CENTENARY OF NERNST’S DISCOVERY OF ZIRCONIA ELECTROLYTES - REVIEW OF ZIRCONIA-BASED ELECTROCHEMICAL TECHNOLOGIES

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ABSTRACT

In 1899, W. Nemst published a paper entitled “On the Electrolytic Conduction of Solid Bodies at Very High Temperatures” in Zeitschrift für Elektrochemie. In this paper, Nemst reported his discovery of ionic conduction in solid zirconia at high temperatures and described his experiments, observations, and conclusions on the electrical conduction of the material. Since that time, the science and technology of zirconia electrolytes has advanced significantly. Zirconia electrolytes are the fundamental building block for solid oxide fuel cells, oxygen generators, electrolysis cells, oxygen sensors, and integrated ceramic reactors. This paper is written to mark the centenary of the discovery and discusses certain aspects of several important zirconia-based electrochemical technologies.

INTRODUCTION

In 1899, Professor Dr. W. Nernst published a paper entitled “On the Electrolytic Conduction of Solid Bodies at High Temperatures” in Zeitschrift für Elektrochemie (1). In this paper, he reported the experimental results and other observations to demonstrate and confirm ionic conduction in zirconia for the first time. The key results and observations given in this paper include:

- Pure zirconia had very low conductivity but mixtures of zirconia with other oxides such as magnesium oxide showed high conductivity at high temperatures.
- Nernst observed that the color of the mixture was white and clear, an indication of ionic conduction (not electronic or metallic conduction).
- Electrolysis experiments confirm the ionic conduction nature of the mixture.
- Oxygen is required for the ionic conduction in the mixture.

Since that time, it has become known that doping zirconia with other oxides enhances the ionic conductivity. The oxygen ion conducting properties of doped or stabilized zirconia have been studied extensively. The material has been developed for use as solid electrolytes and has become the basis for a number of important electrochemical technologies, including solid oxide fuel cells (SOFCs), oxygen separators and concentrators, electrolysis cells, oxygen sensors, and integrated reactors.
SOLID OXIDE FUEL CELLS

SOFC technology is the most important application of zirconia electrolytes. The SOFC has been developed for use as a clean and efficient power source operating on a variety of fuels (2). A SOFC cell typically consists of a stabilized zirconia electrolyte sandwiched between two electrodes (the anode and cathode). The common zirconia electrolyte for SOFCs is based on yttria-stabilized materials (YSZ). With hydrogen fuel and oxygen oxidant, a SOFC cell produces less than 1 V. Therefore, for practical uses, SOFC cells are connected in electrical series to build voltage. A component, referred to as an interconnect, connects the cathode of one cell to the anode of the next in a SOFC stack. For YSZ-based SOFCs, the other cell materials are strontium-doped lanthanum manganite for the cathode, nickel/YSZ for the anode, and doped lanthanum chromite for the interconnect (3). Current SOFCs operate at about 1000°C and atmospheric pressure. Figure 1 shows, as an example, a microstructure of a SOFC cell.

![Microstructure of SOFC Cell](image)

Figure 1. Microstructure of SOFC Cell (Fabricated by Tape Calendering)

At present, SOFCs have been tested for tens of thousands of hours. Power systems up to 100 kW have been operated. The current trends in the development of SOFC technology have focused on two areas: (i) to operate the fuel cell at high pressures (3 to 10 atmospheres) (4) and (ii) to reduce the operating temperature to below 800°C (5). Operating a SOFC at elevated pressures leads to increase in cell voltage, thus power output for a given current. In addition, the elevated operating pressure enables SOFC integration with a gas turbine in a hybrid system with significant increase in efficiency. Operating a SOFC at reduced temperatures provides several advantages including wider choice of cell and ancillary materials, longer cell life, reduced thermal stress, and potentially lower fuel cell cost. One important feature of reduced-temperature operation for SOFCs is the possibility of using low-cost metals for the interconnect.
SOFC zirconia electrolytes have been fabricated by a variety of processes, and each fabrication process has been selected depending on the specific stack design. For example, electrochemical vapor deposition (EVD) has been used to produce zirconia electrolytes for the sealless tubular design; plasma spraying for the segmented-cells-in-series design; and tape casting for the flat-plate design (2). Recently, other techniques have also been developed and evaluated for making thin (1 to 25 micrometers) electrolytes for reduced-temperature SOFCs. Table 1 lists a selected number of these fabrication processes.

