Effect of potassium carbonate on electrode materials for advanced combustion MHD generators

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NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

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Overview

- MHD electrode materials
- HVOF torch test
- Potassium seed injection
- Refractory metal electrodes
- Oxide ceramic electrodes
- Summary and conclusions

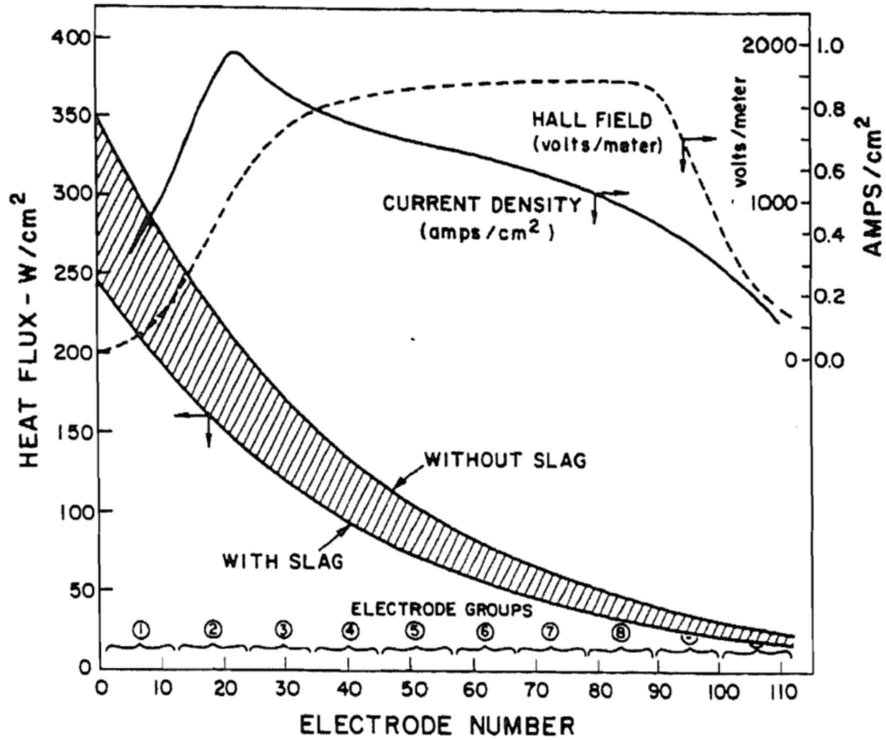
MHD Laboratory, National Energy Technology Laboratory, Albany, Oregon (Photo: NETL, 2017)

MHD Electrode Material Requirements

Pushing the limits of material performance

- High operating temperature
- High electrical conductivity
- Adequate thermal conductivity
- Electrochemical corrosion resistance
- High-velocity particle erosion resistance
- Thermal shock resistance
- Arcing resistance

220 kW MHD channel



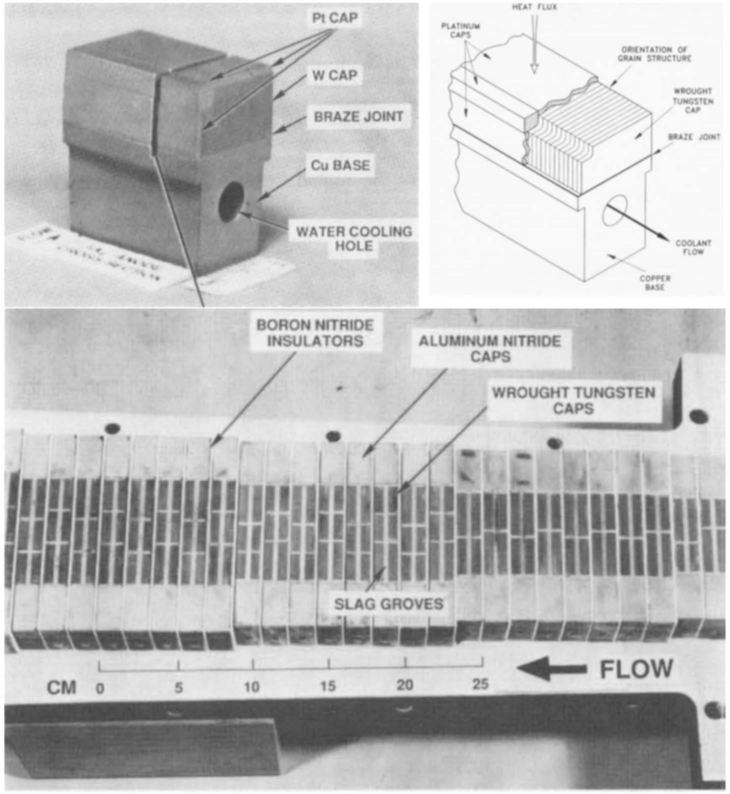
S. Petty, A. Demirjian, A. Solbes, Electrode phenomena in slagging MHD channels, in: 16th Symposium on Engineering Aspects of MHD, Pittsburgh, PA, 1977, pp. VIII.1.1-VIII.1.12.

Metallic Electrodes

Cold (arcing) mode operation

- **Advantages**
  - High electrical conductivity
  - Mechanically robust
  - Resistant to thermal-shock
  - Ease of fabrication
- **Disadvantages**
  - Lower operating temperature
    - Higher heat loss
    - Higher boundary voltage drop
    - Possibility of seed-induced shorts
  - Oxidative evaporation

MHD literature
Tungsten
Molybdenum
Tantalum
Niobium
Copper alloys
Steel alloys
Nickel alloys



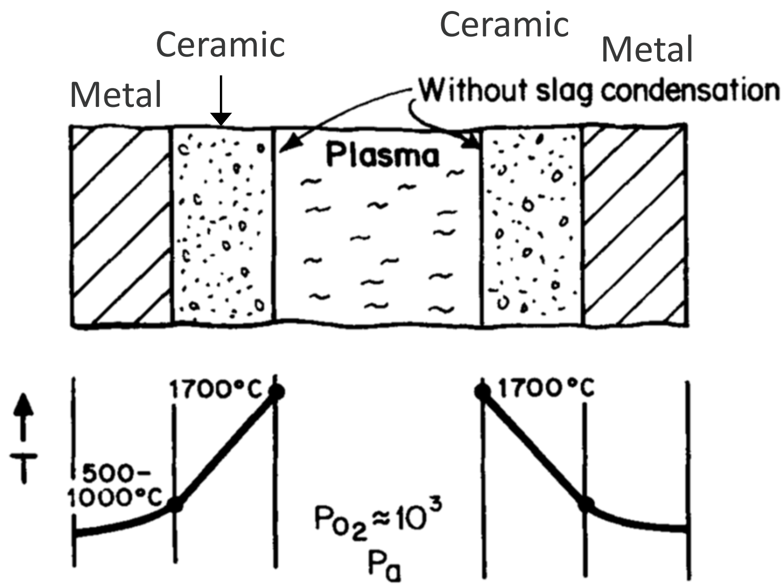
L.C. Farrar, J.A. Shields, Tungsten and tungsten-copper for coal-fired MHD power generation, JOM-J Min Met Mat S, 44 (1992) 30-35.

