Benchmarking Advanced Water Splitting Technologies: Best Practices in Materials Characterization

Ellen B. Stechel
Arizona State University
Email:ellen.stechel@asu.edu

HydroGEN STCH Questionnaire
(Distributed May 2018)
Summary of Responses
25 Responses as of November 6, 2018

Background and motivation: We aim to develop standards for benchmarking performance, so comparisons between materials, concepts, and literature from different research groups can be made in future and to lower the barrier for new researchers entering the field. In addition to units, metrics, and system boundaries; cycle-specific standardized operating conditions, community-accepted benchmarking, and protocols developed through this exercise are strongly encouraged to include in publication.

A questionnaire was sent to EMN project leads, National Lab Capability Node Leads, academic and international experts in the Spring of 2018. The goal of this effort was to collect broad feedback across the water splitting community with a specific target of obtaining at least a 50% response rate from EMN Level 1 Node Leads and Project PI's.

As part of the questionnaire, respondents were asked if they wished to provide feedback to the proposed test framework. Access to the draft framework documents were provided to those leading breakout sessions at the Fall workshop.

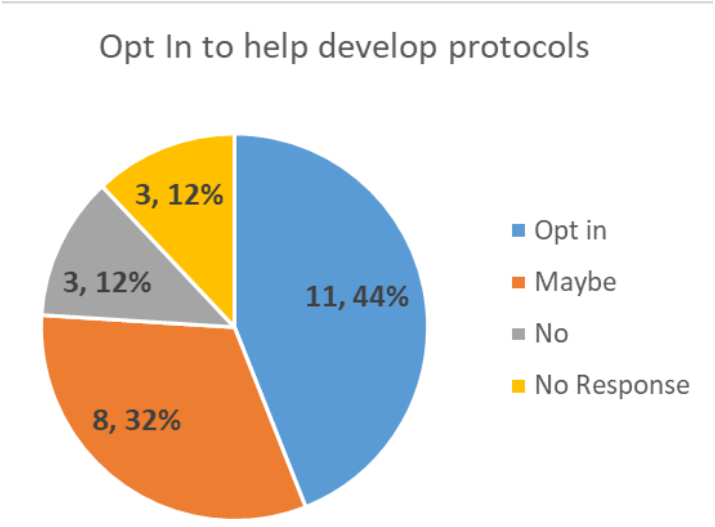
The original survey that was sent to participants can be found on the HydroGEN Data Hub and is publicly available at the link:

https://datahub.h2awsm.org/dataset/2018-stch-benchmarking-questionnaire/resource/53a60590-1eca-4fc0-9449-c38d3ceb332b

The following two tables illustrate the feedback received to date (November 2018) by type of institution and by specific institutions. See summary report below for detailed feedback.

Affiliation	Sent	Responses	% Response
EMN	18	12	67%
Domestic (Non EMN)	18	10	56%
International	11	3	27%
Total	47	25	53%

Institutions	Count
Arizona State University	4
Center for Energy, Energy, and Technology (CIEMAT)	1
Colorado School of Mines	2
ETH-Zurich	1
Georgia Institute of Technology	2
Greenway Energy	1
Massachusetts Institute of Technology	1
Northwestern University	1
Sandia National Laboratories	4
University of Colorado Boulder	3
University of Maine	1
National Renewable Energy Laboratory	3
CSIRO Energy, Australia	1
Grand Total	**25**



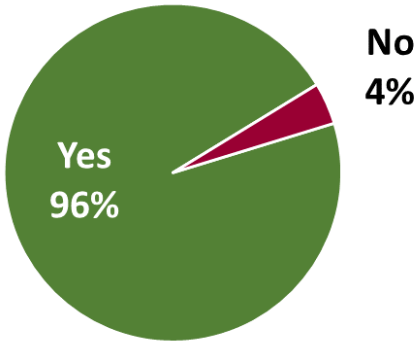
List of Acronyms:

atm	Atmosphere
BET	Brunauer, Emmett and Teller
DNI	Direct normal irradiation
EMN	Energy Materials Network
Pa	Pascal
PI	Principle Investigator
pO_2	Partial pressure of oxygen
ppm	Parts per million
RRT	Round Robin testing
sccm	Standard cubic centimeters per minute
SFR	Stagnation flow reactor
STCH	Solar thermochemical hydrogen
T	Temperature
TGA	Thermogravimetric Analyzer
WHSV	Weight hourly space velocity

Summary of STCH Questionnaire Responses

PART I. What standard conditions should we use to benchmark redox active metal oxides for solar thermochemical water splitting?

