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Performance and post-test characterization of an OTM system in an experimental coal gasifier

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Abstract

An early design of oxygen transport membranes (OTM) developed and fabricated by Praxair have been tested at 850-900°C in an experimental coal gasifier using a blend of Illinois and Powder River Basin (PRB) coals. Oxygen flux was measured and found to be stable over approximately 80 hours of gasifier operation. Study of interactions between the OTM and coal ash and gas phase impurities indicated that the OTM components remain chemically and structurally stable against coal ash and do not show any indication of solid or liquid (slagging) compound formation. The structure of the active fuel oxidation layer in the OTM exposed to the coal gas also remained stable and no interactions between the consecutive layers (porous support/fuel oxidation layer/gas separation layer/oxygen incorporation layer) were identified in the tested OTM system.

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31 Performance, Stability and Ash
32

1. Introduction

High temperature ceramic oxide based oxygen transport membranes (OTM) offer flexibility of operation ranging from clean coal combustion and efficient power generation to syngas production for a variety of industrial applications [1-10]. Selective separation of oxygen from an oxidizing gas stream is achieved through the transport of oxygen ions through dense ceramic membranes under an imposed oxygen chemical potential gradient or an applied electrical potential. An overview of the oxygen transport membrane technology and its applications in the above-mentioned industrial processes, including power generation with near-zero greenhouse gas emissions, has been recently published in a review article by Gupta et al. [11].

Challenges in terms of efficiency and gas phase pollutants such as SO_x , NO_x , and PM's in conventional coal-based power generation have been well documented in the literature [9-11]. Approaches for improving power plant efficiency along with reduction in greenhouse gas emissions have also been studied and reported [12-15]. In a retrofit situation using oxy-fuel combustion [16], pure oxygen would replace air required for combustion, and the oxygen would be supplied nominally via a cryogenic air separation unit (ASU). The above power plant configuration, however, imposes a significant energy penalty due to parasitic power requirements of the cryogenic ASU [11]. An oxygen transport membrane system, on the other hand, provides high purity gaseous oxygen for efficient and clean combustion of fossil fuels in integrated gasification combined cycle (IGCC) systems or coal fired oxy-fuel combustion boilers and allows for the development of cost-effective system configurations amenable for the capture and sequestration of CO_2 [16-18]. In comparison to the cryogenic and pressure swing processes, the distinct advantages of the oxygen production by dense ceramic membranes are that they can

be integrated into a process cycle or unit operation leading to capital cost savings and reduced operating costs for power cycles with CO₂ capture and compression [14].

The Advanced Power Cycle (APC) has been developed by Praxair to incorporate ceramic oxygen transport membranes (OTM) into coal-fired power plants in order to facilitate carbon dioxide capture, depicted in Fig. 1. The process includes coal being reacted in an oxygen-blown gasifier to generate synthesis gas. A cyclone or a candle filter removes fines from the synthesis gas, before the synthesis gas is fed to an OTM partial oxidation reactor (OTM POx). In the POx unit, the reaction between oxygen generated by the OTM tubes and synthesis gas provides heat, increasing the temperature of the synthesis gas. Power is then recovered by expanding the hot synthesis gas. After expansion, the synthesis gas is fed to the OTM boiler.

In the OTM boiler, synthesis gas reacts with oxygen produced from the OTM tubes. The exiting flue gas consists of ~ 45% H₂O, 52% CO₂, with a balance of N₂, SO₂, and O₂ is fed to a convective section of the boiler for further steam generation and boiler feed water preheating. The flue gas exiting the FGD scrubber consists mainly of CO₂ (>95%) and is compressed in a multistage compressor to >2000 psia for transport to the sequestration site.

