SAND2018-0802R

REPORT SUMMARY TEMPLATE

Directions: Fill in the below. Submission must be a minimum of 3 to maximum of 5 pages in length.

1. **Project Title / Sub-program:** High Performance Reduction/Oxidation Metal Oxides for Thermochemical Energy Storage (PROMOTES) / CSP

2. **FOA / Award** #: ELEMENTS / DE-FOA-0000805

3. **Principal investigator:** Andrea Ambrosini, Sandia National Laboratories
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4. **Other Participating Organizations:**
Georgia Institute of Technology: Prof. Peter Loutzenhiser, Prof. Sheldon Jeter
Arizona State University: Dr. Ellen Stechel
King Saud University: Prof. Hany Al-Ansary

5. **Project Schedule:**
    1. Initiation Date: June 6, 2014
    2. Dates of Intermediate Phase Completions or Go/No-Go Points
    3. Expected Completion Date (Original and Current Plan, if different): April 30, 2018 (Original: May 31, 2017)

6. Project Scope:

Thermochemical energy storage (TCES) offers the potential for greatly increased storage density relative to sensible-only energy storage. Moreover, heat may be stored indefinitely in the form of chemical bonds via TCES, accessed upon demand, and converted to heat at temperatures significantly higher than current solar thermal electricity production technology and is therefore well-suited to more efficient high-temperature power cycles. However, this potential has yet to be realized as no current TCES system satisfies all requirements. This project involves the design, development, and demonstration of a robust and innovative storage cycle based on redox-active metal oxides that are Mixed Ionic-Electronic Conductors (MIECs). We will develop, characterize, and demonstrate a first of its kind 100kWth particle-based TCES system for direct integration with combined-cycle Air Brayton based on the endothermic reduction and exothermic reoxidation of MIECs. Air Brayton cycles require temperatures in the range of 1000-1230 °C for smaller axial flow turbines and are therefore inaccessible to all but the most robust storage solutions such as metal oxides. The choice of MIECs, with exceptional tunability and stability over the specified operating conditions allows us to optimally target this high impact cycle and to introduce the innovation of directly driving the turbine with the reacting/heat recovery fluid. The potential for high temperature thermal storage has direct bearing on next-gen CSP, and an appropriate investment for SETO.

Summary of technical targets and technical innovations that address them.

Area of Focus	How the Project Team Will Fulfill the Focus Area Intent
Maximize Efficiency	MIEC exhibits reversible and deep reduction with fast kinetics yielding high first-law energy recovery. High temperature reoxidation allows for high second law efficiency.
Process Eng.	The process is simple and directly coupled to the Air Brayton cycle, thereby minimizing losses.
Reactor Engineering	Reactors directly coupled to solar input and power cycle and leverage the existing design and operational experience. Heterogeneous reactions with air and O_2 simplify product separation.
Heat and Mass Transfer	Energy efficient particle conveyance. Heat transfer fluid (air) used directly in the reoxidation reactor and in the power cycle, creating direct-contact heat exchange with storage medium.
Catalysis	No catalysts are required to effect the redox reaction for TCES.
Modeling	Includes system-level techno-economics, reactors (thermodynamic, macro/micro heat & mass transfer, structural), multi-phase CFD, optical ray-tracing, etc. Validation via on-sun/lab testing.
Materials	MIECs are highly tunable, robust, and proven under extreme conditions. They are not corrosive, toxic, flammable, or volatile. A very attractive baseline is in hand.
On-Sun Testing	The team will utilize GIT’s $5kW_{th}$ solar simulator, Sandia’s $16kW_{th}$ solar furnace and King Saud University’s $300kW_{th}$ solar tower to test, validate, and demonstrate materials/designs.

