Praxair, Inc.

O_2-Selective Materials to Lower the Cost of Oxygen

In the mid-1990s, American industries were looking for ways to save energy, cut costs, and contribute to environmental cleanliness, either through improved work processes or new technologies. For example, furnace operators in various industries were interested in converting from air to oxygen (O_2)-enriched air for their combustion processes, but were prevented from doing so by the high cost of oxygen. Oxygen or oxygen-enriched air reduces energy consumption by 25 percent to 60 percent and reduces environmental emissions. However, oxygen prices would have to be reduced by at least 25 percent to provide incentive for most furnace operators to commit the resources necessary to convert to O_2-based processes. Praxair, Inc., the second-largest supplier of industrial gases worldwide, wanted to develop highly efficient O_2-selective materials (materials used to separate oxygen from air) that could be used in sorption or membrane air separation systems. This technology could reduce the cost of oxygen by 25 percent to 50 percent, a sufficient incentive for industrial furnace operators to convert to O_2-enhanced combustion processes.

Due to financial limitations, Praxair was unable to independently fund this long-term project. In 1994, the company was awarded co-funding from the Advanced Technology Program (ATP). By the end of the three-year project, Praxair had successfully developed materials that are highly selective for oxygen. It is unclear whether this class of materials can be applied economically to air-separation systems; however, they may be useful initially in niche commercial applications. In 2003, Praxair has continued to work to bring these materials closer to commercialization through a Department of Energy-funded project in which they are attempting to separate nitrogen and oxygen from air. Although this is a slightly different application, it uses essentially the same class of materials.

COMPOSITE PERFORMANCE SCORE

(based on a four star rating)

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Research and data for Status Report 94-01-0111 were collected during October - December 2002.

Praxair Develops First-Generation Air-Separation System

In the 1950s, industrial gas companies began to recognize the potential of using noncryogenic systems for separating oxygen (O_2) from air. (Cryogenic separation is a distillation process that occurs at very cold temperatures.) By the late 1960s, Praxair, Inc., the second-largest supplier of industrial gases worldwide, had developed a pressure swing adsorption (PSA) unit for producing oxygen using molecular sieves it had invented in the 1950s. The molecular sieve materials used in current commercial PSA systems separate air by selective adsorption of nitrogen. Praxair determined that the PSA process provided a practical vehicle for using O_2-selective sorbents to generate oxygen at a reduced cost. However, there were no commercial O_2-selective materials that met the performance requirements.

In the mid-1980s, Praxair developed the first generation of hollow-fiber membrane systems for air separation, which led to even greater interest in O_2-selective materials. Membrane systems produce nitrogen very efficiently, but the oxygen that was produced had very low purity due to limitations in the selectivity of the membrane materials.

In 1994, when Praxair applied for the ATP award, the company had already spent six years, through an in-house research program, investigating and evaluating the potential benefits of O_2-selective materials in PSA and membrane systems. This preliminary work indicated that equilibrium-based O_2-selective sorbents containing transition element complexes (TECs) had the best chance of overcoming the high-risk technical barriers. A TEC is a combination of a transition element ion to provide an oxygen-binding site and a series of groups provided by organic components to modify the oxygen interaction characteristics.

Praxair Focuses on Advancement of O_2-Selective Materials

Praxair's goal was to develop O_2-selective materials as sorbents for PSA systems and to establish their practicality for use in membrane systems. Preliminary assessments indicated that the cost of producing oxygen could be reduced by 25 percent to 50 percent. In addition, replacing the nitrogen (N_2)-selective sorbents that were being used in PSA systems with this new material could reduce power consumption by 50 percent and production costs by more than 25 percent for oxygen, with purities in the 40 percent to 90 percent range.

Oxygen or oxygen-enriched air reduces energy consumption by 25 percent to 60 percent and reduces environmental emissions.

Although such a technological breakthrough would revolutionize the industrial gas business and the industries it supplies, the research and development (R&D) challenges would be considerable. In 1994, financial limitations had forced Praxair to channel all resources available for R&D into those activities that were most likely to succeed and that would provide the most immediate return on investment. Therefore, Praxair proposed the project to ATP for funding and received a three-year, $1.22 million award.

Lower Oxygen Costs Would Spur Economic Growth

Praxair believed that lowering the cost of oxygen by 25 percent to 50 percent would enable many manufacturers, especially in steel-making, glass-making, and petroleum refining, to switch from air to oxygen or oxygen-enriched air for their combustion processes. This would dramatically improve their manufacturing processes, resulting in less pollution, higher productivity, and lower production costs. For example, switching to oxygen can reduce fuel consumption by 60 percent. The total savings potential for processes that currently use oxygen and for those that could be converted to oxygen or oxygen enrichment was estimated at $378 million annually.

In the long term, this savings could lead to economic growth, increased U.S. competitiveness, and more jobs. In the near term, as individual companies made the investments necessary to change from air to oxygen, other beneficiaries would include equipment suppliers, architecture and engineering firms, construction contractors, and material suppliers.

Material Design Guidelines Are Defined

Praxair's primary goal was to develop a new O_2-selective material that could be used for commercial air separation as a sorbent in PSA systems and that had the potential to lower the cost of oxygen by at least 25 percent. In addition, the company planned to develop high-performance membranes that could be used to separate oxygen from air and other gases via facilitated surface transport (that is, the oxygen would be transported across the membrane, assisted by O_2-selective sites embedded in the membrane). The membranes would be used if sorbent costs were too high.