Ceramic Electrodes

Hot (diffuse) mode operation

- **Advantages**
  - Higher operating temperature
    - Lower heat loss
    - Lower boundary voltage drop
  - Chemical stability
- **Disadvantages**
  - Lower thermal-shock resistance
  - Ionic charge conduction
  - Difficult to fabricate

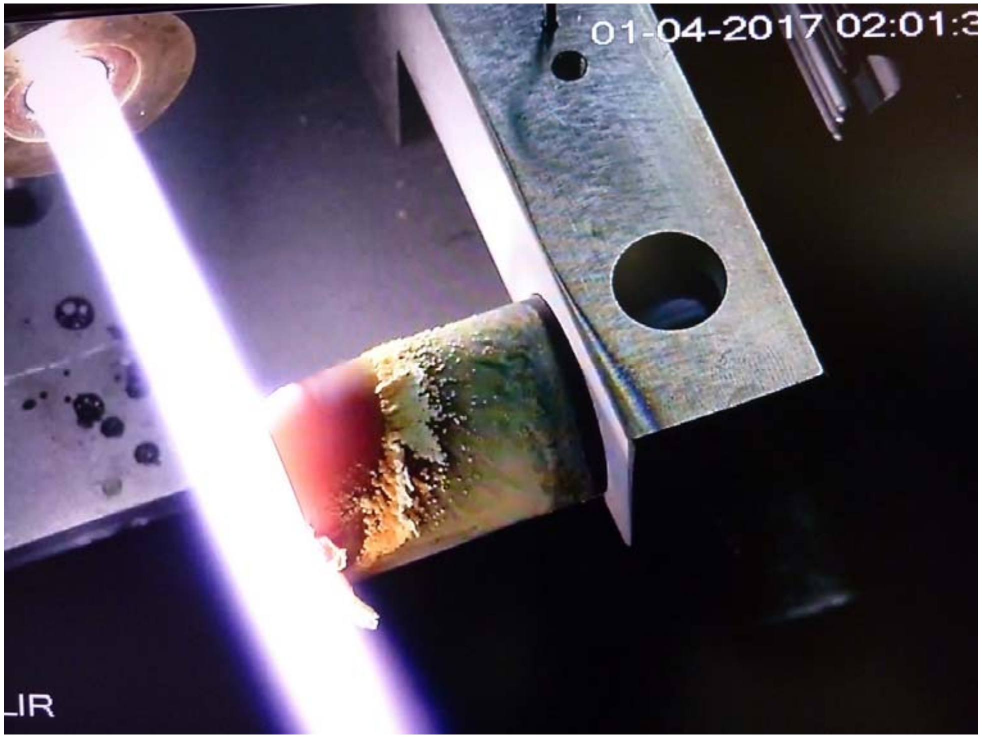
MHD literature
Zirconia-based
Hafnia-based
Chromite-based
Carbide-based
Alumina-based
Ceria-based
$MoSi_2$-based



J. Mizusaki, W.R. Cannon, H.K. Bowen, Electrochemical degradation of ceramic electrodes, J Am Ceram Soc, 63 (1980) 391-397.

High-Velocity Oxy-Fuel Torch Test

- HVOF torch test parameters
- CFD simulation results
- Potassium seed injection



Formation of tungsten oxide and potassium tungstate on tungsten in oxy-kerosene flame seeded with potassium carbonate (Photo: NETL, 2017)

Typical HVOF Torch Operating Parameters

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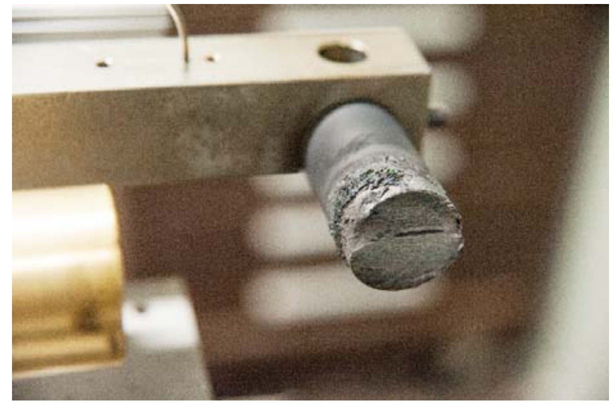
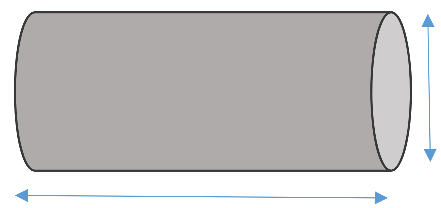
Fuel:	**kerosene (K-1)**
Oxidizer:	**oxygen**
Carrier:	**argon**
Seed:	**potassium carbonate**

Fuel flow rate	16.3 ± 0.2 L/hour
Oxidizer flow rate	611 ± 4 SLPM
Carrier gas flow rate	15.7 ± 0.1 SLPM

