ION CONDUCTING CERAMIC ELECTROLYTES:
A CENTURY OF PROGRESS

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ABSTRACT

The evolution of sodium, oxygen and hydrogen ion conducting ceramic electrolytes will be traced with particular attention given to oxygen ion conductors. These materials such as the stabilized zirconias are critical to the commercial success of oxygen sensors, the solid oxide fuel cell (SOFC) and devices separating oxygen from air. They also can play significant roles as protective coatings for other oxygen ion conductors and in the synthesis of sodium-ion conducting ceramic composites. This overview will also include an assessment of mixed ionic/electronic conducting oxides employed in oxygen separation devices, the partial oxidation of methane, and in the development of composite anode and cathode structures in the SOFC. The development of rechargeable beta batteries for electric vehicles and load leveling energy storage systems employing sodium-ion conducting β'"-Al2O3 electrolytes will be placed into perspective with the evolution of SOFC power generation systems.

INTRODUCTION AND HISTORICAL PERSPECTIVE

At the beginning of the 20th century, research began on polycrystalline ceramic electrolytes. In 1916 Rankin and Merwin (1) discovered what they believed to be a new polymorph of Al2O3 and named it beta-alumina (β-Al2O3). This designation was retained even when it was determined later that the material contained ~ 10 mol % Na2O (2) and was actually a sodium aluminate. β-Al2O3 was used commercially as a glass-furnace refractory before it was 'rediscovered' to be a good conductor of sodium ions with an ionic conductivity at 300°C of ~ 0.07 S/cm. β'"-Al2O3 was subsequently discovered with a higher Na2O concentration (~ 13 mol % Na2O) and with a significantly higher sodium-ion conductivity of ~ 0.25 S/cm (2,3). Furthermore, oxides such as Li2O and/or MgO in solid solution, and at concentrations of ~ 2.6 and ~ 10 mol %, respectively, were required to stabilize the β"-Al2O3 phase during sintering/annealing and to enhance the sodium ion conductivity (2,3). The cation dopants (Li+ and/or Mg2+ substituting for Al3+) are compensated electrically by mobile interstitial sodium ions situated in two-dimensional conduction planes, i.e. 2[LiAl3+] = [Na+] or [MgAl1/2] = [Na+]. By the early seventies, thin-walled β"-Al2O3 electrolyte tubes could be fabricated by several processing routes with acceptable ionic conductivities, negligible electronic conductivity, sufficient mechanical strength, and electrochemical stability/durability at 300-350°C in the presence of liquid sodium and sodium polysulfide (3,4). Kummer and Weber (5) at the Ford Motor Company had announced the commercial development of rechargeable beta batteries for electric vehicles and load leveling energy storage systems employing sodium-ion conducting β"-Al2O3 electrolytes.
feasibility of the Na/S storage battery, which led subsequently to the development of the companion Na/NiCl₂ battery (6). Successful pilot-plant developments of these two batteries, both employing the β"-Al₂O₃ ceramic electrolyte, have occurred in the United States, Great Britain, Germany and Japan on electric vehicle traction batteries designed for electric vehicles and load leveling energy-storage systems for electric utilities and industrial applications. Traction batteries depending on their size (15-130 kWh) as well as the capacity of the unit cell (10-40 Ah) contain between several hundred and several thousand cylindrical cells, each with a central β"-Al₂O₃ electrolyte tube. Load leveling battery systems can be several MWh in size. A large-scale 6 MW (8 hour discharge or 48 MWh) rechargeable Na/S battery system is on test in Japan containing some 48,000 tubular cells each with a capacity of 632 Ah. β"-Al₂O₃ electrolyte tubes, with thin walls (1-2 mm), diameters between 25 and 50 mm and lengths up to 500 mm have been fabricated and successfully tested in many traction batteries in electric vehicles driven on interstate highways and in large scale load-leveling batteries in electric utilities or situated at industrial sites (3,4).

