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OXYGEN PRODUCTION USING SOLID-STATE ZIRCONIA ELECTROLYTE TECHNOLOGY

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ABSTRACT

High purity oxygen is required for a number of scientific, medical, and industrial applications. Traditionally, these needs have been met by cryogenic distillation or pressure swing adsorption systems designed to separate oxygen from air. Oxygen separation from air via solid-state zirconia electrolyte technology offers an alternative to these methods. The new technology has several advantages over the traditional methods, including reliability, compactness, quiet operation, high purity output, and low power consumption.

INTRODUCTION

The Process

Solid-state zirconia electrolyte technology is made possible by the fact that zirconia is one of a number of materials that is electrically insulating but that can conduct ionic oxygen. Because of this attribute, zirconia can be used as the electrolyte in an electrolytic or galvanic cell. In either case, the zirconia is sandwiched between two gas permeable electronically conducting electrodes. The electrolytic cell, Figure 1, is the basis for the oxygen separation cell.

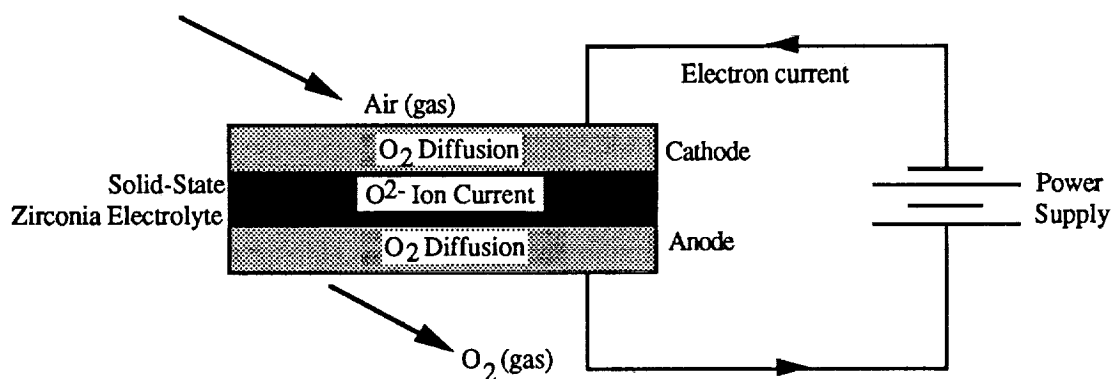
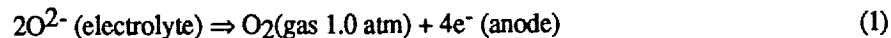


Figure 1. Electrolytic Cell (Oxygen Separation Cell)

The energy necessary to drive the separation process is supplied by the power supply. Oxygen in the air diffuses through the cathode to the cathode-electrolyte interface. Under the influence of the applied voltage, oxygen molecules are dissociated and reduced to oxygen ions, O^{2-} . As an ionic species, oxygen enters the crystal lattice of the electrolyte and moves toward the anode. At the anode, each ion gives up its two electrons which then enter the anode and return to the power supply, completing the circuit. The oxygen atoms recombine into O_2 and diffuse out through the anode. Because the zirconia conducts only oxygen ions, the gas on the output (anode) side of the cell is pure oxygen. Equation 1 describes the reaction.



To impart oxygen ion conductivity to the material, pure zirconia (ZrO_2) must be doped with another oxide such as calcia (CaO) or yttria (Y_2O_3). [1] Each dopant cation (Ca^{2+} or Y^{3+}) replaces a Zr^{4+} ion; the net result is that the doped crystal is electrically neutral without having all oxygen ion sites filled. These oxygen ion vacancies impart in the substance an appreciable oxygen ion conductivity. Because the ionic conductivity is a strong function of temperature, the typical operating temperature of solid-state zirconia electrolyte cells is 1000 C.

Thermodynamic Considerations

The laws of thermodynamics play a major role in determining the power consumption of any oxygen separation system.

Oxygen separation in the solid-state zirconia electrolyte oxygen separator is driven by the current provided by the power supply. Part of the overall power consumption is due to the thermodynamically reversible process of separating oxygen from nitrogen and the other gases that make up air. The rest of the power consumption is caused by irreversible processes including electrical resistance in the electrodes, ionic resistance in the electrolyte, and parasitic effects that occur at the electrodes.

