Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels (DE-FC26-97FT96052)

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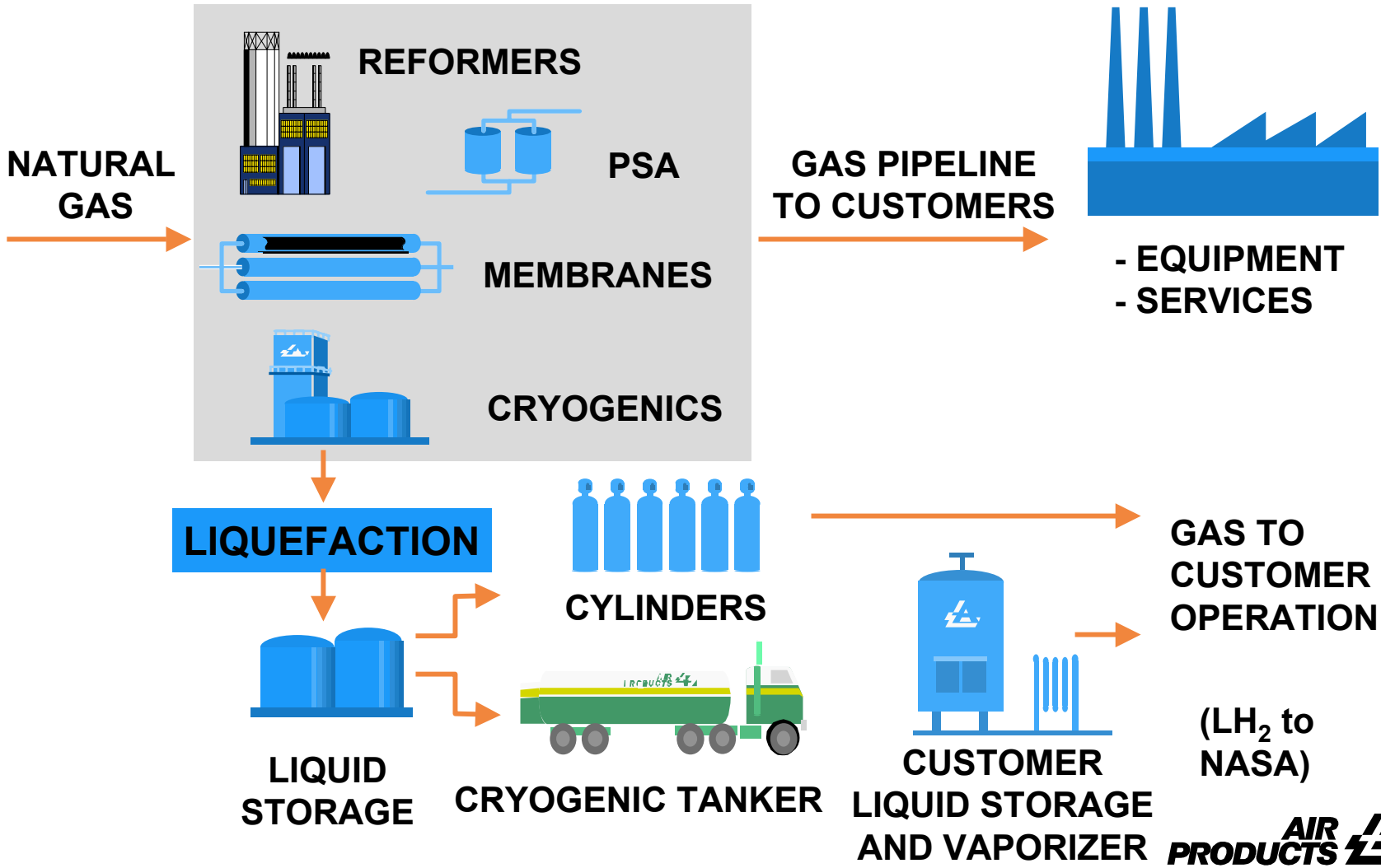
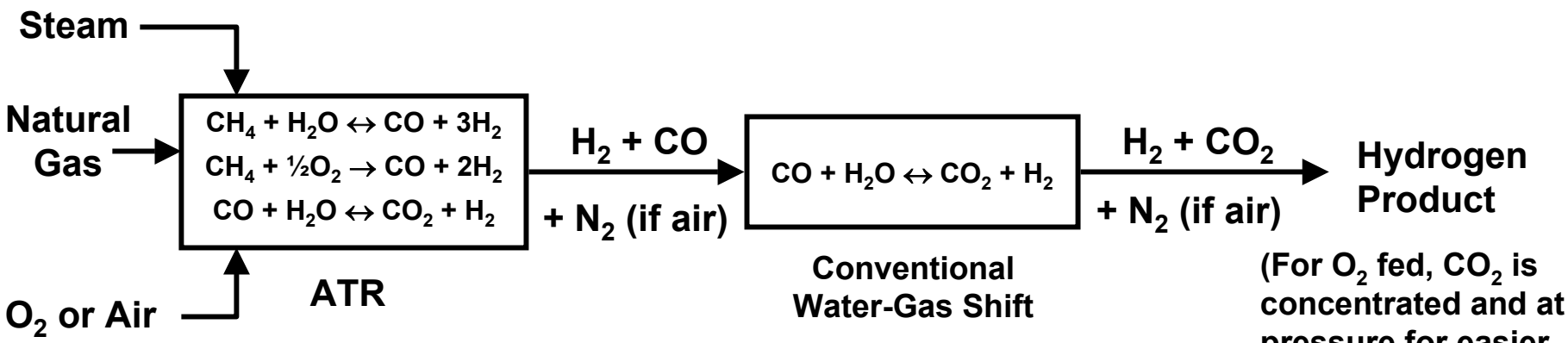
Air Products Is the Global Leader in Hydrogen Supply

