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2021 MRS Fall Meeting

EN14.19: Hydrogen Production VI

EN14.19.05

Liquid Metal Alloys for Hybrid Thermo-Electro-Chemical Water Splitting Cycles

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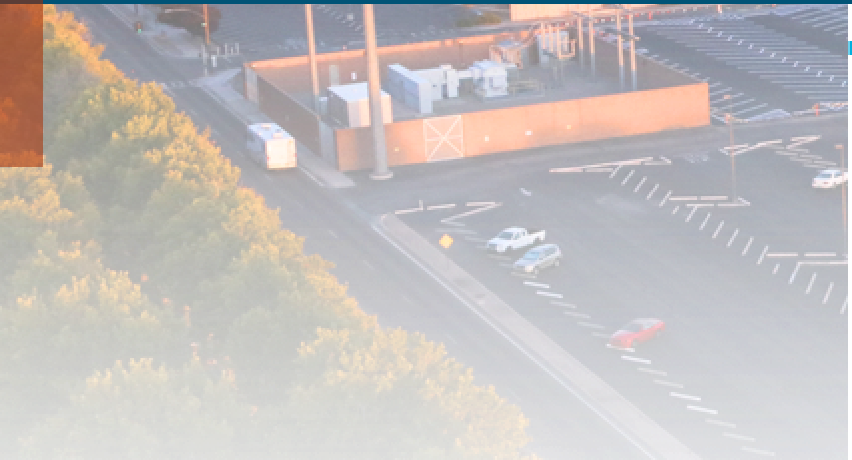

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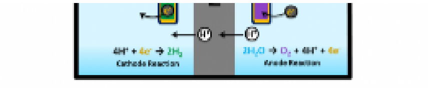
Challenge: Green hydrogen production

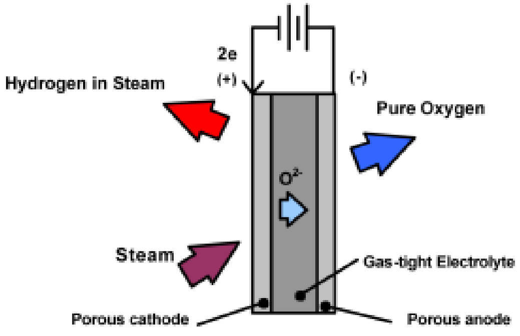
- As climate change worsens, there is increasing interest in H_2 as a fuel, heat source, and reducing agent for decarbonization
- H_2 is currently sourced by reforming hydrocarbons, resulting in CO_2 waste stream
- Numerous renewable pathways for H_2 production via water splitting are under development, but efficiency and cost must be improved
- High temperature processes of interest for potential high efficiencies and ability to leverage process heat & electricity from concentrating solar and nuclear energy, but challenges exist

Low-temperature electrolysis

- Catalyst deactivation
- Cell degradation
- Thermal stresses
- Electrode sintering

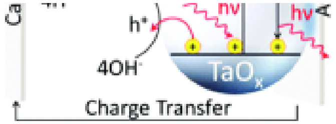


High-temperature electrolysis

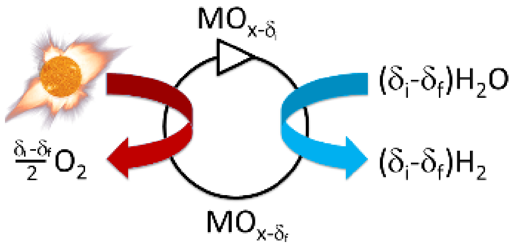


Photoelectrochemical

- Ultra-high temperatures (> 1400 °C)
- Expensive construction materials
- Thermal stresses

