HydroGEN
Advanced Water Splitting Materials

Advanced Water-Splitting Technology Pathways Benchmarking & Protocols Workshop

Breakout Session Summaries
Solar Thermochemical (STCH)

October 29 - 30, 2019

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Executive Summary

For Solar thermochemical hydrogen (STCH) there were discussions about metrics, standards (beyond the state-of-the-art ceria), measuring the thermodynamics of the redox active material, measuring kinetics, efficiency calculations, durability, and the role and challenges for materials discovery using Density Functional Theory (DFT). Those discussion focused on draft protocols and what will be required before the protocols can be expected to be publication ready. In addition, there were breakout discussions about a high level roadmap for materials, for reactors and systems, and for ancillary components. It was agreed that there is still no consensus on optimal operating conditions or how to achieve them and as a result, moving from a material to efficiency to cost remains a difficult challenge for the community.

STCH Breakout Sessions

Breakout Session #	Session ID	Technology	Topic	Lead
1	S1-A	STCH	STCH Technology Roadmap Review & Discussion: Materials	Andrea Ambrosini
1	S1-B	STCH	STCH Metrics -Units and Operating Boundaries (Protocol)	Chris Muhich
2	S2-A	STCH	STCH Technology Roadmap Review & Discussion Reactors and Systems	Ivan Ermanoski
2	S2-B	STCH	STCH Standards: beyond Ceria (Protocol)	Jonathan Scheffe
4	S4-A	STCH	STCH Thermodynamics (Protocol)	Andrea Ambrosini
4	S4-B	STCH	STCH Kinetics (Protocol)	Tony McDaniel
5	S5-A	STCH	STCH Durability (Protocol)	Ivan Ermanoski
5	S5-B	STCH	STCH Density Functional Theory	Tony McDaniel
6	S6-A	STCH	Wrap-up/Bringing it to Closure and Next Steps: STCH Active Materials	Tony McDaniel
6	S6-B	STCH	Wrap-up/Bringing it to Closure and Next Steps: STCH What's Missing	David Ginley

Session Summary

Session ID: S1-A
Title: STCH Technology Roadmap Review & Discussion: Materials
Facilitator: Andrea Ambrosini

Summary of discussion

- Materials portion of roadmap (thermodynamics, kinetics, durability, auxiliary) were discussed
- Main discussion around timing of certain elements of roadmap

Consensus and/or dissenting opinions

- Computational techniques should be included in Roadmap (across several sub-tasks)
- Most Durability tasks should be pushed back to later in roadmap
- Need to standardize thermodynamic characterization and standards
- We shouldn't limit ourselves to materials that are "better than ceria" – too nebulous

Key Take-Aways

- Durability is difficult to define/measure until we have a reactor design (need to consider form factor, reactor conditions…)
  - Are there any tests we can perform that are irrespective of reactor design, e.g. chemical stability?
- Kinetics can be difficult to measure; how do we define?
- Does "Auxiliary" refer to all aspects of H_2 production or only the aspects that are directly funded by STCH?

Action Items

- Refine Roadmap

Session Attendee List

Session ID: S1-A
Title: STCH Technology Roadmap Review & Discussion: Materials
Facilitator: Andrea Ambrosini

Name	Affiliation
Andrea Ambrosini (facilitator)	Sandia National Laboratories
Robert Bell (note taker)	National Renewable Energy Laboratory
Stephanie Byham	U.S. Department of Energy
Eric Coker	Sandia National Laboratories
Levi Irwin	U.S. Department of Energy (via phone)
Sai Gautam Gopalakrishnan	Princeton University
Samantha Millican	University of Colorado Boulder
Jie Pan	Michigan State University
Alicia Bayon Sandoval	CSIRO, Australia
Ellen Stechel	Arizona State University
Michael Toney	SLAC, Stanford Linear Accelerator
Shang Zhai (note taker)	Stanford University

Session Summary

Session ID: S1-B
Title: Metrics -Units and Operating Boundaries (Protocol)
Facilitator: Christopher Muhich

Summary of discussion

- Materials metrics should take a 3 tiered system
- There was debate as to what the "delta" metric should be
- There was a discussion of how to determine a standard "0" or a fully oxidized state of the system
- There was debate over how to do the efficiency analysis and what it should include
- The group did not talk about the Protocol that was drafted.

