Sputtered thin films for very high power, efficient, and low-cost commercial SOFCs (DE-FE0031656) – 24 month program

Sean Bishop (PI)
Redox Power Systems, LLC
College Park, MD, USA

9/17/18
9 am

Kick-off meeting with NETL

Introduction to Redox Project Team

- **Sean Bishop (PI), Director, Materials R&D**
  - 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 2 large Dept. of Energy SOFC projects (NETL)
  - Project management experience leading teams of dozens of engineers working on materials, subsystems, and systems development
- **Colin Gore, Materials Engineer III**
  - Expertise in SOFC device testing, electrochemical characterization, test stand design, and gas phase analysis
  - Expertise in materials properties characterization
- **Keji Pan, Materials Engineer II**
  - Expertise in materials design
  - Expertise in SOFC processing and manufacturing

Introduction to KDF (key collaborator)

KDF, Inc.

- US-based manufacturer of high volume production sputtering equipment
- Expertise in materials deposition and high volume manufacturing
- Previously developed a preliminary sputtering process with Redox using production equipment

Ammar Derraa¸ Director of Technology at KDF

- PhD in Physics with over 20 years experience in process engineering, device technologies, and capital equipment
- 64 US patents, and has received multiple academic scholarships and awards, and published several scientific publications and presentations, with over 150 citations.

Relevance: Project Objectives

- **Purpose:** Lower cost through dramatic power density increase of SOFC stacks using commercial-scale thin film processing

- **Objectives:**
  - *Achieve dramatic increases in SOFC stack power density using sputtered electron blocking and buffer layers.*
  - *Demonstrate highly active advanced cathode functional layers deposited with sputtering.*
  - *Demonstrate commercial-scale potential of sputtering by optimizing sputter conditions for high throughput with improved metrology techniques for high yield.*

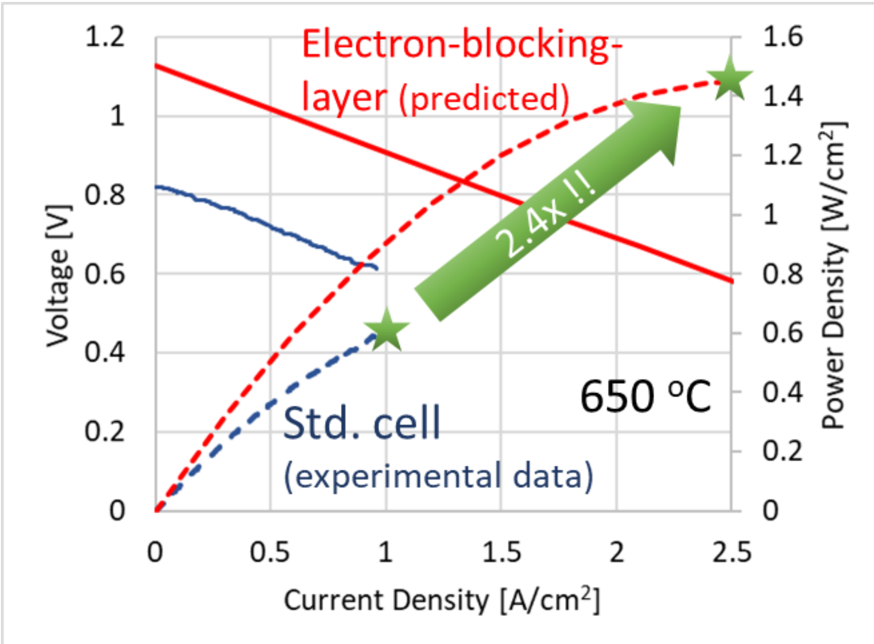
Schematic of Objectives

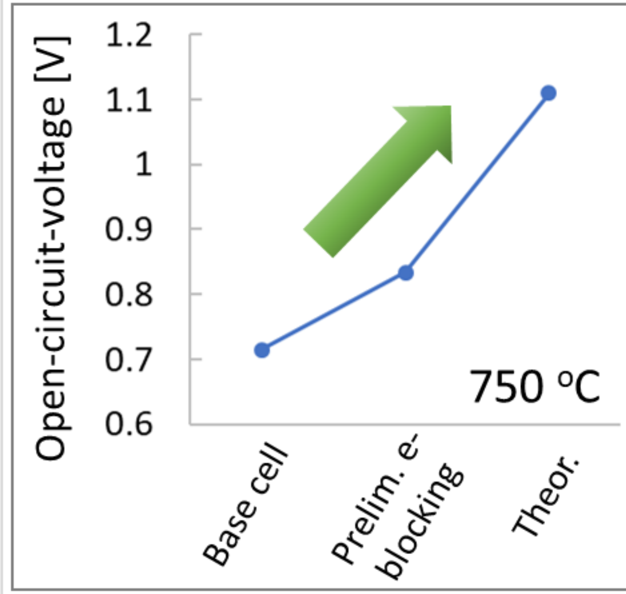
Sputter electron blocking and buffer layers → Optimize substrate fabrication → Optimize sputtering and post-anneal conditions → **Demonstrate cell efficiency and *100% power density* improvement**

