the visible part of the spectrum.

Therefore, the primary problem was to devise a deposition process whereby the lithium stoichiometry could be controlled. The desire to solve this problem was heightened by two events: (i) the difficulty mentioned above - excess electron depletion in films of In₂O₃ and Nb₂O₅; and (ii) recent band structure calculations that we made which indicated that in fully- stoichiometric LiCoO₂ there should be a splitting of the cobalt 3d band into a completely filled lower (t_{2g}) band and an empty upper (e_g) band, and that there should be a band gap ≥ 3 eV between the top of the (essentially oxygen 2p) valence band and the bottom of the e_g band (with transitions between the t_{2g} and e_g bands being parity-forbidden) and, hence, fully lithiated films should be highly transparent over the entire solar spectrum, and particularly the visible portion. (The results of these band structure calculations have been qualitatively verified by similar calculations recently reported by Kemp and Cox²⁶.)

2.4 TC Layers:

For EC windows a low E_p^* is desirable, together with the competing requirement of a high dc conductivity. The requirements are competing in that one way to increase conductivity is to increase the

carrier concentration, but this would raise E_p^* . Therefore, to simultaneously achieve both requirements, it is necessary to obtain a high electron mobility, which can be done by depositing highly ordered films. Furthermore, the TC layers should be blocking to lithium ions. For In_2O_3 , ITO or SnO_2 layers this is not the case, (as we and others have been observing for a number of years³¹). Hence, either alternative TC materials must be used, or additional thin, modestly electronic-conducting, but lithium ion blocking, layers must be synthesized.

2.5. Electrochromic Window Cells Using LiCoO_2 = EC₂ Layer:

Motivated by our calculations and experiments on LiCoO_2 , we proceeded to vary some of the details of our process²⁷. We are now rf-diode sputter-depositing EC window cells with EC_2 layers that exhibit useful visible transparency when the cells are in their "clear," or "bleached," state. Shown in Figure 2 are the optical transmission characteristics of one of the recent, small area (approximately 1 cm^2) cells that have been so fabricated. It should be noted that there is considerable near infrared modulation between the clear (or "bleached") state and the blocking (or "colored") state, with an average of less than 20% transmission in the near infrared (650-2400 nm) when the cell was in the colored state. The data presented in Figure 2 were obtained after the cell had been cycled, in vacuum, for more than 3000 times between the bleached and colored states. The cycling was done by using a triangular voltage with a period of less than 200 seconds. Because of an electronic current leak in the IC layer, and because lithium insertion and de-insertion from the two TC layers is relatively slow, the extrema of the triangular voltage were occasionally adjusted throughout the cycling to maintain a qualitative (i.e., by eye) reversibility of the optical transmission²⁸. Cycling was discontinued on this cell to allow a study of its dynamic lithium composition profile by nuclear reaction analysis^{29,31}. We have subsequently further optimized the fabrication process, especially to obtain a higher bleached state transmission in the blue-green part of the spectrum. This can be seen in Figure 3, which is for another, larger area (20 cm^2), window cell employing a thicker LiCoO_2 film as the EC_2 layer; and shown in Figure 4 is the transmissivity for a window cell identical to that of Figure 2, but in which LiCoO_2 is only 50nm thick.

4. FURTHER DISCUSSION

The results of Figures 2, 3 and 4 indicate that, by using a reactive rf diode sputtering process, monolithic variable reflectivity EC windows, comprised of: $\text{EC}_1 = \text{pc-WO}_3$, $\text{IC} = \text{a-LiNbO}_3$, and $\text{EC}_2 = \text{LiCoO}_2$, (or one of the other layered transition metal oxide compounds, LiMO_2 , e.g., $\text{M} = \text{Ni}$, $\text{Cr}^{25,32}$), can be fabricated to have optical and electrochemical properties approaching those desired for energy management. It is also anticipated that, with further refinements of the fabrication process, such windows will exhibit shorter switching time and lower switching energy than required. Furthermore, considering the materials used (all relatively inexpensive refractory metal oxides), these variable reflectivity EC windows should be both economical and durable.

From the results to date it appears that pc-WO_3 films will satisfactorily meet the requirements for the EC_1 layer of a variable reflectivity EC window; although with reductions in E_r and an increase in E_p^* , improved performance EC windows would result. However, because of the relatively low lithium diffusion coefficient ($< 10^{-10} \text{ cm}^2/\text{s}$) and the low density of states of its conduction band, pc-WO_3 is not a good candidate material for the anode of a rechargeable battery. In that case a lithium alloy is probably a better choice. On the other hand, LiCoO_2 and other layered transition metal oxides of the composition LiMO_2 , where e.g. $\text{M} = \text{Ni}$ or Cr , appear to be very attractive choices for both the EC_2 layer of the EC window and the cathode of a battery^{32,33}.