SYNTHESIS GAS PRODUCTION TECHNOLOGY



Several Companies Are Developing Autothermal Reformers for a Range of Hydrogen Plant Sizes



- Centralized hydrogen production
  - Typically use pure oxygen feed
  - Better economies of scale than SMR for large plants
  - Amenable to carbon capture
- Small stationary hydrogen production
  - Conventional pure oxygen is not economical at these small scales
  - Typically use air feed to ATR
  - N_2 dilution of synthesis gas leads to increased cost of downstream purification

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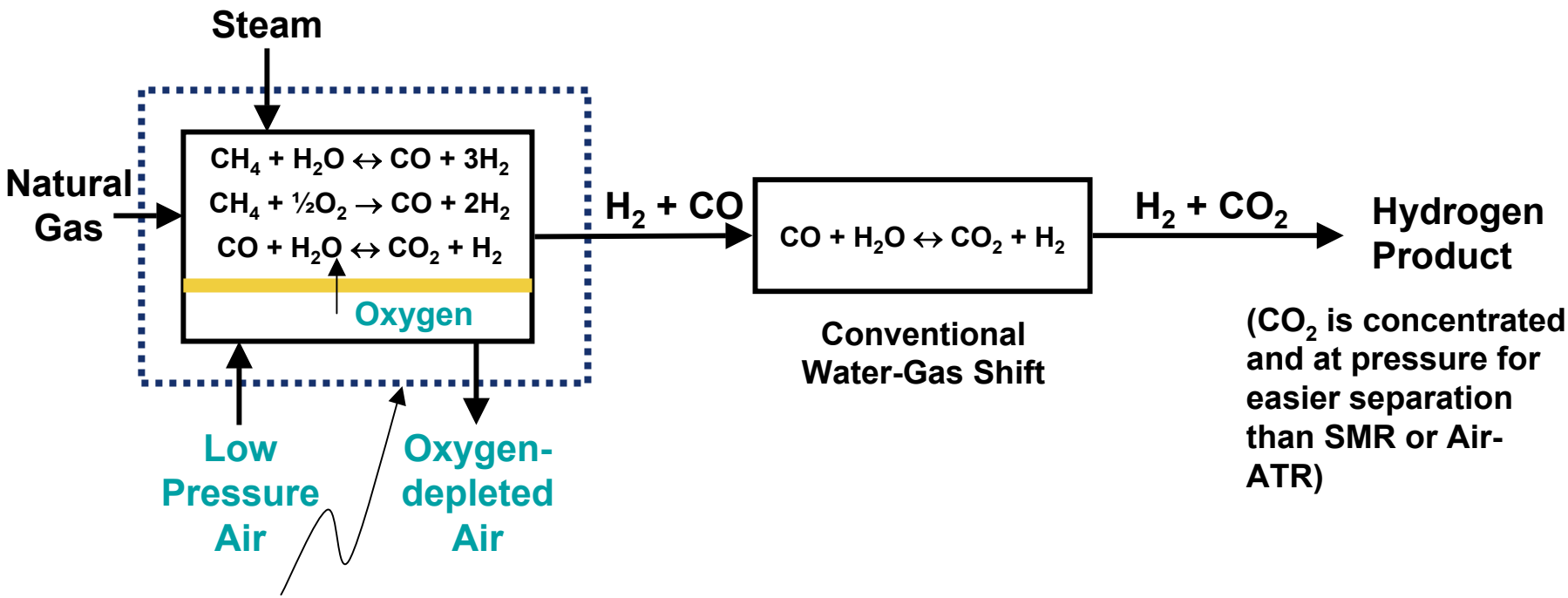
ITM Syngas Technology Provides the Benefits of Oxygen-Based ATR at Significantly Reduced Cost



ITM Syngas Technology

Critical Features:

- Promote steam reforming reaction
- Promote partial oxidation reaction
- Promote oxygen separation from air