1) Do you think reporting the performance of a material given a specific thermodynamic operating cycle (or cycles) at fixed standardized conditions, in addition to "favored" testing conditions, would be useful?

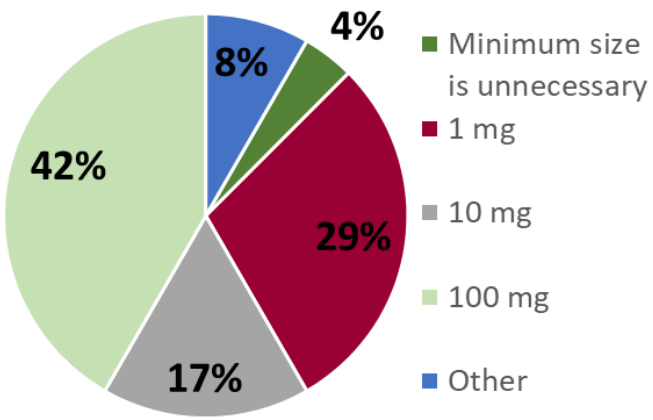


Responses indicated strong agreement that standard conditions would be useful.

Respondents indicated that we should consider optimizing the entire cycle + material, not only the material and that there is a need to standardize a way to compare two materials; while still allowing that cycle conditions that are optimal for one material will necessarily be different from that of another.

Respondents indicated that perhaps a better, more general, and useful alternative would be a characterization of the off-stoichiometry, δ, over a set range of values (of pO_2 and T). Especially if coupled with some standard for equilibration times (i.e. kinetics), particle size, etc.

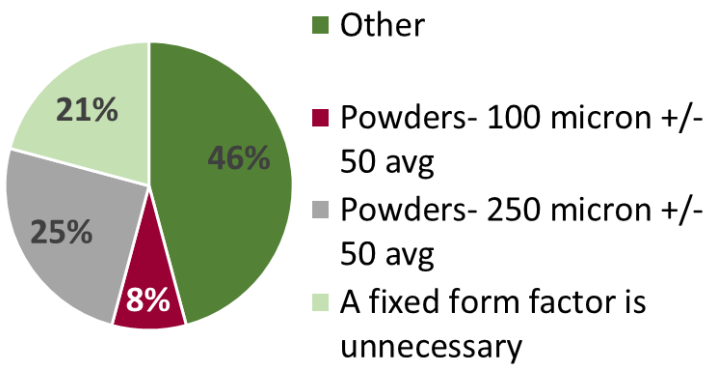
2) Should we choose a minimum material batch size (and permit multiple measurements and round robins), with fixed form factor (porosity, size)?



Respondents were largely in agreement that a minimum batch size was necessary, but the required size was split with the most responses favoring 100 mg batch size.

Respondents indicated that 100 mg is too small, but at a minimum, 100 mg would be needed to be supplied to each round robin participant. Some respondents suggested that there be an ensemble of material samples so that reproducibility and sample-to-sample variation can be assessed. Finally, some respondents suggested that such metrics could be identified and established within the STCH community prior to round robin testing.

3) Should we choose a fixed form factor (porosity, size)?



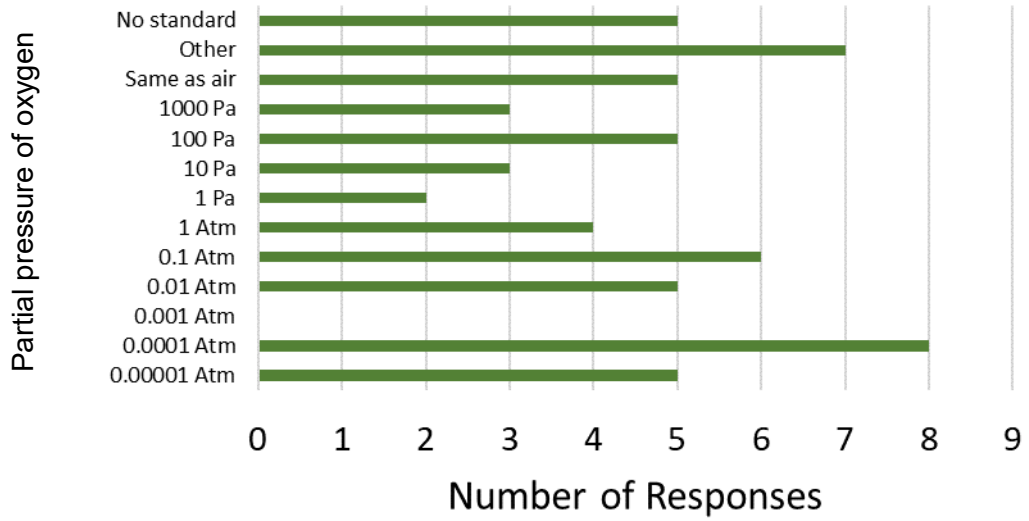
Most responses indicated that a fixed form factor is desired but did not agree on what that the form factor should be.

