

Ultra High Temperature Thermionic Sensor

NETL Crosscutting Research Review Meeting

Scott Limb(PI), Scott Solberg, Arun Jose, Victor Liu

April 28, 2015

Funded under NETL Crosscutting Research: Development of Novel Architecture for
Optimization of Advanced Energy Systems

DE-FE0013062

Program Manager: Barbara Carney

DISCLAIMER: “This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”

HEAT Sensor Project Goal

Harsh Environment Adaptable Thermionics

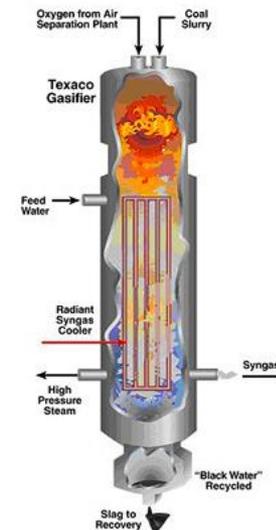
- **Develop sensors that measure process parameters**

- Gasifiers -- harsh fuel, oxidizer and combustion product environment
- High Temperature (750-1600 C)
- High Pressure (up to 1000 psi)

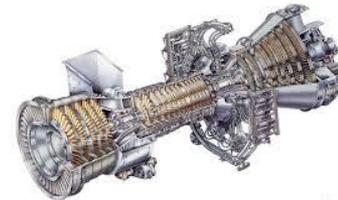
- **Develop sensors that are wireless and self-powered**

- Generate their own energy to operate and wirelessly transmit data
- Avoids wires that may be a reliability or inconvenience concern

Source: GE Energy



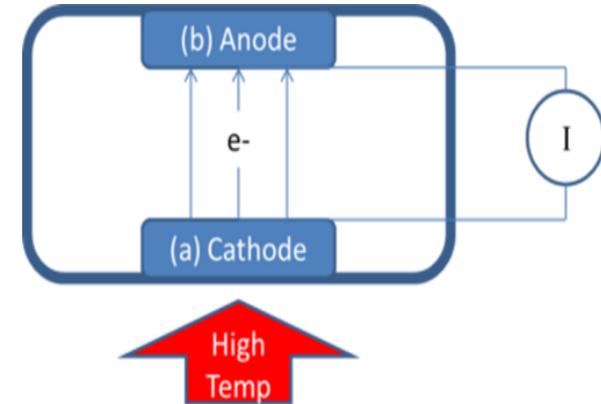
Source: GE Energy



Thermocouple protection system for gasifiers (NETL website)

HEAT Sensor Project Concept

- Use Thermionic Materials as Sensors
 - Heat induced flow of electrons from a metal surface
 - Thermionic emissions occur at high temperature without need for external heater source
- Thermionic Technology
 - Diodes, Triodes, Tetrodes, etc...
 - Amplifier, Oscillators, Power Generation



The 1946 [ENIAC](#) computer used 17,468 vacuum tubes and consumed 150 kW of power

70-watt tube audio amplifier selling for US\$2,680^[31] in 2011, about 10 times the price of a comparable model using transistors.^[32]

HEAT Sensor Project Plan

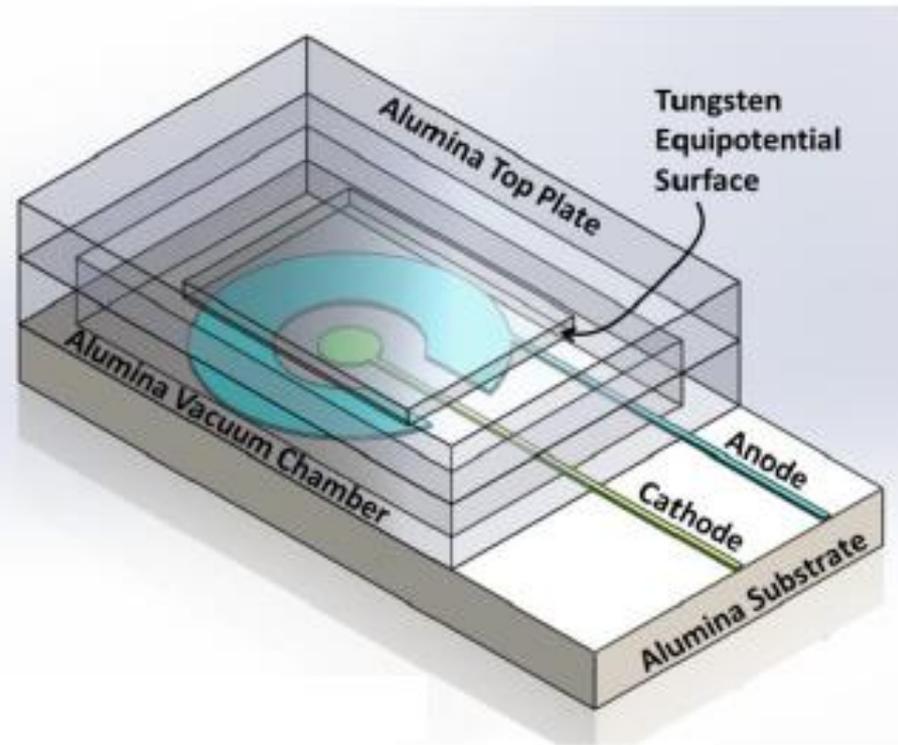
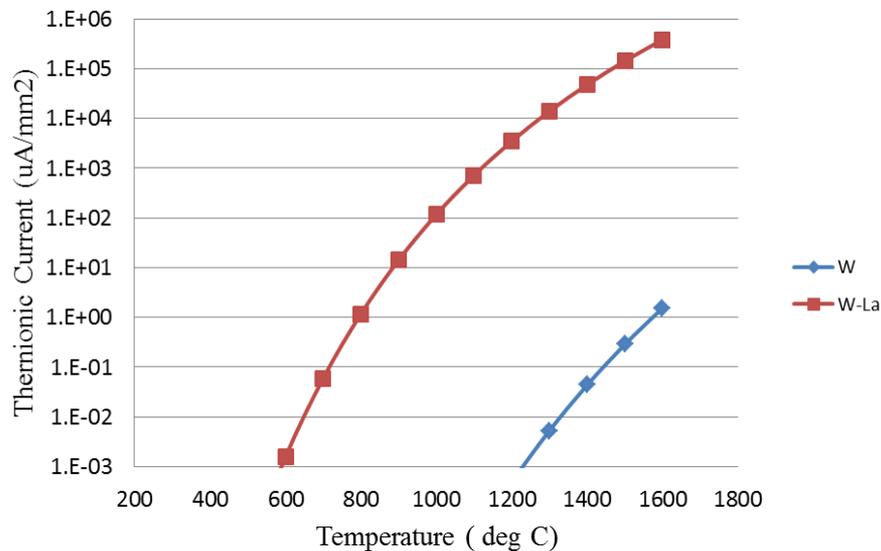
- Model and Pattern Thin Film Thermionic Layers
- Develop Experimental System
- Develop High Temperature Hermetic Package
 - Use High Temperature Co-Fired Ceramics (99.9% pure alumina)
 - Adhesive and Hermetic Sealant Development
- Thermionic Measurements
 - Temperature Sensor
 - Pressure Sensor
 - Circuits and Power Generation