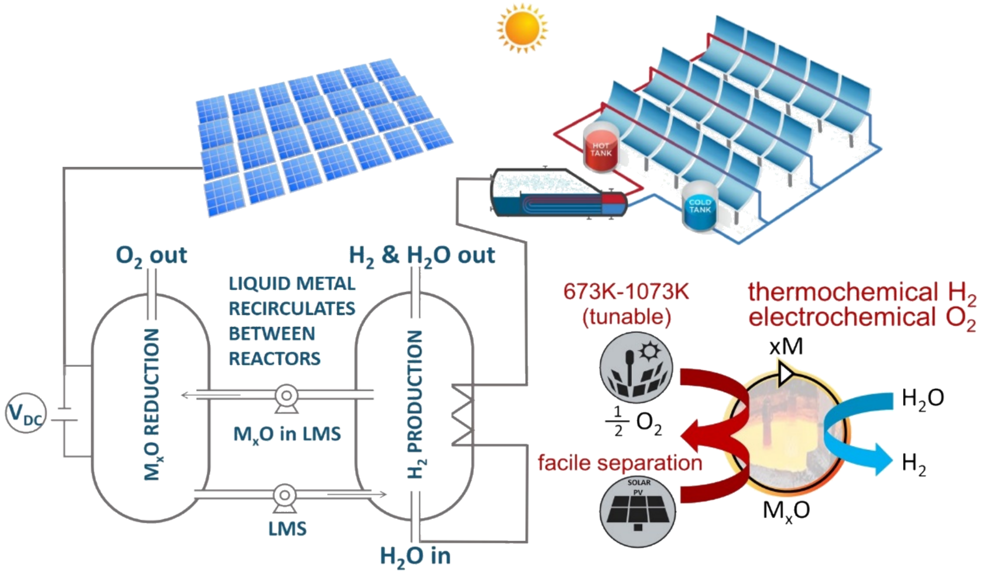


Solar Thermochemical

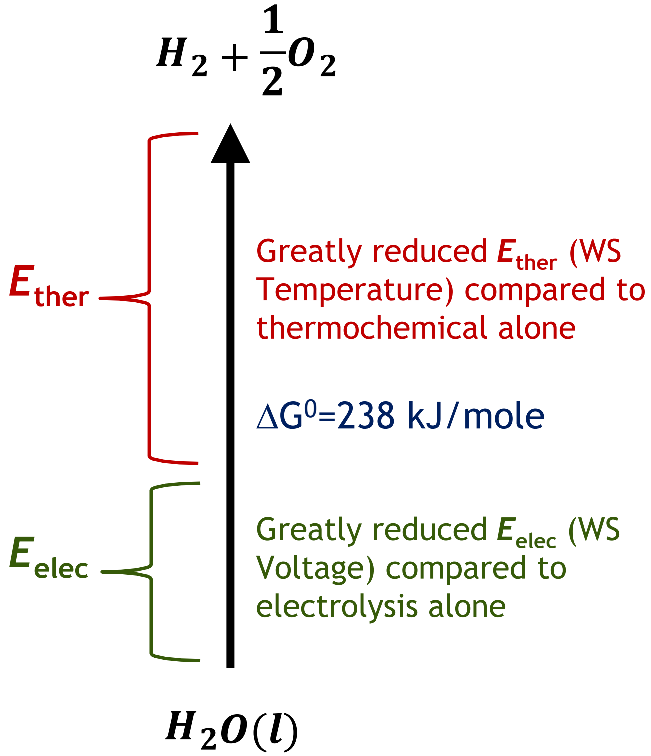


Solution: A Hybrid Thermo- Electro-Chemical Process

A liquid metal solution (LMS) integrated into a hybrid thermochemical-electrochemical process to renewably produce hydrogen by splitting water



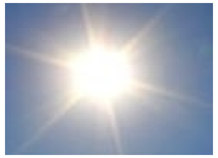
- LMS acts as a conductive medium for heat and electrons to facilitate water-splitting reaction
- Synergy between thermal + electrical energies allows for milder temperatures (< 1000 °C) and decreased electrical requirement relative to conventional electrolysis
- Heat and electricity can be from nuclear reactor or any combination of renewable resources