Yttria-stabilized zirconia (YSZ), currently the electrolyte of choice in many electrochemical systems, was developed in the same time frame as β"-Al₂O₃ (4). Oxides based on ZrO₂ were found to exhibit attractive oxygen ion conductivities (i.e. ≥ 0.02 S/cm @ 900-1000°C) by Nemst in 1900 (7). In 1943 Wagner (8) proposed that oxygen ion vacancies were the mobile species carrying the ionic current. They are generated in the lattice by the solid solution of divalent or trivalent cations (e.g. Ca²⁺ or Y³⁺ substituting for Zr⁴⁺), which also stabilize the material in the cubic-fluorite structure. Subsequently, Wagner and others conducted research on the characterization of stabilized zirconia and other related electrolytes, which included (i) establishing the relation between oxygen ion diffusivity and conductivity via the Nemst Einstein relation (9,10), (ii) measurement of oxygen ion and electron/hole conductivities as a function of stabilizer type and composition, temperature and oxygen partial pressure (11,12,13), (iii) characterization of oxygen permeation and the ionic conducting (or electrolytic) regime (14,15), and (iv) the determination of oxygen ion activities in gases and liquid metals, oxide free energies of formation and diffusion/interfacial kinetic phenomena in oxides from EMF measurements with galvanic cells (15,16). By the seventies, Brown Boveri in Germany (17) and Westinghouse in the United States (18) demonstrated that commercially viable power densities could be achieved for applications of the SOFC. Subsequently, large development efforts have been underway in the United States, Germany, and Japan (19,20). Prototype SOFC power-generation systems, with sealless tubular designs employing thin-film YSZ electrolytes and having maximum power outputs of ~ 200 hundred kilowatts, have been built and tested successfully (21). These systems are constructed from 1152 cylindrical unit cells (~ 180 watts) which are 1500 mm long and with a diameter of ~ 22 mm fabricated with YSZ film ~ 40 μm in thickness supported on a (La,Sr)MnO₃ porous cathode tube with a wall thickness of ~ 1-2 mm.

Electrolytes with higher oxygen ion conductivities and also protonic conductors are being considered as alternatives to YSZ (4,19,20). The evolution of SOFC designs from tubular cells utilizing electrolytes with thick walls (~ 500 μm) to planar cells with thin film (~ 5-10 μm) membranes will be traced. Thin film electrolyte technology in planar cell designs has permitted the SOFC to be operated at significantly lower temperatures (600-800°C) compared to first generation cells operating at 900-1000°C (4). By contrast, beta battery systems operating at ~ 325°C have been developed with tubular β"-Al₂O₃ electrolytes due,
in part, to higher open-circuit voltages (~1.9-2.6 V versus ~1 V for the SOFC) and sealing issues related to the containment of liquid electrode reactants, i.e. sodium and sulfur (4).

The evolution of $\beta''$-$\text{Al}_2\text{O}_3$ and zirconia ceramic electrolytes from the time of conception to the fabrication of components with acceptable performance and durability characteristics has taken some 70 years. These electrolytes have been manufactured for use in commercial and prototype electrochemical systems such as chemical sensors, secondary energy storage batteries, fuel cells, thermoelectric power generators (22), and chemical processing reactors. YSZ electrolytes are also utilized as the ion-conducting phase in composite, two-phase, mixed ionic and electronic conducting electrode systems (23), in the synthesis of sodium-ion conducting $\beta''$-$\text{Al}_2\text{O}_3$/YSZ composite electrolytes (24), and as protective coatings (25,26).

**CERAMIC OXYGEN AND HYDROGEN ION CONDUCTORS**

Currently, ceramic electrolytes with the highest oxygen ion conductivities have two primary crystal structures: (i) the fluorite-cubic structure including compounds based on ZrO$_2$, ThO$_2$, CeO$_2$, and Bi$_2$O$_3$ and (ii) and oxides with the cubic perovskite structure, which can also exhibit interesting levels of protonic conductivity.

**Stabilized Zirconia (ZrO$_2$) Ceramic Electrolytes**

The fluorite cubic structure of ZrO$_2$ is stabilized over a range of temperatures by the addition of divalent (e.g. CaO) or trivalent (e.g. Y$_2$O$_3$, Yb$_2$O$_3$, Sc$_2$O$_3$) oxides, which form solid solutions with ZrO$_2$ over a range of compositions. Oxygen ion transport in YSZ involves the diffusion of oxygen ions on the anion sub-lattice by a vacancy exchange mechanism. Aliovalent dopants (e.g. Y$^{3+}$ and Ca$^{2+}$ substituting for Zr$^{4+}$) are compensated electrically by an appropriate concentration of vacancies on the oxygen ion sublattice, i.e. $2[V_0^{**}] = [Y_2]$ or $[V_0^{**}] = [CaZ]$. Oxygen ion conductivity in the stabilized zirconias is proportional to the oxygen ion diffusivity via the Nernst-Einstein relation. In YSZ, the oxygen ion self-diffusion coefficient is proportional to the concentration of oxygen ion vacancies, $[V_0^{**}]$, which is set by the concentration of Y$^{3+}$ substituting for Zr$^{4+}$. We might expect that as the concentration of Y$^{3+}$continuously increases, the oxygen ion conductivity should increase accordingly. However, the oxygen ion mobility, which is directly proportional to the oxygen vacancy diffusion coefficient, depends on the stabilizer composition resulting usually in a unique composition for maximum conductivity. This dependence on stabilizer concentration is related to the type of chemical bonding and is determined experimentally. In the fully stabilized cubic zirconias, the ionic conductivity at a given temperature passes through a maximum at a unique composition specific to the particular stabilizer (12). Similar behavior has been observed in the conductivity of $\beta''$-$\text{Al}_2\text{O}_3$ as a function of Na$_2$O content.

