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TITLE: Optics and Materials Research for Controlled Radiant Energy Transfer in Buildings

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Annual Project Status Report for FY'91
(Grant DE-FG03-85SF15927)
"Optics and Materials Research for Controlled Radiant Energy Transfer in Buildings"

I. Summary - Technical Highlights

A number of unexpected discoveries during 1991 caused us to redirect our efforts and to depart from the linear project plan proposed for the year. However, (a) the original intent of the plan was carefully respected; (b) the development of practical and robust electrochromic windows advanced significantly; (c) we acquired a much deeper understanding of conduction and chemical processes occurring within the component layers; and (d) our conviction that completely inorganic monolithic electrochromic windows will prove to be robust and cost effective in architectural applications has continued to grow.

Activities sponsored by DOE at Tufts University to develop thin film variable reflectivity electrochromic windows have focussed in five areas in 1991: (1) evaluating the irreversible incorporation of lithium in the counterelectrode material, sputtered indium oxide; (2) responding to evidence that protons substitute for mobile lithium ions in "standard" five-layer electrochromic window structures operating in room air; (3) understanding the electronic and ionic conduction mechanisms in sputtered amorphous lithium niobate, the ion conductor adopted for electrochromic window structures fabricated at Tufts; (4) responding to the discovery that cathodic coloring of the variable reflecting tungsten bronze (Li_xWO_3) is constrained by interaction with the underlying ITO or SnO_2 transparent conductor in conventional electrochromic window structures; and (5) life testing of electrochromic window prototypes.

Counter-Electrode Layer Research

The progressive incorporation of lithium into sputtered indium oxide during cycling, studied in detail by Phillip C. Yu using cyclic voltammetry, undermines the utility of this material as counterelectrode. This work and Dr. Yu's results are described in his doctoral thesis entitled "Characterization of Indium Sequioxide and Niobium Pentoxide for the Application as Counter-Electrodes in an Electrochromic Window" (Tufts University, May 1991) and in an article published in the Proceedings of the Materials Research Society.

The results of Dr. Yu's study were not the only negative indicators for the use of indium oxide as counterelectrode. A suspicion that proton substitution for lithium occurs in electrochromic window structures employing sputtered indium oxide as counterelectrode was confirmed by cycling newly fabricated five-layer devices in vacuum rather than in room air. In the vacuum environment such devices exhibited weaker electrochromic behavior and correspondingly smaller charging currents. Although dependence of electrochromic window operation upon atmospheric water might be acceptable to some, the risks and complications involved in depending upon such an open system were thought too serious to continue with the use of indium oxide as counterelectrode.

Alternative five-layer cells fabricated with sputtered niobium oxide as counterelectrode and devices fabricated with sputtered lithium cobalt oxide as an anodically coloring electrochromic electrode functioned well both in vacuum and in air, and were insensitive to illumination. Cells employing niobium oxide required emfs greater than seven Volts to color at acceptable rates. This we have attributed to electron depletion and space-charge buildup in the n-type niobium oxide. Typical structures require three Volts or less.

