**Title**
CRADA Final Report: Ionically Conductive Membranes Oxygen Separation



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CRADA Final Report
CRADA No. BG7-155(00)

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1. Parties: **Praxair, Inc.** (NYSE:PX) is a global, Fortune 500 company that supplies atmospheric, process and specialty gases, high-performance coatings, and related services and technologies.

2. Title of Project: **Ionically Conductive Membranes Oxygen Separation**

3. Summary of the specific research accomplishments:

The original CRADA proposal stated, "***we propose the efficient electrolytic extraction of oxygen from air using novel thin-film structures consisting of high strength ionic membranes supported on porous, catalytic electrodes.***" In the execution of the CRADA, we accomplished this goal. The LBNL and Praxair teams were able to develop porous ceramic structures onto which dense high-strength, ionically conductive zirconia films were deposited. The faradaic efficiency of these structures for $O_2$ separation from air was shown to be 100%. The final objective of the CRADA was to design and demonstrate a benchtop $O_2$ electrolyzer in year 3. In order to achieve this goal tubular structures had to be developed by LBNL and that technology transferred to Praxair. All these objectives were met, and delivered on time.

4. Deliverables:

| Deliverables Achieved | Party (LBNL, Participant, Both) | Delivered to Other Party? |
|---|---|---|
| Delivery of planar $O_2$ separation disk to Praxair | By LBNL | Yes |
| Delivery of tubular $O_2$ separation structure to Praxair | By LBNL | Yes |
| Burst testing of tubular $O_2$ separation structures | By Praxair | Yes |
| Benchtop $O_2$ electrolyzer built | By LBNL and Praxair | Built at Praxair |
| Benchtop $O_2$ electrolyzer demonstration | By Praxair | At Praxair |

5. Identify publications or presentations at conferences directly related to the CRADA?

Steven Visco gave a talk on the development of porous electrode supported thin-film devices at the Ionic and Mixed Conducting Ceramics Symposia at the 192nd Meeting of the Electrochemical Society in Paris, France, September 1997. Since most of the work done under the CRADA involved patentable inventions, we did not publish during this period.

6. List of Subject Inventions and software developed under the CRADA: (please provide identifying numbers or other information).

The LBNL team was exceptionally prolific in the filing of invention disclosures during the 3-year CRADA with Praxair. This list of disclosures follows:

1) US Patent Application No. 60/239,472, entitled "Improved Electrode-Electrolyte Structure for Solid State Electrochemical Devices" corresponding to Berkeley Lab Case No. CIB-1405P1 entitled "Improved Electrode-Electrolyte Structure for Solid State Electrochemical Devices" by S. Visco, L. DeJonghe, and C. Jacobson;

(2) US Patent Application No. 09/626,022, entitled "Solid State Electrochemical Device Electrode Additives" corresponding to Berkeley Lab Ref. CIB-1406 entitled "Surface Additives for Enhanced Electrode Performance" by S. Visco, L. DeJonghe, and C. Jacobson;

(3) US Patent Application No. 09/626,629, entitled "Structures and Fabrication Techniques for Solid State Electrochemical Devices" corresponding to Berkeley Lab Case No. CIB-1418 entitled "Alloy Support Structure for Ceramic Electrochemical Devices" by S. Visco, L. DeJonghe, and C. Jacobson;

(4) Berkeley Lab Ref. CIB-1653: "Method of Forming Thin Ceramic Films" by S. Visco, L. DeJonghe, and C. Jacobson;

(5) Berkeley Lab Ref. CIB-1654: "Metal/Metal Alloy Additives for Making Thin Ceramic Films" by S. Visco, L. DeJonghe, and C. Jacobson;

(6) Berkeley Lab Ref. CIB-1655: "Integrated Heat Exchanger and Interconnect for Electrochemical Devices" by S. Visco, L. DeJonghe, and C. Jacobson;

(7) Berkeley Lab Ref. CIB-1656: "Metal Current Collect Protected by Oxide Film" by S. Visco, L. DeJonghe, and C. Jacobson;

(8) Berkeley Lab Ref. CIB-1657: "Integrated Electrochemical Device Stack Design" by S. Visco, L. DeJonghe, and C. Jacobson;

(9) Berkeley Lab Ref. CIB-1658: "Novel Electrochemical Device Stack Design" by S. Visco, L. DeJonghe, and C. Jacobson;

7. A final abstract suitable for public release: (Very brief description of the project and accomplishments without inclusion of any proprietary information or protected CRADA information.