Evaluate and develop sputtered CFL → Optimize sputtering and post-anneal conditions → Demonstrate additional power density and cell efficiency improvements

Develop commercial-scale sputter process → Increase sputtering throughput by optimizing deposition conditions and yield → ***Demonstrate high throughput, commercial-scale sputtering!!***

Thin Film Advantages

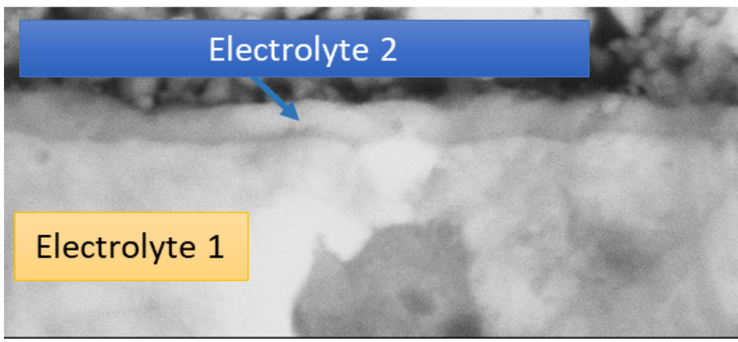




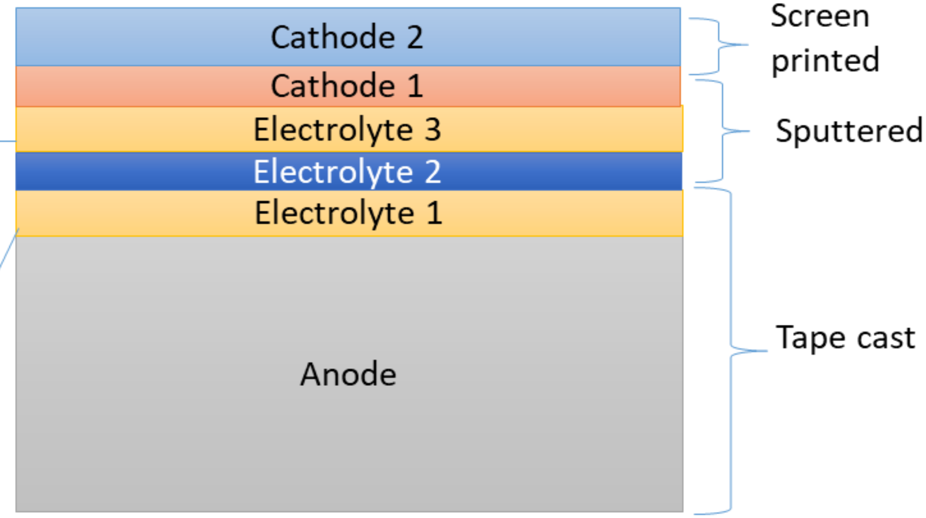
- Thin electron-blocking layer expected to increase Redox GEN1 cell power density by >2x
- Electron-blocking layer eliminates electronic leakage through ceria based electrolyte → ~40% increase in open circuit voltage
- Thin-ness of electron-blocking layer adds negligible resistance
- Takes advantage of high performance Redox GEN1 cell platform

Structure of Cell

SEM cross-section of preliminary Redox sputtered cell



Proposed cell configuration



**layers not to scale*

- Electrolyte 3 provides transition between electrolyte 2 and cathode 1
- Cathode 1 expected to improve electrochemical and structural properties

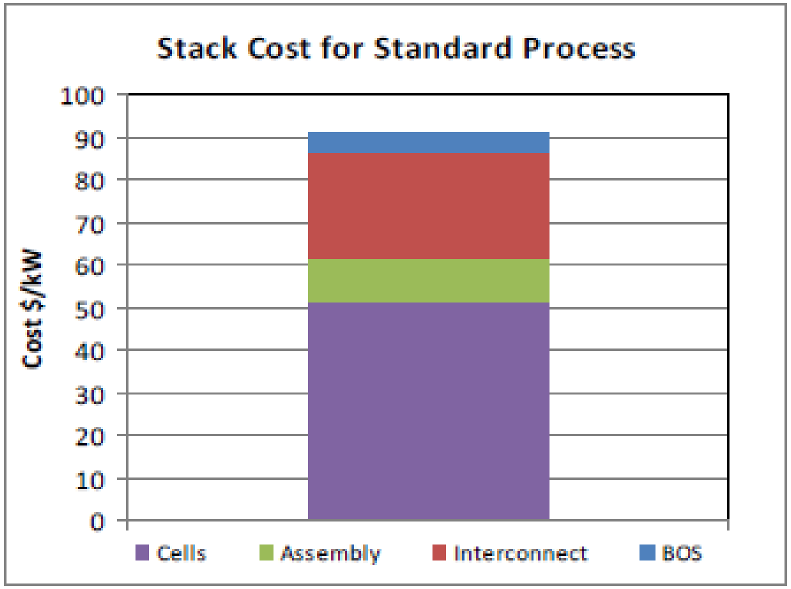
Comparison of Thin Film Deposition Techniques