At the present time, however, there is no obvious "best choice" material for the IC layer for the EC window as well as for other thin film solid state ionic devices. In the case of the EC window, though, there are several important reasons that might lead one to adopt an inorganic electrolyte, and among these are: (i) inorganic electrolytes usually involve the transport of only a single ionic species; (ii) inorganic electrolytes lend themselves to continuous, in-line (as compared to batch) manufacturing processes, (especially reactive sputtering and related physical deposition processes); (iii) monolithic structures (as compared to sandwich, or laminated, structures) are readily fabricated with inorganic electrolytes, thereby avoiding bubble formation and sealing problems during manufacture; and most importantly, (iv) the durability of inorganic films is expected to be high, especially with regard to exposure to a wide range of temperatures and to ultraviolet radiation, particularly because of the normally low reactivity of inorganics. Also, the ionic conductivity and the electronic resistivity of inorganic electrolytes usually increase with increasing temperature, and hence one expects that at elevated temperatures their performance should improve rather than degrade as often occurs with polymer electrolytes.

It should be noted that during the deposition of a multilayer monolithic structure there is the likelihood of interactions between the depositing and the deposited layers that need to be understood and carefully controlled. For example, the degree of lithiation of the EC₁ layer of Figure 1 may affect the stoichiometry and the stress of the IC layer; and the electron potential energy barrier at the interface between these same two layers may be affected by the deposition parameters of the depositing IC layer.

There still remain two major uncertainties that also need resolution: (i) **experimental proof of, and a basic understanding of the deposition conditions that lead to, durable or kinetically-stable monolithic, completely inorganic EC windows as well as other related devices;** and (ii) **demonstration of the existence of one or more economical, high deposition rate synthesis processes for inorganic layers, (but particularly for the inorganic electrolyte).** That is, to insure the success of monolithic variable reflectivity electrochromic windows, and related thin film solid state ionic devices, basic studies of thin film materials syntheses and the fundamentals of thin film solid state ionic materials must continue; however, it is also apparent that some attention must be directed to the development of fabrication processes which are "production-worthy." In particular, a production-worthy process for EC windows should have the following properties:

(a) It should economically provide for rapid, highly controllable (including controlled stress, composition and microstructure profiles), and highly reproducible depositions of large area, active, and especially durable, multilayer structures, on to relatively low temperature substrates. (This includes plastic substrates, which could be used for retrofit window applications.)

(b) It should produce pc-WO₃ films having low values of the Drude loss parameter, E_r. This would have an important beneficial effect on the economics of both producing and operating/maintaining the windows because it would allow for thinner and less optically-absorbing EC₁ and EC₂ layers, which should provide for: shorter switching times, lower switching energies, less strain and, thus, more durable coatings.

To achieve this goal, we believe, methods for increasing reactive rf sputtering rates by a factor of ten or more must be developed, or variants such as reactive magnetron sputtering must be developed and applied. Enhanced ion beam techniques have promise as well (e.g., ion assisted deposition¹⁴ and even direct ion beams deposition techniques).

Although the technology risks associated with the development of a monolithic variable reflectivity

electrochromic window for managing the exchange of radiant energy between buildings or vehicles and their surround have not been eliminated, progress continues on every front and production-processes are now beginning to receive attention; and it is highly probable that what has been learned regarding the production of research electrochromic window cells by rf diode sputtering can be transferred readily to determining the conditions needed to fabricate large-area EC windows as well as batteries and other thin film ionic devices, by one or more of these production-worthy processes.

4. CONCLUSIONS

Probably the primary goal of the thin film solid state ionics scientist is to determine optimum ways to synthesize single and multilayers with highly predictable and kinetically stable ionic and electronic transport properties. As with thermodynamically stable crystalline solids, this generally translates into determining, a priori, not only the composition and structure profiles, but also what growth process should be used. However, in the case of thin films, like other kinetically stable solids (e.g., ceramics), there is an added burden as well as opportunity - namely to determine the optimum microstructure profile and the best way to reproducibly achieve it, in single as well as multi-layers.

