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Catalytic membrane reactors for spontaneous synthesis gas production

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Abstract

Over the last several years our work has focused upon determining the interrelationship between crystallographic and thermodynamic properties of solid state metal oxides and how they relate to achieving simultaneous high ionic and electronic conductivity. This work has led to a new class of oxygen anion and electron conducting brownmillerite derived membrane materials which have been incorporated into catalytic membrane reactors (CMRs) for achieving the spontaneous conversion of natural gas to synthesis gas at practical rates with complete materials stability for extended periods.

CMR technology under development at Eltron Research, facilitates the exclusive mediation of oxygen from the atmosphere to a desired reaction site — in this case natural gas partial oxidation to synthesis gas. Because this CMR process is exothermic and eliminates the need for a separate oxygen plant, a significant reduction in synthesis gas production costs may be realized compared to currently available technology. Additionally, NO_x emissions are eliminated since the membrane only mediates oxygen and excludes atmospheric nitrogen. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic membrane reactor; Spontaneous conversion; Natural gas; Synthesis gas

1. Introduction

The use of catalytic membrane reactor (CMR) technology under development at Eltron Research for the spontaneous conversion of natural gas to synthesis gas has important commercial implications. Because the CMR process is exothermic and eliminates the need for a separate oxygen plant, a reduction in synthesis gas production costs may be realized. Additionally, NO_x emissions are eliminated since atmospheric nitrogen is excluded from mediating through the membrane. These dense ceramic membranes are exclusive oxygen anion conductors with oxygen anion transport proceeding from reducing to oxidizing membrane surfaces with electrons mediating from oxidizing to reducing surfaces via the membrane lattice bulk. Principles behind application of this CMR technology for the spontaneous conversion of natural gas into synthesis gas are shown in Fig. 1. These devices behave as short-circuited electrochemical cells, except that no electrical energy is required to drive this thermodynamically downhill process.

Current commercially available technology for synthesis gas production from natural gas is based on the endothermic steam reforming reaction which may be represented by:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

with CO also reacting with water via the water–gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

In contrast, the methane partial oxidation reaction:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

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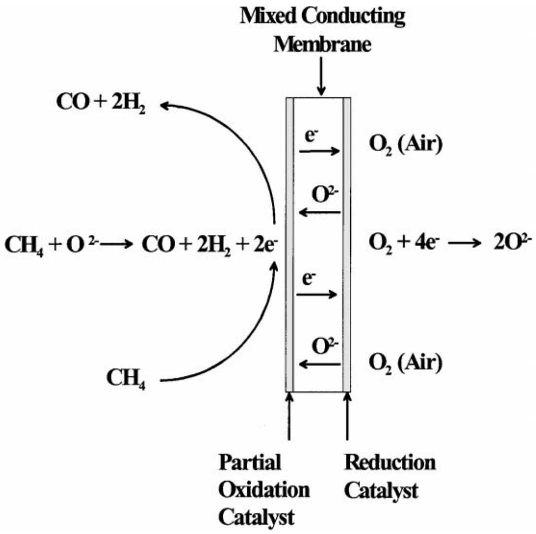

Fig. 1. Schematic of catalytic membrane reactor principles for spontaneous natural gas partial oxidation to synthesis gas.

proceeding across mixed oxygen anion and electron conducting membranes is exothermic, with oxygen being separated from the atmosphere at the membrane reducing surface for subsequent participation in the natural gas partial oxidative reforming reaction at the membrane oxidizing surface.The two formidable technical problems controlling development of CMR technology for achieving the spontaneous partial oxidation of natural gas into synthesis gas have been (1) the ability to mediate a sufficiently high flux of oxygen across the membrane and (2) achieving this for materials which possess high stability — CMRs must be simultaneously stable to natural gas on the partial oxidation surface and air at their reducing surface, all at 900°C.

The majority of work on oxygen separating membranes by others has focused upon perovskite derived lattice. In these materials oxygen anion conduction is controlled mainly through lattice oxygen vacancies. Such vacancies in the perovskite lattice are formed either through doping of the lattice or through the loss of oxygen when the material is exposed to atmospheres of low oxygen partial pressures. However, both of these vacancy formation mechanisms present problems. For example, doping of cations into the lattice can cause association between the dopants and the resulting oxygen vacancies. This leads to high activation energies for ionic conduction. Loss of oxygen by reaction with the atmosphere leads to increases in lattice parameters and eventual phase decomposition, limiting the usefulness of such materials in commercial applications.