→ **Achieves significant cost saving through process simplification**

Combines air separation and synthesis gas production into a single reactor

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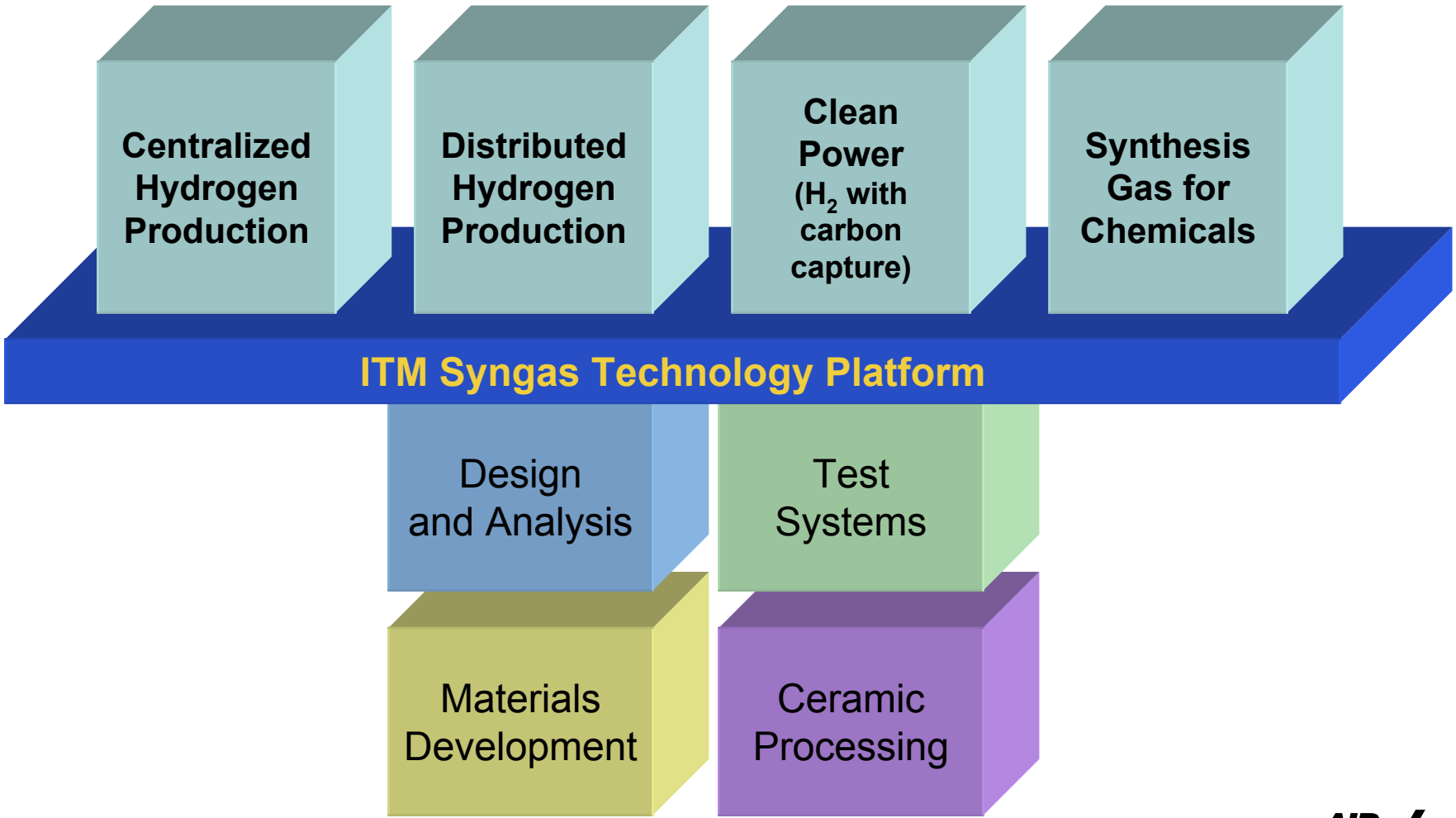
Project Objective: Research, develop, demonstrate ceramic Ion Transport Membrane (ITM) reactor system for low-cost conversion of natural gas to hydrogen and synthesis gas



Three Phase Industry-DOE Project with Broad Development Team

Phase 1

Identified family of high-pressure membrane materials
Verified ceramic-to-metal seal performance
Selected planar membrane over tubular design

Phase 3

15 million SCFD* Pre-Commercial Technology Demonstration Unit

Phase 2

24,000 SCFD* Process Development Unit (PDU)
330,000 SCFD* Subscale Engineering Prototype (SEP)