7. Project Goals:

The project is organized around three principal technical program elements: 1) Materials, 2) Reactors, and 3) Systems Integration. The Materials element includes design and synthesis, characterization and optimization, and demonstration. The Reactors element includes engineering development and design for the two principle operational units: solar reduction and subsequent reoxidation/heat recovery from the oxide. The third element views the System Integration as a whole and links the Materials and Reactors elements to the rest of the system and includes system analysis and engineering tasks related to the balance of system. The goal of the project is to demonstrate a particle system with high energy density thermal storage (1500 kJ/kg) at high temperatures (1200 °C), at an economical cost (\$15/kWh$_t$).

8. Project Objectives:

Project Work Plan:

Materials Development and Model Formation: MIEC metal oxides will be investigated to develop improved TCES materials. A systematic, tiered-approach and successive down-selection will be used to guide the development and choice of a material for the project demonstration. The metrics include the storage capacity and available temperature of the heat, reaction kinetics, cost, and durability. In addition to standard approaches, instrumentation and advanced techniques will be developed and refined to support the materials development effort and to provide high quality data for engineering model development and validation. This includes a stagnation flow reactor coupled to a high flux solar simulator. Storage solutions for the high temperature oxides will be evaluated and initial models of the whole system will be developed to help guide the final selection of state conditions.

Materials Optimization and Mid-Scale Development: Promising materials will be subjected to more detailed laboratory characterization, including thermodynamic quantification, performance under high flux conditions, kinetics and heat transfer measurements, and sintering determination. Quantitative data for the materials will be used to develop the thermodynamic and kinetic models necessary for reactor design. The performance of the materials in the Solar Receiver Reduction Reactor (SR3) prototype will be quantified at laboratory scale and high flux conditions. Reoxidation behavior will be modeled and verified using a laboratory scale system (ROx). System level modeling will continually incorporate all subsystem refinements and determine system level impacts and negotiate tradeoffs as needed.

Validation of technology and path to commercialization: Validation of the SR3 and ROx concepts are important steps to substantiate the PROMOTES concept, to provide data to inform scale-up of the system as a whole, and to underpin the techno-economic models which are necessary to confirm that the goal of < \$15/kWh$_t$ storage costs is achievable. Demonstrating the reduction reaction on-sun at reasonable scale (100 kW$_t$) on-sun is a necessary step in the path to commercialization.

Key Equipment and Facilities: **Sandia** operates the National Solar Thermal Test Facility (NSTTF), where particle receiver concepts are under investigation (Ho, et al). Materials capabilities at Sandia include: synthesis, simultaneous TGA/DTA/DSC, scanning electron microscopy, elemental analysis, powder x-ray diffraction, and thermal conductivity analysis. High-performance computing resources are available for detailed computational fluid dynamics modeling of complex, coupled processes. **Georgia Tech** will utilize the High Flux Solar Simulator (HFSS) which provides an external source of intense thermal radiation closely approximating the heat transfer characteristics of highly concentrating solar systems, and allows for the reproducible experimentation essential for the development of the solar thermochemical technologies. **King Saud University (KSU)** recently constructed a 300-kW$_{th}$ central receiver test facility. As the first facility designed specifically for testing solid particle receiver concepts and associated thermal energy storage, it will provide unique test capabilities for intermediate scale component testing. **Arizona State University** identifies and solves key project risks, including technical, execution, staffing, infrastructure, and stakeholder risk.

9. Project Organization and Responsibilities:

We are currently working with CoorsTek, Inc. on particle scale-up and development.

10. The Challenges:

The most innovative aspects of the proposed effort also embody the most risk. The most significant technical risk is that suitable redox-active materials satisfying the thermodynamic, kinetic, and transport metrics will remain elusive. Additionally, the dynamic and extreme environment to which the MIECs will be exposed creates the potential for materials to degrade or fail before reaching time-on-stream requirements. These risks are mitigated by a materials development effort constructed around making modifications to an attractive and stable material previously identified and characterized by members of the team. Regarding the solar receiver, the risk is minimized by leveraging the team's previous efforts, providing not only experience and a technical base. While the ROx reactor is unique, we will generate and utilize computational methods that span from high-fidelity simulations to parametric optimizations to identify the appropriate design space, and then use bench scale testing to quantify the performance in that design space.

