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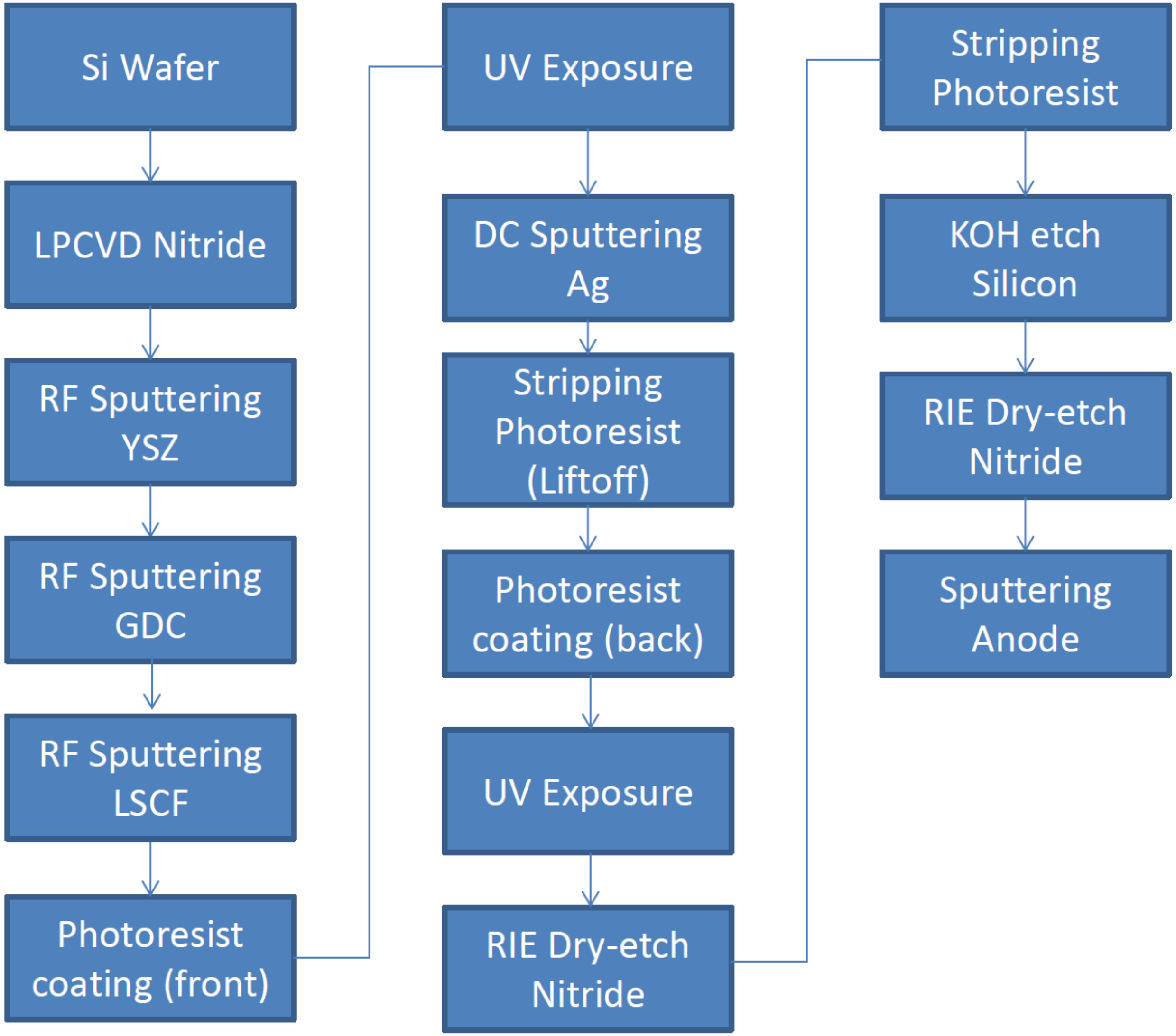
Si Energy Systems, LLC
28.086
An Allied Minds Company

The Cell Variability Project

Key steps in the cell fabication

- **Process Steps (in laboratory scale process)**
  - **Acquire 6” (100) silicon wafer from a vendor.**
  - Form low stress SiN layers on both sides of the wafer by LPCVD.
  - *(Currently performed by an external MEMS foundry)*
  - Sputter YSZ electrolyte (RF sputtering) – 30-40 nm
  - Sputter GDC interlayer (RF sputtering) – 40-50 nm
  - Sputter LSCF cathode (RF sputtering) – 40-50 nm
  - Photoresist coating on LSCF surface (spin-coating).
  - UV Exposure and photoresist development.
  - Sputter Ag current collector – 250 nm.
  - Photoresist coating on back side. UV exposure and photoresist development.
  - Dry-etch of backside SiN layer by RIE.
  - Strip remaining photoresist. (Front and back sides)
  - Wet etching of silicon by KOH solution.
  - Dry-etch of front side SiN layer by RIE.
  - Sputter anode oxide layer – Ni-GDC (DC-RF co-sputtering) – 60 nm

