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, λ =900 nm and colorless at -0.8 V with a transmittance of 74% at λ=500 nm. The optical modulation is limited to 400-1500 nm and there is no activity in the thermal infrared. The switching time is a function of temperature and time for coloring reaction was slower than the bleaching reaction. 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 mirrors 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 range 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 changes the spectral response. The performance of the device is based on the insertion of lithium ions 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 are 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. The active material in the anode was V_2O_5 and it functions as an ion storage layer. The stiffness to the structure is provided by indium tin oxide (ITO) that also functions 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 X 6 cm X 0.5 cm. Figure 1 shows the schematic structure of the device.

The tests consisted of determining the 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 hysterisis in the current-voltage profile and the coloring reaction has a higher current density than 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 \( \lambda = 450 \text{ nm} \) and 1100 nm. The transmittance of the device was
74\% at \( \lambda = 500 \text{ nm} \) (colorless state-bleached) and 5\% at \( \lambda = 900 \text{ nm} \) (green). 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 a 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 \(1.8 \text{ V}\) and measuring the transmittance at \(700 \text{ nm}\) as a function of time. A switching time of 75 seconds was measured for the transmittance to decrease to 50\%. A further 10\% decrease in transmittance to 40\%, occurred in 23 minutes.

The colored-to-bleached 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 increase in the switching observed 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 through 10 respectively. 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 indicated marginal increase in the transmittance when the temperature is increased from 23°C to 45°C. At 10°C the percent transmittance decreased by 6\% compared to that measured at 23°C. The temperature dependency is attributed to the conductivity of the solid electrolyte which increases with increase in temperature.

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. There is no spectral response in the wavelength region 6-10 micron that corresponds to the infra red region.
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 for the coloring process from a bleached state was higher than that of the bleaching reaction in the reverse direction.

4. The data suggests modulation of energy in the visible region. There is no spectral activity from 6 - 10 microns that corresponds to the infrared region.

5. The device is capable repeated cycling.
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PURPOSE

TO DEVELOP FILM STRUCTURES BASED ON ELECTROCHROMISM FOR THERMAL CONTROL OF SATELLITE SUBSYSTEMS
ADVANTAGES

- ELECTROCHROMIC DEVICE IS LIGHT WEIGHT, IT HAS OPTICAL MEMORY, ELECTRICALLY TUNABLE, SPECTRAL SELECTIVITY AND WIDE RANGE OF OPERATING TEMPERATURE.

- POTENTIAL REPLACEMENT FOR HEATERS, LOUVERS AND HEAT PIPES
DESCRIPTION

- AN ELECTROCHROMIC DIVICE IS A THIN FILM BATTERY CONTAINING ELECTROCHROMIC ELECTRODES SEPARATED BY A SOLID ELECTROLYTE.
- CHARGING AND DISCHARGING CHANGE THE SPECTRAL RESPONSE
- LITHIUM INSERTION INDUCES SPECTRAL RESPONSE.
FIGURE 1

SCHEMATIC OF THE ELECTROCHROMIC DEVICE

Li_xWO_3 + V_2O_5 ↔ WO_3 + Li_{y}V_2O_5

(COLORED)

(BLEACHED)
EVALUATION OF THE PROTOTYPE

- DEVICE ASSEMBLED BY NREL
- USES WO$_3$ AND V$_2$O$_5$
- PARAMETERS: SPECTRAL RANGE, MODULATION, TEMP., VOLTAGE PROFILE, AND CYCLE LIFE
FIGURE 2

VOLTMOMGRAMS OF THE ELECTROCHROMIC DEVICE
AT 22°C AT A SWEEP RATE OF 10 mV/s
FIGURE 3

TRANSMITTANCE AS A FUNCTION OF WAVELENGTH FOR THE ELECTROCHROMIC DEVICE

0.0V

1.7V for 1hr

TRANSMITTANCE (%)

WAVELENGTH (nm)
FIGURE 4
COLORING/BLEACHING SWITCHING TRANSIENTS AT 45°C
FIGURE 5

COLOR-TO-BLEACHED SWITCHING TRANSIENT AT 30°C
FIGURE 6

COLORED-TO-BLEACHED SWITCHING TIME AT 0°C
FIGURE 7

SPECTRAL RESPONSE AT 23°C IN THE COLORED STATE

(%) TRANSMITANCE

80 68 56 44 32 20 400 600 800 1000 1200 1400 nm
FIGURE 8
SPECTRAL RESPONSE AT 30°C IN THE COLORED STATE
FIGURE 10

SPECTRAL RESPONSE AT 0°C IN THE COLORED STATE

TRANSMITTANCE (%)

nm

400 600 800 1000 1200 1400

20 30 40 50 60 70
FIGURE 11

VARIATION OF TRANSMITTANCE AT A WAVELENGTH OF 610 nm
FIGURE 12

TRANSMITTANCE AT $\lambda = 700$ nm DURING REPETITIVE CYCLING AT 30°C
CONCLUSIONS

- Capable of repeated cycling
- Bleaching process
  - State is 74% and that in the bleached
  - The transmittance in the colored
- Spectral regulation in the visible

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