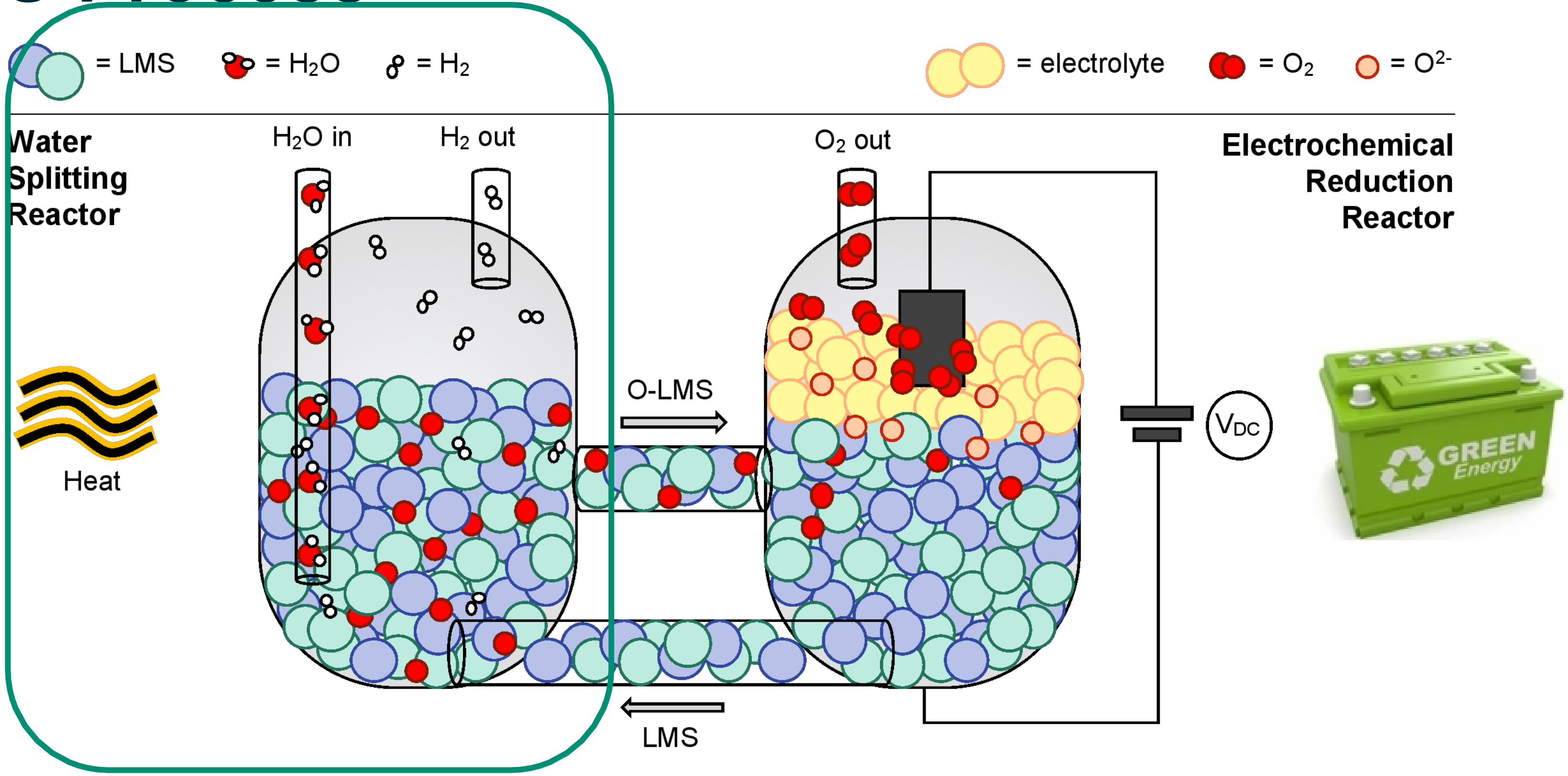
Interplay between temperature and electrochemistry allows us to tailor the hybrid cycle to particular thermal source