From the above we have seen that, in the case of the variable reflectivity EC window, to obtain the desired electronic transport properties at optical frequencies, the EC and TC layers should be highly ordered, with a minimum concentration of point defects. Furthermore, for pc-WO_3 , which is currently unique among known EC materials, (unique in regards to exhibiting high reflectivity modulation, at least over the near infrared portion of the solar spectrum), the requirement of a high degree of structural order puts a constraint on the stoichiometry. In particular, having oxygen stoichiometry is a necessary (but not sufficient) condition for attaining structural order. This is because oxygen deficiency leads to extended defects, i.e., crystallographic shear planes, and an associated undesirable amount of electron scattering¹³. We have also seen that achieving full lithium and oxygen stoichiometry in films of LiCoO_2 (and other related layered transition metal oxides) probably would provide for an a priori desired set of optical and charge storage properties, useful for EC windows and batteries, respectively.

Also, in the case of the IC layer, (of either an EC window or a thin film battery), to obtain high σ_{Li} and $\langle \rho_e \rangle_{\text{eff}}$ it appears that just the opposite is needed - i.e., highly disordered structures are most desirable. Additionally, for the IC layer, with appropriate processing it may be possible to achieve high $\langle \rho_e \rangle_{\text{eff}}$ both by achieving high intrinsic electronic resistivity and by synthesizing electronic potential energy barriers at both interfaces of the layer. This, in turn, would lead not only to high $\langle \rho_e \rangle_{\text{eff}}$ but also to stable operation at relatively high voltages.

Finally, from what has been discussed above, the structure and composition, and therefore most of the physico-chemical properties, of solid state ionic thin films and devices are sensitively determined by the deposition parameters. Therefore, if the rest of the world is going to benefit from the labors of the thin film solid state ionics community, one of the most important research and development hurdles that must be overcome by that community is to devise production-worthy deposition processes, especially by establishing further a basic understanding of the interrelationships between the deposition parameters of such processes and the properties of the resulting deposited layers and devices.

5. ACKNOWLEDGEMENTS

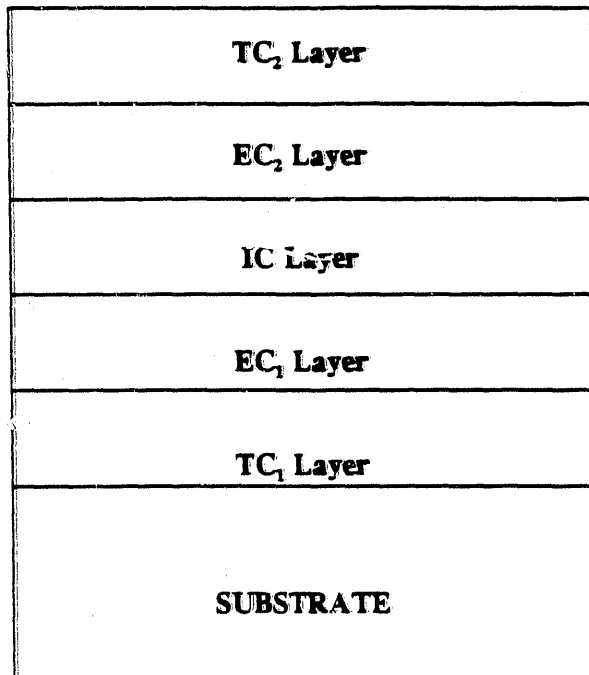
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6. REFERENCES