Table 1
Selected Fabrication Processes for Thin Zirconia Electrolytes

| Process             | Description                                                                                   | Ref. |
|---------------------|----------------------------------------------------------------------------------------------|------|
| Coat Mix Process    | YSZ layers are applied on a partially sintered porous anode by vacuum slurry coating.         | (6)  |
| Dip Coating         | Zirconia films are formed on porous electrode substrates immersed in YSZ slurries or colloidal suspensions. | (7)  |
| Electrophoretic     | YSZ particles are deposited from a suspension onto a substrate electrode of opposite charge upon application of a DC electrical field. | (8)  |
| Deposition          |                                                                                              |      |
| Spin Coating        | YSZ films are produced on a dense or porous substrate by spin coating a sol-gel precursor.    | (9)  |
| Sputtering          | YSZ films are sputter-deposited from metal targets on porous electrode substrate using an electric discharge in an oxygen/argon mixture. | (10) |
| Tape Calendering    | YSZ films are formed on an electrode support by rolling YSZ and electrode tapes between a two-roll mill. | (11) |
| Vapor Deposition    | YSZ films are deposited on a substrate by spraying atomized precursor droplets across a heated environment | (12) |

Other thin-film techniques investigated for zirconia electrolyte fabrication include vapor-phase electrolytic deposition, spray pyrolysis, vacuum evaporation, liquid injection plasma spraying, laser spraying, jet vapor deposition, electrostatic spray deposition, and plasma metal organic chemical vapor deposition.

**OXYGEN SEPARATORS/CONCENTRATORS**

Zirconia electrolytes have been used in a number of gas separation/concentration applications. One typical example is oxygen concentration/separation/compression devices. For example, air separation using zirconia electrolytes has been considered as an alternate oxygen production process other than air liquefaction (13). The common construction of these devices is a stack of cells connected in electrical series, each cell consists of a zirconia membrane and two electrodes. Unlike the SOFC, same materials can be used for the anode and cathode since both electrodes are exposed to oxidizing environments (oxygen and air). The operating principle of these devices is based on
oxygen ion conduction in stabilized zirconia, and the driving force for oxygen separation is a potential (voltage) applied across the zirconia electrolyte. During operation, oxygen in the inlet gas stream is reduced to oxygen ions at the cathode. Oxygen ions conduct through the electrolyte and are combined (oxidized) at the anode to produce pure oxygen.

Zirconia-based oxygen separators/generators offer several attractive features including all solid state, no moving parts, 100% pure oxygen, and efficient oxygen generation. The potential uses include commercial oxygen production and oxygen separation for military aircraft, land vehicles, and shipboards. Because of high oxygen selectivity and high operating temperature, zirconia electrolytes can be used as filters to provide protection from contaminants. The oxygen ion conduction of zirconia allows only oxygen ions to pass through it, and the high operating temperature quickly degrades chemical and biological contaminants. In addition, zirconia electrolytes can be used to generate compressed oxygen. This type of device can extract oxygen from air at ambient pressure and simultaneously compress the oxygen to, for example, 2,500 psig for high-pressure applications (14).

**ZIRCONIA ELECTROLYSIS CELLS**

Zirconia electrolysis cells are ceramic devices that electrochemically reduce an oxygen containing reactant to generate oxygen and other products. The operation of a zirconia electrolysis cell is the reverse of that of a SOFC. In the zirconia cell case, a direct-current power source provides the electron flow from the anode to the cathode in the external circuit. The oxygen containing reactant, fed to the cathode, accepts electrons from the external circuit and converts to oxygen ions and other gaseous products. Oxygen ions conduct through the zirconia electrolyte to the anode and combine to form oxygen gas and release electrons to the external circuit. Two examples of the use of zirconia cells are electrolysis of steam to produce oxygen and hydrogen (15) and oxygen generation from carbon dioxide (16).

