Transparent Thermochromic Smart Window Film

Argonne National Lab
Jie Li, Principal chemical engineer
jieli@anl.gov, 630-252-8656
Project Summary

Timeline:
Start date: April 1, 2019
Planned end date: March 31, 2022
Key Milestones
1. Achieved ultra-small M-phase VO2 (<50 nm) via flow synthesis; Feb. 2020
2. Demonstrated VO2/PVB smart film; April 2021

Budget:
Total Project $ to Date:
• DOE: $1,114k
• Cost Share: $248k

Total Project $:
• DOE: $1,492k
• Cost Share: $373k

Key Partners:
Florida A&M university
University of Chicago
Lawrence Berkley National Lab
National Renewable Energy Lab

Project Outcome:
This project is to develop advanced energy-efficiency and low-cost VO2 based thermochromic window film by using theoretical simulation and design of films; 2) scalable liquid-phase flow synthesis of M-phase VO2 nanoparticles; and 3) scattering-controlled composite thin film manufacturing.

We have successfully accomplished film designs, synthesized M-VO2 with diameter down to 13 nm and demonstrated refractive match coating. The smart film optimum study is under progress. One (1) patent pending, two (2) software and five (5) papers
### Team

<table>
<thead>
<tr>
<th>Dr. Jie Li, PI, Principal Chemical Engineer (ANL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expert in advanced materials and process technology, Lead the project and contribute VO2 nanoparticle synthesis using continuous flow hydrothermal reactor, prepare and characterizations of smart films</td>
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<table>
<thead>
<tr>
<th>Dr. Ralph T. Muehleisen, Co-PI, Principal Building Scientist (ANL)</th>
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</thead>
<tbody>
<tr>
<td>Expert in building science, thermodynamics, and metamaterials for acoustics and vibration. Provide leadership and technical to market guidance as well as knowledge of building construction and performance requirements.</td>
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<table>
<thead>
<tr>
<th>Dr. Bayaner Arigong, Co-PI, Assistant Professor (FAMU)</th>
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<tr>
<td>Arigong is an expert in applied electromagnetic device and transformation optics design, will bring the skills for smart film design including nanocomposite film and metasurface design.</td>
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<thead>
<tr>
<th>Dr. Matthew Tirrell, Co-PI, Dean and Professor (UC)</th>
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<tbody>
<tr>
<td>Expert in creating novel, functional self-assembled structures focusing on tailored nanomaterials. Contribute to scattering control at VO2/polymer interface in the composite film via refractive index match coating</td>
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<thead>
<tr>
<th>Dr. Charlie Ćurčija, Co-PI, Scientist V (LBNL)</th>
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<tbody>
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<td>Expert and leading scientist in the R&amp;D of thermal and optical performance of windows, Provide guidance on the project, contribute energy calculations and characterization of film performance</td>
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<tr>
<th>Dr. Robert Tenent, Material Scientist V (NREL)</th>
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<tr>
<td>Expert in development of new materials for improved electrochemical devices with focus on cost-effective, manufacturing friendly methods for the production of materials for both energy generation (PV) and efficiency (smart windows). Contribute to new film ageing test to the ASTM Standards</td>
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### Team