Process Steps



Cell Variability Project

Objective/Scope

"To understand the root causes of performance* variation that exists in coupons tested from the same wafer batch"**

— **Performance is defined as: (i) Peak/initial power/current density and (ii) degradation rate*
— ***Tested on the Same tester*

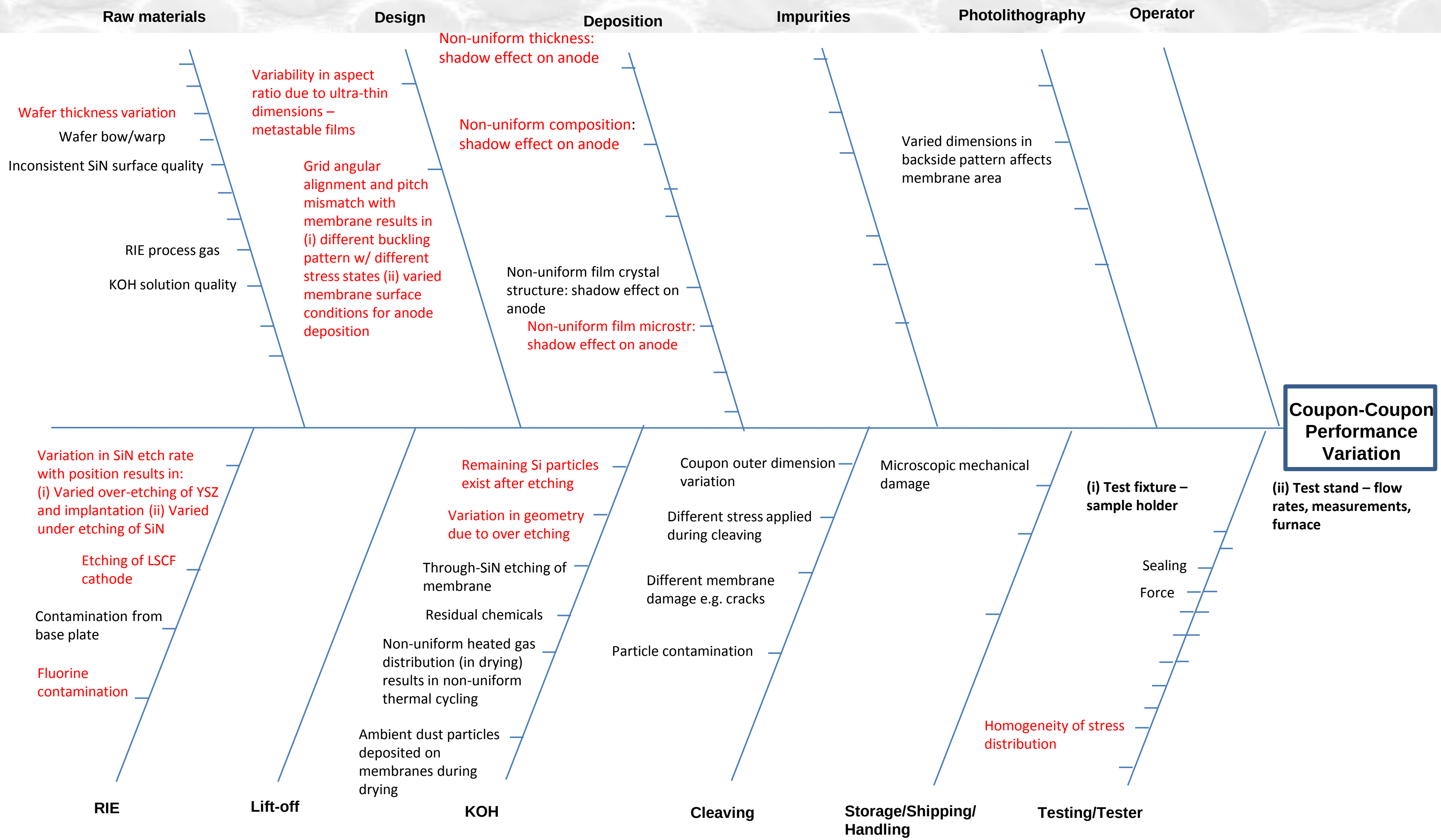
Down-Selection Methodology

- Data suggests less variation is observed using ceramic substrates compared to free-standing membranes
- Two fish bones addressing root causes for performance variation in each case were created and subtracted:

Free-standing membranes fishbone − Ceramic substrates fishbone = Most likely root causes

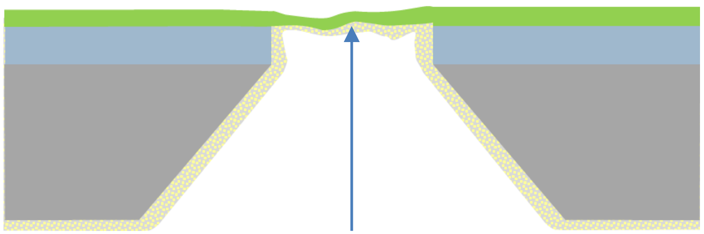
- Common root causes were subtracted **if and only if** items have same impact in both systems (e.g. variation in substrate thickness has different implication for free-standing coupons so remains as a likely root cause)