Consensus and/or dissenting opinions

δ- plot should have 2 y axes so we can have multiple representations, this came down to three – δ/total number of O, δ/# of atoms, Number of O – δ. No further agreement was made. Consensus from 2018 was δ/# of atoms.

Agreed that the thermodynamic model of system efficiency is important and should be conducted over an array of system assumptions.

However, there was descent as to how to calculate efficiency and what to include.

Key Take-Aways

- Tear 1 – δ- plot, phase analysis, composition analysis
- Tear 2 – detailed thermodynamics of the material, possibly efficiency analysis
- Tear 3 – all other properties of interest

Action Items

- δ- normalization – Sanders
- Efficiency modeling standardization – Ermanoski
- Form team to review the protocol - Stechel

Session Attendee List

Session ID: S1-B
Title: Metrics -Units and Operating Boundaries (Protocol)
Facilitator: Christopher Muhich

Name	Affiliation
Ivan Ermanoski	Arizona State University
Wei Li	West Virginia University
Anthony McDaniel (note taker)	Sandia National Laboratories
Christopher Muhich (facilitator)	Arizona State University
Michael Sanders	Colorado School of Mines
Jonathan Scheffe	University of Florida
Alan Weimer	University of Colorado Boulder

Session Summary

Session ID: S2-A

Title: STCH Tech Roadmap Review & Discussion: Reactors & Systems

Facilitator: Ivan Ermanoski

Summary of discussion

- Discussed the roadmap draft at the highest level, to identify gaps, if any
- Agreed that the details should be done by a small group, offline.
- Focused on "reactors" and "systems" sections of the roadmap.
- Need consensus on 2023+ outcomes and the timelines in general.

Consensus and/or dissenting opinions

- No major gaps in roadmap
- Need for much work on adding appropriate level of detail

Key Take-Aways

- No major gaps identified in roadmap
- Possibly need to add heat recovery other than solid-solid to the roadmap
- Need for consensus on the scale for integrated long-term testing for the various components. The target power is probably ~ 10kW (with wide margins)
- Need to generate a simpler/shorter roadmap for outreach purposes.

Action Items

- Evaluate and refine specific details listed in the existing roadmap [Ivan Ermanoski will own coordinating this activity]
- Al Weimer will work Air Products regarding opportunities in oxygen separation

Session Attendee List

Session ID: S2-A

Title: Technology Roadmap Review & Discussion: Reactors and Systems

Facilitator: Ivan Ermanoski

Name	Affiliation
Ivan Ermanoski (facilitator)	Arizona State University
Wei Li	West Virginia University
Anthony McDaniel (note taker)	Sandia National Laboratories
Samantha Millican	University of Colorado Boulder
Jie Pan	Michigan State University
Michael Sanders	Colorado School of Mines
Ellen Stechel	Arizona State University
Alan Weimer	University of Colorado Boulder

Session Summary

Session ID: S2-B
Title: STCH Standards: Beyond Ceria (Protocol)
Facilitator: Jonathan Scheffe

Summary of discussion

- Building on the existing protocol for Ceria
- Foundationally using TGA Measurements
- Use initial measurements in TGA as baseline for field
- Build to more standard water splitting systems

Consensus and/or dissenting opinions

- New standard material defined by consensus LaSrMnO3 – starting with commercial materials from Merck
- Need to have a two stage approach to developing standards

Key Take-Aways

- Stagewise standards development from TGA standards to ultimately water splitting standards
- Have baseline synthesis one laboratory and baseline measurements in another.
- Round robin test should be done

Action Items

- NREL to develop materials and curate them for Ceria and (La,Sr)MnO_3 as standards
    - Powders
    - Ceramic
- SNL to measure standards under controlled reproducible thermodynamic protocol

Session Attendee List

Session ID: S2-B
Title: STCH Standards: Beyond Ceria (Protocol)
Facilitator: Jonathan Scheffe

