Enabling Clean Coal Power Generation: ITM Oxygen Technology

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Air Products and Chemicals, Inc.
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Excerpted text

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Abstract
In the late 1980s Air Products identified a class of perovskite ceramic materials with high flux and separation selectivity for oxygen ions. These materials have become the basis for a novel class of air separation technologies, referred to as ion transport membranes (ITMs). Along with partners and through partnership with the U.S. Department of Energy, Air Products has made substantial progress in developing ITM Oxygen technology into a cost-effective method of oxygen production. ITM Oxygen integrates well with advanced power generation processes, as well as with traditional energy-intensive industrial processes requiring oxygen.

The team has successfully demonstrated expected performance of commercial-scale modules in a prototype facility that produces up to 5 tons per day (TPD) of oxygen. Continued operation of this unit has verified thermal and pressure cycle performance and has tested a number of component designs and operating scenarios for next phase scale-up. Design of the next phase pilot unit is complete and operation is planned in 2012. This Intermediate Scale Test Unit (ISTU) is designed to produce up to 100 TPD of oxygen integrated with turbomachinery and coproduction of power. Data from the 100 TPD unit will provide the design basis for a much larger plant that could produce 2000 TPD. In parallel, work has also begun to expand ceramic fabrication capacity to support these demonstrations.

This paper will present an overview and update of the ITM Oxygen development effort, including testing of commercial-scale ceramic modules and operating scenarios; next-phase scale-up designs; ceramic manufacturing expansion work; and developing industrial power process integrations and economic analyses toward gasification, oxy-combustion, and other energy-intensive industrial applications. A commercialization timeline will be discussed.

Introduction
Worldwide energy use is projected to grow significantly over coming decades as developing economies gather momentum. Coal will likely play a significant role in the production of that energy. To compete with other feedstocks and processes, and with the added complication of carbon constraints, power generation from coal will need to use the most advanced technologies available. Two of these are gasification and oxy-combustion, which enable high efficiency power production and generate a CO₂-rich by-product stream suitable for capture. However, both gasification and oxy-combustion make use of large quantities of oxygen, which today is sourced from cryogenic air separation facilities. Cryogenic air separation is a reliable technology, but one which constitutes, for example, 15% of the cost of an integrated gasification combined-cycle (IGCC) power plant. Moreover, cryogenic technology is mature and is therefore unlikely to undergo future cost reduction coming from step-out technology improvements. A new air separation process is needed to support the role of coal in the future energy mix.
**Background**
In the late 1980s, Air Products identified a class of perovskite ceramic materials with high flux and separation selectivity to oxygen that can form the basis for cost-efficient air separation membranes. These materials separate oxygen from air at high temperature in an electrochemically driven process. The oxygen in air is ionized on the surface of the ceramic and diffuses through the membrane as oxygen ions, driven by an oxygen activity (partial pressure) gradient to form oxygen molecules on the other side. This process is represented schematically in Figure 1. Impurities such as nitrogen are rejected by the membrane. In addition, these materials conduct electrons as well as ions, meaning that no external source of electrical power is required—the entire separation is driven by an oxygen partial pressure ratio across the membrane. Detailed descriptions of the materials and electrochemical processes can be found in ref. i, ii, iii. The air separation system that results from the use of such ceramic oxygen ion transport membranes (ITMs) produces a hot, pure oxygen stream and a hot, pressurized, oxygen-depleted stream from which significant amounts of energy can be extracted.

Because of the requirement to feed a high-pressure oxygen-containing gas to the membrane separator, and the production of the hot high-pressure off-gas stream, ITM Oxygen systems advantageously integrate with turbomachinery-based power cycles. Compressed air, obtained directly from an air compressor or extracted from the compression side of a gas turbine, is heated to 800–900 °C, and supplied to the membrane. A portion of the oxygen is extracted by the membrane, and the resulting oxygen-depleted non-permeate off-gas can be expanded in a hot gas expander or combustion turbine to recover useful work. Further downstream processing in a heat-recovery-steam-generator (HRSG) can result in an overall product mix of oxygen, power, and steam.