1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007

Tested membranes at elevated pressure for over 6 months

Fabricated full planar membrane module for PDU

Membranes tested in PDU

Fabricated commercial-size planar membrane

* std. cu. ft. per day of synthesis gas

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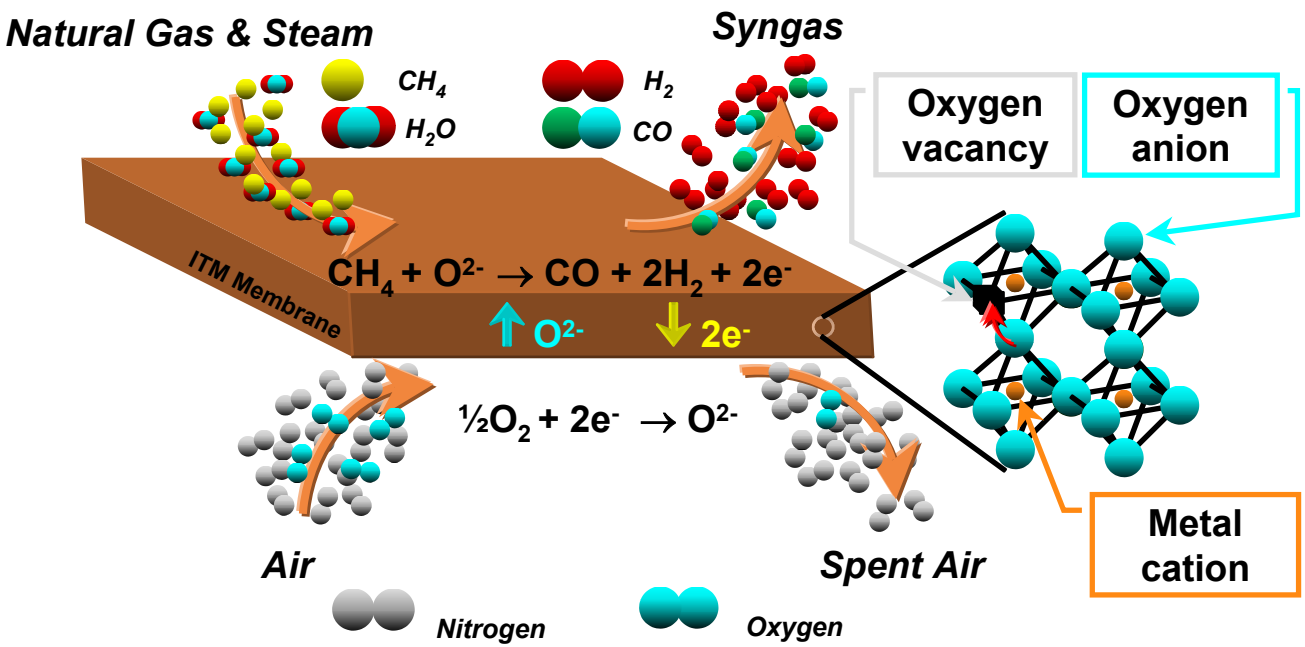
A Revolutionary Technology Using Ceramic Membranes

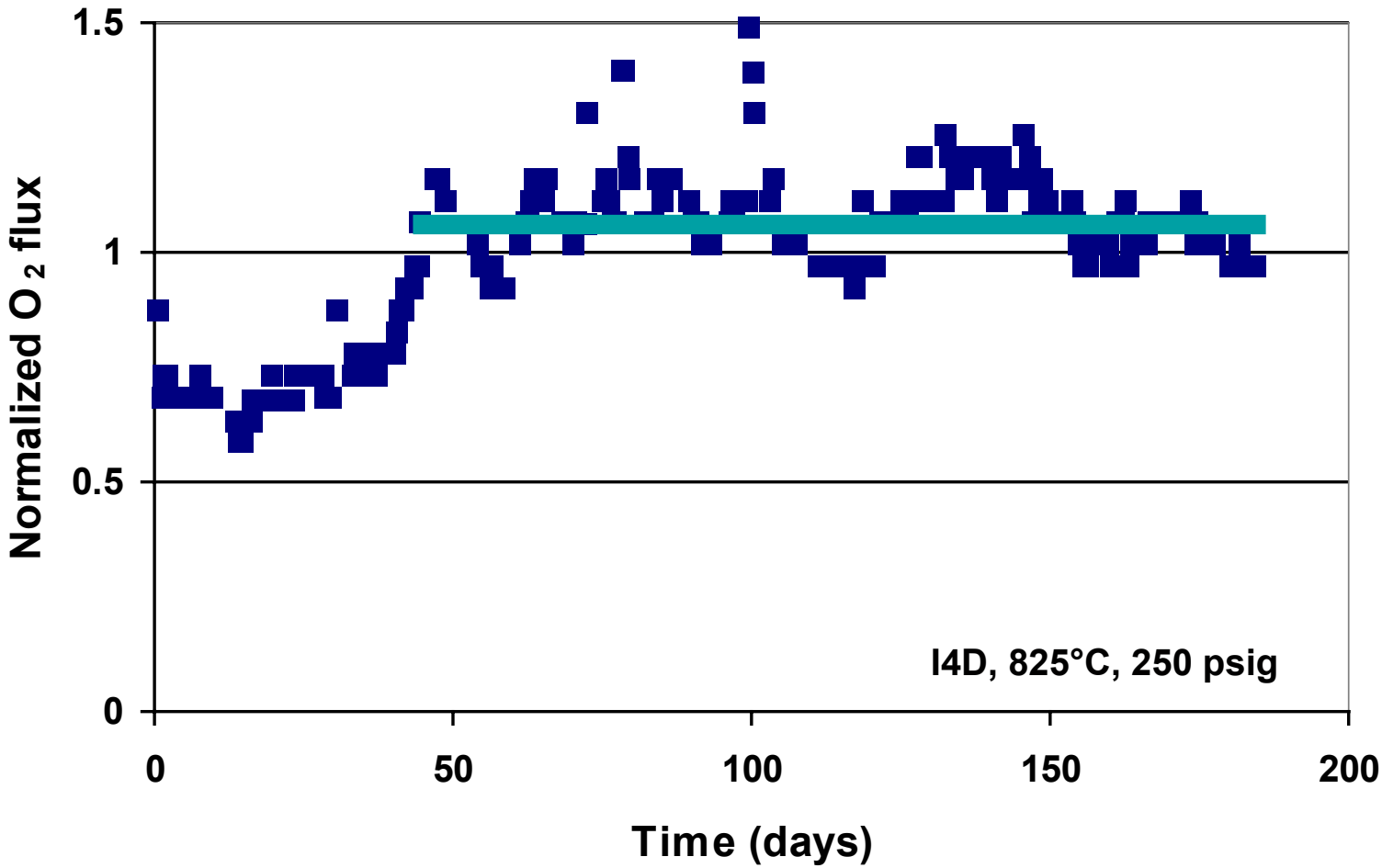
- Ion Transport Membranes (ITM)
  - Non-porous multi-component ceramic membranes
  - High oxygen flux and high selectivity for oxygen
  - Operate at high temperatures, typically over 700 °C
- ITM Syngas combines air separation and methane partial oxidation into a single unit operation, resulting in significant cost savings