Name	Affiliation
Andrea Ambrosini	Sandia National Laboratories
Alicia Bayon Sandoval	CSIRO, Australia
Robert Bell	National Renewable Energy Laboratory
Eric Coker	Sandia National Laboratories
David Ginley (note taker)	National Renewable Energy Laboratory
Sai Gautam Gopalakrishnan	Princeton University
Christopher Muhich	Arizona State University
Jimmy Rojas	Stanford University
Jonathan Scheffe (facilitator)	University of Florida
Shang Zhai	Stanford University

Session Summary

Session ID: S4-A
Title: STCH Thermodynamics (Protocol)
Facilitator: Andrea Ambrosini

Summary of discussion

- Discussed best practices for a testing candidate materials for water splitting and determining the thermodynamics. TGA is sufficient for this test. Best practices in terms of order or experimentation, sample size, pressure, etc. were discussed.

Consensus and/or dissenting opinions

- The TGA gives sufficient information for determining if a material splits water and its rough thermodynamics
- Need data above and below the steam line in pressure
- The protocol discussed is a “second tier” test for water splitting, after a quick and dirty, and a before an extensive mapping for higher precision thermodynamics
- Medium-low pO_2 is difficult to obtain by many labs (the pO_2 “cliff”). How do we address that?

Key Take-Aways

- Need points above, on, and below steam line (recommended two above, one on, two below).
- Need the low temperature low T/low pO_2 point to correctly model thermodynamics.
- Thermodynamics are path independent, can run in isothermal pressure changes or isobaric temperature changes. But need to confirm a couple points are the same for the material in isothermal or isobaric.

Action Items

- Control and report experimental pressure independent of altitude (e.g. pressure transducer on TGA outlet)
- Investigate alternate low pO2 low temperature methods such as a Coulombic titration cell
- Need to look at what gas mixtures are readily achievable before setting numbers
- Refine protocol document

Session Attendee List

Session ID: S4-A
Title: STCH Thermodynamics (Protocol)
Facilitator: Andrea Ambrosini

Name	Affiliation
Andrea Ambrosini (facilitator)	Sandia National Laboratories
Alicia Bayon Sandoval	CSIRO, Australia
Robert Bell (note taker)	National Renewable Energy Laboratory
Eric Coker	Sandia National Laboratories
Ivan Ermanoski	Arizona State University
Sai Gautam Gopalakrishnan	Princeton University
Wei Li	West Virginia University
Michael Sanders	Colorado School of Mines
Christopher Muhich	Arizona State University
Ellen Stechel	Arizona State University
Shang Zhai	Stanford University

Session Summary

Session ID: S4-B
Title: STCH Kinetics (Protocol)
Facilitator: Anthony McDaniel

Summary of discussion:

The need for kinetic protocols was established and details were debated. Conversation focused on deriving ONE specific protocol for the water oxidation reaction over powdered material using a flow reactor. How the experiment is designed and performed was discussed. How the data is analyzed and presented was discussed.

Consensus and/or dissenting opinions

- Everything about the how the experiments are designed and conducted matters and will influence the result.
- Prioritize development of **one** method: *water oxidation* of *non-stoichiometric oxides* over *powder* using a *flow reactor* (fully dense particle, 10-100µm sieved to narrow size distribution, gas transport effects must be eliminated or otherwise accounted for [Haile-like criteria?], use water vapor diluted by inert gas over a range of concentrations, gas composition measured by mass spectrometry).
- Material must be stable (cycled until redox behavior invariant).
- Thermal and chemical methods of reduction acceptable (must verify and/or fix initial delta).
- Measure data over a specified range of re-oxidation extent (TBD).
- Model-based analysis required, standardized analysis method TBD.

Key Take-Aways

- Rate of oxygen exchange in STCH oxides governed by three fundamental processes (not considering decomposition).
  - Surface mediated reactions
  - Transport of anions, cations, electrons, holes in the solid
  - Crystallographic rearrangement of atoms
- Magnitude of oxygen chemical potential determines rate controlling process, rate controlling processes may transition from on to another during oxidation reaction.
- Everything matters.

Action Items

- McDaniel: Lead the effort to writing a solid second draft of protocol.
- Scheffe: Help edit protocol to final form.

