

Solid-State Ionic Devices

by Eric D. Wachsman and Enrico Traversa

Solid-state ionic devices can be used to harness chemical energy to produce electricity in a fuel cell (SOFCs), convert one chemical species to another (both with and without application of an electric potential), separate one chemical species from another, or detect chemical species by producing an electric signal. SOFCs were described in a companion article in this issue, and in this article we focus on some of the other applications of solid-state ion conducting materials.

Solid-State Electrolytic Devices

Numerous electrolytic devices are made possible by solid-state ion conducting materials, whereby an applied electric potential is used to drive specific chemical reactions. Examples include high temperature steam electrolysis, upgrading of hydrocarbons, and pollution control (e.g., NO_x reduction).¹ Among these, ceramic oxygen generators (COG) are receiving the greatest attention for medical and aerospace applications because they can readily produce a pure oxygen gas stream from ambient air.

Compact COGs are being developed to provide a continuous supply of oxygen-enriched air for people with breathing disorders. Similarly, these devices can enrich the breathing oxygen concentration for high altitude aircrafts. More recently this technology has sparked the interest of NASA for space exploration. Because of the distance involved, if we are to travel to other planets in the future, we need to utilize available planetary resources (*in-situ* resource utilization, or ISRU) for life support and propellant production. An example is NASA's plan to send a manned mission to Mars. In order for this to be feasible this mission will require the utilization of the Mars CO_2 atmosphere to produce the propellant for the return trip and oxygen, both for breathing and the fuel oxidant. The technology envisioned to make this possible is based on a COG converting CO_2 to O_2 and CO. Experimental results demonstrating the efficacy of this technology are shown by the Faradaic oxygen production from CO_2/CO gas mixtures² in Fig. 1. This technology also has potential for mine safety, military, and emergency response applications.

Ion Transport Membranes and Membrane Reactors

Gas separation and purification is one of the most important industrial chemical processes. Major advances in

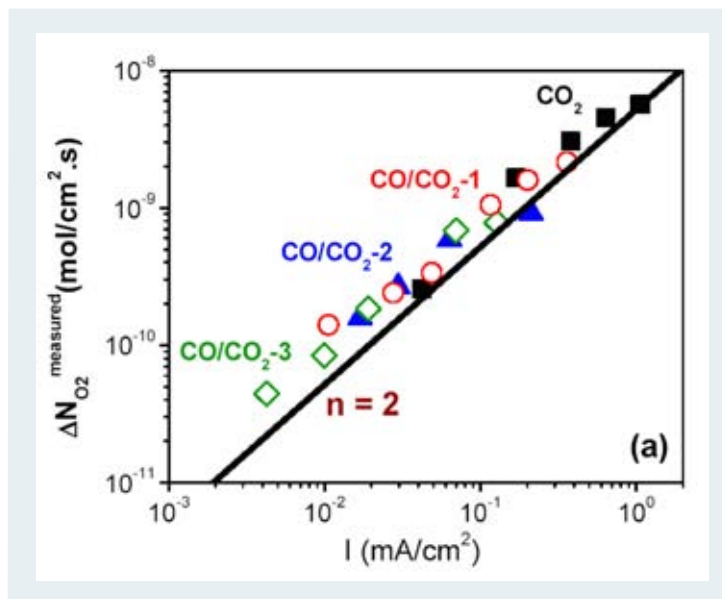


Fig. 1. Faradaic production of O_2 from CO/CO_2 gas mixtures in a ceramic oxygen generator (from Ref. 2).

gas separation technology have been achieved using membranes, either porous³ or dense (e.g., Pd alloys for H_2 separation⁴), operating under a pressure (total or partial) gradient. Among these, ion transport membranes (ITM) are receiving a lot of attention due to their unique properties and ability to integrate with other chemical processes. In fact, recent advances in ITM technology present the possibility for a dramatic reduction in the cost of producing pure O_2 , as well as converting petroleum, coal, and even biomass-derived feed stocks to H_2 and other “value added” hydrocarbons. Because of this potential, several major corporations are actively pursuing development of this technology.