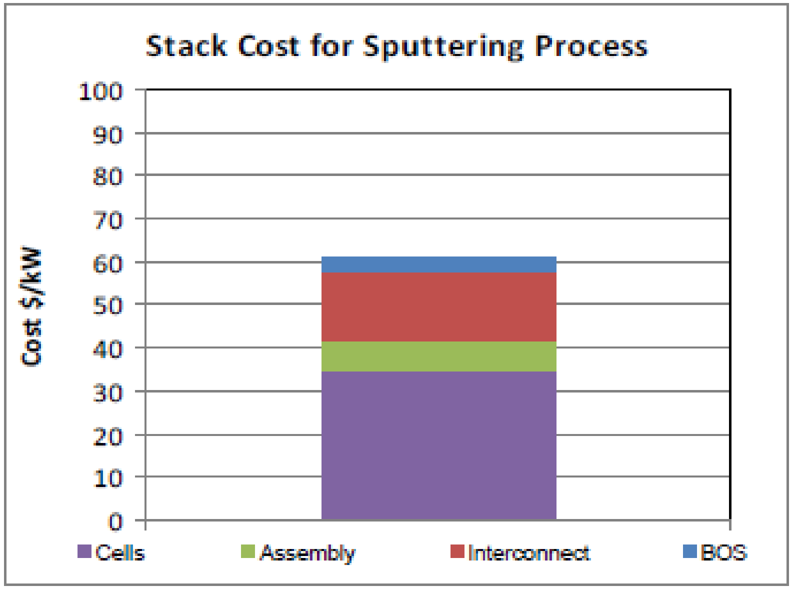
Film deposition technique	Advantage	Key Limitation
Sputtering	Uniform films and near room temperature deposition	
Chemical Vapor Deposition (CVD)	Uniform films	High reaction temperature and corrosive gases
Sol-gel method	Inexpensive	Coating uniformity challenges, multiple coats typically needed with high temperature firing
Thermal spraying	High deposition rates	Difficult to achieve uniform, dense, thin electrolyte
Pulsed laser deposition (PLD)	Versatile	Low throughput (low deposition rate and small deposition area), typically uses high temperature deposition
Electrophoretic deposition	Very high deposition rates	Requires electronically conductive substrate and high temperature anneal
Atomic layer deposition (ALD)	Uniform very thin films	Slow deposition rates, often uses complex precursors
Other conventional processes (e.g., calendering, screen printing, tape casting)	Inexpensive	Requires high firing temperature to achieve high density and typically produces thick films (>> 1 um)

Sputtering is the most attractive technique

Cost of Sputtering

Study on conventional yttria-stabilized zirconia (YSZ) electrolyte SOFCs



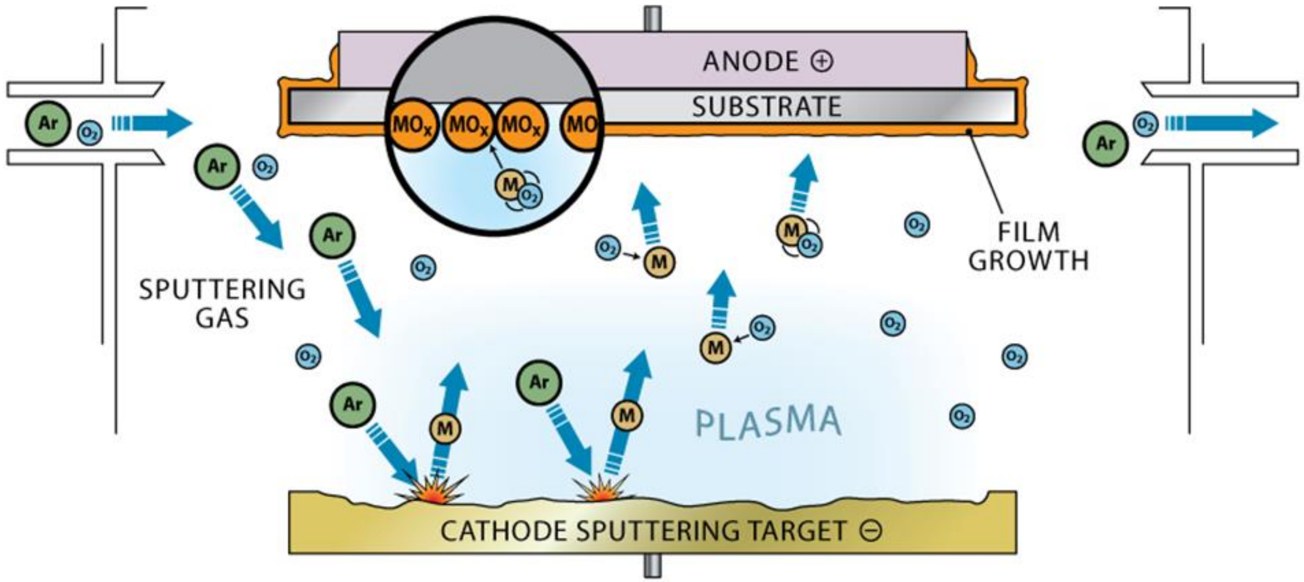


M. R. Weimar, D. W. Gotthold, L. A. Chick, and G. A. Whyatt, "Cost study for manufacturing of solid oxide fuel cell power systems," PNNL Rep., p. 22732, 2013