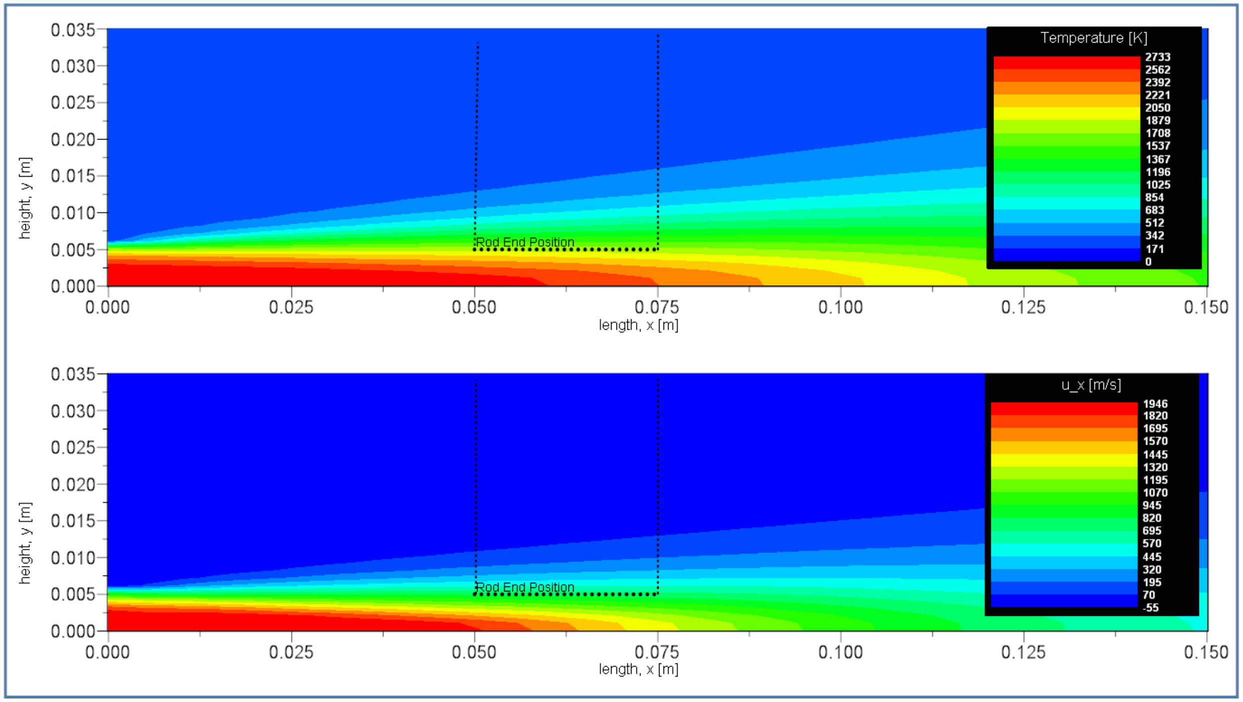
Holder temperature
(K-type thermocouple)



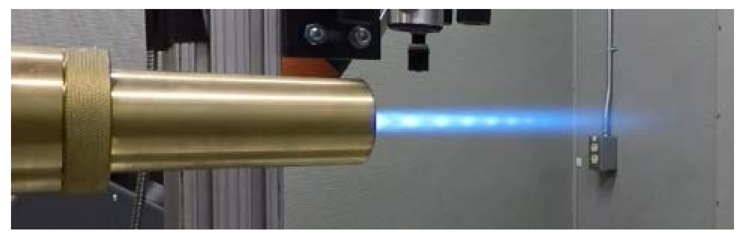


(top) sample holder temperature measurement
(bottom) sample geometry and dimensions

CFD Simulation of HVOF Working Fluid

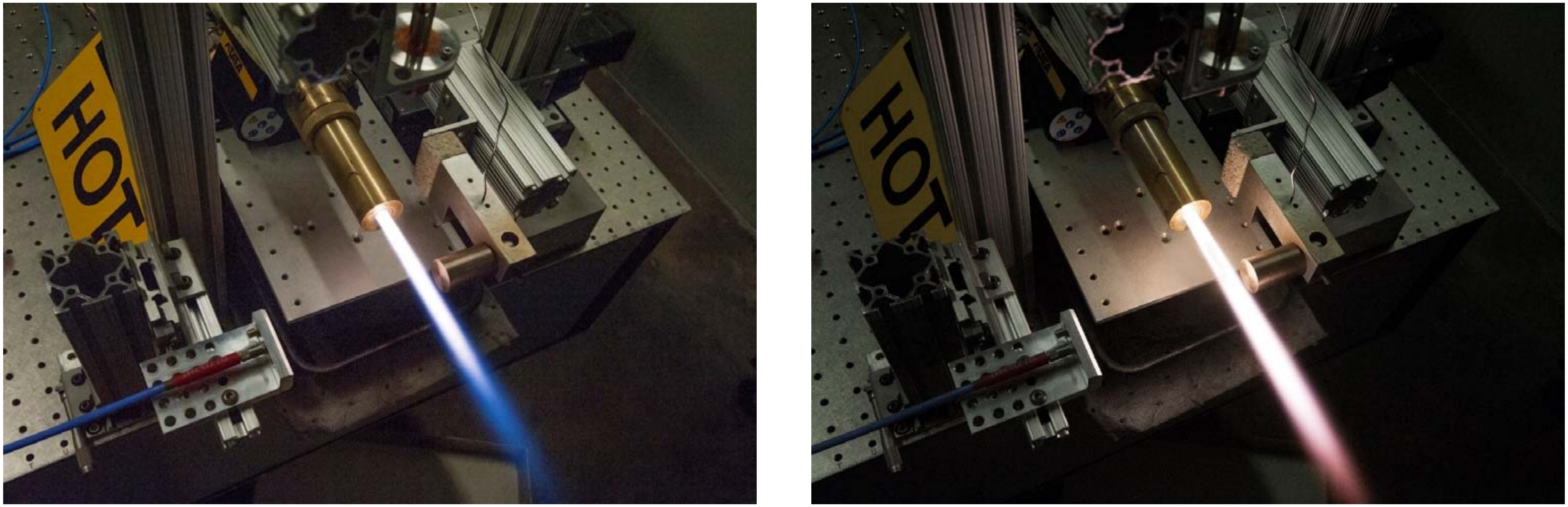


- Estimated temperature is between 1700 to 1900 K
- Gas velocity is between 700 to 800 m/s



Shock diamond structure in HVOF flame
R. Woodside, et al. "IPT – Direct Power Extraction," Crosscutting Technology Research Review Meeting, 2016