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<thead>
<tr>
<th>Name</th>
<th>Position/Institution</th>
<th>Expertise</th>
<th>Collaborations</th>
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<tbody>
<tr>
<td><strong>Cathy Milostan, Market &amp; Technology Development Analyst</strong></td>
<td>U.S. DEPARTMENT OF ENERGY - OFFICE OF ENERGY EFFICIENCY &amp; RENEWABLE ENERGY</td>
<td>Expert in techno-economic analysis, market assessment, and business development. Work with team on TEA and with Dr. Muehleisen on finding investment and industry partners.</td>
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<tr>
<td><strong>Dr. Wei Chen, Chemist, (UC/ANL)</strong></td>
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<td>Expert in synthesis of polymeric materials with well-defined molecular weight, microstructure, and functional group; Contribute to functionally graded nano-coatings for engineered VO2/polymer interface for scattering control.</td>
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<td><strong>Jacob Jonsson, Principal Scientific Engineering Associate (LBNL)</strong></td>
<td></td>
<td>Expert in fenestration optical properties measurement, including solar spectral transmittance, reflectance, as well as complete bi-directional scattering distribution. Contribute on film optical performance characterizations.</td>
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<tr>
<td><strong>Dr. Kowsalya Rasamani, Postdoctoral researcher (ANL)</strong></td>
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<td>Expert in nano-material synthesis, characterizations. Work with Jie Li on VO2 nanoparticles synthesis, smart film preparation and optical characterizations.</td>
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<tr>
<td><strong>Dr. Kai Mai Tran, Research Aide (Rice University)</strong></td>
<td></td>
<td>Expert in nano-material synthesis, characterizations. Work with Jie Li on high-throughput synthesis of VO2 nanoparticles and material characterizations.</td>
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<tr>
<td><strong>Dr. Sovan Banerjee, Postdoctoral Researcher (UC)</strong></td>
<td></td>
<td>Expert in block copolymer synthesis, surface coatings, and characterizations. Work with Matt/Wei on GCP synthesis, core-shell coating, and smart film preparation/characterizations.</td>
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<tr>
<td><strong>Elizabeth Rasmussen, Research Aide (University of Washington)</strong></td>
<td></td>
<td>Expert in flow synthesis of MOF materials under supercritical CO2, computer simulation of supercritical fluids. Work with Jie Li on high-throughput flow synthesis of VO2 nanoparticles and VO2 particle characterizations.</td>
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Advanced windows technologies are required to reduce ~30% energy loss. Existing dynamic window film technologies (including electrochromic, thermochromatic) have the potential, but are too costly to be widely acceptable.
Concept: VO2 Nanocomposite Thermochromic Window Film

How it works

Advantages

- Switch adaptively & automatically depending on temperature (passive)
- Always allow visible light in
- Save both heating & cooling energy, >18% annually
- NanoVO2 enables high solar energy modulation and visible light transmittance
- Potentially more economic and affordable due to single active layer structure
Challenge - State of the Art & Technical Gaps

State of the Art

- **Nanoparticle film** emerges as a breakthrough thermochromic film tech which outperforms conventional bulk film in IR control (Figure left and image right).
- **Nanocomposite film** shows the best performance versus other material options (figure left upper).

Technical Gaps

- But **conflict** exists between $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$.
- To have high performance smart film, **ultra-small (<50 nm) M-phase** VO2 nanoparticles are required.\(^2\)
- NanoVO2 synthesized mostly by the batch reactor method is expensive, poor in quality control with **limited scalability**.\(^3\)

> Need economic/reliable nanoparticle/film technology


\(^3\): $5.67/g (NN1918 Nano Vanadium Oxide (VO2) Powder from Stanford Advanced Materials, 2020.

Our Approach & Objective

Enable a new generation of smart, high-efficient, low-cost *thermochromic* dynamic window films

- **Approach I:** Use the computational method, rather than “trial-and-error”, to design/optimize high-performance transparent VO2/polymer films

- **Approach II:** Demonstrate ultra-small (M) phase VO2 nanoparticles with average diameter < 50nm by developing a rapid scalable continuous flow hydrothermal (CFHT) synthesis, rather than using autoclave, that can synthesize high quality material at reduced product cost

- **Approach III:** Use RI-matching coating of VO2 to simultaneously enhance visible light transmittance and solar energy modulation

- **Objective:** Fabricate reliable and repeatable composite films satisfying ASTM E3119/20-17 with $T_{\text{lum}} > 50\%$, $\Delta T_{\text{sol}} > 15\sim 40\%$ and $T_{\text{conv}} \sim 35^\circ\text{C}$
Approach I: Theory Analysis

Smart Film – Modeling Theory
-- towards ideal solar modulation and light transmission

\[
\begin{align*}
\text{Air} & \quad \text{VO2} \quad \text{Substrate} \quad \text{Air} \\
\theta_0 = 90^\circ & \quad d_1 \quad d_2 \quad \theta_i = 90^\circ \\
N_0 & \quad N_1 \quad N_2 \quad N_i \\
\text{outer layer} & \quad \text{layer 1} \quad \text{layer 2} \quad \text{inner layer}
\end{align*}
\]

The total reflection and transmission coefficients:
\[
\begin{bmatrix}
1 \\
0
\end{bmatrix}
= M_{d_1} \cdot N_1 \cdot M_{d_2} \cdot N_2 \cdot M_{d_2} 
\]

\[
\begin{bmatrix}
1 \\
0
\end{bmatrix}
= \begin{bmatrix}
\frac{1}{s_j} \\
\frac{1}{s_i}
\end{bmatrix} \cdot N_j \cdot \begin{bmatrix}
\Delta_p(d_i) \\
0
\end{bmatrix} \cdot \begin{bmatrix}
\frac{1}{s_j} \\
\frac{1}{s_i}
\end{bmatrix}
\]

\[
\Delta_p(d_i) = \frac{N_i - N_j}{N_i + N_j} \cdot \exp \left( \frac{2 \pi N_i d_i}{\lambda} \right)
\]

