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OXYGENATION OF HYDROCARBON FUELS
TO HIGH-VALUE-ADDED PRODUCTS

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DISCLAIMER

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to

Contract No. W-31-109-ENG-38 between the U.S. Department of Energy and the

University of Chicago.

BACKGROUND OF THE INVENTION

5   As oil companies search further into remote regions and to greater depths in

their attempts to maintain adequate oil supplies, they encounter ever-increasing

amounts of unusable natural gas, which consists mostly of methane. The upgrading

of this natural gas to value added products, such as easily transportable fuels, is

driven by the abundance of natural gas discoveries in remote areas and the disparity

10   in prices of petroleum liquids versus gas on a BTU cost basis. Over the past several

years, extensive efforts have been focused on both the direct and indirect conversion of methane to value-added products, particularly easily transportable fuels. The direct conversion routes involve some form of partial oxidation of methane to methanol, formaldehyde, or olefins. This is a difficult approach because it is complicated by significant competitive side reactions that result in low selectivities to the desired products. Moreover, the reaction must be carried out at high temperatures in the gas phase. The reaction products are more reactive than the starting material, and the competitive gas-phase reactions lead to deep oxidation. Any technological breakthrough in the direct conversion of methane could have a significant economic impact in the industrial sector.

The indirect routes for the conversion of methane involve oxidation of methane to form syngas ($CO + H_2$) in a first stage either by steam reforming, direct partial oxidation or a combination of both, and then converted into upgraded products such as paraffins, olefins, oxygenates, waxes, and mid-distillate fuels in a second stage by the application of Fischer-Tropsch technology. The indirect route, and in particular the syngas step, is usually very energy- and capital-intensive (steam reforming is highly endothermic), operating at high pressures and temperatures. The cost of syngas production by steam reforming can be at least 60% of the integrated cost of the total plant.

Although direct partial oxidation of methane using air as a source of oxygen is a potential alternative to today's commercial steam-reforming processes, downstream processing requirements cannot tolerate nitrogen (recycling with

cryogenic separations is required), and pure oxygen must be used. The most significant cost associated with partial oxidation is that of the oxygen plant. Any new process that could use air as the feed oxidant and thus avoid the problems of recycling and cryogenic separation of nitrogen from the product stream will have a

5   dominant economical impact on the cost of a syngas plant, which will be reflected in savings of capital and separation costs.

Dense ceramic membranes represent a class of materials that offer potential solutions to the above-mentioned problems associated with natural gas conversion. Certain ceramic materials exhibit both electronic and ionic conductivities (of

10   particular interest is oxygen ion conductivity). These materials not only transport oxygen (functioning as selective oxygen separators), but also transport electrons back from the catalytic side of the reactor to the oxygen-reduction interface. As such, no external electrodes are required, and if the driving potential of transport is sufficient, the partial oxidation reactions should be spontaneous. Such a system will operate

15   without the need of an externally applied electrical potential. Although there are recent reports of various ceramic materials that could be used as partial oxidation ceramic membrane, little work appears to have been focused on the problems associated with the stability of the material under methane conversion reaction conditions.

20   Perovskites in the system La-Sr-Fe-Co-O (LSFC) have been shown to not only exhibit both oxygen ionic and electronic conductivity but also appreciable oxygen permeabilities (≈ 2 orders of magnitude higher than that of stabilized

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zirconia) at temperatures $\approx 800°C$. These perovskites are thus a natural candidate for methane conversion, where large quantities of oxygen are required.

Ceramic materials in the family $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ are considered promising materials for oxygen permeation at elevated temperatures. Researchers have

5 investigated the oxygenation permeation of several materials with different values for x and y. The stability of those materials under actual gas conversion conditions however, is somewhat problematic.

A variety of formulations in the system La-Sr-Co-Fe-O have been synthesized, and reactor tubes according to these formulations have been fabricated.