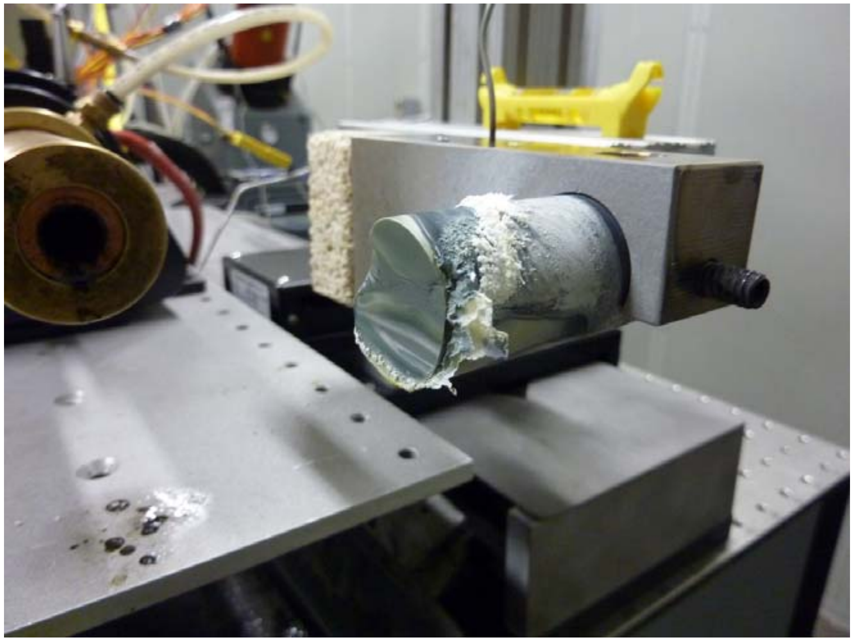
Potassium Carbonate Seed Injection



(left) Oxy-kerosene HVOF flame; (right) with potassium carbonate seed injection Photo: NETL, 2017)

Refractory Metal Electrodes

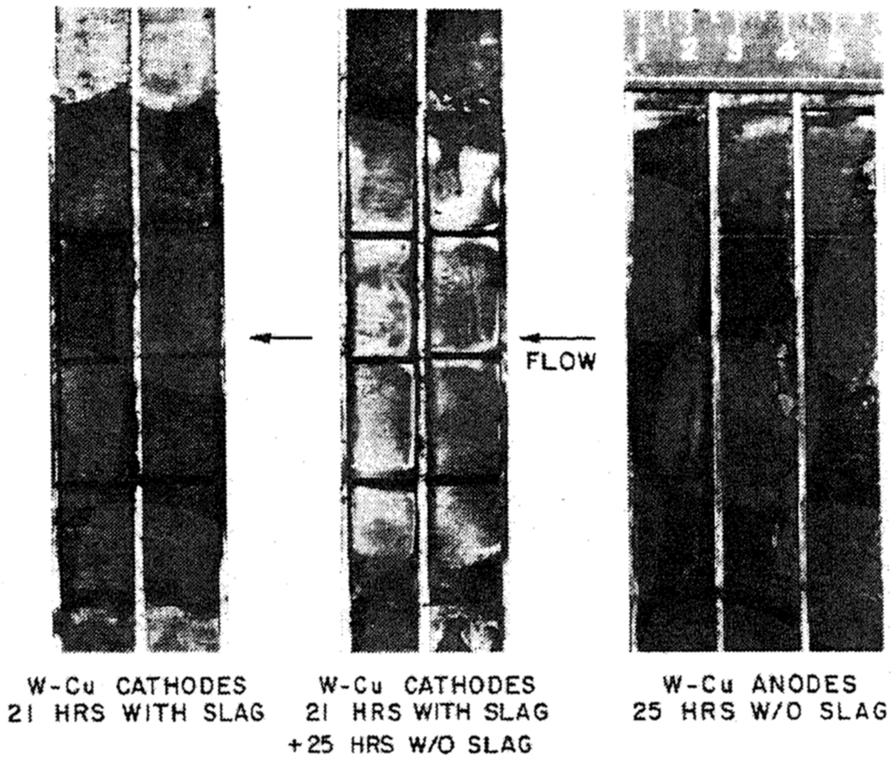
- Tungsten and tungsten-copper pseudoalloys
- Temperature measurements
- Electrode mass change
- Reaction products
- Surface reactions
  - Reactive evaporation
  - Potassium tungstates



Tungsten sample after exposure to potassium carbonate in HVOF test. (Photo: NETL, 2017)

Tungsten and Tungsten-Copper

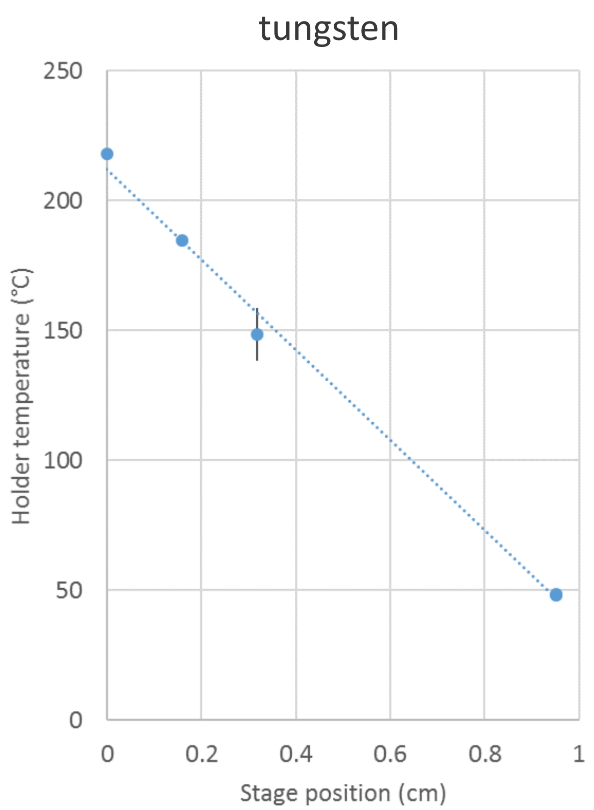
- **Tungsten ($T_{m.p.}$ = 3422 °C)**
  - Rosa (1961)
  - Zhimerin et al. (1969)
  - Bitiurin et al. (1969)
  - Petty et al. (1977)
  - Natesan et al. (1991)
  - Farrar and Shields (1992)
- **Tungsten-copper pseudoalloy**
  - Heywood et al. (1969)
  - Petty et al. (1977)
  - Farrar and Shields (1992)