The options of, “Particles, dense, 1mm”, and “Particles, porous, 1mm, 50% porosity” were presented but neither were selected. It was pointed out that porous powders may have low bulk density but high H_2 production per mass, so no standard is appropriate. It was also pointed out that porosity may be difficult control and that porosity is not one of the important factors to control for. It was noted that fine powders are easy to produce and adequate for much of the testing. One respondent pointed out that porosity depends on the synthesis method and the calcination conditions. Therefore, it would be advantageous to use similar physicochemical properties (e.g. surface area, porosity, particle size). The respondent suggested that having the same physicochemical properties is not critical, but the method of synthesis and fabrication should be reported with the material performance. Some wondered if some materials were dependent on the porosity for their performance, for example, due to heat or mass transfer limitations, while others may not require porosity. As a result, the suggestion is to have flexibility on the form factor.

Respondents noted that while a fixed form factor would be useful, that it might be necessary to define a different form factor for various classes of analytical techniques. Several respondents commented on reporting properties such as surface area, porosity (when applicable), particle size distributions, and crystalline size. It was also suggested that multiple (2-3) options for the form factor might be better than just one and that for a head-to-head round robin, a common form factor would be preferable and two better yet, for example, a fine power (representative of the thermodynamics) and a dense material (1 mm particle) to gain insight into bulk utilization.

On multiple questions respondents expressed a concern that our standards should not result in giving a preference to a specific reactor design.

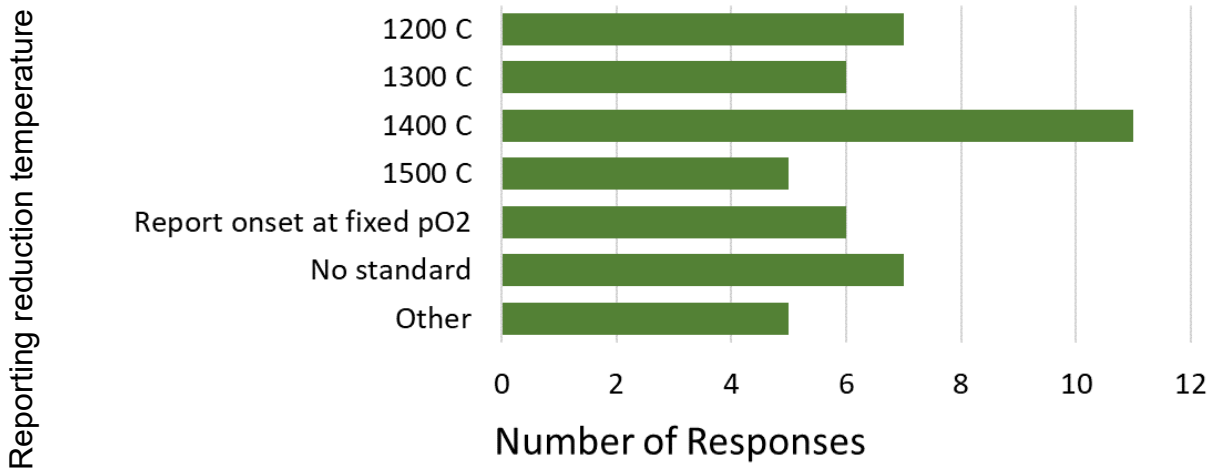
4) Should we choose one or several standards for operating partial pressures of oxygen in reduction? If so, what pO_2 values should ALWAYS be reported for benchmarking? (Choose all that apply)



Like Question 3, Question 4 got a lot of inputs suggesting that the difficulty and the richness of the opportunity are in determining standardized protocols.