Thermodynamic and process economic analyses indicate that the ITM Oxygen process produces oxygen at a significantly lower cost than conventional cryogenic processes. The high selectivity to oxygen separation afforded by the membrane and its rapid oxygen flux result in compact membrane devices with little pressure drop, resulting in >30% reduction in the cost of oxygen. One implementation of an ITM Oxygen membrane in a power cycle is shown in Figure 2. A pressurized air stream is extracted from a gas turbine and fed to the ITM unit after passing through a direct combustor to raise the feed temperature to 800–900 °C; oxygen-depleted off-gas from the membrane unit, at substantially the same pressure as the feed air, is reinserted into the combustion turbine for conversion of its thermal and hydraulic energy to shaft work. The compressed air not extracted from the gas turbine goes directly to the combustion turbine (not shown). By contrast, if the air is fed to a cryogenic air separation unit (ASU) instead of the ITM Oxygen unit, the heat in the air stream would be rejected, and much of the pressure energy would be expended during the oxygen extraction.

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**Figure 1:** Mixed-conducting ion transport membrane. Oxygen anions move counter to electrons at high temperature in the same material under an oxygen activity gradient.

**Figure 2:** Simplified process flow diagram of an ITM Oxygen unit integrated into a power cycle.
A block diagram of this concept as implemented in an integrated gasification combined cycle (IGCC) facility is shown in Figure 3. The ITM Oxygen system shown here operates fully integrated with the main gas turbine of the IGCC plant, but good benefits can be realized in partially integrated cycles as well. Alternate process cycles are applicable for oxy-fuel combustion power plants with CO₂ capture or other energy-intensive industrial production plants. Examples of these would be iron and steel, metallurgical, hydrometallurgical, glass, cement, oil refineries and petrochemicals.

Collaborative development with the Department of Energy
The potential for coproducing oxygen and power or producing oxygen with relatively little power input has interested the DOE and others in developing this technology further for advanced applications requiring low cost oxygen. Air Products and the DOE entered into a Cooperative Agreement in 1998 to develop ITM Oxygen membrane technology to the point of precommercialization in a three-phase program. The overall goal of the program is to reduce the cost of oxygen by one-third over conventional cryogenic distillation-based technology.

The development effort has focused on identifying key technical objectives and addressing them comprehensively with a multidisciplinary, multi-organizational team approach. The program addresses the following areas, among others: materials development, ceramic processing, integration of membrane systems with turbomachinery, mechanical design, ceramic and system reliability, oxygen production performance, and process safety.

Phase I of the program, which focused on the technical feasibility of the approach, was completed in 2001. A material was chosen from a class of perovskite ceramics as the basis for further scale-up. The material has a combination of properties sufficient to meet commercial requirements for performance and operating life, including high oxygen flux, good material strength at high temperature, and resistance to system contaminants such as sulfur. In addition, the material is amenable to standard ceramic processing techniques which facilitate the design and manufacture of multi-layer, planar wafer structures.

A schematic of the planar wafer design is shown in Figure 4. Four wafers are shown joined to a common oxygen withdrawal tube. Each wafer consists of two thin outer membrane layers through which the oxygen ions diffuse. The thin layers on the top and bottom of the wafer are supported by a porous...
layer which is itself supported by a slotted layer. Hot, high-pressure air flows between the wafers. Oxygen passes from the air outside each wafer, through the thin outer membrane layer, through the pores of the porous layer and into the slots of the innermost layer. Oxygen is collected at the center of each wafer in a tubular region formed by the joined wafers and passes out of the module through a ceramic tube sealed to a metal pipe. The high-pressure air on both sides of each wafer creates compressive stresses within the ceramic which stabilize the wafer. The planar design also makes for a very compact separation device while facilitating good gas phase mass transfer. All of the layers are made of the same ceramic material, and therefore expand and contract together during temperature changes.