Basic Temperature Sensor

Richardson's Law

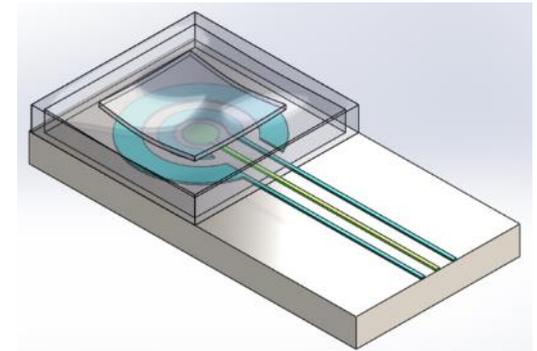
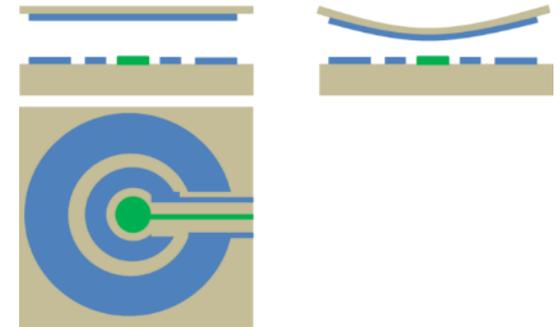
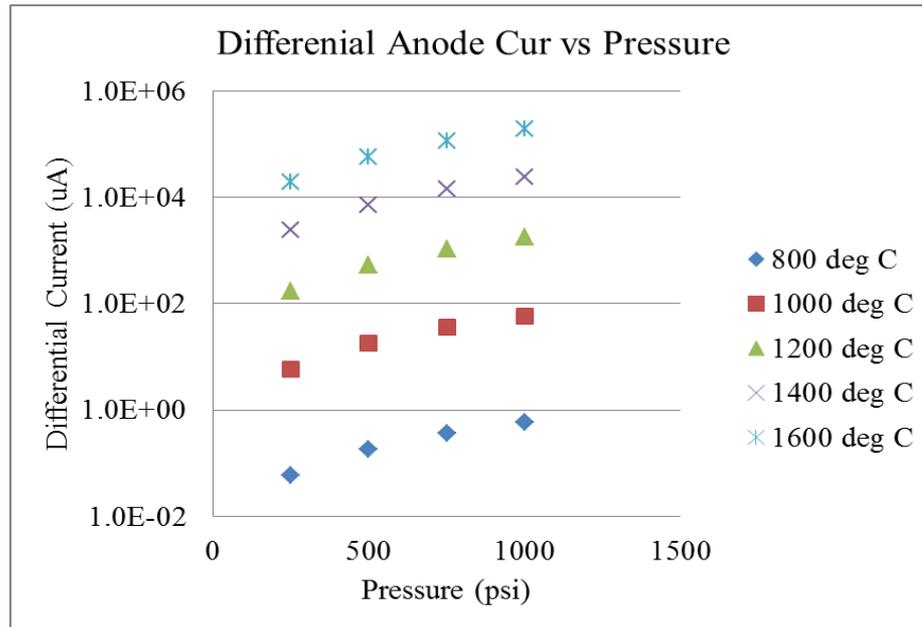
$$J = A_G T^2 e^{\frac{-W}{kT}}$$

