HydroGEN
Advanced Water Splitting Materials

Advanced Water-Splitting Technology Pathways Benchmarking & Protocols Workshop

Breakout Session Summaries
Photoelectrochemical (PEC) Water Splitting

October 29 - 30, 2019

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Executive Summary

For PEC, there was a lot of discussion on the technology roadmap in terms of its timeline, connection to protocols and the need for separating roadmaps for established materials vs. emerging materials. As a result, a PEC Roadmap team was established to meet regularly to further develop the roadmap. There was general agreement that device stability and scalability are the bottleneck for the technology, and protocols related to these areas should be in the priority list. In addition, scaling studies should also inform/guide materials processing pathways & component performance criteria. It was recognized that many PEC protocols relate to basic materials properties were well established in the community and can be implemented into the SOP format for easy use. Protocols relate to real world conditions, such as varying illumination, temperature and low concentrated sunlight conditions were identified as gaps. It was recommended to leverage and bridge with LTE specifically on membrane and catalyst related testing protocols, but also recognized that membrane and catalyst stability testing should include illumination and diurnal cycles for PEC. There was also general agreement that advanced spatially resolved techniques, such as pH imaging, are important and there is opportunities to leverage beam-line facilities for new techniques and advanced measurements.

PEC Breakout Sessions

Breakout Session #	Session ID	Technology	Topic	Lead
1	P1-A	PEC	PEC Technology Roadmap Review & Discussion - Materials	Roel van de Krol
1	P1-B	PEC	PEC Technology Roadmap Review & Discussion - Components and Devices	Frances Houle
2	P2-A	PEC	PEC Light absober and Protective Layer Requirements & Tests	Nicolas Gaillard
2	P2-B	PEC	PEC Catalyst and Electrolyte Requirements & Tests	Adam Weber
4	P4-A	PEC	PEC Photoelectrodes: Spatially Revolved Energetics and Transports	Shannon Boettcher
4	P4-B	PEC	PEC Photoelectrodes: Stability and Accelerated Stress Tests	Tom Jaramillo
5	P5-A	PEC	PEC New Materials Screening, Theory and Operando Characterization	Francesaca Toma
5	P5-B	PEC	PEC Device Testing Protocols, Standard Formats and Scale-up	James Young
6	P6-A	PEC	Wrap-up/Action Item Assignment: PEC Materials	Shu Hu
6	P6-B	PEC	Wrap-up/Action Item Assignment: PEC Components and Devices	Shane Ardo

Session Summary

Session ID: P-1A

Title: PEC Technology Roadmap - Materials

Summary

- PEC with concentrated light could be interesting (but only up to ~10x)
- PEC membrane optimization needed
- Gaps in existing protocols & efforts for e.g. varying illumination conditions and electrochem. compressed H_2

Consensus/Dissenting Opinions

- Development of new absorbers with high-throughput methods is challenging; may be more useful to develop passivation/ protection layers with HT techniques
- Should roadmap be general for entire community or aligned to DOE target of $2/kgH2?

Key Take-Aways

- Roadmap should distinguish between legacy materials and new absorbers (different priorities & timelines)
- Identify suitable funding pathway for long-term activities (e.g. work on new absorber materials)

Action Items

- Make decision tree for new absorbers
- Define well-defined sets of operating conditions for different device concepts/classes
- Identify ideal/relevant market for PEC hydrogen (e.g. compatibility with sea water, impurities, etc)

Session Attendee List

Session ID: P-1A

Title: PEC Technology Roadmap - Materials

Name	Affiliation
Shane Ardo	UC Irvine
Jason Cooper	LBNL
Nicolas Gaillard	Univ. of Hawaii
Shu Hu	Yale Univ.
Shinjae Wang	Rutgers Univ.
Dave Palm	Stanford Univ.
Chris Topping	Tetramer Technologies
CX Xiang	Caltech
Tadashi Ogitsu	LLNL
Roel van de Krol	Helmholtz-Zentrum Berlin