The total reflection and transmission:
\[
R = r_{0i} \cdot r_{0i}^* , \quad T = \frac{N_i}{N_0} \cdot t_{0i} \cdot t_{0i}^*
\]

\[
\text{ideal}
\]

\[\text{State-of-the-art technique}\]

\[
\text{Solar modulation} (\%) = \frac{\text{Luminous transmission in metal-phase} (\%)}{100}
\]

Approach II: Material Synthesis (ANL)

Motivation: Nanomaterial is expensive! Developing a rapid, scalable modern flow synthesis method using (cheap) water as the solvent is the key to achieve low-cost VO₂ & smart film.


Continuous Flow Hydrothermal (CFHT) Reaction under Supercritical H2O

Uniqueness
- Ultrafast reaction (sec. vs days)
- One-step synthesis of crystal structures (no annealing needed)
- Low-dielectric SC water being particularly suited for (high-quality nanomaterials)
  1. making ultra-small oxide (VO₂) nanoparticles (<50 nm)
  2. coating organic ligands
  3. easing particles separation
- Rapidly heating/cooling (for nano VO2)
- Simple, “green”, fast and scalable process without CO₂ emission
- Feasible automation via ML/AI
Approach III: Controlling VO$_2$/polymer interface scattering (UC)

### Problem:
Trade-off between visible light transmittance ~ solar energy modulation

### Our solution:
- Design & coat a low-refractive-index (RI 1.3) Gradient Copolymers (GCP) on VO$_2$ particles (RI 3.0) for effective RI to match RI (1.5) of matrix polymer*

\[
\frac{I}{I_0} \approx e^{-3V_p x r^3 \left(\frac{n_p}{n_m} - 1\right)}
\]

- Apply low refractive index fluorinated polymer (RI ~ 1.33 – 1.4)
- Assume spherical VO$_2$ nanoparticles diameter = 50 nm
- Resulting in thickness of grafted polymers is ~ 40 nm.
- Increase compatibility by mixing fluorinated and PMMA with ratio of ~40 – 50% (Note: RI of PMMA ~1.49 and VO$_2$ ~3.0)

*Our method: Gradient copolymers of poly(methyl methacrylate) (PMMA) and low-refractive-index poly(perfluoroalkyl methacrylate) (P13FOMA) are identified as a candidate of the VO$_2$ nanoparticle surface coating.

- Chemical compositions of the copolymer and property of each segment
A successful project enables

1. **optimum design** of VO2/polymer composite films with highest solar modulation, guiding film preparation.

2. A “green” and scalable **continuous flow hydrothermal (CFHT) process** under supercritical water, rather than a batch autoclave, that can rapidly (seconds vs days) manufacture target ultrasmall(<50 nm) m-phase VO2 nanoparticles at low cost;

3. A demonstrated **thermochromic film** with $T_{lum} > 50\%$ and $\Delta T_{sol} > 15\text{~}40\%$ made by a scalable slot-die coater. (with controlled haze,<1% and $T_{conv.}$)

4. A new TC film product with cost controlled $< 12/ft^2$

5. **>18\%** heating/cooling energy saving annually

6. **Two patents, two software and 4~5 publications**
Impacts – Techno-Economic Analysis

Societal Impact:
• Greater energy efficiency (EE) (>18% annual heating/cooling savings) by reducing energy loss from windows to support net zero energy buildings and global mandates for de-carbonization.

Technology & Market Impact:
• Technology competitive advantages: higher visibility plus dynamic energy savings at lower cost (< $12/ft²) than low-e films (~$15/ft²) and current thermochromic films (~$30-$50/ft²).
• Building owners & consumers: lower costs for shorter paybacks than low-e films (low-e films re-install issues & longer paybacks, especially in northern climates).
• Window film vendors & manufacturers: opportunities to enhance solar films with more heat reduction & visible light transmission (3M Prestige50(50% VLT) & Night Vision(15%-35% VLT)).