The planar wafers were scaled to their full commercial dimensions and produced in volume on a pilot production line using standard ceramic tape-casting technology. The production activities established the feasibility of achieving low-cost production required to meet overall economic targets. Multi-wafer modules were constructed, and the modules were operated under commercially relevant high-temperature, high-pressure conditions in pilot-scale experiments. Oxygen production exceeded commercial flux and purity targets. Detailed process economic studies reconfirmed the overall, market-disruptive benefits of the technology. (See ref. iv)

Further scale-up of ceramic devices requires stacking and joining a number of commercial-size wafers to make multi-wafer modules. The commercial concept of an ITM Oxygen separation vessel is shown in Figure 5. It contains an array of multi-wafer modules (in green) in a common flow duct and connected through a series of manifolds to an oxygen header below. Each commercial-scale module produces about one (1) ton per day (TPD) of oxygen. Many modules are arrayed in parallel and series to meet the production requirements of a large tonnage oxygen plant.

In Phase II, commercial-scale modules capable of producing up to 0.5 TPD of oxygen were built by cojoining multiple wafers to form a unified ceramic device. The modules are also fitted with a terminating end cap and ceramic oxygen product pipe. All joints are ceramic, such that the entire device is composed of the same ceramic, thus minimizing the potential for differential stresses caused by nonuniform expansion across the body of the device. Figure 6 shows four ITM Oxygen modules awaiting testing after fabrication.

Figure 5: Schematic of commercial ITM Oxygen vessel showing ITM Oxygen modules (in green) arranged in a flow duct and connected to a common oxygen header. The vessel is shown only partially full of modules to expose the oxygen gas manifold tubes below.

Figure 6: Commercial-scale ceramic ITM Oxygen modules. Each module is capable of producing 0.5-TPD of oxygen.
The pilot plant or subscale engineering prototype (SEP) was designed, constructed and commissioned in Sparrows Point, Maryland during the final portion of Phase II. This unit features a prototype ITM pressure vessel which holds six commercial scale modules in a 2 by 3 array. Each module has a dedicated permeate train with vacuum pump and controller, flow and purity measurement. The SEP is located adjacent to a commercial cryogenic industrial gas plant and is deployed in a recycle loop configuration, taking makeup gases from the commercial plant and recycling and recompressing its own offgas as the balance of the feed. The feed stream to the membranes is first heated by recuperative heat exchange with the non-permeate stream, then brought to final temperature by an induction heater. Nominal membrane operating conditions for the unit are 800–900 °C, 200 psig feed pressure, and <1 atm permeate pressure. The SEP is equipped with sufficient flow capability to simulate feed gas velocities anticipated in commercial service. An aerial photograph of the SEP is shown in Figure 7. Figure 8 shows detail of the flow duct and module configuration.

Air Products carried out the first experiment in the SEP in January 2006. As of July 2011, the SEP has operated for a total onstream time of over 850 days. Expected values of purity and flux have been measured during multiple runs, including oxygen purities reaching 99.9%.

Initial runs have been done using modules capable of producing a half-ton per day of oxygen. Modules equipped with ceramic-metal seals are loaded into the pressure vessel and connected to the oxygen permeate piping. A flow duct is placed around the modules to give a flow path with minimal excess space between duct walls and modules to minimize bypass of feed air. The cold wall vessel lid is bolted in place to finish preparation for the run.

