Red-Ox Robust SOFC Stacks for Affordable, Reliable Distributed Generation Power Systems

Award No. DE-FE0027897

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Redox Power Systems, LLC

Project Kickoff 11/16/2016

NETL Project Partners

- *Center for Advanced Life Cycle Engineering* (CALCE) at the Univ. of Maryland
- *Univ. of Maryland Energy Research Center* (UMERC)

Introduction to Redox Project Team

- Bryan Blackburn, CEO/CTO
  - Expertise in SOFC materials /stack / reformer development, design/test of electrical and mechanical systems, and manufacturing
  - Currently PI on 4 large Dept. of Energy SOFC projects (EERE, NETL, ARPA-E)
  - Project management experience leading teams of dozens of engineers working on materials, subsystems, and systems development
- Thomas Langdo, VP of R&D
  - Expertise in the design, fabrication, and manufacturing of advanced materials, solid state devices, and microelectronics
  - Expertise in SOFC materials scale-up, techno-economic analyses, and stack development
- Sean Bishop, Sr. Materials Engineer
  - Expertise in materials characterization, processing, design and defect modeling
  - Expertise in thermal and chemical expansion of materials and stoichiometry
  - Project management experience for large R&D groups at MIT and Kyushu University (Japan) focused on SOFC and related materials characterization and development

Introduction to Partner Organizations

- CALCE
  - Prof. Michael Pecht
    - world leader in accelerated testing, electronic parts selection, supply-chain management
    - led first academic research facility in the world to be ISO 9001 certified
    - developed techniques for extending the lifetime of batteries and related devices under real world operating conditions
  - Prof. Peter Sandborn
    - expert in system life-cycle and risk economics for various technologies
    - experience in analyses for return on investment, design for availability, and maintenance optimization for energy technologies
- UMERC
  - Prof. Eric Wachsman
    - active in NETL SOFC degradation investigations for more than a decade
    - developed unique techniques for investigating degradation of cathode materials
    - ceramic anode material used in this project developed through a multiyear UMERC/Redox effort

Relevance: Project Objectives

- **Purpose:** To develop a high power density solid oxide fuel cell (SOFC) stack that is **red**uction-**oxi**dation (red-ox) stable for robust, reliable, and lower cost distributed generation.

- **Objectives:** To improve the red-ox stability of Redox stacks while reducing costs through:
  - the scale-up and optimization of all-ceramic anode material processing and cell fabrication for lower cost manufacturing;
  - the determination of all-ceramic anode degradation mechanisms and optimization of anode compositions/geometries for enhanced red-ox stability;
  - the demonstration of a 1-2 kW stack that is more robust for red-ox cycling with the use of accelerated, lifecycle, and failure testing; and
  - the demonstration of at least a 10% reduction in system cost and at least a 30% reduction O&M costs compared to a system without a red-ox stable stack.

Key SOFC Stack Degradation Issues

- Degradation mechanisms of the cell components include
  - coarsening of the microstructure over time
  - decomposition of materials
  - interfacial chemical reaction of electrode materials with electrolyte at the interface
  - layer delamination
  - coking and sulfur poisoning of the anode
- Furthermore, nickel cermet anodes are also prone to re-oxidation, which causes a volume change of >60% that can mechanically damage the anode or other components

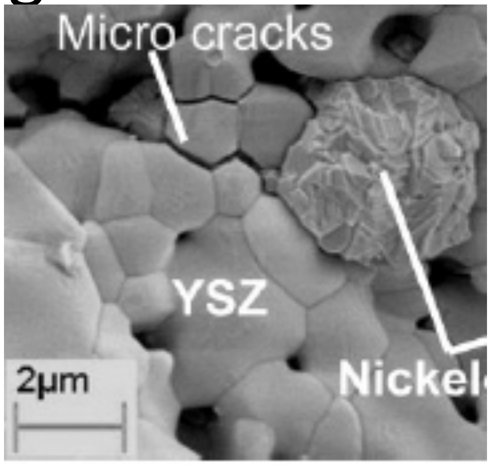
Red-Ox Cycling: Why is it Important?

- The main limitation for Ni-based cermet anodes (e.g. NiO/YSZ) is poor stability in red-ox cycling

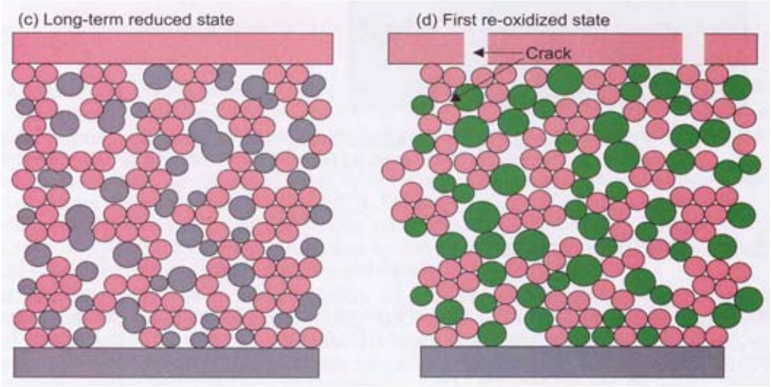
- Red-ox cycles can be expected during long-term fuel cell operation
  - unexpected fuel supply interruptions
  - high fuel utilization under high current loads
  - gas sealing failures
- Re-oxidation can result from abnormal conditions in fuel supply system
  - fuel starvation and a subsequent increase in the oxygen partial pressure above the Ni thermodynamic oxidation threshold
  - oxygen ingress into the anode through pinholes and other defects in the electrolyte, or through imperfect gas seals
- SOFCs have to cope with possible red-ox cycling during transient states
  - start-up/shut-down
  - cell conditioning protocols (first operation)
  - thermal cycling or thermal runaway conditions
  - reforming dynamics

Red-Ox Cycling and Ni-cermet Anodes

- Nickel cermet anodes offer a good balance between power density, structural strength, and efficiency
- But, ultimately will fail upon red-ox cycling
  - As much as 69% volume change
  - Less than desirable robustness creates the risk for long-term reliability issues (microcracks)
  - Fast kinetics for reduction-oxidation of nickel at high temperatures (failure can be fast)
  - Irreversible changes to microstructure during red-ox cycling can lead to severe degradation in electrical and mechanical properties (failure can be slow)