For accurate and/or efficient operation of an electrochemical device such as an oxygen sensor or the SOFC, conduction in the electrolyte must be ionic with a very low electronic transference number over a wide range of oxygen partial pressures. In YSZ at 1000°C, n-type electronic conduction does not become dominant until the oxygen partial pressure decreases below ~$10^{-22}$ atm well below the oxygen chemical potential at the anode (~$10^{-20}$ atm). In air, the transference number of the electron hole conductivity is < $10^{-2}$. The extent or range of oxygen partial pressures for the ionic conducting or
electrolytic domain increases as the temperatures is dropped below 1000°C. It becomes progressively narrower as the temperature is increased over 1000°C (15). By contrast, the electronic transference number in β"-Al₂O₃ is very low, ~ 2x10⁻⁶ @ 350°C (2,3).

**Doped Ceria (CeO₂) Ceramic Electrolytes**

Ceria (CeO₂) has the fluorite structure and, unlike zirconia, does not need to be stabilized. However, it must be doped with lower valent cations to introduce significant ionic conductivity. Like the cubic stabilized zirconias, ceria-based compounds doped with Y₂O₃ (YDC), Gd₂O₃ (GdDC), Sm₂O₃ (SmDC), SrO (SrDC), and others become oxygen ion conductors when oxygen ion vacancies are created on the anion sublattice by the substitution of cations of lower valence (e.g. Sr²⁺, Y³⁺, Gd³⁺, etc) for Ce⁴⁺. Referring to Table 1, we find that GdDC and SmDC have ionic resistivities at 800°C, which are lower than YSZ by factors ranging between about 5 and 6, thus making these materials possibly attractive choices for the SOFC electrolyte (20). Unfortunately, ceria compounds undergo reduction at low oxygen partial pressures leading to the onset of electronic conductivity, i.e. 2Ce⁴⁺ + O₂ → (1/2)O₂(g) + V_0^{**} + 2Ce⁴⁺ or, alternatively, O₂ → (1/2)O₂(g) + V_0^{**} + 2e⁻. The formation of Ce³⁺ in the lattice by reduction of Ce⁴⁺ leads to the creation of mobile electronic defects, which impart electronic conductivity by electrons hopping between tetravalent cerium ions in the structure. The relative ease of reducing tetravalent cerium severely restricts the range of oxygen partial pressures over which the transference number for ionic conduction is equal to 1 (19,20,25,26).

**Table 1. Area Specific Resistance, ASR, (Ω cm)² of 10 μm Thick Electrolytes.**

| Composition                     | Ionic Resistivity, ρ (Ω cm) | ASR, ρt (Ω cm²) |
|---------------------------------|---------------------------|----------------|
|                                | 600°C   | 800°C | 600°C | 800°C |
| ZrO₂ + 8 mol % Y₂O₃            | 630     | 54    | 0.63  | 0.054 |
| ZrO₂ + 10 mol % Y₂O₃           | 400     | 56    | 0.40  | 0.056 |
| ZrO₂ + 4 mol % Y₂O₃            | 206     | 27    | 0.21  | 0.027 |
| + 4 mol % Yb₂O₃                | 60      | 12    | 0.06  | 0.012 |
| ZrO₂ + 10 mol % Sc₂O₃          | x = 0.15, y = 0.15        | 45   | 7     | 0.05  | 0.007 |
|                                | x = 0.20, y = 0.05        | 40   | 11    | 0.04  | 0.011 |
| CeO₂ + 20 mol % Sm₂O₃          | 30      | 9     | 0.03  | 0.009 |
| CeO₂ + 20 mol % Gd₂O₃          | 37      | 12    | 0.04  | 0.012 |
| Bi₂O₃ + 25 mol % Y₂O₃          | 14      | 3     | 0.01  | 0.003 |

One approach to the development of an electrolyte employing stabilized ceria, which is compatible with a very reducing environment, is to deposit a thin layer (5-10 μm) of YSZ (or yttria-stabilized thoria) on the fuel-electrode side of a thicker (125 - 150 μm) and higher conductivity baseline ceria membrane. The resulting two-layer composite electrolyte will be stable at the reducing electrode, while its overall ionic resistivity will be significantly lower than the high resistivity of the thin coating. Ceria does not reduce to its metal in the fuel atmosphere of the SOFC. However, it does become a mixed conductor with an ionic transference number significantly less than 1.0 when the oxygen...
partial pressure drops below a critical value. The function of the YSZ protective layer is to suppress the development of electronic conductivity in the baseline electrolyte by acting as a blocking electrode for electronic current (25,26).

