Zero-Emmision Power Plants Using Solid Oxide Fuel Cells and Oxygen Transport Membranes

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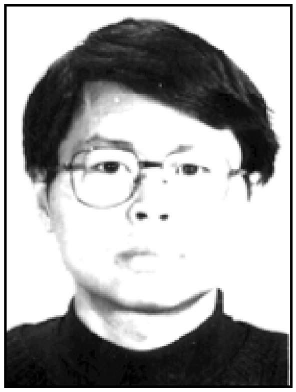

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Objectives

- Develop the technology to make zero-emission power plants, based on solid oxide fuel cells (SOFCs) and oxygen transport membranes (OTMs) possible.
- Demonstrate complete combustion of simulated SOFC fuel exhaust containing 15% residual CO and H_2, using an appropriately selected OTM material and architecture.
- Demonstrate stable operation of the OTM under typical operating conditions.
- Develop conceptual designs for the SOFC/OTM module(s).

Key Milestones

- Demonstrated consistent, complete oxidation of a simulated SOFC depleted fuel effluent using both short and long, closed end, tubular PXAB2 OTMs, resulting in dried afterburner effluents of 98% to 99.5% CO_2, 0.5 to 2% O_2 and N_2, and no detectable CO or H_2.
- Demonstrated stable operation of both short and long OTMs under typical operating conditions for over 3500 and 2700 hours, respectively.
- Developed a preliminary conceptual design for an OTM-based afterburner unit for a 10-kWe and 250-kWe SOFC, including the basic associated balance of plant, as well as preliminary startup, shutdown, and transient protocols.

Approach

Siemens Westinghouse Power Corporation (SWPC) has teamed with Praxair to develop the technology that would enable development of zero-emission, Vision 21 power plants based on solid oxide fuel cells (SOFCs) and ceramic oxygen transport membranes (OTMs). Our approach to achieve a zero-emissions SOFC power system is to modify the SOFC module and system design to incorporate an afterburner stack of tubular membranes using the Praxair OTM technology. The SOFC technology, in addition to producing electric power at high efficiency, also separates oxygen from the air, thus the anode exhaust from the SOFC stack is free of nitrogen. However, the SOFC modules that have been developed to date, have combined the anode exhaust with the vitiated air exiting the cathode in a combustion chamber located at the top end of the SOFC stack. Combining those exhaust streams yields a "seal-less" stack. The resulting exhaust stream, which is primarily vitiated air, makes the separation of CO2 difficult and expensive.

Our approach for a zero-emission SOFC power system is to modify the design of the SOFC module in order to maintain separation of the fuel cell anode gas from the vitiated air. The anode gas, or depleted fuel stream, which contains approximately 15% residual H_2 and CO, is then directed to an OTM afterburner, being developed by Praxair. The OTM afterburner is supplied with air and the depleted fuel. The OTM will selectively transport oxygen across the membrane to oxidize the remaining H_2 and CO in the depleted fuel. That oxidized depleted fuel stream consisting of CO_2 and H_2O is then routed to a condenser. The water vapor is condensed, leaving only the CO_2 in gaseous form. That CO_2 can be compressed and sequestered, resulting in a zero-emission power generation system operating on hydrocarbon fuel.

Praxair has been developing oxygen separation systems based on mixed electronic and oxygen ion conducting ceramics for a number of years. The oxygen separation membranes find applications in synthesis gas production, high purity oxygen production and gas purification. In the OTM afterburner application, the chemical potential difference between the high-temperature SOFC depleted fuel gas and the supplied air provides the driving force for oxygen transport.

The focus of the program is to develop ceramic oxygen transport membranes that are chemically and mechanically stable in the SOFC depleted fuel environment, and have adequate oxygen flux to economically oxidize the SOFC depleted fuel to completion. After setting targets for the cost and oxygen transport flux for the OTMs, lead candidate materials are characterized for physical, chemical and mechanical properties. Selected materials are fabricated into tubular OTMs and tested by supplying simulated SOFC exhaust gas and air to opposite sides of sealed membranes in high temperature laboratory scale reactors. Finally, conceptual designs for integrating the SOFC and OTM modules were prepared.

Results

A number of experiments have been carried out in which the residual fuels contained in simulated SOFC exhaust gas are oxidized in laboratory-scale OTM reactors. In the laboratory-scale reactors at Praxair, constructed as part of this program, 6”-8” closed-one-end, ceramic OTM tubes are sealed into high temperature metallic housings. Fresh air is fed to the inside of the OTM tube and the simulated, fuel-depleted SOFC exhaust gas is directed to the outside of the OTM tube. The OTM and seal assembly are contained within an Al_2O_3 muffle, and an external furnace is used to maintain an OTM temperature of approximately 1000°C. A schematic of a typical experimental reactor set-up is shown in Figure 1. Praxair completed a 3500-hour life test of a tubular OTM in July, 2002. The results of the full 3500 hours of operation are summarized in Figure 2, which presents the dried OTM afterburner fuel exhaust composition as a function of time. The vertical line at approximately 200 hours corresponds to the end of fuel-flow adjustments. During the fuel-flow adjustments, the flow rate of the simulated SOFC exhaust to the OTM tube is slowly increased until the amount of excess transported oxygen in the dried exhaust is minimized. We generally refer to this operating condition as the cusp of fuel clean-up. From that point through the test conclusion, the observed oxygen flux through the OTM tube remained stable. As is shown in Figure 2, the dried OTM exhaust composition fluctuated around 98%-99% CO_2, 0.5%-1.5%O_2.and 0%-0.5% N_2. Except for brief transients during water saturator tank re-fills and fuel cylinder change outs, no residual H_2 or CO was recorded down to the gas chromatograph limits of detection (< 10 ppm).