Fishbone Diagram: Subtracted Fishbone – Coup.-to-Coup. Perform. Variation

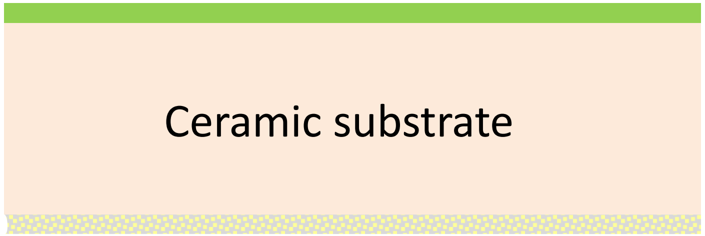


In red = down-selection based on scientific judgement and data

Films on Ceramic Substrate vs. Freestanding Films: Bridging the Gap



Free-standing membrane



By consideration of: (i) differences between the two systems (ii) root causes from subtracted fish bone addressing variation in initial power/current density **and** degradation rate, there are four ranked (likelihood and difficulty) areas of focus:

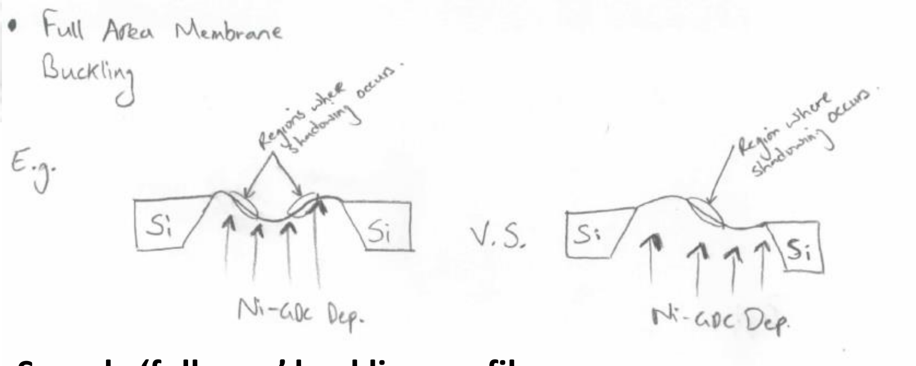
1. Buckling structure variation
2. Variation in over-etching of YSZ by RIE
3. Variation due to metastable ultrathin films
4. Membrane dimensional variation

Hypothesis #1

"Buckling structure variation between coupon membranes results in <u>local</u> differences in Ni-GDC anode microstructure, composition and stress"

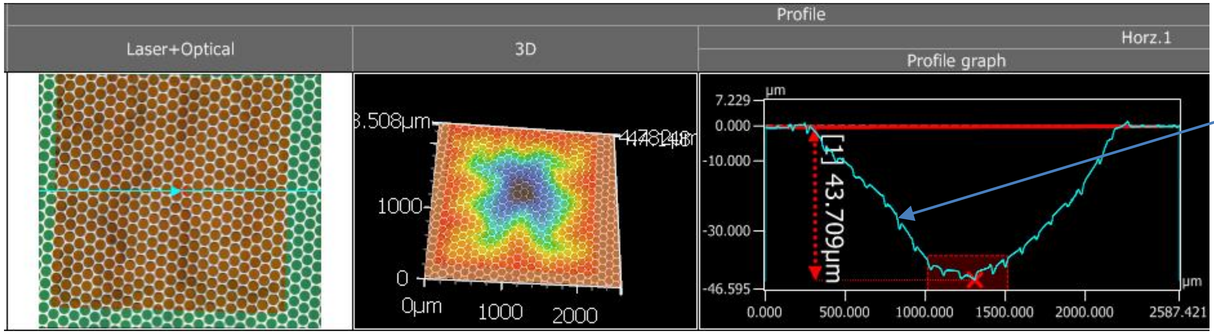
- The resulting variation in Ni-GDC 'initial conditions' leads to a variation in evolution of local microstructure and resulting composition of Ni-GDC on heating <u>even prior to start of data acquisition</u>
- Net result → variation in electrochemical performance and initial degradation behavior (which may occur prior to data acquisition for some coupons)

Hypothesis #1 Explained



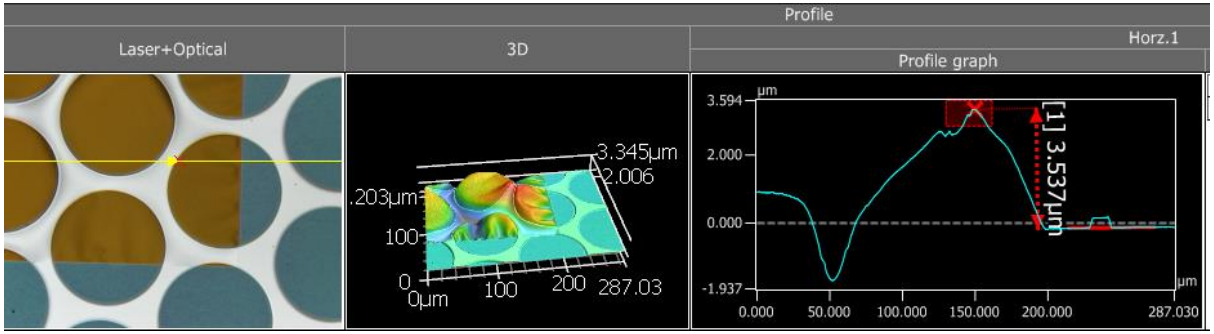
Different buckling patterns and membrane displacement will affect growth of Ni-GDC due to shadowing and differences in surface state e.g. film curvature