Journal of Power Sources 195 (2010) 5452–5467



J. Electrochem. Soc., 152 [11] (2005) A2186-A2192

Alternate Approaches to Red-Ox Stable Stack

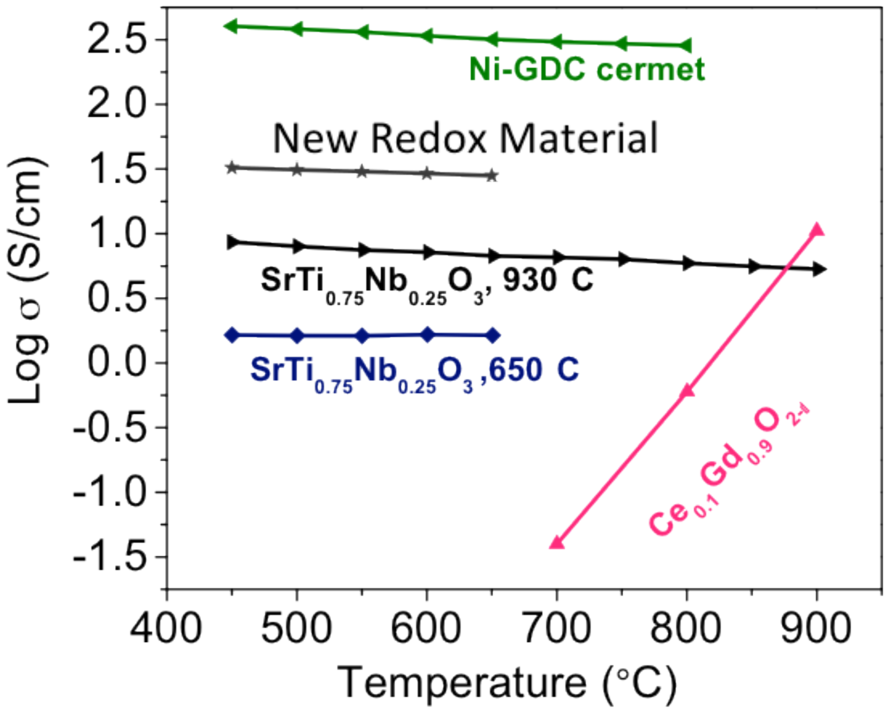
- Metal-supported SOFCs
  - A metal-supported SOFC with a thin anode helps reduce impact of red-ox cycling
  - Processing difficulties make such cell/stack approaches difficult
    - generally results in lower power densities and thus higher costs
- Ceramic anode supported cells
  - Various materials developed
    - titanates (e.g., $SrTi_{0.75}Nb_{0.25}O_3$)
    - molybdates (e.g., Sr_2MgMoO_6)
    - chromates (e.g., $La_{0.2}Sr_{0.7}Cr_{0.5}Mn_{0.5}O_{3-\delta}$)
    - ferrites (e.g., $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$)
    - vanadates ($La_{0.8}Sr_{0.2}VO_{3-\delta}$)
  - Conductivity sufficient but not outstanding
  - Require high temperature pretreatment to activate conductivity
    - therefore cannot leverage advantages of lower temperature operation (e.g., lower TEC mismatch)

Potential System Solutions and Tradeoffs

- Control system malfunctions, emergency-stop situations, and natural gas supply disruption are real possibilities
- Safety gas system is one way to deal with this
  - Help with respect to catastrophic failure but with increased cost and size
    - More than 1.5 times the physical size
    - Potentially contributes to doubling of the levelized cost of electricity (LCOE) if stack needs to be replaced every 2-3 years
- Does not address long-term performance issues associated with seal degradation

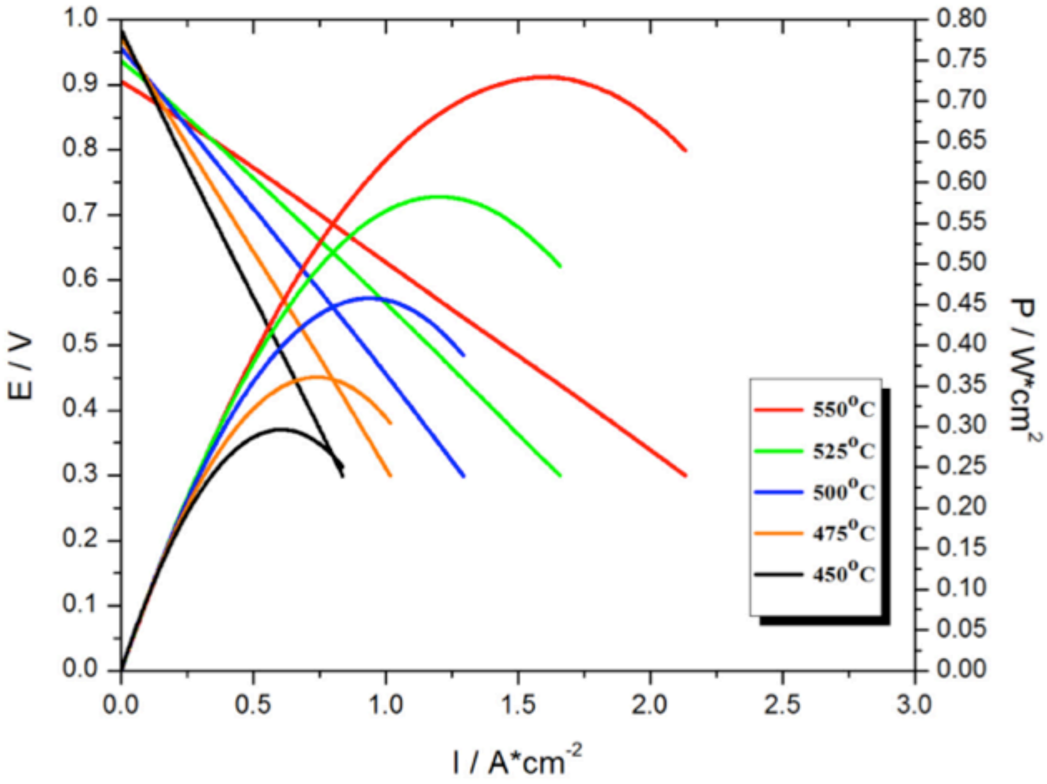
Redox's Approach: A New Ceramic Anode Support

- Ceramic anode…minor non-stoichiometry should create only small dimensional change
  - Minimize internal stress
  - Chemical tolerance
  - Engineer thermal expansion coefficient
- New Redox material
  - High conductivity ~ 20 S/cm when activated below 650°C
  - Alternatives must be activated >900 °C and still have lower conductivity
    - SNT pretreated at 930°C: 8.2 S/cm
    - SNT pretreated at 650°C: 1.7 S/cm
  - Most other materials lack compatibility with GDC electrolytes



Temperature dependent DC conductivity of ceramic anodes in comparison to standard Ni-GDC anode measured in reducing gases.