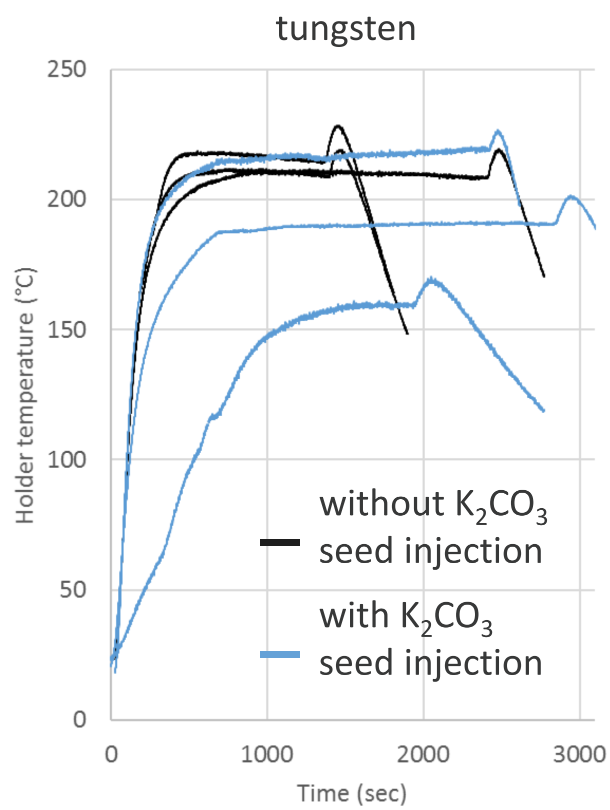


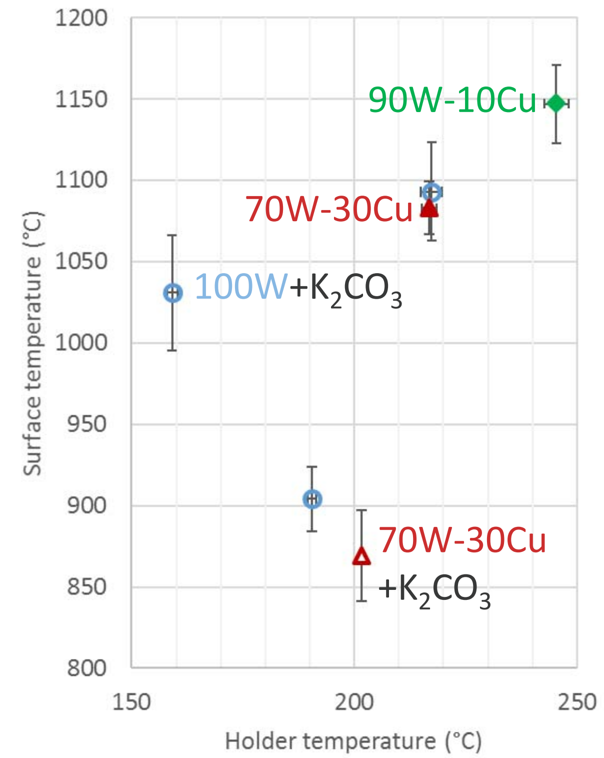
S. Petty, A. Demirjian, A. Solbes, Electrode phenomena in slagging MHD channels, Proceedings of the 16th Symposium on Engineering Aspects of MHD, Pittsburgh, PA (1977) VIII.1.1-VIII.1.12.