Respondents noted that precise choice is not so important, but it is important that pO2 is determined and reported. Preferably not below say 10^{-4} atm, because kinetics can be affected at low pO_2, and hamper reproducibility. It is also important to have relatively low pO2 as too reducing of an environment may risk decomposing materials. Depending on the instrumentation being used, the lowest pO_2's may be hard to control. Also, a key factor often overlooked is the effect of ambient pressure. Many analytical instruments vent to atmosphere, meaning the actual pressure within the instrument is similar to ambient pressure. This can be vastly different between the mountain states and the coast, and can influence the results

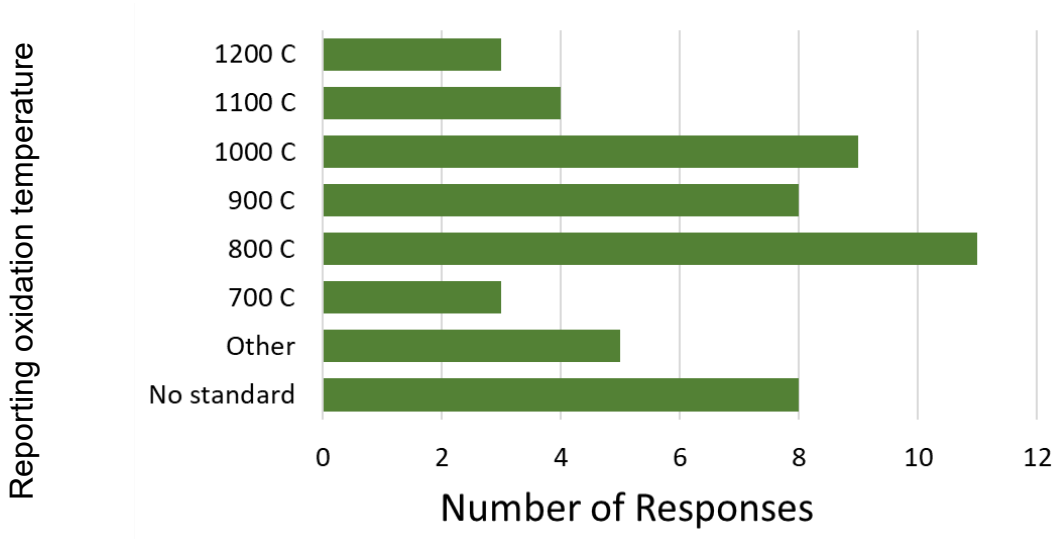
5) Should we choose one or several standards for reduction temperature? If so, what reduction temperature values should ALWAYS be reported for benchmarking? (Choose all that apply)



Most respondents agreed that a standard would be useful but did not agree on exactly what standard should be set. Some respondents suggested temperatures in between values.

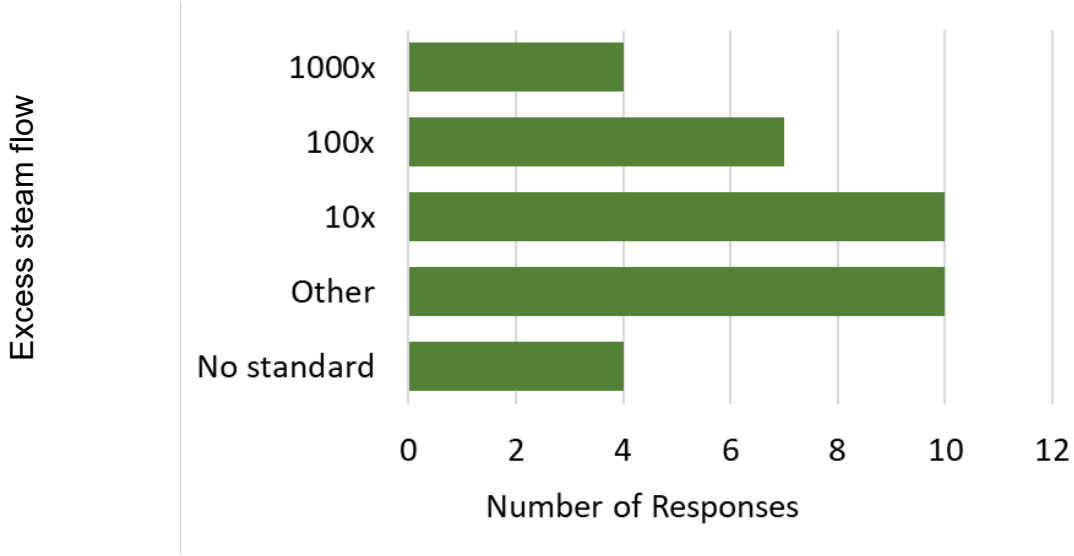
Respondents noted that no standard should be chosen as reduction temperature will be sample-dependent. Some may work better under different re- duction temperatures than those recommended. Temperature must be reported along with pO_2, but suitable temperatures may vary with material. We should be careful to not choose a temperature so high that it risks decomposing (or melting the material). For example, ceria will survive (and likely require) 1500°C, but some perovskites/ferrites would not survive; we do not want to risk eliminating a promising material because of that.

