Development and Evaluation Framework of a Tungsten Trioxide and Nickel Oxide Electrochromic Variable Emissivity Device for Satellite Thermal Control

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In orbit, satellites experience temperatures as high as 400K and as low as 200K in orbit, necessitating a dynamic thermal control solution that ensures electronic system functionality throughout the duration of an orbital period. One potential option is discussed – the tungsten trioxide (WO₃) and nickel oxide (NiO) electrochromic variable emissivity device (VED) – as a low-cost and easily-integrated thermal control option to be applied to the surface of a 2U CubeSat in a 500-kilometer altitude low-earth orbit (LEO). Electrodeposition and chemical bath deposition of WO₃ and NiO, respectively, exhibit reliable cyclic stability and coloration ability, with more advanced film characterization and emissivity measurement techniques discussed as future work.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>a</td>
<td>albedo</td>
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<tr>
<td>α</td>
<td>absorptivity</td>
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<tr>
<td>$A_s$</td>
<td>surface area</td>
</tr>
<tr>
<td>$\beta^*$</td>
<td>critical Beta angle</td>
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<tr>
<td>$\varepsilon$</td>
<td>emissivity</td>
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<tr>
<td>$h$</td>
<td>orbit altitude</td>
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<tr>
<td>$I$</td>
<td>current</td>
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<tr>
<td>$Q_{sun,a}$</td>
<td>total heat from sun and albedo</td>
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<tr>
<td>$Q_{IR}$</td>
<td>total heat from earth’s infrared</td>
</tr>
<tr>
<td>$Q_{gen}$</td>
<td>total heat generated internally</td>
</tr>
<tr>
<td>$\dot{q}_{IR}$</td>
<td>heat flux from earth’s infrared</td>
</tr>
<tr>
<td>$\dot{q}_{sun}$</td>
<td>heat flux from sun</td>
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<tr>
<td>$R$</td>
<td>earth’s radius</td>
</tr>
<tr>
<td>$r$</td>
<td>reflectivity</td>
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<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
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<tr>
<td>$T_B$</td>
<td>blackbody temperature</td>
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<tr>
<td>$T_s$</td>
<td>surface temperature</td>
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<tr>
<td>$t$</td>
<td>transmissivity</td>
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<tr>
<td>$\tau$</td>
<td>orbit period</td>
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<tr>
<td>$V$</td>
<td>voltage</td>
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I. Introduction

Thermal control technology remains at the forefront of aerospace system development in military, scientific, and commercial disciplines: with growing efforts towards both the miniaturization and commercialization of satellite technology [1], a need for more robust and dynamic thermal control emerges to mitigate loads experienced in space [2]. All waste heat within the system – either absorbed externally from the environment or generated internally from power-dense and heat-dissipative electronics – must be rejected to regulate internal temperature, ensure electronic functionality, and extend system lifespan.

Passive thermal control options have been well-documented to achieve successful temperature regulation by radiating waste heat out into the environment. Extended surfaces like thermal fins [1], [3] or conductive honeycombs [1], [4] may be attached to the satellite or internal electronic structure as heat sinks, but may contribute to unnecessary system weight. Tailoring material finish – like adding reflective white coatings, emissive metal oxides coatings, or reflective blankets [5],[6] – offer lightweight alternatives to surface extensions, but only reflect and reject heat at discrete amounts designed for heat exchange from high-temperature to low-temperature environments.

Actively-powered, dynamic thermal management techniques have been proven to offer more flexibility in satellite mission design than their passive counterparts [1], [7]. If a satellite surface can switch between high-emissive and low-emissive states, energy can be optimized to prevent both system overheating and freezing in direct sunlight and deep space, respectively. Physical shudders like thermal louvers [1], [8] allow for variable heat exchange between reflective (shudders-closed) and emissive (shudders-open) states, but also may increase system weight, present high risk of failure, and require tailored design for each application.

With scalability in mind, a dynamically-responsive electrochromic variable emissivity device (VED) prototype is presented as a lightweight alternative to previous thermal control techniques. When deposited onto an electrically-conductive substrate, the complementary electrochromic thin film properties of WO₃ and NiO display a reversible color modulation between dark blue and dark brown to transparent, respectively. When integrated into the satellite system, the completed VED cell has a target temperature regulation range of +/- 35°C in orbit and a target emissivity range of 0.85 in the high-emissivity, colored mode and 0.3 in the low-emissivity, transparent mode.