Value Proposition:
Argonne used nano technology to develop thermochromic smart window films with higher transparency & greater reduction in winter heat loss/summer heat gain (at a lower cost than ‘low-e’ window films) to deliver >18% annual heating/cooling energy cost savings for building owners & consumers.
Progress I: Theory Analysis (Composite film & design tool)

- **Modeling theory** is developed to characterize the optical property of smart film composed of VO2 nanoparticles
- **Optimization algorithm** is developed to improve the solar modulation and transmission
- **Two publications**: 1 journal paper (Applied Physical Lett.) 2 conference paper (CLEO)
- **Design tool** is developed for film performance analysis
- **Software** has been compiled to calculate optical properties.
- **More options** applying different methods will be integrated
Energy savings by climate and thermochromic parameters

- Range of potential thermochromic parameters:
  - Glazing configurations: 5
  - Dark state transmittance: 4
  - Light state transmittance: 3
  - Transition temperature: 4
  - Climates: 5
  - Orientations: 4
  - Lighting controls: 2
  - Surface number: 2
  - Total runs: 19,200 plus 200 baseline runs for comparison

- 3 separate sets of surface plots showing total energy consumption and energy savings:
  - \( T_{\text{sol}}(\text{low}) \) vs Transition Temperature
  - \( T_{\text{sol}}(\text{hi}) \) vs Transition Temperature
  - \( T_{\text{sol}}(\text{low}) \) vs \( T_{\text{sol}}(\text{hi}) \)
Impact of COVID 19 on experiment work ……

- **Experimental work** has been significantly affected by COVID-19 locking down, we have no or limited access to the Lab.

- We have been managing to generate as much data as possible.

- Most work focused on **VO2 nanoparticle synthesis**, and **smart film research** started from January 2021.
Demonstrated it is feasible to obtain high-quality of 1) uniform and 2) small (<50 nm) and 3) M-VO2 using our CFHT tech.

240 bar@450°C, 1 L precursor feed in 30 mL/min, 130 ml/min SC water(75% pulsar)

Averaged particle size via DLS: 36-42nm

Plot shows we created primarily M-VO2, where 5.5L & 3.5L solutions have peaks that match M1&M3, not A&B
Progress II: Optical Performance (Pristine VO2@PVB films)

✓ Optimum solar modulation exists in certain domain of 1) film thickness and 2) VO2 load, which depends on VO2/polymer interface.

(A) Transmittance (%)

- 23 °C
- 90 °C (dropcasted on coverslip)
- 86 μm film thickness

Solar modulation @1200 nm : 22.4 %

Wavelength (nm)

(B) Transmittance (%)

- CFHR-VO2
- (dropcasted on coverslip)
- 134 μm film thickness
- 23 °C
- 90 °C

Solar modulation @1200 nm : 20.9 %
Progress II: Applying Capping Method (Adding More Functions)

1) DECANOIC ACID (DA) CAPPING

- VO2 diameter 13 nm (>99.9%)
- Precursor concentration: 0.0356M
- Using higher conc. to increase yield

2) CTAB CAPPING

- VO2 diameter 33 nm (>97.8%)
- Precursor concentration: 0.0356M
- Stable for multiple days

Particles migrate from H2O into hexane
Progress III: Synthesis of GCP & GPC Characterization

 ✓ Method: Ruthenium Catalyzed Living Radical Polymerization Reaction

- Ethyl α-chlorophenyl acetate
- PMMA-grad-P13FOMA
- PMMA-grad-P13FOMA-block-PMOS
- Core-shelled PMMA-grad-P13FOMA-block-PMOS coated SiO₂@VO₂
Progress III: RI-match performance of GCP-Coated VO₂/PMMA Films

Parametric studies of varying GCP-coated VO₂@SiO₂ particle concentrations & coating thickness
✓ confirms that GCP coating efficiently matches the RI of the VO₂ particles with dispersion matrix ~range=1.55-1.60.

TEM of GCP coated VO₂@SiO₂

A. PMMA (Mn 1,20,000 g/mol, 687 nm thickness)
B. PMMA+GCP 41 (710 nm)
C. PMMA+VO₂@SiO₂ CFHR (10 wt% loading, 710 nm)
D. PMMA+VO₂@SiO₂ CFHR (10 wt% loading, 690 nm) + GCP

**Papers (5):**

- Banerjee et al., “VO2/polymer Based Smart Inorganic Hybrid Thermochromic Window Coating: Design Strategy, Recent Progress and Future Prospect”, in preparation for *Progress in Polymer Science*.
- Banerjee et al., “Match Refractive Index of VO2 Nanoparticles with PMMA matric using Fluorinated Gradient Copolymers”, in preparation for *Polymer Chemistry*.

