Solid Oxide Membrane (SOM) Electrolysis of Magnesium: Scale-Up Research and Engineering for Light-Weight Vehicles

Metal Oxygen Separation Technologies, Inc. (MOxST)

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Presenter: Steve Derezinski, MOxST CEO

DOE Annual Merit Review May 12, 2011

Project ID: LM035

Overview

- Timeline
  - April 20, 2010 – May 19, 2011
  - 98% complete
- Budget
  - Total: $843,143
  - DOE: $843,143
  - FY 10: $456,983
  - FY 11: $386,160
- Barriers
  - Zirconia (YSZ) robustness
  - Raw material purity
  - Energy budget
- Partners
  - Boston University Prof. Uday Pal
  - Oak Ridge National Laboratories

Objectives and Relevance

Magnesium for light-weight vehicles:

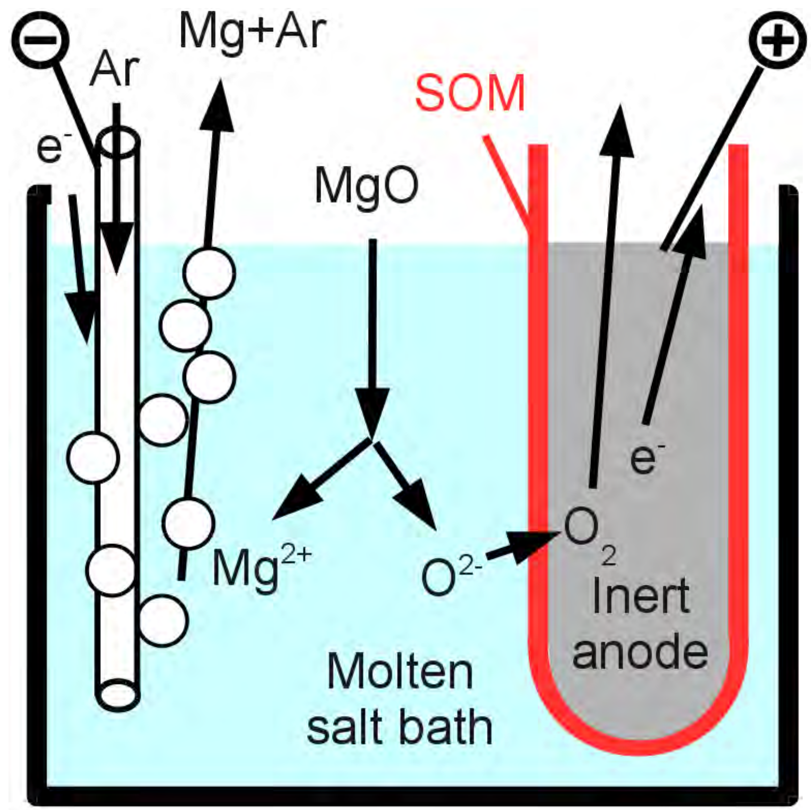
- Lowest-density engineering metal
- Excellent stiffness-to-weight
- Low manufacturing costs
- Good recyclability

Production at **low cost** with **zero emissions** would improve life-cycle performance and help industry to use magnesium in light-weight vehicles

"The overall goal of this one-year project is to **answer key research questions** enabling MOxST to **assess the feasibility and cost** of operating a SOM Electrolysis cell which will produce **tens of tons of magnesium per year**"

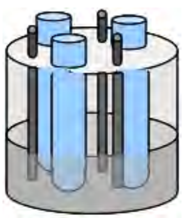
Magnesium Process Approach

- Electrolysis in molten salt at 1150-1300º C
- SOM (YSZ) protects anode from harsh liquid electrolyte bath and separates Mg from O_2
- Argon stirs electrolyte and dilutes Mg vapor
- High current and energy efficiency



MOxST Scale-Up Path

Research crucible
1-3 tubes
Shallow immersion

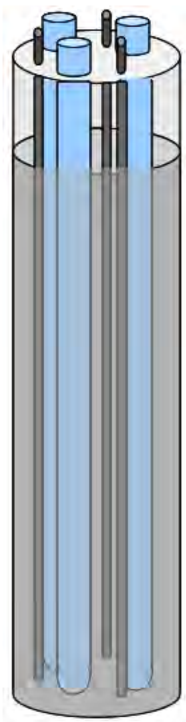


Robustness & Scale-up development

Design of pre-production prototype

This project →

Stage two crucible
3+ tubes
Deep immersion

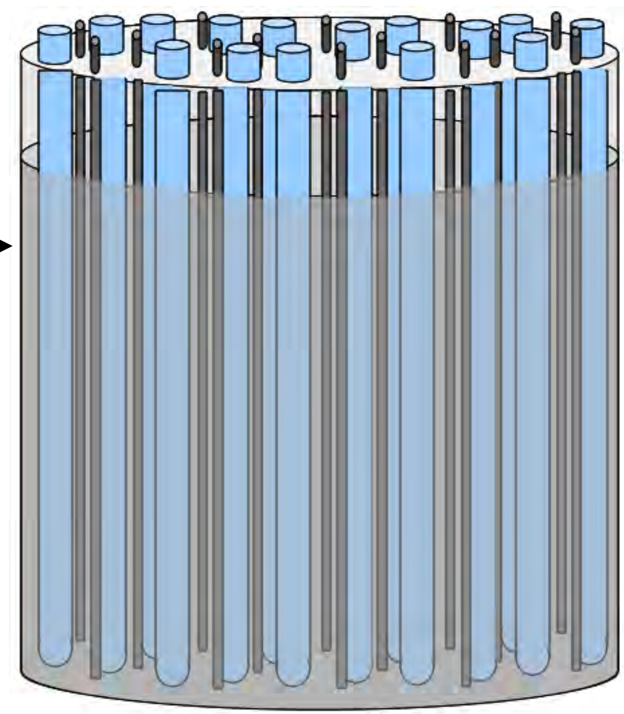


2011-2012 →

Build 12-tube pre-production prototype

Design production machine

Full-scale crucible
Many tubes
Deep immersion

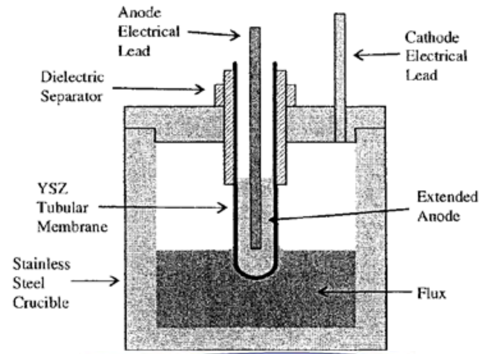


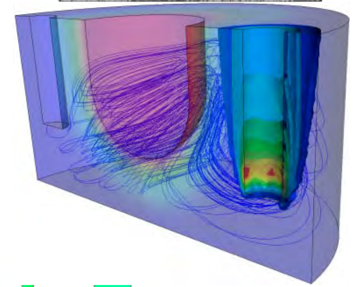
Technical Accomplishments and Progress

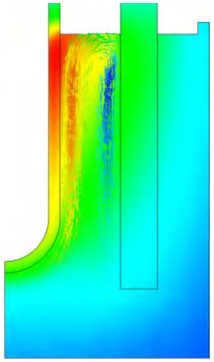
- Zirconia (YSZ) robustness: additive for stability, 100-hour electrolysis test, 500-hour molten salt exposure test
- Obtained MgO material composition, ran limited tests of impurity removal features
- Completed energy analysis and budget
- Operated at 8” immersion 60 A max current
- Condenser temperature and argon flow control determine liquid condenser success
- FEA modeling and scale-up design