Basic LMS Process

< 573 K

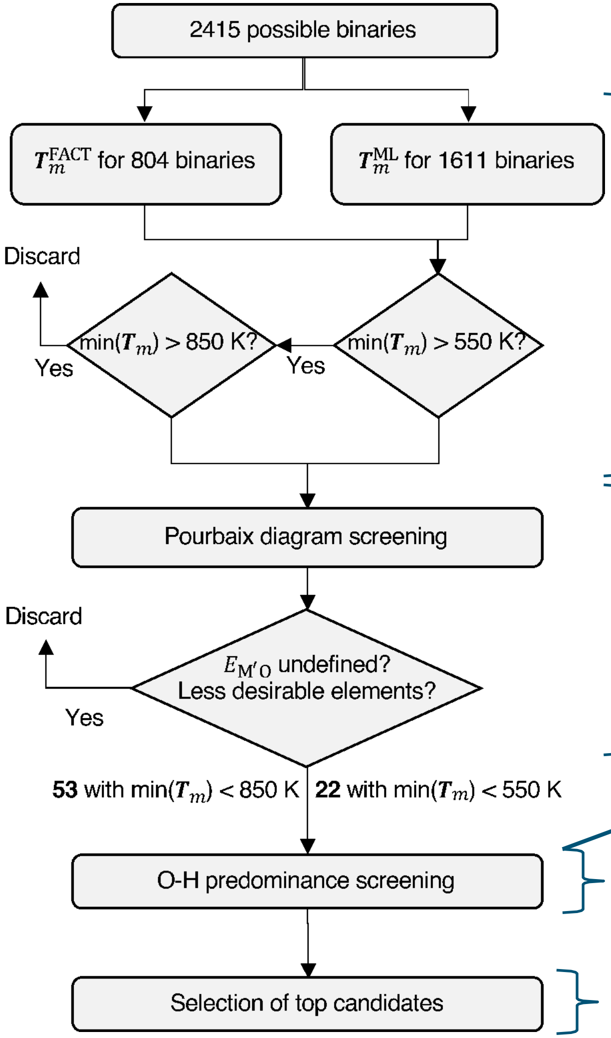


≤ 850 K



- Two-step cycle:
  - Thermochemical steam reduction of LMS producing hydrogen and solid metal oxide (O-LMS)
  - Thermo-electrochemical reduction O-LMS back to LMS with the subsequent oxygen evolution
- LMS requires at least one redox-active metal to split H_2O (M) and one less reactive or inert carrier (M′) to maintain liquidus phase

Alloy Selection Using Machine Learning*



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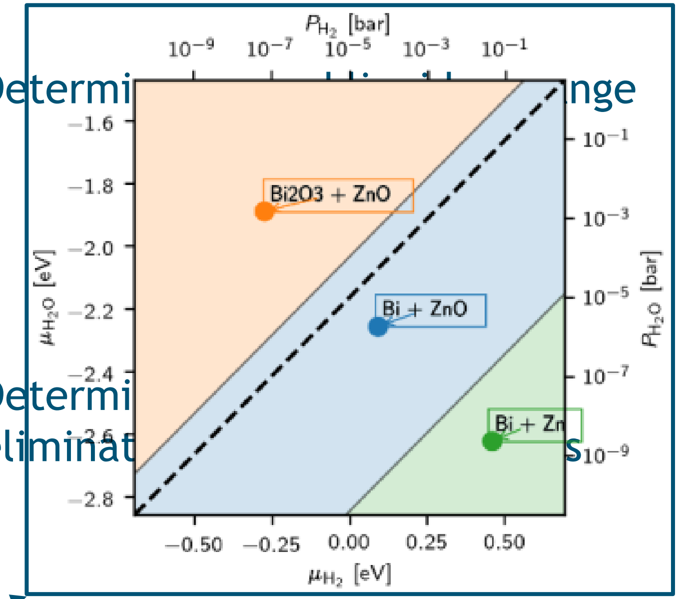
Determi… eliminat… …s



Predict equilibrium products of water-splitting reactor @ P_{H2}, P_{H2O}, T

Screen all binary candidates

- Mined all Materials Project (MP)[1] compounds for M-M'-O-H phase diagram
- Applied an ML descriptor that transforms DFT formation enthalpy to finite T Gibbs energies: e.g.,

$$\Delta G_f(T) = \Delta H_{f,DFT}(0\,K) + \delta G_{ML}(T)$$

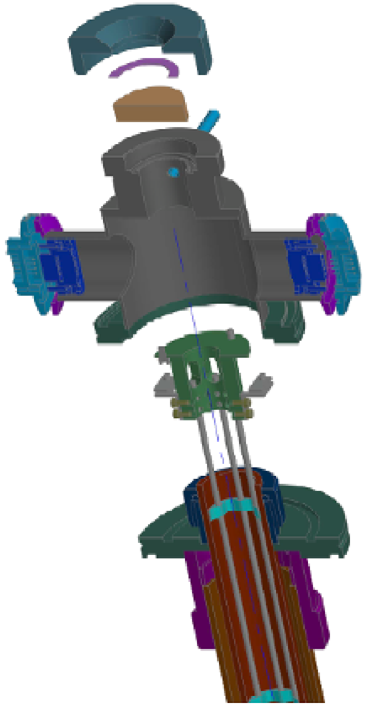
- Compute thermodynamic potential @ μ_{H_2}, μ_{H_2O}, T
- Reconfigured MP machinery to perform Gibbs minimization and predict the *predominant* (stable) phases in this ensemble