Sample 'full area' buckling profile



Profile contains local variations, likely corresponding to 'grid membrane buckling' shown below, another potential buckling structure variability

Sample grid membrane buckling profile



Hypothesis #2

“Variation in SiN etch rate with position results in varied over-etching of YSZ and implantation, affecting (i) as-deposited Ni-GDC microstructure and/or YSZ/Ni-GDC interface (ii) evolution of Ni-GDC microstructure during heating/testing”

- Net result → variation in electrochemical performance and initial degradation behavior (which may occur prior to data acquisition for some coupons)

Hypothesis #3

“Variability in aspect ratio due to ultra-thin dimensions – metastable films result in performance variation”

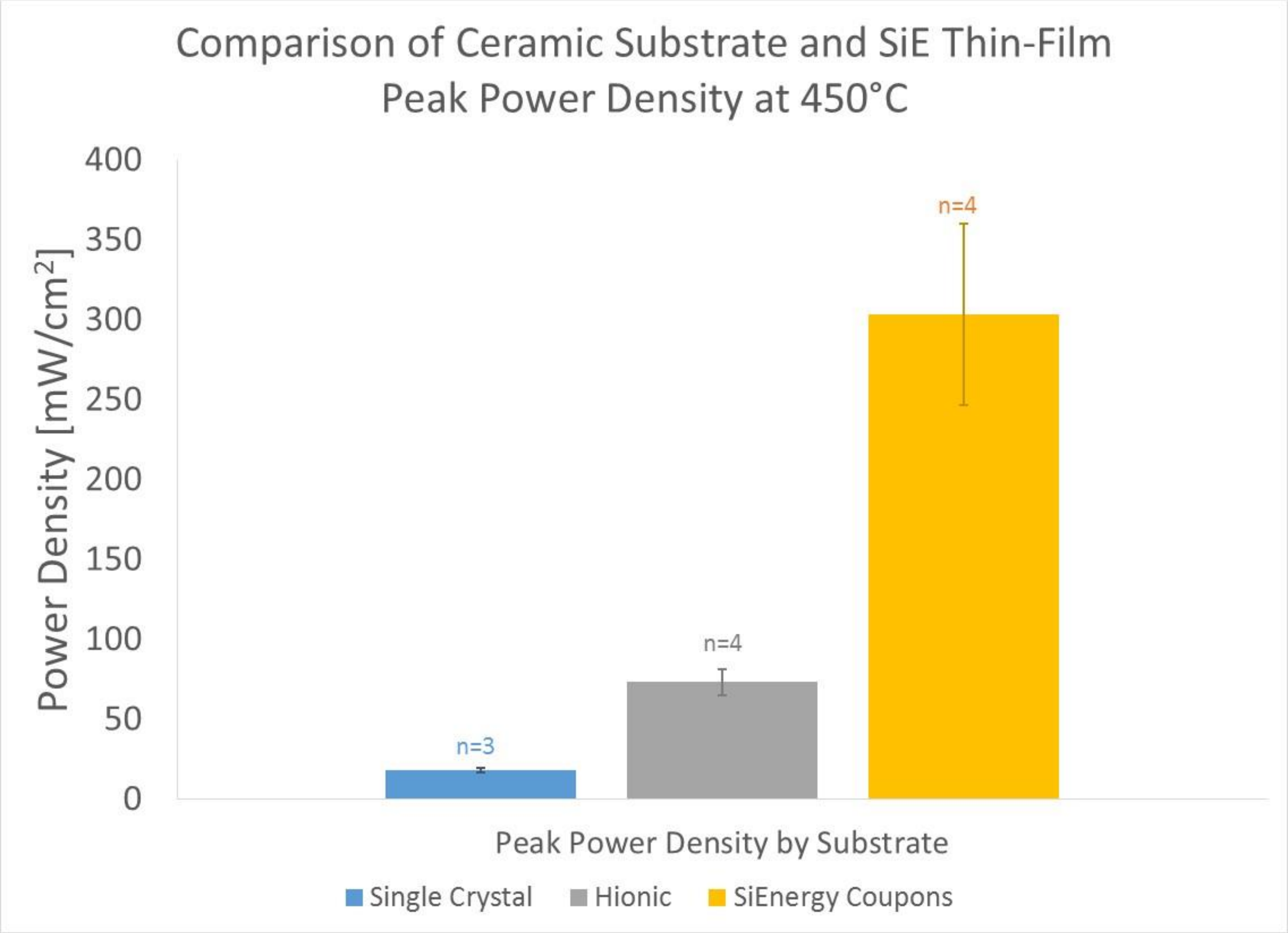
Hypothesis #4

“Variation in membrane dimensions results in variation in performance”