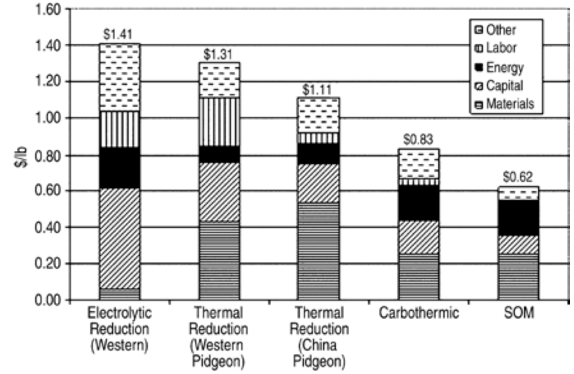
SOM Electrolysis Prior Work

- 1-tube apparatus with failure-critical metal-ceramic joint
- 40-hour zirconia salt exposure tests
- 3-tube experiments at 3" immersion depth
- 1-tube axisymmetric and 3-D FEA models of electrolysis cell
- Cost model by Sujit Das (ORNL)



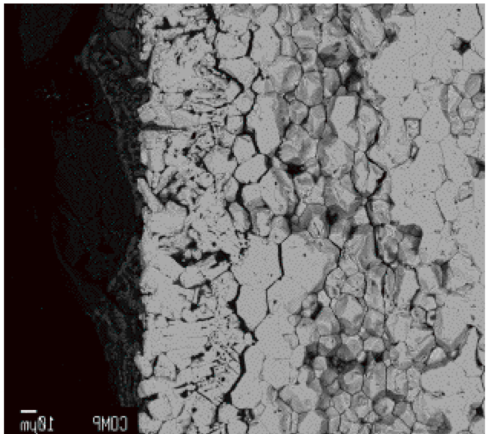


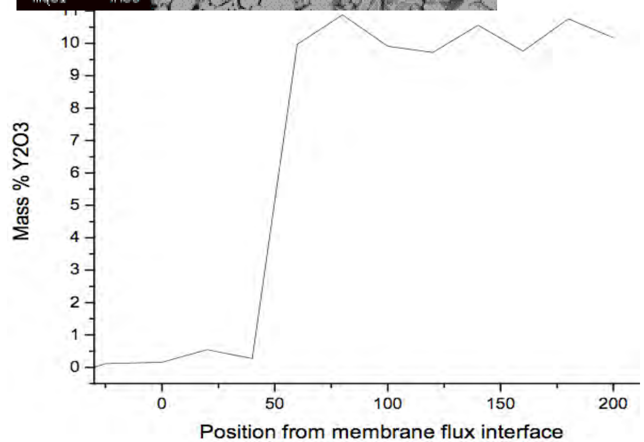




Molten Salt Additive for YSZ

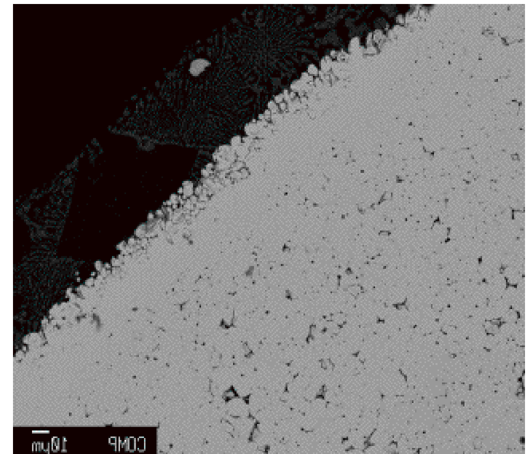
No additive

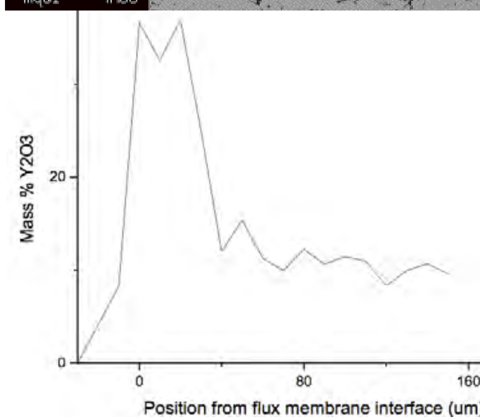




Y depletion, porosity, grain boundary attack, acicular phase

With additive





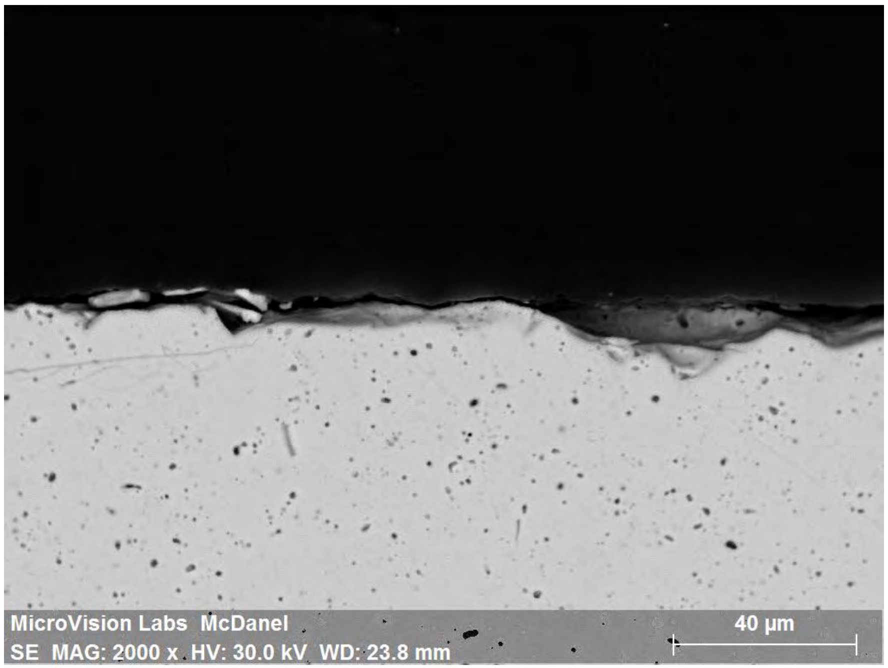
No porosity, Y *enrichment* near YSZ surface