Session Summary

Session ID: P-1B

Title: TRRD - Components & Devices

Summary of discussion

- Roadmaps should be more specific for each component/device (e.g. vapor fed, optical concentration)
- Protocols should be expanded to encompass broader scope of component/device options
- Consider defining roadmaps to also achieve durability and efficiency targets

Consensus

- Timelines for scale-up are unrealistic
- There are many opportunities to expand on the list of protocols
- Focused connections between roadmaps to protocols will require that components/devices be broken down into subsets as there is no good one-size-fits-all option

Key Take-Aways

- Need for separate roadmaps and protocols (e.g. established materials + protection vs. new oxide materials)
- Roadmap items require small edits (e.g. missing demonstration system beyond cost), but protocols have major gaps in breadth **(We have a huge list of items!)**

Action Items

- Redefine roadmaps for specific cases
- Add many protocols to current list and identify for which component/device each should be used, starting with PEC book by Chen, Dinh, and Miller (ISBN: 978-1-4614-8298-7)
- Write!

Session Attendee List

Session ID: P-1B

Title: TRRD - Components & Devices

Name	Affiliation
Shane Ardo	UC Irvine
Micha Ben-Naim	Stanford
Frances Houle	LBNL
Zetian Mi	Univ. of Michigan
Francesca Toma	LBNL
James Vickers	DOE
Adam Weber	LBNL
James Young	NREL
Guosong Zeng	LBNL

Session Summary

Session ID: P-2A

Title: PEC Light absober and Protective Layer Requirements & Tests

Summary

- Focused primarily on materials (not enough time to address components and devices)
- Updated excel spreadsheet with comments
- Consider updating SOP to real life conditions (e.g. catalytic activity at 10X, 100 mA/cm^2)

- **Consensus**: Methods to characterize key properties of solar absorbers (e.g., carrier life time, diffusion length, mobility, electronic/structural stability) are missing.
- **Dissenting opinions**: solid-state structures (i.e. p/n junctions) are not necessary the best/easiest approach to characterize materials (forming contacts can be challenging)

Key take-aways

- Additional information could be extracting from existing methods (e.g., refractive index from UV-vis)
- Existing protocols methods should be updated with state of the art methods (photothermal deflection spectroscopy)
- Key protocols, such as stability testing, are missing.

Action items

- SOP Draft on solid-state characterization
- Further review existing protocols:
  - PEC-P-1 Photoelectrode fabrication and area Rev2_Oct24
  - PEC-P-2 Light Sources Calibration Rev2_Oct24
  - PEC-P-3 Tandem IPCE Rev2_Oct24
  - PEC-P-7 Band Energetics Rev2_Oct24
  - PEC-P-9 On Sun Testing Rev2_Oct24
- Update/format old protocols with new SOP template

Session Attendee List

Session ID: P-2A

Title: PEC Light absober and Protective Layer Requirements & Tests

Name	Affiliation
Jason Cooper	LBNL
Micha Ben-Naim	Stanford
Shane Ardo	UCI
Zetian Mi	Univ. of Michigan
Francesca Toma	LBNL
James Young	LBNL
Hu Shu	Yale
James Young	NREL
Shinjae Hwang	Rugters
Dave Palm	Stanford
Roel Van der Krol	Helmholtz-Berlin
Nicolas Gaillard	Hawaii Natural Energy Institute

Session Summary

Session ID: P-2B

Title: PEC Catalyst and Electrolyte Requirements & Tests

Summary of discussion

Discussed how PEC test requirements differ from LTE protocols

Examined

- Membrane Conductivity Protocol
- Membrane Permeability Protocol

Catalyst Protocol

Needed Protocols

Consensus and/or dissenting opinions

Need understanding of circumstances that materials/device will see: electrolyte conditions/ temperatures 60-80 (Not RT) / transparency of membrane.

For membrane performance permeability is sufficient but solubility and diffusivity could also be measured

Key Take-Aways

Membrane stability tests must include illumination (solar spectrum)

Catalyst tests must be diurnal, difficult to accelerate as we do not fully understand low-activation energy processes that fast sweep ignores.