1. R.B.Goldner and R.D.Rauh, *Solar Energy Materials* 11, 177 (1984).
2. R.B.Goldner, T.E.Haas, G.Seward, K.K.Wong, P.Norton, G.Foley, G.Berera, G.Wei, S.Schulz and R.Chapman, *Solid State Ionics* 28-30, 1715 (1988).
3. R.B.Goldner, F.O.Amtz, G.Berera, T.E.Haas, G.Wei, K.K.Wong, P.C.Yu, *Proc.SPIE* 1536-34 (July 1991).
4. R.Bevington and A.H.Rosenfeld, *Scientific American* 263, 77 (1990).
5. Private communication with Dr.G.Manfre, FIAT Corp., Turino, Italy.
6. T.E.Haas and R.B.Goldner, "Fundamentals of Electrochromism in Metal Oxide Bronzes," Chapter of book, "Large Area Chromogenics," edited by C.M.Lampert and C.G.Granqvist, Vol.IS 4, 170, SPIE Optical Engineering Press, Bellingham, WA (1990).
7. R.B.Goldner, G.Berera, F.O.Amtz, T.E.Haas, B.Morel and K.K.Wong *Proc. Electrochem.Soc.* 90-2, 14 (1990).
8. F.Wooten, "Optical Properties of Solids," Academic Press, NY (1972).
9. P.J.Wiseman and P.G.Dickens, *J.Solid State Chem.* 17, 91 (1976).
10. R.J.Cava, A.Santoro, D.W.Murphy, Sm.Sahurak, and R.S.Roth, *J.Solid State Chem.*, 50, 121 (1983).
11. J.F.Owen, K.J.Teegarden and H.R.Shanks, *Phys.Rev.* B18, 3827 (1978).
12. G.Berera, R.B.Goldner, F.O.Amtz, K.K.Wong, A.Ciaccia, M.Welch, T.E.Haas, L.Jauniskis, *Proc.Mat.Res.Soc.* 210, 69 (1991).
13. R.B.Goldner, A.Brofos, G.Foley, E.L.Goldner, T.E.Haas, W.Henderson, P.Norton, B.A.Ratnam, N.Weis and K.K. Wong, *Solar Energy Materials*, 12, 403 (1985).
14. F.O.Amtz, R.B.Goldner, B.Morel, T.E.Haas and K.K.Wong, *J.Appl.Phys.* 67, 3177 (1990).
15. J.J.Pankove, "Optical Processes in Semiconductors," Dover Publications Inc., N.Y.
16. T.E.Haas, R.B.Goldner, G.Seward, K.K.Wong, G.Foley, and R.Kabani, *Proc.SPIE* 823, 81 (1987).
17. J.B.Bates, N.J.Dudney, B.C.Sales, J.D.Robertson, R.A.Zuhr, G.R.Gruzalski, and C.F.Luck, *Proc. Mat.Res.Soc.* 210, 569 (1991).
18. A.Glass, K.Nassau and T.J.Negran, *J.Appl.Phys.*49, 4808 (1978).
19. P.C.Yu, T.E.Haas, R.B.Goldner and S.F.Cogan *Proc.Mat.Res.Soc.* 210, 63 (1991).
20. Phillip C.Yu, "Characterization of Indium Sesquioxide and Niobium Pentoxide for the application as Counter-Electrodes in an Electrochromic Window," Ph.D. Thesis, Tufts University (1991).
21. M.Marezio, *Acta Crystallography* 20, 723 (1966).
22. W.Veppner and R.A.Huggins, *J.Electrochem.Soc.* 124, 1569 (1977).
23. T.E.Haas, R.B.Goldner, G.Wei and E.Candela, Paper 111 of the 18th Northeast Regional Meeting, American Chemical Society, Orono, Maine (Jul.31 - Aug.3, 1988).

24. G.Wei, T.E.Haas and R.B.Goldner, Proc.Electrochem.Soc. 90-2, 80 (1990).
25. Guang Wei, "Lithium Cobalt Oxide Thin Films: Preparation and Characterization for Electrochromic Applications," Ph.D. Thesis Tufts University (1991).
26. J.P.Kemp and P.A.Cox, J.Phys.: Condens.Matter 2, 9653 (1990).
27. Patents being applied for.
28. The extrema never exceeded 2.8 Volts (TC₂ positive) and -1.0 Volts (TC₁ negative).
29. I.Golicheff, M.Loeuillet and Ch.Engelmann, J.Radioanalytical Chem. 12,233 (1972); and A.Sagara, K.Kamada and S.Yamaguchi, Nucl.Instr. and Meth. in Physics Research B34, 465 (1988).
30. Measurements are being performed by W. Lanford and C. Shepard at SUNY, Albany, NY.
31. R.D.Rauh, et al. Appl.Opt.24, 2281(1985); R.B.Goldner, et al. Appl.Opt.24, 2283(1985).
32. B.Morel, "Elaboration et etude de films a proprietes electrochromes et d'electrodes transparentes. Application a la realisation de dispotifs electrochromes 'tout solide'," Ph.D. Thesis, L'Universite de Bordeaux I (1991).
33. M.G.S.R.Thomas, P.G.Bruce, and J.B.Goodenough, Solid State Ionics 17, 13 (1985).