Ceramic Anode Cell Performance



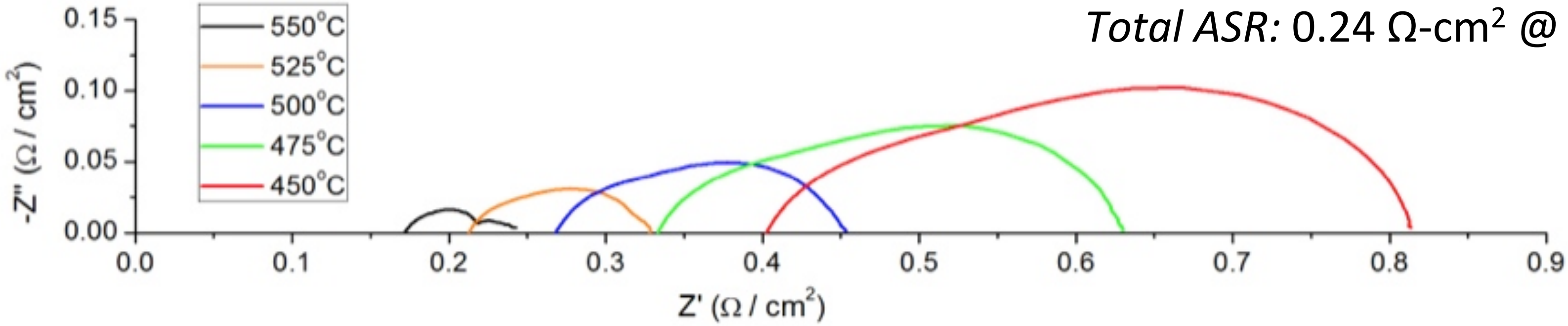
I-V characteristic for ceramic anode-supported cell with a GDC electrolyte in humidified H_2 at various temperatures.

Peak Power Density

~0.75 W/cm^2 @ 550°C

~0.3 W/cm^2 @ 450 °C

Nyquist plot of the impedance spectra for the same cell.



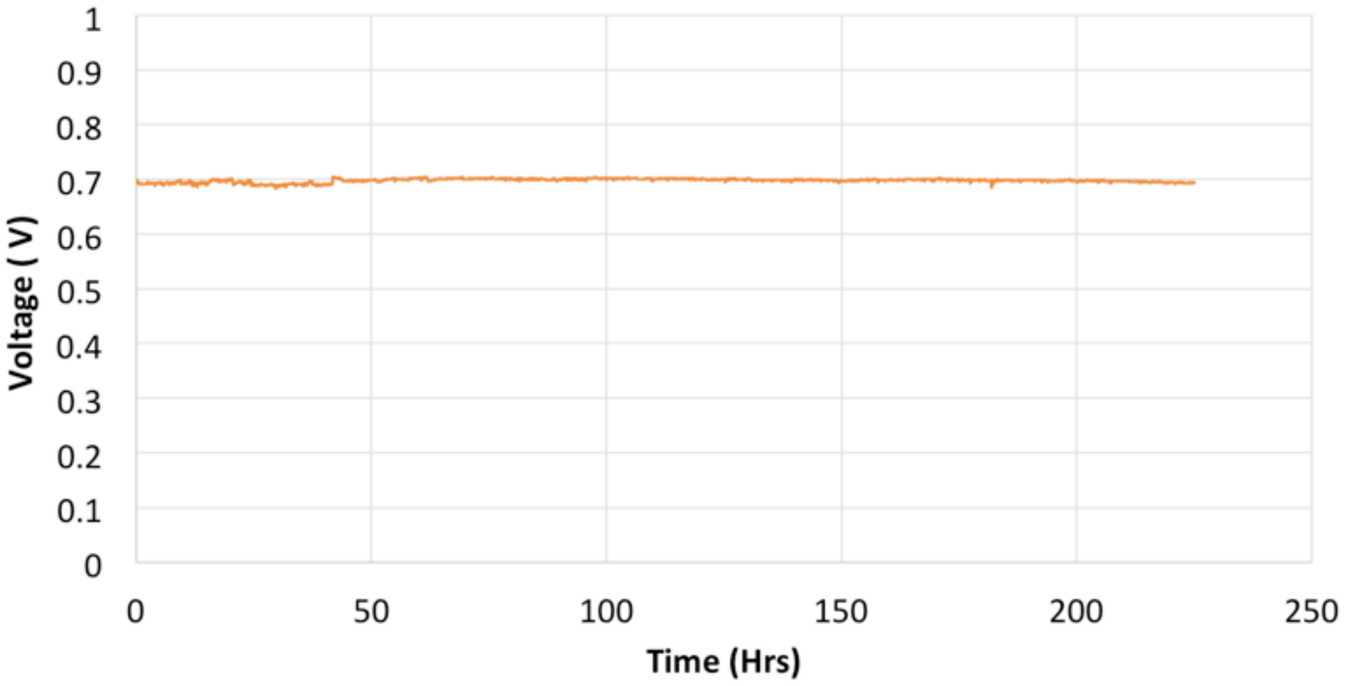
Ohmic ASR: 0.17 Ω-cm^2 @ 550°C

Total ASR: 0.24 Ω-cm^2 @ 550°C

Ceramic Anode Cell Operational Stability

Long-term Stability

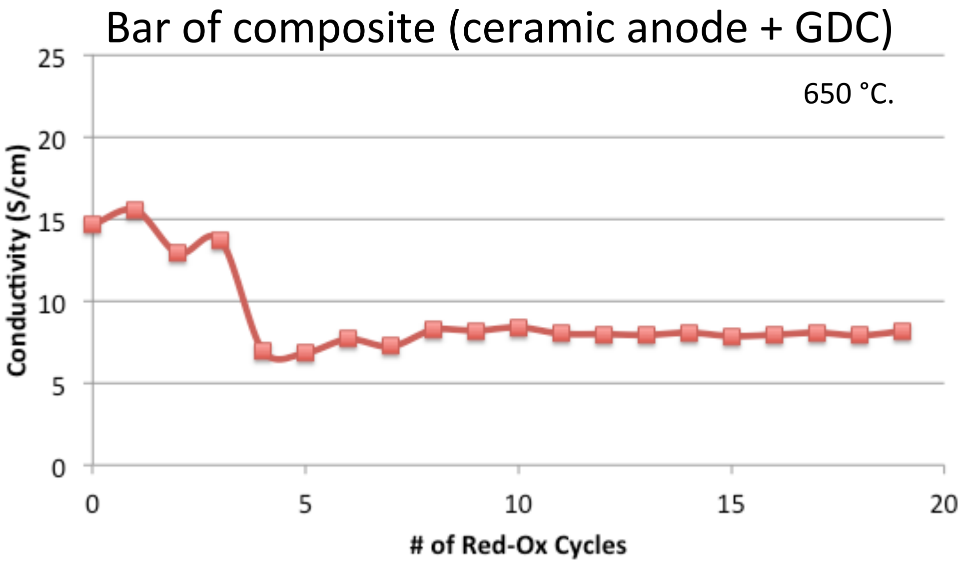
Using reformate gas mixture (> 15% CH_4) at ~500 °C with a fixed current density of 0.2 A/cm^2.