**Stabilized Bismuth Oxide Ceramic Electrolytes**

Bi$_2$O$_3$ stabilized with Y$_2$O$_3$ in the fluorite cubic structure has an ionic conductivity substantially higher than that in YSZ by nearly a factor of 45 at 600°C for the composition 25 mole % Y$_2$O$_3$ as can be seen in Table 1. The pure form of the cubic phase has a higher conductivity (> 1 S/cm) near its intrinsic oxygen vacancy concentration of ~ 25%. Of all the oxygen ion conductors, the bismuth oxide compounds are the most conductive. Cubic Bi$_2$O$_3$ undergoes a phase transition to the monoclinic polymorph below 730°C. It can be stabilized at lower temperatures by additions of various rare earth oxides (e.g. Y$_2$O$_3$, Er$_2$O$_3$, WO$_3$, and alkaline earth oxides such as CaO, BaO and SrO (27). Stabilizer concentrations of at least 25 mol% Y$_2$O$_3$ stabilize the cubic structure at temperatures below 730°C (27). The higher conductivity of stabilized bismuth oxide compared to YSZ offers the possibility for its use as the electrolyte in the SOFC at reduced temperatures. However, several disadvantages are inherent with this material. The range of oxygen partial pressures over which the material remains an ionic conductor is limited. Degradation in ionic conductivity due to ordering and phase decomposition are possible for long term exposure at temperatures below 730°C (28). The tendency for the cubic phase to transform can be minimized by the addition of ZrO$_2$ or ThO$_2$ dopants in solid solution that suppress cation diffusion (28). Unfortunately, the electrolyte will eventually reduce to bismuth metal at oxygen pressures ≤ 10^-9 atm at 800°C. Practical use of this material requires protection from direct exposure to the fuel gas environment by a technique similar to that outlined for ceria-based electrolytes (26). Even with a protective coating, internal reduction may occur at the interface with the coating leading to the formation of molten Bi and structural instability.

**Oxygen and Hydrogen (Protonic) Ion Conductors with Cubic Perovskite Structure**

Many oxides with the perovskite structure exhibit significant oxygen ion conductivity (20). Most of these materials have lower ionic conductivities than the YSZ electrolyte (19,20). However, one perovskite, LaGaO$_3$ (i.e. LSGM) doped with Sr and Mg, is a potential electrolyte for the SOFC due to its relatively high oxygen ion conductivity (29). This material, over a wide range of compositions, should be superior to CeO$_2$ compounds because electronic conduction does not occur in the reducing atmosphere of the SOFC anode. It is expected to be a pure ionic conductor in that none of the constituent cations (i.e. La, Sr, Ga or Mg) are variable valent. Simultaneous substitution of Sr and Mg for La and Ga, respectively, leads to the formation of oxygen ion vacancies, i.e. [Vo**] = (1/2)[[SrO$_2$] + [MgO$_2$]]. Oxygen ion resistivities given in Table 1 for selected compositions are comparable to the most conductive of the CeO$_2$-based electrolytes (29).