ITM Syngas Technology Challenges

- Materials
  - Stable Performance
  - Catalysis
- Reactor Design
  - Configuration (Planar vs. Tubular)
  - Seals
- Ceramic Processing Development
- Process Scaleup

Long-Term Flux Stability Demonstrated Under High Pressure Hydrogen Production Conditions



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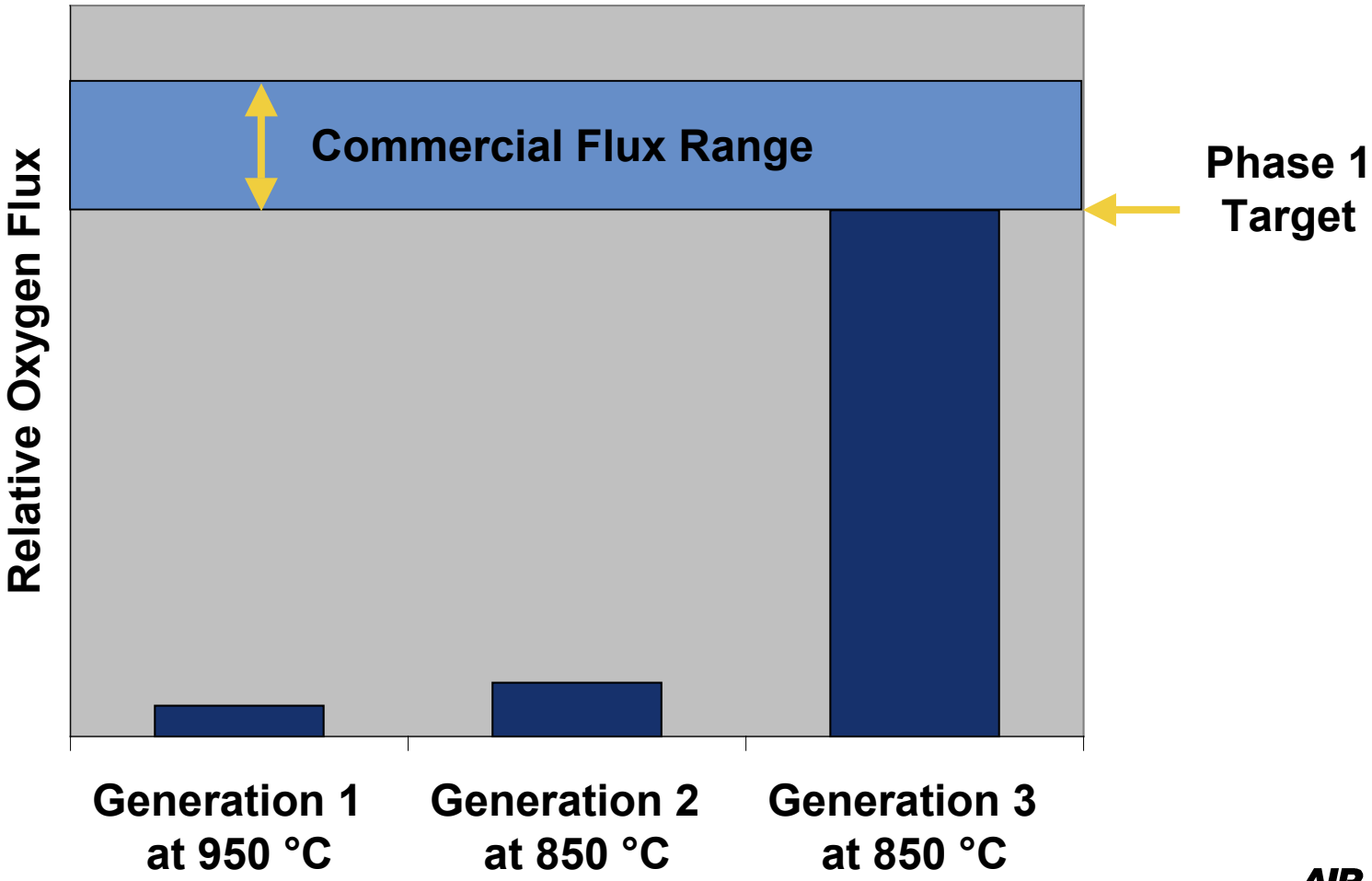
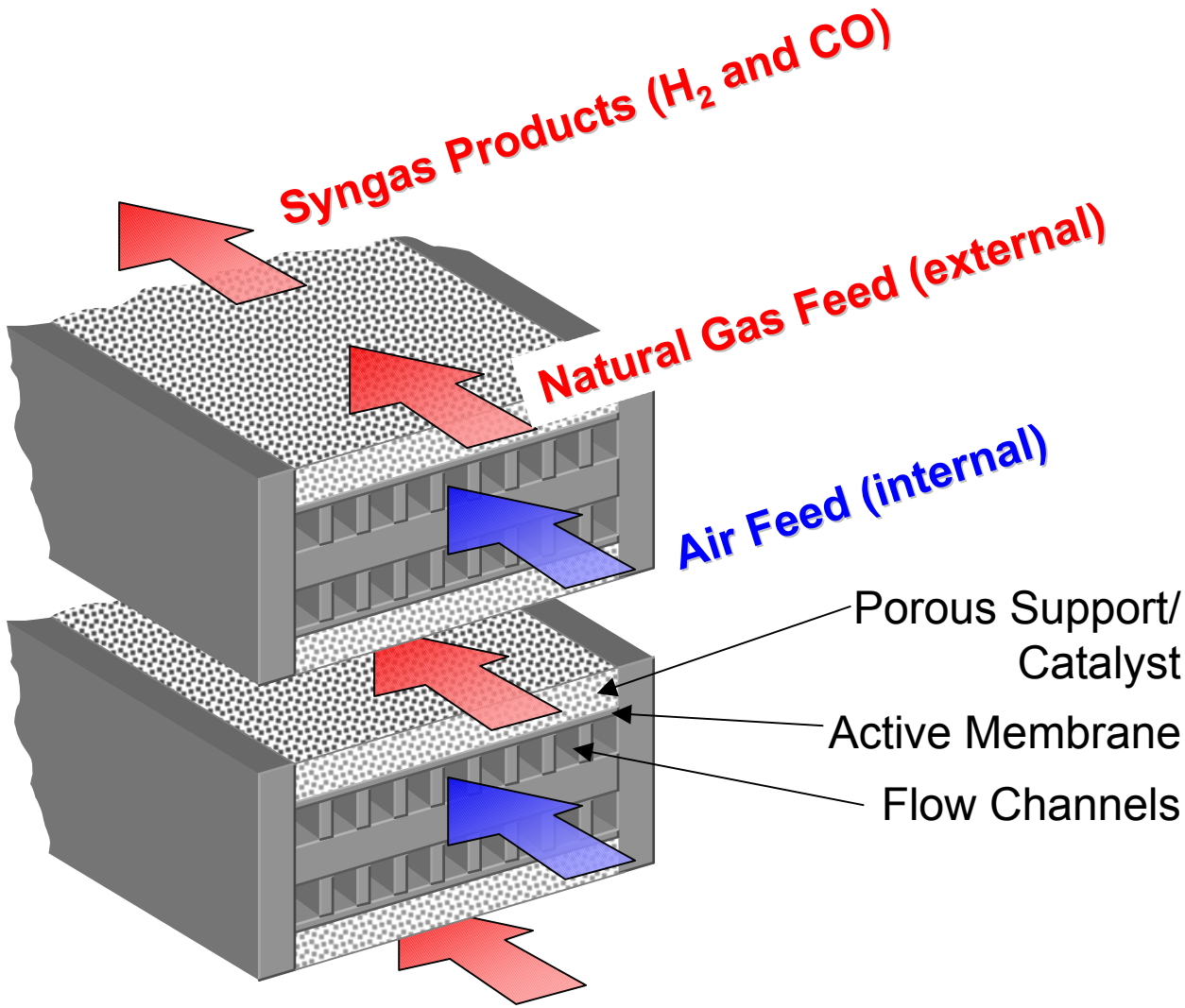
Excellent Progress in Achieving Membrane Flux Target