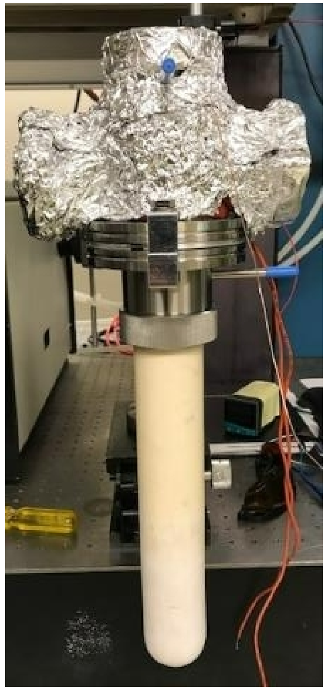
[1] Jain, A., et al. "The Materials Project: A materials genome approach to accelerating materials innovation," *APL Materials* **2013, 1 (1), 011002.**

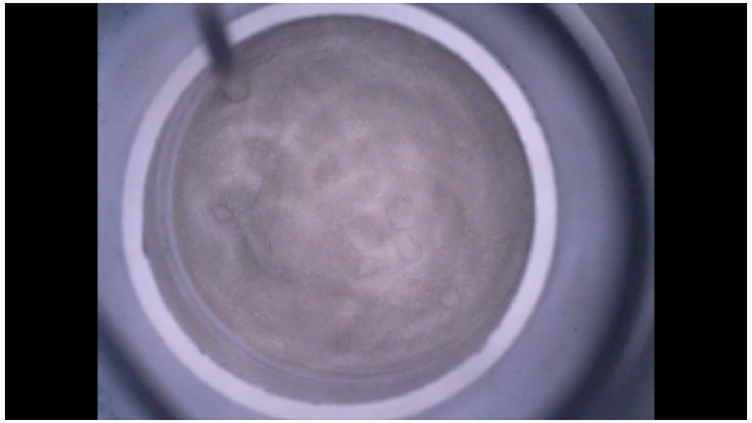
* A oversimplification. (Witman, M., *et al*. "Machine learning assisted screening and discovery of liquid metals for reversible, low temperature water-splitting," *in prep.)*

Test Run: Sn in Flow Reactor

- Designed and fabricated stagnation flow reactor
- Characterize alloy thermochemistry and electrochemistry
- Control gas composition, residence time, pressure, and temperature
- Optical access for video and laser-based probes