Temperature Measurements

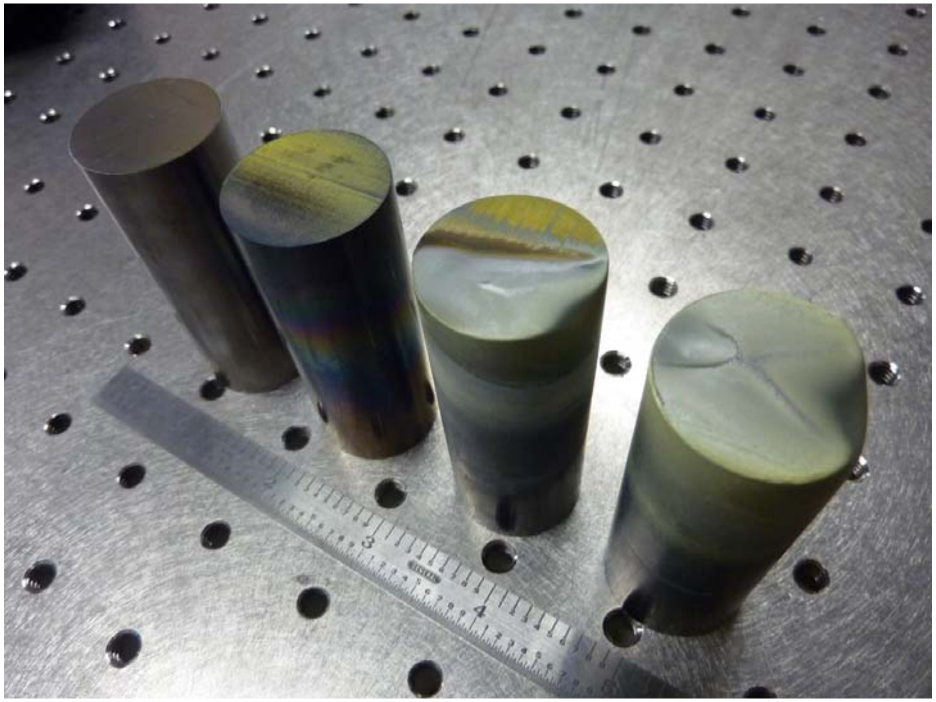
As a function of position and time



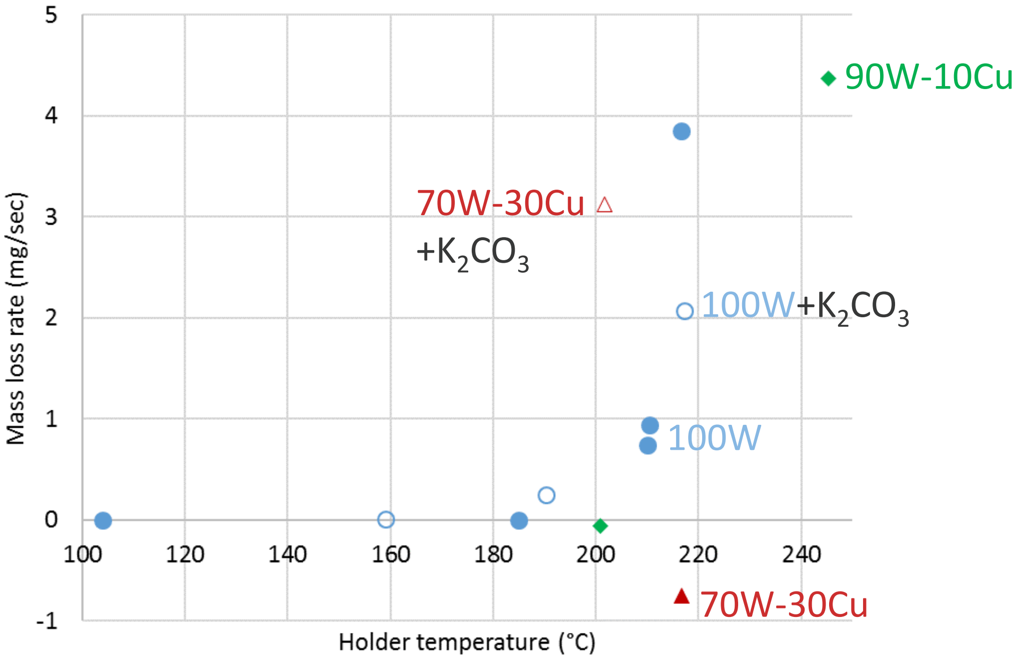




Mass Change Measurements



Tungsten electrodes (Photo: NETL, 2017)



Reaction Product Characterization

$HW_6O_{21}^{5-}(aq) + 3H_2O(l) \rightleftarrows 6WO_4^{2-}(aq) + 7H^+(aq)$

polytungstate ion — tungstate ion

M.I. Nave, Y.-c.K. Chen-Wiegart, J. Wang, K.G. Kornev, Precipitation and surface adsorption of metal complexes during electropolishing. Theory and characterization with X-ray nanotomography and surface tension isotherms, Phys Chem Chem Phys, 17 (2015) 23121.

Energy-dispersive x-ray spectroscopy

$WO_3 + K_2WO_4$

18% (mole/mole) W

9% (mole/mole) K

Balance O

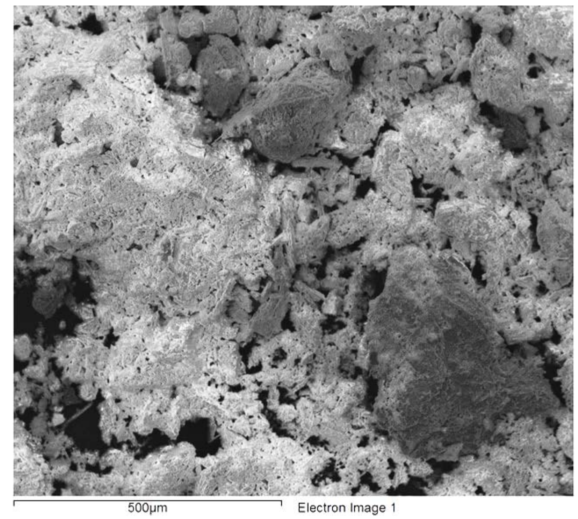
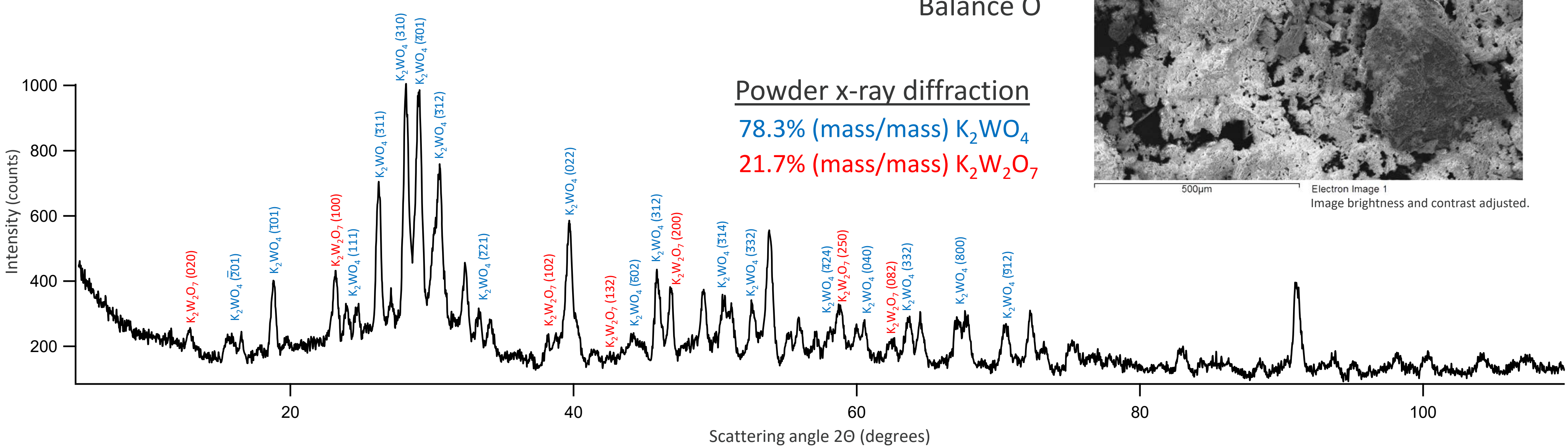


Image brightness and contrast adjusted.