Scientists at the Lawrence Berkeley National Laboratory (LBNL) in a collaborative effort with Praxair Corporation developed a bench-top oxygen separation unit capable of producing ultra-high purity oxygen from air. The device is based on thin-film electrolyte technology developed at LBNL as part of a solid oxide fuel cell program. The two teams first demonstrated the concept using planar ceramic disks followed by the development of tubular ceramic structures for the bench-top unit. The highly successful CRADA met all technical milestones on time and on budget. Due to the success of this program the industrial partner and the team at LBNL submitted a grant proposal for further development of the unit to the Advanced Technology Program administered by the National Institute of Standards. This proposal was selected for funding, and now the two teams are developing a pre-commercial oxygen separation unit under a 3-year, $6 million dollar program.

8. Benefits to DOE, LBNL, Participant and/or the U.S. economy.

The global market for industrial oxygen is estimated at $20 Billion annually, of which the U.S. market is over $2 Billion. The dominant technology for the production of commercial oxygen is cryogenic distillation. The high capital equipment costs for cryogenic $O_2$ limits this technology to large installations. The distribution of oxygen from a central cryogenic plant is largely accomplished by shipment of $O_2$ in high-pressure cylinders. For every 1 pound of $O_2$ moved in this manner, 5 pounds of steel are transported. This inefficiency of this distribution network is a direct result of centralized production of $O_2$. Accordingly, the market for on-site generation of high purity oxygen has been estimated at roughly $1 billion in the U.S. In order to capture this market the commercial generator must have competitive operating costs, long life, and reasonable capital cost. The electrolytic generator under development by LBNL and Praxair can meet those demands. Consequently, the benefits to the U.S. economy could include significant job creation, introduction of an energy efficient process for on-site $O_2$ generation, and significant revenues to a U.S. corporation. The benefit to DOE would include technical spillover to the solid oxide fuel cell development efforts.

9. Financial Contributions to the CRADA:

| | |
|---|---|
| DOE Funding to LBNL | $550K |
| Participant Funding to LBNL | $185K |
| Participant In-Kind Contribution Value | $375K |
| Total of all Contributions | $1,110K |

## Schedule of the 3-year LBNL Effort under the LBNL/Praxair CRADA

| ID | Task Name |
|---|---|
| 1 | **Oxygen Separation CRADA** |
| 2 | **LBNL Effort** |
| 3 | **Small Planar Oxygen Generator: Year 1** |
| 4 | Fabrication of porous support |
| 5 | Deposition of YSZ membrane |
| 6 | Deposition of oxygen electrode |
| 7 | Testing of small planar LBNL device |
| 8 | Delivery of planar LBNL device to Praxair |
| 9 | Longterm (1000 hr) testing |
| 10 | Characterization of microstructures |
| 11 | Theoretical modeling |
| 12 | **Scaleup to Tubular Oxygen Generator: Year 2** |
| 13 | Fabrication of tubular porous support |
| 14 | Deposition of YSZ membrane |
| 15 | Deposition of oxygen electrode |
| 16 | Testing of tubular device at LBNL |
| 17 | Delivery of tubular LBNL cell to Praxair |
| 18 | Mechanical testing of tubes |
| 19 | Modeling studies |
| 20 | Initiate design of benchtop unit |
| 21 | **Construction of Benchtop Unit: Year 3** |
| 22 | Co-design benchtop unit |
| 23 | Sealing and manifolding of tubes |
| 24 | Fabrication of tubular cells for prototype |
| 25 | Fabricate electrolysis unit |
| 26 | Troubleshooting of prototype |
| 27 | Benchtop unit built |
| 28 | Demonstration and testing of unit |