Session Attendee List

Session ID: S4-B
Title: STCH Kinetics (Protocol)
Facilitator: Anthony McDaniel

Name	Affiliation
David Ginley	National Renewable Energy Laboratory
Anthony McDaniel (facilitator)	Sandia National Laboratories
Samantha Millican	University of Colorado Boulder
Jie Pan	Michigan State University
Jimmy Rojas	Stanford University
Jonathan Scheffe (note taker)	University of Florida
Michael Toney	SLAC National Accelerator Laboratory
Alan Weimer	University of Colorado Boulder

Session Summary

Session ID: S5-A
Title: STCH Durability (Protocol)
Facilitator: Ivan Ermanoski

Summary of discussion

Recapped last year's discussion, and picked up with remaining items. Largely achieved consensus on early and advanced durability testing, with *in-situ* testing yet to be addressed in detail.

Consensus and/or dissenting opinions

- For early stage durability testing, confirmed 20 cycles (after break-in), relevant pO_2, T, indication of asymptotic O_2 capacity, no H_2O splitting. Added:
  - Heat/cool rate: 10K/min or faster
  - Dwell time: 30 min or less
- For advanced stage confirmed 200 cycles, stable kinetics, and acceptable mass loss, and specified:
  - No reprocessing between cycles
  - Structure checks
  - Postponed mechanical stability to in-situ testing

Key Take-Aways

- In the early stage, durability screens are meant to discard materials quickly that degrade rapidly
- Screening should be doable by common equipment in the field, such as TGA

Action Items

- Ivan Ermanoski: send draft protocol to Eric Coker for revisions.
- Ivan Ermanoski: start drafting 2^{nd} level durability testing protocol

Session Attendee List

Session ID: S5-A
Title: STCH Durability (Protocol)
Facilitator: Ivan Ermanoski

Name	Affiliation
Andrea Ambrosini	Sandia National Laboratories
Stephanie Byham	U.S. Department of Energy
Eric Coker	Sandia National Laboratories
Ivan Ermanoski (facilitator)	Arizona State University
Wei Li	West Virginia University
Katie Randolph	U.S. Department of Energy
Michael Sanders	Colorado School of Mines
Alicia Bayon Sandoval (note taker)	CSIRO, Australia
Michael Toney	SLAC National Accelerator Laboratory

Session Summary

Session ID: S5-B
Title: STCH Density Functional Theory
Facilitator: Anthony McDaniel

Summary of discussion

Focused on the variety of applications DFT is applied to for STCH research, including high throughput screening and structural prediction.

The benefit of community *discussion* of best practices was affirmed. Also discussed whether creating a DFT protocol was feasible and/or useful.

Consensus and/or dissenting opinions

- No consensus on whether DFT protocols are needed or would be useful (do not want to specify exact equipment or method).
- No consensus on whether Peer review is sufficient.
- Difficulty in determining a "right answer" when it comes to tradeoffs between chemical accuracy and high throughput.
- Hard to enforce standards on wider community; people working in this field do not provide sufficient details when reporting results.
- Accuracy need to be to be effective (or convincing) for screening (0.1 eV, errors <10-25 kJ/mol absolute? to claim it is a good candidate to split water).
- Clear metrics needed for ΔS and ΔH (methodology, accuracy, etc.).
- Magnetic ordering, is it important at high temperature.

Key Take-Aways

- There are a variety of uses for DFT in the STCH community.
- Will likely find it difficult to find consensus on many issues.
- Better to inform and guide as oppose to stipulate.
- Recognized the need for continued group discussion.

Action Items

- Determine if other technologies are interested in a cross cutting meeting talking about how DFT is used in HydroGEN before next workshop.
- Have regular online meetings to discuss best practices in STCH DFT
- Begin working on a suggested protocol/best practices.

Session Attendee List

Session ID: S5-B
Title: Density Functional Theory
Facilitator: Anthony McDaniel

Name	Affiliation
Robert Bell (note taker)	National Renewable Energy Laboratory
David Ginley	National Renewable Energy Laboratory
Sai Gautam Gopalakrishnan	Princeton University
Anthony McDaniel (facilitator)	Sandia National Laboratories
Samantha Millican	University of Colorado Boulder
Christopher Muhich	Arizona State University
Jonathan Scheffe	University of Florida
Ellen Stechel	Arizona State University

Session Summary

Session ID: S6-A

Title: Bringing it to Closure and Next Steps: STCH Active Materials

Facilitator: Anthony McDaniel

Summary of discussion

Reviewed all breakout sessions on active materials (kinetics, thermodynamics, DFT, durability, and auxiliary materials as well as compatibility with structural materials). Affirmed that taking a tiered approach to developing protocols is best because it is easier to prioritize goals and focus on singular objectives.