The electrochromic thin films are deposited onto fluorine-doped tin oxide (FTO) glass slides and are assembled opposite each other, separated by a resin-printed spacer that houses a lithium perchlorate (LiClO₄) electrolyte layer suspended in a polymethyl methacrylate (PMMA) polymer matrix. A full VED cell assembly schematic is shown in Figure 1.

![Figure 1: Fully-Assembled VED Schematic](image-url)
Coloration in the VED cell results from a combination of oxidation-reduction reaction with Lithium ion intercalation. WO$_3$ colors blue on the partial oxidation of the film and Lithium ion intercalation, and NiO colors brown on the partial reduction of the film and rejection of the intercalated Lithium ions. As a result, the coloration of both films are complementary and optical densities are additive. Reversing the applied voltage polarity results in coloration loss (bleaching) of both films. The bleach-coloration states are shown in the Figure 2 schematic, with corresponding pictures of bleached and colored slides for each metal oxide.

![VED Bleach-Coloration States](image)

**Figure 2: VED Bleach-Coloration States**

II. Preliminary Thermal Analysis

For a small satellite in low-earth orbit, the expected thermal environment is modeled assuming steady state conditions and assume heat contributions from the following sources: direct sunlight, heat reflected off of earth’s surface (albedo), infrared heat emitted from earth’s surface, and heat generated internally from electronics (Figure 3). For initial temperature estimates, the model does not distinguish satellite faces, assumes a unity view factor [9], and assumes that the VED is in the high-emissive state.

The system is evaluated by applying the conservation of energy, rewriting using the Stefan-Boltzmann law, and isolating surface temperature. Direct sunlight and albedo heating are coupled as follows:

\[ Q_{sun,a} = (1 + a)\dot{q}_{sun}A_s \]  (1)

and total infrared heat is found as follows:

\[ Q_{IR} = \dot{q}_{IR}A_s \]  (2)

Total heat sources can be summed:

\[ Q_{in} = Q_{IR} + Q_{sun,a} + Q_{gen} \]  (3)

![Heat Sources Along Orbit Path](image)

**Figure 3: Heat Sources Along Orbit Path**
and total heat flux is assumed to be constant at 3W for preliminary analysis. Assuming energy is conserved, surface temperature is isolated as follows:

\[ T_s = \left( \frac{Q_{in}}{A_s \sigma \varepsilon} + T^4_H \right)^{\frac{1}{4}} \]  

(4)

The steady-state assumption – that the VED surface temperature will remain constant with respect to time – is only valid for orbit configurations with constant exposure to sunlight. The angle of the orbit plane with respect to the sunlight vector (the orbit Beta angle, Figure 4) strongly influences steady state behavior for the system. For a given orbit altitude, there exists a critical Beta angle [9] at a given orbit altitude where the satellite will spend no portion of the orbit in earth’s shadow and maintain constant exposure to sunlight. An expression for critical Beta angle can be written as follows [9]:

\[ \beta^* = \arcsin \left( \frac{R}{R + h} \right) \]  

(5)

where \( R \) represents earth’s radius at 6378 km. For an orbit at an altitude of \( h = 500 \) km, this angle is \( \beta^* \approx 68^\circ \). Figure 4 displays graphically the fraction of orbit to be spent in eclipse for a given Beta angle, whose shape is validated with similar figures in literature [9], [10].

Figure 4: Eclipse Fraction as Function of Orbit Beta Angle
III. Theory and Methods

A summary of the deposition, characterization, model validation, and calorimetric emissivity measurement methods are discussed below.

A. Thin Film Deposition and Coloration

WO₃ films are deposited through continuous voltage deposition (CVE) and NiO films are deposited through chemical bath deposition (CBD). The simple equipment requirements and manufacturing scalability lend both methods to be attractive options for low-cost deposition. The resulting films are semitransparent and diffusive.

NiO chemical bath deposition is prepared following the procedure outlined by Han et al., with modifications in the slide pre-treatment and drying procedures [11]. FTO slides are cleaned using the RCA-1 cleaning procedure [12] and placed in a 0.125M potassium persulfate (K₅S₂O₈) and 0.5M nickel(II) sulfate hexahydrate (NiSO₄•6H₂O) bath at room temperature, then stirred continuously for 20 minutes and rinsed with deionized (DI) water. Films are then annealed in steps starting at 120°C (10 minutes), increasing to 200°C (10 minutes), and holding at 300°C (90 minutes).