OTM technology within the OTM Boiler and the OTM POx units in the Advanced Power Cycle utilizes the large gradient in oxygen partial pressure between the fuel and air side to drive and transport oxygen through the membrane. In its simplest form, a mixed conducting ceramic perovskite–fluorite dense composite film serves as the oxygen transport membrane when exposed to an oxygen gradient established between anodic (fuel) and the cathodic (oxidant) atmospheres. A schematic of a mixed ionic-electronic (MIEC) based oxygen ceramic membrane is shown in Fig. 2. Significant research over the last decade has resulted in the identification, selection, testing and optimization of several A and B site doped perovskites (electronic/ionic

conductors) and doped zirconia (ionic conductor) for devices operating at $\sim 1000^{\circ}\text{C}$ [11-27]. Mechanistic understanding of the OTM system and the behavior of various perovskite–fluorite materials under OTM operating conditions can be found in the recently published article by the authors [11]. Although some results have been reported for select membrane and electrode configurations [28-32], the performance data is only captured by maintaining an oxygen partial pressure gradient using air at the feed side and reducing gas (e.g. H_2 and CO) at the permeate side. OTM system performance in a real coal gas atmosphere with post-test characterization has not previously been reported in the literature.

This study provides the performance of fluorite – perovskite dual phase composite based OTM tubes tested in a gasified coal blend, which consisted of a high-sulfur bituminous Illinois coal and a sub-bituminous low-sulfur North Antelope Powder River Basin (PRB) coal. Post-test characterization of the tubes is performed to understand the materials degradation resulting from solid–solid interactions and solid–gas interactions during the exposure to the gasifier environment and electrochemical operation. The approach for the evaluation of the component structure (bulk, interface and surface) along with identification of the chemical composition and development of mechanistic understanding utilizes analytical tools and techniques such as FESEM, EDS, XRD, and DSC.

2. Experiments

2.1. OTM device materials

A tubular OTM device consisting of three layers (oxygen incorporation layer, gas separation layer and fuel oxidation layer) is fabricated and supported on porous $\text{Zr}_{0.942}\text{Y}_{0.058}\text{O}_{1.971}$ for mechanical strength. The air-side porous oxygen incorporation layer is made of 50 vol%

(La_{0.8}Sr_{0.2})_{0.98}MnO_{3-δ} perovskite and 50 vol% Zr_{0.802}Sc_{0.18}Y_{0.018}O_{1.901} (10Sc1YSZ) fluorite. The dense separation layer consisted of nominally 40 vol% (La_{0.825}Sr_{0.175})_{0.94}Cr_{0.72}Mn_{0.26}V_{0.02}O_{3-δ} and 60 vol% 10Sc1YSZ. The fuel-side porous fuel oxidation layer is comprised of nominally 60 vol% (La_{0.825}Sr_{0.175})_{0.96}Cr_{0.76}Fe_{0.225}V_{0.015}O_{3-δ} and 40 vol% 10Sc1YSZ. The thickness of the three layers is in the range of 20 to 30μm. The details on the materials chosen and fabrication of the OTM device is mentioned elsewhere [33-34].

2.2. Coal-based OTM gasifier

An OTM reactor, shown in Fig. 3, was constructed at the University of Utah to test the performance of OTM tubes in a coal-derived syngas fuel [35-36]. A Hot Oxygen Burner (HOB), developed by Praxair, was used to generate a highly preheated oxygen stream, that was then mixed with pulverized coal in a gasification section to produce coal synthesis gas (syngas). The HOB is a compact, high-intensity burner that uses a small amount of natural gas burned in the oxygen stream to create a slightly vitiated, very hot oxygen jet that enhances coal gasification reactions through the promotion of high gasification temperatures and high particle heating rates. The products from the gasifier are a highly reactive coal char and a syngas fuel. There is no residual oxygen in the syngas, since the gasifier is operated under very fuel rich conditions. Praxair designed the HOB gasifier concept to generate activated carbon from coal. A scaled-down version was designed and fabricated by Praxair and sent to the University of Utah to attach to the OTM reactor (OTMR) to facilitate the generation of coal syngas in the small-scale OTMR.

