



Energy Materials Network  
U.S. Department of Energy



**HydroGEN**  
Advanced Water Splitting Materials

# Advanced Water-Splitting Technology Pathways Benchmarking & Protocols Workshop

## Breakout Session Summaries Technology Pathway: *Solar Thermochemical Hydrogen*

October 24-25, 2018

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# S1-A Session Summary

Session ID: S1-A (Jim Miller Facilitator)

Title: Performance Metrics - Units, System Boundaries

Summary: The discussion began to define a minimum set of metrics that should be reported, e.g. thermodynamic values, physical properties, rates etc. The group was generally unsatisfied with this & focused instead on identifying a single data set or plot that could be universally understood and from which other calculations and comparisons could be drawn.

## Key Take-aways:

- Field needs something that is analogous to the I-V curve for electrolysis
  - Thermodynamic map of a material  $p_{O_2}$ ,  $T$ ,  $\delta$
- Agreement we need a standard way to measure redox extent ( $\Delta\delta$ )
  - For  $M_xO_{y-\delta}$ :  $\delta/(xM + yO)$
  - Standardize to O, not  $O_2$ .
  - This normalizations helps to deal with Cp, etc.
- Boundaries for Metrics (efficiency)
  - Thermal: Net Q, Products at Standard States
  - Solar: Need standardized locations or conditions

## Dissenting opinions/concerns

- Some prefer  $H_2/kg$ , or % of O metric rather than molar normalization.
- No agreement yet on a single global metric ( $\$/unit H_2$ , sunlight (or thermal) to  $H_2$ ,
  - Is the goal an understanding of efficiency or the business case, or both?
- Bad idea to specify a std. cycle (conditions)
- $\Delta\delta$  needs context, What couples to  $\Delta\delta$ ?
  - $H_2O/H_2$  ratio, etc?
  - Time frame to achieve  $\Delta\delta$ ?

## Action Items

- There was some agreement on the need for reporting a variety of other materials properties that impact performance and practicality, but aren't metrics per se. These could include Cp, durability (m.p., volatility, loss of activity),  $\$/kg$  material, density, m.w., etc.
- Kinetics – discussed in other sections. Is there a “must be at least this good” criteria?



# S2-A Session Summary

Session ID: S2-A (David Ginley Facilitator)

Title: Standard materials and form factors

## Summary of discussion

- The overall discussion looked at all aspects of the development of STCH material standards for high and low temperature processes. The discussion included sourcing, synthesizing and characterizing and curating samples for broad distribution. Key is the necessary characterizations to be done prior to distribution. There was also considerable discussion on what materials sets should be employed.
- The discussion also looked at the long term evolution of the standards process as STCH evolves.

## Key Take-Aways

- We must define a set of parameters and methods that can be broadly employed
- Need to define multiple standards for various temperature ranges specifically 1500 C and 1200 C for the former use CeO<sub>2</sub> and a perovskite at the lower temperature.
- There needs to be a set of well established best practices and well established measurement protocols
- Initial thermodynamic standards are key ultimately kinetic standards are desirable.

## Consensus and/or dissenting opinions

- For the standards while it is ideal that they have water splitting efficiency there is also a use for highly reproducible defect behavior with no water splitting properties, albeit not applicable to all protocols
- Key is understanding in addition, the curation of standards is also a key to defining such issues as shelf and storage stability, environmental reactivity, best handling practice. Note sufficient materials need to be made and curated for broad dissemination.
- Ultimately two standards may not be sufficient for the diversity of STCH approaches.

## Action Items

- A group was identified to begin to define standards as
  - High temperature 1500 C using CeO<sub>2</sub>
  - Low temperature 1200 C defect controlled materials – perovskite
  - Low temperature 1200 C water splitting materials - also perovskite
  - Methods to control the materials and curate them for broad dissemination.