ITMs are based on dense, high-temperature, ion-conducting ceramics, typically perovskite oxides. In the oxygen-ion conductors, an oxygen-ion moves from a filled (O_O^\times) to a vacant ($\text{V}_\text{O}^{\bullet\bullet}$) oxygen site through a fixed cation lattice (M_M^\times). Therefore, the actual charged solid-state ionic species involved in oxygen-ion transport are $\text{V}_\text{O}^{\bullet\bullet}$. In the proton-conducting oxides the proton is associated with an oxygen site ($\text{OH}_\text{O}^\bullet$) and hops between adjacent oxygen sites. Because oxygen and hydrogen are transported through lattice sites (vs. porous membrane diffusion), the gas separation selectivity is essentially infinite. This is a dramatic improvement in selectivity over porous gas separation membranes that employ size exclusion (the difference in size between gas molecules relative to the pore size) as the mechanism for separation.³ In addition,

ionic transport is a thermally activated process and high ionic conductivities, ~ 1 S/cm, are achieved in the 600–1000°C temperature range. While these high temperatures create several materials issues, they are compatible with typical industrial gas processing (e.g., catalytic oxidation and steam reforming) temperatures resulting in a more efficient thermal integration.

This advantage in thermal integration provides the opportunity for ITMs to be used in membrane reactors. Membrane reactors can circumvent thermodynamic equilibrium limitations by *in situ* removal of product species, thus permitting greater product yields.⁵ Not only do membrane reactors result in greater yields, but the product is already purified removing the need for downstream purification processes.

The major functional components of these reactors are the reaction catalysts (e.g., oxidation, steam reforming, and water gas shift) and the oxygen-ion or proton transport (or O_2 and H_2 separation, respectively) membranes, which are described below.

Oxygen-ion transport membranes — Oxygen-ion transport membranes are based on metal oxides (such as $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{M}_x\text{O}_3$ perovskite-type oxides) that exhibit both ionic and electronic (mixed) conductivity. For O_2 separation these oxides are typically p-type semiconducting oxides so that a high degree of electron-hole (h^\bullet) conduction is obtained under oxidizing conditions. Because of their significant electronic conductivity, these mixed ionic-

electronic conductors (MIEC) have an internal electrical short and the ionic species will selectively permeate through a dense film of the material under a partial pressure gradient. The potential permeation flux rates of these materials are extremely high. For example, based on the results of Teraoka, *et al.*⁶ and assuming the flux is bulk diffusion limited, calculated O₂ flux rates through a 50- μm -thick membrane of La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O₃ at 600°C are 22400 L (STP) h⁻¹•m⁻² of membrane surface area under an 0.21 atm P_{O₂}-gradient. The governing equation under these conditions is the Wagner Equation (described in The Chalkboard article in this issue).

Because of the potential high O₂ flux of these materials under a simple air P_{O₂}-gradient, major industrial gas suppliers are developing ITMs to produce pure O₂ from air. By siting one of these ITM units next to a hydrocarbon processing unit, dramatic improvements in the conversion efficiency is achieved because the N₂ is removed prior to reaction of O₂ with the hydrocarbon feed stream. Due to the thermal compatibility of these membranes with, for example, catalytic oxidation processes, membrane reactors are under development to integrate the partial oxidation of hydrocarbons, such as natural gas, to syngas using an oxygen-ion transport membrane, as shown in Fig. 2. The integrated process further improves efficiency and reduces cost.

Proton transport membranes — A series of perovskite-type oxides (e.g., BaCe_{1-x}M_xO₃, where M is a metal acceptor dopant) have been shown to have high proton conductivity at elevated temperatures.^{7,8} These materials are receiving considerable attention because of their numerous applications as H⁺ electrolytes in fuel cells, hydrogen

pumps, electrolyzers, and gas sensors.⁹ BaCe_{1-x}M_xO₃-type protonic conductors have sufficient ionic conductivity to obtain comparable flux rates to the oxygen-ion conductors. However, they have insufficient electronic conductivity. The electronic conductivity is necessary to balance the transport of charge through the material. Further, it is desirable that the electronic conductivity is n-type (e⁻ conduction) so that electronic conductivity is obtained under low P_{O₂} conditions. If comparable electronic conduction can be obtained with the BaCe_xM_xO₃-type protonic conductors, they would be excellent H₂ permeation membrane materials, equivalent to palladium alloy films, but with the potential advantages of higher temperature operation (for thermal integration) and lower cost.