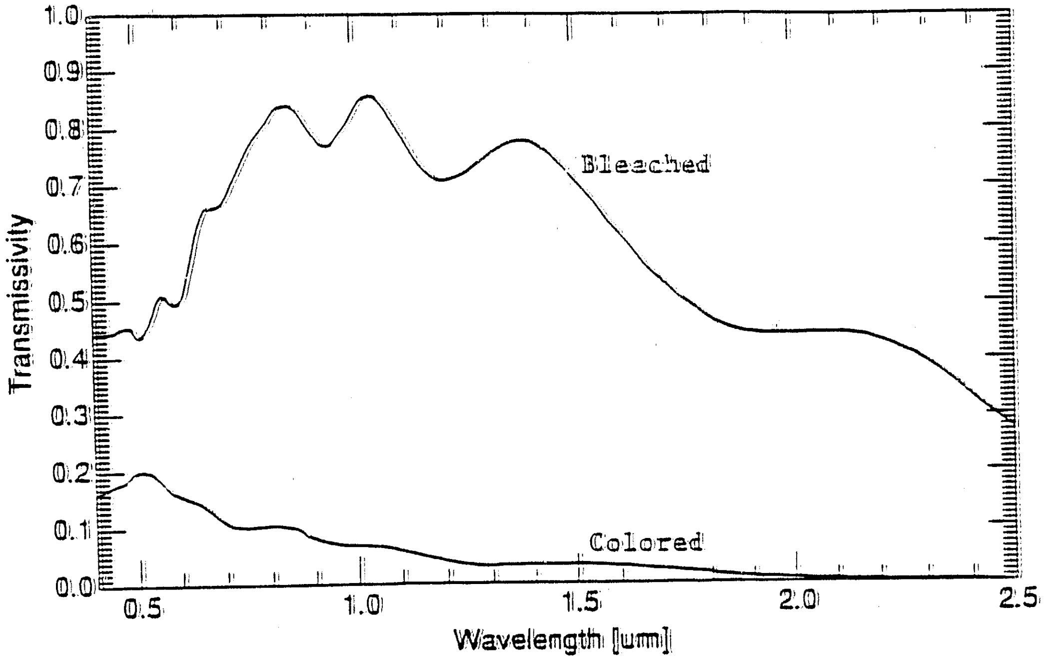

Figure 1. Transmission spectra for a six-layer complementary electrochromic window sample (H197) before and after coloring. It is comprised of the following layers: (1) ITO - 120nm; (2) lithium blocking layer, 30-nm; (3) tungsten trioxide, 100nm; (4) amorphous lithium niobate; 400nm; (5) lithium cobalt oxide, 50nm; and (6) reduced indium oxide, 100nm.

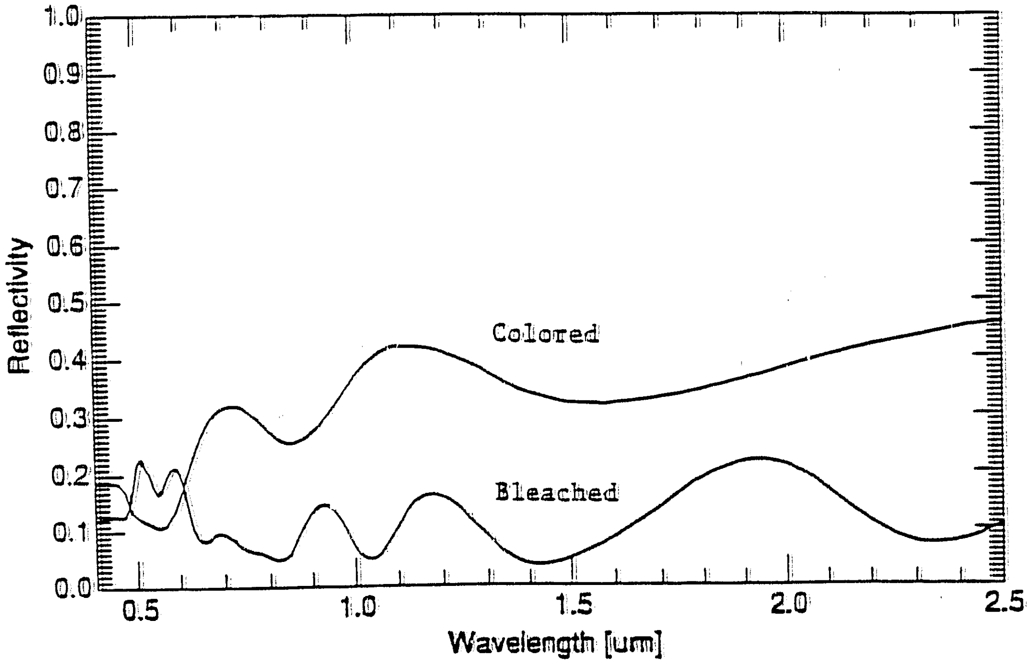

Figure 2. Reflection spectra for a six-layer electrochromic window sample (H197) before and after coloring. For details see Figure 1.

Because of the above results and in response to earlier results by Guang Wei supporting theoretical predictions of strong anodic electrochromism in lithium cobalt oxide, we committed to the development of sputtered films of this material to supplant indium oxide as counterelectrode. Dr. Wei reported in detail on her study of electrochromic character of lithium cobalt oxide in her doctoral thesis in 1991 and in a previous publication [Proc.of Electrochem.Soc.Conf.on Electrochromic Materials, 90-2, 80 (1989)]. Although the transparency limit of lithium cobalt oxides produced by straightforward sputtering was originally marginal in the visible spectrum, we have since found process variations which improve it. This work continues.