# S2-B Session Summary

Session ID: S2-B (Jim Miller Facilitator)

Title: Detailed thermodynamics  
Operating Conditions and Methodology

Summary: Driven by agreement we need something analogous to an I-V curve, a “thermodynamic map”. Underlying assumption was that TGA is the method of choice (not electrochemical titration or sealed bomb experiments, except in special circumstances).

## Concerns/Other Opinions

- When do we need better than this, and what techniques should we use?
- What about hybrid splitting cycles – how do we evaluate them relative to this framework?
- Does data represent equilibrium?
  - Sample break-in?
  - Approach points from both reducing and oxidizing directions

## Recommended Minimum Map:

- 25 points minimum
- Bounded by 800 and 1500 °C
- 5 temps minimum (inclusive of bounds)
- 5 pO<sub>2</sub> values min at each T
  - pO<sub>2</sub> range ~10X, 100X above and below, and one near pO<sub>2</sub> of H<sub>2</sub>O at given T.
- Alternative – vary T for given gas composition to collect similar data set
  - ensure the area is adequately mapped, e.g. at high T and pO<sub>2</sub> where the steam curve is flat

## Action Item

- The use of gas mixes to establish low equilibrium pO<sub>2</sub> values in flowing systems needs to be more thoroughly validated and/or established.
  - E.g. what is the rate of H<sub>2</sub>/H<sub>2</sub>O or CO/CO<sub>2</sub> homogeneous equilibration reaction as a function of T?
  - Do we have to rely on the active materials we are evaluating to help establish the equilibrium – if so, is it universally going to work?



# S3-A Session Summary

Session ID: S3-A (Andrea Ambrosini Facilitator)  
Title: “Quick and Dirty” Thermodynamic Screen

## Summary of discussion

- What parameters constitute a “quick” screen?
- Who can perform screening?
  - Established researchers, wider solid state community (explore materials designed for other purposes)
- How do we perform analysis?
  - TGA seems obvious answer, but are there other means?
  - Does it matter?

## Key Take-Aways

- Necessary to agree on what makes a material “promising” and under what conditions screening should occur
- There is more than one way to skin a cat (i.e., screen a material): TGA, flow reactor, computational methods, combinatorial chemistry
- There may be other indicators accessible by quick screening methods to identify promising materials, e.g., optical changes, conductivity, something we haven’t thought of yet.

## Consensus and/or dissenting opinions

### Consensus:

- Most important parameters: (1) O<sub>2</sub> evolution upon reduction; (2) Onset temperature of reduction; (3) Redox is repeatable over several (11) cycles; (4) reaction must occur within specified period of time
- Direct measurement of water splitting is not a “quick and dirty” experiment

### Dissent:

- TGA is the best method to screen a material
  - Not everyone can afford a TGA/experiment too complicated vs. TGA is a std. piece of equipment and is most efficacious method

## Action Items

- Determine measurement parameters (pO<sub>2</sub>, T<sub>high</sub>/T<sub>low</sub>, desired rate)
- Seek BES/DOE funding for establishing screening methods
- Continue activities to encourage participation of non-STCH groups, e.g. Symposia at conferences, publication of screening methods and desired metrics



# S3-B Session Summary

Session ID: S3-B (Ellen Stechel Facilitator)

Title: Extracting thermodynamic variables from theory and experiment

## Summary of discussion

- Goal: It is important that we develop protocol to extract data from thermodynamic measurements
  - Underlying assumptions: TGA measurements (mass loss) for detailed thermodynamic measurements will have its own protocol
- Most of the discussion focused on entropy and role of defect models.
- Some discussion on alternatives to TGA.