Some perovskites (e.g. BaGd$_x$Ce$_{(1-x)}$O$_{(3-x/2)}$, BCD) and mixed perovskites (e.g. BaGd$_{(0.5+x)}$Nd$_{(0.5-x)}$O$_{(3-x)}$, BCN) are generating interest because of their protonic conducting characteristics (30,31,32,33). In the presence of water vapor, interstitial hydrogen ions can be generated by the reaction, H$_2$O + Vo** = O = 2Hf^+ (20). In the
limit of a low partial pressures of water vapor, \( P(H_2O) \), the concentration of mobile hydrogen ions and hence the protonic conductivity would be proportional to \([H_f^+]\) and, thus, to \([P(H_2O)]^{1/2}\). In this limit, the concentration of oxygen vacancies, \([V_o^{**}]\) in the BCD and BCN materials, is constant and fixed by the concentration of Gd. As the partial pressure of water vapor \( P(H_2O) \) is increased, the solubility of \( H_2O \) in the structure increases, protonic conductivity increases and the oxygen ion conductivity decreases due a decrease in \([V_o^{**}]\). In fully saturated material, the ionic conductivity is almost entirely due to protonic conduction. Hydroxyl ions can also be generated in a water vapor atmosphere by a defect reaction of the type, \( H_2O + O_o + V_o^{**} = 2OH_o^* \). Hydrogen ions attached to oxygen ions can migrate in the lattice as \( OH^- \) ions by a vacancy exchange mechanism. A conduction process with lower activation energy could involve the Grotthus mechanism in which protons migrate by hopping from one oxygen site to another. Many cerates and closely related materials are unstable in \( \text{H}_2\text{O} \)-containing atmospheres and decompose at temperatures < 600°C by a reaction of the type, \( \text{BaCeO}_2 + \text{H}_2\text{O} \rightarrow \text{Ba(OH)}_2 + \text{CeO}_2 \) (34). The mixed perovskite (BCN) compounds are potential SOFC electrolytes. They are stable in the presence of water vapor and have relatively high protonic conductivities. Finally, since CO cannot be used as a fuel in a SOFC utilizing only a protonic conductor, the ideal electrolyte might actually be a mixed protonic and oxygen-ion conductor.

**Ionic Resistivity and Area Specific Resistance (ASR)**

To achieve a maximum specific power density \( (P/A)_{\text{max}} \) of \(~ 1 \text{ W/cm}^2\) in the SOFC, the area specific internal ionic resistance (ASR) of the electrolyte (\( \rho_t \)) should be significantly below \(~ 0.25 \text{ \Omega cm}^2\) (4) at the cell operating temperature (i.e. \( \text{ASR} = (P/A)_{\text{max}} \left( \frac{U_o}{2} \right)^{3/4} \)) with the open circuit voltage, \( U_o \sim 1 \text{ volt} \). By comparison, for a maximum power density of \(~ 1 \text{ W/cm}^2\) in a Na/S battery cell with an \( U_o \) of \(~ 2 \text{ volts} \), the cell ASR should be \( < 1 \text{ \Omega cm}^2\). A \( \beta'\)-\( \text{Al}_2\text{O}_3 \) tube with a 1 mm wall and a sodium ion resistivity at 300°C of \(~ 5 \text{ \Omega cm} \) will contribute \(~ 0.5 \text{ \Omega cm}^2\) to the cell ASR with the balance coming primarily from the sulfur electrode (4). In Table 1, ASR values are tabulated at 600 and 800°C for several SOFC candidate electrolyte materials with a range of oxygen ion resistivities \( \rho \), which are fabricated into membranes with a wall thickness, \( t \), of \( 10 \mu m \) (12,13,29).

The YSZ electrolyte thickness in tape cast structures is typically 150 \( \mu m \) leading to a SOFC cell ASR of \(~ 0.15 \text{ \Omega cm}^2\) or higher at 1000°C (35). In cell designs with thin film configurations for the electrolyte (4,20), YSZ thicknesses will vary between 5 and 40 \( \mu m \) leading to significantly lower contributions to the ASR of the cell (i.e. \( \leq 0.05 \text{ \Omega cm}^2\)). In these situations, the electrodes are the major contributors to the internal resistance of the cell. Some of the early segmented in-series SOFC cell designs employed YSZ ceramic tubes with wall thicknesses \(~ 500 \mu m \) (17). The electrolyte contributed significant internal resistance \(~ 0.5 \text{ \Omega cm}^2\) to the cell, which led to unacceptably low power densities at 1000°C (17). ASR values \(~ 0.1 \text{ \Omega cm}^2\) at 600°C can be achieved with the use of thin film (5-10 \( \mu m \)) \( \text{Yb}_2\text{O}_3/\text{Y}_2\text{O}_3 \) and \( \text{Sc}_2\text{O}_3 \) stabilized zirconias and also LSGM electrolytes. YSZ electrolytes will be suitable for SOFC operation at somewhat higher temperatures (\(~ 800°C\)) and possibly even at lower temperatures around 600°C providing the electrolyte thickness is on the order of 5 \( \mu m \) or less. Electrolytes based on ceria (\( \text{CeO}_2 \)) and \( \text{Bi}_2\text{O}_3 \) have attractive resistivities at temperatures below about 800°C.
Unfortunately, these materials have problems related to the development of electronic conductivity or chemical stability in highly reducing atmospheres (4,25,26,28).