10 These tubes were tested for conversion of methane and it was found that one particular composition, $SrCo_{0.05}FeO_{3-x}$, is more stable than any other composition in this family of materials. Reactors fabricated using this formula yielded good methane conversion results. This formulation is disclosed in U.S. Patent application serial number 08/212,251, filed March 18, 1994, and incorporated herein by

15 reference. Even though the material disclosed in USSN 08/212,251 exhibits greater stability than other related compositions, there are certain problems associated with it. The reactor tubes fracture at regions slightly away from the hot reaction zone (the temperature of the hot reaction zone is > 800°C, while the temperature at the failure regions is about 700 °C). This may be due to slow oxygen permeation at lower

20 temperatures through the perovskite material from air side to methane side. The slow oxygen permeation retards the refurbishing of any oxygen lost from the lattice

sites in the perovskite and thus causes the material to decompose, and eventually fail by cracking.

Accordingly, it is an object of the present invention to provide a stable reactor tube composition for directly converting methane to value-added-products that is

5   capable of using oxygen as the feed oxidant.

It is another object of the present invention is to provide a stable ceramic reactor tube for converting low hydrocarbons to high value products that exhibits greater stability when exposed to a reducing gas environment for extended time periods.

10   Yet another object of the present invention to provide a stable reactor tube for converting low hydrocarbons to high value products that has a compositions that exhibits both ionic and electronic conductivity as well as appreciable oxygen permeabilities.

SUMMARY OF THE INVENTION

15   A hollow tube reactor for partial oxygenation of hydrocarbon fuels to high-value-added products may include an outer tube of a perovskite having the general formula ABO_3, where A and B are cations having mixed electronic and ionic conductivity; an inner tube of doped-zirconium oxide; and, a middle tube bonded between the outer tube and the inner tube, the middle tube transitioning from an

20   excess of perovskite at its boundary with the outer tube to an excess of zirconium oxide at its boundary with the inner tube. Oxygen from air which passes over the outer tube is transported through the outer, middle, and inner tubes where it reacts

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with methane gas passing through the inner tube, generating partial oxidation

products. The A and B sites on the perovskite outer tube each contain a mixture of A

metal ions and B metal ions. It is preferred that the perovskite exhibits oxygen ionic

and electronic conductivity and substantial oxygen permeabilities at temperatures of

5   about 800°C. More specifically, the perovskite would have the general formula Sr_α

$(Fe_{1-x} Co_x)_{\alpha+\beta} O_\delta$, where x is a number in a range from 0.01 to 1, α is a number in a

range from about 1 to 4, β is a number in a range upward from 0 to about 20, and δ is

a number which renders the compound charge neutral.

A reactor for conversion of methane and other low-hydrocarbon gases into

10   high-value-added products may also comprise a functionally gradient hollow tube

having an inner layer of a ZrO_2 based mixed conductor in contact with highly

reducing methane gas; an outer layer of a mixed metal oxide composition that

demonstrates oxygen ionic conductivity and electronic conductivity, and in contact

with an oxidizing atmosphere; a middle layer of material transitioning from an

15   excess of the ZrO_2 based mixed conductor mixed metal oxide at its boundary with the

inner tube to an excess of the mixed metal oxide composition at its boundary with

the outer tube. The oxygen from the oxidizing atmosphere in contact with the outer

tube is transported through the outer, middle, and inner tubes where it reacts with the

methane gas in contact with the inner tube, generating partial oxidation products.

20   The outer layer of a mixed metal oxide composition preferably has the general

formula $Sr_\alpha (Fe_{1-x} Co_x)_{\alpha+\beta} O_\delta$ where x is a number in a range from 0.01 to 1, α is a

number in a range from about 1 to 4, β is a number in a range upward from 0 to about 20, and δ is a number which renders the compound charge neutral.