Lowering the cost of oxygen would dramatically improve manufacturing processes, resulting in less pollution, higher productivity, and lower production costs.

Praxair's approach in developing both the O_2-selective sorbents and the membranes would employ TEC sites. Although there had been attempts by others to use sorbents that incorporate TEC sites, the results had not been cost effective.

Praxair defined a series of material design guidelines so that the company could assess project progress and guide materials development. A material would be considered successful if it met all of the following characteristics:

- **High (oxygen loading) under process conditions.** Oxygen loading is the equilibrium amount of oxygen sorbed by the TEC and is a function of temperature and pressure. Oxygen loading is important because it determines the amount of sorbent needed in a PSA process; thus, it affects manufacturing plant size and, therefore, the manufacturer's capital costs.

- **Fast oxygen interaction rates.** The rate at which oxygen is taken up and released affects sorbent productivity in a process cycle, power, and oxygen recovery.

- **Low cost.** The material cost should be consistent with favorable economics for commercial processes at the performance levels achieved.

- **Adequate lifetime under conditions of use.** TEC sorbent lifetime is the time between sorbent installation and replacement in a PSA system. Unless the lifetime is sufficiently long (the target was greater than 10 years), it will be a major contributor to both capital and operating costs.

- **Minimal hazards.** The sorbent should pose no threat to users or the environment under normal operation or under non-ideal conditions. Sorbent that is used up should be suitable for recycling.

At the beginning of the project, there was no single material that met all of these performance requirements. Praxair's greatest challenges were to increase the lifetime of the sorbent and decrease its cost.

Alternative Applications Considered for New O_2-Selective Materials

With the assistance of academic researchers from Clarkson University, the State University of New York, and Iowa State University, Praxair investigated a number of approaches to materials development. By the end of the project, the company had achieved some success in reaching its original goals. Praxair developed several new materials that were highly selective for oxygen. However, it was unclear at the time whether these materials could be used economically for air separation in PSA or membrane systems. Therefore, Praxair did not pursue these goals after the ATP funding ended. However, Praxair recognized that the properties of the adsorbents produced during the ATP-funded project could potentially be used to produce high-purity nitrogen or to purify nitrogen streams that contain oxygen in a low concentration. Praxair produced approximately two kilograms of the most promising adsorbent.

The company identified a potential application in the aluminum industry that could lead to significant energy savings if the cost of high-purity nitrogen and coproduct oxygen required by the application could be reduced and the product could be commercialized. Within a year after this ATP-funded project ended, Praxair applied for and received funding from the Department of Energy to develop coproduct nitrogen and oxygen from air. Through this project, the company anticipated that it would be able to continue work on the materials developed in the ATP-funded project to bring them closer to commercialization.

Conclusion

Praxair did not reach its goals to develop a new oxygen (O_2)-selective material that could be used commercially as a sorbent for air separation in pressure swing adsorption (PSA) or membrane systems and to lower the cost of oxygen by 25 percent. However, since the ATP-funded project ended, the company has taken the properties of the adsorbents that were developed and is now using them to develop processes to produce coproduct nitrogen and oxygen from air.

Praxair developed several new materials that were highly selective for oxygen.

Since the project's conclusion in 1998, Praxair has been granted three patents for the following: a method for producing nitrogen using O_2-selective adsorbents, a separation process that uses O_2-selective sorbents, and a PSA method for producing an O_2-enriched gas.

PROJECT HIGHLIGHTS
Praxair, Inc.

Project Title: O_2-Selective Materials to Lower the Cost of Oxygen (Advanced Sorbents for Reducing the Cost of Oxygen)

Project: To synthesize, characterize, and demonstrate oxygen-selective materials for use as sorbents in air-separation systems.

Duration: 3/1/1995-2/28/1998
ATP Number: 94-01-0111

Funding (in thousands):

ATP Final Cost	$1,220	51%
Participant Final Cost	1,180	49%
Total	$2,400	

Accomplishments: Praxair developed several new materials that are highly selective for oxygen, which have other potential applications.

Since 1997, Praxair has also been granted the following patents:

- "Method for production of nitrogen using oxygen selective adsorbents"
  (No. 5,735, 938: filed January 15, 1997, granted April 7, 1998)
- "Pressure swing adsorption method for production of an oxygen-enriched gas"
  (No. 6,475,265: filed October 22, 1998, granted November 5, 2002)
- "Process for separation of oxygen from an oxygen containing gas using oxygen selective sorbents"
  (No. 6,183,709: filed January 4, 1999, granted February 6, 2001)

Commercialization Status: The O_2-selective materials developed during this ATP-funded project have not been commercialized. However, as of 2003, Praxair has continued work on their development through a project with the Department of Energy.

Outlook: At this time, it is unclear whether the class of materials developed under this ATP-funded project can be applied economically to the separation of air in pressure swing adsorption systems or membrane systems. According to Praxair, however, it is possible that the materials can be used commercially for niche applications. For example, the company is currently determining whether the materials could serve a role in applications such as oxygen removal from gases or in food packaging.

Composite Performance Score: *

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