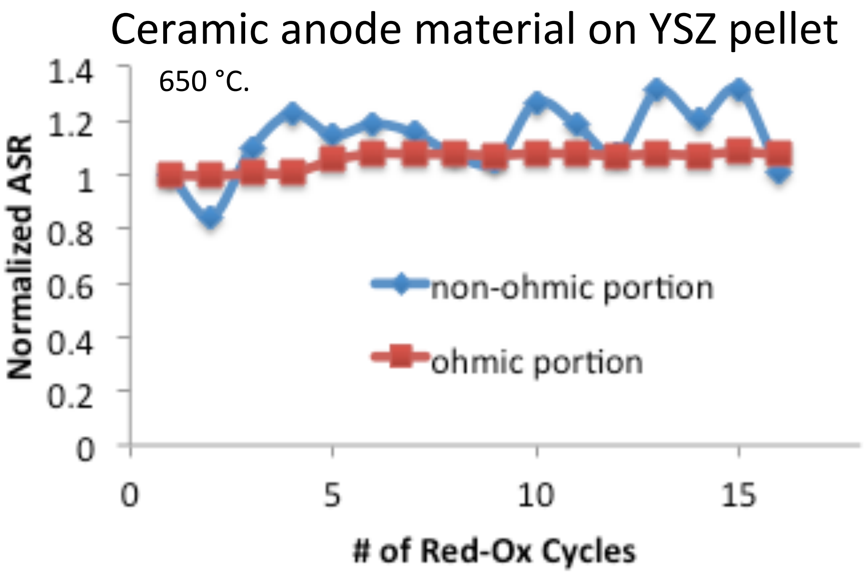
Summary

- Relatively high open circuit voltage and high power density even at low temperatures
- Stable performance with degradation rate < 0.3% per 1000h
- Additional optimization is possible (focus of this project)

Red-Ox Cycling Stability of New Ceramic Anode


Bar of composite (ceramic anode + GDC)

650 °C.

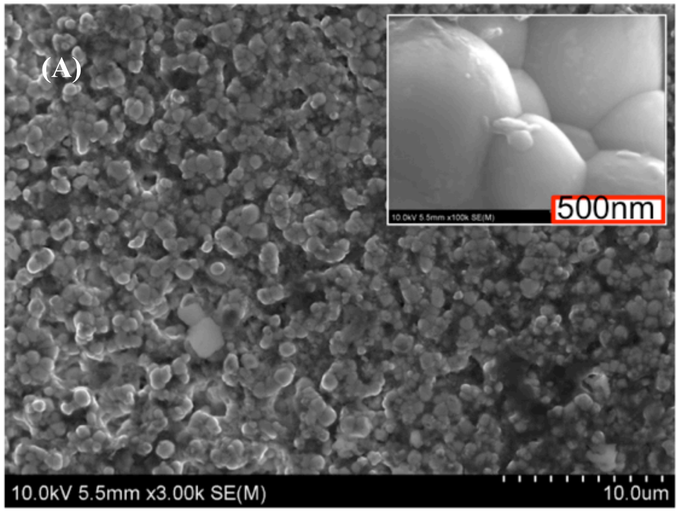

Ceramic anode material on YSZ pellet

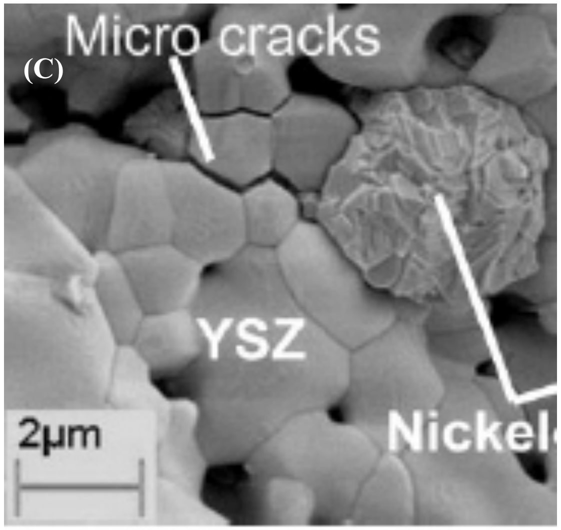
650 °C.

- Alternating between 10% H_2/N_2 (initial) and air
- After first few cycles, slight decrease in conductivity, attributed to sample preparation rather than intrinsic property of the material
- Conductivity relatively stable even after 20 cycles

- Three-electrode symmetric cell arrangement
- Successive red-ox cycles in air and 5%H_2/N_2 with a N_2 purge in between each change in gas composition
- Almost no change in ohmic and non-ohmic contributions to ASR

Red-Ox Cycling Stability of New Ceramic Anode





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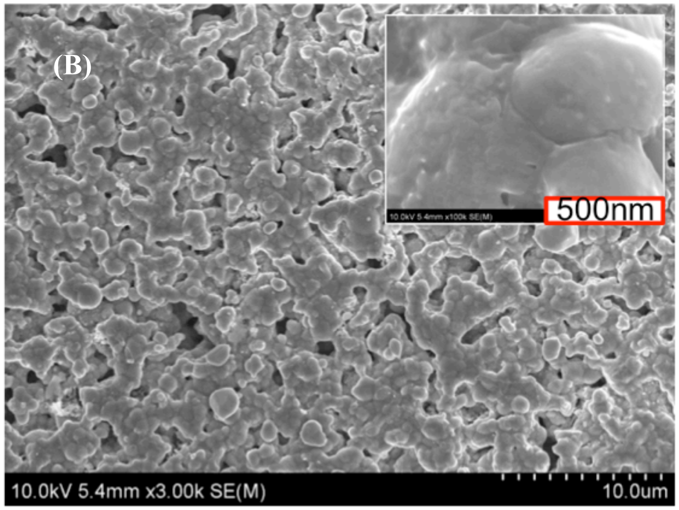