- Despite high capital equipment cost, sputtering results in predicted ~30% reduction in SOFC system cost
- Reduction in cost largely associated with dramatic increase in power density and resulting decrease in amount of components and assembly hours needed

Sputtering Fundamentals

Reactive Sputtering

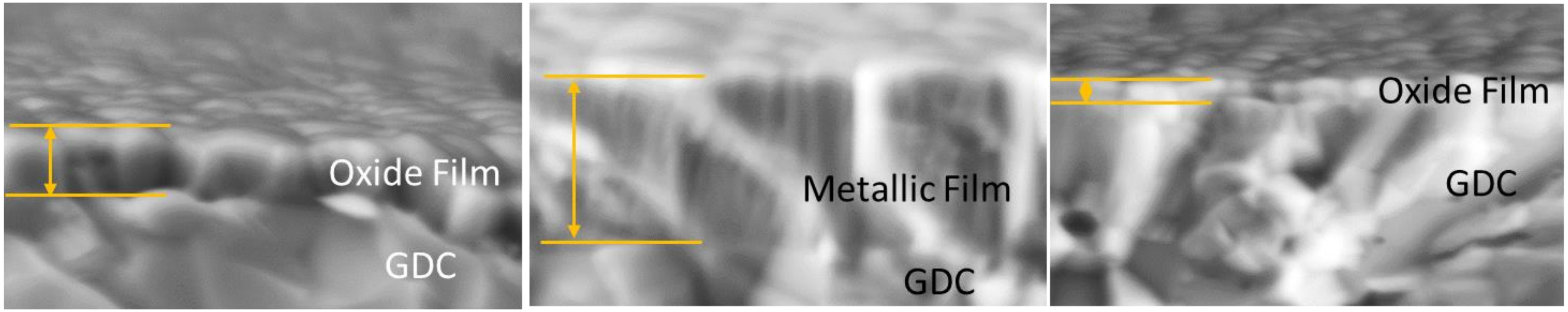


Ref.: Clear Metals Inc.

- The sputtering gas (Ar) is accelerated using DC bias to the sputtering target, bombarding it and releasing metal atoms
- Metal atoms react with O_2 and deposit on the substrate
- Process parameters include: sputter pressure, O_2 pressure, DC bias, and sputter time

Preliminary Sputtering by Redox

Key parameters tune film morphology

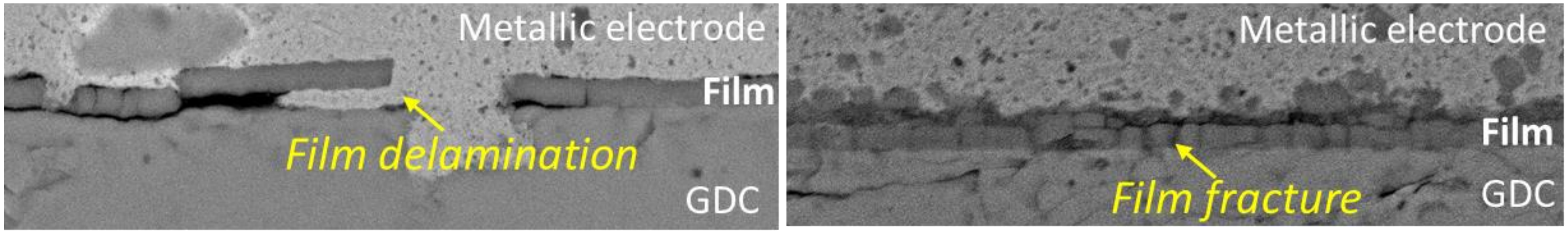


→Thick, dense oxide

→Very thick, dense metal

→Thin, dense oxide

Cell design (e.g., electrode type) impacts post-SOFC-test film microstructure



Oxide electrodes largely avoid above poor post-test microstructures (see earlier slide)