Achieved through advances in supported thin-film planar membranes and catalysts



Planar Membrane Systems Have Significant Advantages

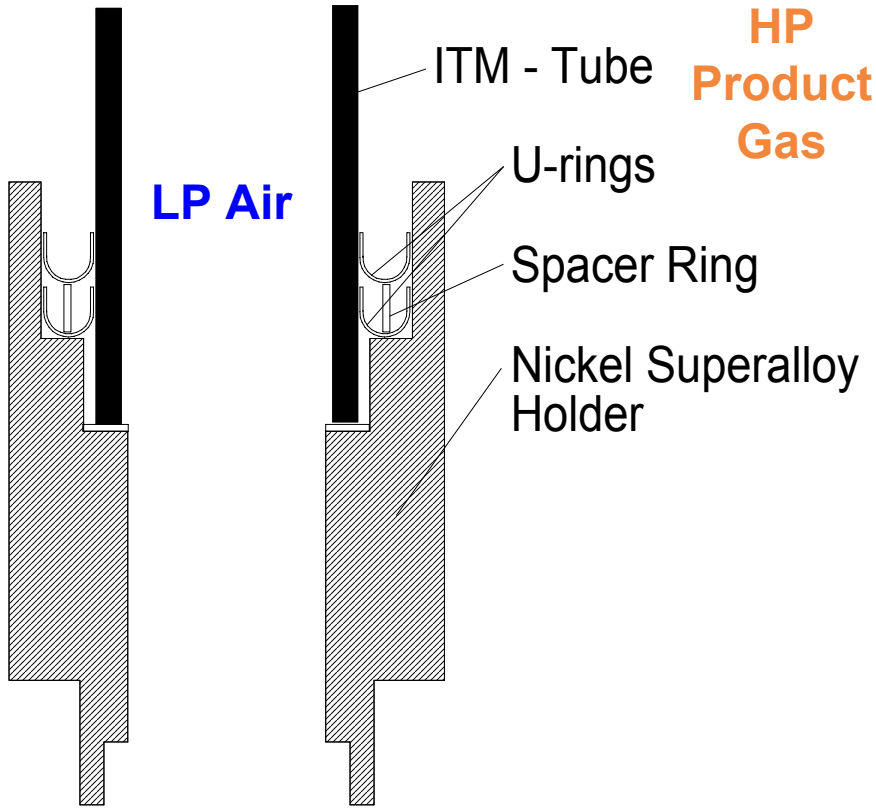
- Microchannel design
- Good mass and heat transfer
- Compactness
- Minimizes number of ceramic-to-metal seals
- Amenable to standard ceramic processing methods