6) **Should we choose one or several standards for re-oxidation temperature? If so, what re-oxidation temperature values should ALWAYS be reported for benchmarking? (Choose all that apply)**



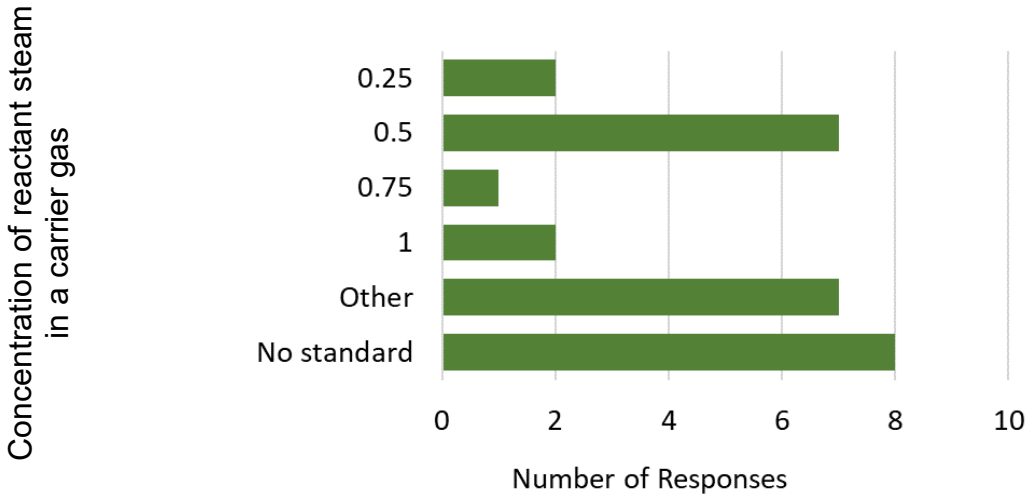
It was noted that suitable temperatures may vary with material. A standard re-oxidation temperature could make some materials look better or worse than they really are, depending on how close that standard is to their optimum re-oxidation temperature. As with reduction, it is better to provide a range of oxidation temperatures in short term cycles (e.g., three cycles) to find the best conditions for each material and be able to compare them under the maximum/minimum possible reduction/re-oxidation temperatures.

7) **Should we choose one or several standards for excess steam flow over stoichiometric reactant? If so, what excess values should ALWAYS be reported for benchmarking? (Choose all that apply)**



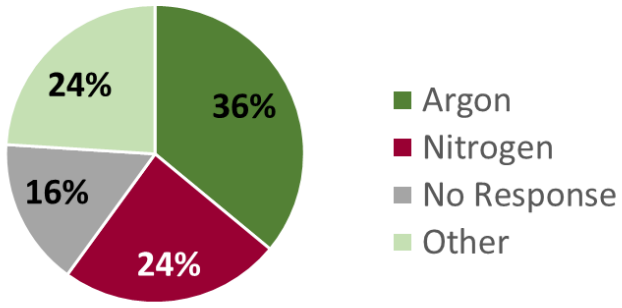
It was noted that excess steam flow is a bit hard to measure but ideally once would perform under different flow rates of steam. The minimum will be always the one that will give the best efficiency (from the articles of thermodynamic analysis the minimum flow of steam maximizes the efficiency). Probably, the key aspect here is to find the minimum flow of steam that provides fast enough kinetics (e.g. cycles of 15 minutes under isothermal conditions). It could be better to fix the time of reaction and find the minimum steam flow.