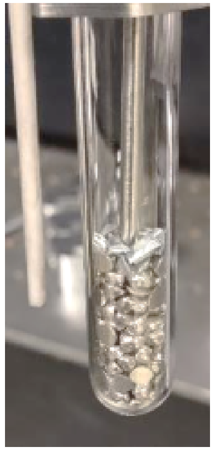


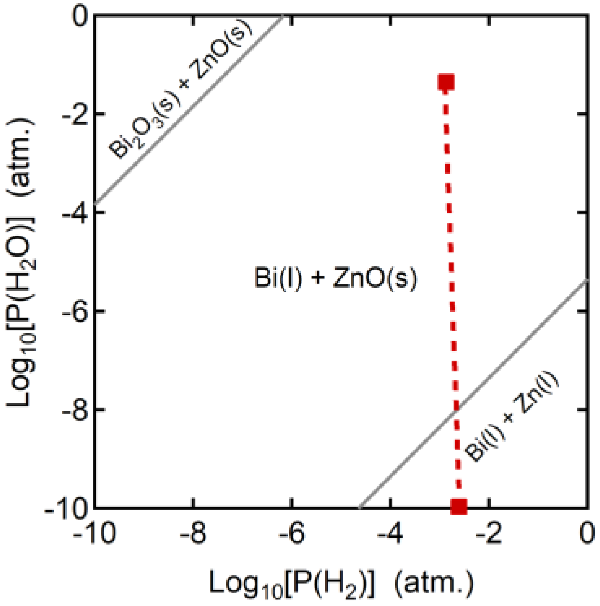


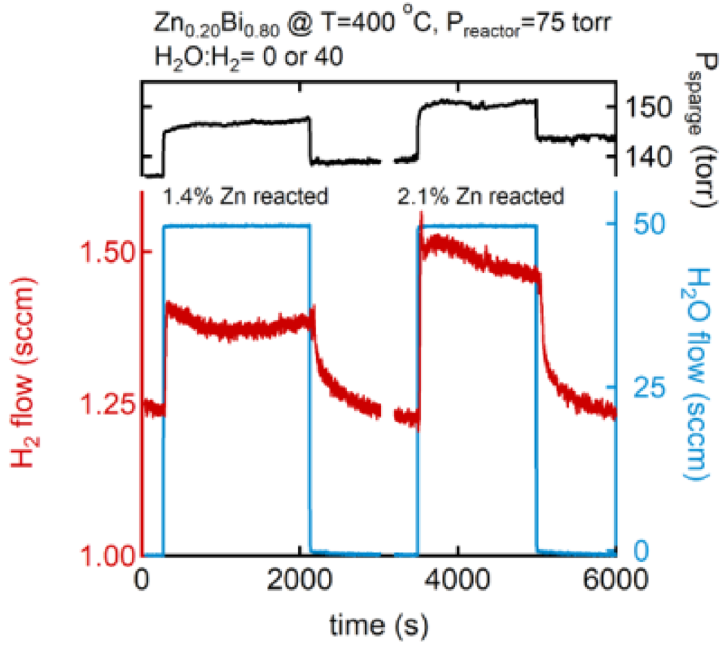


- Time lapse video while heating ~15 K/min in 5% H_2 from room temperature to 723 K
- Reduction of water by Sn produces H_2 and oxidizes Sn surface layer
- Thin SnO_2 layer appears to inhibit further oxidation

H_2 Production in $Zn_{0.2}Bi_{0.8}$ Alloy



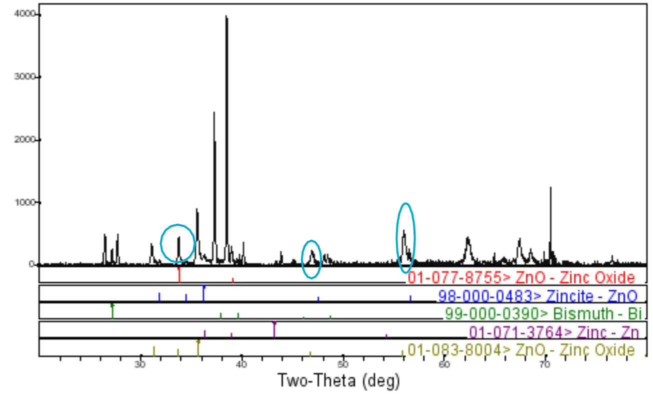


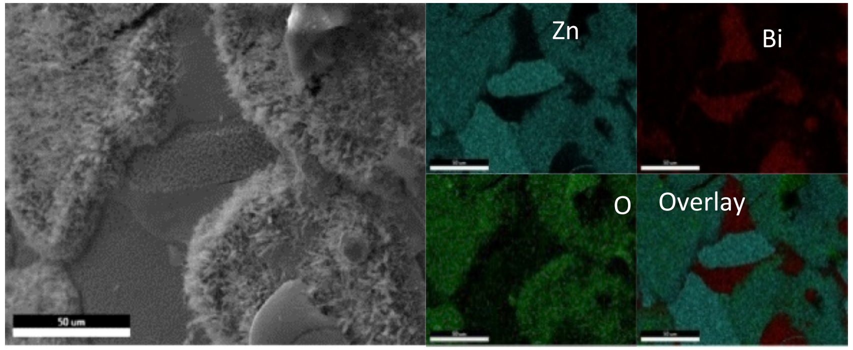


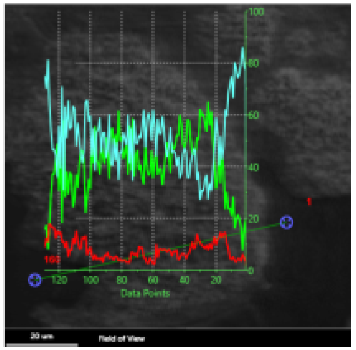
- Adjust $P(H_2O)/P(H_2)$ ratio in melt
- Transition from liquid to ZnO(s) formation region
- H_2 production observed, but utilization much lower than expected
- Why?
  - Incorrect thermodynamic predictions?
  - Experimental conditions, e.g. mixing? Mixing in the system is performed by a sparger