**Figure 1. A monolithic variable reflectivity electrochromic window.
(TC = transparent conducting, EC = electrochromic, IC = ion conducting.)**

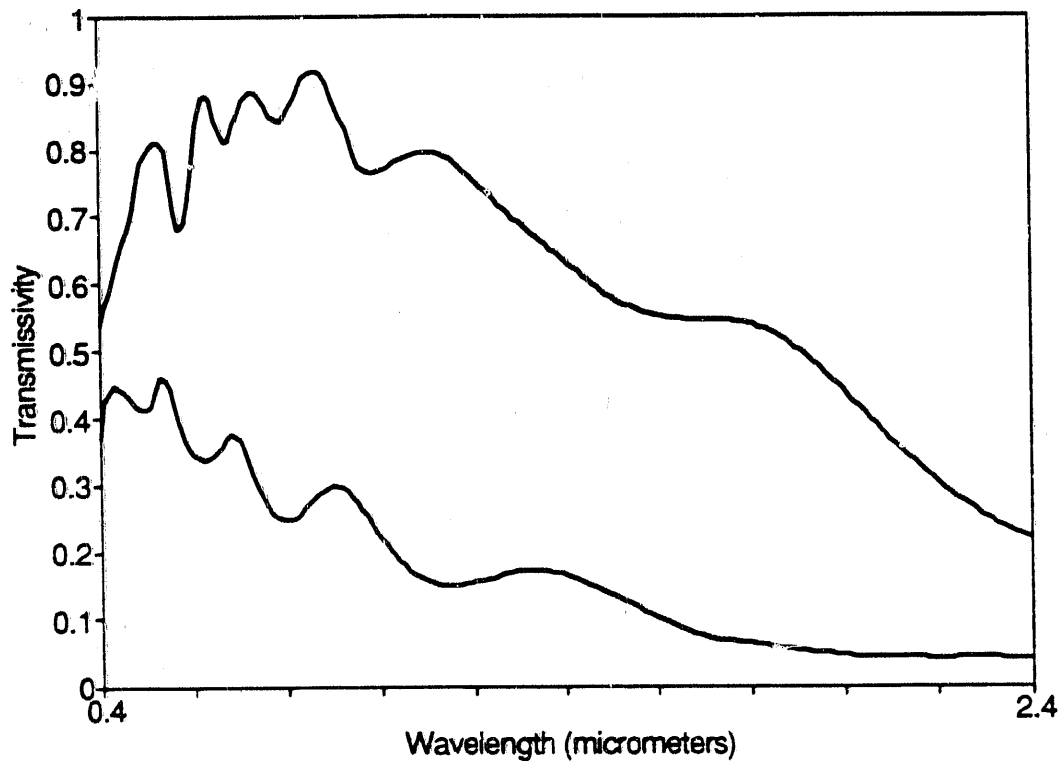


Figure 2. Optical transmissivity for a monolithic variable reflectivity electrochromic window cell of 1 cm² area. Composition: TC₁ = ITO (150 nm thick), EC₁ = pc-WO₃ (150 nm thick), IC = α-LiNbO₃ (500 nm thick), EC₂ = LiCoO₂ (120 nm thick), and TC₂ = In₂O₃ (reactively evaporated, 100 nm thick). All layers except TC₂ were deposited by rf diode sputtering. TC₂ (+) to obtain lower ("colored" state) curve.