NOTE: All YSZ samples are off-the-shelf tubes

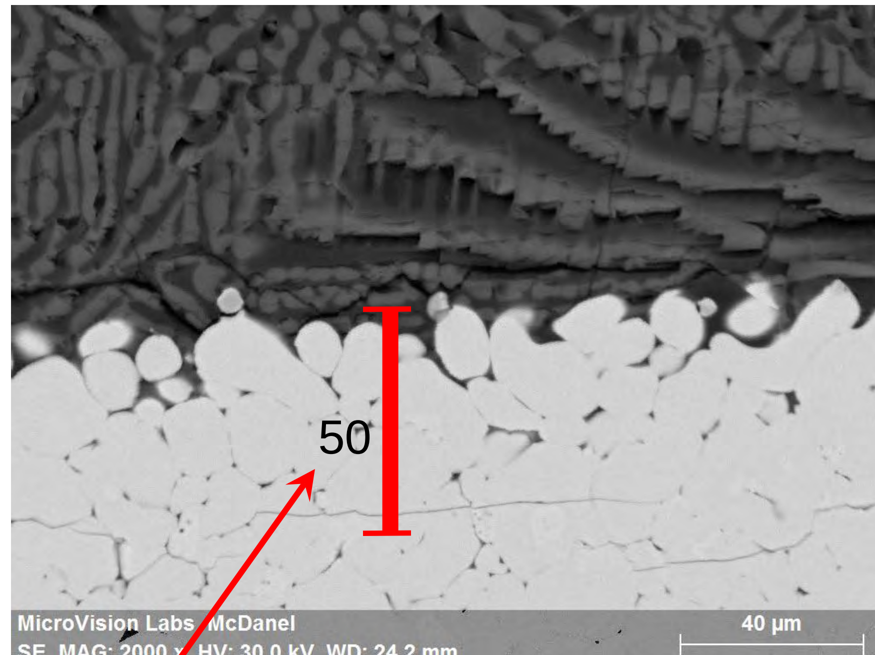
Long-Term Zirconia (YSZ) Tests

100-hour static membrane test

As Received



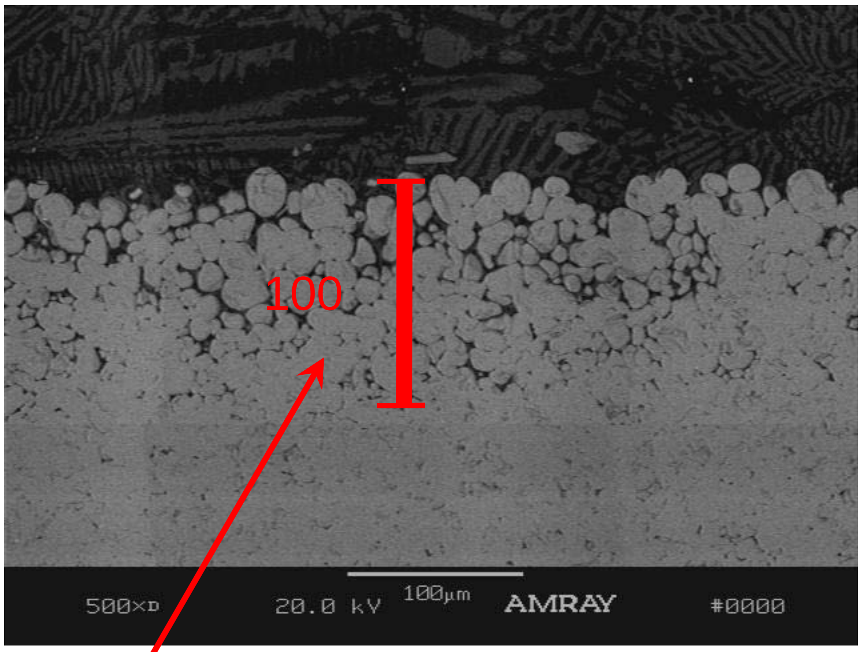
After 100-hour exposure



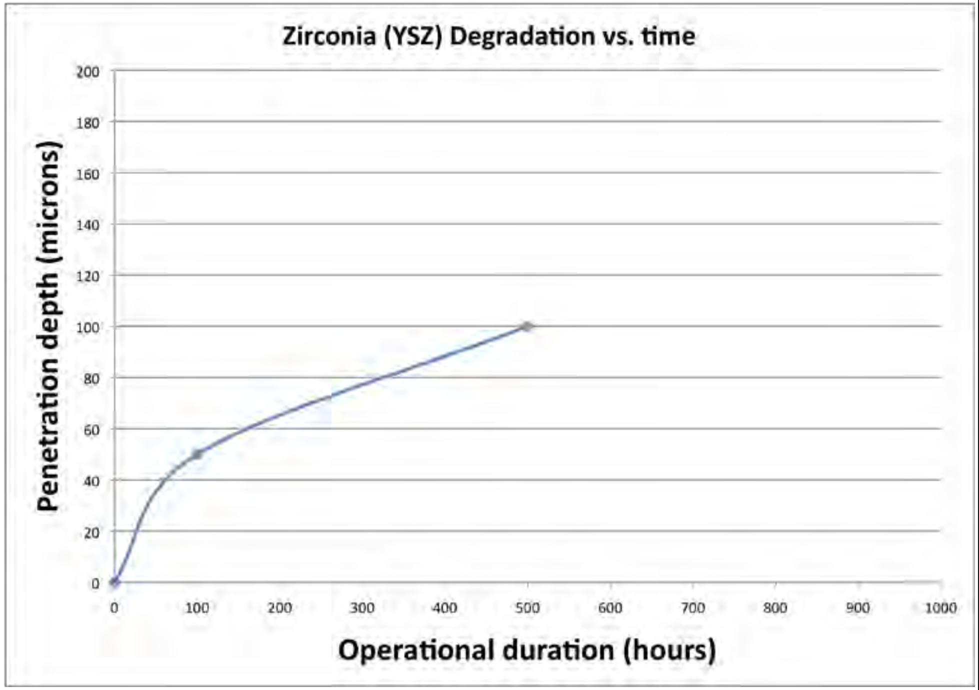
~50 µm layer after 100 hours

Long-Term Zirconia (YSZ) Tests

- 500-hour salt exposure



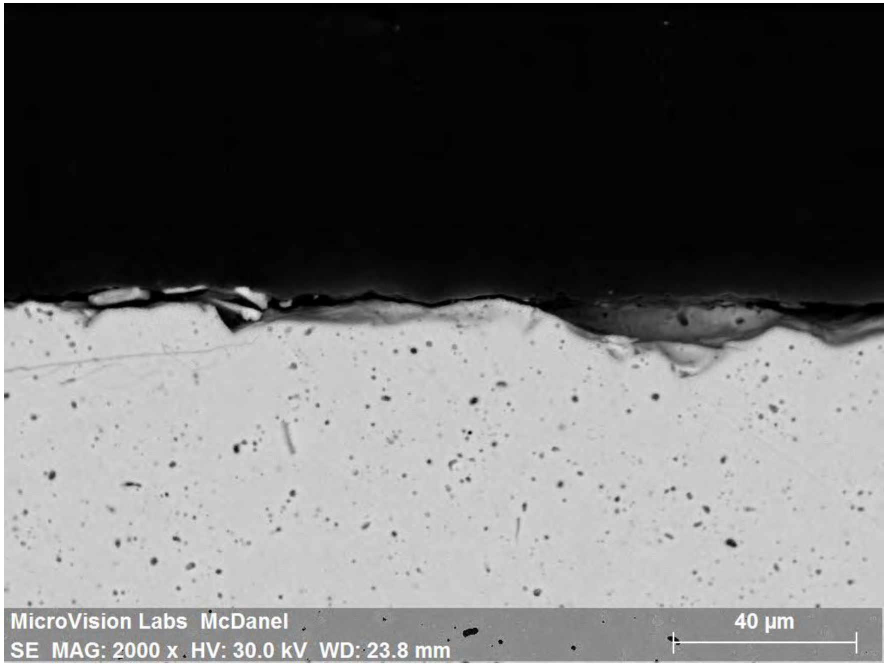
~100 µm layer after 500 hours