11. Milestone Status:

The majority of Milestones have been met or are on course to do so. Key results include the identification and synthesis of a material that meets the project metrics, the construction of the stagnation flow reactor to evaluate materials, design of a storage bin, the design and construction of bench-scale SR3 and ROx reactors to characterize the reduction-reoxidation performance of the reactive particles, extensive modeling and validation of thermodynamics, transient heat transfer, particle flow, oxidation kinetics, and increasingly sophisticated systems with techno-economic analyses based on the results of the modeling and characterization mentioned above. Several more recent advances are listed in Section 13.

However, several challenges have also resulted in delays or pivots on Milestones. These include:

- Particle scale-up for the SR3 demonstration proved more expensive and complicated than anticipated. This was due in part to the difficulty in finding a supplier to synthesize a custom composition (CAM28) in the quantity required and within budget—250 kg seems too large for an experimental batch but too small for most companies to justify the effort. Successful negotiations with CoorsTek have put the effort back on track, but the delays have resulted in missed (delayed) milestones, such as final SR3 reactor design and technoeconomic analysis, and necessitated a no-cost extension of the PoP to Apr 30, 2018.
- The ultra-fast reoxidation of the working material hindered attempts to quantitatively characterize the reduction kinetics of the oxide on-schedule or on-budget. That Task and Milestone (3.3) were thus eliminated.
- ES&H and design considerations regarding testing the ROx reactor under pressure would have resulted in unacceptable delays and cost overrun. Task/Milestone 2.5 was modified to test at ambient instead and use the data obtained in a validated model to predict performance at increased pressures.

12. Scalability / Replicability / Impact:

Robust techno-economic and systems analyses have been an integrated part of this project from the beginning. This involves the systematic exploration of the dynamic inter-relation between component and system designs, operating conditions, mass and energy flows, and normalized costs, in order to identify the most impactful opportunities and enablers for materials, components and operating parameters. Patents (pending award) were filed regarding the materials of interest and TCES technology, thus protecting the financial investments of potential commercial partners.

Upon the conclusion of this project, activities requiring attention for scaling will include commercial solutions for removing and reintroducing the air from the Brayton power cycle. MIEC production scale-up will require development to the quantities required for a large CSP plant. This chemical engineering challenge can leverage the capabilities of existing metal oxide industry and apply them to these specific materials. Finally, commercialization will require resizing and optimization of vessel designs, process flows, and the receiver. These efforts will be adaptations of the developed technology and will be significantly de-risked by the proven performance and the materials and process characterization resulting from the research. A major challenge remains economic uncertainty surrounding widespread deployment of CSP, particularly in the US, and the adoption of air Brayton as a power cycle for future plants.

13. Project Results:

1. Major recent accomplishments

- Identified high-performing oxide at T > 1000 °C ($CaAl_{0.2}Mn_{0.8}O_{3-\delta}$, “CAM28”)
- Demonstrated particle-fluid reactor/heat exchanger operation at the lab scale

- Coupled reactive CFD model with optimization algorithms to optimize performance of ROx as a function of geometry, flow rates, particle thermodynamics, and inlet state points over a range of scenarios and scales
- Developed novel solar thermochemical inclined granular-flow reactor (STINGR) concept for reduction of reactive metal oxides
- Developed design-stage heat and mass transfer model for 5 kW_{th} STINGR using Co_3O_4/CoO binary metal oxide energy storage media to validate, then applied to CAM28 particles
- Designed 100 kW_{th} scale STINGR with a 6-petal secondary concentrator for experimentation with CAM28 particles at the King Saud University heliostat field
- Techno-economic analysis identified a path to \$0.06/kWh LCOE and to < \$15/kWh_{th} storage