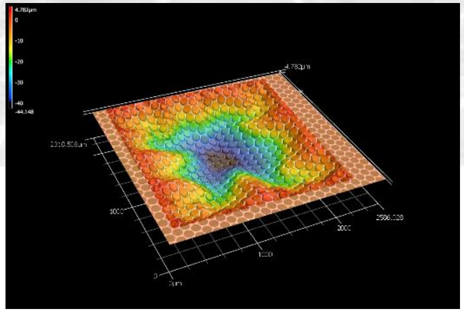
Prioritization of Hypothesis Testing Tasks

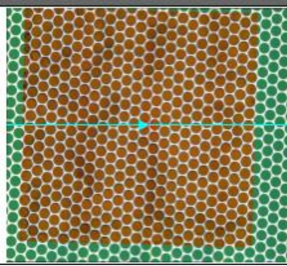
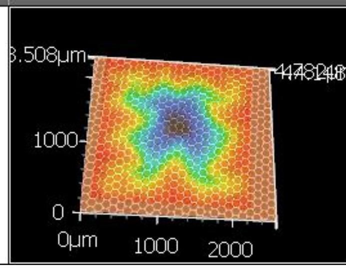
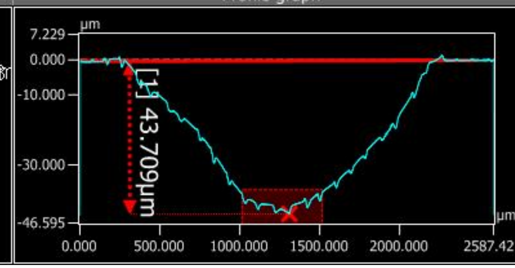
Tasks associated with hypothesis testing tasks are broken down into 3 categories:

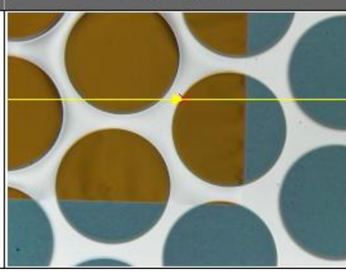
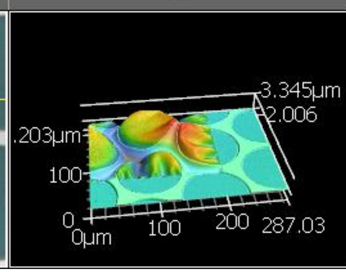
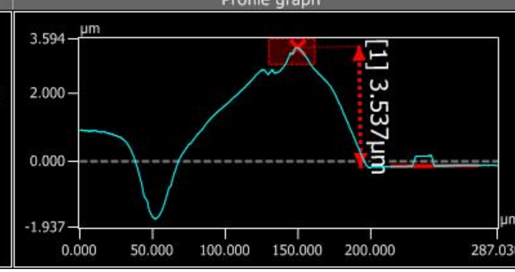
- High priority: tasks which must be completed as soon as possible
- Medium priority: tasks which must be completed but may be subjected to delay due to resources
- Low priority: tasks which are on the fishbone that are ranked less likely due to data and/or scientific judgement



- Greater variation in peak power density exists for SiE freestanding films compared to the same films deposited on thick ceramic substrates



File name	Profile			
	Laser+Optical	3D	Horz.1	
			Profile graph	Measured values
Stitch				No. / Measurement name / Measured value / Unit 1 / Line - Point1 / 43.709 / µm

File name	Profile			
	Laser+Optical	3D	Horz.1	
			Profile graph	Measured values
Membrane Corner				No. / Measurement name / Measured value / Unit 1 / Line - Point1 / 3.537 / µm

Effect of Test Procedure

- For a repeatable test procedure it is possible that peak performance may appear varied if measurements initiate at testing temp and Ni-GDC microstructural evolution varies for each sample prior to testing temperature