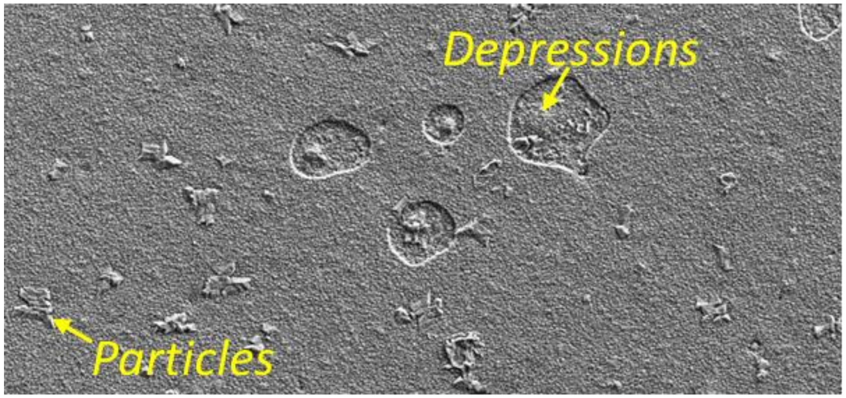
Project Objectives

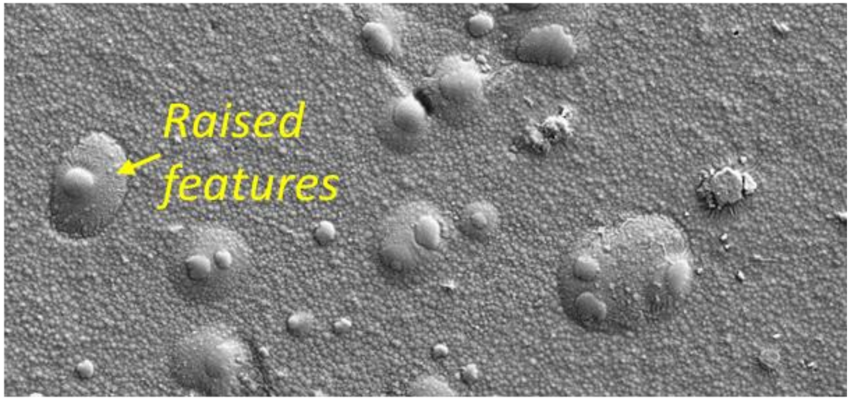
Tasks

1. Project management
2. Optimize electrolyte and buffer layer deposition process
3. Optimize processing parameters for sputtered cathode functional layers
4. Scale-up sputtering process

2.1. Optimize electrolyte and buffer layer deposition process: Optimize substrate

Examples of extreme surface defects observed on sputtered Redox cells





Improve processing conditions

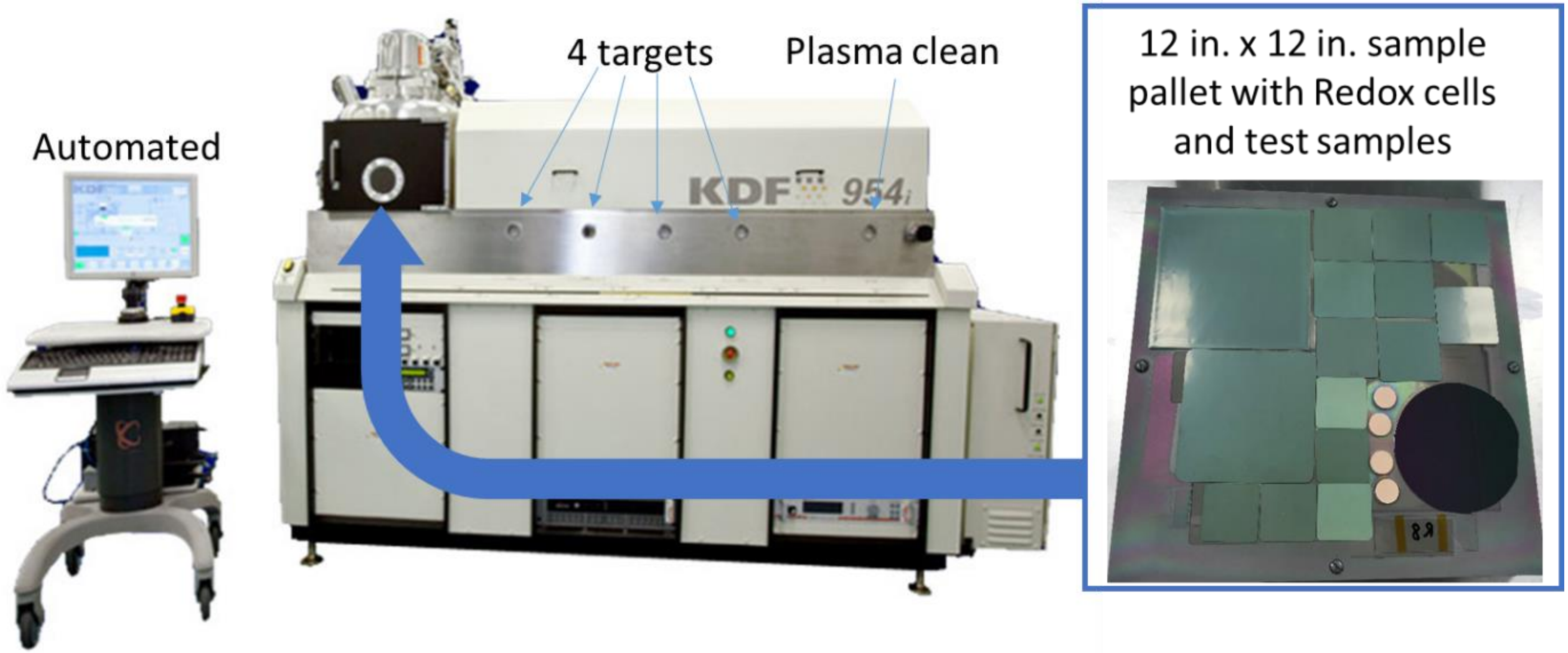
- Tape casting process
- Cell fabrication process
- Room cleanliness