2. Up to 5 of the most recent, significant publications and a short description of the significance

- Schrader, A. J.; De Dominicis, G.; Schieber, G. L.; Loutzenhiser, P. G., "Solar electricity via an Air Brayton cycle with an integrated two-step thermochemical cycle for heat storage based on Co_3O_4/CoO redox reactions III: Solar thermochemical reactor design and modeling." *Sol. Energy* **2017,** *150*, 584.
  - *Detailed mass and heat transfer analysis for a 5 kW(th) scale prototype*
- Evan Bush, H.; Schlichting, K.-P.; Gill, R. J.; Jeter, S. M.; Loutzenhiser, P. G., "Design and Characterization of a Novel Upward Flow Reactor for the Study of High-Temperature Thermal Reduction for Solar-Driven Processes." *J. Sol. Sci. Eng.* **2017,** *139* (5), 051004.
  - *Development of upward flow reactor for particle characterization*
- Babiniec, S. M.; Coker, E. N.; Miller, J. E.; Ambrosini, A., "Doped calcium manganites for advanced high-temperature thermochemical energy storage." *Inter J Energy Res* **2016,** *40* (2), 280.
  - *New material outperforms any reported oxide TCES material operating above 1000 °C*
- Miller, J. E.; Ambrosini, A.; Babiniec, S. M.; Coker, E. N.; Ho, C. K.; Al-Ansary, H.; Jeter, S. M.; Loutzenhiser, P. G.; Johnson, N. G.; Stechel, E. B. "High Performance Reduction/Oxidation Metal Oxides for Thermochemical Energy Storage (PROMOTES)." In *Proceedings of the ASME 10th International Conference on Energy Sustainability*, ASME 10th International Conference on Energy Sustainability, Charlotte, NC, JUN 26-30, 2016; Amer Soc Mechanical Engineers: Charlotte, NC, 2016.
  - *Overview of PROMOTES project*
- Schrader, A. J.; Muroyama, A. P.; Loutzenhiser, P. G., "Solar electricity via an Air Brayton cycle with an integrated two-step thermochemical cycle for heat storage based on Co_3O_4/CoO redox reactions: Thermodynamic analysis." *Sol Energy* **2015,** *118*, 485.
  - *Thermodynamic analysis of TCES cycle efficiency*

3. Any relevant intellectual property to emerge from the project

Full Inventor List	**Patent Title**	**Date Filed**	**Appl. #**
A. Ambrosini, J.E. Miller, D.D. Gill	Thermal Energy Storage and Power Generation Systems and Methods	9/4/2015	14846201
P. Loutzenhiser and S. Jeter	An Air Brayton Cycle Integrated with Solar Thermochemical Storage	3/10/2015	62130,847 (provisional)
S. M. Babiniec, E. N. Coker, J. E. Miller, A. Ambrosini	Redox-Active Oxide Materials for Thermal Energy Storage	6/1/2016	15170314

14. Budget Tables:

The Project has seen several cost variances and modifications as it has progressed over the last three years. Many of these modifications were made during SOPO negotiations between Budget Years. The Milestone changes are described above in Sect. 11. Prolonged SOPO negotiations of several months between Phases 1-2 and 2-3 resulted in an extended PoP and a budget shortfall in Phase 3; the budget was augmented by DOE by \$80k to compensate. Personnel changes included the departure of two PIs over the course of the project; this resulted in some transitions but did not impact program Milestones.

Total Project Funding by Source:

- DOE - \$3,450,000
- Cost Share (In Kind) – \$909,793

Total - \$\$4,359,793

Quantity of Work (Person-Months):

PI – 19.81 person-months

Other SNL personnel – 52.90 person-months

Sub-awardees – 49.56 person-months (estimated, including in-kind cost share, if any)

- ASU – 6.51 person-months (estimated)
- GA Tech – 25.25 person-months (estimated)
- King Saud University – 17.80 person-months (estimated)

