High throughput, in-line coating metrology development for SOFC manufacturing (DE-FE0031178) – 24 month program

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Redox Power Systems, LLC, College Park, MD

Project Partner:
Mike Ulsh and Peter Rupnowski
NREL, Golden, CO

11/30/2017

Introduction to Redox Project Team

- **Sean Bishop (PI), Sr. Materials Engineer**
  - Expertise in materials characterization, processing, design and defect modeling
  - Expertise in thin film coatings and characterization
  - Project management experience for large R&D groups at MIT and Kyushu University (Japan) focused on SOFC and related materials characterization and development
- **Bryan Blackburn, CTO**
  - Expertise in SOFC materials /stack / reformer development, design/test of electrical and mechanical systems, and manufacturing
  - Currently PI on 3 large Dept. of Energy SOFC projects (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

Introduction to Partner

National Renewable Energy Laboratory (NREL)

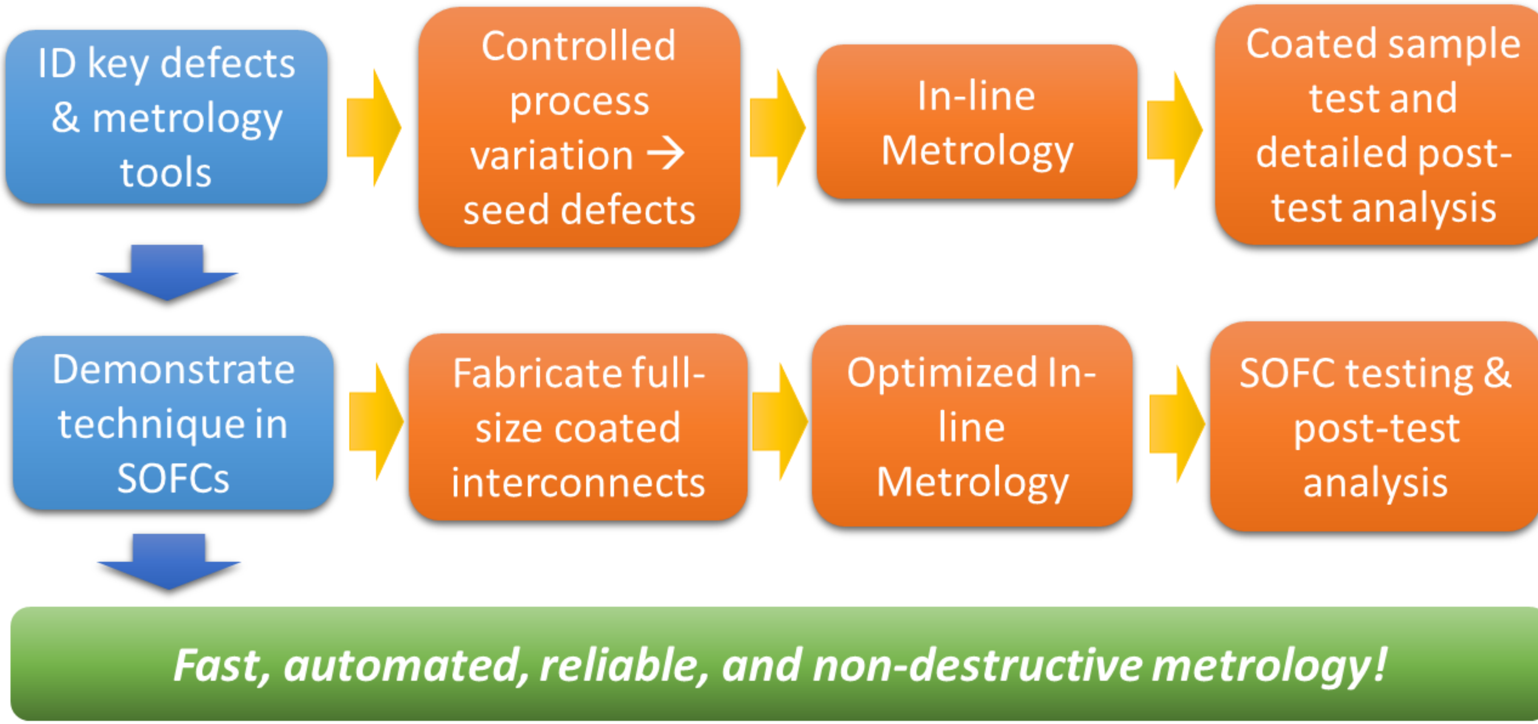
- **Mike Ulsh, Sr. Engineer and Fuel Cell Manufacturing Project Lead**
  - Expertise in evaluating and developing diagnostics for in-line quality control for manufacturing of fuel cell component materials
  - Expertise in studying impact of manufacturing defects on durability and performance of components
  - Interacts with industry on understanding and addressing barriers to high-volume production of fuel cell materials and systems
- **Peter Rupnowski, Materials Scientist**
  - Expertise in manufacturing level metrology techniques for SOFCs, polymer electrolyte fuel cells, and solar cells