Start-up of the process involves a series of pressure, flow and temperature ramps whose rates are set to minimize stresses due to thermal and chemical expansion of the ceramic. The membrane material has a relatively large coefficient of thermal expansion along with a chemical expansion as oxygen vacancies are created in the lattice structure at elevated temperature. Changes in oxygen partial pressure as well as temperature can create stresses in ceramic parts which must be managed in order to maximize ceramic reliability. (See ref. v.)
Once the full temperature and pressure conditions are reached, the pressure on the interior of the modules is reduced to subatmospheric levels to reach the desired oxygen partial pressure driving force conditions for the unit. Oxygen flow rate and purity from individual modules are monitored continuously once steady state is achieved. The product oxygen is ultimately vented to atmosphere. To allow the vitiated non-permeate stream to be recycled while keeping the feed stream at the oxygen concentration of air, makeup oxygen is metered into the process through a control valve which maintains the inlet oxygen content equivalent to air.

Results
Multiple runs have been performed at the SEP in order to investigate a number of operating parameters. Insulation type and configuration have been optimized. Various types of ceramic-to-metal seals have been tested, as have a range of start-up and shutdown schedules designed to maximize ceramic reliability while reducing start-up and shutdown times. Multiple banks of modules were tested, and their ability to withstand rapid transients in process conditions was studied. Full scale 1-TPD modules were tested, as were various mechanical components designed for use in the next scale-up unit. A summary of key experimental findings is given below.

1-TPD module testing
Two 1-TPD modules were loaded and tested in the SEP during Run 16 in February 2010. Figure 9 shows a photograph of the modules installed in the flow duct. Purity and flux were monitored over a range of process conditions. Oxygen product rate was measured at up to the expected 1 ton per day, as shown in Figure 10. For these modules, the membrane active layer thickness was somewhat larger than typical values, reducing flux.

A significant development effort was focused on control of contaminants in the process air. A getter configuration was chosen which gives a good balance of high surface area and low pressure drop, along with good commercial availability. Testing of this getter has proceeded both in lab scale experiments and at the SEP. Good results for the getter were confirmed in SEP Run 19, which occurred from October 2010 to January 2011, with 640 hours of continuous fluxing and 887 hours fluxing overall for the run. (A laboratory experiment in which a sub-scale module operated successfully for 7900 hours had been conducted in 2008.) This test included two successful thermal cycles on half-TPD modules with return to original purities and fluxes as shown in Figure 11. In addition, two significant process upsets occurred and were survived with minimal reduction in product quality.
More recent work at the SEP includes performance testing of components and design concepts for process units planned for the ISTU, discussed below.

**Future work**

The ITM Oxygen development program is currently focused on design and construction of an intermediate-scale test unit (ISTU), sized for a nominal 100 TPD of oxygen production. The ISTU will provide design and scale-up data necessary for a nominal 2000-TPD test facility by the middle of the decade. In this development scenario, world-scale ITM Oxygen plants for IGCC and other large clean energy applications would be available by around 2017.

The primary goal of the ISTU is to test large arrays of ITM Oxygen modules housed in a common pressure vessel while operating coupled to dedicated turbomachinery configured for power generation. The testing will enable further scale-up of the vessel system and verify process control schemes required to maintain membrane module integrity and turbomachinery performance. In addition, performance verification will be accomplished for scaled-up supporting systems, such as heat exchange, contaminant control, and oxygen vacuum systems.

The basic ISTU process configuration is shown in Figure 12 as a simplified block flow diagram. The arrangement comprises two separate subsystems: one making power, consisting of the air compression train, low-temperature recuperator, combustor, and hot gas expander; and the other making oxygen, consisting of a high-temperature recuperative heat exchanger, an indirectly fired heater, the ITM vessel, and an oxygen cooling and compression train. As such, the power production process can be operated somewhat independently of the ITM process, thus isolating each system from the other, especially during start-up and other transients, and thereby increasing the overall reliability of the process. Notably, the natural demarcation between these two subsystems occurs on the cool side of the high-temperature recuperator, denoted in Figure 12 by the red dashed line, which allows selection of standard control system hardware to accomplish the desired compartmentalization.

