5. Electrochromic Displays Based on WO₃

B. W. Faughnan and R. S. Crandall

With 9 Figures

Electrochromic displays based on thin films of WO₃ as the active layer are reviewed with emphasis on the basic mechanisms of the electrochromic effect. These include the concept of double injection of electrons and protons into the WO₃ film, resulting in the formation of a colored tungsten bronze HₓWO₃. It is suggested that the broad optical absorption band which peaks at λ = 0.95 µm arises from an electron transfer between tungsten ions.

A detailed theory of the dynamics of coloring and bleaching is presented. In the coloring mode, the WO₃-electrolyte interface and the x-dependence of the chemical potential of HₓWO₃ play a critical role. Speed limitations due to diffusion of electrons or protons in the WO₃ film are shown to be unimportant for practical devices. During bleaching, the positive and negative charges must be separated and exit from opposite sides of the film. The limitation on the bleaching speed is the space charge limited current flow of protons through the bleached portion of the film.

Various methods of preparing WO₃ films are discussed. Methods of measuring the water content of films and its relationship with film reproducibility and device performance are emphasized.

Device performance, starting with the simplest WO₃-film/proton-electrolyte system, is considered. Equations for coloring and bleaching speeds are developed. More complicated devices including liquid electrolytes in which positive ions other than protons are used and all solid state devices are described.

Finally, the critical problems of device lifetime and degradation mechanisms are reviewed.

5.1 Background Information

5.1.1 Electrochromic Displays

An electrochromic material has the property of changing color when a voltage is applied across the material, or alternately, a current is passed through it. This color change should be reversible when the voltage is removed or when the polarity of the voltage or current is reversed. Known electrochromic materials are both inorganic and organic, and the color change may be from clear or
transparent to colored, or from one color to another color. The last case is characteristic of organic materials.

An electrochromic display device utilizes one of the above materials usually in the form of a thin film, to build a passive display. The characteristics of electrochromic displays are: low-voltage operation (1.5 V down to approximately 0.4 V), low power requirements [somewhere between liquid-crystal displays (LCD) and light-emitting diode (LED) displays], storage of the display without power dissipation, potentially low cost and simplicity in building, and possibility of an aesthetically pleasing display with good contrast and wide viewing angle.

The last characteristic probably has provided the motivation for work in this area; that is, the desire to obtain a display which looks better than an LCD display, whose device properties it most closely resembles. One area of keen interest has been small displays suitable for watches or calculators, but somewhat larger displays suitable for automotive or aircraft use remain an attractive possibility.

5.1.2 Historical Outline

One of the first discussions of electrochromism was by Platt [5.1] who coined the term. However, a field-induced increase in optical density goes back to Franz and Keldysh [5.2], who explained the shift of optical absorption caused by an electric field. The Franz-Keldysh effect depends on the shift of an optical absorption band caused by an electric field, requires high voltage and usually results in a small optical density (OD) change. This is to be contrasted with the low-voltage effect discussed in this review. This low-voltage electrochromic (EC) effect occurs only when charge is injected and can result in large optical-absorption changes.

Perhaps the earliest example of this EC effect, as well as the simplest, is the creation of F centers in an alkali halide crystal when a voltage is applied between two metal electrodes attached to opposite faces of the crystal, which is heated to about 700°C [5.3]. Briefly, the effect occurs because electrons injected from the negative pointed electrode are trapped at anion vacancies thereby forming F centers. Charge neutrality and current continuity is maintained by anion vacancy motion originating from the positive electrode. This implies a net mass transport of anions to the positive electrode where halogen gas is evolved. If the electrode potentials are reversed, hole centers are produced accompanied by the release of alkali metal at the negative electrode.

This simple example illustrates most of the requirements for an electrochromic material. First of all, it must have a color center, or some optical absorption in the visible. A second feature is the presence of mixed conduction; i.e., electronic and ionic conduction. This is necessary since charge neutrality must be preserved. These requirements severely restrict the range of available materials. In the example above, the crystal must be heated to 700°C to raise its