Relevance: Project Objectives

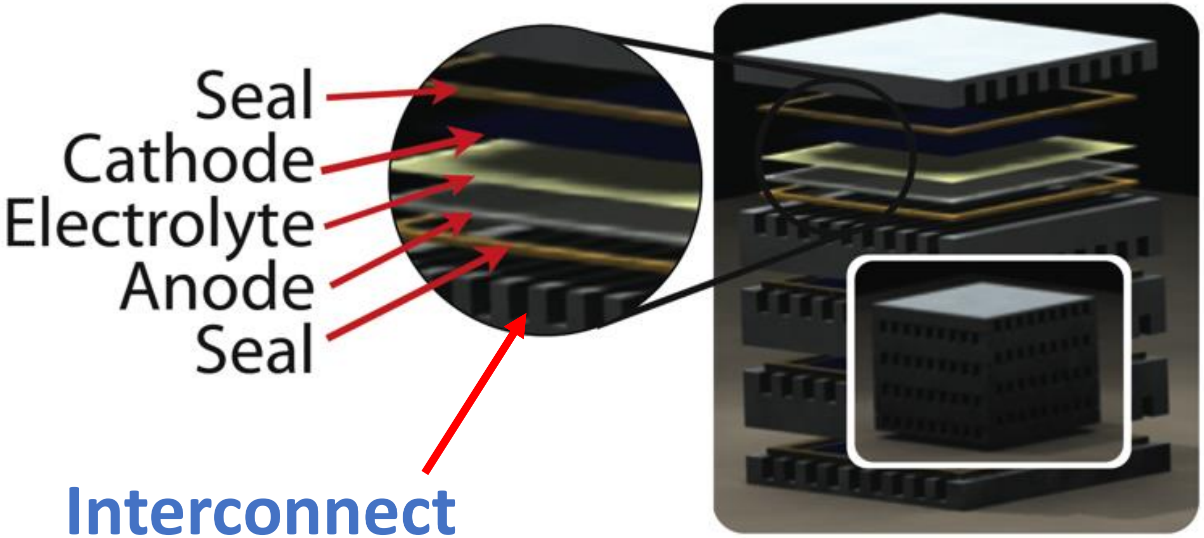
- **Purpose:** Lower cost and increase lifetime of SOFC stacks using high throughput, in-line, early defect detection techniques on protective interconnect coatings.

- **Objectives:**
  - *Identify key interconnect coating and substrate defects that lead to coating failure through the use of detailed characterization methods (e.g., microscopy, XRD, EDS, electrochemistry);*
  - *Assess capabilities of in-line metrology techniques, e.g., optical profilometry (Redox) and thermography (NREL), to probe these defects, or evidence thereof;*
  - *Demonstrate long-term performance of short stacks (1 to 3 cells) using coated interconnect having a low defect count, as identified by in-line metrology.*

Schematic of Objectives



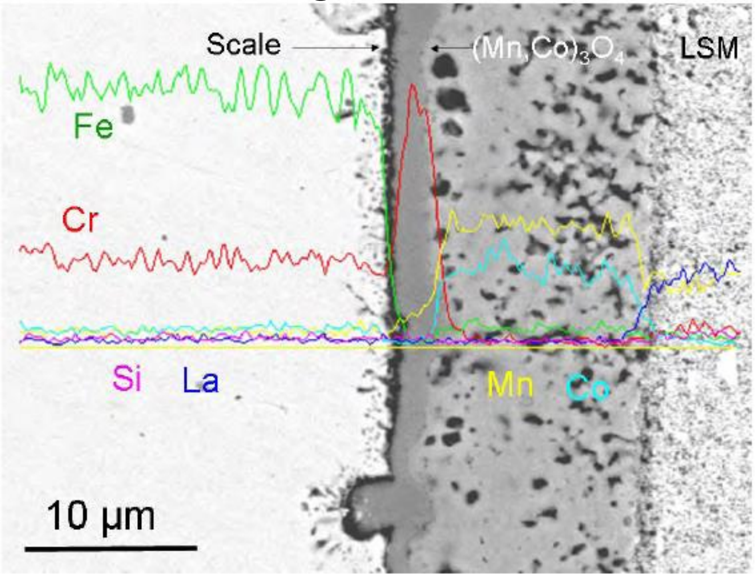
The SOFC Interconnect



- Transfers current from cathode to anode
- Dense gas barrier between anode and cathode compartments
- May serve as a gas distribution layer
- High temperature stability typically requires use of Cr containing alloys (e.g., stainless steel and Crofer)

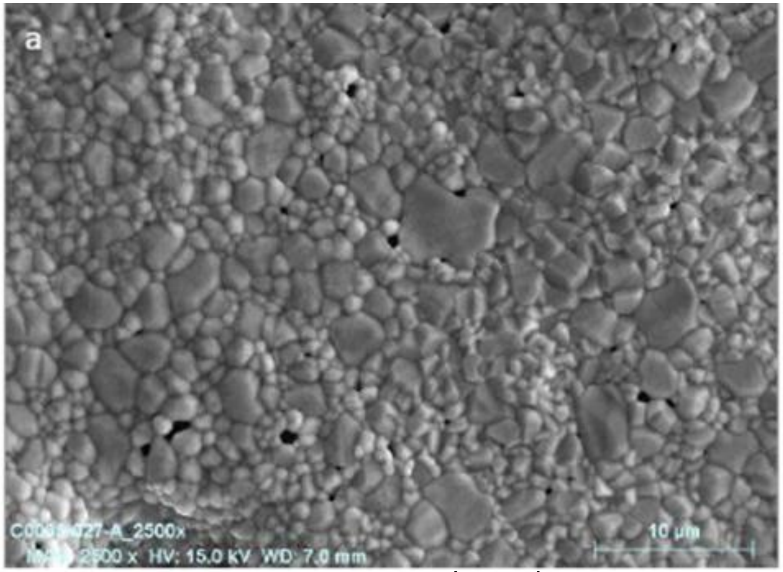
Role of the Interconnect Coating

Coating cross-section



PNNL report ID: PNNL- 17568, May 2008

Coating surface



ECS Transactions, v. 68, i. 1 (2015) 1569

Protective coating applied to the interconnect surface:

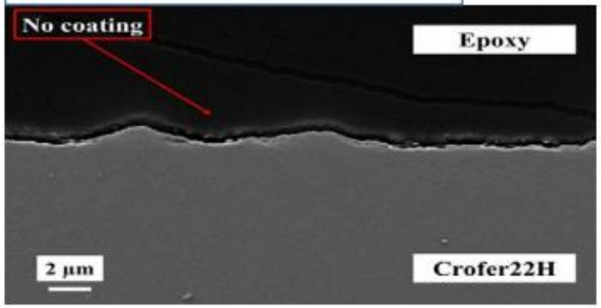
- Barrier to Cr transport from the interconnect to the electrode (prevent cathode poisoning)
- Barrier of inward oxygen migration to the interconnect (block resistive oxide film growth)

$(Mn,Co)O_4$ (MCO) is a commonly used barrier coating layer

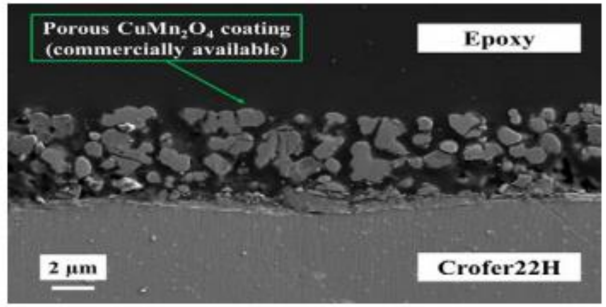
Defects in coating (e.g., porosity, cracks) inhibit coating and SOFC performance

Cell Performance Degradation depends on Interconnect Coating Quality

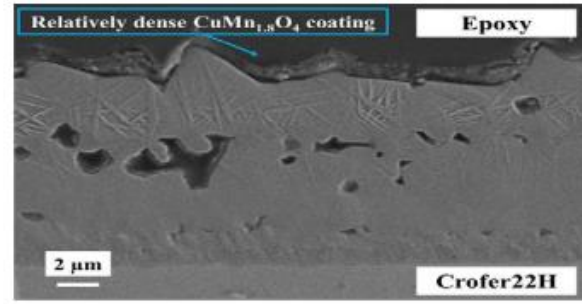
(a) No Coating



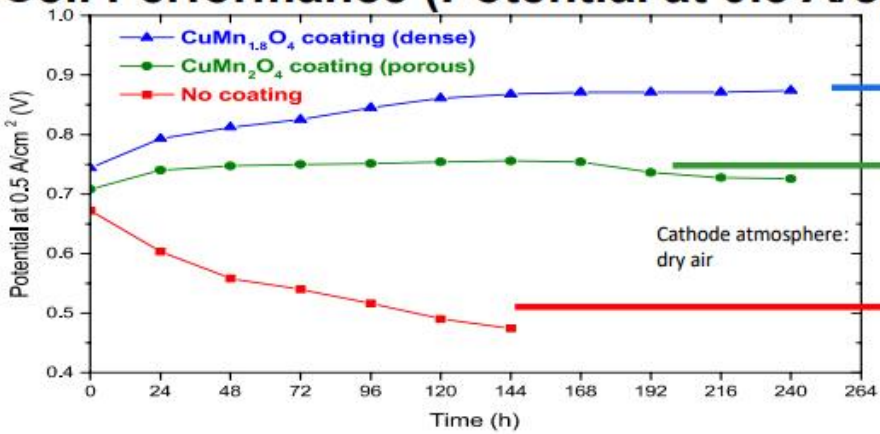
(b) Commercial (Fiaxell) $CuMn_2O_4$ Spinel Coating



(c) BU $CuMn_{1.8}O_4$ Spinel Coating



- **Cell Performance (Potential at 0.5 A/cm^2) as a Function of Time:**



No observable degradation

Degradation after Cr gettering capacity of coating exhausted

Degradation was observed from the begining

6/20/2017

S. Gopalan, 18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting, June 2017, Pittsburgh, PA

Key Coating Defects

Defect	Impact on SOFC	Severity
Through thickness crack	Cr induced degradation	High
Delamination	Increased coating resistance	High
Spallation	Increased coating resistance and Cr induced degradation	High
Coating porosity	Increased coating resistance, decreased coating mech. integrity	Low-Medium
Coating-substrate interface porosity	Increased coating resistance, increased delamination risk	Medium
Inhomogeneous or out-of-spec. coating thickness	Non-uniform current distribution (hot spots), high coating resistance, and/or non-uniform layer stress	Low-Medium
Inhomogenous or incorrect coating composition	Incorrect electrical, mechanical, and materials compatibility properties	Medium

Many defects exist

- Level of their impact on cell performance not well documented
- High throughput defect detection techniques not characterized or well-developed