Can borrow LTE protocols but need to account for light and electrolyte including other ions/electrolytes

Action Items

Protocol for stability test should include membrane characterization.

- Permeability
- Physical characterization
- Chemical characterization possibly

Set standard catalyst deposition techniques for testing – concerns about binders.

Test cells for >1000h tests must be improved beyond simple H-cell (cell itself can have trouble due to counter electrode, pastes, etc).

Session Attendee List

Session ID: P-2B

Title: PEC Catalyst and Electrolyte Requirements & Tests

Name	Affiliation
James Vickers	DOE
CX Xiang	Caltech
Guosong Zeng	LBNL
Srinivas Vanka	Umich
Frances Houle	LBNL
Huyen Dinh	NREL
Chris Topping	Tetramer
Walter Drisdell	LBNL
Tadashi Ositsu	LLNL
Adam Weber	LBNL

Session Summary

Session ID:P-4A

Title: PEC Photoelectrodes: Spatially Revolved Energetics and Transports

- **Summary of discussion**
  - Want to measure local corrosion which is materials dependent – local excitation? Local "siphon"
  - Want to measure local pH, which might allow for identifying local distributions of activity
    - X-ray techniques, optical fluorescence (confocal of 2-photon), scanning probe, local conductance
  - Want to measure local product distributions
  - Want to measure potential (electrostatic, electrochemical)
  - Photocarrier distribution (*n, p, r, g*) - spectroscopies?
  - Restructuring/structure
    - FIB tomography
    - Operando AFM surface imaging

- **Consensus and/or dissenting opinions**
  - Most proposed techniques and methods are difficult, requiring specialized tools and expertise.
  - Simple lab-scale techniques, like EC Raman, would be useful.

- **Key Take-Aways**
  - Techniques not readily accessible on routine basis, but creates opportunities to develop unique node capability at labs
  - Opportunity to leverage and facilitate ALS usage
  - Local properties are important, but specific approaches are highly materials dependent, complicating analysis
  - New technique development could be expensive, need development funding

- **Action Items**
  - Match existing capabilities to needs (exploration phase)
  - 2 photon pH mapping (LBNL?), explore beamline capabilities for mapping, confocal (Boettcher?)
  - CX, Shannon, Francesca write perspective on spatially resolved measurements?

- **Prioritization**
  - Local pH measurement

Session Attendee List

Session ID:P-4A
Title: PEC Photoelectrodes: Spatially Revolved Energetics and Transports

Name	Affiliation
Dave Palm	Stanford U
Gary Moore	ASU
Adam Weber	LBNL
Tadashi Orirsu	LLNL
Srinivas Vanka	U. Michigan
Guosong Zeng	LBNL
Shinjae Hwang	Rutgers
CX Xiang	Caltech
Shannon Boettcher	U. Oregon
Siwei Liang	LLNL
Jason Cooper	LBNL

Session Summary

Session ID: P-4B

Title: PEC Photoelectrodes: Stability and Accelerated Stress Tests

Summary of discussion

- What do we want in a PEC durability test?
- Possible measurable quantities
  - J, V, H_2/O_2 rate, material spectroscopy, material dissolution, visual inspection, charge passed
- Desired measurement conditions
  - 2 vs. 3 electrode
  - Illumination – constant, cycling,
- Measurement criteria – How stable is stable?
- Goal of protocol – R&D diagnostic or "gold-standard"?

Consensus/Dissenting Opinions

- There is a need for a standard, rigorous test for unassisted water-splitting.
- Goal of measurement: H_2 produced (mL) and charge passed (C), both in absolute terms & per surface area
- Details of illumination cycle

Key Takeaways

- The protocol should be a "gold standard" for unassisted water-splitting for entire PEC device
- Ideally this test would help the community move technology forward
- Conditions should be kept realistic/rigorous - unassisted water-splitting, illumination cycling, realistic gas atmosphere, measure H_2 and O_2.