1.2+1.4. Identify and Optimize Pre- and Post-Sputter Treatments

https://www.cismst.org/en/technologien/waferprocessing/

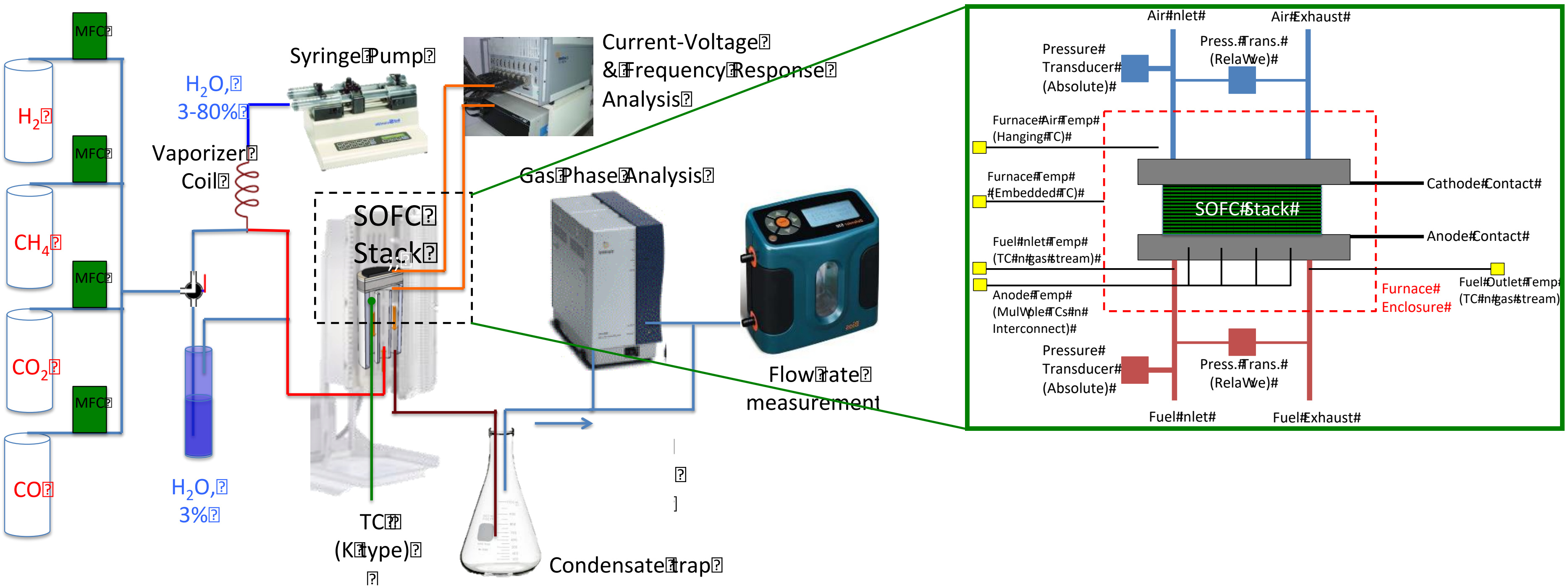
- Take advantage of semiconductor industry knowledge
- Substrate pre-clean steps (RCA clean)
- Anneals

1.3. Optimize Sputtering Conditions



- Commercial scale sputtering systems available to process large sample batches at high throughput with multiple targets
- Redox will work with KDF, a commercial-scale sputter system manufacturer, to fabricate sputtered thin films
- Redox will also use small-scale sputter equipment available at the University of Maryland Nano-fabrication center

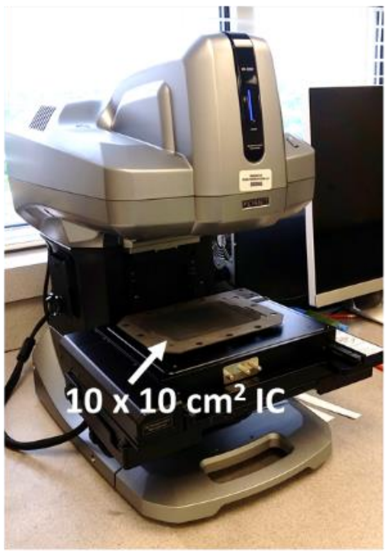
1.5. Test Sputtered SOFCs



- SOFC testing of mini-cells, 5 cm x 5 cm, and 10 cm x 10 cm cells
- Use advanced electrochemical testing, gas analysis, and system parameter monitoring test stations at Redox

1.6. Post-Test Characterization

Optical profilometry capabilities at Redox (Keyence VR and VHX)



High throughput

High resolution (1000x)