To overcome such problems Eltron has developed mixed oxygen anion and electron conducting membranes derived from the brownmillerite structure. This structure has the general composition $A_2B_2O_5$ and is attractive as an oxygen anion conductor since it can support a large population of oxide ion vacancies, both ordered and disordered, as well as a variety of substituents in the A and B lattice sites (Fig. 2a). This structure may be compared to the perovskite structure (Fig. 2b) where B metal atoms occupy only octahedral sites with no inherent oxide ion vacancies.

The rationale for selecting specific A and B lattice substituents within the $A_2B_2O_5$ brownmillerite structure has evolved in part from recent studies performed at Eltron [1–4] which have identified clear correlations between crystallographic and thermodynamic parameters relating to the activation energy for ionic transport. These parameters include: (1) the average metal–oxygen bond energy within the lattice; (2) lattice free volumes, obtained by subtracting the ionic volumes of cations and O^{2-} in the unit cell from the overall crystallographic unit cell; (3) the parameter r_{critical} (r_c) which corresponds to the radius of the opening between the two A site cations and one B site cation through which the mobile anion must pass, and (4) lattice polarizability towards ionic migration. Eltron is currently applying this rationale to the selection of new brownmillerite derived materials for use as mixed conducting membranes.

Of all the potential applications for mixed oxygen anion and electron conducting materials, the spontaneous partial oxidation of methane to synthesis gas (syngas) is one of the most commercially important. Syngas can serve as a precursor for a variety of products such as methanol, higher alcohols or Fischer–Tropsch products. This process is currently performed industrially but requires oxygen on a large scale, which is expensive. By performing this reaction with a membrane reactor, oxygen is separated directly from air. This allows air to be used as the oxidant, greatly reducing syngas production costs.

In addition to the natural gas partial oxidation reaction, Eltron has been studying the combined partial

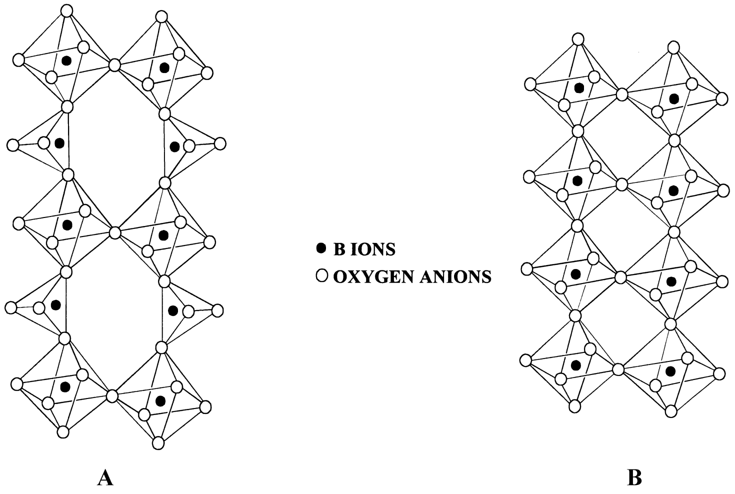

Fig. 2. Comparison of brownmillerite (A) and perovskite (B) structures. A cations are omitted for clarity.

oxidation/steam reforming and partial oxidation/CO_2 reforming reactions, similar to industrial autothermal reforming. In these processes, steam or CO_2 is added to the methane feedstream. This serves two purposes. First, since the natural gas partial oxidation reaction is highly exothermic and the steam and CO_2 reforming reactions are highly endothermic, heat generated can be used to drive the reforming reactions. This allows for better thermal control of reactions within the membrane reactor. The second purpose for a mixed feedstream is that the syngas product composition can be varied. Specifically, the addition of steam in the feedstream increases the H_2:CO ratio in the synthesis gas product stream while the addition of CO_2will decrease the H_2:CO ratio. The specific composition desired will depend upon the eventual end use of the syngas product.

In order to promote the partial oxidation reaction utilizing a mixed conducting membrane, the ceramic membrane material needs to be formed into an appropriate configuration. In practice, one side of this reactor is exposed to air. The membrane reactor then serves to separate oxygen from the atmosphere. This oxygen is then transported as oxide ions through the membrane where it goes on to react with the methane present on the second side of the membrane yielding syngas as previously shown in Fig. 1.

