

IV.E.5 Hydrogen Reactor Development and Design for Photofermentation and Photolytic Processes

Daniel M. Blake (Primary Contact) and Cheryl Kennedy

National Renewable Energy Laboratory

1617 Cole Blvd., MS 3322

Golden, CO 80401

Phone: (303) 384-7701; Fax: (303) 384-6363; E-mail: dan_blake@nrel.gov

DOE Technology Development Manager: Roxanne Garland

Phone: (202) 586-7260; Fax: (202) 586-9811; E-mail: Roxanne.Garland@ee.doe.gov

Subcontractor:

Nuclear Filter Technology, Inc., Golden, CO

Start Date: November 2004

Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop advanced renewable photolytic hydrogen generation technologies.
 - By 2015, demonstrate engineering-scale biological system to produce molecular hydrogen (H₂) at a plant-gate cost of \$10/kg (kilogram) projected to commercial scale.
 - By 2015, demonstrate direct photoelectrochemical (PEC) water splitting at a plant-gate H₂ production cost of \$5/kg (projected to commercial scale).
 - The long-term objective is hydrogen cost competitive with gasoline.
- Assist DOE with the identification of solar reactor concepts and related materials needs in support of photobiological and PEC H₂ production.
- Reactor concepts
 - Review literature; work with program scientists and engineers, and industry.
- Materials needs
 - Determine time-zero properties (solar transmittance, molecular oxygen [O₂] and H₂ permeability, tensile strength, and cost) of polymers—polycarbonate (PC), acrylics, polyethylene terephthalate (PET), and fluoropolymers.
 - Conduct accelerated and outdoor weathering tests for polymers and other materials of construction.
 - Identify and begin to test strategies for reducing hydrogen permeability, if necessary.

Technical Barriers

This project addresses the following technical barriers from the Biological Hydrogen Production (3.1.4.2.5) and the Photoelectrochemical Hydrogen Production (3.1.4.2.6) sections of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- AA. Systems Engineering
- AG. Systems Engineering
- AT. Systems Engineering
- AB. Diurnal Operation Limitations
- AH. Diurnal Operation Limitation

Technical Targets

This project is identifying materials of construction and reactor design concepts that can be used to implement photobiological and PEC production of hydrogen from water using sunlight as the energy source. The ultimate reactor design and materials of construction will have an impact on the system cost and performance for these solar water-splitting processes. As a result, the cost targets for these technologies are major drivers for this project:

- Photoelectrochemical hydrogen production targets are \$22/kg in 2010 and \$5/kg in 2015.
- Photobiological hydrogen production cost targets are \$30/kg in 2010.
- The long-term goal is hydrogen at a price competitive with gasoline.

Approach

- Develop large-area solar reactors for photobiological and PEC water-splitting systems.
 - Assemble database of existing literature on reactors and materials.
 - Identify candidate transparent materials and other materials of construction.
 - Measure key properties (e.g., transmittance, H₂ and O₂ permeation rates, mechanical properties, and cost).
 - Perform outdoor and accelerated weathering tests on candidate materials of construction.
 - Identify reactor concepts with the potential to meet the process requirements.
 - Provide data for techno-economic process analyses.

Accomplishments

- Assembled literature database with over 200 references.
 - Identification of solar reactor concepts is under way.
 - Compiled list of important material properties.
- Selected candidate transparent material families: polycarbonates, fluoropolymers, acrylics, and polyesters.
 - Multi-year weathering tests are in progress (“piggybacking” on work in the DOE Solar Programs).
- Obtained H₂ and O₂ permeation parameters for a range of polymers.

Future Directions

- Remainder of FY 2005
 - Provide input on reactor configurations, materials of construction, and annual solar energy availability to the systems engineering for photobiological hydrogen production.
- FY 2006
 - Begin to address reactor issues raised by the techno-economic analysis that will be completed in FY 2005.
 - Identify strategies for reducing hydrogen permeation rates (if needed).
 - Continue materials testing and evaluation.
 - Work with material vendors to identify methods to overcome materials issues.
 - Identify reactor concepts and begin to identify design issues.

Introduction

NREL is working on the following activities as part of this project: algal hydrogen production from water using sunlight, PEC hydrogen production from sunlight, dark-phase fermentative hydrogen production, and photofermentation of hydrogen from alcohols and waste acids. All of these processes have promise and have been demonstrated at the laboratory scale. Designs for solar reactors, materials of construction, and system layouts, however, have not been identified.