ELECTROCHEMICAL SYSTEMS BASED ON OXYGEN ION CONDUCTORS

Oxygen Sensor

The oxygen sensor was the first major commercial application of oxygen ion conducting YSZ ceramics (36). Two types of oxygen sensors have been commercialized to date: Lambda (\(\lambda\)) voltage sensors for the control of emissions and optimization of fuel economy in automobiles worldwide and current sensors utilized in large heating systems and industrial boilers to ensure safe and efficient operation with minimal environmental pollution. Oxygen sensors have also been developed to control the level of dissolved oxygen in liquid metals. Voltage (potentiometric) sensors operate a temperatures \(\geq 350^\circ C\), while current (amperometric) sensors normally operate at temperatures \(\geq 600^\circ C\). The voltage sensor operates on the principle of a galvanic cell operated under an open circuit (zero current) mode, i.e. Pt/O\(_2\) (exhaust gas) // YSZ or YPSZ // O\(_2\) (air)/Pt. The oxygen partial pressure (in atm) in the exhaust gas is related to the open circuit voltage (\(U_0\) in volts) of the sensor, the partial pressure of oxygen in air (0.21 atm) and absolute temperature (T), via the Nernst relation, i.e. \(P(O_2 \text{ in exhaust gas}) = 0.21 \exp(-46,437U_0/T)\).

The parameter, which is computer controlled via feedback from an automotive oxygen sensor, is the fuel/air ratio in the IC engine. It is monitored by the ratio \(\lambda\) of oxygen actually used for the combustion of a fuel to the amount of oxygen that is required for stoichiometric combustion. Automotive sensors typically operate in the vicinity of \(\lambda = 1\). In contrast to automotive applications, fuel combustion for heating systems cannot be kept at \(\lambda = 1\) for long periods of time. A certain amount of excess oxygen (i.e. \(1.00 \leq \lambda \leq 1.03\)) is required to avoid formation of soot, CO and hydrocarbons, which can over time lead to explosive conditions and can also contribute to unhealthy emissions. Current sensors, which are used to determine the oxygen partial pressure in a hot exhaust gas stream, involve the measurement of ionic currents passing through a small oxygen pump utilizing a YSZ electrolyte. They operate in the higher \(\lambda\) regime.

The central structural element of an oxygen sensor is an yttria stabilized (YSZ) or partially stabilized (YPSZ) polycrystalline zirconia tube, which is closed at one end with the following approximate dimensions: OD \(\sim 10-15\) mm, length \(\sim 60-90\) mm and wall thickness \(\sim 1-2\) mm. Both the inner (air) and outer (fuel gas) surfaces of the electrolyte tube are covered with porous, catalytically active and electronic conducting electrodes, which generally contain platinum. To protect the outer electrode of a voltage sensor from physical abrasion and contamination, a porous ceramic coating is normally applied. Oxygen sensors are exposed to rapid changes in temperature requiring substantial resistance to thermal shock cracking. Thus, YPSZ ceramics are frequently employed because of their higher fracture toughness characteristics leading to improved tolerance to thermal shock. The YSZ ceramic technology developed for the oxygen sensor was the starting point in the fabrication of early SOFC cells with tubular designs.
The solid oxide fuel cell is referred to as the ‘ceramic fuel cell’ since the electrochemically active components are composed of ceramic materials (4,17,18,19,20): (i) impervious YSZ electrolyte, (ii) porous Ni/YSZ cermet as an electronically conducting anode, (iii) porous (La,Sr)MnO₃ (LSM), a p-type semiconducting cathode, and (iv) an impervious (La,Mg)CrO₃ ceramic interconnect. In the SOFC, a fuel such as hydrogen and/or carbon monoxide is electrochemically oxidized by the reduction of oxygen to oxygen ions at the cathode/electrolyte interface, transport of oxygen ions across the YSZ membrane, and oxidation of the fuel at the anode/electrolyte interface. The electrons generated at the anode are then transported through the external working circuit to the cathode where they react with O₂ and generate oxygen ions.

Early SOFC designs (17) employed tubular YSZ electrolyte segments (OD ~ 25 mm, length ~12 mm, and wall thickness ~ 0.4-0.5 mm). Thin (100-300 μm) porous anodes and cathodes were deposited on the surfaces of these tubes by flame or plasma spraying. Many tubular segments could be assembled in a series string of unit cells by sealing the dense ceramic cell interconnect to the anode of one cell and the cathode of the adjacent cell. Because of the relatively high ionic resistance of the YSZ supporting electrolyte, the specific power which could be achieved with this design was rather low (~ 0.2 W/cm² @ 1000°C). However extended tests with cells of this design demonstrated very long lifetimes (~ 28,000 hours) for all of the basic cell components currently in use today (17).