Ion-Conducting (Electrolyte) Layer Research

At the present time, although there is no obvious "best choice" material for the IC layer for the electrochromic window, there are several important reasons that might lead one to adopt an inorganic electrolyte. 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 the wide range of temperatures and to ultraviolet radiation which building windows will experience, 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 was for these reasons that our research has and continues to focus on inorganic electrolytes; and a recent communication from a colleague at the University of Bourdeaux indicating that their polymer electrolytes have not been robust at elevated temperatures has reinforced this decision.

A study of the electrical properties of sputtered amorphous lithium niobate in standard device structures and in metal-(ion conductor)-metal structures indicates electron conduction is strongly dependent upon the properties of the interface between the ion conductor and cathode but is also influenced by conditions obtaining during deposition of the lithium niobate. Bulk ion conductivity exceeding 0.05 microSiemens/cm is obtained in lithium niobate sputter deposited in a pure argon ambient whereas the ion conductivity of such films deposited in the presence of oxygen is somewhat lower. This work is nearing completion and will be reported by K. K. Wong in his doctoral thesis in early 1992.

Window Devices Research

Reduced levels of transmission and reflection modulation in typical five-layer electrochromic window cells after many cycles has been traced to significant sharing of lithium between the tungsten bronze (layer 2) and the underlying ITO or SnO2 transparent conductor. We have been studying the use of a thin sputter-deposited lithium blocking layer between these layers to prevent lithium exchange with the ITO without severely compromising electron conduction. Results for the optical transmission and reflection before and after coloring of such a cell, now having six layers, are presented in Figures 1 and 2. This particular cell employs a 30-nanometers thick lithium blocking layer (layer 2) and a 50-nanometers of lithium cobalt oxide as an anodic electrochromic counterelectrode (layer 5).

Life testing of five-layer electrochromic window cells with a lithium cobalt oxide as anodic electrochromic counterelectrode (layer 4) has been extended to 9000 cycles (equivalent to 24-years at one cycle per day) at a temperature of 60 degrees Celsius (140 degrees F). These tests were performed in an

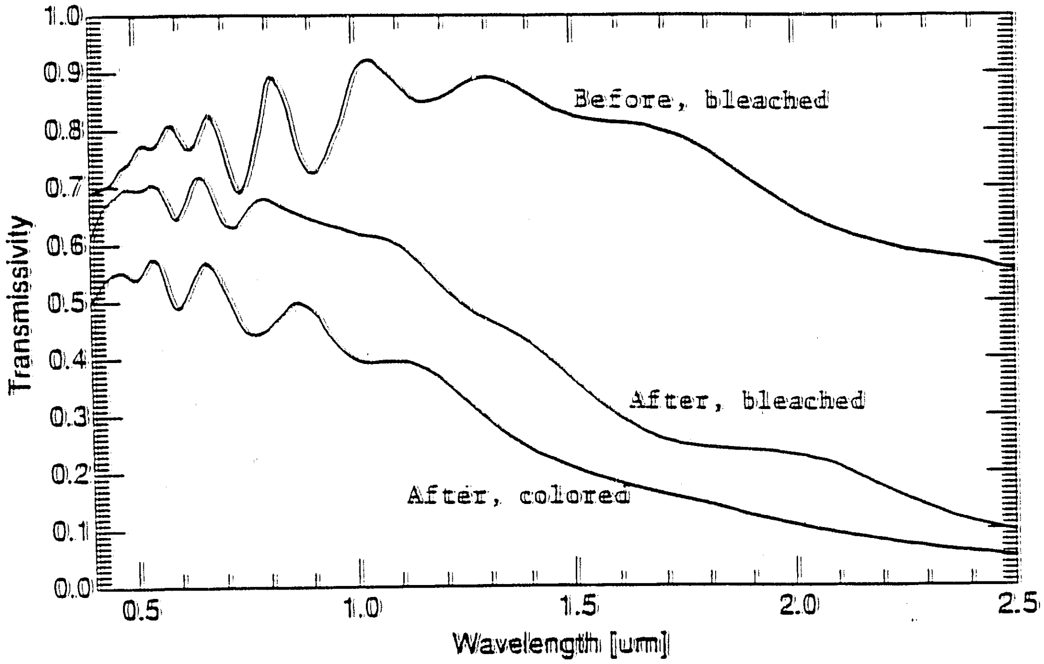

Figure 3. Life test results. Transmission spectra of a five-layer complementary electrochromic window sample (H193) before and after 9000 cycles at 60-degrees Celsius. The decrease in transmission modulation is attributed to loss of lithium to the ITO contact.