Thermionic Current of W vs W-La



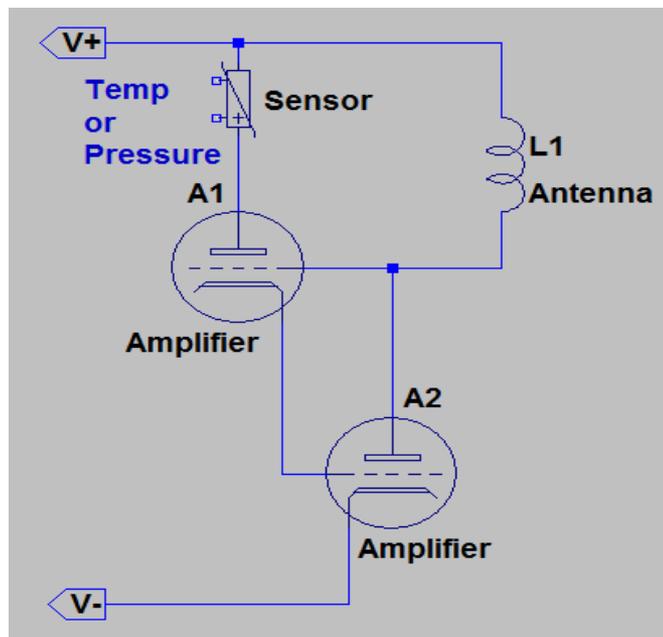
Pressure Sensor

Simulation

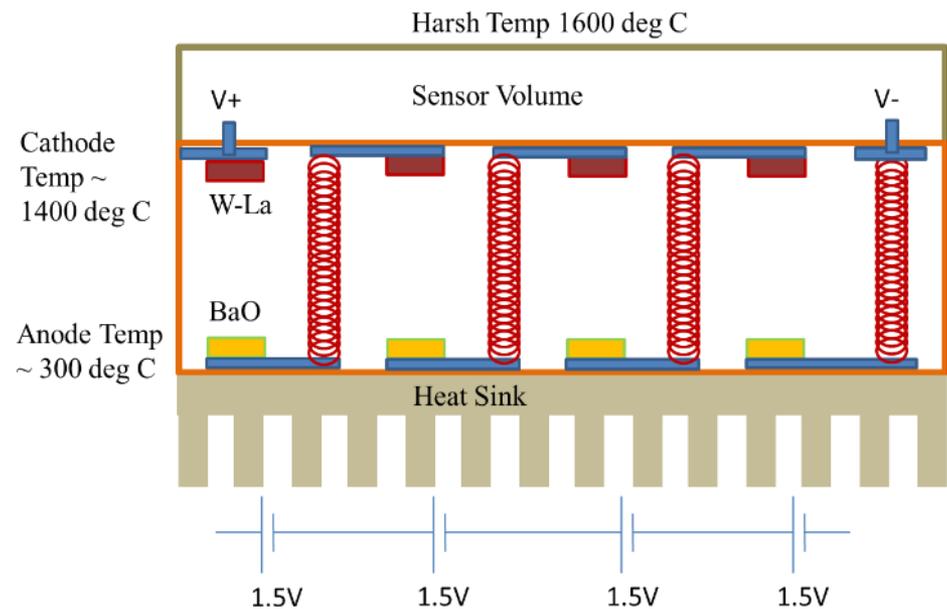


Autonomous Power & Wireless Transmission

Wireless Transmission Circuit Example



Power Generation Concept



50 mA/mm² max current

Vacuum Tubes vs HEATS Platform

Characteristics	Vacuum Tubes	HEATS Platform
Operating vacuum level	Similar	Similar
Package hermetic sealing temperature	<300 C	> 1300 C
Package operating temperature	<300 C	> 1300 C
Package dimensions	~ cm	~ mm

Hermetic Seal Development

- Encouraging initial results using Alumina Paste
 - Fired @ 1350C
 - $<3.4e-4$ mbar base pressure
 - Our target is $<1e-4$ mbar
- Planned Improvements
 - Explore application method and firing procedure
 - Seal area and structure modification
 - Decrease paste particle size
 - Add CTE matched high temperature glass filler

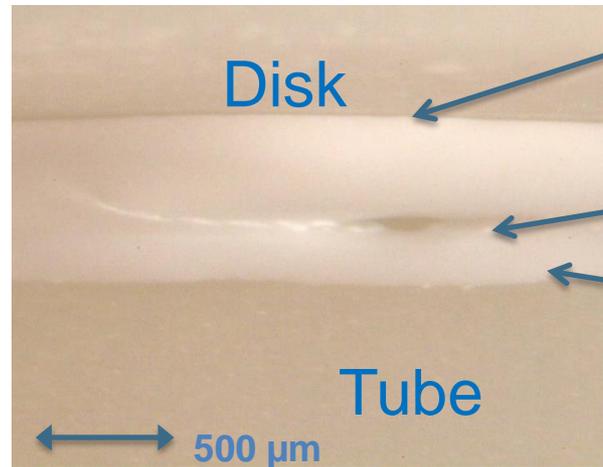


Sample
Connection
Port



Hermetic Seal Development

- Important parameters
 - CTE match (thin glue line)
 - Need melting component to fill in pores (sealing temperature)
 - Surface wettability during curing (additives and surface preparation)
 - Structural thermal stability of substrates
- Secondary importance
 - Paste particle size
 - Drying temperature

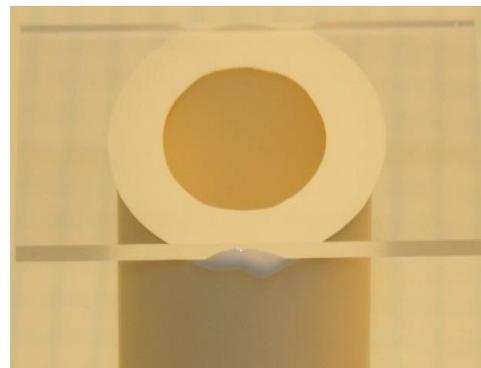


Slight separation between fired excess paste blob and disk.