The reversible part of the power consumption is manifested by a voltage across the oxygen separation cell called the Nernst voltage. This voltage is a function of the difference in oxygen partial pressure on the two sides of the cell; the greater the difference, the greater the voltage. For a 1000 C cell separating oxygen from air at atmospheric pressure, the Nernst voltage is 44 mV.

Because the ionization reaction takes place inside the cell (at the cathode-electrolyte interface), the structure of the electrodes can have a major effect on cell performance. Gaseous oxygen may diffuse through pores in the electrodes, or it may diffuse through the electrode material itself. Because the presence of electrodes will reduce the rate of oxygen transport to and from the zirconia electrolyte, regions of oxygen starvation and oxygen enrichment are formed at the cathode and anode respectively. The presence of these starved and enriched regions results in an increase in the Nernst voltage. This (irreversible) enhancement of the Nernst voltage is sometimes called gas-phase polarization. A major portion of the development work performed at JPL has been directed toward development of electrode materials that minimize gas phase polarization.

ADVANTAGES OF SOLID-STATE ZIRCONIA ELECTROLYTE OXYGEN SEPARATION

Separation of oxygen from air or other oxygen-containing gases by the solid-state zirconia electrolyte technique has several advantages over traditional methods of separation like cryogenic distillation or pressure-swing adsorption.

Separation of oxygen by solid-state zirconia electrolyte technology lends itself well to modular construction, and thus is easily scaled. JPL has developed patented circular oxygen separation cells that can be stacked, forming a multi-cell stack; multiple stacks can be manifolded together within a common furnace to form a multi-stack module. The modularity inherent in the technology also simplifies maintenance procedures.

Equation 1 indicates that transfer of four electrons is required to conduct each oxygen molecule (O_2) through the electrolyte. Thus it is a simple matter to control the rate of oxygen production by controlling the current applied to the cells. This feature reduces the storage requirements of oxygen separation units and allows operators to better match production to demand. On a small scale, solid electrolyte cells could be used to meter precise amounts of oxygen to partial oxidation processes.

The basic solid electrolyte separation cell has no moving parts. This fact contributes to the high inherent reliability of the technology. The lack of moving parts, combined with the continuous, rather than batch, nature of the process result in a quiet, vibration-free system.

Because the separation of oxygen from air by a solid-state zirconia electrolyte cell is an electrochemical process, the oxygen output stream is 100 percent oxygen. Other separation schemes, such as cryogenic distillation or pressure swing adsorption, cannot produce oxygen of this purity due to the basic processes used.

APPLICATIONS OF SOLID-STATE ZIRCONIA ELECTROLYTE TECHNOLOGY

Medical

Solid-state zirconia electrolyte technology has been proposed for several medical applications. Because of the modularity of the technology, application in home, hospital and portable settings are feasible. A block diagram of a home medical unit is shown in Figure 2.

A blower gathers fresh air and forces it through a series of small recuperative heat exchangers. Then, after passing through the startup heater, the air enters the zirconia oxygen separation module. The module separates approximately 50 percent of the oxygen from the input air stream. The oxygen and oxygen depleted air streams pass through heat exchangers before leaving the unit. The heat exchangers thus serve to preheat the input air, reducing the load on the startup heater, and cool the output streams, reducing the amount of waste heat leaving the unit.