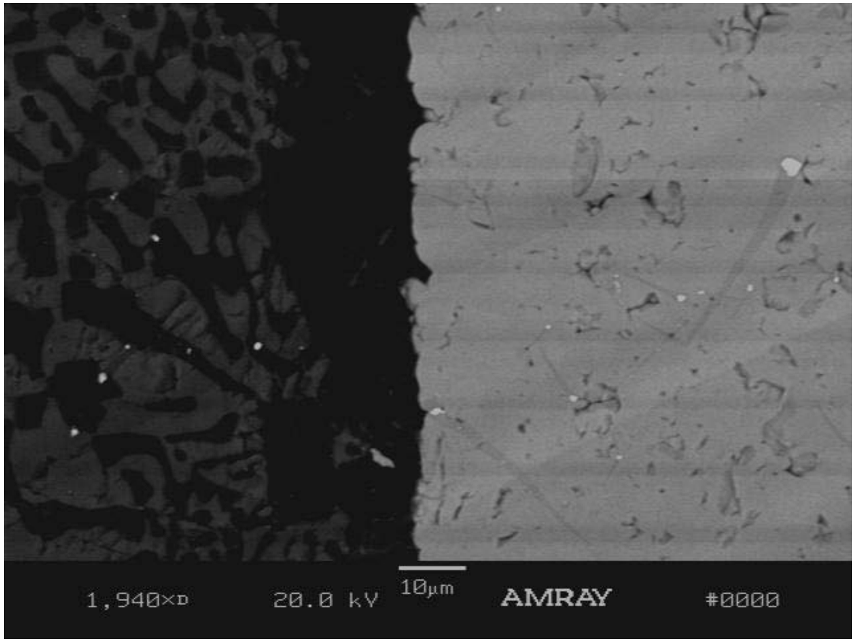
Asymptotic degradation characteristics

100-hour Electrolysis

As Received



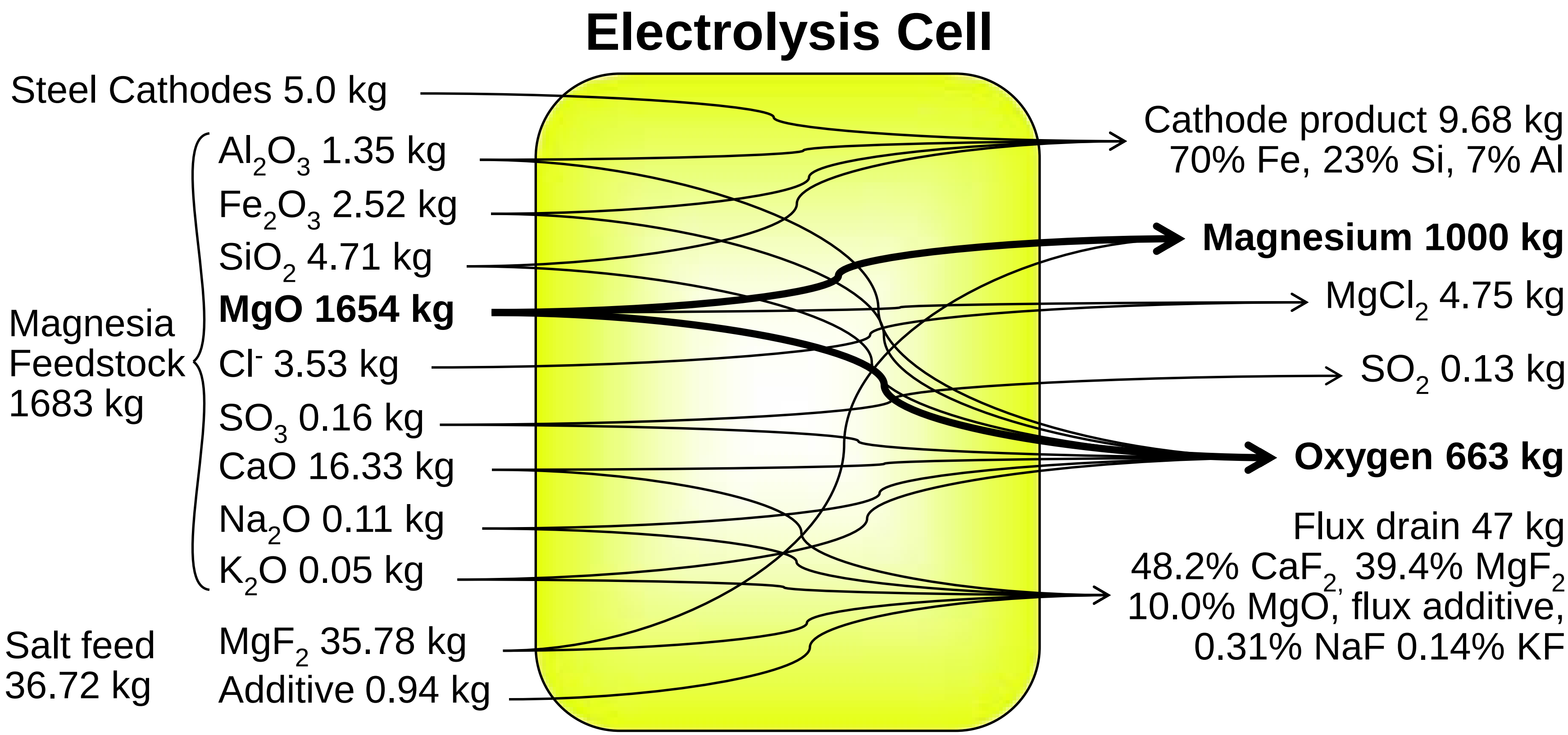
After 100-hour Electrolysis



Off-the-shelf Zirconia (YSZ) Stability Summary

- Additive eliminates porous layer in YSZ
- Magnesia-stabilized zirconia (MSZ) stable but low conductivity
- Based on data likely 4,000-8,000 hour YSZ lifetime
- Further optimization of YSZ is possible