Because of the dramatic potential of these materials in H₂ production, several groups including Argonne National Lab, Georgia Tech, and the University of Florida, have been developing mixed protonic-electronic membrane materials. Most of the earlier work focused on developing composite membranes of the proton conducting oxide and a metal phase for electronic transport;¹⁰ however, more recent work has shown that by use of a multivalent dopant cation, n-type electronic conduction can be achieved in a single phase material.¹¹⁻¹³

Ultimately these two MIEC membranes can be combined in series, and integrated with partial oxidation, steam reforming, and water gas shift catalysts, also in series, to optimize the thermodynamics of hydrogen production. The first membrane separates O₂ from air (with infinite selectivity) and reacts any of the hydrocarbons in the feed to form CO and H₂, facilitated by an oxidation catalyst. The second membrane separates the H₂ (also with infinite selectivity) providing a pure H₂ gas stream. As the process gas stream continues through the reactor, any hydrogen that has not been separated

will tend to oxidize to H₂O. A water gas shift catalyst, with the introduction of additional H₂O, in the later part of the reactor could push the conversion to higher H₂ yields.

Exhaust Sensors

Undoubtedly, oxygen sensors (λ probes) are the most widespread and successfully implemented solid state ionic device today (Fig. 3). Comprised primarily of an oxygen-ion conducting electrolyte (yttria-stabilized zirconia) with a Pt electrode on the exhaust (sensing) side and another Pt electrode on the air (reference) side, it generates a voltage via the Nernst equation due to the difference in P_{O₂} between the two sides.

By monitoring the exhaust P_{O₂}, these sensors have been used to control the air-to-fuel ratio (λ) near stoichiometric combustion, of essentially every automobile produced during the last 30 years. While initially deployed to work with the three-way catalytic converter to reduce air pollution, they also produce the additional benefit of improved fuel efficiency. The three-way catalytic converter combined with λ probe control of the air-fuel ratio, has been the pioneering technological breakthrough to minimize pollutant emissions from automotive exhaust gases, simultaneously reducing the concentrations of both oxidizing (CO and HCs) and reducing (NO_x) exhaust pollutants.

However, regulations for vehicle pollutant emission are becoming increasingly stringent worldwide, and proposed limits cannot be met using conventional three-way catalytic converter and λ probe control. For instance, recent regulations require On-Board Diagnostic (OBD) systems to control exhaust pollutants. The current OBD systems monitor the converter efficiency through the measurement of the oxygen content up-stream and down-stream of the converter using two λ probes but does not directly monitor the actual pollutant concentrations.¹⁴ In contrast, emission control and fuel efficiency could be further improved by deployment of sensors capable of directly detecting CO/HCs and NO_x in the exhaust gas stream, in addition to O₂, to provide improved feedback for automotive engine control.

A recent strategy to improve fuel efficiency (and thus reduce overall emissions) is to operate the engine under lean-burn combustion. However, the high oxygen concentration hinders the NO_x reduction reaction in the catalytic converter, making necessary the implementation of a transient NO_x storage process. When the engine is operated in lean conditions CO and HCs are rapidly oxidized and NO_x is adsorbed on the catalyst surface. Then the engine operation is shifted to rich-

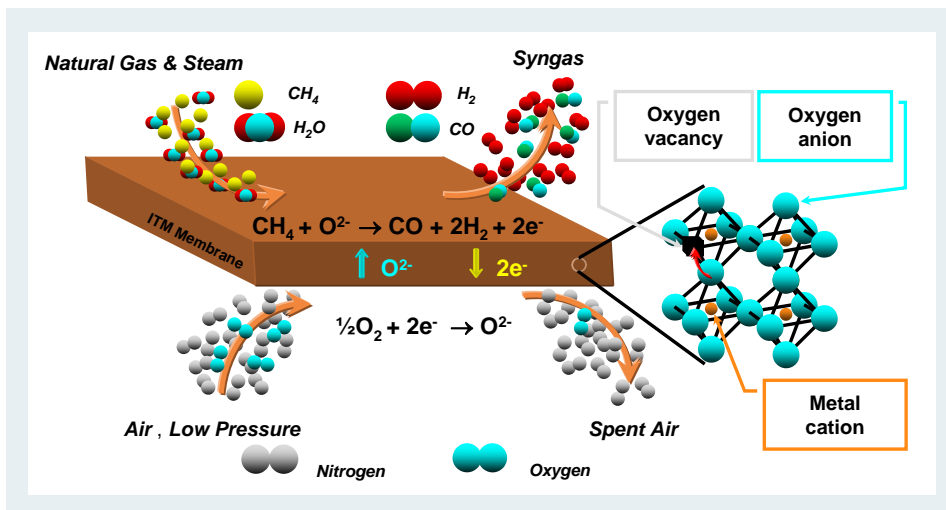


Fig. 2. ITM Syngas technology being developed by Air Products.