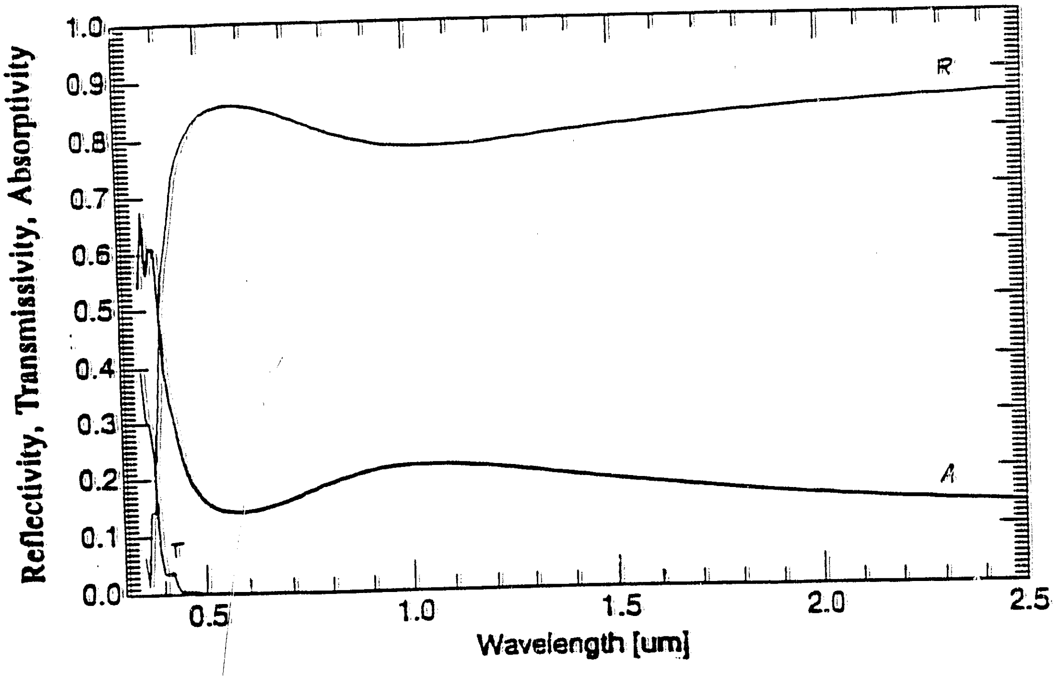

Figure 4. Simulated transmission and reflection spectra of a complementary electrochromic window comprised of substrate (n = 1.5) and the following five layers: (1) transparent conductor, 100nm, n = 2; (2) Drude film, 200nm, Egamma = 0.2eV, Eplasma = 6.2eV, epsilon_b = 4.0; (3) ion conductor, 500nm, n = 2.2; (4) Drude film, 200nm, Egamma = 4eV, Eplasma = 0.5eV, epsilon_b = 4.0; and (5) transparent conductor, 100nm, n = 2.

pure argon ambient to preclude any possible reaction with componen of room air. The elevated temperature was chosen to simulate challenging conditions in which electrochromic windows would be used (excepting for the absence of air). We expected the higher temperatures to accelerate the appearance of undesired phase transitions within component layers and the occurrence of chemical reactions which might bind lithium. The reduced transmission modulation apparent after this exercise regimen (see Figure 3) is believed due to the irreversible accumulation of lithium within the ITO transparent contact as described above. To test this hypothesis, life testing is planned for a six-layer device employing a lithium blocking layer.

Efforts to obtain closure between optical measurements (for example see Figures 1 and 2) and optical modelling including Drude effects are proving to be very useful. The complex optical properties displayed by sample electrochromic windows in various states of charging can now be largely unwound and traced back to optical constants, Drude parameters, and thicknesses of individual layers. This capability also places us on the threshold of designing reflective mode electrochromic windows with desired optical properties in the visible, e.g transmissivity and tint, while permitting effective management of radiant transfer over the entire solar spectrum.

Figure 4, a result of modelling, has served us as an example of what might be achieved and, in 1992, will be used as a basis for judging working devices. This model assumes realistic values for all the optical properties of the various layers, the most extreme being the Drude parameters, namely a plasma energy of 6.2eV and a loss parameter of 0.2eV, for the electrochromic tungsten bronze in its maximally lithiated state. Although the latter parameters have been obtained from measurements on bulk crystalline sodium tungsten bronze, evidence is mounting that these can be achieved with lithium tungsten bronze films produced by sputtering. The figure demonstrates for this model electrochromic window structure in its colored state that the very low transmissivity over the entire solar spectrum is principally due to free carrier **reflection** of incident radiation, not absorption.