Improved power densities (~ 0.29 W/cm² @ 1000°C) were achieved by reducing the YSZ electrolyte thickness to ~ 100-150 μm. This reduction in electrolyte thickness was achieved by introducing a porous ceramic tube (initially alumina and subsequently zirconia) as the support structure for the series connected segmented cells (17). Porous anode (~100 μm), dense YSZ, and porous cathode (150-200 μm) layers were deposited sequentially on a porous support tube. This design was further simplified by depositing single layers of a porous anode (100-200 μm), an impervious YSZ electrolyte film (~ 40 μm), and a porous cathode (~ 1400 μm) on a zirconia support tube with a wall thickness of ~ 1.2 mm and a length up to 50 cm (4,20). However, the high sheet resistance associated with the large circumferential current flow paths in the electrodes led to relatively low output power densities (~ 0.20 W/cm²). This cell with a sealless tubular design was further simplified by eliminating the ancillary porous support tube. In the modified design, a porous LSM cathode tube (with a 1-2 mm wall and now 150-cm in length) provided the entire support for the cell. Even in the new air electrode supported (AES) sealless tubular design (4,20,21), the maximum output power density was still relatively low, i.e. ~ 0.22 W/cm² @ 1000°C with a cell ASR ~ 0.6 Ωcm².

To improve the power density and permit operation at temperatures below 800°C and possibly below 650°C, anode-supported planar cell designs are under development (37). In these designs, the conductive Ni/YSZ anode (250-2000 μm thick) provides mechanical support for the electrolyte film (5-10 μm) and the porous LSM cathodic current collector (25-100 μm thick). In the anode-supported planar cell, the ratio of active electrolyte area to cell volume is significantly increased (A/V ≥ 2 cm⁻¹) and the thickness of the YSZ electrolyte film is reduced to ≤ 10μm leading to cell ASR values ≤ 0.15 Ωcm² @ 800°C. Anode supported cells employing YSZ films with improved catalytically active anode
and cathode structures have maximum output power densities of 0.8 W/cm² @ 650°C and 1.8 W/cm² @ 800°C (37). At the lower temperatures of operation, the ceramic interconnect can be replaced by a flexible metallic component and compliant seals can be introduced enabling the assembly of mechanically flexible cell stacks.

In anode-supported cell designs (37), the electrolyte is no longer the highest resistance component and its contribution to the cell ASR is small. Factors related to minimizing ohmic and non-ohmic losses due to concentration polarization in the electrodes and electron transfer processes at the electrode/electrolyte interfaces are now critically important. The redesigned electrodes are composite mixed ionic and electronic (or metallic) conductors (23) involving two contiguous solid phases and contiguous interconnected porosity. The two solid phases in the composite functional electrodes (~15-20 μm) are an electronic conductor (i.e. Ni metal in the anode and LSM in the cathode) and the oxygen ion conducting YSZ electrolyte phase. The YSZ phase extends beyond the impervious electrolyte and well into the functional porous electrode structures on either side of the electrolyte. The anode and cathode layers adjacent to the electrolyte are designed to maximize the number of three phase boundaries (TPB) between the electronic conductor (Ni or LSM), the YSZ electrolyte and the gas phase (23).

Planar cells can also be designed with flat YSZ plates providing mechanical support for the thinner anode and cathode components of the cell (35). The thickness of the YSZ electrolyte cannot be much below 150 μm placing a lower limit on the ASR of the cell (typically ≥ 0.15 Ωcm² @ 1000°C) and thus limiting the achievable power density to values ≤ 0.6 W/cm². Furthermore, these all-ceramic cells are rigid, difficult to assemble, and they are more susceptible to thermal shock and mechanical failure.

Other Applications of Oxygen Ion Conductors and Mixed Conducting Oxides

Three additional applications for either ionic or mixed ionic/electronic conducting ceramics will be outlined briefly: (i) synthesis of composite β"-Al$_2$O$_3$/YSZ sodium ion conducting electrolytes, (ii) separation of oxygen from air either by voltage or pressure driven devices for medical and space/aircraft applications, and (iii) the partial oxidation of methane in the synthesis of syngas (H$_2$ + CO) as the gaseous fuel source for the SOFC.