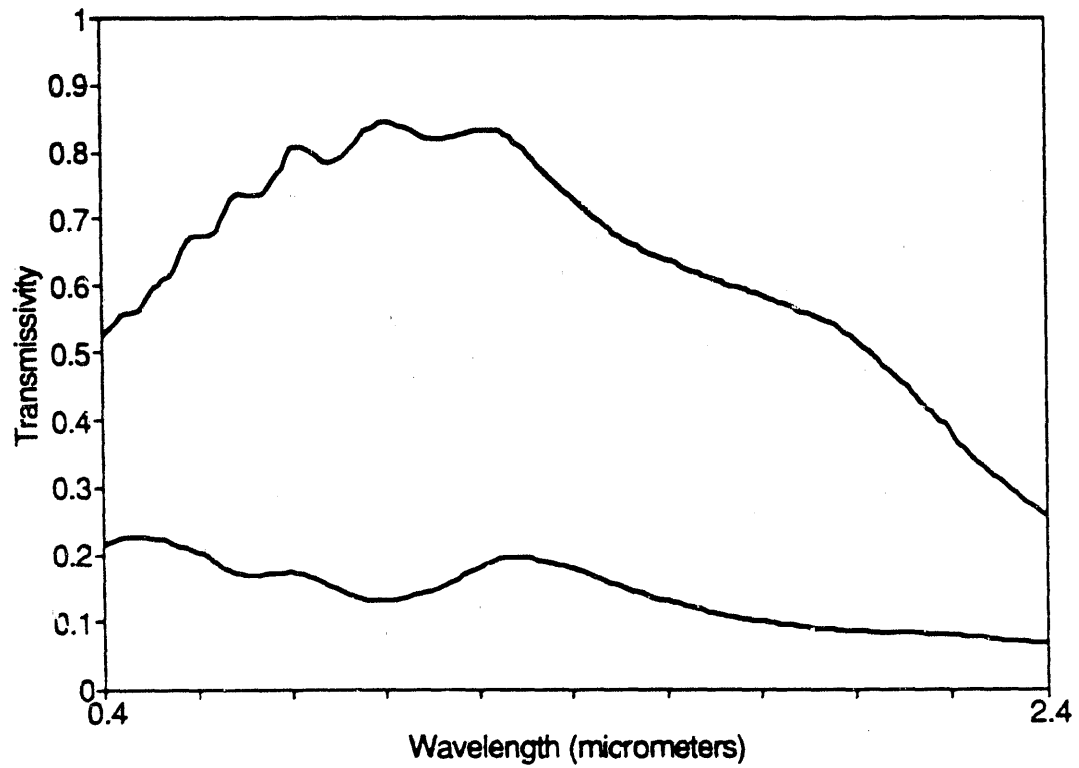


Figure 3. Optical transmissivity for a monolithic variable reflectivity electrochromic window cell of area = 20 cm² of the same composition as, (but with the thickness of the LiCoO₂ layer twice), that of the cell of Figure 2. TC₂ (+) to obtain lower ("colored" state) curve.

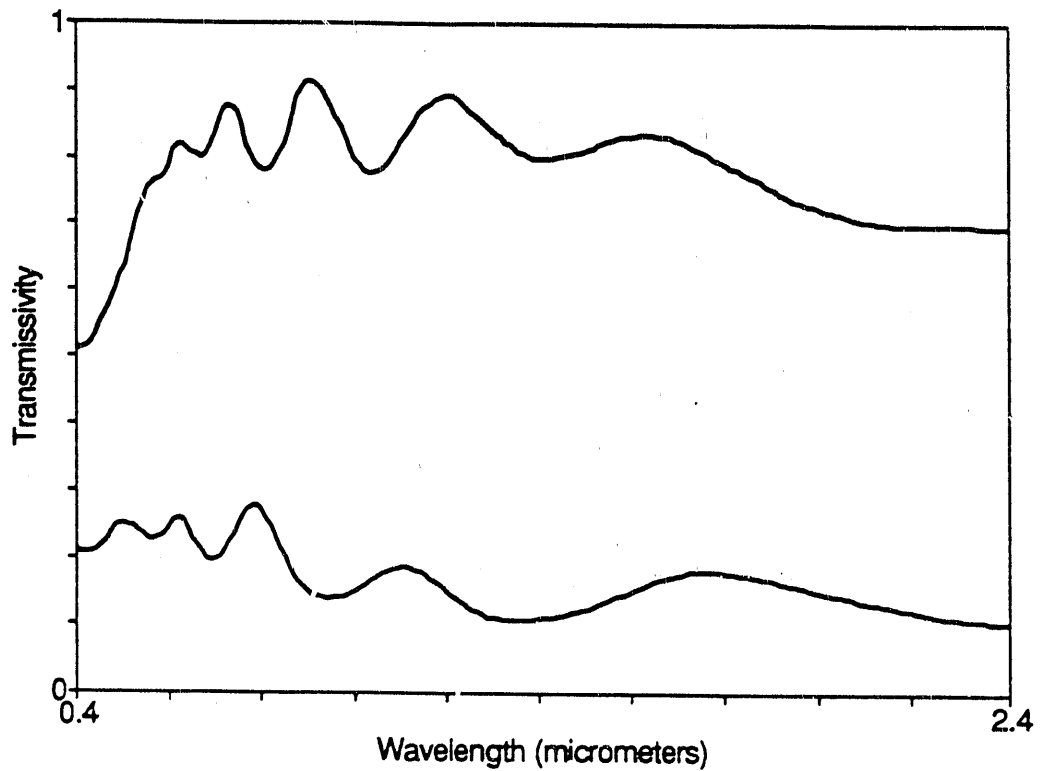


Figure 4. Transmissivity for a monolithic variable reflectivity electrochromic window cell of area = 1 cm². Composition is the same as that of Figure 2, except the LiCoO₂ thickness is 50nm. TC₂ (+) to obtain lower ("colored" state) curve.

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