Material and Impurity Flows

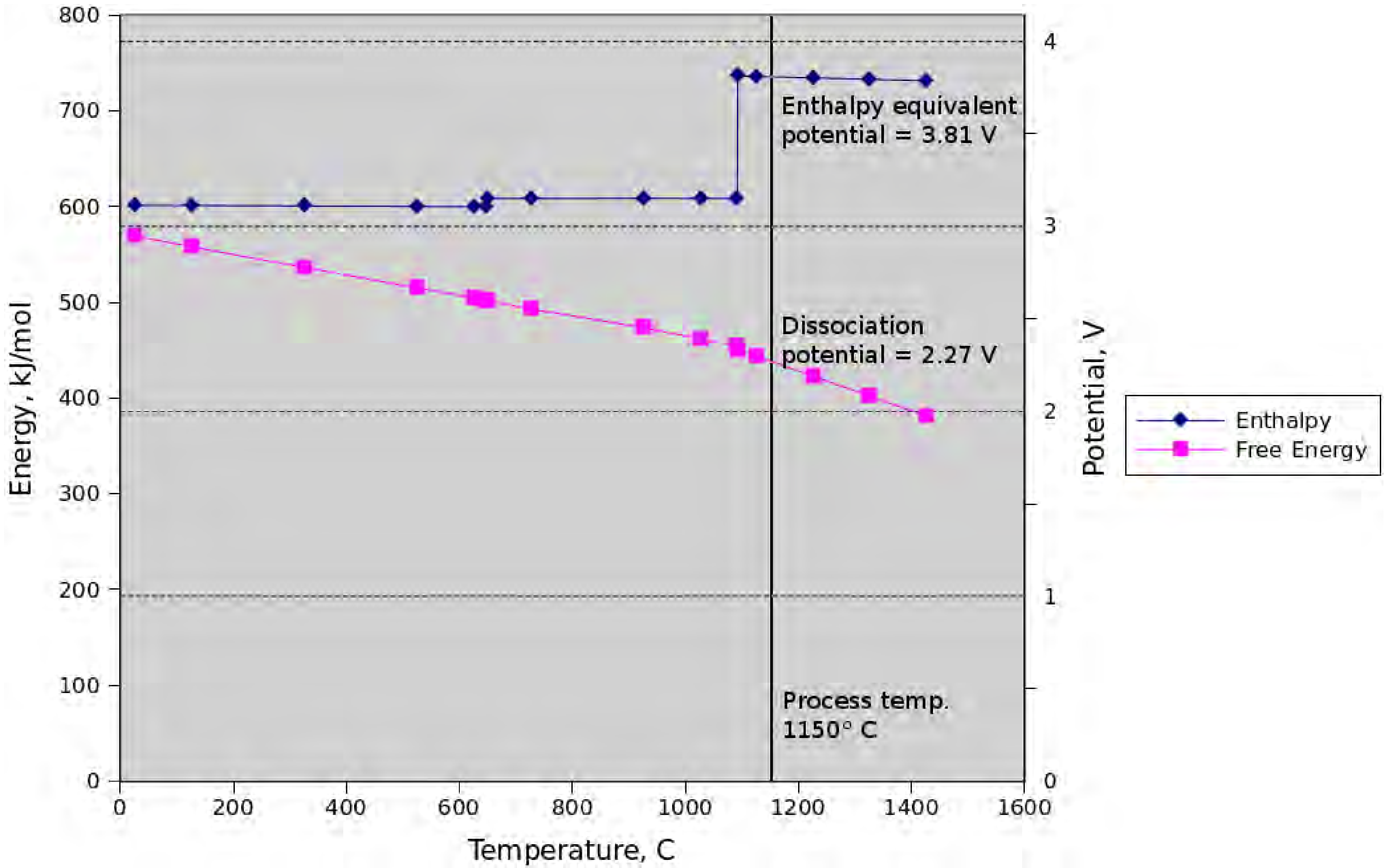


Inline purification → use moderate-purity MgO (*cf.* Bayer process)