Coating Qualification State of the Art

Most common

Technique	Measured parameter	Automation for interconnect	Speed for large area scan	Non-destructive
Tape peel test	Film adhesion	Yes	Fast	Yes
Mass	Film thickness	Yes	Fast	Yes
Scratch test	Film adhesion	Yes	Slow	No
SEM/EDS/TEM	Cracks, pores, film uniformity, subsurface defects /composition	No	Slow	No
XRF	Composition	Yes	Slow-Medium	Yes
Indentation	Mechanical properties	Yes	Slow	Possibly
Ellipsometry	Film thickness	No, requires uniform substrate	Fast	Yes
X-ray tomography	Microstructure	Yes	Slow	Yes
X-ray diffraction	Composition	Yes	Slow	Yes
Raman Spectroscopy	Local atomic arrangement	Yes	Slow	Yes

- Fast techniques yield only limited information (only rough estimate of coating thickness and adhesion)
- Other common measurements are labor intensive, destructive, and typically only evaluate a small part of the specimen
- Less common measurements are too slow for rapid evaluation or only for featureless substrates

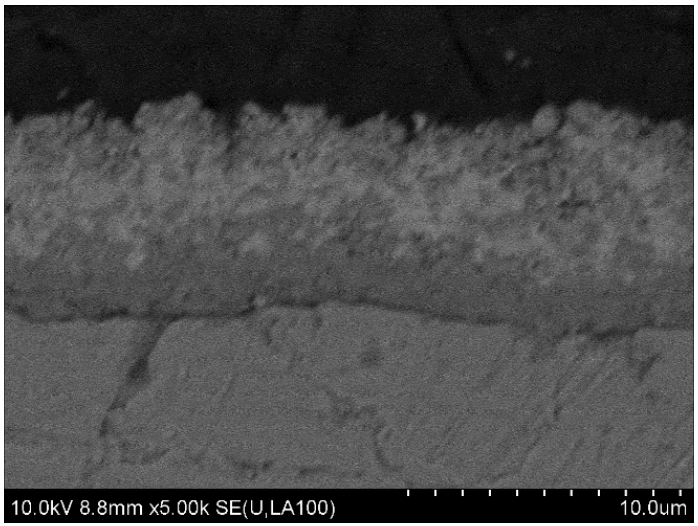
Redox Approach

Technique	Measured parameter	Automation for interconnect	Speed for large area scan	Non-destructive
Optical Profilometry	Cracks, pores, film uniformity	Yes	Fast	Yes
Optical Reflectance	Cracks, pores, film uniformity	Yes	Fast	Yes
Thermography	Cracks, pores, film uniformity, subsurface defects	Yes	Fast	Yes

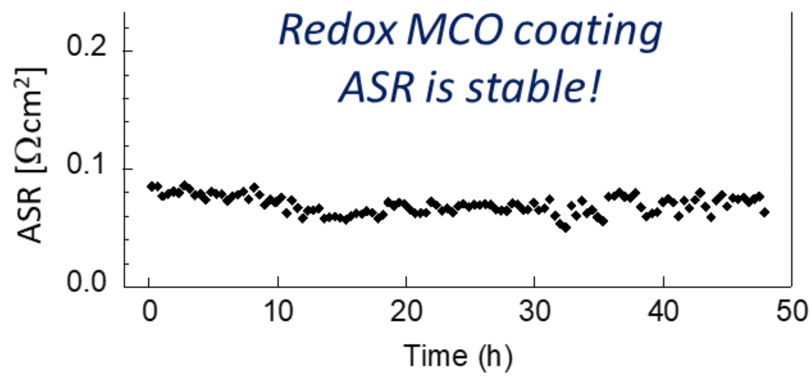
High-throughput, in-line techniques for manufacturing-scale defect identification

Coating Fabrication at Redox

- Sprayed MCO coatings followed by standard annealing methods (reducing atmosphere followed by oxidation to achieve, dense oxide coating)



SEM cross-section of MCO coating on stainless steel developed at Redox



- Obtain commercial coatings for comparison (e.g., Fiaxell)

Project Objectives

1. Identify key interconnect coating and substrate defects that lead to coating failure through the use of detailed characterization methods (e.g., microscopy, XRD, EDS, electrochemistry);
2. Assess capabilities of in-line metrology techniques, e.g., optical profilometry (Redox) and thermography (NREL), to probe these defects, or evidence thereof;
3. Demonstrate long-term performance of short stacks (1 to 3 cells) using coated interconnect having a low defect count, as identified by in-line metrology.

1. Identify Key Interconnect Coating and Substrate Defects

- Deposition of coatings on interconnect test coupons and full-size (~10 cm x 10 cm) interconnects.
- Procurement of commercially coated substrates for tests and benchmarking of Redox coatings.
- ASR Testing of coupons in SOFC-like environments (e.g., annealing in air at 650 ^{o}C)
- Detailed post-test characterization of coatings, including morphology and compositional characterization with SEM and EDS of cross-sections and phase purity with XRD
- Intentional introduction of defects (e.g., cracks, porosity) in coatings by control of processing parameters (e.g., deposition rate, particle fraction, temperature of thermal treatment).
- Identification of key coating-related defects that lead to degradation of SOFC performance (e.g., increase in coating resistance, Cr contamination of cathode).