Any residual char particles exited through the outlet of the gasifier and encountered a particle impact plate to drive them into the ash hopper. The syngas exiting the gasifier was directed up into the OTM reactor, as shown in Fig. 3. By use of this configuration, the OTM tube avoided

125 direct contact with the largest of the char and residual ash mineral particles in the coal. Only the
126 very fine particulates remained entrained and entered the main OTM reactor chamber.
127 Additionally, the fuel gas that interacted with the OTM tubes possessed a high concentration of
128 active fuel species.

129 The OTM reactor consisted of three separate sections, as shown in Fig. 4. Section 1 (Fig. 4a)
130 contained the hot oxygen burner (HOB) for the production of high-temperature oxygen for use in
131 reacting with coal in the gasifier to produce syngas. The HOB was connected to a mixing zone
132 where the coal was introduced and allowed to react with the hot oxygen jet. This zone served as
133 the gasification chamber. This overall section also included the particle impact plate to reject the
134 largest of the coal and ash particles. Section 2 (Fig. 4b) housed the OTM tubes and was designed
135 to provide sufficient contact with coal volatiles and gasification products. Section 3 (Fig. 4c) was
136 the exhaust section, which also contained a natural gas torch that served as an afterburner for any
137 unreacted syngas fuel. The reactor and the OTM tubes were first preheated to the target operating
138 temperature for the OTM tubes, using electrical heating panels that were located between the
139 refractory and Insboard insulation, and supplemented by some heat input from the torch
140 afterburner. Included on the right side of the reactor were sampling ports (Fig. 4b). These ports
141 were used to sample synthesis gas before and after interaction with the OTM tube, when the
142 OTM was positioned in the middle port. The ports were also used for extractive sampling of
143 entrained solids.

144 2.3. *Oxygen flux measurement and gas composition analysis*

145 OTM tubes (Fig. 5), were tested in the synthesis gas derived from a coal blend comprised
146 of a high-sulfur bituminous Illinois coal and a sub-bituminous low sulfur North Antelope Powder
147 River Basin (PRB) coal. The Illinois coal was blended at 50 wt % to 50 wt % with the PRB. The

analysis of each coal is given in Table 1. The OTM reactor was operated in the temperature range of 850-950°C for 80 h. Gas chromatography (Varian Micro GC) was used for the identification of major species in the synthesis gas. A detailed characterization of the syngas fuel produced from gasification of the coal blends in the HOB was carried out on a sample of the syngas collected using a Tedlar bag, and the analysis was performed by ALS Environmental.

The oxygen transport rate, or oxygen flux, across the OTM membrane was calculated using the following equation:

$$J_{O_2} = \frac{F_{in}x_{O_{2in}} - F_{out}x_{O_{2out}}}{A} \quad (1)$$

Where J_{O_2} is the oxygen flux, F_{in} is the inlet air flow rate, F_{out} is the outlet air flow rate, $x_{O_{2in}}$ is the mole fraction of oxygen in the inlet air, $x_{O_{2out}}$ is the mole fraction of oxygen in the outlet air and A is the active area.

2.4. Post-test characterization

OTM tubes tested while using the Illinois/PRB coal blend in the experimental coal gasifier were analyzed for surface, interface and bulk structure, as well as chemistry interactions between the OTM and surface ash deposits and electrochemically active cell components. Ash deposits were removed from the OTM using scotch tape, and samples were examined using a scanning electron microscope (FEI - ESEM Quanta 250, Hillsboro, OH). Energy dispersive spectroscopy (EDS) attached to the SEM was used for elemental compositional analysis. The porous support tube surface and selected fractured samples obtained from the OTM units were also analyzed for microstructure, chemistry, and elemental distribution using SEM-EDS.

X-ray diffraction (BRUKER-D8 ADVANCE, Bruker AXS Inc. Madison, WI) was used to identify the ash deposit and secondary compounds. The scan step was 0.02° using CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$).