**Software (2):**

1) Optical design of nanocomposite thermochromic films (Frank, Bayaner, 2020); 2) Energy calculation of thermochromic films (Curcija, LBNL, May 2021)

**Presentations (3):**


**Awards (2):**

- 2nd Prize, Oak Ridge Chapter of *ASM Annual Student Poster Competition*, Undergraduate Division (Jackson Spurling);
- 3rd Prize, *Materials Science & Technology Conference* Student Poster Competition, Undergraduate Division (Jackson Spurling)
Remaining Work: Film optimization + scale-up

1. Correlate theory and experiment and optimize solar modulation using **inverse design**

2. **Increase solar modulation** by using **surface modified VO\textsubscript{2}** by organic ligands;

3. **Reduce VO\textsubscript{2} conversion temperature** and **control film color** by doping element (W, Mg, Sn, 68\(^\circ\)C to 35\(^\circ\)C);

4. Conduct **optical** (LBNL) and **ageing tests** (NREL) of smart films to Standard ASTM E3119/20-17 to confirm suitability/durability of PVB matrix and PET substrate materials;

5. Finalize **energy saving calculations** of our final TC films using LBNL newly developed software.

**DA-CAPPED VO\textsubscript{2} FILM shows improved transparency.** Its optical modulation is under investigation.
Stakeholder Engagement (Project is in Mid-Stage)

- **Stage:** Project is in the *middle* stage of development
- **Scale-up:** Talked with *Corning Advanced Flow reactor* for material process scale-out/up
- **Pilot:** Coordinating with *Cardinal Coated Glass and 3M* to enable large area of smart film by conducting the pilot and commercial scale roll-to-roll film preparation using their exiting coaters and characterize film performance during the maturation stage to expedite development;
- **Field testing:** *Franklin Energy/Argonne Lab* will be willing to support for field test and demonstration
- **Techno-economic analysis (TEA):** continuing TEA with experimental data & customer discovery to identify market growth, competitive niches, early adopters & beta testers
- **DOE TCF** is supporting on process scale-up to manufacture enough VO2 materials for making large area of smart films
Thank You

Argonne National Lab
Jie Li, Principal chemical engineer
jieli@anl.gov, 630-252-8656
REFERENCE SLIDES
Project Budget

Project Budget: $1,492,026 for FY19 - FY22.
Variances: No budget variances
Cost to Date: $1,114,00 (75%)
Additional Funding: $250k TCF from OTT/DOE

<table>
<thead>
<tr>
<th>Budget History</th>
<th>Apr. 2019 – FY 2020 (past)</th>
<th>FY 2021 (current)</th>
<th>FY 2022 – Apr. 2022 (planned)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Cost-share</td>
<td>725k</td>
<td>181k</td>
<td>420k</td>
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<tr>
<td>DOE Cost-share</td>
<td></td>
<td>105k</td>
<td>347k</td>
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<tr>
<td>Cost-share</td>
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<td>87k</td>
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# Project Plan and Schedule

## Project Schedule

**Project Start:** April 2019  
**Projected End:** April 2022

<table>
<thead>
<tr>
<th>Task</th>
<th>FY2019-20</th>
<th>FY2020</th>
<th>FY2021</th>
<th>FY2022</th>
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<tbody>
<tr>
<td><strong>Past Work</strong></td>
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<tr>
<td>T1 Ultra-small VO2 nanoparticle synthesis: - Average VO2 diameter &lt;50 nm</td>
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<tr>
<td>T2 Theory for cloaking VO2</td>
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<td>T3 Energy modeling</td>
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<td>T4 VO2/Polymer composite film ---LT&gt;60%; Tsol &gt; 15% ~ 40%</td>
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<tr>
<td>T5 Milestone: VO2@matrix RI matchingcoating</td>
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<tr>
<td><strong>Current/Future Work</strong></td>
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<tr>
<td>T6 Film optimization via surface coating</td>
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<tr>
<td>T7 tuning film color@ conv. temp. via doping</td>
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<tr>
<td>T8 Film performance@ageing test</td>
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<tr>
<td>T9 T2M activities</td>
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- **Completed Work**
- **Active Task (in progress work)**
- **Milestone/Deliverable (Originally Planned) use missed**
- **Milestone/Deliverable (Actual) use when met on time**