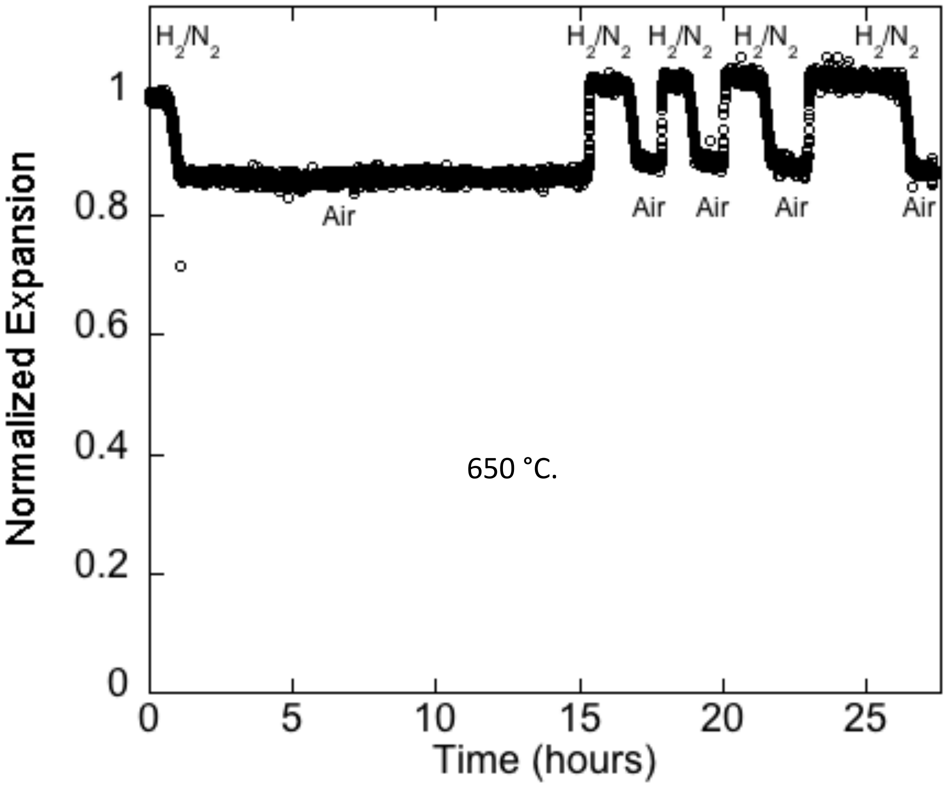
(A) SEM showing ceramic anode before exposure to reducing gas

(B) SEM showing ceramic anode after 9 red-ox cycles, illustrating that no major reconstructions or other changes occur, aside from some minor texturing of grains.

(C) A comparison showing the micro-cracks that form during red-ox cycling of a conventional Ni-YSZ cermet.

Red-Ox Cycling Stability of New Ceramic Anode

- XRD (not shown) shows the absence of impurity phases when the sample is reduced at 650 °C in hydrogen for 24 hours
- Dilatometer used to measure dimensional changes of ceramic anode pellet during red-ox cycling (H_2/N_2 mix → N_2 purge → air) using an atmosphere-controlled quartz reactor

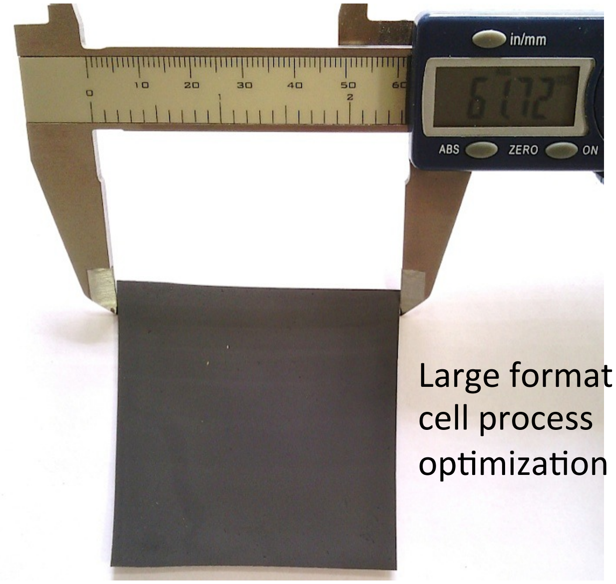


- ~0.12% linear expansion in switch between a reducing and oxidizing gas environment, which amounts to a <0.4% volume expansion
- Considerably better than 69% volume change for Ni→NiO

Project Objectives

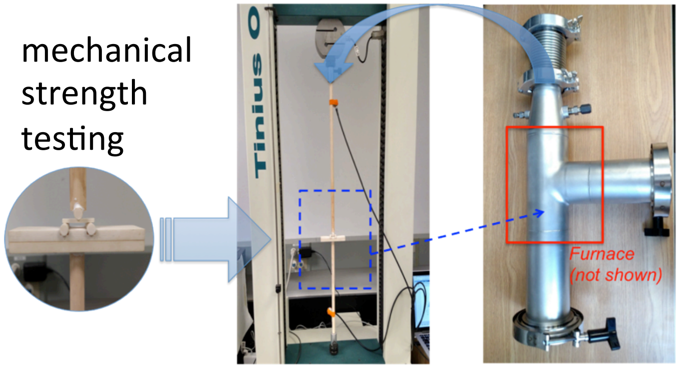
1. Scale-up and optimization of all-ceramic anode material processing and cell fabrication for lower cost manufacturing;
2. Determination of all-ceramic anode degradation mechanisms with an optimization of anode compositions and geometries for enhanced red-ox stability of the optimized, robust cells;
3. Demonstration of a 1-2 kW stack that is more robust for red-ox cycling with the use of accelerated, lifecycle, and failure testing; and
4. Demonstration of at least a 10% reduction in system cost and at least a 30% reduction O&M costs compared to a system without a red-ox stable stack.

1. Optimize Large Format Red-Ox Stable SOFC



Large format cell process optimization

mechanical strength testing



Alumina 3-point bend fixture

Universal Test Machine

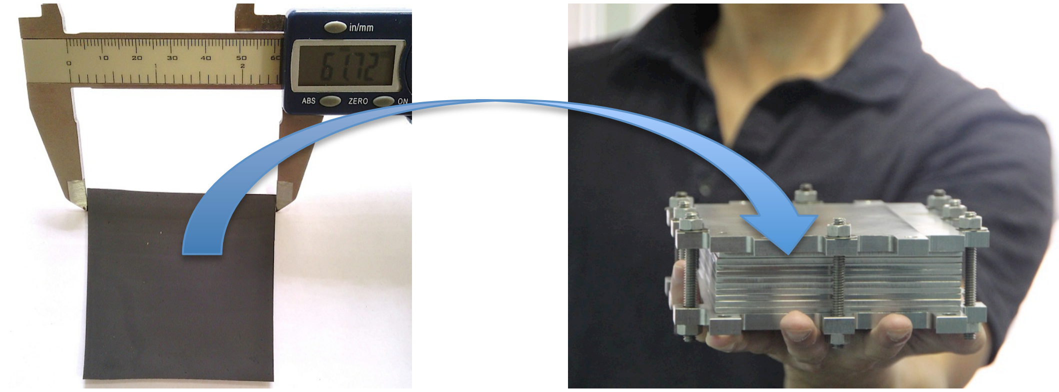
Atmosphere/ temperature control for mechanical tester

Atmosphere and temperature controlled fixture for mechanical testing of cell materials under relevant conditions and to be used in conjunction with computational modeling.