Zirconia electrolysis cells have been developed for hydrogen production from steam. The advantages of this process compared to conventional water electrolysis include favorable thermodynamics and improved reaction kinetics at high temperatures. Multicell stacks have been assembled from small cylinders of zirconia electrolyte coated on both sides with porous electrodes. A specific energy consumption of 3.2 kW/cubic meter of hydrogen has been demonstrated.

Zirconia electrolysis cells have been considered for oxygen production from carbon dioxide for use as propellant and life support in Mars in-situ resource utilization production plants. In this concept, carbon dioxide from the Martian atmosphere (mean pressure of 640 Pa and mean temperature of 200K) is pressurized, heated, and passed through a zirconia electrolysis cell. The gas is reduced inside the cell to carbon monoxide and oxygen. The oxygen formed is separated from the gas mixture by the zirconia electrolyte. The oxygen is finally liquefied and stored for its final use. Figure 2 shows, as an example, the voltage/current curves of a laboratory-scale zirconia cell stack (3-cell) being developed for this application.
The most important commercial application of zirconia electrolyte is oxygen sensor for automobile combustion control (17). This type of sensor is essentially an oxygen concentration cell. It is simply constructed with a closed-one-end zirconia tube with appropriate electrodes deposited on both sides of the electrolyte tube. When the two sides of the sensor are exposed to different oxygen partial pressures $P_1$ and $P_2$, an electromotive force (emf) develops across the electrodes given by the Nernst equation:

$$\text{emf} = \frac{RT}{4F} \ln \left( \frac{P_1}{P_2} \right)$$

where $R$ is the gas universal constant, $T$ is the temperature, and $F$ is the Faraday. If $P_1$ is the known reference oxygen partial pressure and emf and $T$ are measured, the unknown $P_2$ can be obtained from the above equation. In an automotive oxygen sensor, air is normally in contact with the inner electrode. The outer electrode is exposed directly to the exhaust gas. Over the typical 350° to 800°C exhaust gas operating conditions, the zirconia sensor output will be about 50 mV when the exhaust is lean, and about 900 mV when the exhaust is rich. Zirconia electrolytes are fabricated by conventional ceramic processing techniques such as isostatic pressing. The outer electrode is exposed to the hot, abrasive gases of the engine exhaust. Because of this, the outer electrode surface is plasma sprayed with a protective layer such as magnesia-alumina spinel. Figure 3 shows an example of a schematic diagram of an oxygen sensor. The advantages of this type of sensor are (i) quick and continuous measurement, (ii) electrical signal output suitable for electronic control systems, and (iii) accuracy and simple design. In addition, zirconia electrolytes have also been used for oxygen sensing in other high-temperature environments such as iron and steel melts (18).

**OXYGEN SENSORS**

Figure 2. Voltage/Current Curves of Three-Cell Stack for CO$_2$ Electrolysis at 800°C
INTEGRATED CERAMIC REACTORS

Zirconia electrolytes have been considered for use in ceramic reactors for chemical conversion (18). An example is the integrated reactor concept. The reactor is a ceramic composite structure consisting of two layers: the selective layer and the catalytic layer. Theoretically, an integrated reactor requires no, or very little, external energy to drive the process. The selective layer permits the migration of the reactant but rejects other impurities. As the reactant travels into the catalytic layer, it is converted to a product (Figure 4). The product is swept by convection forces for collection.

One example is an integrated reactor for hydrocarbon oxidation and hydrogenation processes. The selective layer of this reactor is made of stabilized zirconia and ceria or titania, which provides a mixed oxygen ion and electron conducting function. The
catalyst layer consists of porous zirconia impregnated with a metal oxide catalyst, which provides the ion conducting function. Air flows on the selective side, and hydrocarbon gas flows on the catalytic side. Oxygen ions pass through the mixed conducting layer and catalytically react with the hydrocarbon in the porous catalytic layer. The product is separated from the porous layer while electrons pass through the mixed conducting layer to balance the system.

The key benefits of the integrated reactor include lower reagent requirements, higher conversion efficiencies, and lower costs. Another feature of the reactor is that, by changing operating parameters such as temperature, thickness of the selective and catalytic layers, the system can be tailored to manufacture a wide spectrum of other products.

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