Differential scanning calorimeter (DSC; DSCQ100-TA) analysis was conducted on the ash deposit to understand its melting characteristics. The DSC experiment was conducted in air with ~10 mg of powder in the temperature range of 600-1200°C at a 20°C/min heating rate.

3. Results and Discussion

3.1 Operation of the OTM Reactor

The operating conditions required for the Hot Oxygen Burner (HOB) to sustain stable gasification resulted in the HOB/gasifier combination generating syngas at flowrates substantially higher than could be consumed by a single OTM tube. Thus, much more syngas fuel was generated than was needed for testing. The high flow of syngas required an afterburner to be installed on the OTMR prior to the exhaust.

The main operational parameters that could be adjusted to affect the OTM performance were tube temperature, flow rate of air to the OTM and the H_2 content in the fuel. The O_2 flux of the OTM was linear with temperature. As temperature increased, O_2 flux increased as well. The flow rate of air through the OTM mainly affected the operating temperature of the OTM. The air flow was therefore optimized to give a maximum O_2 flux within the operating temperature range of the OTM. Higher air flow rates caused adverse cooling effects on the OTM, while too low of flowrates reduced the available partial pressure of O_2 within the membrane. Once the optimum flow rate of air was found, the subsequent tests used the same operating conditions.

As previously mentioned, the flow of syngas was much higher than the flux of O₂ through the OTM. The syngas was not continuously sampled. During sampling, the flux of the O₂ through the OTM was not affected since the flow rate of syngas is much higher than is needed for a single OTM tube. The sampling of a small part of that syngas did not have any measurable effect on the OTM tube performance.

The O₂ flux through the OTM was also affected by the H₂ concentration in the syngas. Syngas fuels with higher H₂ levels produced a higher O₂ flux. Fig. 6 illustrates normalized O₂ fluxes for two different syngas fuel compositions. The O₂ fluxes are scaled according to the highest O₂ flux measured from both data sets. The n_{H2}/n_{CO} molar ratio is an indication of which mixture has the higher concentration of H₂ in the fuel. As shown in Fig. 6, the higher n_{H2}/n_{CO} ratio gives a higher normalized O₂ flux for a given temperature range.

3.2 Oxygen flux and gas chromatography analysis

During operation, a single OTM tube was typically positioned in either the middle port or top port of the OTM section (Section 2). The gradient in oxygen partial pressure facilitated oxygen transport from the air side to the fuel side of the OTM tube. The exterior of the OTM tube was exposed to the coal-derived syngas produced in the HOB/Gasifier section (Section 1), and the syngas had a very low oxygen partial pressure.

Air was fed continuously through a lance tube into the OTM tube annulus, and oxygen-depleted air was continuously removed from OTM tube. An oxygen analyzer (Yokogawa ZR 402G) was used to measure the fraction of oxygen in the oxygen-depleted air. Mass flow meters were used to measure the flow rate of fresh air into the OTM tube, and the flow rate of oxygen depleted air out of the OTM tube. The oxygen transport rate, or oxygen flux, across the OTM membrane was calculated using Eq. (1).

During a short test campaign performed on OTM tubes in syngas derived from the blended Illinois/PRB coal, no discernible performance degradation was observed. Performance consistency over time is illustrated in Fig. 7 for various operating temperatures. After performance testing of OTM tubes in coal-derived syngas environments, buildup of loose and fixed ash on the outside of the OTM tube, i.e. the porous substrate surface, was observed. Repeated tests were performed to determine if the loose ash negatively affected the tube performance through the introduction of additional mass transport resistance. The loose ash was removed from the surface of the OTM tube through an air blower after the OTM had been cooled down. It can be seen in Fig. 8 that the O₂ flux measurements with and without the loose ash are consistent over a range of operating temperatures. This result suggests that the collection of loose ash on the outside surface did not add a significant resistance to the transport of H₂ and CO to the OTM active layers.

In actual operation, both ash and char may be present in contact with the OTM tubes depending on the system configuration and extent of coal gas clean-up employed. The flow of char and ash into the OTM zone of the reactor was measured using an isokinetic sampling probe at two different points in the reactor during one of the tests. The sampled solids flow was between 2.15 and 2.56 g/s.