- Appendix

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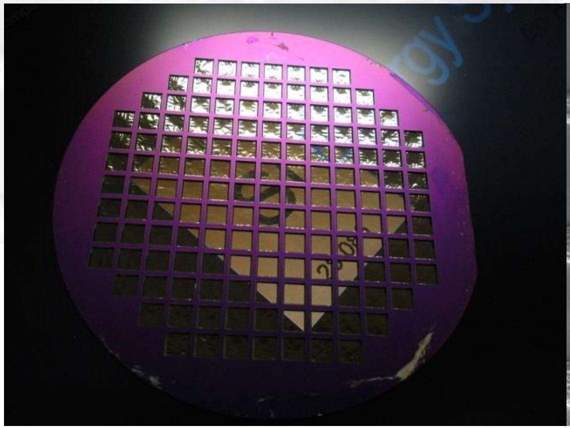
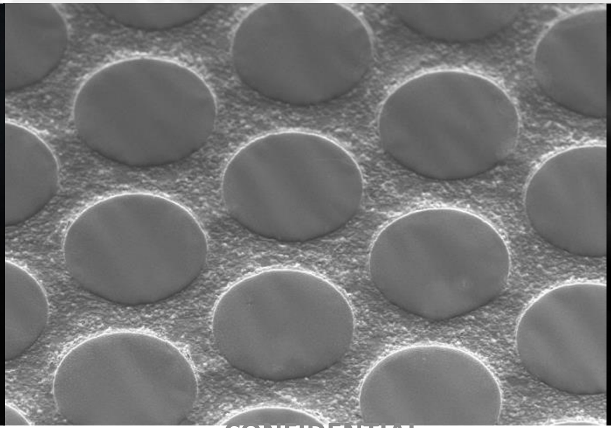
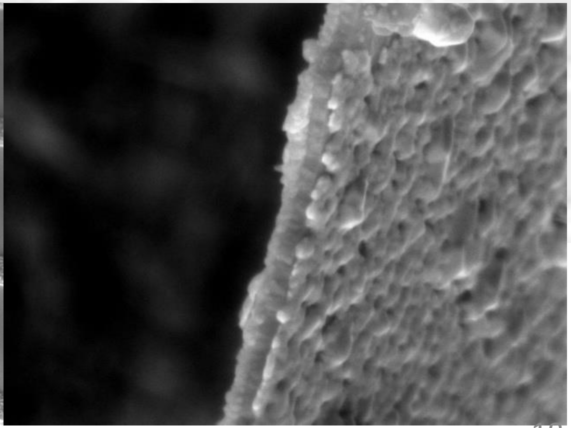
Thin Film Solid Oxide Fuel Cells:

Breakthrough Technology for Affordable Clean Energy

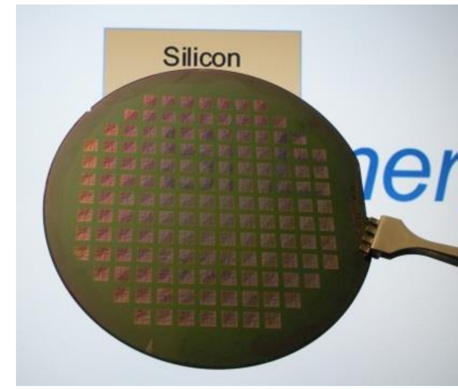


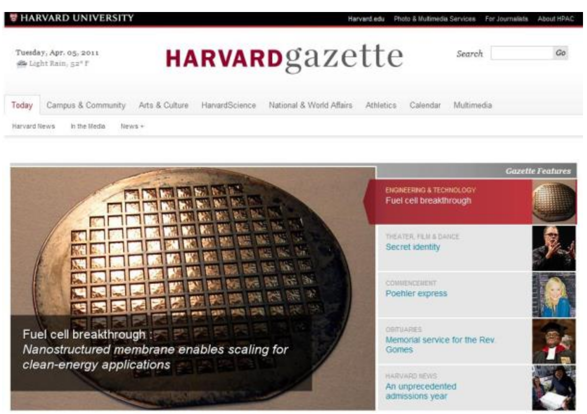




Company Overview

- SiEnergy Systems is a Harvard University spin-off commercializing thin film solid oxide fuel cells.
- SiEnergy team demonstrated the ***FIRST*** macro-scale thin film solid oxide fuel cells in 2010.
- After three years of research activity at Harvard University, the company has moved to an off-campus location in Cambridge, Massachusetts.





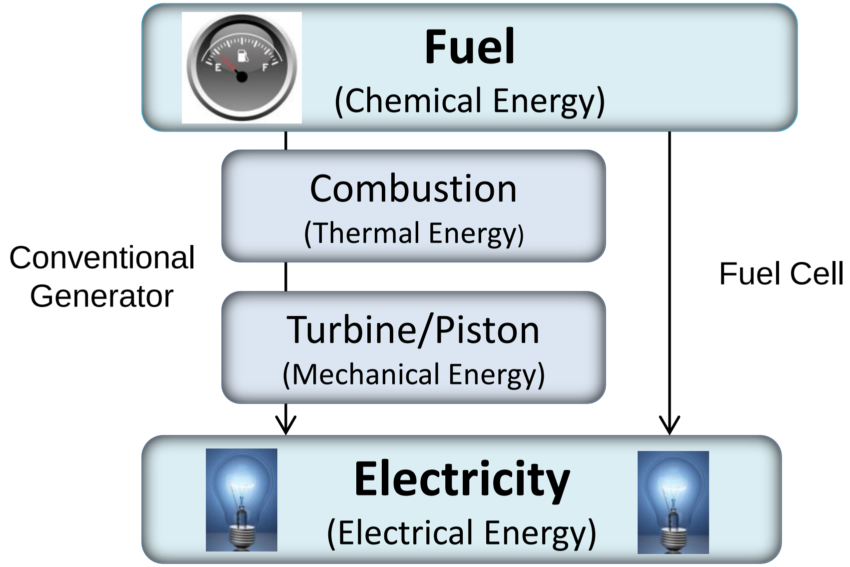
nature nanotechnology

Forbes

EE Times

Solid oxide fuel cell (SOFC)