Task Description

- Optimize shrinkage and sintering parameters for a target cell camber of < 100 µm/cm without pinholes;
- Scale-up production demonstration using roll-to-roll lamination and other techniques for low cost manufacturing;
- Optimize performance with improved catalyst infiltration
- Develop improved metrology techniques such as x-ray and thermal imaging to improve quality control and thus reliability;
- Use defect seeding to test both the defect metrology methods and validate performance, reliability, and lifecycle cost models;
- Determine the impact of red-ox cycling on electrical, mechanical, catalytic, and electrocatalytic properties;
- Determine the long-term stability of the materials for continuous cycles of reduction-oxidation using techniques such as dilatometry;
- Determine the cell degradation of the anode under normal operating conditions (relevant to stack), and under accelerated / life-cycle oriented conditions with a focus on red-ox cycling

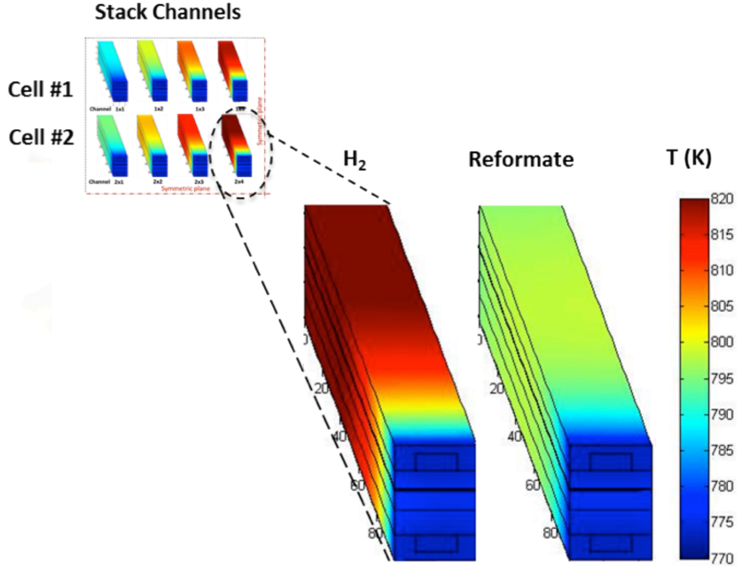
2. Develop Red-Ox Stable Stack



Task Description

- Evaluate red-ox stability of interconnect coatings and optimize as necessary
- Develop red-ox stable anode current collectors / contact pastes
- Characterize and if necessary develop red-ox stable sealing configurations
- Modify Redox computational model for all-ceramic anode, incorporating electrochemistry and mechanical properties under relevant red-ox cycling conditions
- Perform thermo-mechanical studies related to stress within cell / stack developed during assembly, heating, and operation
- Optimize stack designs through parametric studies to improve fuel distribution and minimize thermal gradients under normal operation, load following, and shutdown conditions

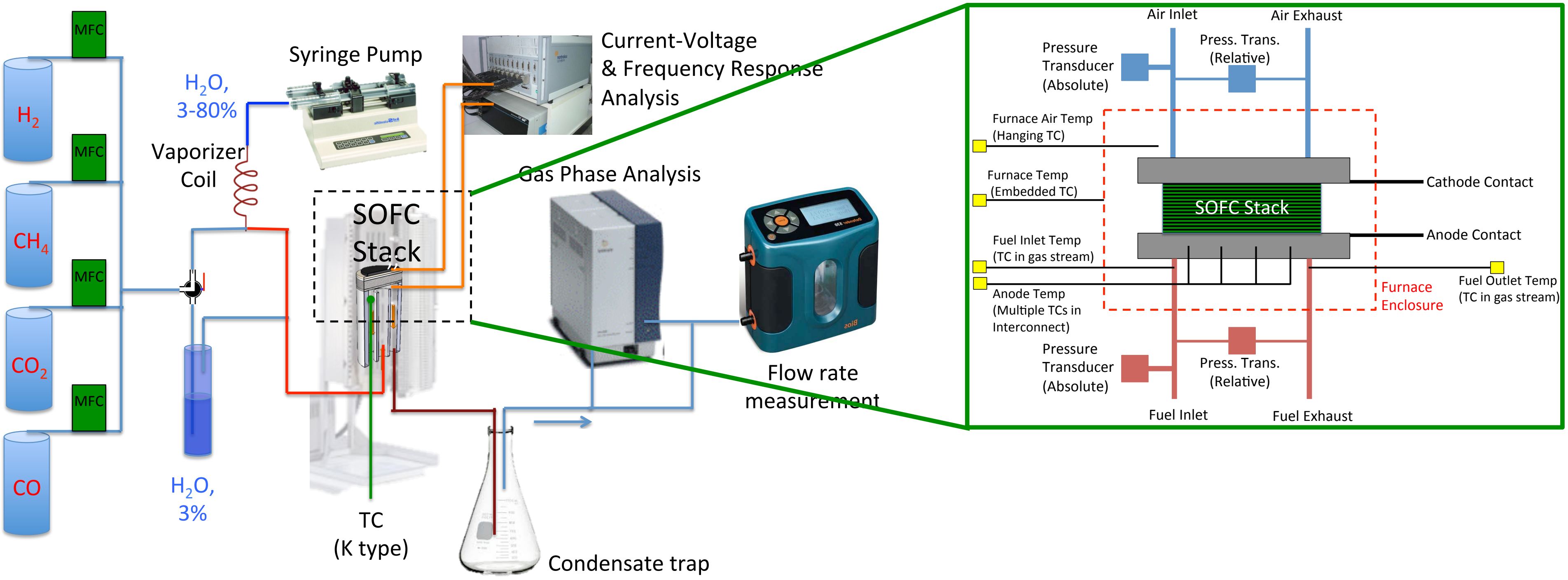
Multi-Physics Computational Modeling



- Takes into account thermochemical and physical properties of materials
- Captures kinetics of electrochemical and heterogeneous reforming reactions within anode
- Includes impact of thermal gradients on mechanical stress

Component	Metric	Goal
Anode interconnect coating	ASR (Ω-cm^2)	ASR increase < 20% through 20 cycles, baseline cell ASR < 0.2 ohm-cm^2 at 650 °C.
Anode current collector	ASR (Ω-cm^2)	ASR increase < 20% through 20 cycles baseline cell ASR < 0.2 ohm-cm^2 at 650 °C.
Gasket	Leak rate (cc/min/cm)	<0.5% increase in external fuel leak after 20 cycles, baseline is 1% of fuel flow
Seal	Leak rate (cc/min/cm)	<1% increase in fuel cross-over leak after 20 cycles, baseline is 1% of fuel flow