Gas chromatography results collected with a Varian Micro GC provided compositional information for major species in the synthesis gas produced, and these results are shown in Table 2. The fuels produced from the gasification of the coal blends in the HOB were also sampled and collected in Tedlar bags, and those samples were analyzed by ALS Environmental for concentrations of CH₄, C₂H₄, C₂H₆, H₂S, COS, CS₂, NH₃, HCN, and Cl. The results of these analyses are presented in Table 3.

3.3 OTM device after testing: Macroscopic observations

Significant buildup of loose ash on the porous substrate, which is the outside of the OTM tube used in this configuration, was observed after the completion of the testing campaigns. The post-test OTM tubes were disassembled and the tubular section was removed from the fixture. The surface exposed to coal gas showed ash deposit formation as shown in Fig. 9a. The ash deposit was loose and separated easily from the porous support tube as shown in Fig. 9b.

3.4 Post-test characterization

3.4.1. Ash deposit – Morphology and elemental analysis

The porous support tube surface was analyzed by SEM and EDS techniques to examine the possibility of interaction, molten compound formation and surface pore closure. Surface analysis and the morphology of the ash deposit are shown in Fig. 10a, b and c. Powder agglomerates consisting of smooth and powdery ash are observed. The ash particles deposit at the pore surfaces, however, remain loose as shown in Fig. 10d, e and f. There is no indication of surface compounds or molten phase formations at the support tube surface. It is postulated that the molten phase present in the ash deposit formed via vaporization in the gasifier at elevated temperatures, and was then carried in the gas stream where it condensed in cooler regions and deposited on the OTM surface. SEM-EDS elemental analysis identifies the ash chemistry as shown in Fig. 10c and f.

XRD patterns of the ash deposit are compared with standard JCPDS files for the identification of compounds. Complex silicates containing alkali, alkaline earth and transition metals are identified as possible compounds, as shown in Fig. 11. A literature search was subsequently carried out to understand the melting behavior of the silicates. It was postulated, based on the melting point, that the ash deposit on the OTM surface will not form liquid

compounds under the experimental conditions (surface temperature $\sim 1000^{\circ}\text{C}$). A complementary DSC analysis on the ash deposit was also performed in air to understand the melting characteristics. Our observations indicated endotherms (indicative of melting) above 1000°C , as shown in Fig. 12. This result confirms that the ash deposit will not adhere to the OTM surface in liquid form, as the melting point of the ash constituents are above the OTM operating temperature.

3.4.2. OTM tube cross-section: Microstructural analysis

Fig. 13 shows micrographs of the tested OTM tube cross-section. The oxygen incorporation layer, dense gas separation layer, fuel oxidation layer and porous support layer interfaces remain stable, as shown in Fig. 13. An interface reaction layer is not identified. Smooth interfaces and lack of inter-diffusion is observed at the oxygen incorporation and fuel oxidation layer interfaces. No interaction between OTM active layers and coal ash is identified, as shown in Fig. 13. SEM-EDS analysis of each active layer and the interface between them does not indicate any secondary phase formation in the bulk as well as at the interface, as shown in Fig. 13b and d. Such microstructural features can be attributed to (a) thermochemical stability of the compounds under the exposure conditions and (b) short reaction times. No evidence of sulfur is detected in the fuel oxidation layer as shown in the active layer elemental analysis (Fig. 13d).

4. **Conclusions**

OTM tubes were tested in a reaction chamber coupled to a coal gasifier, and oxygen flux was measured over the temperature range of $850\text{--}900^{\circ}\text{C}$. Short-term stability of OTM operation in a high-sulfur atmosphere, and robustness of the material when exposed to direct coal ash contamination was demonstrated. Ash deposits did not form detectable reaction products when in

contact with OTM tubes. Molten ash constituents, observed on the OTM surface, were most likely formed by mineral vaporization at the elevated temperatures in the gasifier zone, followed by condensation in cooler regions of the reactor. Porosity was maintained in the oxygen incorporation layer. No interfacial compound formation was observed between the separation and activation layers.