8) **Should we choose one or several standards for concentration of reactant steam in a carrier gas? If so, what values should ALWAYS be reported for benchmarking? (Choose all that apply)**



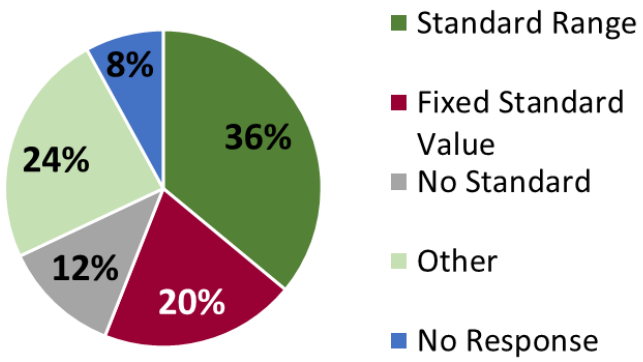
Some respondents were unsure about this question, suggesting discussion needed. Some felt that re-oxidation in the presence of a carrier gas should be optional.

9) Should we choose a standard carrier gas for re-oxidation? If so, what carrier gas?



Several respondents were unsure on whether we need to be concerned about this. Others expressed concerns about both N_2 and Ar. One respondent commented that this is mostly irrelevant for materials development and less so for reactor and costs or heat transfer.

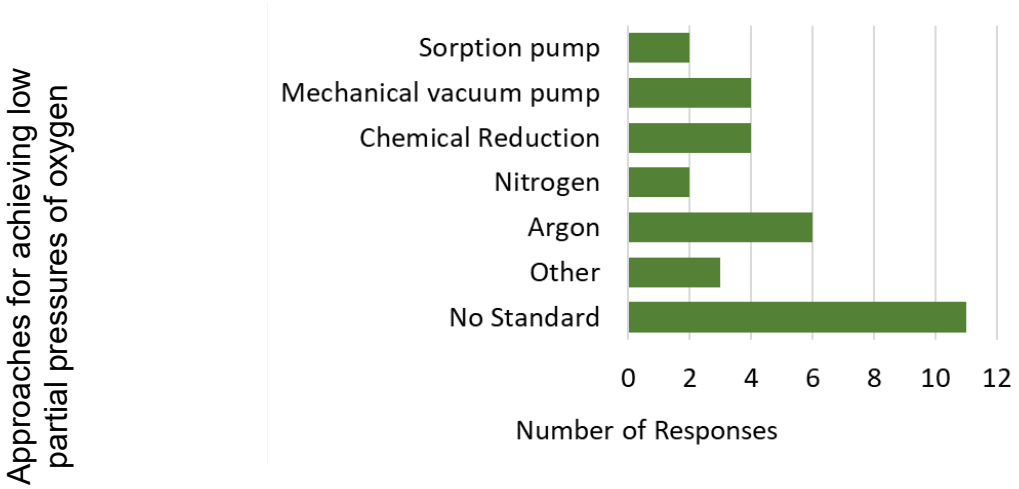
10) Should we standardize gas flow rates for kinetic measurements? If so, what kind of standards?



Respondents noted that we will need much more than a gas flow rate standard. We must decide on reactor form factor, residence time, method of detection, etc., just like in electrochemistry to guarantee transport effects (heat and mass) are not biasing the measurement. Different reactor types may have different dependencies on flow rate. It was suggested that it may be worthwhile to have a standard experimental apparatus (e.g., Sandia's SFR) for kinetics.

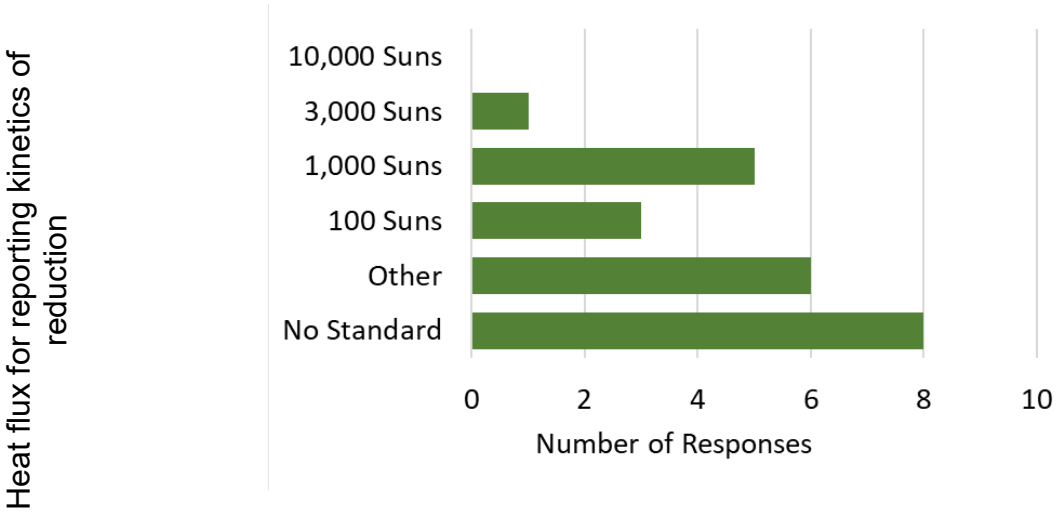
PART 2. What standard method should we use to achieve low partial pressure of oxygen when benchmarking redox active metal oxides for solar thermochemical water splitting?