User Facility: Hitachi SU-70 SEM/EDS

- Optical metrology
- SEM/EDS
- XRD
- SIMS and XPS depth profiling

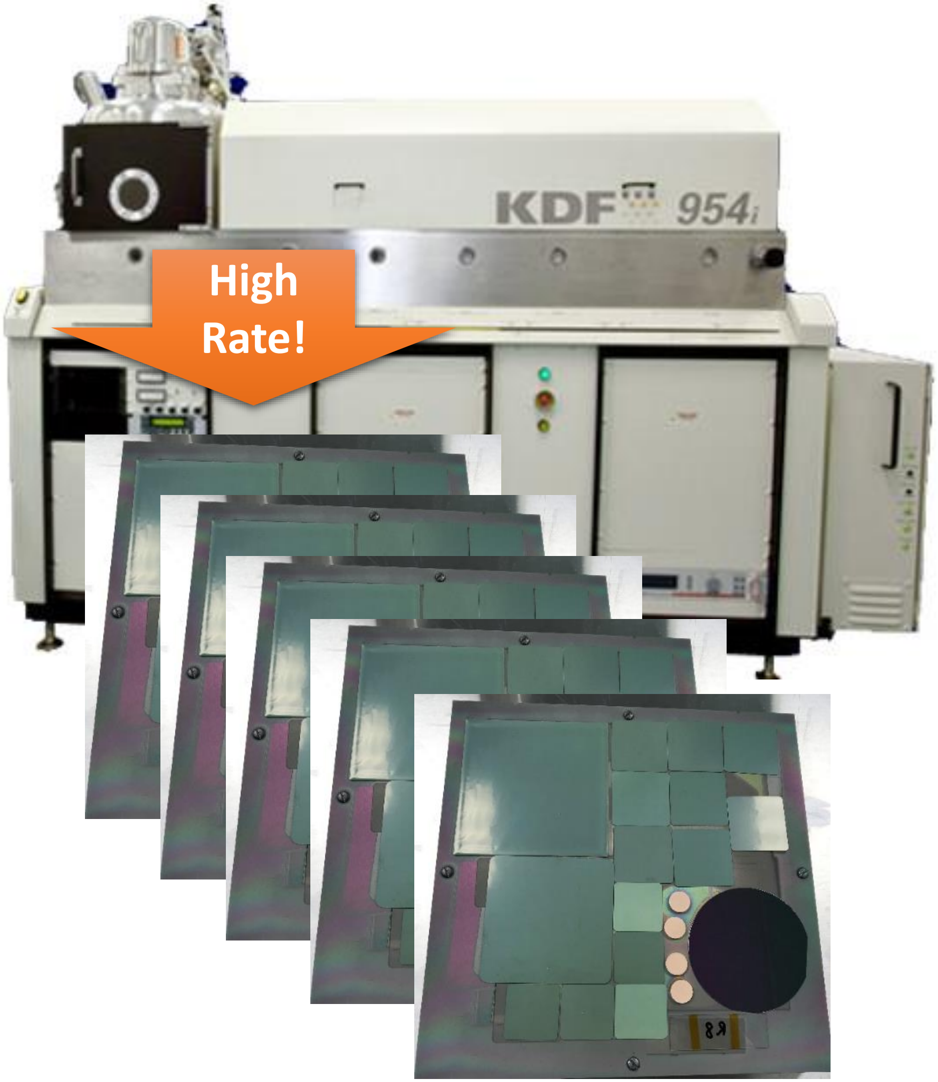
3. Optimize Processing Parameters for Sputtered Cathode Functional Layers

Develop and evaluate the cathode functional layer using cells developed in task 2

1. Optimize sputtering deposition conditions
   - Film density
   - Film microstructure
2. Identify and optimize post-process treatments
3. Test sputtered SOFCs
4. Post-test characterization