YSZ (or YPSZ)/Al$_2$O$_3$ composite ceramics formed by sintering preformed mixtures of zirconia and alumina powders have been used as precursors in the fabrication of impervious β"-Al$_2$O$_3$/zirconia composite electrolytes by vapor phase reaction (24). In the precursor, α-Al$_2$O$_3$ and the oxygen ion conductor (YSZ or YPSZ) are both present in amounts (30 to 70 % oxygen ion conductor) to form continuous matrices of each phase. This unique synthesis technique will work providing the zirconia phase is an oxygen ion conductor, e.g. fully stabilized YSZ at ≥ 8 mol% Y$_2$O$_3$ or Y$_2$O$_3$-stabilized tetragonal + cubic phase zirconia @ 4.5 mol% Y$_2$O$_3$ (YPSZ). In this process, the precursor α-Al$_2$O$_3$/zirconia composite, in the form of a thin-walled (≤ 2 mm) structure, is placed in a powder mixture containing Na$_2$O, Li$_2$O, and Al$_2$O$_3$ having the prescribed composition (4) for β"-Al$_2$O$_3$ (i.e. 8.85 wt.% Na$_2$O, 0.75 wt.% Li$_2$O and 90.45 wt.% Al$_2$O$_3$). Heat treatment at 1450°C for ~ 8 hours will covert all of the α-Al$_2$O$_3$ in a 1.5 mm thick section completely to the β"-Al$_2$O$_3$ phase assuming diffusion of Na$_2$O into the body takes place from both external surfaces. The rapid kinetics of this process is due to the parallel and
coupled transport of oxygen ions in YSZ (or YPSZ) phase and sodium ions in the growing β"-Al₂O₃ phase. The two phase mixture of alumina and zirconia is converted into an impervious, strong, fine grained and sodium ion conducting composite electrolyte.

The basic cell for the separation of oxygen from air is similar in concept to an oxygen concentration cell operated with a finite current as an oxygen pump. The operating temperatures for an oxygen pump are similar to those for the SOFC. In this device, oxygen gas is continuously reduced to oxygen ions at the air electrode and oxidized to diatomic oxygen gas at the pure oxygen electrode. Depending on the magnitude of the current density, the oxygen partial pressure (in atm) in the vicinity of the interface between the air electrode and the electrolyte can be very low due to local depletion of oxygen. Thus, an opposing Nernst voltage arises that must be overcome to drive current across the cell, i.e. \( U_{\text{Nernst}} = - (2.15 \times 10^{-3} T) \ln[P(\text{O}_2)_{\text{Depleted Air}}] \). This voltage (in volts) is in addition to the voltage drop \( IR_i \), which is generated by the internal resistance of the cell, such that the total driving voltage, \( U \), is given by \( U = IR_i + U_{\text{Nernst}} \).

In a potentially lower cost process, oxygen can be separated from air in an oxygen permeation cell in which ionic and electronic charges are transported across a mixed conducting oxide. In contrast to voltage driven electrochemical transport, the driving force for this process is a gradient in oxygen chemical potential or gradient in the logarithm of oxygen partial pressure. The rate of oxygen permeation through the cell is directly proportional to the differential in oxygen chemical potential at the two electrodes and to the magnitudes of the electronic and/or ionic conductivities in the mixed conductor. In an oxygen permeation cell, electronic charges are not transported in an external circuit. They are electrochemically transported across the mixed conductor along with oxygen ions resulting in the transfer of oxygen atoms from one electrode to the other. The slowest diffusing of either oxygen ions or electronic charge carriers controls the kinetics of transport. A similar electrochemical permeation cell could be employed in the partial oxidation of methane in the production of syngas (38), i.e. \( \text{CH}_4 + (1/2)\text{O}_2 \rightarrow 2\text{H}_2 + \text{CO} \).

Two approaches appear to be practical for the development of mixed ionic and electronic conductors. The first involves doping electrolytes, which are already excellent oxygen ion conductors (e.g. YSZ, LSGM, and other electrolytes with the fluorite, perovskite, pyrochlore or brownmillerite structures), with transition metal ions such as Fe²⁺/Fe³⁺, Ti³⁺/Ti⁴⁺, Ce³⁺/Ce⁴⁺, Co³⁺/Co⁴⁺, etc (38). The variable valent cations provide sources of mobile electronic charge carriers. Another potential approach is to develop two-phase mixed conductors similar to the YSZ/LSM composite cathode being developed for the SOFC consisting of contiguous oxygen ion and electronic conducting phases (23).

**CONCLUSIONS**

Over the last century, sodium ion and oxygen ion conducting ceramic electrolytes have been developed with suitable electrical and mechanical properties, which have made possible the development of many electrochemical systems including the oxygen sensor, beta energy storage battery, solid oxide fuel cell, alkali metal thermoelectric power converter, oxygen pump and other applications in chemical processing and synthesis.
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