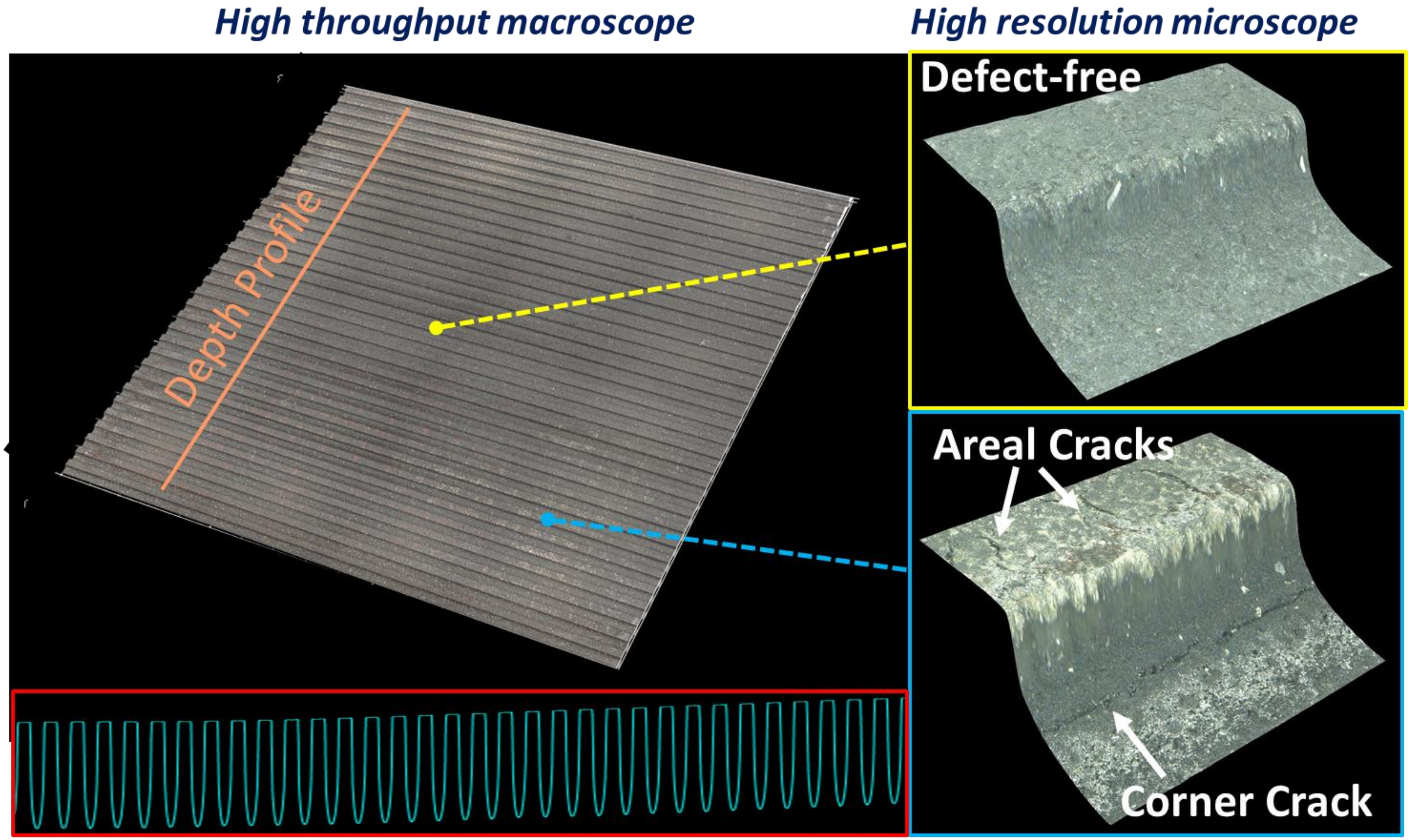
1. Coating Evaluation at Redox

Optical profilometry capabilities at Redox (Keyence VR and VHX)

High throughput ***High resolution (1000x)***

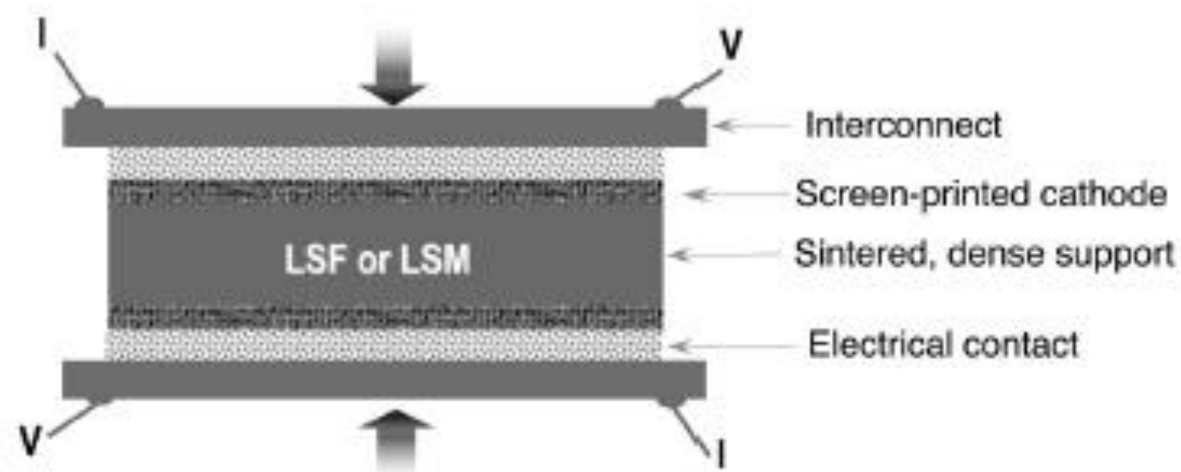
- Optical profilometry at Redox
- SEM, EDS, and XRD available to Redox through UMD

