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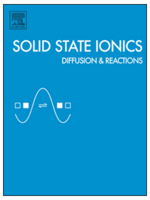

Advances in ion transport membrane technology for oxygen and syngas production

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ABSTRACT

Several decades of research by Air Products and Ceramatec have recently culminated in the construction and operation of a test unit with the capacity to produce up to 100 tons per day of oxygen using planar, ceramic mixed conducting, ion transport membranes (ITM). In the first tonnage operation of this unit, over 16 tons/day of oxygen were produced. Smaller scale experiments demonstrated high purity oxygen production for over 15,000 hours. A parallel development effort has produced planar ceramic mixed conducting membranes to partially oxidize methane to produce syngas.

1. Introduction

Air Products and its partner Ceramatec are developing ion transport membranes (ITM) for oxygen and syngas production. ITMs are ceramic, mixed conducting membranes that conduct oxygen ions at elevated temperatures. They have significant potential in the industrial gas and energy industries. The focus of the development program at Air Products and Ceramatec is ITM membranes for the separation of a pure oxygen product from air, ITM Oxygen, and ITM membranes for the conversion of methane to synthesis gas, a mixture of carbon monoxide and hydrogen, ITM Syngas. Many different organizations have been involved in their own developments of similar membranes and those developments have been reviewed by other authors [1–5]. The purpose of this paper is to review the state of the art of the technology being jointly developed by Air Products and Ceramatec, in particular the scale-up of the technology to large scale process demonstration facilities.

Air Products and Ceramatec have been developing ITM membranes together since the mid 1990's [6]. Significant progress has been made since then. The ITM team currently holds over 90 US patents in the ITM field, with equivalent patents issued in jurisdictions around the world. The patents cover membrane materials [7–10], membrane designs [11–15], ceramic-to-metal seals [16–19], and processes using ITM membranes [20–27]. Progress in both technologies has been aided by cooperative agreements with the US Department of Energy and alliances with industrial partners.

The planar membrane configuration offers a high degree of flexibility in designing membrane modules for optimum flux performance and reliability. The modular membrane systems developed by Air Products and Ceramatec provide a high packing density of membrane for a given volume of reaction vessel and a low ratio of ceramic-to-metal seals to membrane surface area. It is well known that planar compact heat exchangers can achieve higher convective heat transfer coefficients than shell and tube heat exchangers since the heat transfer coefficients are inversely proportional to the hydraulic diameter. Planar compact heat changers can have smaller hydraulic diameters than tubular heat exchangers [28]. Analogously, planar membranes should achieve improved convective heat and mass transfer coefficients relative to tubular membranes resulting from the planar membranes' smaller hydraulic diameters due to the internal micro-channels and close external membrane spacing. Furthermore, the microchannel architecture reduces stresses due to external pressure in the membrane layers of components and, hence, improves reliability.

ITM Oxygen membranes operate under an imposed gradient of oxygen partial pressure to produce a pure oxygen product. Hot, high-pressure air is supplied to one side of a membrane and a pure oxygen

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product is recovered from the permeate side of the membrane. Favorable economics can be obtained when ITM Oxygen is integrated with other high-temperature processes such as Integrated Gasification Combined Cycle [29,30]. Recovery of the energy contained in the hot, high-pressure vitiated air stream after oxygen has been extracted by the ITM membranes permits the co-production of power and steam [31]. This has been one of the drivers for continued development of ITM Oxygen technology by various research groups around the world [32].

The driving force for oxygen flux through ITM Syngas membranes is produced by supplying heated air and a hydrocarbon such as methane to opposite sides of the membrane [33]. Oxygen permeating the membrane oxidizes the methane to produce synthesis gas (syngas), a valuable feedstock for many industrial processes, including the production of ultraclean liquid fuels, hydrogen, and other chemicals. Previously published studies indicated that ITM Syngas could improve the economics of syngas production for gas-to-liquids production [34,35]. Research on ITM Syngas disk membrane designs has been reported previously [36]. The disks described in that study could not support a significant pressure differential across the disk. Also, the reactor systems in which the disks were evaluated were not rated for pressurized operation. To evaluate the performance of new membrane configurations and compositions at elevated pressure, both the reactor design and the disk membrane module had to be modified. The benefits of introducing porous layers and components were described in the previous study, for a disk membrane system operated at near-atmospheric pressure on both sides of the membrane, and whose porous layer composition is identical to that of the dense membrane. This previous work has been extended in two directions: demonstration of operation with an elevated pressure on the reducing side of the membrane, and further flux enhancement by the introduction of catalytic components into the porous layers.

