THERMAL CONTROL USING ELECTROCHROMISM

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ABSTRACT

The applicability of a charge balanced electrochromic device to modulate the frequencies in the thermal infra red region is examined in this study. The device consisted of a transparent conductor, WO₃ anode, PMMA/LiClO₄ electrolyte, V₂O₅ cathode and transparent conductor. The supporting structure in the device is SnO₂ coated glass and the edges are sealed with epoxy to reduce moisture absorption. The performance evaluation comprised of cyclic voltammetric measurements and determination of transmittance at various wavelengths. The device was subjected to anodic and cathodic polarization by sweeping the potential at a rate of 10 mV/sec from -0.8V to 1.8V. The current versus voltage profile indicated no reaction between -0.5 and +0.5 V. The device is colored green at 1.8 V with a transmittance of 5% at a wavelength, \( \lambda = 900 \) nm and colorless at -0.8 V with a transmittance of 74% at \( \lambda = 500 \) nm. The optical modulation is limited to 400-1500 nm and there is no activity in the thermal infrared. The switching time is 75 seconds for transmittance to decrease from 74% to 50%. The device yielded reproducible values for transmittance when cycled between colored and bleached states by application of 1.8V and -0.8V, respectively.
INTRODUCTION

Electrochromism has been the subject of intense study in the past decade. The automatic dimming of rear view mirror for motor vehicles is the first commercial product based on electrochromism. The electrochromic devices exhibit high optical contrast with continuous variation of transmittance, UV stability, optical memory and a wide temperature of operation. An electrochromic device is a thin film rechargeable battery in which an electrochromic electrode is separated by a solid electrolyte from a counter electrode. The rechargeable battery uses the 'rocking chair concept' in which the lithium ions rock between cathode and anode. Charging and discharging of the device change the spectral response. The performance of the device is based on the insertion of lithium ion into the lattice of the electrochromic electrode. The device can be constructed with electrochromic material on either the anode or cathode or in both.

The purpose of this study is to examine the applicability of the thin film electrochromic devices for thermal control in satellites. This device is a lightweight alternative for the heaters, louvers and heat pipes that regulate the satellite temperature. The experimental results obtained using a device supplied by NREL is reported in this study.

DESCRIPTION

The device consists of a solid-state battery composed of thin layers of anode, cathode, and electrolyte assembled in a glass case. The electrochromic layer consisted of WO$_3$ and it functions as a cathode. V$_2$O$_5$ was the active material in the anode and functioned as an ion storage layer. The stiffness to the structure is provided by indium tin oxide that also functioned as a transparent conductor. The solid electrolyte consists of polymethylmethacrylate mixed with LiClO$_4$ and propylene carbonate. The dimensions of the device are 5 cm $\times$ 6 cm $\times$ 0.5 cm. Figure 1 shows the schematic structure of the device.

The tests consisted of determining voltage profile using cyclic voltammetry and measuring the optical spectrum using a spectrophotometer.

VOLTAGE PROFILE

The device was polarized anodically by sweeping the potential from $-0.8$ V to $1.8$ V at a rate of 10 mV/sec and then, polarized back to $-0.8$ V at the same rate in one cycle to obtain the current-voltage profile. The current was negligibly small from $-0.5$ to $0.5$ V and then increased in an exponential manner until $1.8$ V. The device turned green at $1.8$ V and colorless at $-0.8$ V. The coloring and bleaching of the device occurred when the potential sweeps were repeated. Figure 2 shows the potential-current curves for two consecutive cycles. There is hysteresis in the current-voltage profile and the coloring reaction has a higher current density then the bleaching reaction.

SPECTRAL RESPONSE

The device was mounted in the spectrophotometer and electrical connections were made to perform potentiostatic experiments. The transmittance of the device at an applied voltage of $1.7$ V was measured as a function of wavelength. Then, the applied voltage was decreased to $0$ V and the transmittance was again measured. The spectral data indicated that there is optical modulation between wavelength $\lambda = 450$ nm and $1100$ nm. The transmittance of the device was 74% at $\lambda = 500$ nm (colorless state) and 5% at $\lambda = 900$ nm (greenish blue). The device switches from a transmittance
of 71% to 10% at a wavelength of 680 nm as a result of the applied voltage. Figure 3 illustrates the activity of the device in the spectral region from 400 to 1400 nm.

