

THE USE OF CERAMIC MEMBRANE REACTORS FOR THE PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS

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INTRODUCTION

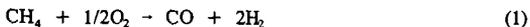
Materials exhibiting mixed ionic and electronic conductivity are of commercial interest due to their application in fields such as oxygen separation, membrane reactors for oxidation reactions and electrocatalysis. Much of this work has focused on metal oxides crystallizing in the perovskite structure. For example, early work¹⁻³ studied compounds selected from $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$. In this work, electrical and ionic conductivities were measured on a range of compositions and it was found that oxygen ion conduction was controlled mainly through oxygen vacancies in the lattice, indicating the importance of this structural feature in achieving high oxygen permeability.

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.⁴ 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 been studying ionic conductors⁵ and mixed ionic and electronic conductors based on the brownmillerite structure. This structure has general composition $\text{A}_2\text{B}_2\text{O}_7$ and is attractive as an oxide ion 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. The structure consists of BO_6 octahedral layers sharing vertices with a layer of BO_4 tetrahedra (Figure 1a). This difference in coordination sphere of B metal ions lends itself to controlled substitution. Depending on the particular metal ions, some distortion may be present in the polyhedra. This structure may be compared to the perovskite structure (Figure 1b) 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 $\text{A}_2\text{B}_2\text{O}_7$ brownmillerite structure has evolved in part from recent studies performed at Eltron⁶⁻⁸ which have identified clear correlations between perovskite crystallographic and thermodynamic parameters relating to the activation energy for ionic transport. These parameters include: 1) the average metal-oxygen bond energy within the perovskite, 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 materials for use as mixed conducting membranes.

Of all the potential applications of mixed ionic electronic conducting materials, the partial oxidation of methane to synthesis gas (syngas) is one of the most exciting and commercially important. The partial oxidation reaction of methane and oxygen to yield syngas is:



The syngas can then 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, the oxygen is separated directly from air. This allows air to be used as the oxidant, greatly reducing syngas production costs.

In addition to the partial oxidation reaction, Eltron has been studying the combined partial 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 partial oxidation reaction is highly exothermic and the steam and CO_2 reforming reactions are highly endothermic, the heat generated from the partial oxidation reaction can be used to drive the reforming reactions. This will allow for better thermal control of the reactions within the membrane reactor. The second purpose for a mixed feedstream is that the composition of the syngas product can be varied. Specifically, the addition of steam in the feedstream will increase the H_2 :CO ratio in the synthesis gas product stream while the addition of CO_2 will 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 reactor shape such as a thin plate, tube or monolith. In practice, one side of this reactor is exposed to air. The membrane reactor then serves to separate oxygen from the air. 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. A schematic illustration of this process is shown in Figure 2.

In addition to Eltron, several other research groups are studying the use of mixed conducting ceramic membrane reactors for the partial oxidation of methane to syngas. One group, Mazenec et al. at BP Chemicals, have been studying materials as partial oxidation membrane reactors.^{9,10} For example, they fabricated a membrane of composition $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_x$ into a tube and operated it for >1000hr at 1100°C as a partial oxidation reactor.¹⁰ A second group, consisting of a team from Amoco and Argonne,¹¹ has been studying materials derived from intergrowths of the perovskite structure. Specifically, materials of composition $\text{SrCo}_{0.5}\text{FeO}_x$ have been fabricated into tubular membrane reactors and used to convert methane to syngas at 900°C at rates of 2-3scc/min-cm². High methane conversion was achieved and reactors were operated for 40 days.

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 sintered disks and tubes. These disks and 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 a long-term performance testing of >3000hr.

EXPERIMENTAL

Mixed conducting membrane materials were prepared by standard ceramic processing techniques. Metal oxides and carbonates, serving as the starting materials, were thoroughly mixed and calcined at 1200-1300°C until the desired brownmillerite 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 shapes were formed by pressing: uniaxial pressing in the case of disks and isostatic pressing in the case of open-both ends and closed-one-end tubes. 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 $\text{CuK}\alpha$ radiation and experimental densities of sintered disks and tubes were determined using Archimedes' method. All materials studied in membrane reactors were single-phased and >90% of theoretical density.

Membrane reactors for the partial oxidation of methane to syngas were fabricated using sintered disks and open-both-end and closed-one-end tubes. Sealing of the 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. 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 heating the water bubbler. 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.