Only zinc gets into product (few ppm), not a problem for alloys

Flux drain and salt feed → developing options for salt recycling

Magnesium Oxide Dissociation Energy



Data source: NIST Chemistry WebBook webbook.nist.gov

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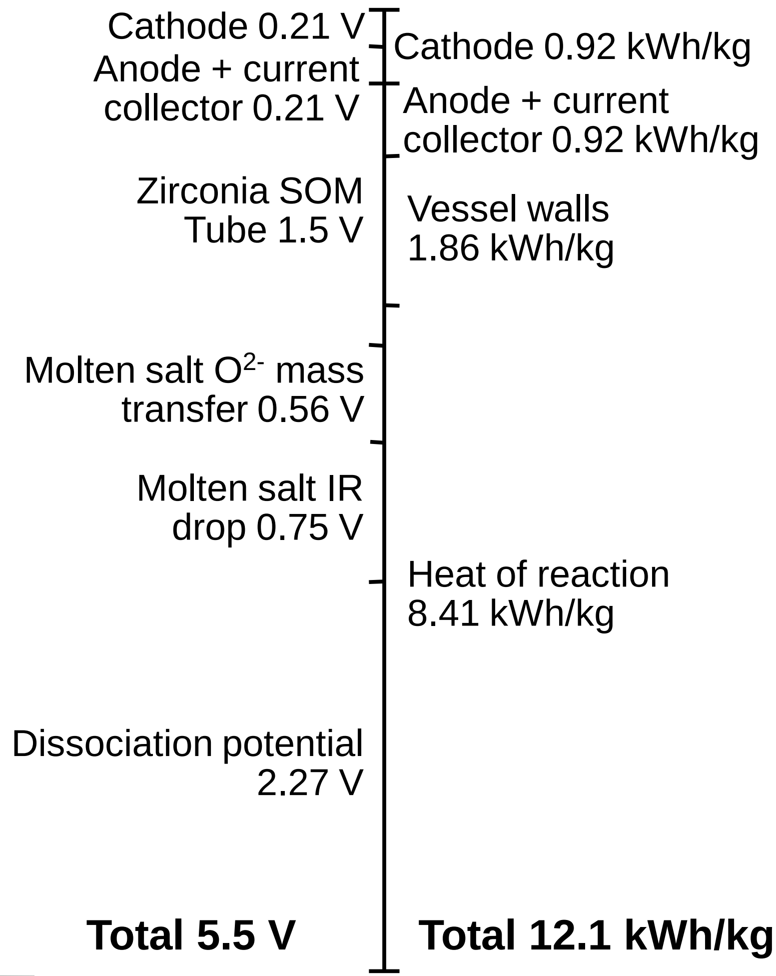
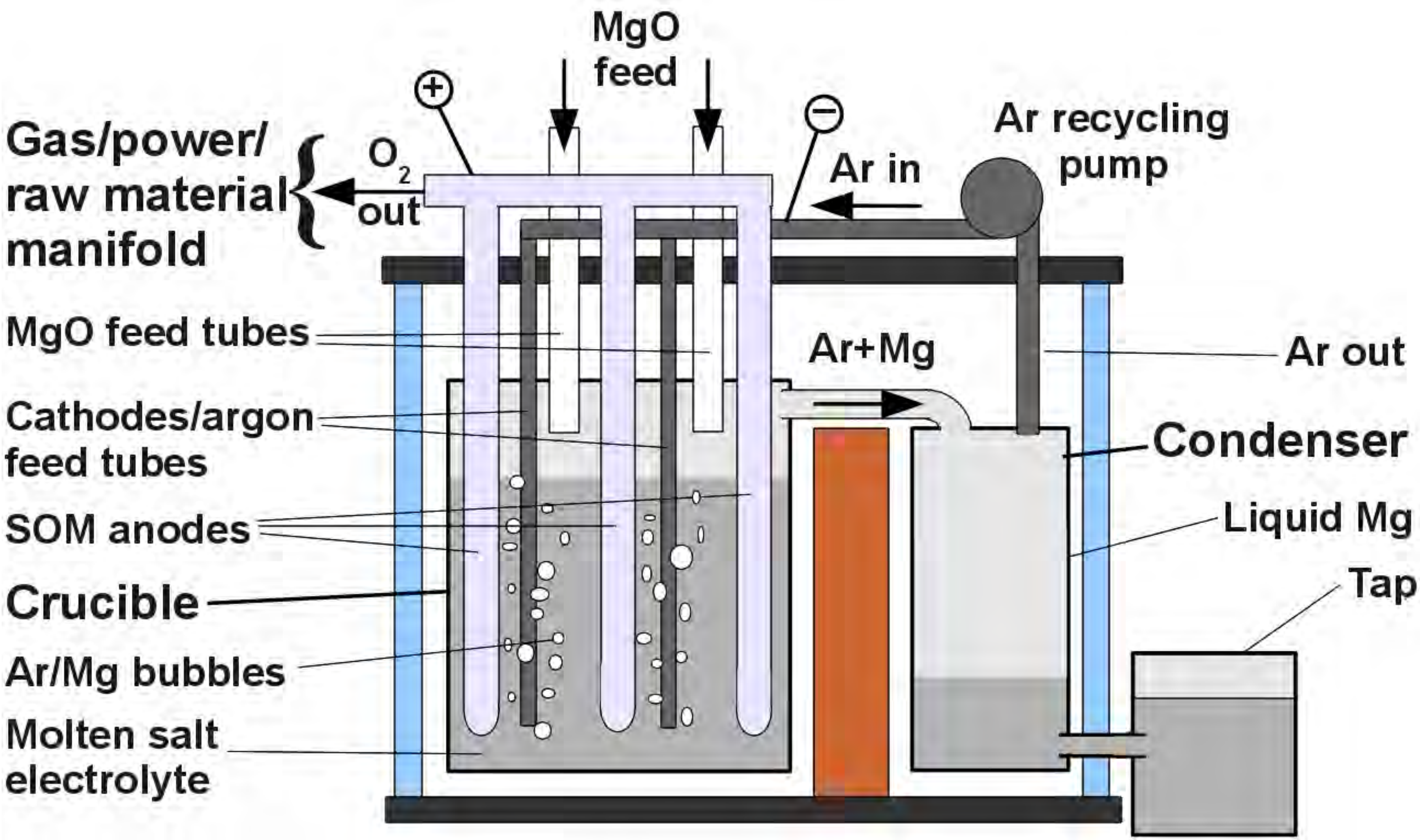
Magnesium Energy Budget

- Operate at 5-6.5 V
- Free energy budget:
  - $\Delta G_{rxn}/nF$=2.3 V
  - IR losses 2.7-4.2 V
- Enthalpy budget:
  - ΔH_{rxn}=8.4 kWh/kg
  - Losses via leads, etc. total 2.6-5.9 kWh/kg
- Vapor Efficiency: 58-76%
- Liquid Mg efficiency: 48-63%



MOxST Electrolysis Components



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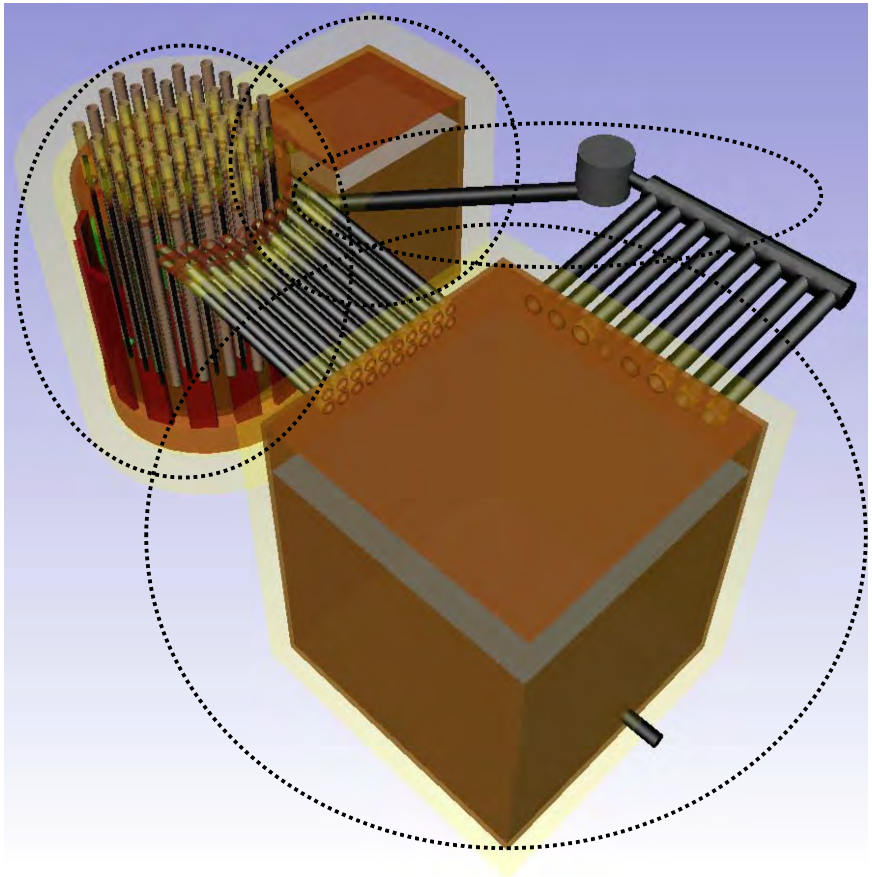
Preliminary Design Concept

- Components:
  - Electrolysis crucible
  - Condenser & tank
  - Argon recycling
  - Molten salt removal
  - Cold trap and power supply (not shown)
- Bounding box: 6.5×4.5×3.9 ft.
- Power: 5-6.5V 10kA