Ceramic Wafer Stack

Ceramic-to-Metal Seal Designs Have Been Extended to Planar Membranes

- Successfully tested with tubular membranes during several six-month tests
- Compliant metallic sealing elements (U-rings)
- Multiple elements for improved seal and added mechanical stability
- Elements open to high pressure side to take advantage of pressure activation



U. S. Patent #6302402

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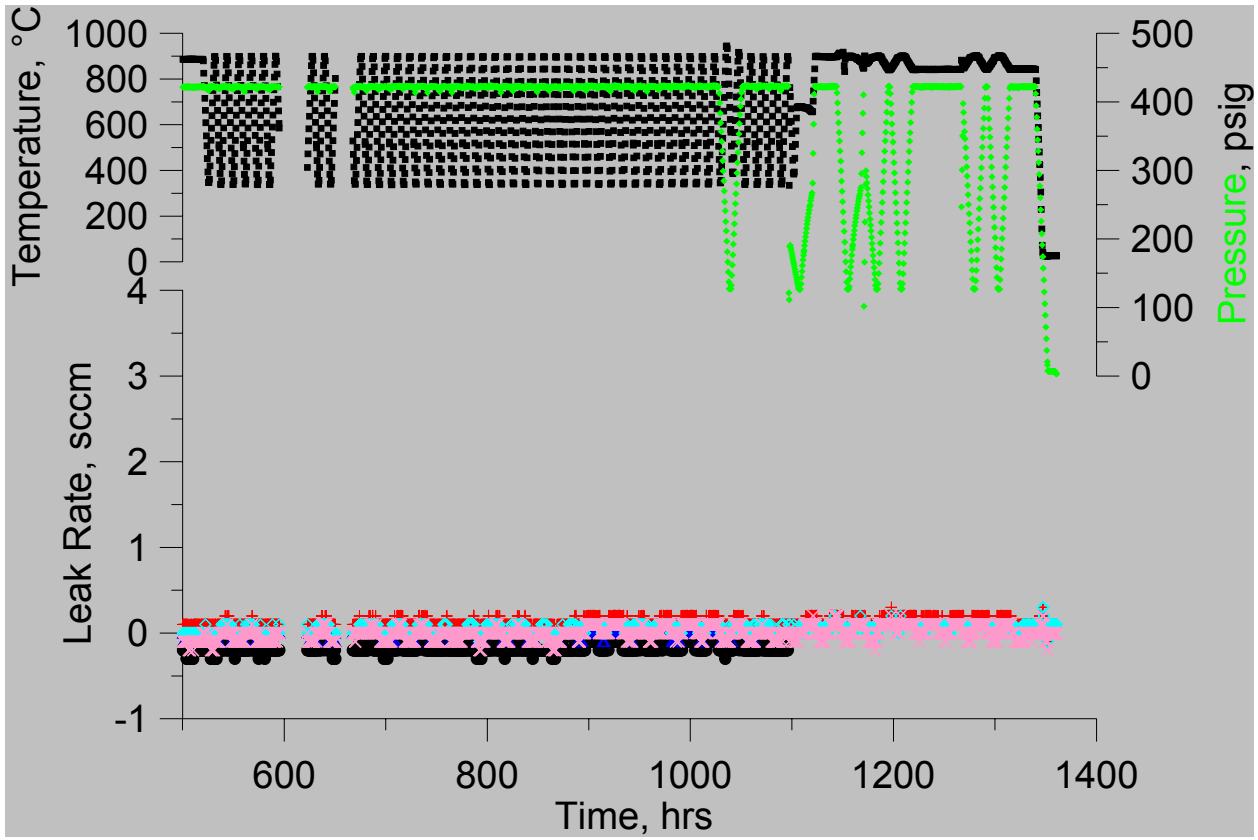
PDU Module Seals Remained Leak Tight During Thermal and Pressure Cycling



Seals demonstrated leak-tight performance

- **232 days static test (900°C, 250 psig)**
- **Over 50 thermal cycles (300 to 900°C, 425 psig)**
- **8 pressure cycles (125 to 425 psig, 850-900°C)**

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Ceramic Processing Infrastructure Is In Place

Using Conventional Processing Methods

High Speed Laser Cutter

Lamination and Cutting Operations

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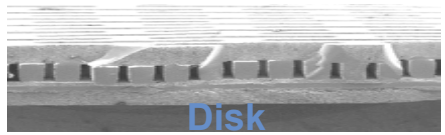
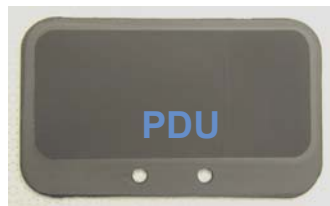
Rapid Scale Up Of Membrane Size and Function