SOFC Advantages

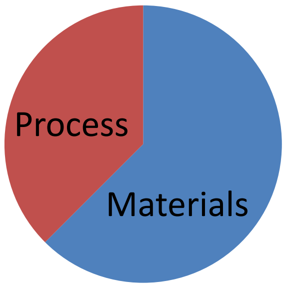


- **Clean and quiet.**
- **Scalable (mW to MW).**
- **Highly efficient.**
  - 50-60% Electrical
  - 80-95% Combined heat and power

SOFC Challenges

(Cost and Durability)

<u>Thick rare-earth oxide materials</u>

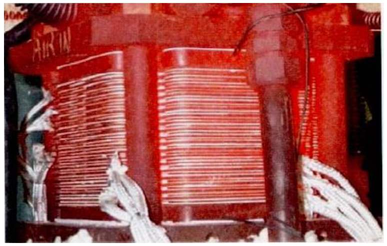


5kW SOFC stack cost

- Materials cost constitutes >50% of SOFC stack cost.

<u>High temperature operation</u>

(750°C or higher)



- High temperature operation limits materials choice and durability.

The Technology

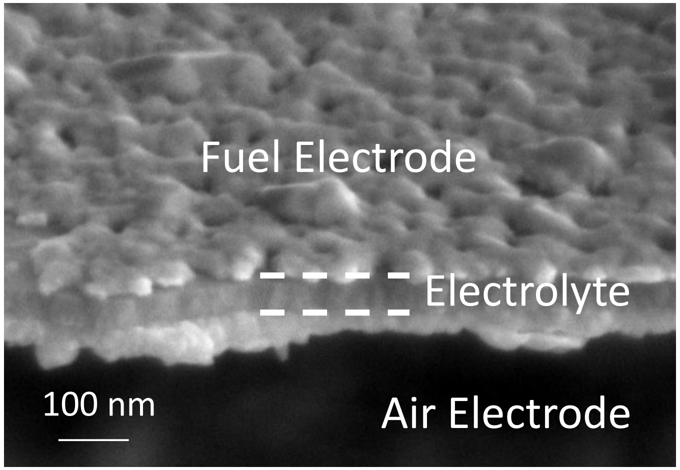
Nanometric Thin Film SOFC

Material cost reduction

- SiEnergy's rare-earth material usage is less than one-thousandth of the conventional SOFC.

Low operating temperature

- SiEnergy operates SOFC at 350-550 °C, which is by far the lowest among SOFC developers.
- Low operating temperature enables better durability and broader materials choice for system components.

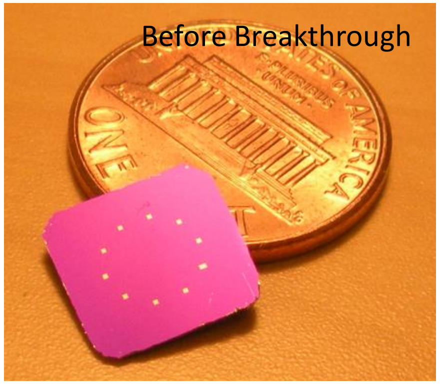


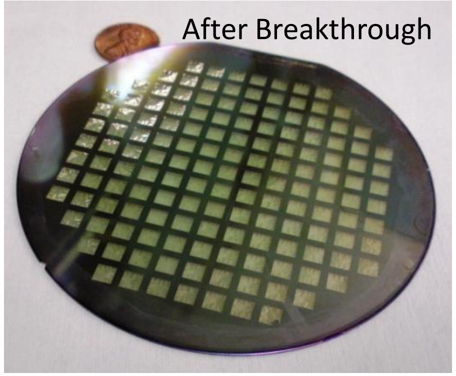
Tsuchiya et al., *Nature Nanotechnology* (2011).

The Breakthrough

Scalable nanometric thin film SOFC

- SiEnergy invented a support structure to scale active area of thin film SOFC from micrometer to centimeter scale. (X 1,000)
- SiEnergy holds exclusive license of core intellectual property from Harvard.



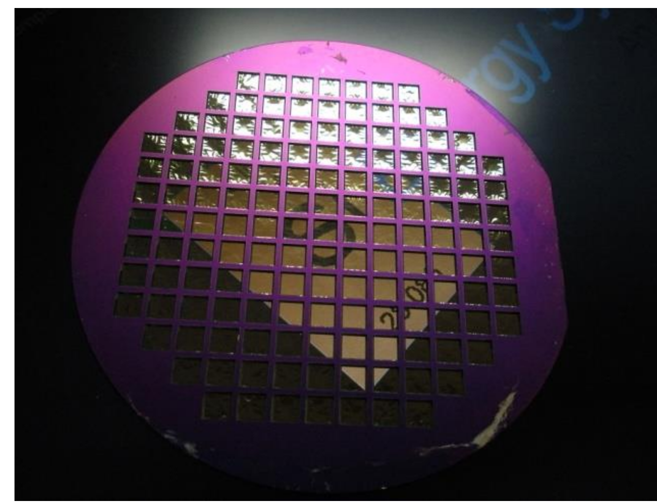


Goals and Objectives

SiEnergy is developing <u>Thin Film Low Temperature</u> SOFC that brings highly efficient, and affordable clean energy systems for broad application.