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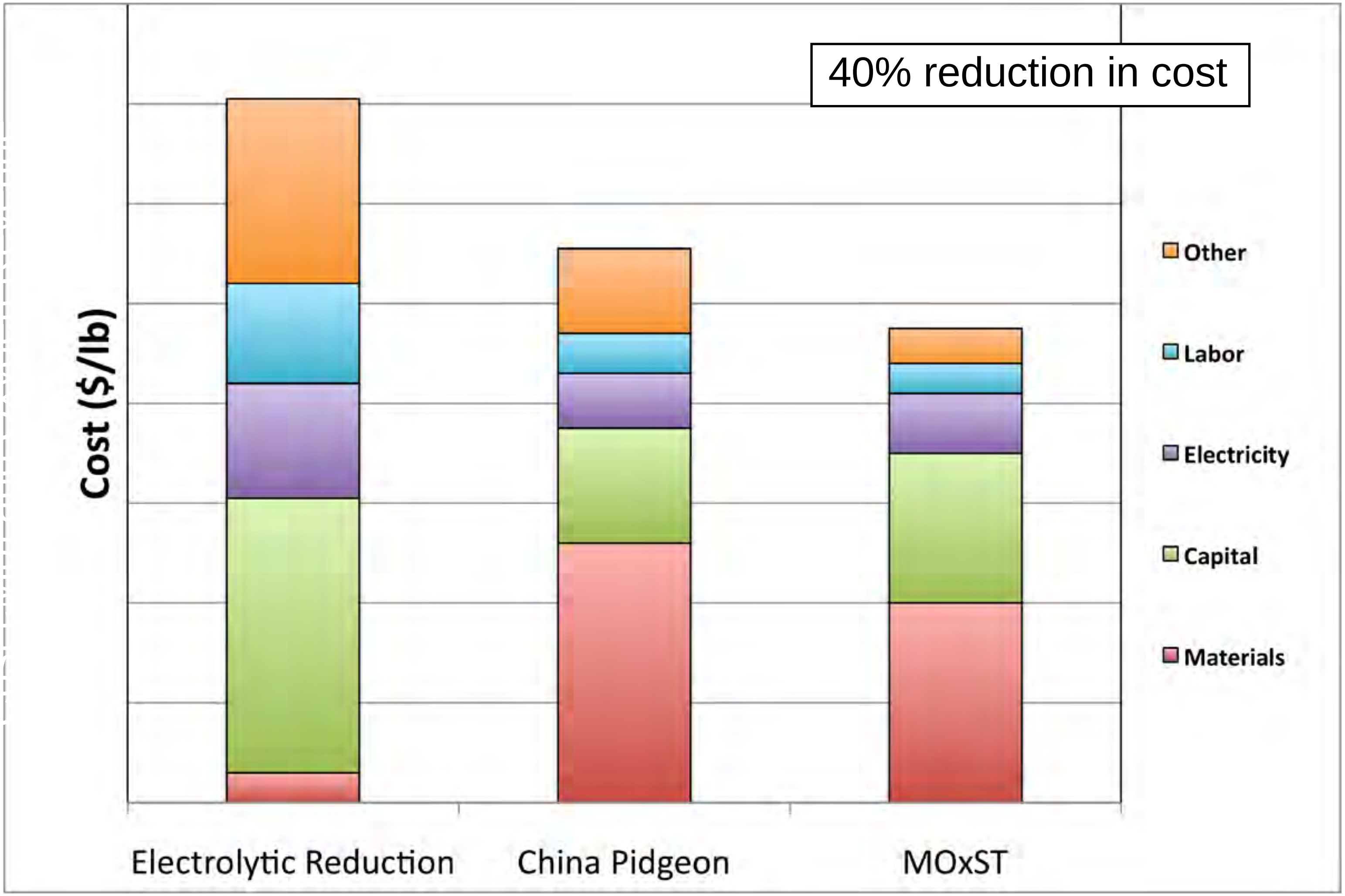
MOxST Magnesium Cost stack
(comparable plant sizes)



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Collaboration with Boston University

- Cell design:
  - Contributed new robust design for SOM tubes eliminating high-temperature seal
- Zirconia robustness
  - Performed half of electrolysis tests
  - Discovered correlation between electrolysis and static exposure to molten salt
  - Performed half of static exposure tests
  - Fundamental current efficiency studies
  - Membrane and product characterization

Proposed Future Work

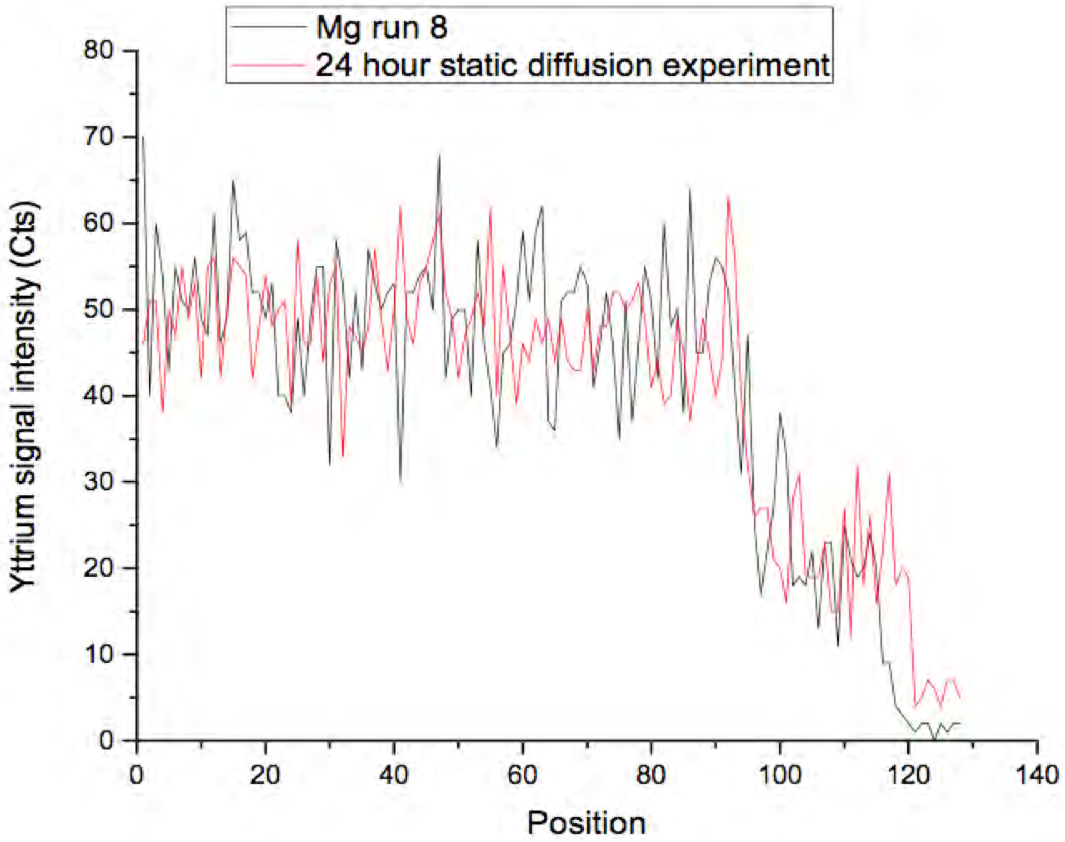
- Optimize zirconia (YSZ) formulation and process for long-term operation in molten salt
- Design, build and test prototypes in new configuration at larger scale
- Produce metal using prototypes and test composition and suitability for vehicle parts
- Further refine technical, cost, energy, GHG and other emissions modeling
- Begin site selection and development for pilot plant