Action Items

- Details still to decide – illumination cycle, electrolyte
- Draft a protocol incorporating the parameters discussed here.
- Discuss among session members

Session Attendee List

Session ID: P-4B

Title: PEC Photoelectrodes: Stability and Accelerated Stress Tests

Name	Affiliation
Micha Ben-Naim	Stanford
Roel van de Krol	HZB
James Young	NREL
Chris Topping	Tetramer
Frances Houle	LBNL
Walter Drisdell	LBNL
Shu Hu	Yale
Nicolas Gaillard	Hawaii
Zetian Mi	Michigan
Josh Spugeon	Louisville
Shane Ardo	UC Irvine
Tom Jaramillo	Stanford

Session Summary

Session ID: P-5A

Title: PEC Materials, Theory and Operando Characterization

Discussion summary

- What is the technology target?
- Do we need new materials?
- What do we need from theory?
- What do we need from operando characterization?

Consensus and/or dissenting opinions

- New materials useful but not practical on this timescale – focus on existing materials
- DFT less useful than larger-scale modeling
- Debate on feasibility of low-cost III-Vs
- Basic science vs. optimization – operando study of degradation mechanisms to feed into scale-up

Key Take-Aways

- Aim at both planar and particle cell technologies
- Use existing materials, Si and perovskites worth consideration
- Basic science on degradation needed

Action Items

- Work on Si device architectures
- Reach consensus on electrolyte composition
- Generate SOP for operando studies
- Strategize operando studies of degradation, , couple to supernode on III-V thin film cells

Session Attendee List

Session ID: P-5A

Title: PEC Materials, Theory and Operando Characterization

Name	Affiliation
Francesca Toma	LBNL
Walter Drisdell	LBNL
CX Xiang	Caltech
Jason Cooper	LBNL
Shu Hu	Yale
Siwei Liang	LLNL
Huyen Dinh	DOE
Shannon Boettcher	U. of Oregon
Shane Ardo	UCI

Session Summary

Session ID: P-5B

Title: PEC Device Testing Protocols, Standard Formats and Scale-up

Summary of discussion

- Each attendee briefly described the PEC cells used in their laboratory
- Motivations for scaling studies were discussed in light of not having true PEC absorbers stable enough to be worth demonstrating at scale
- Protocol priorities were discussed
- Research roles were discussed, e.g. applied research may focus on durability and scaling while basic research may focus on understanding newer absorbers and catalysts

Consensus and/or dissenting opinions

- Scaling studies should inform/guide materials processing pathways & component performance criteria
- Where applicable, component-level protocol should be based on LTE protocol or PV protocol, as a starting point
- "Integrated" PV-electrolysis may be used as an acceptable model system for evaluating PEC scaling
- Open questions: What defines PEC vs PV-electrolysis? Are definitions needed? Can the distinction reflect a techno-economic promise of PEC vs PV-electrolysis?

Key Takeaways

- All attendees use custom reactors/cells of either glass and/or polymer, and still "epoxying" electrodes
- Little to no standardization of cell/reactor design
- Scaling up will present challenges in terms of electrolyte conductivities, but also in materials synthesis translatability
- Impurities & cleaning of chassis materials may be a significant challenge to demonstrations
- Progress in PEC durability will also help advance and make scaling studies worthwhile

Action items

- Several component and device protocol already have first drafts
- Protocol likely not beneficial for the three "spatial resolved", more fundamental and specialized techniques
- Device stability/durability protocol development should be prioritized and based-on or cross-referenced with the Materials durability protocol

Session Attendee List

Session ID: P-5B

Title: PEC Device Testing Protocols, Standard Formats and Scale-up

Name	Affiliation
James Young	NREL
Dave Palm	Stanford
Srinivas Vanka	Univ. of Michigan
Josh Spurgeon	Louisvile
Chris Topping	Tetramer
Frances Houle	LBNL
Shinjae Hwang	Rutgers
Micha Ben-Naim	Stanford
Nico Gaillard	U. of Hawaii
Roel Van de Krol	Helmholtz-Berlin
Tadashi Ogitsu	LLNL

Session Summary

Session ID: P-6A
Title: Wrap-up/Action Item Assignment: PEC Materials

- Add and populate protocols identified from the workshop.
- Leverage protocols from LTE and see how we can integrate/modify them to use in PEC.