11) Should we choose one or several standard approaches for achieving low partial pressures of oxygen? (Choose all that apply)



Respondents suggested some additional methods including a high-temperature O_2 transport membrane. It was noted that all approaches are viable and resulting data can be used to determine the most cost-effective method.

12) Should we choose a standard heat flux for reporting kinetics of reduction? (Choose all that apply)



Respondents felt that this is highly system dependent but there should be a clear effort to separate the effects of thermal limitations from intrinsic kinetics.

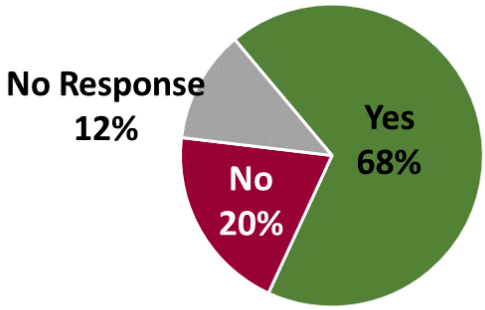
PART 3. What standard number of cycles should we use to report cyclability?

13) Should we choose a standard number of cycles and should we always ignore the first one, two or three cycles? (Choose all that apply)

Standard number of cycles	Responses	Weight (%)
Other	3	12%
No Response	2	8%
No Standard	1	4%
Ignore 1st One	9	36%
Ignore 1st Three	9	36%
Ignore 1st Two	2	8%
100 Cycles	10	40%
10 Cycles	9	36%
1000 Cycles	4	16%
25 Cycles	1	4%
200 Cycles	1	4%
500 Cycles	0	0%

Respondents noted that 10 is probably not enough, but 100 may be onerous for some labs. Where Initial durability cycling should be somewhere between 50-100, and long-term durability should jump up to at least 1000.

14) Should we have standards and benchmarks for computational thermodynamics?



Overall respondents felt the need for standards and benchmarks. Three of the five “no’s” seemed to be respondents who either did not feel qualified or did not understand the question or did not know of a way to standardize. One “no” indicated No standards but report the approach. One did not clarify.

PART 4. What metrics should we always report?

15) What metrics should we always report? (Choose all that apply)

Possible answers	# Responses	% Responses
Total hydrogen per mole of oxide (suitably normalized, such as per metal cation, or per oxygen in the fully oxidized state)	17	8.5%
Solar to hydrogen (with fixed optical efficiency and fixed operating cycle(s))	14	56.0%
Other	2	8.0%
No specific ones	1	4.0%

Additional suggestions for metrics included:

- Solar to H_2 and H_2 production per mass and per volume of active material.
- Total hydrogen per mol/gram of metal should be reported for materials research.
- H_2O conversion (% of H_2O converted into H_2, integrated over the oxidation step).

PART 5. Further Input?

16) Comments and/or questions that we missed regarding standards and benchmarking conditions

There should perhaps be experimental requirements for some of the tests, e.g. it is not permissible to remove a sample mid-test and re-grind it up. There should also be some reporting of characterization (and changes) before and after testing, e.g., particle size, sintering, morphology, and/or crystal structure (including phase changes, impurities, and phase segregation).

Each experiment or computational study should assess and characterize all sources of un- certainty and propagate them through the analysis to the extent feasible.

I understand that for some of the STCH materials is somehow premature, but I believe that a standardized way to calculate the installed costs, even if very preliminary, should be discussed, along with a standardized definition of the efficiency (solar to H_2).