1. Optical Profile of Coated Interconnect



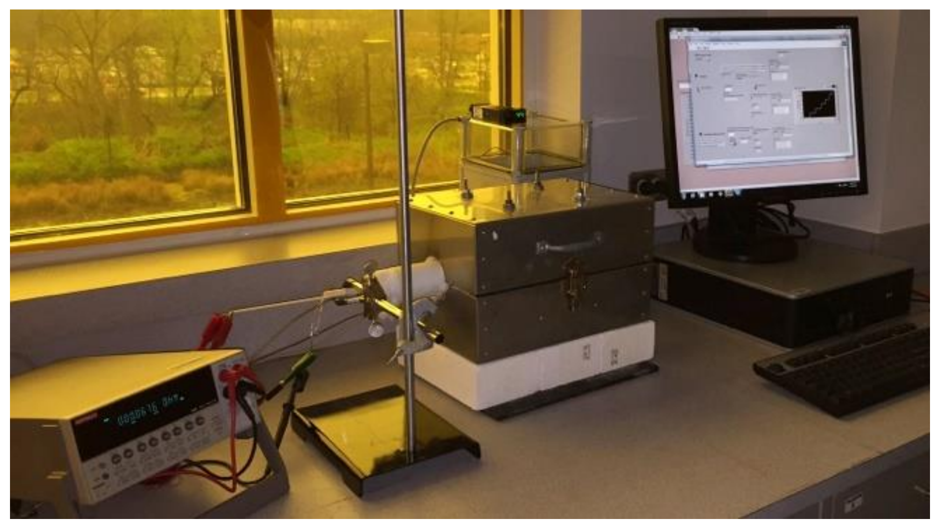
Develop methods to rapidly identify defective coatings

1. Coating Electrical Evaluation



International Journal of Hydrogen Energy, v. 32 (2007) 3648

Setup at Redox to evaluate area-specific-resistance (ASR)

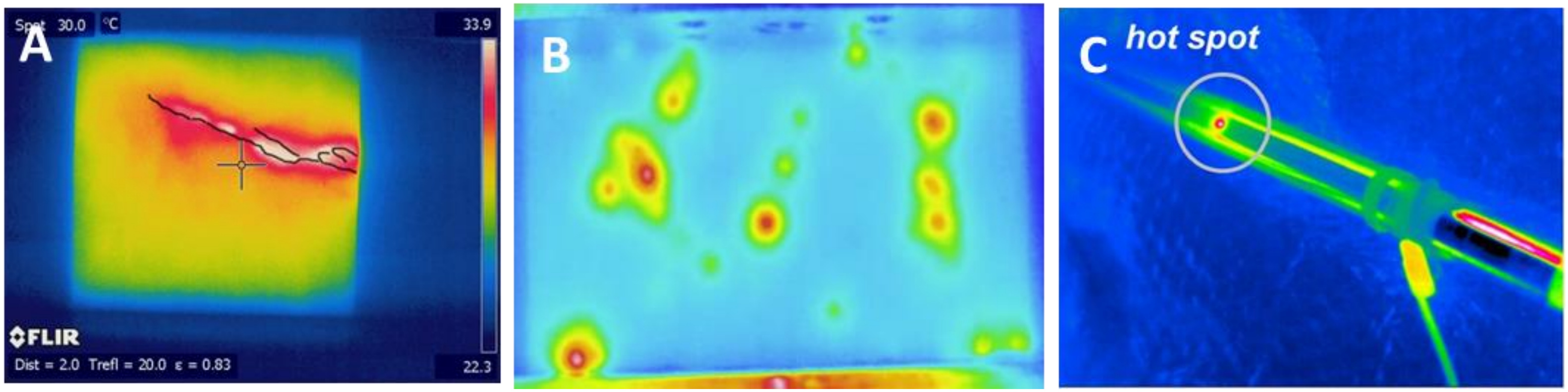


2. Assess Capabilities of In-Line Metrology Techniques

- Evaluation of high throughput optical profilometry techniques at Redox, and optical and thermography techniques at NREL to identify inhomogeneities (i.e., defects) in interconnect test coupons before and after coating.
- Optimization of in-line metrology (e.g., down-select available techniques, improve data analysis methods, optimize metrology hardware parameters) to demonstrate that key coating-related defects or evidence of their existence can be identified.
- Screening MCO coated full-sized interconnects for key defects with in-line metrology techniques to identify defect-free and defective components.