As a means to develop commercially viable ceramic membrane reactors for the partial oxidation of natural gas, Eltron has prepared novel mixed conducting brownmillerite materials and successfully fabricated them into tubes. These tubes have been incorporated into membrane reactors for the partial oxidation of methane. These materials have shown complete chemical and mechanical stability under expected operating conditions, including continuous long-term performance testing for over 1 year.

2. Experimental

Mixed conducting membrane materials were prepared using conventional ceramic processing techniques. Metal oxides and carbonates, serving as the starting materials, were thoroughly mixed and calcined at 1200–1300°C until the desired solid state phase was formed. These powders were then reduced in particle size using an attrition mill after which they were mixed with a standard binder. Membrane tubes were formed by isostatic pressing. After forming, the green bodies were densified by sintering in air at 1200–1400°C.

Membrane materials were characterized by X-ray diffraction (XRD) using Cu kα radiation and experimental densities of sintered tubes were determined using Archimedes' method. All materials studied in membrane reactors were single-phase and >90% of theoretical density.

Sealing of reactors was achieved using glass seals. In all reactor experiments, air was used as the oxidant. 80% methane in helium was used primarily as the feedstock on the membrane partial oxidation surface. However, experiments in which CO_2 or steam were added to the methane were also performed. CO_2 was added by mixing gases prior to entry into the reactor. Steam was added by sparging the methane:helium feedstream into a water bubbler. The concentration of the steam with respect to the methane was varied by adjusting the water bubbler temperature. The humidity of the incoming and effluent streams was measured with commercial humidity sensors. Gas chromatography was used to analyze the syngas product stream as well as any leakage of air across the membrane.

3. Results and discussion

One of the most important properties necessary for industrial use of this technology is long-term stability of the membrane materials under actual operating conditions. Eltron catalytic membrane reactor technology has demonstrated stable continuous performance for over 1 year. This reactor consisted of a dense closed-one-tube. The outside of the membrane tube contained an adherent partial oxidation catalyst consisting of a dispersed metal supported on a mixed conducting oxide. The inside of the tube was coated with a mixed conducting catalyst which served as the oxygen reduction catalyst. The experiment was performed at atmospheric pressure and 900°C. Following voluntary termination of the reactor after over 1 year there was no evidence for membrane material chemical instability following SEM and EDS investigations.

At this time the performance of our CMRs at 900°C may be summarized as: syngas production rate — $60\,\mathrm{ml/min\,cm^2}$, equivalent O_2 flux $\simeq 10$–$12\,\mathrm{ml/min\,cm^2}$ (corresponding oxygen anion conductivity $> 1\,\mathrm{S\,cm^{-1}}$), H_2:CO ratio — ~1.9–2.0, CO selectivity — >96%, throughput conversion — 90% CH_4, 70% O_2.

As discussed above, Eltron has also studied combined partial oxidation/steam reforming reactions. In a typical example, an open-both-ends tube served as the membrane reactor. Steam was added to the methane stream and the CH_4:H_2O ratio was varied and measured as discussed above. The experiment was performed at atmospheric pressure and 900°C. The amount of H_2 produced decreased initially and then increased as a function of increasing H_2O in the feedstream. Additionally, the H_2:CO ratio in the product stream increased as expected. Also important was the observation that typically greater than 90% of the H_2O in the feedstream was consumed in the combined reactions. This indicates that the premise of combining these two reactions within a ceramic membrane reactor is valid.

In a similar fashion, the combined partial oxidation/CO_2 reforming reactions have also been studied. The amount of syngas produced initially increased and then decreased with increasing CO_2 content in the feedstream. The H_2:CO ratio decreased as expected. These results validate the concept of spontaneously promoting the combined CH_4 partial oxidation reaction with the CH_4/CO_2 reforming reactions within membrane reactor technology being developed here.

4. Conclusion

A unique class of dense exclusive oxygen transport membrane materials has been identified. Incorporation of these membranes into a CMR configuration has demonstrated stable, continuous performance for over 1 year at practical rates for the spontaneous conversion of natural gas into synthesis gas.

References

[1] A.F. Sammells, R.L. Cook, J.H. White, J.J. Osborne, R.C. MacDuff, Solid State Ionics 52 (1992) 111.
[2] A.F. Sammells, R.L. Cook, Solid State Ionics 45 (1991) 311.
[3] R.L. Cook, R.C. MacDuff, A.F. Sammells, J. Electrochem. Soc. 137 (1990) 3309.
[4] M. Schwartz, B.F. Link, A.F. Sammells, J. Electrochem. Soc. 140 (1993) L62.