II. The **best devices of 1990** were 20 cm^2 cells comprised of the following five layers:

1. ITO - 160 nm by rf sputtering in oxygen at 440°C.
2. Crystalline WO3 - 100 nm by rf sputtering in oxygen at 440°C.
3. Amorphous lithium niobate - 350 nm by rf sputtering in argon or argon-oxygen at 40°C or less.
4. Indium oxide - 120 nm by rf sputtering in argon-oxygen at 160°C.
5. Indium oxide - 100nm by reactive evaporation of indium in low-pressure oxygen at 300°C.

With these we obtained consistent electrical yields exceeding 85%. In early life strong optical modulation was obtained but it progressively deteriorated over 3000 cycles at room temperature. This decay is attributed to the irreversible loss of lithium to either or both of the ITO and indium oxide layers.

III. The **best devices of 1991** were 2 cm^2 cells comprised of the above layers excepting for layer 4 which is LiCoO2 - typically 50 - 100 nm thick, deposited by rf sputtering in argon-oxygen or oxygen ambients. The few devices made with 20 cm^2 active area were too leaky to be useful. We are presently seeking a recipe providing an attractive combination of static and modulated optical properties. Representative transmission curves for the colored and bleached states are shown in Figure 5 (reproduced from the accompanying paper presented at the Lake Louise 8th International Solid State Ionics Conference).

The problems with this structure are as follows:

1. Progressive loss of lithium to the underlying ITO.
2. The maximum visible transmission obtained in the bleached state is approximately 70%.

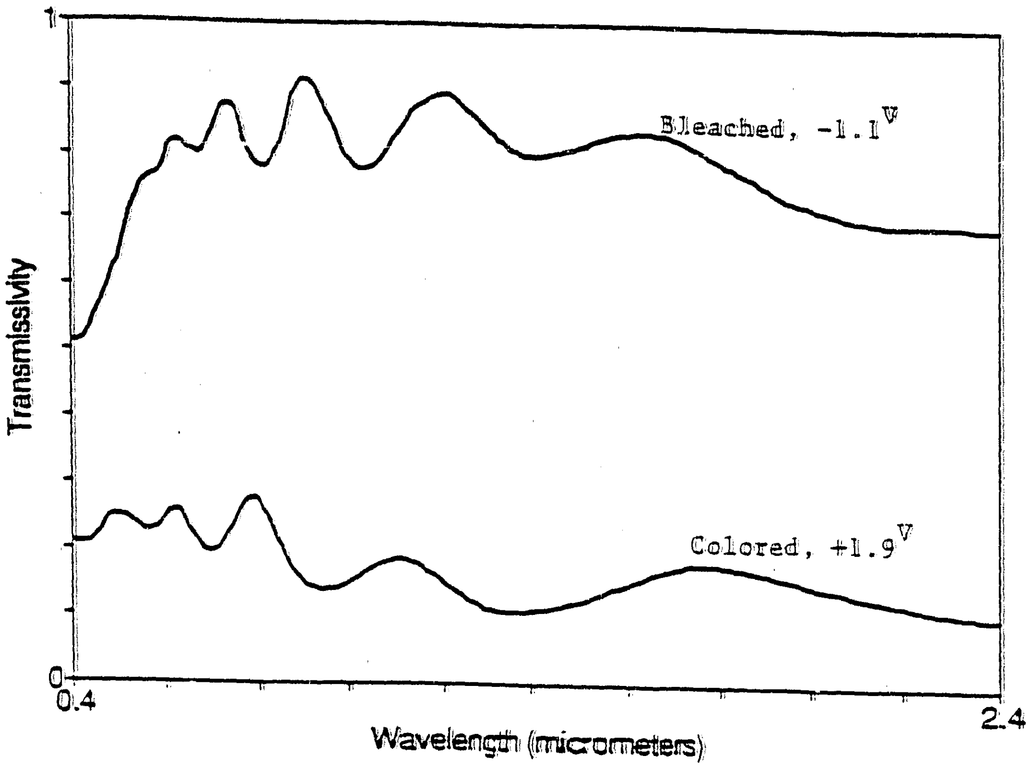

Figure 5. Transmission spectra for a late 1991 five-layer complementary electrochromic window sample (H187) in colored and bleached states (colored state, +1.9 Volts; bleached state, -1.1 Volts).