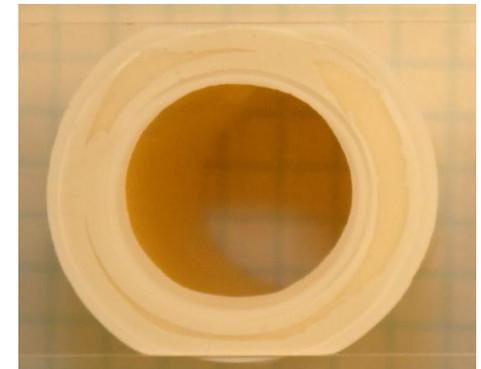
A few obvious cracks

No obvious grain growth

Paste, fired at 1500°C.



Sample after sealing but before any drying



Sample after drying (<300 C bake)
Delamination is clearly visible

Hermeticity Testing

- Multiple paste formulations tested by measuring Tungsten oxidation weight gain
 - Package tungsten powder using sealing paste
 - Bake in air for set period of time
- Failed paste formulations showed oxidation of W (yellow) and volume expansion
- Promising paste formulation showed minimal mass gain at prolonged 1200C temperature soaks
 - 1.463 gr W initially
 - 7 mg gain after 130 hrs
 - $\sim 1 \text{ e-}5 \text{ bar cc/s}$; Spec -- $< 1\text{e-}7 \text{ bar cc/s}$
- 1mm thick HTCC plates had some curvature after curing



Sample 20140819-C,
ready to apply lid.

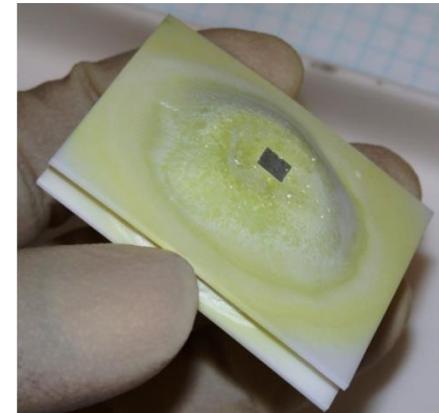


On hotplate, after applied lid
(this paste flakes off when dry)



Fired @ 1600°C in N₂
(darkened in reducing environment)

Used PARC paste
20140731 for sealing.



Re-fired for 30 hours in air at 1200°C

Tungsten oxidation → bad seal

Hermeticity Testing

- Used single layer alumina plate to minimize plate curvature during curing
- Soaked for over 2500 hrs at 1300C.
- Cycled to room temperature 3x and repeatedly cycled between 1000C to 1300C.
- Outgassing was further reduced by an high temperature cycle of 1400C.