A test of a longer, commercial demonstration size OTM tube has also been performed in the SWPC test facility. This test was carried out for 2700 hours and similar results were obtained. No residual CO or H_2 fuel could be detected in the dried OTM exhaust and the oxygen flux through the OTM remained stable for the duration of the test. The tube also survived a number of thermal cycles and relatively rapid changes in SOFC exhaust fuel content that simulated conditions likely to be experienced when operating full size (250 kWe-1 MWe) SOFC systems.

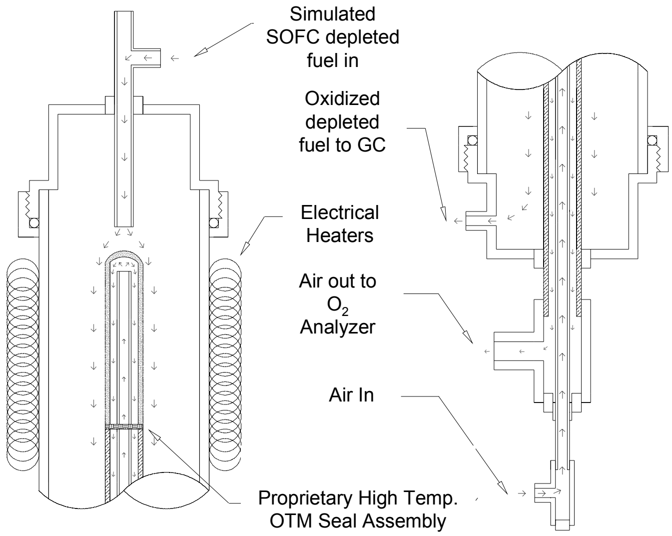

Figure 1: *Schematic of a laboratory-scale reactor at Praxair.*

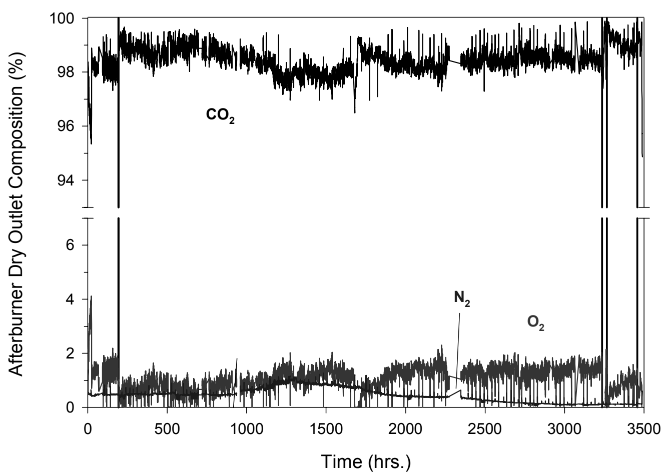

Figure 2: *Dried outlet composition.*

A conceptual design for an OTM-based afterburner designed to fully oxidize the exhaust stream of a 250-kWe SOFC has been largely completed by Praxair. The concept is modular in nature and has been designed to ensure that it is readily scaleable. The fuel and air flows, and energy balance in an SOFC power system are similar to the Zero Emission SOFC power system, although the energy from the oxidation of the depleted fuel is not available to the SOFC module in the ZE system. That depleted fuel energy is now oxidized in the OTM afterburner. That relatively small shift of energy availability will cause some resizing of recuperators, etc. With adequate insulation and a relatively large recuperator, the OTM afterburner would require no additional energy (beyond the depleted fuel and air) to function. The resulting ZE power system efficiency would be only marginally lower than a standard SOFC power system with the incorporation of the OTM afterburner.

There are two ways to integrate the OTM afterburner with the SOFC system. In one method, the OTM afterburner is comprised of a separate module that is close-coupled to the SOFC module. In the other method, the OTM afterburner tubes are located inside the SOFC generator module in a section downstream of the SOFC. SWPC and Praxair have jointly developed a preliminary P&ID for the combined SOFC and OTM afterburner system. For first demonstrations of the technology we have opted for the former approach (i.e. separate, close-coupled modules). This approach leads to more flexibility in designing strategies to facilitate startup, shutdown, and transient operation of the SOFC and afterburner units. Based on these drawings, cost estimates for both early and mature technology are being generated.

Conclusions

The technical feasibility of using oxygen transport membranes as a means to oxidize the residual fuel that would be contained in an SOFC anode gas that has not been combined with vitiated air has been demonstrated in laboratory scale reactors at both Praxair and Siemens Westinghouse Power Corporation. Conceptual designs for the OTM module and method of integration with the SOFC have been developed. Work is ongoing to ensure that the OTM materials are stable, not only in the relatively 'clean' environment of a laboratory scale reactor, but also in the environments likely to exist when the OTM tubes are built into a commercial demonstration sized reactor.