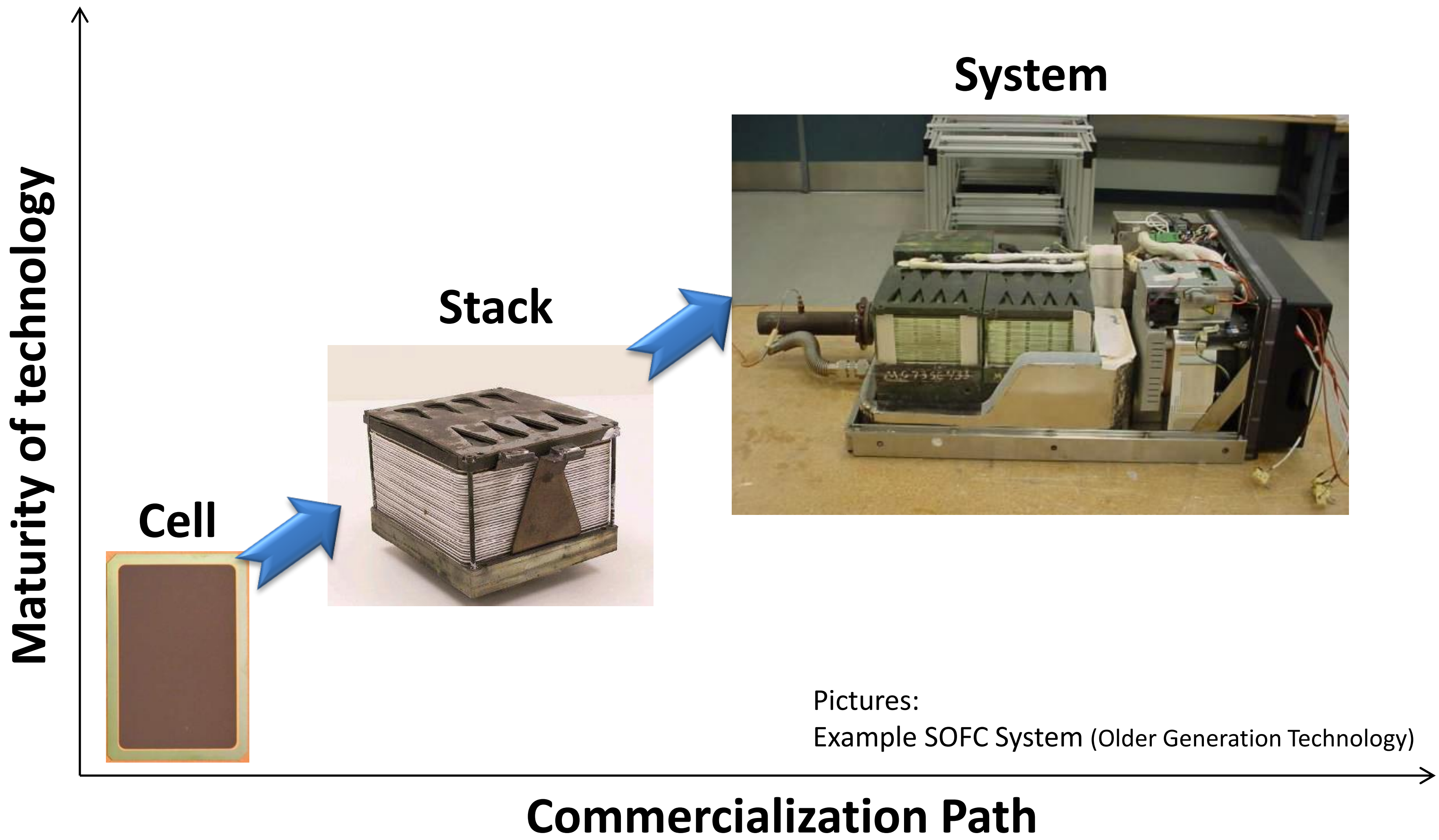
Example Portable FC System
17” (D); 8” (W); 11” (H)

Example Residential FC System
26” (D); 24” (W); 39” (H)



SiEnergy’s thin film fuel cell wafer

Development plan/goals - 1



Development plan/goals - 2

First Product (Gen 1)

100 W fuel cells for remote power sources

Silicon supported cell

SiEnergy provides clean, quiet, and affordable option to extend run time of batteries in remote locations.

Main Product (Gen 2)

1-5 kW fuel cells for small-scale distributed generation

Metal supported cell

SiEnergy will provide highly efficient, safe, and reliable on-site power generation at an affordable price.