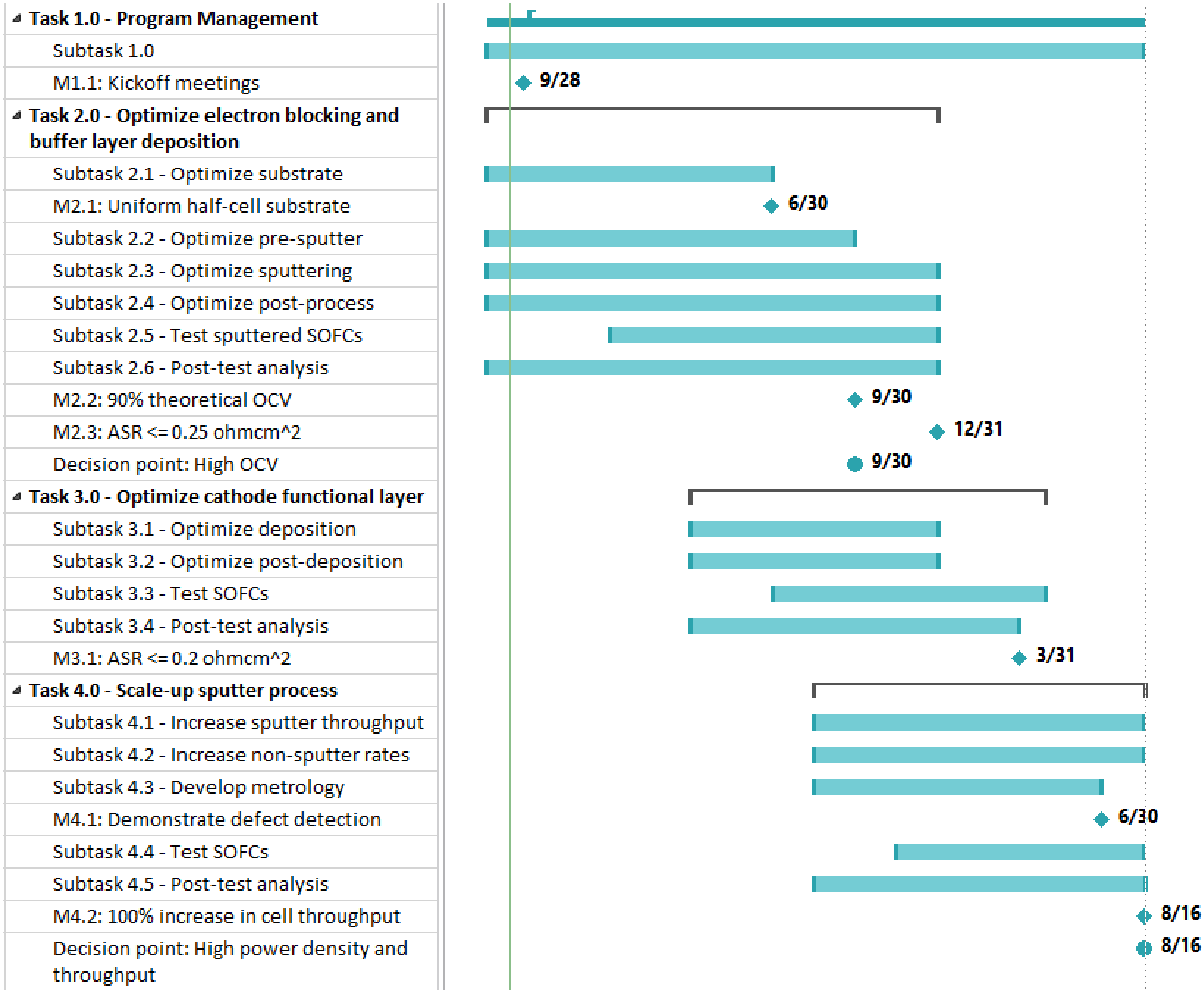
4. Scale-Up Sputtering Process

1. Increase sputtering throughput
2. Increase throughput of non-sputtering processes (e.g., pre- and post-processes)
3. Develop high throughput metrology tools
4. Test sputtered large-scale SOFCs
5. Post-test analysis



REDOX

Gantt Chart



Milestones

Milestone	Project Accomplishment	Due	Success Criteria
2.1	Fabricate uniform substrates	Q4 (6/19)	Achieve uniform GDC electrolyte for sputtering
2.2	Demonstrate large increase in cell OCV with sputtered electron blocking layer	Q5 (9/19)	Achieve ≥ 90% (> 1 V) theoretical OCV with sputtered films at 650 ^{O}C on Redox GEN1 half-cells
2.3	Demonstrate sputtered electron blocking layer and buffer layers do not impact GEN1 ASR	Q6 (12/19)	Achieve ASR of ≤ 0.25 Ω-cm^2 with sputtered electron blocking and buffer layers at 650 ^{O}C on Redox GEN1 half-cells
3.1	Demonstrate cathode functional layer improves GEN1 ASR	Q7 (3/20)	Achieve ASR of ≤ 0.2 Ω-cm^2 and power density ≥1.4 W/cm^2 with sputtered cathode functional layer at 650 ^{O}C on Redox GEN1 half-cells
4.1	Identify high throughput metrology techniques for cell characterization	Q8 (6/20)	Demonstrate ability to detect defective cells with high throughput metrology techniques
4.2	Demonstrate commercial feasibility (fabrication throughput and electrochemical performance)	Q9 (8/20)	Demonstrate 100% increase in sputtered cell fabrication rate with ASR of ≤0.2 Ωcm^2 and power density ≥1.4 W/cm^2 on Redox GEN1 half cells

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:				
Microstructure and composition of sputtered films does not benefit OCV or decrease ASR	Med	High	Med	All processing steps, including substrate fabrication, substrate pre-treatment, film deposition, post-deposition annealing will be examined in detail to optimize film microstructure. Experts in film deposition are involved in this project.
Cathode functional layer does not provide decreased ASR	Med	Low	Low	Improved ASR from cathode functional layer is not necessary to achieve largest impact of program, i.e., very large power density increase and demonstration of commercial-scale sputtering
Metrology techniques are not adequate to identify key defects	Low	Med	Low	Thin film characterization techniques are widely known and available
Rapid throughput of sputtering technique not demonstrable	Low	High	Med	Sputtering with commercial equipment is high throughput. Film thicknesses in this project are thin enough that time on machine is expected to be low enough for high throughput