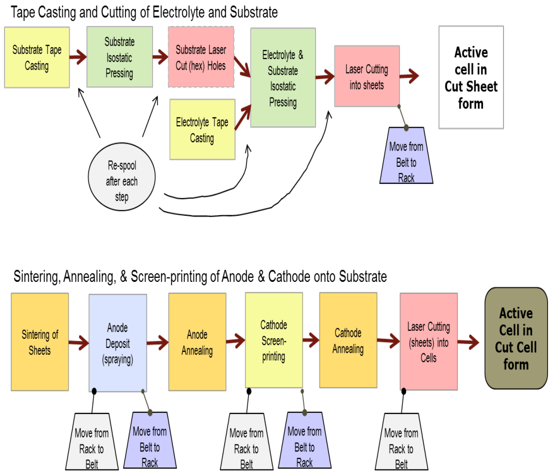
3. Demonstrate 1-2 kW Red-Ox Robust Stack



Stack Lifecycle Analysis Modeled and Evaluated Using:

- Strength, creep, and acoustic emission spectroscopy data of stack materials & components
- Multiphysics modeling of components
- Long-term measurements under normal operational conditions
  - Power output, voltage changes, component conductivity
- Accelerated stack testing under extreme temperature and load
- Modeling of material and operational costs over lifetime of stack

4. Demonstrate Reduced System and O&M costs with TEA



Tape Casting and Cutting of Electrolyte and Substrate

Substrate Tape Casting → Substrate Isostatic Pressing → Substrate Laser Cut (hex) Holes → Electrolyte & Substrate Isostatic Pressing → Laser Cutting into sheets → Active cell in Cut Sheet form

Electrolyte Tape Casting → Electrolyte & Substrate Isostatic Pressing

Re-spool after each step

Move from Belt to Rack

Sintering, Annealing, & Screen-printing of Anode & Cathode onto Substrate

Sintering of Sheets → Anode Deposit (spraying) → Anode Annealing → Cathode Screen-printing → Cathode Annealing → Laser Cutting (sheets) into Cells → Active Cell in Cut Cell form