III. Spending Summary by Budget Category

	Approved Budget per SF-424A					
Budget Categories per SF-424a	**BP 1**	**BP 2**	**BP 3**	**Total**	**Cumulative Costs**	**% of Original Plan**
a. Personnel	\$309,758	\$415,927	\$126,817	\$852,502	\$998,563	117%
b. Fringe Benefits				\$0		
c. Travel	\$13,500	\$10,386	\$8,500	\$32,386	\$23,770	73%
d. Equipment				\$0		
e. Supplies	\$46,080	\$81,820	\$50,000	\$177,900	\$63,442	36%
f. Contractual	\$724,861	\$777,978	\$735,733	\$2,238,572	\$1,727,998	77%
g. Construction				\$0		
h. Other		\$4,000		\$4,000		
i. Total Direct Charges	**\$1,094,199**	**\$1,290,111**	**\$921,050**	**\$3,305,360**	**\$2,813,772**	**85%**
j. Indirect Charges	\$434,769	\$408,919	\$210,745	\$1,054,433	\$995,403	94%
k. Total Charges	**\$1,528,968**	**\$1,699,030**	**\$1,131,795**	**\$4,359,793**	**\$3,809,175**	**87%**
DOE Share	\$1,243,104	\$1,377,437	\$829,459	\$3,450,000	\$3,138,287	91%
Cost Share (In Kind) - Arizona State	*\$6,415*	*\$6,673*	*\$0*	***\$13,088***	*\$13,506*	*103%*
Cost Share (In Kind) - Georgia Tech	*\$74,833*	*\$70,314*	*\$35,069*	***\$180,216***	*\$186,812*	*104%*
Cost Share (In Kind) - King Saud	*\$204,616*	*\$244,606*	*\$267,267*	***\$716,489***	*\$470,570*	*66%*
Total Cost Share	***\$285,864***	***\$321,593***	***\$302,336***	***\$909,793***	***\$670,888***	74%
Cost Share Percentage	18.7%	18.9%	26.7%	20.9%	17.6%	15.4%

1. Budget above only reflects the Originally Planned Budget and does not include the additional \$80k increment sent by DOE for BP3, which was sent to compensate for higher than anticipated costs that occurred for BP3 SOPO negotiation.
2. Cost Share information from partners had not yet been provided for FY18 Q1, so Cost Share is as of FY17 Q4.

I. Major Task/Milestone Schedule (Abbreviated for space)

M.S.	**Milestone Description**	**Performer**	**Task Start Date**	**Milestone Completion**		
				End Date	**Percent Complete**	**Notes**
M1.1	*Material identified that meets project metrics*	*SNL*	*6/1/14*	*5/31/15*	*100%*	*$CaAl_{0.2}Mn_{0.8}O_3$ (CAM28)*
M1.2	*Validate that SFR can achieve heating rates and be used characterize materials*	*GIT*	*6/1/14*	*5/31/15*	*100%*	
M2.1	*Demonstrate accurate determination of kinetic parameters*	*SNL/GIT*	*6/1/15*	*8/30/16*	*50%*	*Oxidation kinetics not determined*
M2.2	*Identify design that achieves receiver outlet >1000 °C and meets metrics*	*SNL*	*6/1/15*	*8/30/16*	*100%*	*Solved for Co_3O_4/CoO*
M2.3	*Demonstrate particle temperature between 1000 and 1350 °C at lab scale*	*GIT*	*6/1/15*		*75%*	*CAM28 not yet tested due to scale-up delays*
M2.4	*Reactor design completed w/ modelling*	*SNL*	*6/1/15*	*8/30/16*	*100%*	
M2.7	*Validate that the system can achieve goal metrics*	*ASU*	*6/1/15*	*8/30/16*	*100%*	
M3.1	*SR3 achieves temperature and efficiency metrics and validity of models*	*GIT*	*9/1/16*		*50%*	*Testing delay due to CAM28 scale-up.*
M3.2	*ROx achieves temperature and efficiency metrics and validity of models*	*SNL*	*9/1/16*		*70%*	*. CAM28 tests delayed.*
M3.4	*Scaled demonstration of SR3*	*KSU/GIT*	*9/1/16*		*40%*	
M3.5	*System cost meeting define metric*	*ASU*	*9/1/16*		*60%*	*Awaiting results from ROx and SR3 tests on CAM28.*