## Key Take-Aways

- Ultimately  $\Delta G$  is what is important (making  $\Delta S$  important)
- If we believe  $\Delta H$ , why don't we believe  $\Delta S$ ?
  - No extrapolation for  $\Delta H$
- Could do DSC to get  $\Delta H$ , but still cannot get  $\Delta S$  without a "ton" of measurements;
  - Still requires extrapolation
  - Often does not agree with Van't Hoff experiments – what is correct?
- Doesn't really matter what method we use as long as everyone uses the same for material comparison – ok if it is not exact
- Often Van't Hoff approach and defect model are used together

## Consensus and/or dissenting opinions

We asked the question can we reliably extract entropy from Van't Hoff extrapolation? Some responses

- Depends on how the data looks
- Problem: experiments generally done under very small range so extrapolation is extreme and assumption of linearity may be incorrect
- Some suggested that we need large temperature range (e.g., 800 to 1500°C) to improve extrapolation (still it is an extrapolation).
- Is the Van't Hoff approach the best approach to get  $\Delta S$ ?
- Defect modeling to extract reaction equilibrium
  - Not robust across materials; can get non-sensible results
  - Can be important if there is curvature in the results

## Action Items

- Explore adiabatic calorimetry or drop calorimetry: e.g., engage Alex Navrotsky to do calorimetry for comparison to determine if we need to develop a calorimetry node.
- Long term– determine if different methods discussed give the same result which is best to standardize on
- Short term – until someone does the cross referencing study, having one standard method is probably the best solution
- Plan to develop a protocol, initially based on TGA and Van't Hoff



# S4-A Session Summary

Session ID: S4-A (Tony McDaniel Facilitator)

Title: Detailed Kinetic Screening

## Summary of discussion

- Identified 3 fundamental processes that control redox kinetics (anion/cation transport, crystal lattice rearrangement, surface mediated processes).
- Experimental and theoretical protocols will be different for studying each process.
- Need to identify and address needs of both fundamental and applied R&D communities when considering protocols.

## Consensus and/or dissenting opinions

- Protocols to measure material kinetics are needed.
- Universal protocols will be difficult to establish and based on “classes” (e.g., material type, rate controlling mechanism, form factor, etc.).
- Metrics are needed for screening materials (how to decide to keep or toss?).
- Material stability must be established before kinetic studies commence.

## Key Take-Aways

- Various experimental methods (i.e., reactor types and measurements) were proposed as best practice for kinetic studies of each mechanism “class”.
- Imperative to account for and/or eliminate the effects of instrument response on measurements (e.g., fast materials require fast methods).
- Establishing and informing ways to improve kinetics is beneficial.

## Action Items

- Did not get this far, maybe next time.



# S4-B Session Summary

**Session ID: S4-B (Ivan Ermanoski Facilitator)**  
**Title: Systems and Techno-economic Analyses**

## Summary of discussion

System performance TEA are complex and, with a lot of history, and will not be solved in one hour. Ultimately, these are the parts of STCH that will interface with those outside of the community. Need to maintain as an ongoing activity to include state of the art in the field, including relevant developments that currently fall outside of the FCTO programs, such as solar concentration. Take care to avoid codifying approaches/prescriptions that no longer reflect the state of the art.

## Consensus and/or dissenting opinions

Agreed that an ongoing activity is the best approach for both systems performance analysis and TEA. There is a need to further develop, regularly update, and document methodologies, embody into community-accepted open-source code, and make available via web interface. It would also be useful if system and TEA code could generate quantities to interface with H2A to continue to enable cross-technology comparisons. 6-month working group meeting cadence deemed appropriate, and annual code updates.

## Key Take-Aways

Interesting takeaway, in addition to remainder of summary: even our colleagues in the hybrid cycle community were not familiar with the system performance analysis methodology currently used by STCH groups. The need for communication outside of the two-step STCH is evident.

## Action Items

Volunteers from the session will reach out to others in the community to gauge interest in participating in systems performance and TEA working groups. Should the activity proceed, interface with similar activities initiated under SolarPACES Task II.





# S5-A Session Summary

Session ID: S5-A ( Tony McDaniel Facilitator)

Title: “Quick and Dirty” Kinetic Screening

## Summary of discussion

- Vigorous debate about needs, how best to achieve a meaningful “quick and dirty” material assessment based on kinetics, and how this information will be used.
- Achieved consensus on measurement bounds (e.g., redox temperatures and time to conversion).