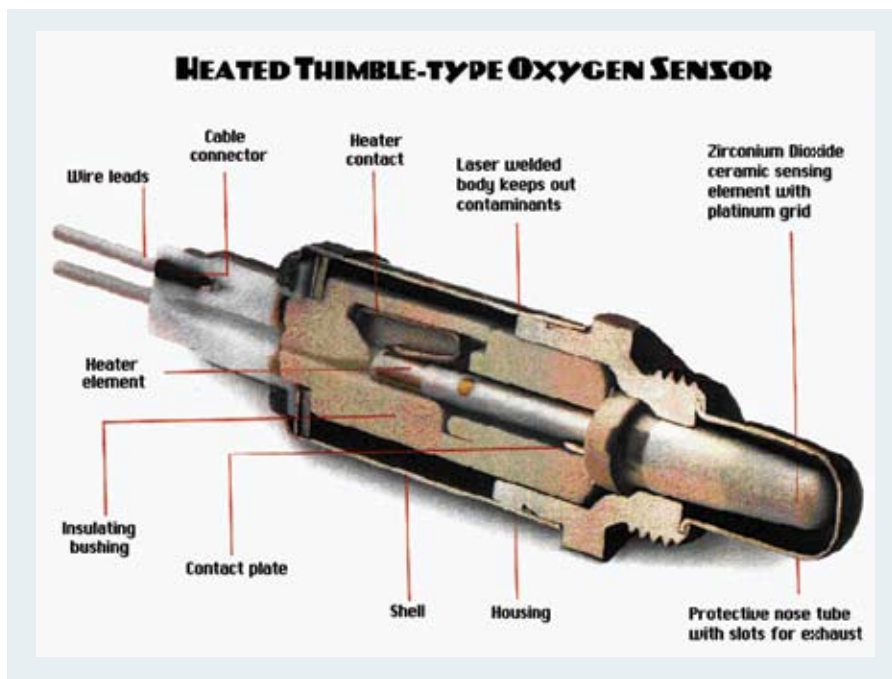


Fig. 3. Cross-section of an oxygen sensor.

burn conditions for a few seconds and the adsorbed NO_x is reacted with the temporarily higher CO and HC concentrations. After this catalyst regeneration, the engine is returned to lean-burn operation. Proper operation of this method requires the availability of a sensor to measure NO_x conversion as well as slip from the spent catalyst.¹⁵

Development of solid-state sensors, similar to the λ probe, that can directly measure CO/HCs and NO_x , has been an area of tremendous research effort. However, in contrast to the λ probe these sensors are based on a non-Nernstian potential mechanism, typically with both electrodes in the same gas stream. They are comprised of the same YSZ electrolyte and a metallic electrode (e.g., Pt), but the other electrode is typically an oxide electrode and the difference in potential generated between the two electrodes results in a non-Nernstian potential that is sensitive to the gaseous species of interest (CO, HCs, or NO_x). These sensors seem to be the most promising to meet all of the requirements needed for exhaust gas monitoring.¹⁶ From a manufacturing point of view, these sensors are only a modification of the λ probe, by substitution of one of the Pt electrodes with an oxide, and can therefore easily be implemented into mass production and practical use.