The WO₃ films are deposited following the method described by Vijayakumar et al., with some modifications to deposition time and drying temperatures [13]. FTO slides are cleaned using the same RCA-1 cleaning procedure, and the precursor solution uses 2.062g of Na₂WO₄•2H₂O dissolved into 250 mL of DI water. 3.06 mL of 30% hydrogen peroxide (H₂O₂) solution is pipetted into the tungstate solution and stirred for 15 minutes. The solution pH is monitored and adjusted with drops of 70% perchloric acid (HClO₄) to a pH of 1.8. Using a three-electrode setup, a constant -1V potential (versus Ag/AgCl) is applied for 200 seconds, after which the slide is rinsed in DI water and annealed at 90°C for 120 minutes. This same fixture design is used for cell coloration post-annealing within a 1.0M LiClO₄-PC electrolyte solution.

B. Sample Characterization Methods

Cyclic voltammetry via a Squidstat Plus Potentiostat is used to perform life cycle testing on individual films and evaluate ion build-up in the films over time. A three-electrode Potentiostat setup is used to isolate the working electrode from the counter electrode and changes in the solution [14], incorporating the FTO as a working electrode, platinum mesh counter electrode, and Ag/AgCl as reference electrode. Linear voltage sweeps are also performed on both WO₃ and NiO samples to evaluate coloration quality and peak redox voltages. Specifically, a positive voltage sweep (shown in Figure 3a) is used to test the coloration of the NiO film and bleaching of the WO₃ and a negative voltage sweep (shown in Figure 3b) is used to test the bleaching quality of the NiO film and coloration of the WO₃ film. Because these films are complementary, the presence of Lithium ions (negative voltage) in the WO₃ film and absence of Lithium ions (positive voltage) in the NiO film results in the colored state of the VED. Conversely, the absence of Lithium ions in the WO₃ film and presence of ions on the NiO film results in the bleached state of the VED when used in the same circuit.
Transmission testing is used to further characterize the uniformity of both films. Using an Ocean Optics Red Tide USB 650 NIR-VIS-UV spectrometer and an Ocean Optics HL-2000-LL Halogen Light Source, transmission tests are calibrated with a blank FTO slide and film transmission results are recorded at nine points at locations (Figure 4).
C. Thermal Model Validation Methods

The structure shown in Figure 5 is meshed into Thermal Desktop and used to perform numerical simulations, with steady state results validated in MATLAB, to catalog the thermal conditions of various orbits to be implemented into in-lab emissivity test set-ups. Transient system behavior is simulated in Thermal Desktop for two arbitrary Beta angles both greater than and less than the critical Beta angle, $\beta = 60^\circ$ and $\beta = 90^\circ$, to guide mission design with collaborators and the launch provider.

![Satellite Mockup, Exploded View (Panels Stowed)](image)

D. Calorimetric Thermal Vacuum Set-up

As is a standard in aerospace thermal analysis, a calorimetric thermal vacuum chamber set-up is used to measure emittance from the device [15] and evaluate VED performance in vacuum conditions. Within a 1000 sq. cm vacuum chamber, the test sample is secured to a thermal control lab heater. The sample and the heater are housed in a copper enclosure to prevent heat loss into the environment. A schematic of this setup is shown in Figure 6.

Applying a version of the conservation of energy shown in Eq. 4 but instead isolating for emissivity – with a surface temperature $T_s$ matching those of the thermal model and the blackbody temperature $T_B$ obtained from averaging the temperature readings from the thermocouples – Eq. 6 is obtained. Input energy in Eq. 3 ($Q_{in}$) is represented by the product of current ($I$, amperes) and voltage ($V$, Volts).

$$\varepsilon = \frac{IV}{\sigma A_s (T_s^4 - T_B^4)}$$

(6)
A perfect blackbody emissivity is assumed, though more realistic values of $\geq 0.95$ will be incorporated, pending blackbody foil selection inside the chamber. Zero heat loss is also assumed between the TC Lab and the sample and assume temperature perturbation from material conduction between the copper enclosure and the blackbody foil box is negligible.

IV. Preliminary Results

Qualitative deposition, optical analysis, and thermal modeling results are discussed below.

A. Thin Film Deposition Results

NiO chemical bath deposition and WO$_3$ electrodeposition results are shown in Figure 7 in their respective bleached and colored states. The films are deposited in their bleached state, colored, and bleached again (one coloration cycle) for the bleached films in Figure 7a and 7c.
In the visible spectrum, CVE has produced highly saturated coloration results and can be reversed to a uniformly clear bleached state. The chemical bath deposition results yield similarly saturated but less uniform coloration results, with a less distinct bleached state. Although not pictured, CVE also yielded consistently saturated coloration results for multiple slides in a batch.