Individual action items:
Adam Weber: Review membrane related protocols and bridge LTE protocols and PEC protocols in membrane benchmarking.
Tadashi Ogitsu: Perspective pieces on benchmarking PEC OER theory.
Walter Drisdell: Interface with super nodes on corrosion in the scale-up efforts. Draft a table for requirements and things you can get out from in situ X-ray techniques in current nodes.
Siwei Liang: Add more details onto 3D printing nodes at LLNL
Dave Palm/Tom Jaramillo: Draft protocols for stability testing for individual components, more specifically for photoelectrodes.
Jason Cooper: Protocol for bandgap measurements for light absorbers.
Shu Hu: PEC roadmap team, legacy materials vs. needs for new photoabsorbers.
Roel van de Krol: Roadmap team, protocol for minority carrier diffusion length, connect with EU benchmarking activities.
CX Xiang: pH imaging/sensing perspective (Shannon, Francesca, Harry), roadmap team.

What can be improved for the next HydroGEN meeting and other discussions:
1) way to inform or get information from other technology.
2) wrap up session can be together if the group is small.
3) where you would host the protocols.
4) standard materials and based line measurements using super nodes.

Session Attendee List

Session ID: P-6A
Title: Wrap-up/Action Item Assignment: PEC Materials

Name	Affiliation
CX Xiang	Caltech
Tadashi Ogitsu	LLNL
Walter Drisdell	LBNL
Siwei Liang	LLNL
Dave Palm	Stanford
Jason Cooper	LBNL
Shu Hu	Yale
Roel van de Krol	Helmholtz Berlin
Adam Weber	LBNL

Session Summary

Session ID: P6-B
Title: Wrap-up/Action Item Assignment: PEC Components and Devices

Action Items

- Form a Team from attendees led by session chair (meet monthly(?) via Zoom (+ Roel or Sophia?))
- Enumerate challenges / categories (living document) with cost targets in mind
- Update/write previous PEC white papers / EES pubs to indicate state-of-the-art and identify next step directions (https://www.energy.gov/sites/prod/files/2014/03/f12/pec_white_papers.pdf; http://pubs.rsc.org/en/journals/articlecollectionlanding?sercode=ee&themeid=837e7e9a-52c0-407d-9105-ed82fab8feda)
- Identify road map(s): Longer-term European road maps with steps along the way (e.g. PV + electrolysis); do all technologies need to be on the same timeline?
- Redefine near-term roadmaps for specific cases: start by merging MYRD&D (2015; https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22; https://www.energy.gov/sites/prod/files/2015/06/f23/fcto_myrdd_production.pdf) with "current" roadmap, which will prioritize protocols from devices to components to materials (Shu Hu's section) (e.g. for semiconductors (http://www.itrs2.net/, e.g. 2009)
- Cross-cutting PEC work to connect efforts to tackle a cross-project challenge and possibly cross-cutting across H2@Scale projects in general (complementary to super nodes)
- Occasional meetings for progress/overview (AMR or Tech Team with attendees by PIs with funded PEC projects and node leaders to help execute roadmap)
- Roadmap as way to collaborate (not to define G/NG / milestone decisions)
- Acknowledge the need for targeted science (super nodes working on scale-up; single PI science)

Session Attendee List

Session ID: P6-B
Title: Wrap-up/Action Item Assignment: PEC Components and Devices

Name	Affiliation
Shane Ardo	UC Irvine
Micha Ben-Naim	Stanford
Nico Galliard	Hawaii
Frances Houle	LBNL
Francesca Toma	LBNL
James Young	NREL
Guosong Zeng	LBNL