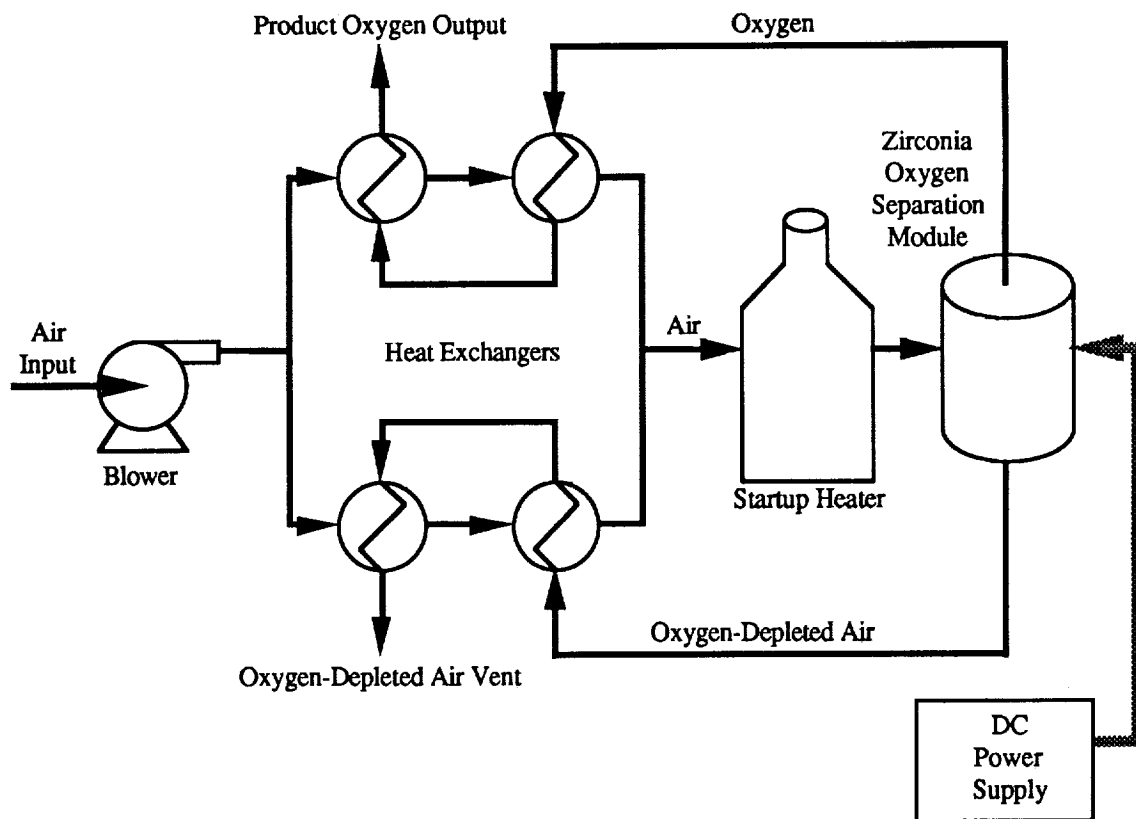


Figure 2. Home Medical Oxygen Supply Unit

Industrial

Solid-state zirconia electrolyte technology has also been considered in a number of industrial applications. A similar system to that shown in Figure 2 is used in an industrial application. Of course, the size is much larger depending on the quantity of oxygen required. The inherent modularity of the zirconia electrolyte technology permits the construction of units ranging from a few liters/min of oxygen to tons per day. Applications considered for this technology include hospital supply, fish farming, weld shop and metal fabrication, coal gasification, and basic metal refining.

Aerospace

The inherent high reliability of the zirconia oxygen separation process makes the technology attractive for several aerospace applications.

Feasibility studies are currently underway at JPL to determine the suitability of solid-state zirconia electrolyte technology for application in spacecraft-borne sensor coolers. In this application, the zirconia cell would be used as an oxygen pump in a closed-loop Joule-Thomson cooling cycle. The lack of vibration-inducing moving parts makes this scheme especially attractive for sensitive optical systems.

Another application for the technology in space is In-Situ Resource Utilization (ISRU). ISRU refers to the utilization of resources available in space, such as Lunar soil or Martian atmosphere, for propellants, life support, and fabrication. Solid-state zirconia electrolyte technology has been identified as a key element in systems to extract oxygen from Lunar soil air and the Martian atmosphere.

JPL ACCOMPLISHMENTS

Project History

JPL has been working in the field of solid-state zirconia electrolyte technology since 1978. In 1984, the U. S. Department of Energy funded an effort intended to develop oxygen separators for use in coal-fired power plants. JPL made several major accomplishments in the development of this technology during the DOE effort [2, 3]. These accomplishments were focused on cell geometry design, component fabrication techniques, and cell testing.

Cell Geometry

A major factor affecting solid-state zirconia electrolyte oxygen separation cell performance is cell geometry. The presence of ionic resistivity dictates that the zirconia electrolyte should be made as thin as possible. Zirconia tubes are in common use but the wall thickness is very large (~1mm). In this case, electrodes are applied on both the inside and outside surfaces of the tube. Air is passed through the center of the tube, and oxygen is conducted through the tube wall to the outside. In addition to the wall thickness, another major drawback to this geometry is the fact that the supply air is depleted of oxygen as it travels the length of the tube; there is little oxygen left in the air by the time it reaches the far end of the tube. This oxygen starvation increases the oxygen partial pressure difference across the cell and results in an increased Nernst voltage and higher power consumption.

