**PURPOSE**

Photoelectrochemical (PEC) hydrogen production using sunlight to directly split water is one of the paramount enabling technologies for a future where hydrogen is widely deployed as an energy carrier. The “traditional” semiconductor-based PEC material systems studied to date, in particular the simple metal oxides such as TiO₂, WO₃ and Fe₂O₃, however, have been unable to meet all the performance, durability, and cost requirements for practical hydrogen production. Technology-enabling breakthroughs are needed in the development of new, advanced materials systems. Toward this end, the IEA Hydrogen Implementation Agreement Annex-26, working in close conjunction with the U.S. Department of Energy’s “Working Group on PEC Hydrogen Production” is bringing together international experts in analysis, theory, synthesis and characterization from the academic, industry, and national laboratory research sectors across the world, with exciting and important results on several fronts.

**FRAMEWORK SUMMARY**

The specific technical goal of this Annex is the research and development of new semiconductor materials for stable and efficient PEC hydrogen production systems. In order to meet this goal Annex-26 has formulated a comprehensive “Task” structure, listed below, to serve as the central organizational framework for Annex activities. A more detailed breakdown of the key sub-tasks is illustrated in Figure 1. Annex-26 relies heavily on individual Tasks and Task Leaders to coordinate collaborative efforts in international PEC R&D and facilitate the PEC materials breakthrough process.

- Task A: PEC Materials R&D Administration
- Task M: PEC Focus Materials
- Task S: PEC Standardized Materials Testing/Screening
- Task C: PEC Materials/Interface Characterizations
- Task T: PEC Materials Theory
- Task D: New PEC Materials Discovery
- Task E: Techno-Economics Analyses

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<th>TASK 26</th>
<th>ADVANCED MATERIALS FOR WATERPHOTOLYSIS</th>
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**VITAL STATISTICS**
ACTIVITIES AND RESULTS IN 2010

New laboratory-scale performance benchmark of STH conversion efficiency with a GaAs/GaInP2 photoelectrode system (Figure 2). Demonstrated the potential to exceed 16% STH in outdoor certification tests, achieved through component and device optimization. (NREL)

Initiation of “III-V Surface Validation Study” to develop and validate new dynamic models of hydrogen production and corrosion at III-V semiconductors with aqueous solutions. (NREL)

UV/Soft X-ray/electron spectroscopic tools for evaluating optoelectronic and chemical properties of PEC materials’ surfaces and near-surfaces are vital to the validation of dynamic interface models. To date, excellent agreement has been observed in XES spectra between theory and experiment for the three compounds InP, GaP, GaInP2 (Figure 3). Although further refinement is necessary, this validation of the theoretical models will allow derivation of the exact position of valence band maximum by comparing experiment and theory. (UNLV)

Development of thin-film copper chalcopyrite material systems for lower-cost alternatives to the III-V systems for efficient PEC water splitting (Figure 4), which provides the opportunity for bandgap tailoring based on composition. (UHawaii)

Development of new MoS2 nano-particle catalysts and concurrent development of novel macro-structures for integration into practical photovoltaic water splitting devices (Figure 5); including macroporous scaffold consisting of a transparent conducting oxide (TCO) upon which the MoS2 nanoparticles can be vertically integrated for support, confinement and electronic contact. (Stanford)

Specific material systems (SrTiO3:Rh combined with BiVO4 in the presence of an Fe3+/Fe2+ redox couple, and RuO2-TaON and Pt-TaON mixture with I3-/I- redox couple) have demonstrated spontaneous water-splitting under visible light but STH efficiencies remain extremely low. The search for effective HER and OER photocatalyst materials for Z-scheme systems is ongoing. (Japan)

Integrated PEC water-splitting devices have been successfully demonstrated based on a thin film WO3 water oxidation cell driven by two underlying series-connected dye-sensitized solar cells. (TUS, Japan)

A novel approach to PEC interface enhancement has been demonstrated via surface treatments of tungsten oxide particles. Significant enhancement in the water oxidation reaction at enhanced surface sites in the WO3 particles have been observed, offering performance improvements in PEC and hybrid PEC systems for hydrogen production (AIST, Japan).

Impressive progress has been made in the investigation of bi-layered metal oxide thin film systems for PEC water splitting, which can provide solutions for corrosion and charge extraction issues. (POSTECH, South Korea)

Achieved a new benchmark level in the performance of low-cost nanostructured iron oxide materials. The cost and durability of this earth-abundant material continues to
warrant further research and development. (NanoPEC, EU)

Work is being done to increase the performance of hematite photoelectrodes for absorbing light in water-splitting, including pretreatment with ultrathin layers of treaethoxysilicate. (NanoPEC, EU)

Work continues on the refinement of the “Standardized Methodologies for PEC Measurements and Reporting” effort and on the development and deployment of the “International PEC Sharepoint Site.”

Figure 2: Enhanced PEC solar water-splitting performance in NREL GaAs/GaInP2 resulting from recent device optimizations.

Figure 3: X-ray Emission Spectroscopic (XES) validation of the DOE PEC Working Group’s Surface Validation Study’s theoretical model of the III-V interface developed at Lawrence Livermore National Laboratory, showing excellent agreement with experimental result obtained at UNLV.
Figure 4: Device configuration and performance curve of multi-junction hybrid photoelectrode based on copper gallium diselenide demonstrating 4.3% STH solar water splitting efficiency.

Figure 5: Innovative approach to the development of PEC photoelectrodes using nano-catalysts loaded onto electron-conducting meso-structured scaffold, showing a candidate Transparent Conducting Oxide (TCO) scaffold material based on indium tin oxide nano-rod.
FUTURE WORK

ACTIVITIES AND/OR TARGETS FOR 2011

Primary efforts in the next six months will be toward the completion of the Annex-26 Final Report. In addition, further work is planned in continued construction of the SharePoint Site work spaces for annex participants, in integration of new participants involved with the DOE Solar Fuels Innovation Hub, and in vetting and publishing of the recent technical advances. A proposal to potentially extend the Annex-26 for the purposes of completing documentation and information management on the new SharePoint site will be drafted. Topics for a potential follow-on Annex, for example focusing on PEC interfaces or PEC multi-junction devices, will be drafted.

ACTIVITIES AND/OR TARGETS BEYOND 2011 (VERY BRIEFLY)

A proposal to potentially extend the Annex-26 for the purposes of completing documentation and information management on the new SharePoint site will be drafted, and is expected to be ready for presentation at the Fall 2011 Executive Committee meeting. Topics for a potential follow-on Annex, for example focusing on PEC interfaces or PEC multi-junction devices, will be drafted by Annex-26 Experts and presented to the Executive Committee when ready.

R&D Challenges in the area of PEC hydrogen production materials and systems are being met through international collaborative efforts. New crystalline (“first generation”), thin film (“second generation”) and nano-particle (“third generation”) materials are emerging with potential for efficient utilization of sunlight for water splitting; however significant research is still needed in the understanding and optimization of PEC interfaces into practical hydrogen production devices.

REFERENCES

SELECTED KEY PUBLICATIONS


• JMR Focus Issue on Photocatalysis for Energy and Environmental Sustainability, Journal of Materials Research, 2010, 25(1)


• The U.S. DOE’s Annual Merit Review and Peer Evaluation:  http://www.hydrogen.energy.gov/annual_review.html