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. An example of the long-term stability of Eltron's brownmillerite-based membrane materials is shown in Figure 3. In this experiment, a closed-one-end tube, 3.5cm long, served as the membrane reactor. The tube had an inner diameter of 8.6mm and a 1.2mm wall thickness. The outside of the tube was coated with a partial oxidation catalyst consisting of Ni supported on a perovskite-type metal oxide. The inside of the tube was coated with $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ which served as the oxygen reduction catalyst. The experiment was performed at atmospheric pressure and 900°C.

As shown in Figure 3, the reactor has been operating for >3000hr with a syngas production rate between 10-15ml/min-cm² with a H_2 :CO ratio that varied from 1.8 to 2, close to the expected value of 2. At ~700hr, there was a complete loss of activity because the methane tank serving the reactor ran empty. When the methane tank was replaced and the methane concentration returned to the previous value in the feed, the reactor resumed syngas production at a slightly lower, but steady rate. The reason for the lower production rate after restarting the reactor is not known but may be due to some loss of activity due to catalyst deactivation. No change in the H_2 :CO ratio was observed after restarting the reactor. In addition to the syngas production, the CO_2 formed in the product was also monitored and was never more than 1-2% of the CO production rate indicating that no deep oxidation was occurring. During the course of this experiment, no evidence for mechanical or chemical instability was observed. Additionally, no leakage into the tube, as measured by the N_2 concentration in the product stream, was observed.

Further evidence of chemical stability is shown by XRD experiments performed on membrane materials operated in syngas production reactors for extended time periods. For example, a reactor fabricated from a sintered disk was operated for > 1000hr at 900°C with a feed of ~80% CH₄ in helium. The oxygen partial pressure of the gas on this side of the membrane was estimated to be < 10⁻¹⁷ atm. After the reactor was voluntarily stopped, XRD was performed on the membrane partial oxidation surface. Figure 4 shows a comparison of this membrane surface with fresh powder. The two patterns are identical which indicates that even after this extended period of syngas production, the membrane material is stable with respect to chemical decomposition under operating conditions. Additionally, the membrane disk maintained its mechanical integrity over the course of the experiment.

As discussed above, Eltron has also studied the combined partial oxidation/steam reforming reactions. In a typical example, an open-both-ends tube served as the membrane reactor. The tube had an effective length of 3.9cm, an inner diameter of 0.7cm and a wall thickness of 1.6mm. The outside of the tube was coated with a partial oxidation catalyst, specifically Ni (40wt%) supported on Al₂O₃. The inside of the tube was coated with La_{0.8}Sr_{0.2}CoO₃ which served as the oxygen reduction catalyst. Steam was added to the methane stream and the CH₄:H₂O ratio was varied and measured as discussed above. The experiment was performed at atmospheric pressure and 900°C.

Figure 5 summarizes the results obtained during this experiment. The amount of H₂ produced decreased initially and then increased as a function of increasing H₂O in the feedstream. Additionally, the H₂:CO ratio in the product stream increased as expected. Also important was the observation that typically greater than 90% of the H₂O 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/CO₂ reforming reactions have also been studied. As a typical example, a sintered disk served as the membrane reactor. The effective surface area was 0.5cm² and the membrane thickness was 1.4mm. One side of the disk was coated with a partial oxidation catalyst, specifically Rh (5wt%) supported on a metal oxide. The opposite side of the disk was coated with La_{0.8}Sr_{0.2}CoO₃ which served as the oxygen reduction catalyst. The feed gas consisted of 80% methane with CO₂ and helium making the balance. The experiment was performed at atmospheric pressure and 900°C.

Figure 6 summarizes the results of this experiment. The amount of syngas produced initially increased and then decreased with increasing CO₂ content in the feedstream. The H₂:CO ratio decreased as expected. These results validate the concept of promoting the combined CH₄ partial oxidation reaction with the CH₄/CO₂ reforming reactions within a brownmillerite-based membrane reactor.

CONCLUSION

Eltron has developed new mixed ionic and electronic conducting ceramic materials based on the brownmillerite structure. These materials have been fabricated into shapes and incorporated into membrane reactors. These membrane reactors have been used to promote the partial oxidation of methane to syngas. The long-term stability of these materials has been demonstrated by the continuous operation of a tubular partial oxidation reactor for > 3000hr. Additionally, the membrane reactors have been used in an autothermal configuration using steam or CO₂ with the methane feed.