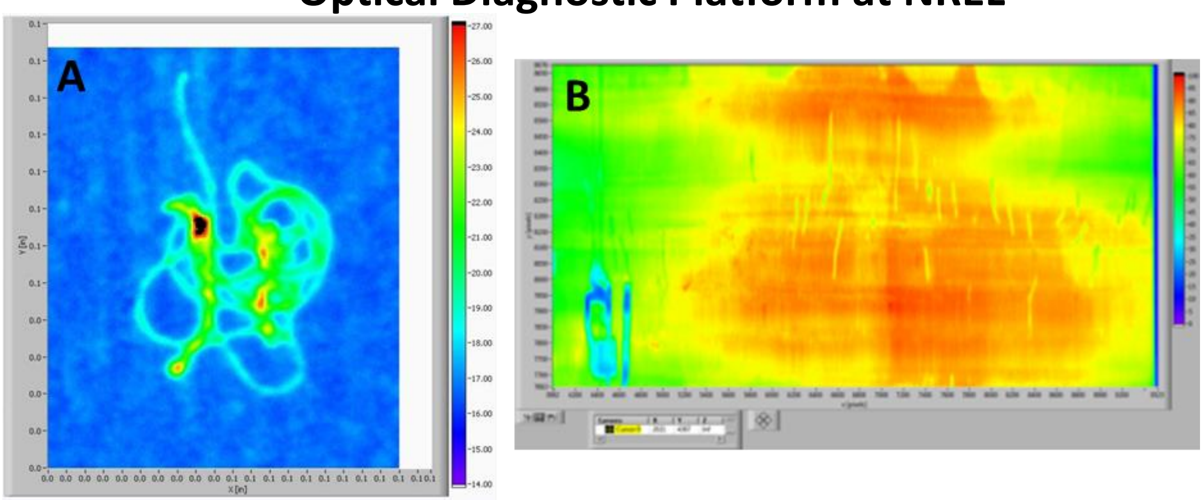
2. In-Line Metrology at NREL

Thermography at NREL



(a) in-plane measurement of a crack on the surface of a GDL, (b) through-plane measurement of shorts in a PEM cell caused by GDL fibers penetrating the membrane during hot-pressing, (c) electrical short identified as hot spot in a tubular SOFC.

Optical Diagnostic Platform at NREL

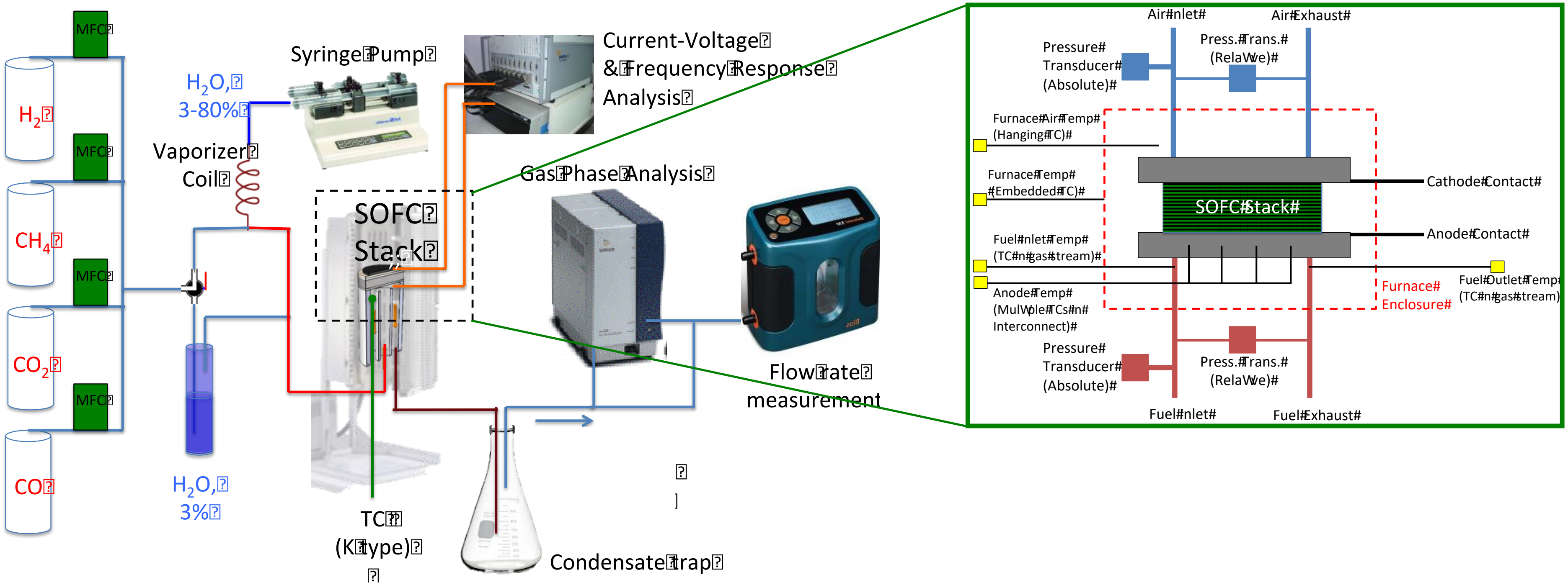


(a) electrolyte-layer scratch in a fired planar SOFC sub-assembly, (b) electrolyte-layer flaws in a tube SOFC cell.