Consensus and/or dissenting opinions

- Thermodynamics (do not need a TGA, other techniques are appropriate to use).
- Kinetics (Tier 1 figure of merit does not need to supply mechanistic details, only an agreed upon “comparator”).
- Durability (several Tiers and merit comparators derived.
- DFT (continued discussions about best practices useful, deriving protocols maybe not).
- A need for cross cutting activities to guide and inform best experimental practices (how to make measurements, how to calibrate equipment, someone mentioned training courses).

Key Take-Aways

- Summarized the day’s discussions.
- Made recommendations for next workshop.

Action Items

- Thermodynamics (actually run a material standard through protocol so that results and applicability can be discussed at next meeting; include data processing).
- Kinetics (fully develop a specific methodology, documented in writing, for discussion and debate; start thinking about other protocols like reduction).
- Durability (finalize Tier 1 protocol).
- Auxiliary materials (start thinking about protocols on interfacial interactions between active materials and structural materials).

Session Attendee List

Session ID: S6-A

Title: Bringing it to Closure and Next Steps: STCH Active Materials

Facilitator: Anthony McDaniel

Name	Affiliation
Andrea Ambrosini	Sandia National Laboratories
Alicia Bayon Sandoval	CSIRO, Australia
Robert Bell	National Renewable Energy Laboratory
Eric Coker	Sandia National Laboratories
Sai Gautam Gopalakrishnan	Princeton University
Anthony McDaniel (facilitator)	Sandia National Laboratories
Samantha Millican	University of Colorado Boulder
Christopher Muhich (note taker)	Arizona State University
Jimmy Rojas	Stanford University

Session Summary

Session ID: S6-B

Title: Bringing it to Closure and Next Steps: STCH What's Missing

Facilitator: David Ginley

Summary of discussion

- Measuring or calculating efficiency is key
  - First Define it.
    - Material efficiency versus system efficiency
  - Then Measure it or Infer it
  - Then Standardize it
- Defining reactor and reactor conditions is important
- Need to develop a system level model to feed into Technology to Market, so we can establish bankability

Consensus and/or dissenting opinions

Need to enforce protocols and get groups to report things like yields.

- Get major research groups to adopt?
- There is pressure to perform given the US funding nature and as a result many groups choose to represent their yields and efficiencies ambiguously, or not at all.

Standardization is critical

Definitions need to be developed

Key Take-Aways

How do we compare efficiencies across technologies, e.g. STH (solar to hydrogen)

- Do not include optical losses?
- Costs can vary substantially depending on plant
- PV plus electrolysis uses efficiency of electolyzer separately form PV
- Better to compare cost than efficiency – e.g. $2 per kg

- How to we capitalize on international collaboration. In the US we are focused on materials and in Europe they ae focused on reactors. Can we develop materials for them?

Action Items

Recommendations for 3rd workshop

- Discuss reactors
- Discuss first law efficiency
- Discuss exergetic efficiency
- Tech-to-market discussion

Do we need a maximum reduction temperature?

- Above 1500 C radiation losses are too great; is there a minimum temperature.
- Other applications where temperature is higher, e.g. gas turbines
- Higher is better thermodynamically but more challenging in terms of material stability and reactor stability and radiation losses
- SETO does something similar with CSP

Need to define standard reaction environment – T, pO_2, etc.

Session Attendee List

Session ID: S6-B

Title: Bringing it to Closure and Next Steps: STCH What's Missing

Facilitator: David Ginley

Name	Affiliation
Ivan Ermanoski	Arizona State University
David Ginley (facilitator)	National Renewable Energy Laboratory
Wei Li	West Virginia University
Jie Pan	Michigan State University
Michael Sanders	Colorado School of Mines
Jonathan Scheffe (note taker)	University of Florida
Ellen Stechel	Arizona State University
Michael Toney	SLAC National Accelerator Laboratory