Indeed, several groups worldwide including Kyushu University, Los Alamos National Lab, the University of Rome "Tor Vergata," and the University of Florida,¹⁷⁻²⁷ have been developing this type of sensors, both for NO_x and CO/HC detection, though with slightly different strategies: namely, some of the groups are developing sensors where the metallic electrode is exposed to

reference air and the oxide electrode to the exhaust gas environment, while other groups are exposing both electrodes to the atmosphere to be detected. A large number of oxides are being tested either for reducing or for oxidizing gas detection. The selection of the oxide is guided by its sensitivity and capability to detect very low concentration, selectivity towards specific gasses, stability at high temperatures, and response time. It has been also found that the

microstructure of the oxide electrode, in terms of morphology and grain size, can significantly affect the sensor response,²⁸ and therefore care should be paid to the electrode fabrication process. Most sensors have been tested in the laboratory, though some reports show tests performed in more practical conditions, such as in real engine exhaust environments.^{29,30}

Solid-state sensors for CO, HCs, and NO_x have been reviewed in recent papers.³¹⁻³³ An example of recent literature results is that of a Pt/YSZ/ Nb_2O_5 sensor, using Nb_2O_5 and Pt electrodes on tape-cast YSZ.³⁴ The EMF response of this sensor to different concentrations of propylene in air, in the temperature range 500-700°C, is shown in Fig. 4. As is typical for these types of sensors, increasing the temperature results in a more stable and faster response, but the amplitude of the EMF decreases. Under exposure to 1000 ppm of propylene in air, the EMF value of Pt/YSZ/ Nb_2O_5 at 700°C was -110 mV, still a remarkably large value for that high of a temperature. In addition, the results for the Pt/YSZ/ Nb_2O_5 sensor were found reproducible and stable: after several days of measurements, the same EMF results were obtained. The cross sensitivity was checked by performing the measurements under exposure to different saturated and unsaturated hydrocarbons, CO and NO_2 in the temperature range 500-700°C. At all the investigated temperatures, the sensor responded best to propylene. For all the gases, a linear dependence of the EMF response was observed. These results indicate that this sensor is a

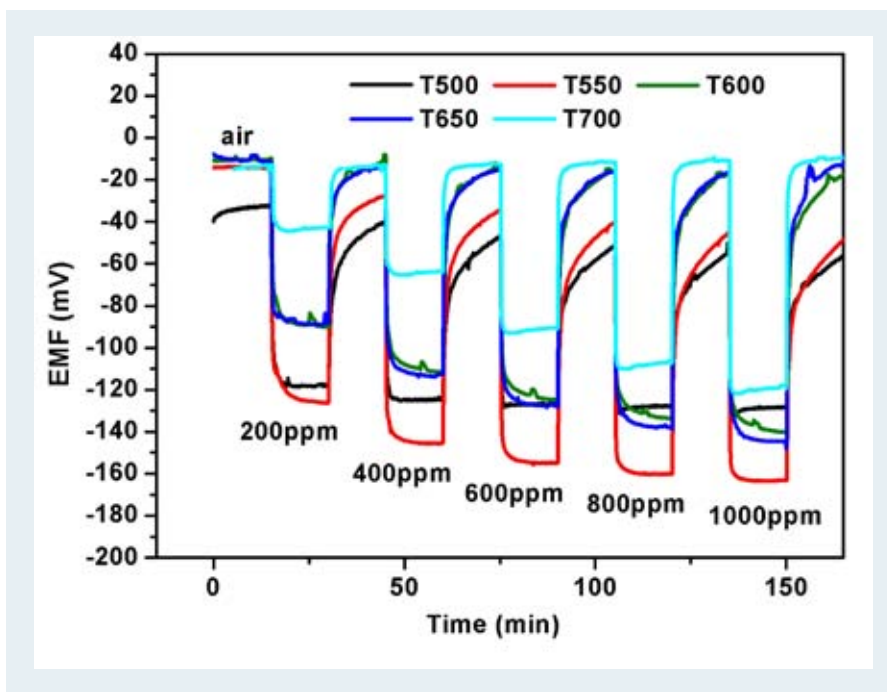


Fig. 4. EMF response versus time of Pt/YSZ/ Nb_2O_5 sensor to different concentrations of propylene in air in the temperature range 500-700°C (from Ref. 34).

Wachsman and Traversa

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potential candidate for monitoring and controlling HCs in automotive exhaust gases.

Summary

Tremendous progress has been made in understanding the defect chemistry and transport in solid-state ion conductors. These materials are attracting increasing attention for a variety of applications, most notable among these being fuel cells for power generation, production of chemicals, oxygen generation for life support systems, and high temperature electrochemical sensors. Oxygen sensors are already a widespread commercial success and many of the other solid-state ionic devices hold similar promise as their performance is improved and cost is brought down through further technical advances and mass production. ■

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