**B. Transmission Results**

Transmission test results are shown for NiO and WO$_3$ samples in both their bleached and colored states. The bleached slide (Figure 7c) yields high – albeit somewhat nonuniform – transmission across the visible and near-infrared wavelengths (Figure 8).
When the same sample is colored (Figure 7d), transmission decreases steeply across the visible spectrum, maintaining transmission more uniformly around 18% in the near infrared wavelengths (Figure 9).

Nine-point transmission test data was limited for NiO chemical bath deposited slides, so transmission is shown only at Point 9 in Figure 10. Both bleached (Figure 10) and colored (Figure 11) yield strong positively-sloped values as wavelengths increase, a feature not shown in the WO$_3$ electrodeposited film. Notably, transmission is highest in the near-infrared wavelengths and limited in the visible spectrum, matching qualitative observations in Figure 7a.
Coloring the same NiO chemical bath sample, transmission decreases by around 20% consistently across all wavelengths (Figure 11).
C. Cyclic Voltammetry Results

Electrodeposited samples of WO₃ are evaluated for cyclic durability and potential ion build-up during repeated oxidation and reduction of the film. Results for five of these cycles are shown in Figure 12 below.

![Cyclic Voltammetry of WO₃ CVE Slide (“Geff”)](image)

The electrodeposited WO₃ slide exhibits ion build-up after the fifth cycle, but minimal build-up in the first four cycles. Similar to the WO₃ deposition, cyclic durability is evaluated for NiO chemical bath-deposited slides for 12 cycles of oxidation and reduction in Figure 13. Cycles 1 through 4 were omitted for clarity – as their results were nearly identical – and only selected cycles after Cycle 5 are shown.
D. Thermal Model Validation

Thermophysical, optical, and material properties for Al-6061 and the VED are assigned to the numerical model, including the maximum expected steady state emissivity and absorptivity of the VED surface at 0.85. Steady state simulation results are shown with a color map (Figure 14) and – by averaging resulting node temperature on the top VED surface – summarized in Table 1.

Table 1: VED Surface Temperature in Steady State

<table>
<thead>
<tr>
<th></th>
<th>Numerical</th>
<th>Analytical</th>
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<tr>
<td>370 K</td>
<td>372 K</td>
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Transient case results for the two arbitrary Beta angles (60° and 90°) illustrate an expected cyclic steady state and true steady state, respectively, in Figure 15. Notably, the 90-degree Beta angle case asymptotes around $T = \sim 378\,\text{K}$, while the 90-degree Beta angle case oscillates between 318K and 377K after four orbit cycles.
V. Discussion

A. Thin Film Deposition and Optical Analysis

Two different film deposition compounds – WO₃ and NiO – and two different deposition methods are used to best evaluate their compatibility as complimentary oxidative-reductive films in the VED assembly, not to compare emissivity modulation between the two compounds. Since the transmission results only demonstrate the deposition uniformity, more robust optical analysis will be necessary to complement calorimetric emissivity measurements in the infrared wavelengths and measure emissivity across all solar wavelengths. Based on Planck’s Radiation Law, electromagnetic radiation is emitted as a function of material, wavelength, and temperature. Assuming equilibrium conditions and normalizing by input energy, light transmitted and reflection from the film is linked to light absorbed (Eq. 6). In thermal equilibrium, energy absorbed per unit time is equal to energy emitted per unit time. Using these principles, future reflectivity and transmission measurements should be used to directly solve for emissivity in the ultraviolet, visible, near-infrared, and infrared wavelengths.

\[
\alpha + r + t = 1 \quad (6)
\]

Calibration of the spectrometer introduces some uncertainty in the transmission results (Figure 8 through Figure 11). Although the data is not displayed, transmission evaluated along the top row of the slide in Figure 8 goes beyond 100% (a theoretically-impossible value). Transmission data also exhibits noise before 490 nm and after 930 nm due to instrument limitations in wavelength range and boxcar averaging in data visualization. With these uncertainties in mind, modest uniformity is shown in the bleached WO₃, showing a difference of 20% between the highest and lowest transmission points (Figure 8). Notably, uniformity and uniformity increases as wavelength increases when the sample is colored and
exhibits lowest transmission at 18% in the near infrared range. This result is promising: since most heat generated and dissipated in the satellite structure is in the infrared wavelengths, a transmission change of around 75% would merit a large increase in absorptivity – and assuming steady state conditions, emissivity – if reflectivity is constant (Eq. 6). However, reflectivity measurements in the current ranges – visible spectrum and near-infrared – and in the infrared via Fourier Transform Infrared (FTIR) spectroscopy must be collected to ensure that reflection of the FTO slide and deposited film is sufficiently low for VED applications.