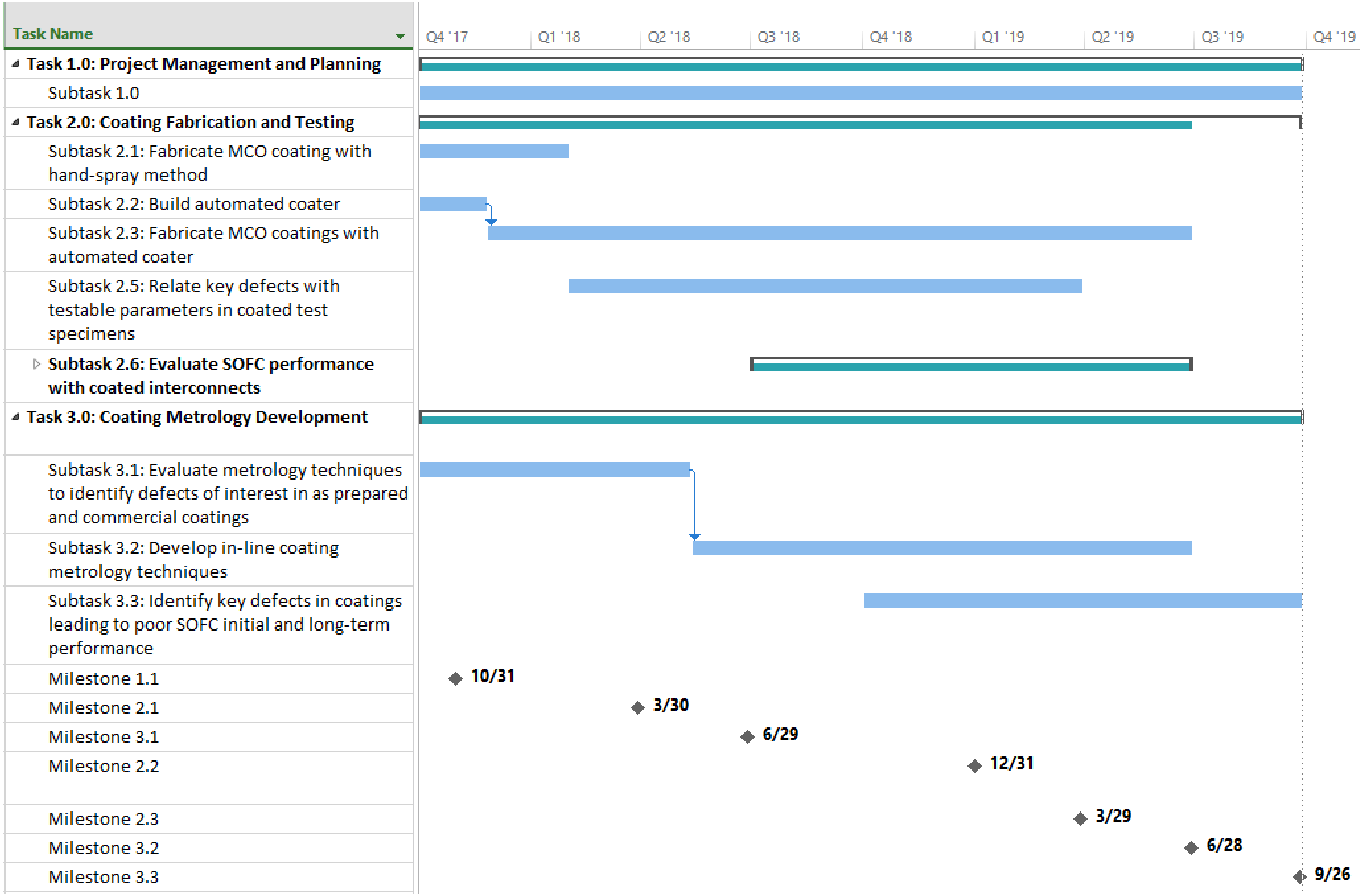
And macroscope at Redox

3. Long-Term Performance of Short Stacks with Low Defect Interconnect Coatings

Demonstration that optimized in-line metrology methodology can successfully detect coating-related defects in full-size interconnects and extend operational lifetime of SOFC stacks.



Project Schedule



Milestones

Milestone	Project Accomplishment	Due	Success Criteria
1.1	Hold a kick-off meeting with NREL and Redox	Q1 (12/17)	Review overall project plan and scope. Formulate more detailed near term plan.
2.1	Demonstrate uniform coatings achievable with automated coater	Q2 (3/18)	Fabricated automated coater system, demonstration of uniform coatings with SEM.
2.2	Demonstrate high stability and low ASR with low defect (determined by in-line metrology) interconnect samples	Q5 (12/18)	Demonstrate ASR of < 0.05 ohm-cm^2 at 650 °C for 1,000 hours
2.3	Demonstrate that low defect coatings on interconnects (screened using in-line metrology) have low volatilization of chromium	Q6 (3/19)	Demonstrate Cr volatization at 650 °C for 1,000 hours as detected using Cr-getter material is < 5 at% increase above baseline.
3.1	Use in-line metrology to identify initial key defects of interest	Q3 (6/18)	Demonstrate capability to identify initial key defects of interest with in-line metrology
3.2	Demonstrate capability to identify as determined in this program key defects of interest with in-line metrology	Q7 (6/19)	Down-selection of initial key defects of interest to defects demonstrated to increase ASR or Cr volatility. Identification of these defects with in-line metrology.
3.3	Demonstrate low cell power degradation per 1,000 hours of low-defect interconnects in SOFCs	Q8 (9/19)	Demonstrate < 0.4% cell power degradation per 1,000 hours of low-defect interconnects used in SOFC short stack (1 to 3 cells) test at a single fixed load at 650 °C

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 detect defects with in-line metrology	Medium	High	Medium	Multiple in-line metrology studies are being evaluated Experts in metrology are subcontracted in the program
Automated coater does not provide uniform coatings	Medium	High	Medium	Redox has previously demonstrated ability to achieve uniform, dense coatings A range of processing conditions will be utilized to optimize coating process, but will extend time for task
ASR and Cr volatility may be excessive	Medium	Medium	Medium	Excessive Cr volatility and ASR may be corrected through coating optimization Despite issue, does not take away from key outcome of project: identification of defects
SOFC cell and stack may degrade too fast	Medium	Medium	Medium	Degradation related to Cr will be alleviated as performed in above risk. Despite issue, does not take away from key outcome of project: identification of defects