These hydrogen-production processes have common characteristics that encourage shared development of system components. For example, PEC, algal hydrogen production, and photofermentation all require a reactor that is low in cost, safe, and efficient at capturing and utilizing light. In addition, the reactor must contain the hydrogen that is produced and provide for efficient hydrogen recovery.

Capturing energy from the sun for the production of hydrogen creates some challenges for materials of construction. The obvious drivers for materials selection are cost and the ability to transmit or concentrate light, but other materials characteristics are equally important. These include gas permeation rates, transmission of the specific wavelengths of light required by the light conversion system, ultraviolet (UV) and chemical stability, biocompatibility, and factors related to strength and impact resistance. Although many of these characteristics have been measured for plastics and glass, it is often difficult to compare results from different sources. Even where standard methods have been used, some materials may have been omitted because the measurements were made for uses other than hydrogen production. Initially, we are focusing on materials for the optical elements of the system because they are the most susceptible to weathering effects. As system designs progress, we will devote more effort to materials for the balance of the system. For example, containment, seals and gaskets, adhesives, piping, and valves will all have to meet rigorous cost and performance standards.

Approach

During the first two years of this work, PC, acrylics, fluoropolymers, PET, and related polymers were selected for continued evaluation based on their known outdoor durability and optical properties. Within these classes of polymers there are wide variations in methods for making them more stable under outdoor conditions or for improving properties such as gas permeability. We conducted a broad literature search, which resulted in a database of reactor concepts, engineering information, and materials of construction for solar applications. This provides a starting point for development of large-area solar reactors for hydrogen production.

Results

By “mining” data from accelerated and real-time weathering of polymers for solar and other outdoor applications that has been done at NREL and elsewhere, we have been able to narrow the list of potential polymers that can be used for transparent optical elements in solar water-splitting reactors. Figures 1–3 present the effect of accelerated and outdoor weathering of PC, fluorocarbon polymers, and PET materials with and without protective coatings or additives. The coatings and additives are added to the polymers to improve resistance to the degradation caused by the UV component of the solar spectrum at the earth’s surface. Accelerated and outdoor data are presented on the same plots of the optical performance as measured by the

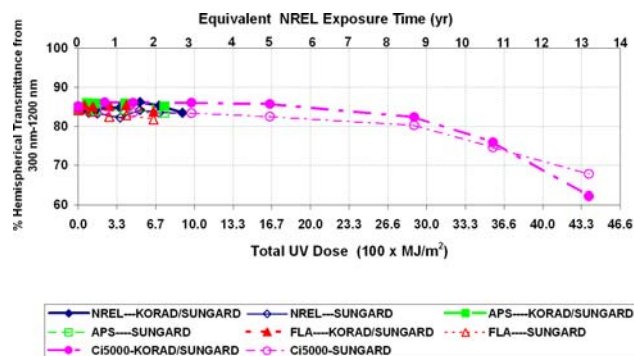


Figure 1. SparTech Plastics Sungard Ultraweatherable PC (Co-extruded PC and Acrylic) with Korad UV Protection Layer as a Function of Accelerated Atlas Ci5000 WOM and Outdoor Exposure in Golden, Colorado, Phoenix, Arizona, and Miami, Florida, After Cleaning

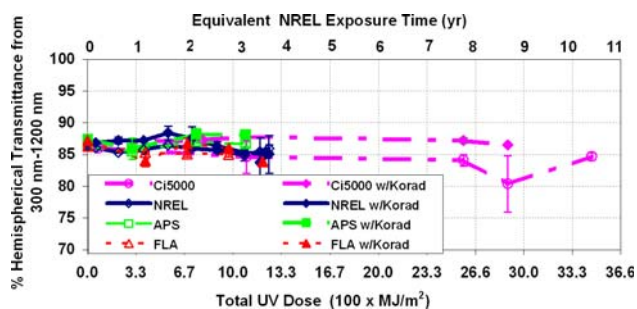


Figure 2. Melinex D387 PET Films with and without Korad UV Protection Layer as a Function of Accelerated Atlas Ci5000 WOM and Outdoor Exposure in Golden, Colorado, Phoenix, Arizona, and Miami, Florida, After Cleaning

hemispherical transmittance, which is plotted versus total UV dose. The National Renewable Energy Laboratory (NREL) uses three outdoor sites: Phoenix, Arizona (designated APS), Miami, Florida (designated FLA), and Golden, Colorado (designated NREL). Accelerated weathering is done in a standard commercial unit. The Atlas Ci5000 Weatherometer (WOM) uses lamps with two times the solar intensities, a temperature of 60°C, and 60% relative humidity. It operates 24 hr/day.