SWITCHING TIME

The time taken by the device to turn to the bleached state from colored state at 45 °C was determined by measuring the transmittance at \( \lambda = 700 \text{ nm} \) as a function of time after application of \(-0.8 \text{ V}\). Figure 4 shows the spectral transient. The transmittance increases to 60% in 240 seconds and to 72% in 900 seconds. The switching time for the reverse process i.e., coloring was determined by applying 1.8 V and measuring the transmittance at 700 nm as a function of time. A switching time of 75 seconds was obtained for transmittance to decrease to 50%. Further decrease in transmittance to 40% occurred in 23 minutes.

The switching time was determined at 30°C and 0°C and the transients are shown in figures 5 and 6 respectively. There is a marked difference in the transient obtained at 0°C.

TEMPERATURE EFFECT

The optical spectrum was determined in the bleached state at 23°C, 30°C, 45°C and 0°C and the results are shown in Figure 7, 8, 9 and 10. The percent transmittance is higher in the colored state at 30°C compared to 0°C, whereas in the bleached state the transmittance is lower at 30°C compared to 0°C. The variation of percent transmittance at \( \lambda = 610 \text{ nm} \) as a function of temperature is plotted in Figure 11. The results indicate that change in transmittance is marginal from 10°C - 45°C whereas at 10°C there is reduction.

REPETITIVE CYCLING

The device was cycled between \(-0.8 \text{ V}\) and \(1.8 \text{ V}\) a number of times and the transmittance at \( \lambda = 700 \text{ nm} \) was measured at 23°C. Figure 12 shows the transients which were reproducible with cycling. The curves indicate a transmittance of 5.9% in the colored state and 69.5% in the bleached state.

THERMAL MODULATION

The spectrographic data indicates activity in the wavelength region 400- 1500 nm. The bleaching and coloring in the visible region demonstrates the ability to modulate energy in the visible region. The data suggests no activity in the thermal infra red when the spectral data is extrapolated to 6 – 10 microns.

CONCLUSIONS

The results of the evaluation point to the following conclusions:
1. The electrochemical current-voltage curves indicate that the device is colored at 1.8 V and bleached at -0.8 V. There is no electrochemical reaction from -0.5 to 0.5 V and the coloring reaction has a higher current.
2. In the colored state the minimum transmittance observed is 5.9% at a wavelength of 700 nm. In the bleached state the transmittance was 74% at a wavelength of 500 nm.
3. The switching time is 240-900 seconds that is higher than expected.
4. The data suggests modulation of energy in the visible region. There is no activity in the infra red region.
5. The device is capable repeated cycling
6. The operational temperature range is 0°C – 45°C.
FIGURE 1. SCHEMATIC OF THE ELECTROCHROMIC DEVICE

\[ \text{ITO} \quad \text{V}_2\text{O}_5 \quad \text{PMMA} \quad \text{Amorphous WO}_3 \quad \text{ITO} \]

\[ \text{Li}_x\text{WO}_3 + \text{V}_2\text{O}_5 \leftrightarrow \text{WO}_3 + \text{Li}_y\text{V}_2\text{O}_5 \]

(COLORED) (BLEACHED)
Voltammograms of the Electrochromic Device at 22°C at a Sweep Rate of 10 mV/sec
Figure 5
Colored-to-Bleached Switching Transient at 30°C
FIGURE 6.

Bleached Switching Time at 0°C
Spectral Response at 23°C in the Colored State
Figure 9
Spectral Response at 45°C in the Colored State
FIGURE 10.

Spectral Response at 0°C In the Colored State
FIGURE 12

Transmittance at $\lambda = 700$ nm During Repetitive Cycling at 30°C