- Proof-of-concept membranes were used to develop processing methods for microchannel devices
- Functional membranes of various sizes have been successfully fabricated using standardized processes

Year	Function	Relative Area	Membrane
FY99-00	**Disks** * Materials * Layer Performance	1	
FY00	**Prelim PDU Wafer** * Fabrication * Integration	30	 
FY01	**PDU Wafer** * Full-Featured * Operating Performance	30	
FY02	**Full-Size Wafer** Integration into Commercial Wafer	160	

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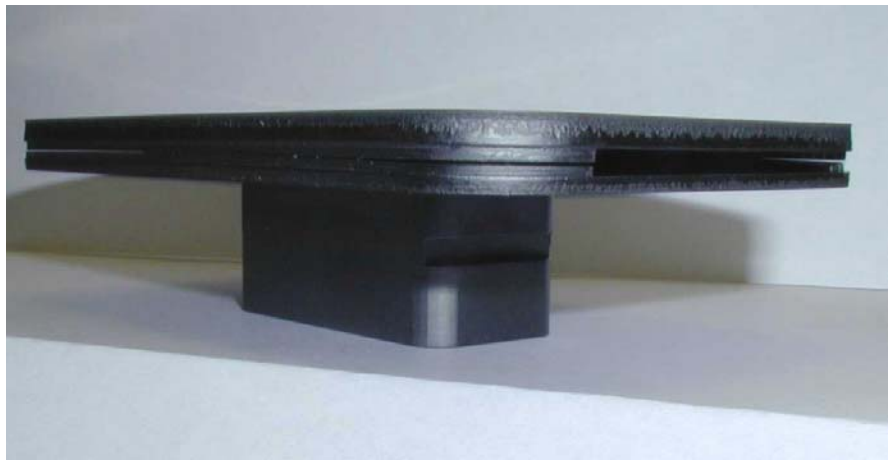
Full Planar Membrane Modules Have Been Fabricated for the PDU

- PDU ceramic membranes contain essential features of full-size commercial membranes
- Ceramic membrane internal features
  - Manifolding and air flow
  - Support greater than 400 psi pressure differential
- Membrane fabrication processes are robust and scaleable



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Process Development Unit (PDU) Tests Membranes at Commercial Conditions

- Objectives
  - Demonstrate performance of ITM Syngas membrane modules
  - Provide data for model validation
  - Test commercial-size wafers
- Capabilities
  - Nominal 24,000 SCFD synthesis gas
  - Pressure: 450 psig
    Temperature: 950°C
  - Residence time similar to a commercial reactor
  - Highly instrumented and PLC controlled
- Status
  - Demonstrated reliable ceramic-metal seals
  - Membrane modules have successfully undergone heat-up, pressurization and testing in syngas environment
  - Continuing to conduct performance runs

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Achieved All Milestones

- **Task 2.1 Commercial Plant Economic Evaluation**
  - ✓ Evaluate ITM Syngas process using PDU data (Q2FY03)
    - Projected hydrogen production costs* are more than 25% below draft DOE targets for 2005
- **Task 2.2 Evaluate ITM Materials and Seals**
  - ✓ Long-term stability tests of tubular membranes and seals at high pressure (Q1FY03)
  - ✓ Select catalysts for the SEP (Q3FY03)
- **Task 2.3 ITM Syngas Membrane & Module Fabrication**
  - ✓ Fabricate modules for additional PDU tests (Q3FY02)
  - ✓ Select SEP membrane module design (Q4FY02)
  - ✓ Commission the PDF (Q4FY02)
  - ✓ Initiate fabrication of SEP (full-size) membranes (Q2FY03)
- **Task 2.4 Nominal 24 KSCFD ITM Syngas PDU**
  - ✓ Demonstrate performance of subscale membrane modules in PDU (Q3FY02)
  - ✓ Performance test second generation sub-scale modules in PDU (Q1FY03)
- **Task 2.5 Nominal 330 KSCFD ITM Syngas SEP**
  - ✓ Initiate design and construction of the SEP reactor (Q3FY02) (Construction deferred due to funding delay)

* 500 KSCFD hydrogen production, 100 units/year

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Milestones for Next Year

- Test catalyzed planar membranes in PDU (Q4FY03)
- Fabricate balance of ceramic components for SEP module (Q2FY04)
- Conduct tests to determine kinetic parameters for membrane and catalysis performance models (Q2FY04)
- Fabricate multi-wafer membrane module for PDU test (Q3FY04)
- Initiate tests to validate full-size membrane design (Q4FY04)

Response to 2002 Reviewer Questions

- Ceramic-to-metal seals have demonstrated excellent performance in long-term static tests, and in thermal and pressure cycle tests
- ITM Syngas processes to produce hydrogen range in efficiency (LHV) from 65 to 74%, depending on plant scale. Efficiency gains can be achieved with additional process integrations. (DOE 2003-2010 target is 70-75%)
- The lower capital costs associated with ITM Syngas technology will lead to lower hydrogen production costs. This will facilitate the transition to a Hydrogen Economy.

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