THE DEVELOPMENT OF A ZIRCONIA CELL FOR GENERATING OXYGEN FROM THE MARTIAN ATMOSPHERE

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Generation of oxygen from the Martian atmosphere for In-Situ Propellant Production (ISPP) has been described as "a potential near-term application of the general concept of producing materials from extraterrestrial sources" (1). Other concepts of extra terrestrial material processing include water electrolysis and extratereestrial soil processing. The concept of ISPP on the surface of Mars has been discussed by investigators too numerous to list in a short abstract (1), experimental development of the processing cell has been very limited (2).

This abstract presents a brief description of experimental development work conducted at the Jet Propulsion Laboratory (JPL) for the U.S. Department of Energy (DOE) on a high temperature, zirconia oxygen separation membrane removing oxygen from air. The discussion of results and concept will center around the separation of air from oxygen and has been discused in greater detail in a prior publication (3). The impact of the Martian atmosphere on the performance of the cell is discussed at the end of the paper.

ZIRCONIA OXYGEN SEPARATION

The oxygen separation ability of zirconia is rooted in the oxygen ion conduction capability of the material. Oxygen vacancies exist in the crystal lattice of the material that provide oxygen conduction sites for transport of oxygen ions through the material. The driving force of this transport is the potential applied across the membrane by a DC power supply.

In operation, the oxygen-containing gas passes over the separation membrane. The membrane consists of the zirconia sandwiched between electronically conductive porous electrodes. Oxygen molecules diffuse through the porous electrode to the zirconia/electrode (cathode) interface. At or near this region, oxygen is decomposed from diatomic molecules to single oxygen ions with a negative valance of two. The electrons are supplied by the DC power supply through the porous electrode. The potential gradient applied by the power supply drives the oxygen ions into the zirconia membrane through the surface oxygen vacancies in the zirconia crystal lattice.

The oxygen ions move through the zirconia from vacancy to vacancy until they appear at the anode zirconia/electrode interface. Here the electrons are given up and are recycled through the power supply thereby completing the circuit. The diatomic oxygen molecule is reformed and diffuses to the free stream surface of the porous electrode.

Energy is consumed by ohmic losses in the electrodes and the electrolyte and by the adverse chemical potential created by "pumping" the oxygen from a low concentration on the supply-side to a higher concentration (100 volume percent) on the oxygen discharge side. A back EMF is generated by this concentration difference. The back EMF represents the chemical potential difference of oxygen across the zirconia membrane and is called the Nernst voltage.

CELL DESIGN

A number of different geometries have been tested as potential cell configurations. These include tubular, square plate, and circular disk geometries. The tubular geometry is readily available from commercial suppliers and represents current state of the art in zirconia manufacture. The tubes are thick walled compared to the requirements for oxygen separation. Square plates are not commercially available but can be made as thin membranes. Stackability of the square plates allows for a series electrical connection which optimizes the power supply. Circular disks offer the same benefits as square plates with the additional benefit of more uniform and lower power consumption per unit area of zirconia.

A patent is pending for the circular disk design. The uniqueness of the circular disk design is in the radial gas flow inward toward the center of the disk. As the supply gas flows towards the disk center, oxygen is removed. The lower oxygen partial pressure causes an increase in the Nernst bucking voltage. With linear flow configurations such as the tube or the square plate, the oxygen partial pressure drops quickly producing a high Nernst bucking voltage and therefore a high power consumption. The radial flow of the circular disk has a reducing active area as the flow moves toward the center, therefore the oxygen removal rate is reduced and the partial pressure of oxygen does not drop as dramatically as with linear flow arrangements.

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A number of circular disk cells were tested using all ceramic casing construction and used both platinum and ceramic electrodes. The ceramic electrode is a electronically conductive perovskite, strontium-doped lanthanum manganite. A maximum of 500 hours with power applied was achieved with 160 hours at a current density of 275 millamps/square centimeter.

MATERIALS FABRICATION

The most important part of the research centers around the fabrication of the materials used in the zirconia module. The separation membrane consists of a sandwich of electrode/electrolyte/ electrode material. The requirements for these sandwiches are:

- electrolyte thickness less than 100 microns
- flat and uniform in thickness
- electrolyte to be gas impermeable
- electrode to have approximately 40 percent porosity
- electrode and electrolyte to be joinable
- capable of design conformity

The requirements were used to evaluate various manufacturing methods. A partial list of methods evaluated including tape casting, slip casting, isopress and sinter, hot isopress, chemical vapor deposition (CVD), and sputtering.

Tape casting was chosen because of its ability to meet the requirements for fabrication as well as the maturity of the technology. Additionally, tape casting permits multiple layer casting and lamination.

Procedures for tape casting including formulation of the ceramic slip used in the casting process and procedures were developed and production of ceramic components was started. In addition to the conventional tape cast products a new formulation using tape casting was developed that was used to produce electrode/electrolyte sandwiches at lower sintering temperatures. The lower sintering temperature eliminates some inherent problems associated with the previous approach to tape cast sandwich manufacture.

MODELLING STUDIES

The performance of the individual cells has been modelled by a finite difference program developed for each of the geometries considered in the test cell development. The modelling programs determine the concentration profiles, pressure profiles, and power profiles as well as local and total voltages and currents for the cell configurations. The modelling effort identified the radial flow circular disk design with axial electron flow as the optimum approach to minimizing the power consumption.

ISSUES RELATING TO THE MARTIAN ENVIRONMENT

There are two primary issues that must be addressed for use of the separation membrane in the Martian environment - 1) electrode type to use on the supply side of the membrane and 2) the magnitude of Nernst bucking voltage. Both isuues are rooted in the lower partial pressure of oxygen in the Martian environment. The lower partial pressure of oxygen requires an electrode that will not reduce. The currently used ceramic electrodes may reduce in cease electronic conductivity in the ISPP application. The bucking voltage due to an increased concentration difference across the membrane will increase the power consumption. Both issues require experimental determination as to the magnitude of difficulties introduced in the ISPP application.

REFERENCES

1. Frisbee, R.H., French, J.R. Jr., and Lawton, E.A. (1987) A New Look at Oxygen Production On Mars - In-Situ Propellant Production (ISPP). Presented at AIAA 25th Aero Space Sciences Meeting, January 12-15, 1987, Reno, Nevada. AIAA-87-0236.

2. Richter, R. (1981) Basic Investigation into the Production of Oxygen in a Solid Electrolyte Process. AIAA-81-1175 June 1981.

3. Suitor, J.W. (1986) Zirconia Oxygen Cell Source. To be published in the Proceedings of the Instrumentation, Components, and Materials Contractors Meeting, September 16-17, 1986. U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, West Virginia.