Powder x-ray diffraction

78.3% (mass/mass) K_2WO_4

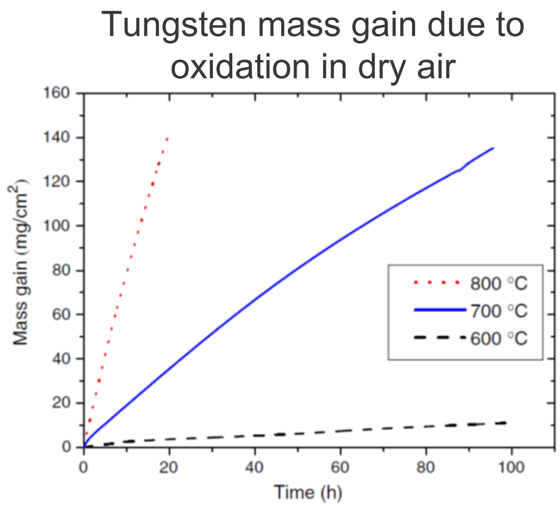
21.7% (mass/mass) $K_2W_2O_7$



High-temperature Surface Reactions

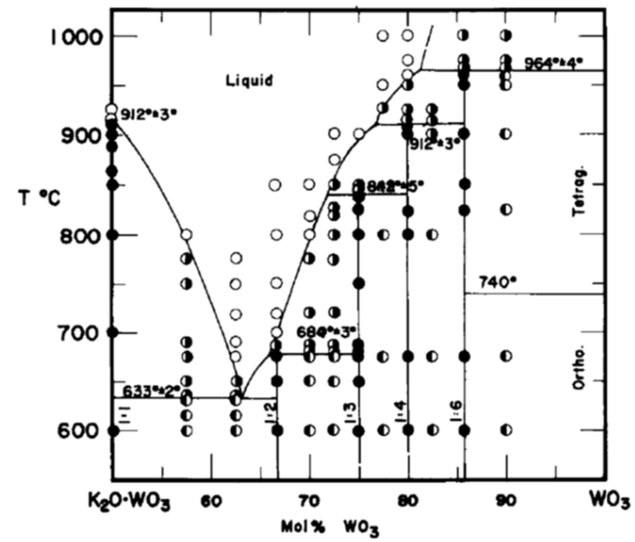
Formation of tungsten(VI) oxide and potassium tungstates

Oxidation of tungsten electrode (Photo: NETL, 2017)



S.C. Cifuentes, M.A. Monge, P. Perez, On the oxidation mechanism of pure tungsten in the temperature range 600-800 °C, Corros Sci, 57 (2012) 114-121.

$$2W(s) + 3O_2(g) \rightarrow 2WO_3(s)$$
$$WO_3(s) \rightarrow WO_3(g)$$



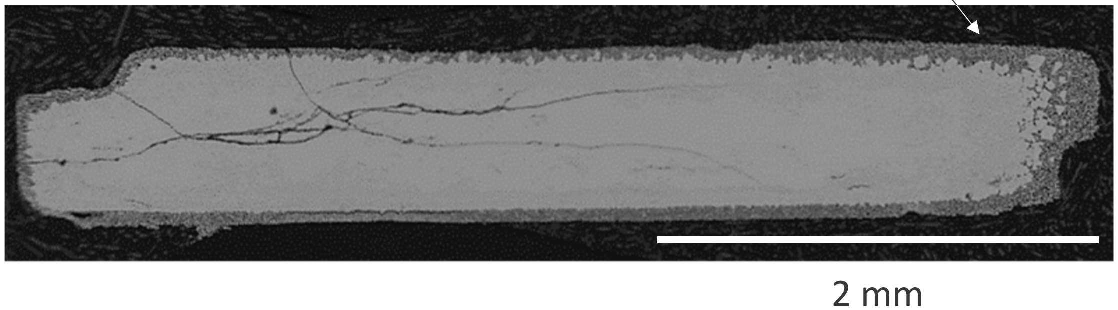
L.L.Y. Chang, S. Sachdev, Alkali tungstates: stability relations in the systems $A_2O \cdot WO_3$-WO_3, J Am Ceram Soc, 58 (1975) 267-270.

$$K_2CO_3(?) + WO_3(s) \rightarrow$$
$$K_2WO_4(l) + CO_2(g)$$

Oxide Ceramic Electrodes

- **Preliminary screening**
  - K_2CO_3 reactivity
  - Fabrication testing
- **ASTM C987 exposure test**
- **Impedance spectrometry**

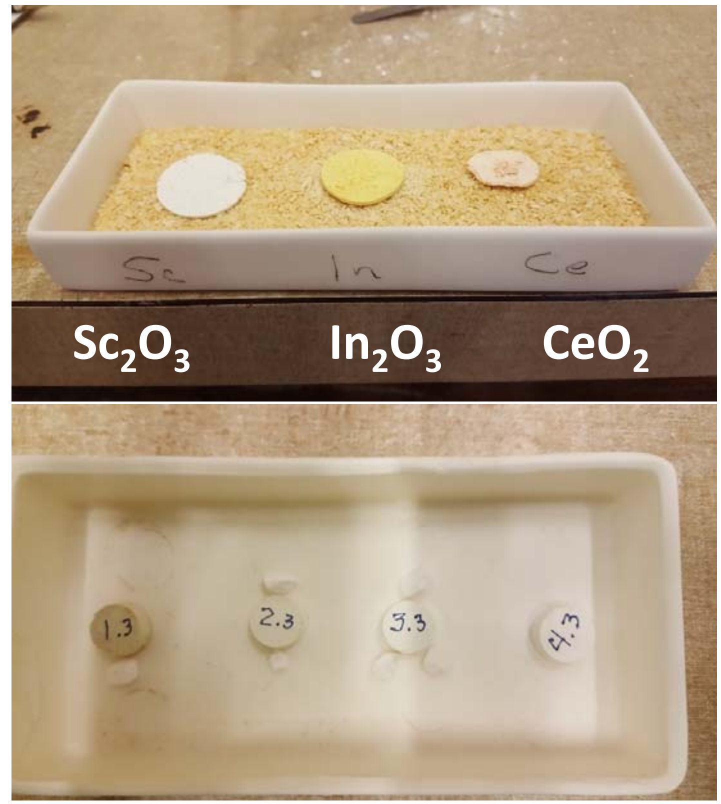
Reaction layer formed at surface of hafnia-ceria-yttria electrode sample after exposure to molten potassium carbonate