The UV dose in accelerated tests is converted to the equivalent amount of time it would take to achieve that dose outdoors (the top scale in each figure). In Figure 1, for example, the optical performance of the PC constructions begins to fall off after a UV dose equivalent to about 5 years outdoors. PET formulations (Figure 2) exhibit promising performance; however, experience with outdoor applications is somewhat limited at present and the outdoor tests have been done only in Golden, Colorado. The fluorocarbon polymers (Figure 3) exhibit very little loss in optical performance out to a UV dose equivalent to nearly 27 years outdoors.

The rate of hydrogen and oxygen loss and potentially oxygen and nitrogen entry into reactors due to the permeability of the materials of construction, particularly that of the transparent cover material, is considered to be a key performance and safety parameter. We found a very limited amount of data on hydrogen permeation through polymers of interest in the literature. More is available for oxygen, water, and nitrogen [1]. In FY 2004, we placed a subcontract with Nuclear Filter

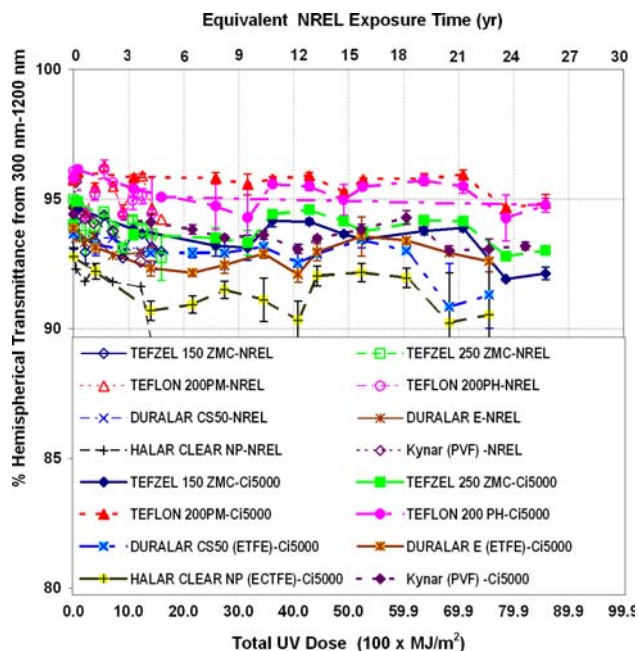


Figure 3. Performance of Eight Fluoropolymers as a Function of Accelerated Atlas Ci5000 WOM and Outdoor Exposure in Golden, Colorado, After Cleaning

Technology, Inc., to develop a method to measure hydrogen permeation rates. The first data for selected polymers became available in FY 2005. In parallel with that work, oxygen permeation rates were collected for the same materials using an instrument (Mocon Oxtran-100) available at NREL. Figure 4 gives values for hydrogen and oxygen permeability coefficients for polymers of interest for the optical elements in photobiological or PEC reactors. The figure also contains hydrogen and oxygen values from the literature. Data for five materials shown on the right side of the figure (indicated by PDL) are from the Polymer Data Library compilation [1]. All of these data are for as-received materials. No data are yet available for polymers that have been subjected to outdoor or accelerated weathering.

Conclusions

- Acrylics have good outdoor durability but are brittle and subject to hail damage.
- PCs are tough but “yellow” and crack outdoors over time. Protection strategies are being evaluated.