## Key Take-Aways

- As in detailed kinetic studies, rate controlling mechanisms must be considered when establishing protocols and reactor configurations.
- “Apples-to-apples” comparisons may be difficult to achieve, must normalize out reactor effects.
- Materials missing “passable” criteria are o.k. (i.e., no hard and fast cutoff), but further justification needed to establish material viability.

## Consensus and/or dissenting opinions

- Kinetic information is important at “Level 1” screening (“Level 0” based purely on thermodynamics).
- “Level 1” must include both reduction and oxidation with actual gas splitting (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ).
- Protocols established that bound both temperature and time (see notes).

## Action Items

- Did not get that far, maybe next time.



# S5-B Session Summary

Session ID: S5-B (Ivan Ermanoski Facilitator)

Title: Durability Protocols

## Summary of discussion

Discussion with agreement on essentially all points of definition, focusing mostly on reasonable qualitative and numerical targets for materials durability in different stages of development.

### Consensus and/or dissenting opinions

Agreed on three tiers of durability testing:

1. Early stage (could be folded into quick and dirty thermodynamics): demonstrate a small number of redox cycles (~20), after 3 break-in cycles that are excluded, in a lab instrument (i.e. *ex-situ*), with an indication of asymptotic behavior with respect to O<sub>2</sub> redox capacity, in the relevant pO<sub>2</sub>, T range, but without H<sub>2</sub>O splitting.
2. Advanced stage, intended before a material is made in sufficient quantities to operate in a reactor: ~200 *ex-situ* redox cycles, in the relevant pO<sub>2</sub>, T range, with periodic confirmation of H<sub>2</sub>O splitting, stable crystal structure, mechanical properties, acceptable mass loss (vapor pressure), and stable kinetics.
3. *In-situ* testing (in a laboratory-scale reactor, on-sun or simulated sun), intended before scale-up to the pre-pilot plant: Includes all relevant operating conditions (temperature, pressure, WS, mechanical, thermal, and other factors expected in operation), ~2000 cycles, with evaluation of all relevant modes of degradation (capacity, kinetics, mechanical, material losses, etc.)

## Key Take-Aways

Durability means different things in different stages of materials evaluation, and these need to be captured and applied judiciously, in order to optimize resources.

## Action Items

Follow up with a working group discussion to finalize/formalize the protocols and standards.



# Session Summary

Session ID: S6-A ( David Ginley Facilitator)

Title: Bringing it to Closure

## Summary of discussion

- We took a step back to review what was discussed and see what items could be brought to closure
- Benchmarking STCH processes, materials, computational? Defining the chemical environment  
Defining what we mean by benchmarking.
- Establish parameters for Ceria as a high temperature standard and seek to define one or more lower temperature materials. This is a priority.
- How can we speed up new materials discovery; i.e., means for rapid assessment

## Consensus and/or dissenting opinions

- Significant consensus for standards and fixed protocols
- Significant energy around having “quick and dirty” protocols
- Very little consensus on whether “quick and dirty” first level screens needs development of new techniques that could be accessible to novice practitioners not just materials scientists with access to high temperature TGAs.
- Significant agreement on metrics and also on durability
- Less agreement on what to normalize on; although moles H<sub>2</sub> per moles of atoms in the active material seemed to be accepted.

## Key Take-Aways

- Question: Can material performance be certified in some manner?
- Should we establish a lab that serves as a testing facility so their results stand without question?
- How easy are we trying to make it so that materials discovery needs experts or can be crowd sourced?

## Action Items

- 1) Standards lead and initial group formed
- 2) Two groups formed with leads identified for “quick and dirty” thermodynamics (the second group taking a longer view of what might be possible.
- 3) Durability Team: Lead and initial team formed.
- 4) Outstanding issues: computational materials was not a focus because we did not know that we had critical mass until too late. Need to set up a working group.