R. Woodside, et al. “IPT – Direct Power Extraction,” Crosscutting Technology Research Review Meeting, 2016

Preliminary Screening Tests

- **Potassium carbonate was combined with candidate oxides and fired at 1600 °C to determine if any new phases are formed**
  - Tested: MgO, Y_2O_3, Sc_2O_3, In_2O_3, CeO_2
  - Potential materials: CaO, SrO, La_2O_3
- **Oxide ceramic coupon fabrication**
  - Densified: $LaYO_3$, $LaY_{0.9}In_{0.1}O_3$, $LaYCaO_{2.96}$, $LaCeYO_{3.04}$, $Y_2Ce_2O_7$
  - Unable to be densified: $La_2Zr_2O_7$



(top) Post-exposure shrinkage of pressed oxide-potassium carbonate pellets after firing. (bottom) Oxide ceramic coupons (Photo: NETL)

Potassium Carbonate Exposure Test

- **Potential chemical reaction products**

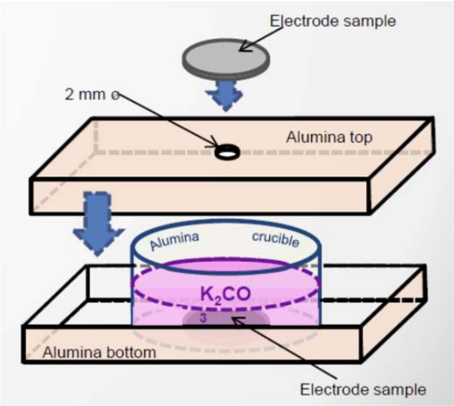
  tungsten → potassium tungstate and polytungstates

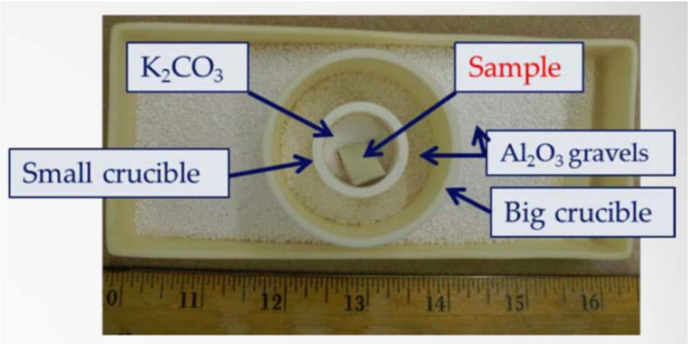
  scandium(III) oxide → potassium scandium oxide, Hoppe and Sabrowsky (1965)

  indium(III) oxide → potassium indium oxide, Lulei and Hoppe (1994)

  cerium(IV) oxide → potassium cerium oxide, Clos et al. (1970)

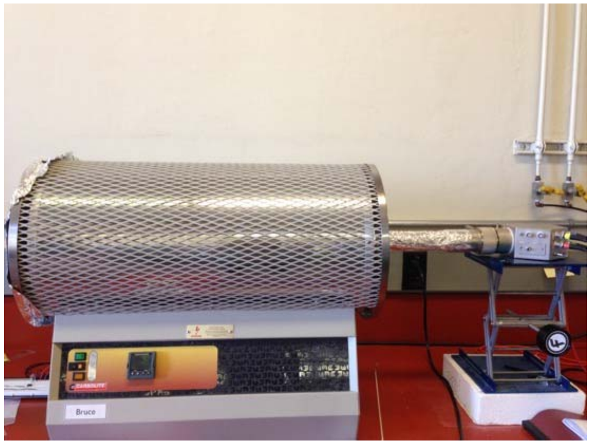
- **Damage mechanisms**
  - New phase formation
  - Grain boundary diffusion
- **Mass loss measurement**

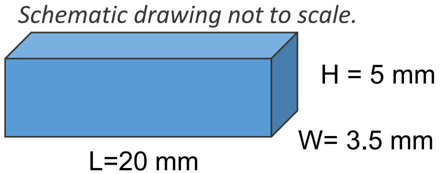




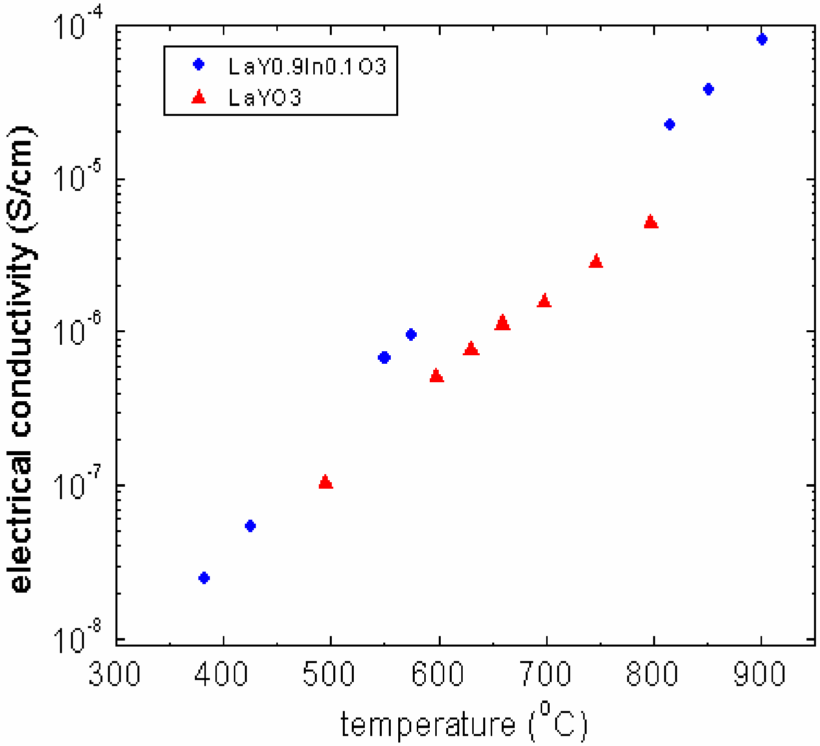
R. Woodside, et al. "IPT – Direct Power Extraction," Crosscutting Technology Research Review Meeting, 2015 and 2016

Impedance Spectrometry





(top) Tube furnace for high-temperature measurements up to 1150 °C;
(bottom) reference sample photograph and dimensions
(Photos: David Cann, Oregon State University, 2016)



at 90% theoretical density

(Photos: Oregon State University)

Acknowledgements

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  - Eric Zeuthen (ORISE)
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