Characterization of Reacted $Zn_{0.2}Bi_{0.8}$ Alloy

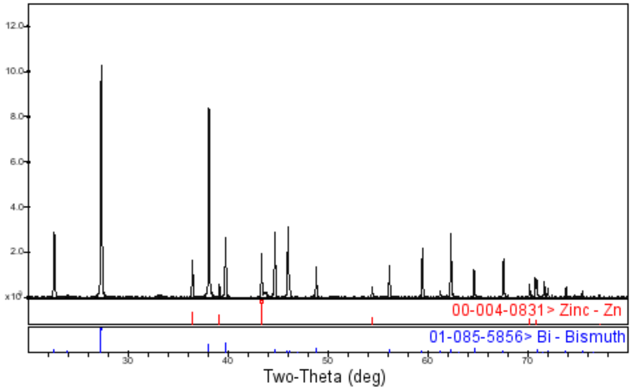
$Zn_{0.20}Bi_{0.80}$ sample collected from the walls of the test tube

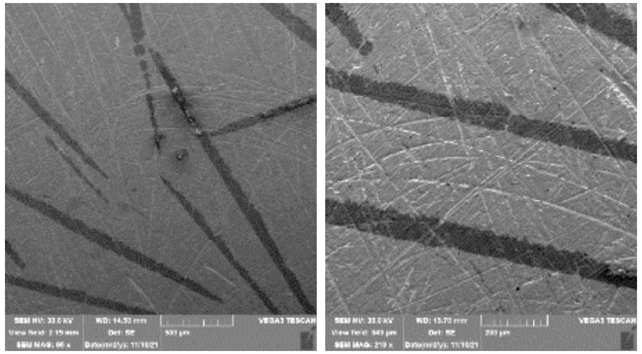


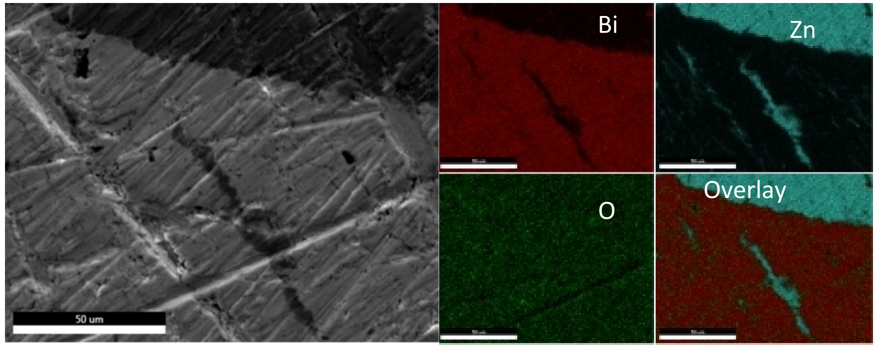




$Zn_{0.20}Bi_{0.80}$ interior X-section







- XRD shows evidence of ZnO (circled) on alloy/tube interface, but three interior cross-sections (only one shown) show only Bi, Zn metal
- SEM images of tube wall show particles of spike-like morphology consisting of Zn and O (EDX map), supported by line scan
- SEM of X-sections show segregation of Bi (light areas) & Zn (dark stripes) with small concentration of O homogeneously dispersed
  - Unsure if signifies presence of MOx or artifact/surface layer; homogeneity and lack of ZnO in XRD implies latter
- Presence of only small amount of ZnO concentrated on sides of tube support low oxidation results and imply that thorough mixing in reactor may not be occurring