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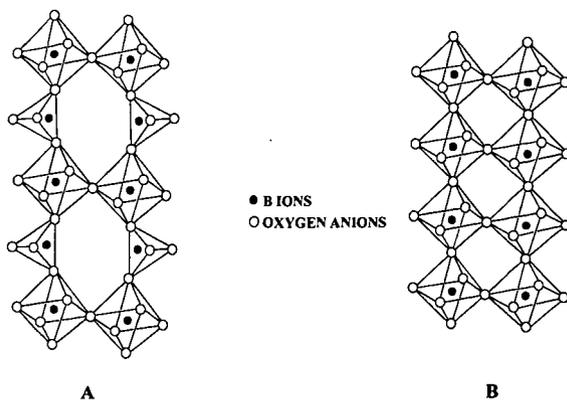


Figure 1. Comparison of brownmillerite (A) and perovskite (B) structures. A cations are omitted for clarity.

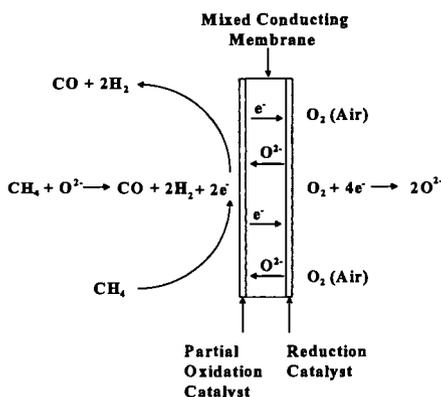


Figure 2. Schematic illustration of processes occurring during the partial oxidation of methane using a ceramic membrane reactor.

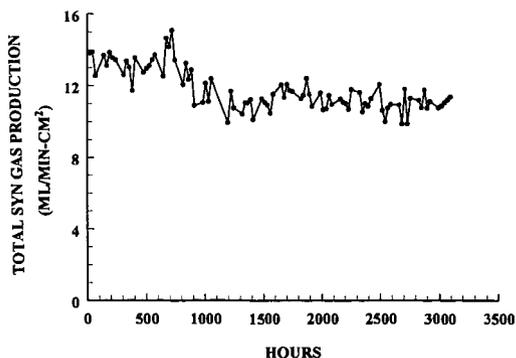


Figure 3. Plot of total synthesis gas production from the partial oxidation of methane using a tubular ceramic membrane reactor showing long-term stability.

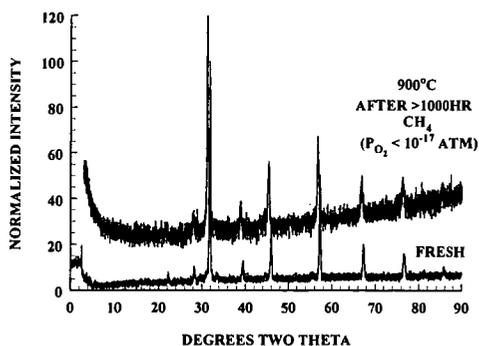


Figure 4. Comparison of XRD patterns for as-prepared membrane material and of the surface of the membrane exposed to methane during the partial oxidation reaction for > 1000 hours at 900°C.

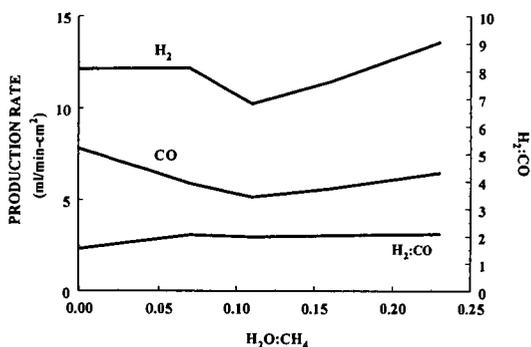


Figure 5. Plots of H_2 and CO production rates and $H_2:CO$ ratio as a function of the $H_2O:CH_4$ ratio in the feedstream for the combined partial oxidation/steam reforming reactions mediated by a ceramic membrane reactor at 900°C.

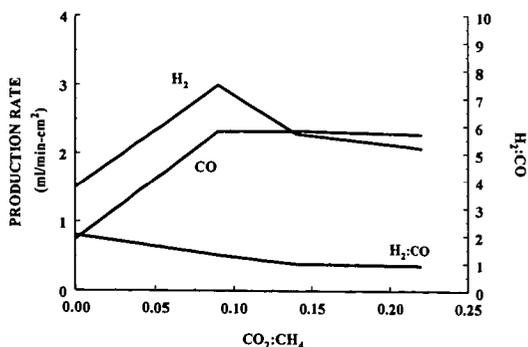


Figure 6. Plot of H_2 and CO production rates and $H_2:CO$ ratio as a function of the $CO_2:CH_4$ ratio in the feedstream for the combined partial oxidation/ CO_2 reforming reactions mediated by a ceramic membrane reactor at 900°C.