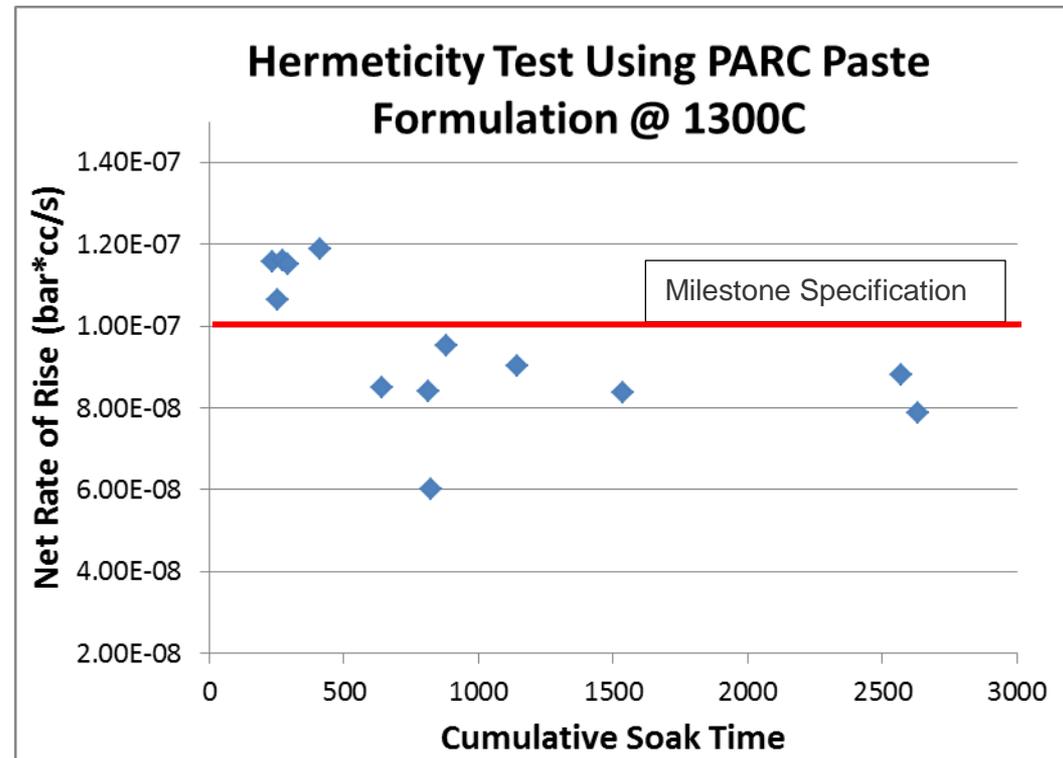


Firing in furnace #2



After firing, can see that some of sealant material flowed

Sample 20140910-A



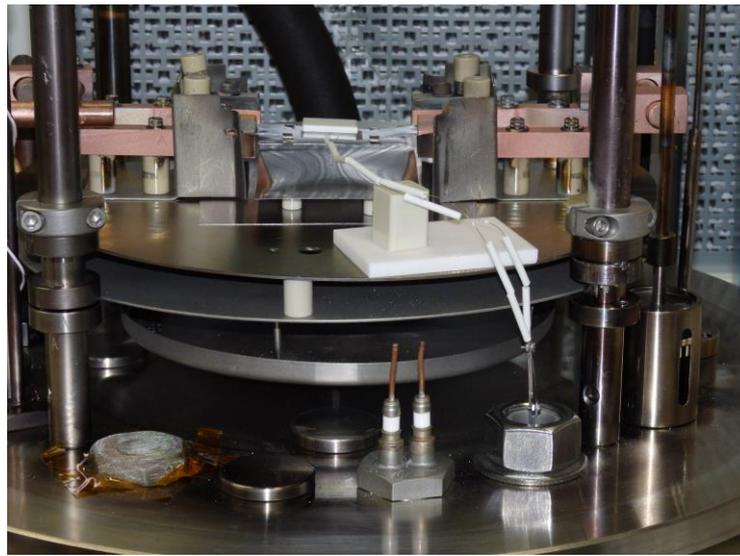
Thermionic Oxygen Poisoning

- Thermionic material oxidized
- Determined background vacuum in MTI tube furnace was too high
 - Getters did not prevent oxidation
 - Reduced current emissions observed
- Could not hermetically seal a package without oxidation of the thermionic material



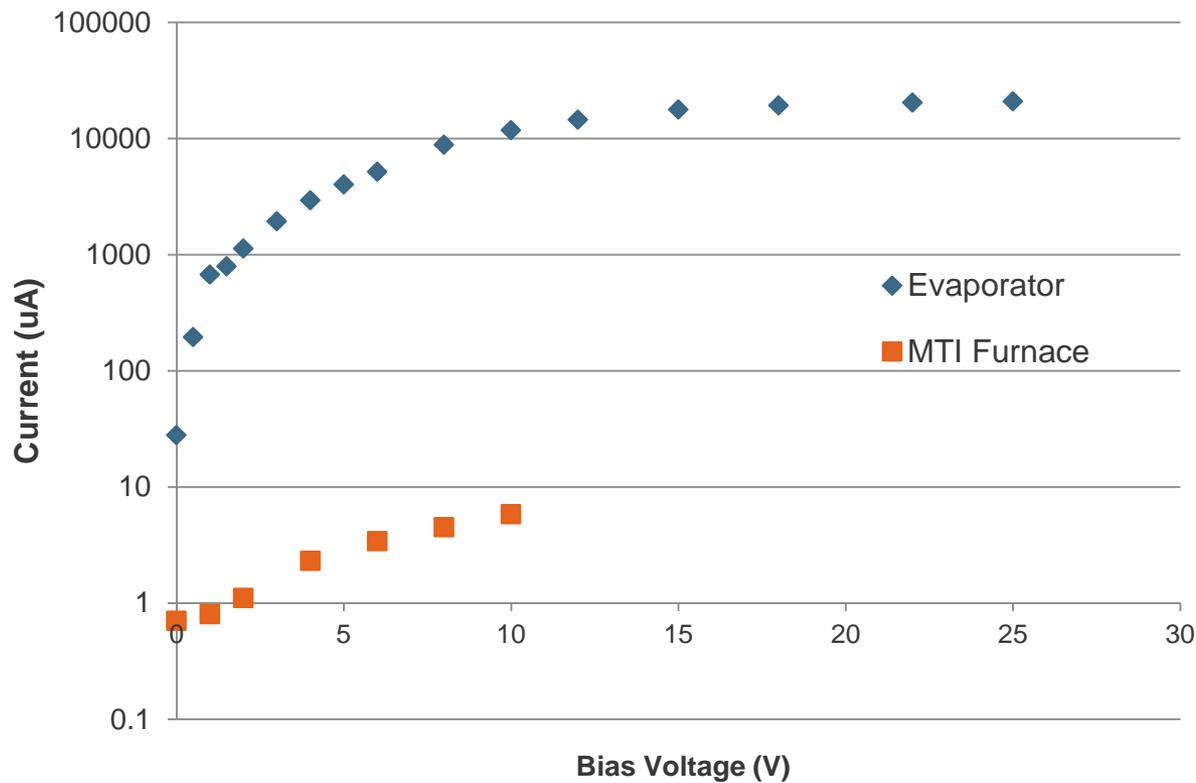
New Test Apparatus

- Converted bell jar evaporator for thermionic testing
- Background pressure – $1e-7$ mbar vs $1e-4$ mbar for MTI furnace
- Temperature control up to 1300C for now (will test to 1600C in future)