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391

Table 1: Ultimate and proximate analysis of coals used in testing campaigns with Praxair OTM tubes (wt%)

Coal Type	LOD (105°C)	Ash (705°C)	C	H	N	S	O (by diff)	Volatile Matter	Fixed Carbon	HHV (BTU/lb)
Illinois	9.65	7.99	64.67	5.59	1.12	3.98	16.65	36.78	45.58	11598
PRB	23.69	4.94	53.72	6.22	0.78	0.23	34.11	33.36	38.01	9078
Ill./ PRB Blend (calc.)	13.44	6.89	62.16	5.82	1.1	0.38	23.66	35.98	43.7	10842
Ill./PRB Blend (measured)	7.88	7.68	64.00	5.29	0.97	2.09	19.97	37.17	47.27	11134

Table 2: Micro-GC data analysis (values in volume %)

	H ₂	N ₂	CO	CH ₄	CO ₂
Illinois/PRB – Campaign #1	18.78	1.04	~32	1.01	43.67
Std. Dev.	0.4796	0.1567	-	0.093	1.6901
Illinois/PRB – Campaign #2	20	0.93	34.84	0.86	42.42
Std. Dev.	1.60	0.62	3.41	0.08	5.54

Table 3: Trace species analysis of syngas generated from two different coal blends (ppm)

Coal Blend & Date	CH ₄	C ₂ H ₄	C ₂ H ₆	H ₂ S	COS	CS ₂	NH ₃	HCN	Cl
Illinois/PRB Campaign #1	3900	470	51	1700	260	6.6	<0.4 3	<0.047	<0.086
Illinois/PRB Campaign #2	5600	1400	88	0.052	340	29	2.3	<0.063	<0.11

Figure Captions

Fig. 1. Process for integration of OTM into power generation cycle with CO₂ Capture.

Fig. 2. Schematic of the operation of a mixed ionic-electronic conducting (MIEC) oxide based oxygen transport membrane.

Fig. 3. Schematic of the Oxygen Transport Membrane Reactor (OTMR) illustrating key process components.

Fig. 4. Schematic showing: a) Section 1, b) Section 2 and c) Section 3 of the OTM Coal Gas Reactor at the University of Utah [36].

Fig. 5. Schematic of an oxygen transport membrane tube.

Fig. 6. Normalized O₂ fluxes as a function of OTM temperature for two different syngas compositions, described by their respective H₂/CO molar ratios.

Fig. 7. OTM performance as a function of operating time in syngas derived from an Illinois/PRB coal blend.

Fig. 8. OTM performance in Illinois/PRB coal derived synthesis gas with and without accumulated ash.

Fig. 9. OTM device after test: a) with ash accumulation and b) after ash removal.

Fig. 10. Ash deposited on the OTM: (a) and (b) powdery deposit, (c) smooth deposit, (d), (e) and (f) localized ash deposit formed on the porous channel. Smooth deposits indicate formation of molten phase.

Fig. 11. XRD pattern obtained from the ash deposit. Chemistry and melting points are also shown.

Fig. 12. DSC analysis on the ash deposit.

Fig. 13. Micrographs of OTM tube cross-section: (a) with all layers (oxygen incorporation layer, gas separation layer, fuel oxidation layer and porous support layer), (b) interface of oxygen

420 incorporation layer and gas separation layer, (c) interface of gas separation layer and fuel
421 oxidation layer, and (d) interface of fuel oxidation layer and porous support layer.

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Figure 1

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Figure 2

Reducing atmosphere (H_2 , CO , CH_4)

Oxidizing atmosphere (O_2)

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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Figure 7

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Figure 8

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Figure 9

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Figure 10

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Figure 11

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Figure 12

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Figure 13