IV. Plans for FY92

The principal challenges for 1992 are the following:

1. Further refine the fabrication processes for lithium cobalt oxide to consistently obtain electrochromic windows cells which exhibit strong reflection modulation and, when bleached, provide improved transparency in the visible.
2. Develop the lithium blocking layer technology.
3. Perform life testing on prototypes incorporating the above advances; use elevated temperatures and room air ambient.
4. Achieve a minimum yield of 50 per cent in fabrication of prototype cells having areas of 20 cm^2.
5. Determine if lithium blocking must be employed to prevent lithium insertion into the top transparent conductor; introduce this layer in the prototype cells if proven to be beneficial.
6. Develop reactive magnetron sputtering deposition techniques for the fabrication of key layers having properties equivalent to or superior to those produced by rf sputtering.

V. Industry, government laboratory, and university involvement and/or contacts:

Airco, American Optical, AT&T, SUNY-Albany, Donnelly, Duracell, Elf-Aquitaine, Eveready, Fiat, Ford, Gentex, GM-Hughes, Geo Centers, GTE, IBM, Indium Corp of American, McDonnell Air, OCLI, ORNL, Pilkington, PPG, Radiation Monitoring Devices Inc., St Gobain, U. Bordeaux.

VI. Publications:

1. P.C.Yu, et al.,"Characterization of indium oxide for use as a counterelectrode in an electrochromic device," Proc.Mat.Res.Soc. 210, 63 (1991).
2. G.Berera, et al.,"A study of the optical bandgap of lithium tungsten trioxide thin films," Proc.Mat.Res.Soc. 210, 69 (1991).
3. G.Wei,"Lithium cobalt oxide thin films: preparation and characterization for electrochromic applications," Ph.D. thesis, Tufts University (May 1991).
4. P.C.Yu,"Characterization of indium sesquioxide and niobium pentoxide for the application as counter-electrodes in an electrochromic window," Ph.D. thesis, Tufts University, (May 1991).
5. R.B.Goldner, et al.,"Progress on the variable reflectivity electrochromic window," Proc.SPIE 1536-34, (July 1991).
6. R.B.Goldner et al.,"Ion-beam based deposition of coatings for electrochromic devices," U.S.Patent 5,051,274 (24Sept1991).
7. R.B.Goldner, et al.,"A monolithic thin film electrochromic window," keynote paper at the thin film ionics session of the 8th International Conference on Solid State Ionics, Lake Louise, (Oct. 1991); and to be published in Solid State Ionics (1992).

Presentations

1. R.B.Goldner, "The Tufts Electrochromics Smart Window - some of its Promise, Progress, and Challenges," invited talk, Hughes Research Laboratory, El Segundo, CA, (4 Jan 1991).
2. T.E.Haas, "The Electrochromic Smart Window: Materials Issues," Cornell Univ.Mat'ls.Sci.Dept. Seminar, (Jan.1991).
3. R.B.Goldner, "Achieving a Solar Energy Economy with Thin Films, invited talk, Boston Research Directors Club Meeting, Lexington, MA (13 Feb. 1991).
4. R.B.Goldner, "The Electrochromic Window and Super Battery - Two Thin Film Devices for a Solar Energy Economy," invited talk, Physical Sciences, Inc., Andover, MA, (22 Feb. 1991).
5. T.E.Haas, "The Reflective Mode Electrochromic Window," invited talk, Royal Society of Chemistry, London, England (3 April 1991).
6. T.E.Haas, "Lithium Cobalt Oxide Thin Films," invited talk, Chemistry Dept. Swiss Federal Polytechnic Institute, Lausanne, Switzerland (8 April 1991).
7. R.B.Goldner, "Progress on the Variable Reflectivity Electrochromic Window," invited talk, Oak Ridge National Laboratory, Oak Ridge, TN, (9 May 1991).
8. R.B.Goldner,"Principles of the Variable Reflectivity Electrochromic Window," invited seminar at the University of Bourdeaux, (June 1991).
9. R.B.Goldner, "The Tufts Electrochromic Window," invited seminar, St.Gobain, Paris, FR (June 1991).
10. R.B.Goldner, et al., "Recent Progress on a Variable Reflectivity Electrochromic Window," Proc.SPIE, San Diego, CA (July 1991).
11. R.B.Goldner, et al., "A Monolithic Thin Film Electrochromic Window," keynote paper at the thin film ionics session of the 8th Solid State Ionics International Meeting, Lake Louise (Oct.1991).

Papers removed and cycled separately -

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