Data

Thermionic Measurement at 1200 °C



Evaporator

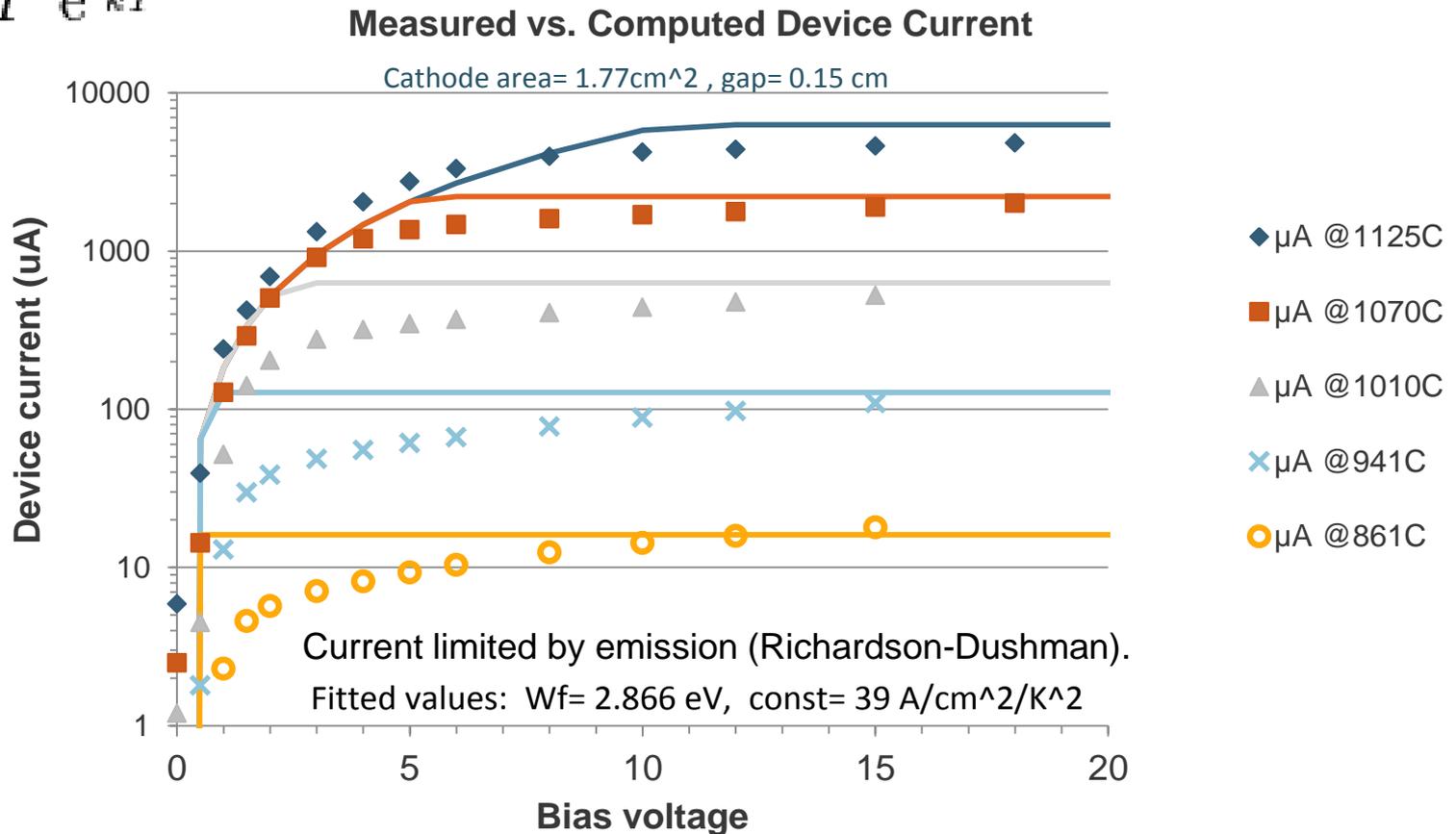


MTI Furnace

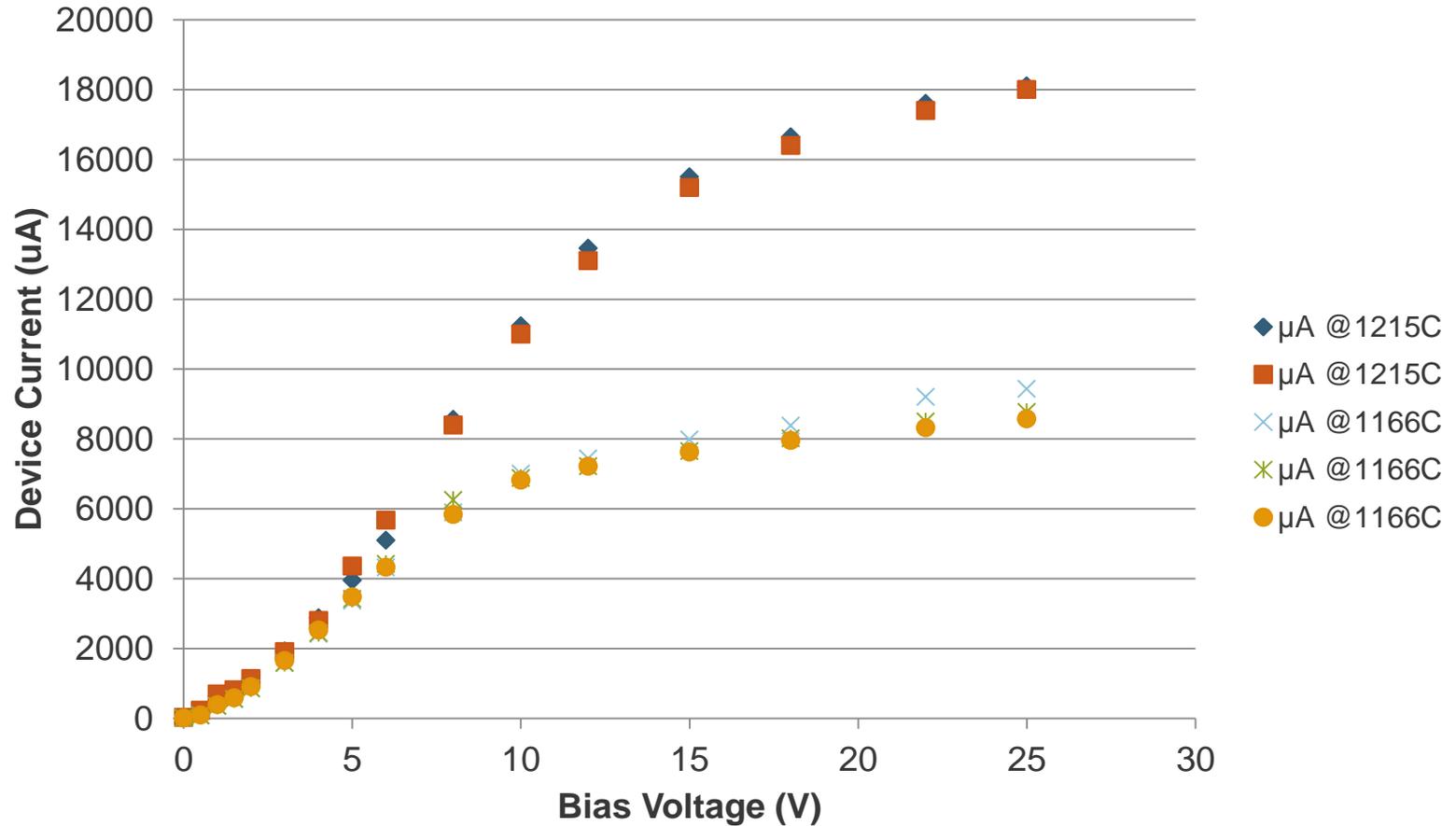


Data – Theory vs Actual

$$J = A_G T^2 e^{\frac{-W}{kT}}$$

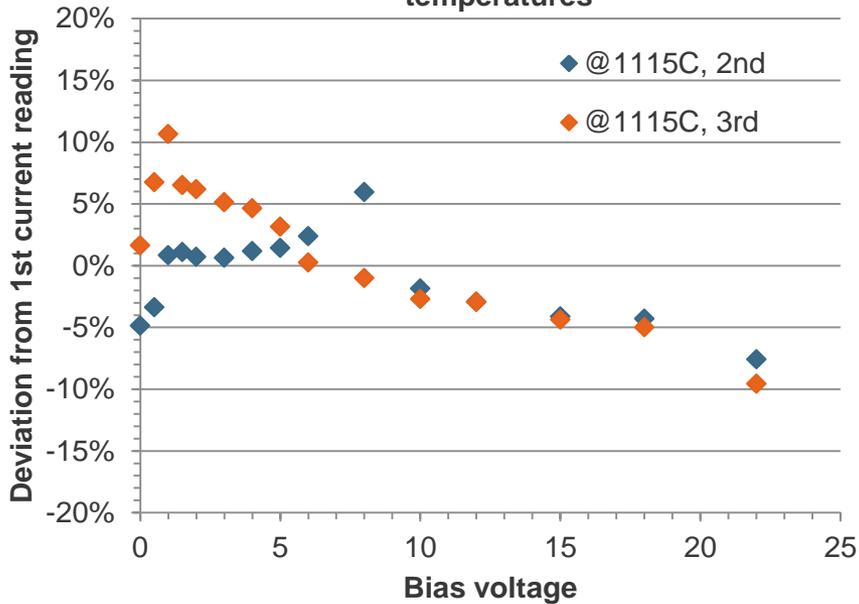


Repeatability

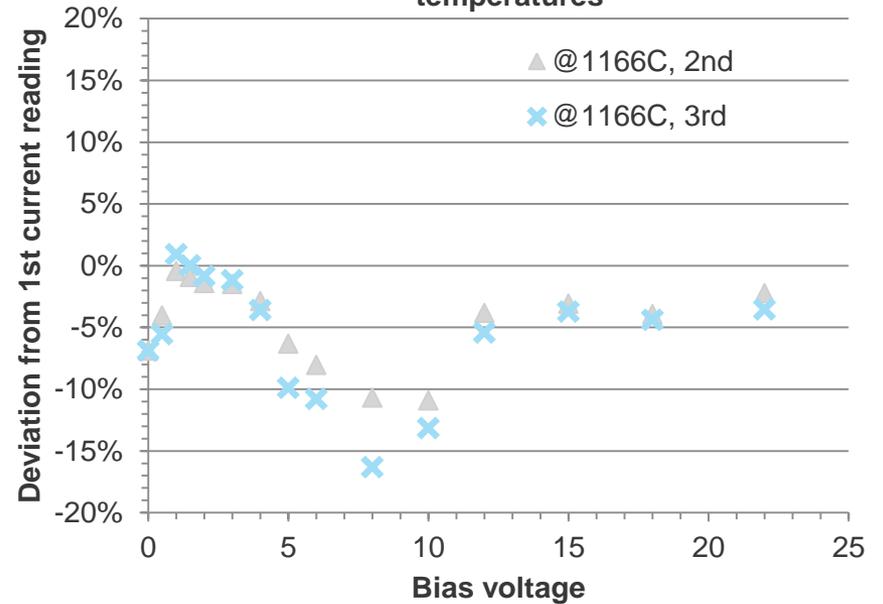