The electrodeposited WO₃ samples yield promising preliminary results for emissivity modulation within the 0.3-0.85 range, but low NiO transmission in the bleached state may inhibit low emissivity overall (Figure 10). Because the NiO component is necessary to complete the oxidation-reduction process, it is important that it yields a high transmission when bleached. Additionally, the highly saturated WO₃ electrodeposition results were replicated during Spring 2022 trials, but have yet to be replicated during Fall 2022 and Winter 2023: the user learning curve to yield deposition results should be considered if future work includes manufacturing samples in large quantities. Manufacturing the chemical bath-deposited NiO films had a similar learning curve, though the results have yet to be consistently replicated in recent trials. Strategies to improve film adhesion to the substrate are being investigated to improve the deposition reliability. Chemical bath-deposited WO₃ and electrodeposited NiO have been tested, but did not yield notable deposition results.

B. Coloration Cyclic Stability

While the electrodeposited WO₃ samples outperforms the NiO chemical bath samples in transmission, the NiO exhibited higher cyclic stability after 12 cycles (Figure 12 and Figure 13). Switching between colored and bleached states induces an ion build-up on the film, which may distort the coloration and yield unreliable emissivity results after several cycles. The thin films must be able to switch between coloration states hundreds of times to provide thermal control for the duration of a satellite lifetime. Consequently, process control techniques for both WO₃ and NiO films will need to be investigated to limit long-term ion build up.

C. Thermal Model Results and Calorimetric Testing Future Work

The current thermal modeling framework – using analytically-validated numerical models in Thermal Desktop – is suitable for verifying steady state behavior against predicted temperatures upon which more complex Thermal Desktop models can be reliably built and integrated into testing. Transient results for the two arbitrary Beta angles (60° and 90°) exhibit expected cyclic steady and true steady state behavior [9], [10].

More rigorous emissivity modulation testing of the VED in Thermal Desktop – coupled with VED placement adjustment to the opposite end of the satellite – must be done to investigate simulated thermoregulatory behavior. For in-orbit emissivity modulation, DynamicSINDA has been used to directly program property modulation as a function of time and temperature, with limited success. This work will continue to be explored in more user-friendly softwares like COMSOL that can more readily incorporate analytical equation-driven properties. These simulations will be critical to informing more rigorous emissivity testing at discrete temperatures and validating experimentally-found system behavior. Developing a reliable thermal model where orbit and material properties can be quickly changed and re-simulated will also be important, as collaborators move closer to the stage of selecting a launch provider who may dictate the chosen orbit. The computational approaches must be flexible enough to
adapt to updated orbit information, extract model behavior and temperatures of interest, and implement them in-lab as the device undergoes testing.

D. Space Qualifications

In addition to short-term future work highlighted in previous sections, longer-term work must be accomplished before launching the device into orbit. Although not discussed in detail, the lithium perchlorate gel-electrolyte layer separating each film sample is vulnerable to air leakage if not sealed properly. Implementing a low vapor pressure electrolyte with high vacuum durability – such as the $n$-butyl methyl imidazolium tetrafluoroborate (BMIM-BF4) polymer substrate [16] – would be a longer-term solution to this problem, and offers an opportunity to scale manufacturing of the proposed VED more readily.

The current deposition substrate – glass FTO slide in both depositions – suitably meet conditions required for in-lab testing, but should be replaced with a lighter, perhaps flexible conductive polymer skin to avoid adding to unnecessary payload weight and to allow for additional customization of device dimensions.

VI. Conclusion

Preliminary thermal analysis and environmental testing framework used to guide the development of a Variable Emissivity Device (VED) is presented, with promise in its ability to selectively reject waste heat from satellites. Electrodeposition and chemical bath deposition were used to deposit $\text{WO}_3$ and NiO thin films, whose preliminary optical testing yielded high transmission across the UV-VIS-NIR spectrum in the low-emissivity state ($\text{WO}_3$) and notably low transmission in the high-emissivity state yields. These preliminary optical tests achieved encouraging results that, with more thorough optical analysis, deposition process control, calorimetric emissivity testing execution, and robust error analysis, is expected to meet the goal emissivity modulation range and goal temperature modulation range.

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References