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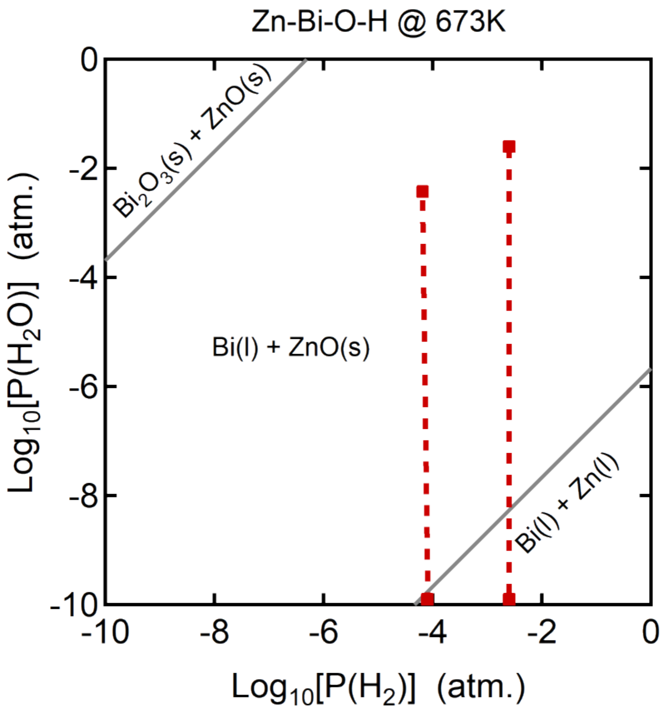
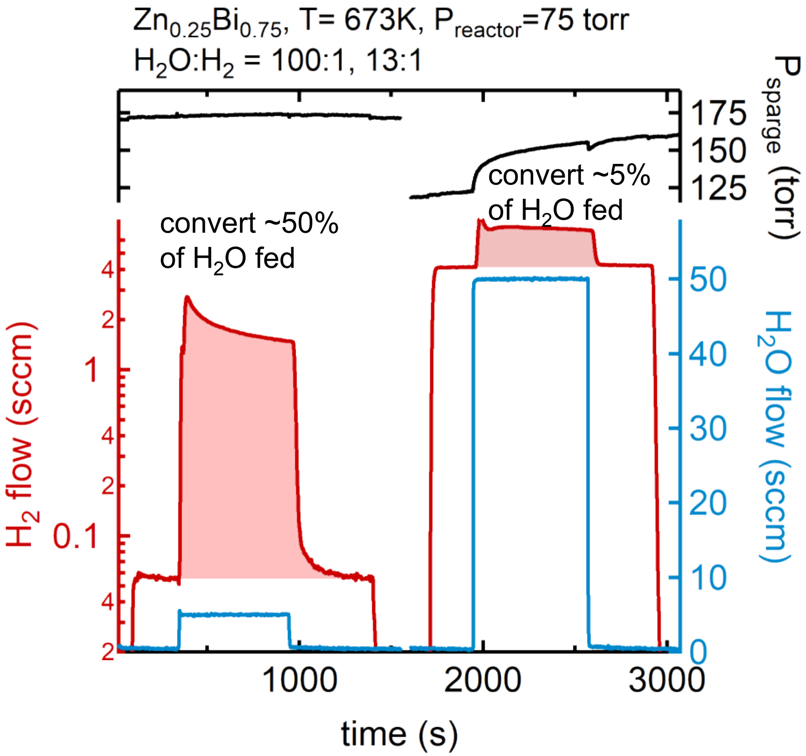
H_2 Production in $Zn_{0.2}Bi_{0.8}$ Alloy, Part II





- Hypothesis: Ineffective sparging results in large bubbles that impede oxidation reaction due to inefficient mixing and lack of interaction between steam and metal
- New sparger with more efficient mixing (smaller bubbles) was added to reactor
  - H_2 production increased by order of magnitude
  - Increasing H_2O flow did not increase conversion percentage, implying bubble formation is likely limiting factor, i.e., the LMS is exposed to the same amount of steam independent of the flow rate

Summary

Conclusions

- Hybridized thermochemical – electrochemical water splitting via liquid metal solutions (LMS) ameliorates the challenges faced by conventional thermochemical and high temperature electrolysis
- Machine learning was utilized to predict metal alloy combinations with favorable performance properties, as well as guide experimental conditions
- A Zn-Bi alloy successfully split water to produce H_2 with up to 50% conversion of Zn → ZnO while remaining liquidus
- Intimate steam-LMS contact is essential, requiring efficient mixing

Next steps

- Post-mortem characterization of Zn-Bi alloys to elucidate oxide compositions, particle size, reaction extent
- Develop efficient mixing methods
- Test additional alloy compositions predicted by machine learning
- Develop thermo-electrochemical metal oxide reduction reactor to regenerate LMS

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