Repeatability

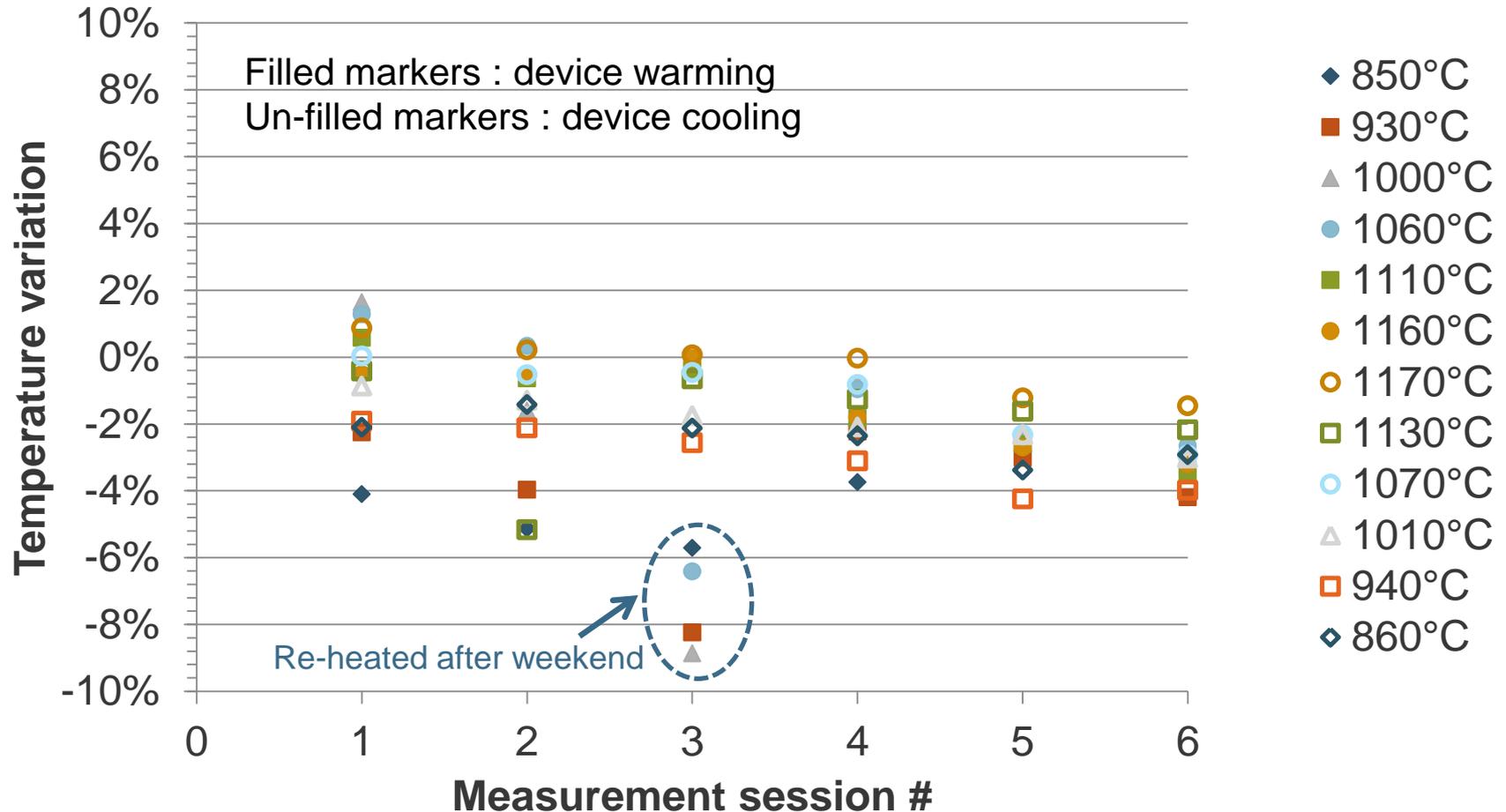
Current reading repeatability at selected temperatures



Current reading repeatability at selected temperatures



Temperature Measurement



Key Milestones

	Device Interconnect	Device Vacuum	Thermionic Material
Milestone 3 Hermetic Seal @ Temp	None	None	None
Milestone 4 Temperature Sensor	Zirconia wire	Active pumping	La
Milestone 6 Pressure Sensor	Zirconia wire	Active pumping	La
Milestone 9a Self powered and wireless	Zirconia wire	Active pumping	La, BaO
Milestone 9b Self powered and wireless	None	Self-contained vacuum with getter	La, BaO