Move from Rack to Belt

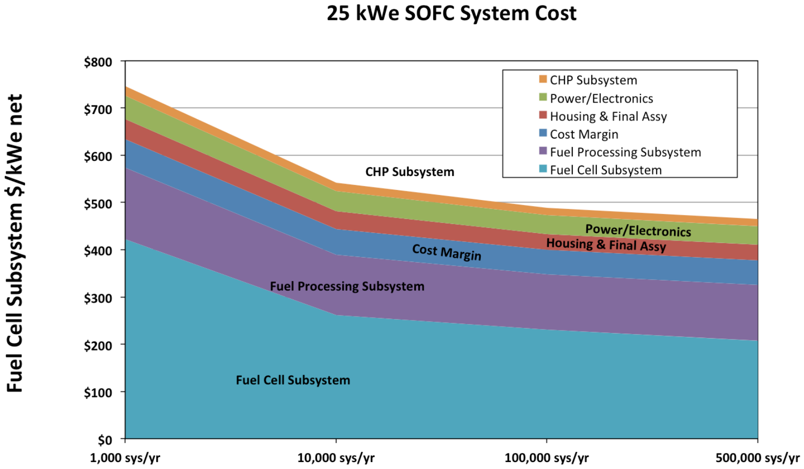
Move from Belt to Rack

Move from Rack to Belt

Move from Belt to Rack

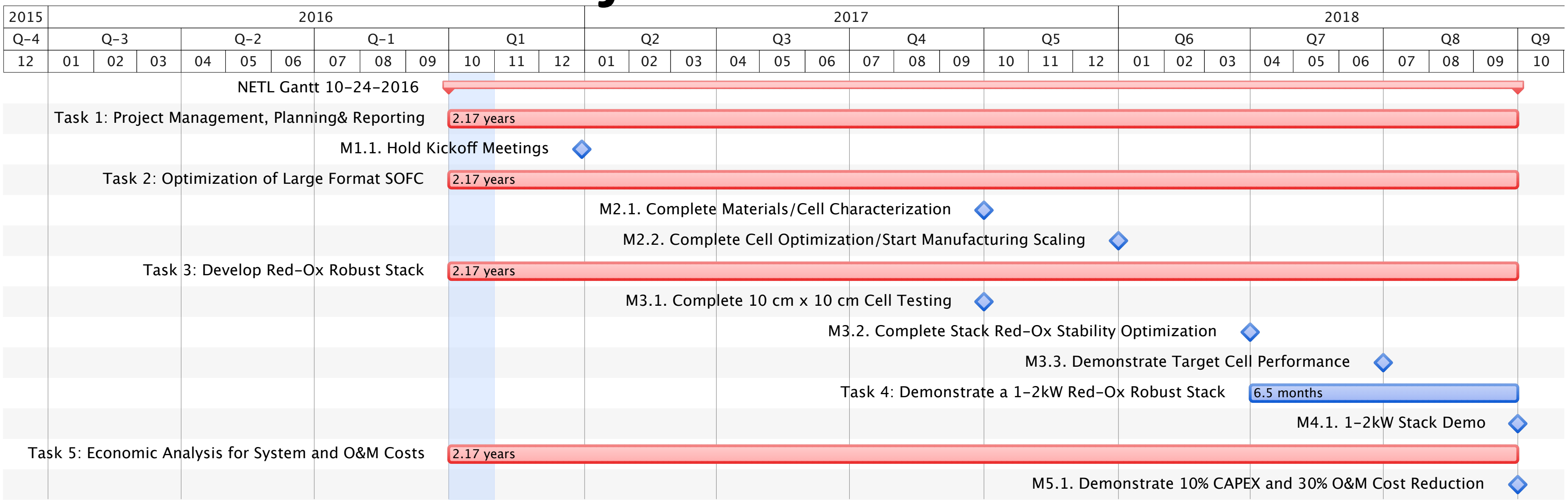
Move from Rack to Belt

Manufacturing Cost Analysis of Stationary Fuel Cells, Strategic Analysis, 2012



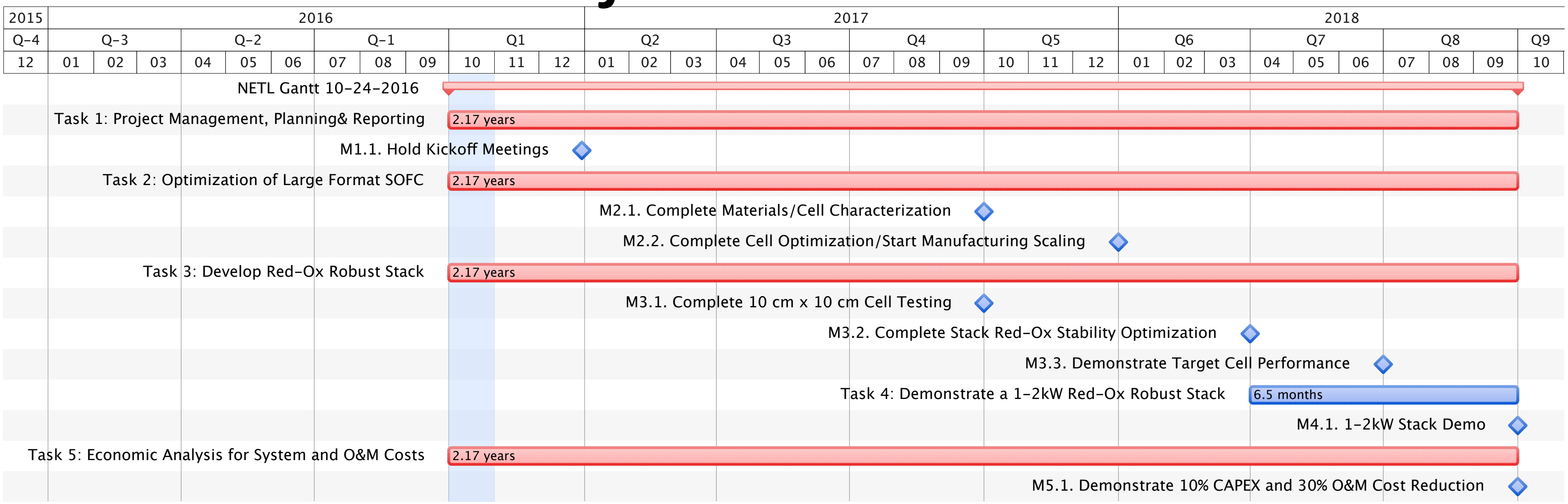
- Detailed study of actual ISO 9001 manufacturing processes and how various automation steps can decrease costs and improve product quality with the red-ox stable stacks;
- Trade studies on how best to form interconnects and seals in light of the design changes that are likely to occur as a result of red-ox stack robustness;
- Sensitivity studies of various aspects of the manufacturing process as it relates to specific design choices for the red-ox stable stack; and
- Use of roll-to-roll manufacturing and other techniques in scale-up efforts to assess the impact on manufacturing cost in high volume.

Project Schedule



WBS	Project Accomplishment	Success Criteria
M1.1	Kickoff meetings with CALCE, UMERC, and Redox production partners.	Review of materials, components, fabrication techniques, and operating conditions with CALCE. Failure test plan, methodology, and protocols documented. Implementation of CALCE recommendations for improved reliability in designs moving forward based on initial materials review.
M2.1	Complete characterization of all-ceramic anode materials & cells and determine degradation mechanisms	Determination of the degradation mechanisms and suitable plan created for resolution in production cells for validation and further testing.
M2.2	Complete main optimization and scale-up to manufacturing.	First qualified production cells have been made and meet all critical target specifications (i.e., cells are ready to test).
M3.1	Complete NOC, accelerated, life-cycle, and failure testing for all-ceramic anode cells	Initial results and predictions on reliability and degradation will be assessed to identify problem areas and potential changes in approach.

Project Schedule



WBS	Project Accomplishment	Success Criteria
M3.2	Stack components optimized for red-ox stability	Stack components will have been demonstrated to meet targets for electrical resistance stability and leak rates for inclusion in red-ox stable stacks.
M3.3	Demonstrate optimized 10 cm x 10 cm red-ox stable cell tested that meets performance metrics	Power Density ≥ 0.75 W/cm^2 at ~0.75 V operating voltage with a degradation rate < 2% when the stack undergoes 20 red-ox cycles.
M4.1	Demonstrate 1-2 kW red-ox stable stack	Hardware demo with 1-2 kW power output which validates and confirm the approach for follow-on commercialization and implementation efforts. Power Density Target ≥ 0.75 W/cm^2 at ~0.75 V operating voltage, and degradation rate demonstrated to be < 2% per 20 red-ox cycles at stack level.
M5.1	Final cost projections based on accelerated testing results and demo performance	Confirmation that proposed stacks and system will meet cost targets for 10% reduction in CAPEX and 30% reduction in O&M. Final lifecycle cost estimates.

Risk Management

Description of Risk	Probability (L, M, H)	Impact (L, M, H)	Overall Degree of Risk (L, M, H)	Risk Management Mitigation and Response Strategies
Technical Risks:				
Cannot scale up the ceramic anode	Medium	High	Medium	• Already successfully scaled > 5 cm by 5 cm • Will optimize that size as we move to a 10 cm x 10 cm cell.
Cannot meet cell degradation and performance targets	Medium	High	Medium	• Identify failure mechanisms using modeling and CALCE advanced life cycle test methods to identify problems and address early in development cycle • Change operating conditions (lower temp and/or reduce operating power density) to improve reliability.
Cannot implement optimized, robust, reliable cell in manufacturing	Medium	High	Medium	• Involve Redox production partners from start • Leverage project team's and partners' deep technical experience and manufacturing knowledge to pursue production worthy solutions.
Cannot demo 1-2kW stack meeting target performance	Medium	High	Medium	• Use Redox production components with demonstrated performance • Leverage current Redox cell and stack development work.
Cannot meet stack reliability targets	Medium	High	Medium	• Change manufacturing techniques for stacks and cells, change operating conditions (lower temp, power density) to improve reliability; • Examine various alternative degradation management approaches; consider alternative stack designs.

Risk Management

Description of Risk	Probability (L, M, H)	Impact (L, M, H)	Overall Degree of Risk (L, M, H)	Risk Management Mitigation and Response Strategies
Technical Risks:				
Facilities not sufficient	Low	Medium	Low	• Redox has enough dedicated test setups for stack R&D efforts. CALCE/UMERC have sufficient facilities to support their efforts as well. • Facility/equipment upgrades can be made, or additional partners involved if necessary.
Right people not available	Medium	High	Low	• Core team is available, and their commitment to project is not a risk. • Redox continues to expand with additional staff to be hired in 2016/2017.
Materials not available	Low	High	Low	• Supply lines have been established for raw materials and production components to meet program needs.
24 month schedule insufficient	Low	Medium	Low	• Redox has broken up the project into a 18 month reliability investigation / optimization / design phase • Final focused 6 month demonstration phase for testing.
Budget Insufficient	Low	High	Low	• Redox will actively manage the project and closely coordinate with the NETL/DOE program manager. • Should the budget be an issue, Redox will work with the PM to re-scope the project or look for additional funding.