This decoupling of oxygen production from power production is facilitated by the development of a separate hot gas expander with its own integrated combustor. The combustor must be capable of operating across the entire range of oxygen concentrations, from normal air to the reduced oxygen content associated with full oxygen production from the ITM, approximately 10 mol% oxygen for the ISTU. In addition, the combustor outlet temperature and expander inlet temperature must be >2,000 °F to compete successfully with other industrial power generation options. This integrated unit is being designed for the ISTU by Williams International as a derivative of their aero-based gas turbine product portfolio. The combustor development is being supported by a 1/3-scale test program currently in progress at Williams.
At the time of this writing, Air Products is in the midst of detailed engineering activities for the ISTU, and the start of construction is imminent. All major equipment is on order; electrical tie-ins are complete; and all environmental permits necessary for construction have been secured. The operation and testing phase of the ISTU project will begin in spring 2012. The test facility will be located at an Air Products commercial air separation plant in Convent, Louisiana.

**Process and economic studies**
Numerous process and economic studies have been conducted on ITM Oxygen, and ITM Oxygen has consistently shown excellent economic performance across multiple applications where oxygen and power are needed. ITM Oxygen technology integrates well with power generation cycles, and studies have shown that ITM Oxygen will result in 25% to 35% reduction in the cost of oxygen compared to conventional cryogenic oxygen plants. ITM Oxygen shows attractive savings toward high-pressure IGCC and decarbonized fuel applications relative to a cryogenic oxygen plant (pumped LOX cycle) and shows even greater power savings toward low-pressure oxygen enrichment and oxyfuel applications relative to a cryogenic oxygen plant (LP cycle). (See ref. iv, vi, vii.)

ITM Oxygen integrates attractively with well-known approaches for CO₂ capture, including pre-combustion capture, post-combustion capture, and oxyfuel combustion capture routes. Different approaches appear optimal toward different applications. Oxyfuel combustion may be targeted toward oxy-combustion end use applications, including new and retrofit pulverized coal power generation with reduced CO₂ emissions. Pre-combustion capture is optimally suited for applications where carbon-free fuel (e.g., hydrogen) is available, for example, in refining (e.g., oxygen for Claus units) or gasification applications such as gas-to-liquids (GTL), coal-to-liquids (CTL), and IGCC power generation. Post-combustion capture is well-suited for applications where common CO₂ recovery equipment may be available for integration, for example, in air-fired coal boilers or retrofit scenarios. Extensive study of ITM Oxygen process cycle development toward power generation with reduced CO₂-emissions was published previously in reference viii. Further engineering study is currently being conducted with input from EPRI and power industry companies toward large-scale power generation with carbon capture, including oxy-combustion (with input from boiler manufacturers) and IGCC (with input from turbine manufacturers).

ITM Oxygen is also attractive to other industries, particularly those using high temperature processes or combustion (e.g., metals processing, pulp and paper, chemicals, petrochemicals, glass) and where oxygen and power are needed. These industries with moderate-scale tonnage oxygen requirements may provide opportunity for early application of ITM Oxygen technology.

**Ceramic manufacturing scale-up**
The ITM Oxygen development program has been focused on ceramic processing development to enable scale-up of ceramic membrane modules to commercial scale. In addition, Air Products, working through its subcontractor Ceramatec, Inc., has been developing methods to manufacture membranes which are scalable to large-scale fabrication operations characteristic of those in the ceramic processing industry.
Conclusions
Excellent results have been achieved in the prototype ITM Oxygen unit, confirming expected membrane performance in terms of flux and purity achieved. Multiple thermal cycles have been performed with unchanged product purity, full size modules were tested and the results of operability testing to date are very positive. These results support and confirm the excellent economic benefits originally projected for the ITM Oxygen technology. Design is nearing completion, and start of construction is imminent on the next step in the scale-up of the technology to an intermediate-scale ITM test facility (100 TPD) to provide a basis for scale-up to plants required for coal gasification, oxy-combustion and clean energy.

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References


v M.F. Carolan et al, US patent #7122072.


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