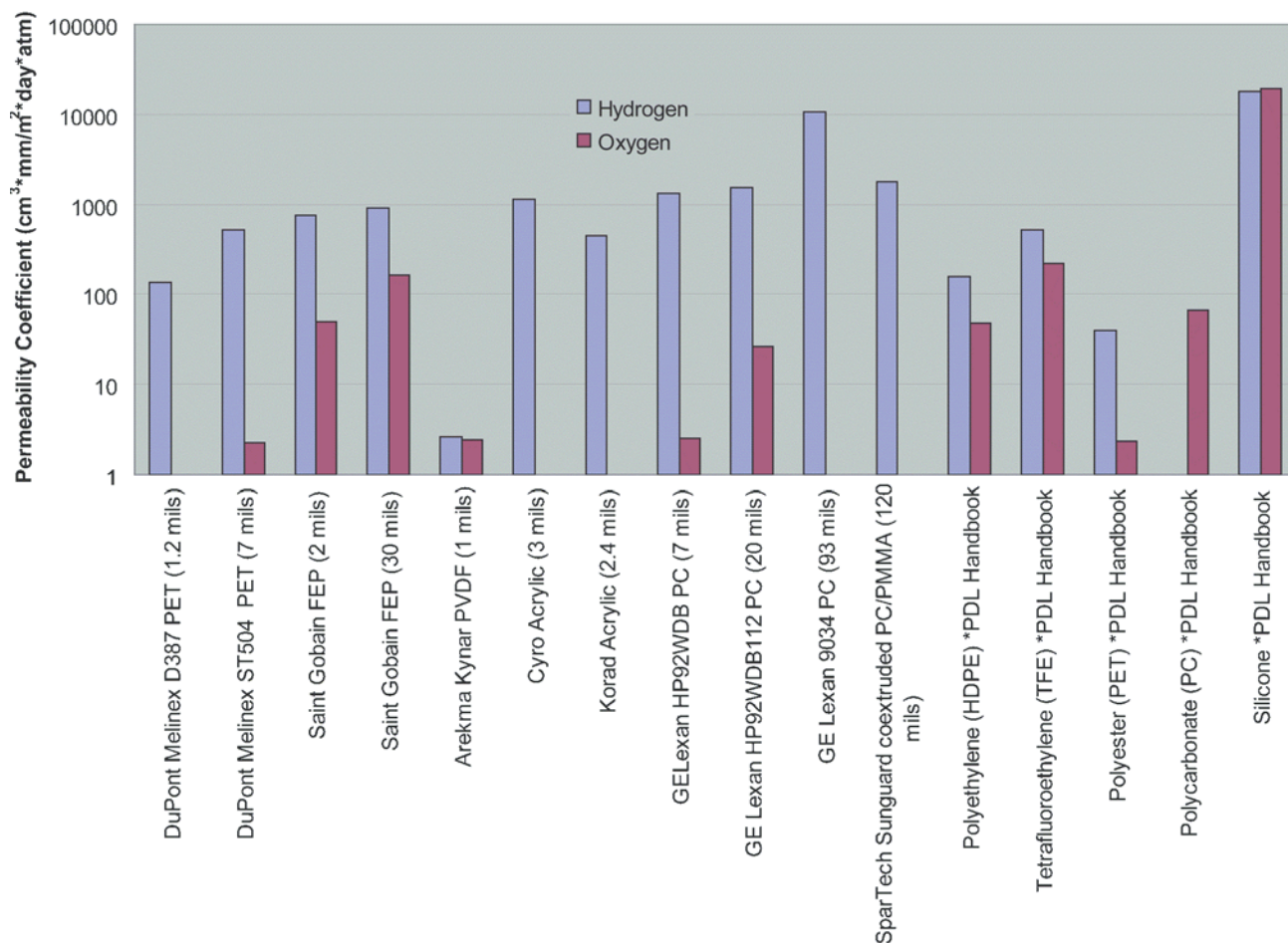


Figure 4. H₂ and O₂ Permeability Coefficients for Selected Polymers

- PET formulations have not yet proven to be durable outdoors but have favorable gas permeation properties. Some have shown encouraging durability in outdoor tests in Golden, Colorado, and in accelerated tests.
- Kynar, a fluoropolymer (PVDF), has very good outdoor durability and favorable gas permeation properties.
- Guidance on gas permeation and other specifications will come from the systems engineering analysis that will be completed in September 2005.

FY 2005 Publications/Presentations

1. Blake, D. M. (2004). Overview of Solar Reactors and Design Considerations. Presented at Photobiology Team Meeting, Oak Ridge National Laboratory, November 3–5.

2. Blake, D. M. (2005). Project Overview. Presented at Hydrogen Technologies Team Meeting, NREL, January 13–14.
3. Blake, D. M., and Kennedy, C. (2005). Hydrogen Reactor Development and Design for Photofermentation and Photolytic Processes. Presented at Hydrogen Program Review, Washington, DC, May 23–26.

References

1. Massey, L. K. (2003). *Permeability Properties of Plastics and Elastomers*. PDL Handbook Series, Plastic Design Library/William Andrew Publishing, Norwich, NY.