Summary

- Significant progress on a new low-cost zero-emissions MgO electrolysis process
- Accomplishments and characteristics:
  - YSZ solid electrolyte is robust at high current
  - High-purity magnesium from low cost MgO
  - High current and energy efficiency, opportunity to capture magnesium condenser energy
  - Pure oxygen by-product reduces net cost
  - Projected net cost is the lowest in the industry
- *Magnesium for light fuel-efficient vehicles!*

Technical Back-Up Slides

Electrolysis Vs. Salt Exposure



Electrolysis and salt exposure lead to nearly identical reaction layers

Energy/Thermo Fundamentals

- Free energy determines voltage needed for reaction to take place

$$\Delta G = -nFV$$

- Reaction kinetics are a function of over-voltage beyond dissociation potential
  - Ohmic resistances in leads, YSZ, molten salt
  - Butler-Volmer overpotentials at cathode and anode interfaces
  - Mass transfer limitation in molten salt
  - High-temperature: ohmic processes dominate

Magnesium Energy Cost

- Each volt = 1 kWh/lb magnesium product

$$1\,V = 1\,\frac{J}{Coul} \times \frac{96485\,\frac{Coul}{mol\,e^-} \times 2\,\frac{mol\,e^-}{mol\,Mg} \times 454\,\frac{g}{lb}}{3.6\times 10^6\,\frac{J}{kWh} \times 24.3\,\frac{g}{mol\,Mg}} = 1.00\,\frac{kWh}{lb}$$

- Therefore: 5-6.5 V = 5-6.5 kWh/lb
- Cost is a strong function of electricity price
  - Upstate New York: 2.5-3¢/kWh → 12-20¢/lb
  - Massachusetts: 8-10¢/kWh → 40-65¢/lb
- Zero GHG except for MgO production

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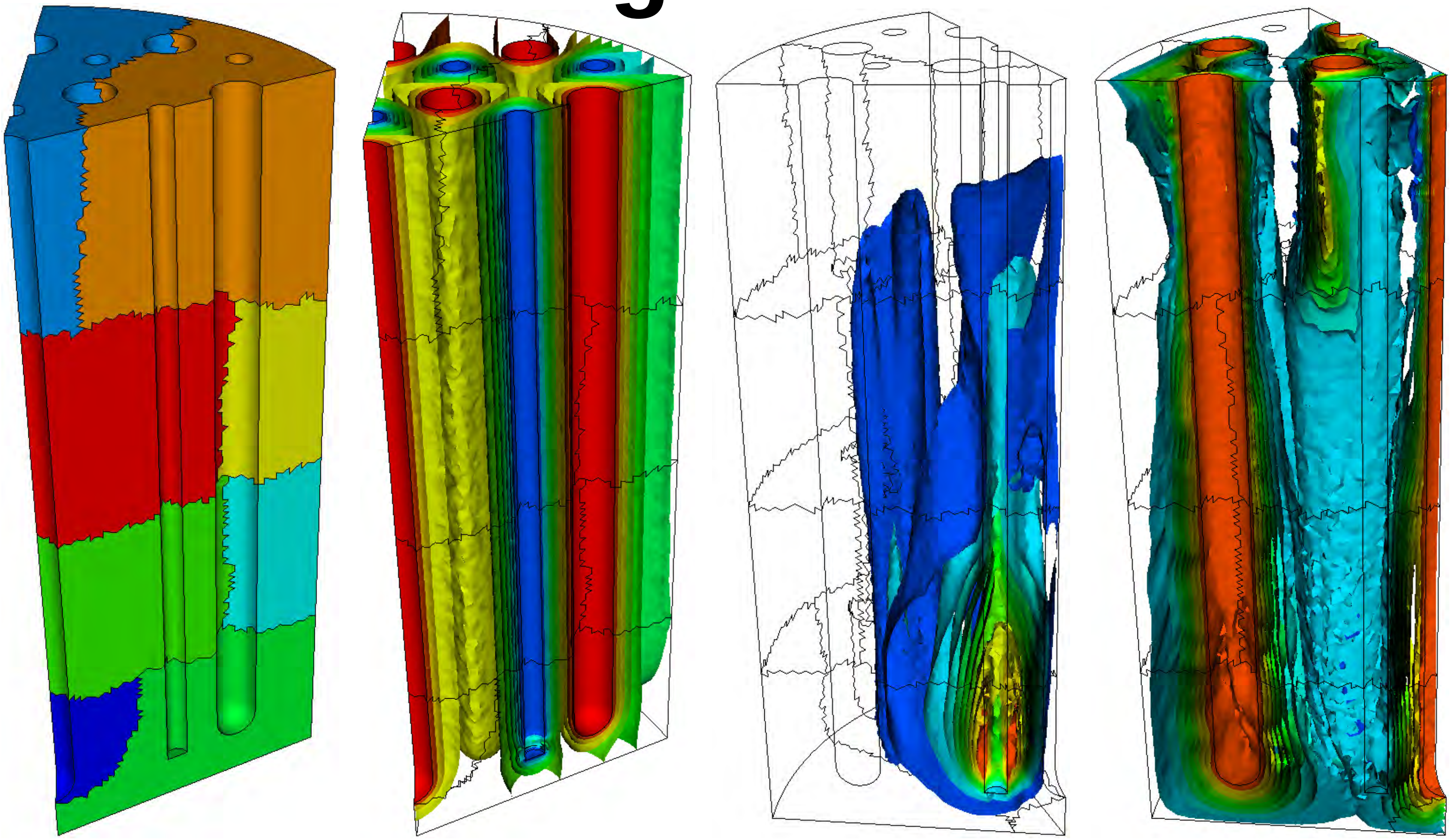
Mathematical Modeling

- Modeling for process scale-up engineering
- Multi-physics 3-D current/fluids/heat/mass transfer FEA model of liquid electrolyte
  - Added Nernst-Planck electromigration to Elmer open source FEA code
  - Ran simulations on research geometries, scale-up unit cells, full crucible geometry
  - Developing new advanced boundary conditions for transport-limited molten salt electrolysis
- Full process current & heat transfer model

19-Tube Wedge Results



CPU partition Electrical potential Argon Temperature

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