JPL addressed the problem of oxygen starvation by developing a cell geometry based on a circular electrolyte disk. As shown in Figure 3, the supply air enters one side of the cell around the circumference of the disk and is directed toward its center by a number of radial ribs. Oxygen is removed as the air travels toward the center of the disk. Because the cell area available to a given quantity of input air is reduced as the center is neared, the increase in Nernst voltage is not as severe as is seen in tubular designs. Computer models indicating the superior performance of this patented design have been confirmed by experimental data. The ribs support the zirconia permitting very thin (~0.05 mm) membranes to be used. The ribs also serve as busbars to carry current to the cell electrodes. [4]

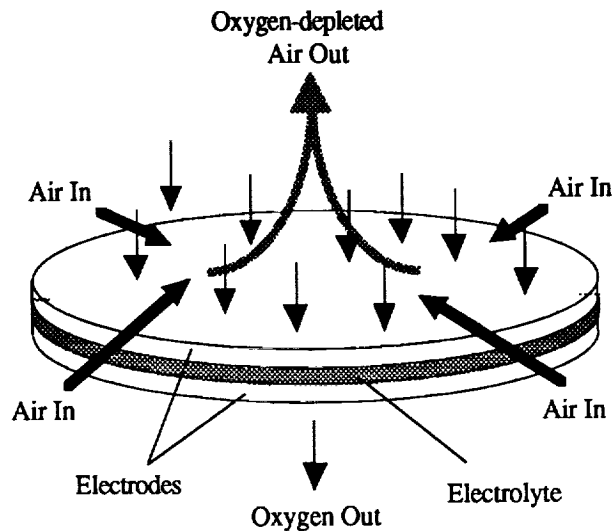


Figure 3. Radial Air Flow, Axial Current Flow Circular Disk Oxygen Separation Cell Geometry (Ribs not shown)

Component Fabrication

JPL developed a patented process for fabrication of the zirconia electrolyte membrane. [5] In this process, conductive ceramic electrodes are applied to the zirconia electrolyte before firing. The method is capable of producing three layer (electrode-electrolyte-electrode) composite oxygen separation membranes with zirconia thickness less than 0.05 mm thick. The firing cycle and temperature were substantially reduced in this patented process. In addition, JPL has developed the ability to fabricate ceramic cell casings.

Testing

As part of the Department of Energy-sponsored effort, JPL built and tested more than sixty single cell oxygen separation units. In addition, ten multicell stacks were tested; three of these were capable of producing 1 standard liter of oxygen per minute each.

Current Work

In addition to promotion of earth-bound applications of the technology, current work at JPL is focussed on studies to determine the suitability of solid-state zirconia electrolyte technology for use in aerospace applications. Two applications under consideration are In-Situ Resource Utilization, in which oxygen would be produced from Lunar soil or the Martian atmosphere, and cryogenic refrigeration, which involves use of a zirconia-based oxygen pump.

TECHNICAL CHALLENGES

The major technological obstacles to commercialization of solid-state zirconia electrolyte technology stem from the high operating temperature required by the process. To eliminate the need for expensive precious metal electrodes and interconnects, JPL's oxygen separation cells use strontium-doped lanthanum manganite (LSM), an electrically conductive ceramic, for both electrodes and cell interconnections. Not only is this material electrically conductive, it is mechanically and chemically stable at 1000 C.

While the problem of expensive interconnects has been eliminated by the use of LSM, sealing of the cells continues to be difficult. The majority of JPL-built separation cells to date have relied upon precision-ground flat seals to contain the the product oxygen. While suitable for use in applications that lack a

requirement for pressurized output, the flat seals are incapable of supporting a pressure differential of more than 4 kPa (0.6 PSI). Follow-on work at JPL will concentrate on development of higher pressure seals.

JPL also intends to examine other oxygen ion-conducting materials such as delta-bismuth oxide. Data reported in the literature indicate that this material has a higher ionic conductivity than doped zirconia, and can operate at a lower temperature.

CONCLUSIONS

JPL has developed an oxygen separation system that is modular and reliable and without moving parts. The power consumption is lower than for other oxygen separation systems. The ceramic fabrication technology has been developed to the point where cells and stacks are easily fabricated. Still required in the development is the successful use of seal technology to provide high pressure, 100 percent purity oxygen to a variety of applications including medical, industrial, and aerospace.

How to License The Technology

Patents held on this technology are the property of the California Institute of Technology. Organizations interested in licensing this technology should contact the California Institute of Technology, Office of Patents and Licensing, (818) 356-4567.

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