2. Materials and methods

2.1. ITM membrane fabrication

Membrane components for ITM Oxygen and ITM Syngas applications are manufactured by similar methods. As shown in the flowchart presented in Fig. 1, the first step of manufacturing is to synthesize powders with the desired ITM material composition using solid state synthesis methods. Subsequently, powder is milled to the appropriate particle size for forming and sintering. Milled powder is combined with solvents, dispersants, binders, and plasticizers to make a suspension with a well-defined viscosity. The slip is cast onto a carrier film and dried to obtain ceramic tapes of varying thicknesses. The tape is then featured, by laser-cutters or mechanical punches, into the dimensions and architecture required for the individual layers of the membrane components. The correct combination of layers is laminated together and then sintered. Modules are made by joining sintered components together in a separate thermal process [37–39].

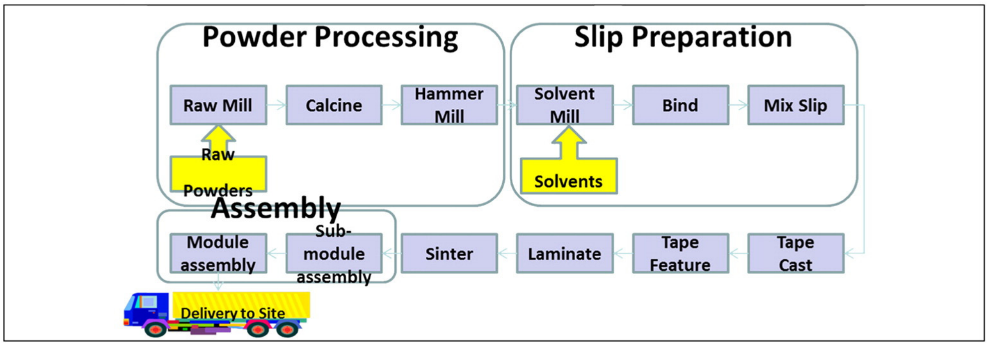

Fig. 1. Flowchart of manufacturing of ceramic ITM membranes.

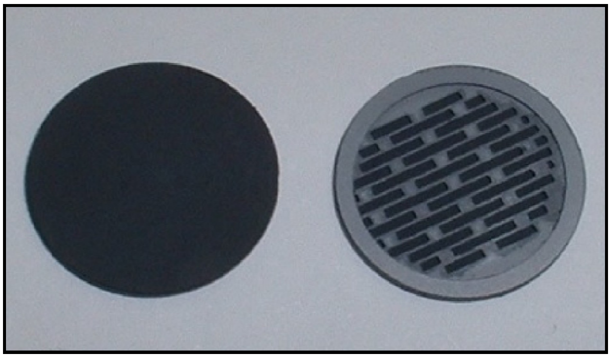

Fig. 2. Sintered PDS disks are shown with the porous layer visible on the left, and the slotted layer on the right.

2.2. ITM Syngas membrane fabrication

2.2.1. Fabrication of green tapes

The powder with a composition of La$_{1-x}$Ca$_x$FeO$_{3-\delta}$ (LCF), where δ makes the compound charge neutral, was prepared through a conventional solid state reaction method. The LCF powder was combined with a dispersant, a binder, a plasticizer, and a solvent to form a slip suitable for tape casting. The slip was first mixed and then rolled ~16 hours to ensure the complete dissolution of the binder. The slip was filtered through a screen and degassed prior to casting on the polyester film by a doctor-blade tape casting method. Four different tapes (thick porous, thin porous, thick dense, and thin dense tapes) were cast for fabrication of different disk architectures. The thickness of the tape was adjusted by the gap of the doctor blade to control a green thickness of <150 μm and <600 μm for thin and thick tape respectively. The porous tapes were fabricated by introducing a suitable pore former to form the porous tape with an open porosity of 30–40%.

2.2.2. DS, PDS, PDPS, and PDPS$_p$ disks manufacture

2.2.2.1. Fabrication of DS disks. Dense-Slotted (DS) disks are composed of 2 different layers: thin dense membrane layer (D, <100 μm sintered) and the slotted layer (S) with rim layers made of thick dense tapes (~500 μm sintered). Two different tapes (1 thin dense, and 2 thick dense tapes) were cut into 16.5 cm × 16.5 cm tiles for the final lamination size. Both slotted and rim layers were first obtained from thick dense tapes and cut by the laser cutting. The DS and rim layers were laminated by a solvent bonding process. After the solvent bonding operation, the DS assembly was further laser-cut into 28 individual PDS disks for thermal processing.

2.2.2.2. Fabrication of PDS disks. Porous-Dense-Slotted (PDS) disks are composed of 3 different layers: a thick porous layer (P, ~500 μm sintered, 30–40% open porosity), thin dense membrane layer (D,

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