BRIEF DESCRIPTION OF THE DRAWINGS

The above-mentioned and other features of the invention will become more

5   apparent and be best understood, together with the description, by reference to the accompanying drawings, in which,

Figure 1 shows a schematic diagram of a membrane reactor for methane conversion in accordance with the present invention;

Figure 2 is a sectional view of the membrane reactor of Figure 1 showing a

10   detailed view of the layers of the membrane;

Figure 4 shows an X-ray diffraction (XRD) characterization of a first LSFC tube, at 850°C in 1% O_2; and 20% O_2;

Figure 5 shows a schematic diagram of a likely phase presentation for a first LSFC tube operating between ambient pressure O_2 and low-pressure O_2;

15   Figure 6 shows an X-ray diffraction (XRD) characterization of a second LSFC tube, at 850°C in 1% O_2; and 20% O_2;

Figure 7 shows methane conversion and selectivities of CO and H_2 in a second membrane reactor with a reforming catalyst; and,

Figure 8 shows methane conversion, CO_2 selectivity and oxygen permeability

20   in a second membrane reactor without a reforming catalyst.

DETAILED DESCRIPTION OF THE INVENTION

As stated previously, a variety of formulations in the system La-Sr-Co-Fe-O have been fabricated as reactor tubes. The composition $Sr\ Co_{0.5}FeO_{3-x}$ has been found to be more stable than any other composition in this family of materials.

However, reactor tubes of this material fracture at regions slightly away from the hot reaction zone of temperatures $>800°C$. This may be due to slow oxygen permeation at lower temperatures through the perovskite material from air side to methane side. The slow oxygen permeation retards the refurbishing of any oxygen lost from the lattice sites in the perovskite and thus causes the material to decompose and eventually fail by cracking.

ZrO_2-based systems with dopants of oxides of Ti, In, Pr, Eu, exhibit mixed conductivity: both electronic and ionic conductivities. The composition of the samples in this system can be adjusted to tailor the material for specific uses. By adjusting the composition a three dimensional composite of a continuous ionically (oxygen ion) conducting ZrO_2 phase and a continuous electronically conducting additive oxide phase can be obtained. ZrO_2 is known to be vary stable in both oxidizing and reducing conditions. The stability of all the additive oxides is not well known, but Eu_2O_3 and In_2O_3 remain in a single phase region for a wide range of oxygen partial pressure conditions. It is expected that the electronic conductivity of the composites to increase as the oxygen pressure is decreased. Considering the favorable properties of oxides of Zr, Eu, and In, a reactor membrane fabricated from the combination of these oxides could be expected to be very stable during

conversion of methane into syngas and other products at elevated temperatures.

Thus, a functionally gradient composition as reactor material is disclosed herein.

Referring to Figs. 1 and 2, a hollow tube 10 for use as reactor material for the

conversion of methane (CH_4) into value-added-products is represented. The

5   membrane 10 is a functionally gradient composition having an outer tube 12 of a

perovskite which is in contact with air, an inner tube 16 of zirconium oxide, ZrO_2,

which is in contact with the methane gas, and a bonding or transition layer 14

between the outer tube 12 and the inner tube 16.

More particularly, the inner tube 16 is a thin, dense layer (about 1-2 mils) of a

10   ZrO_2-based mixed conductor that is in contact with highly reducing methane gas.

The perovskite-type oxide (ABO_3) outer layer 12 is in contact with a more favorable

oxidizing atmosphere, preferably air of at least O_2 and N_2. This ZrO_2 based system

may not have sufficient electronic conductivity. However, the very thin inner-tube

layer 16 can be tolerated in the reactor tube 10 because the electron path lengths are

15   very short and the resistance for the electron transfer will not be very high. The ionic

conductivity will not cause a problem with the passage of the oxygen ion through the

material. The bond layer 14 is a mixture of the ZrO_2 based oxide plus the perovskite

oxide, with the layers transitioning from an excess of perovskite to an excess of

zirconium oxide. These transition layers are necessary to match thermal expansion

20   coefficients and other physical properties between the two different materials.

The outer perovskite layer 12 is a mixed metal oxide composition that demonstrates oxygen ionic conductivity and electronic conductivity. Specifically, the outer layer 12 has the general formula

$$Sr_\alpha (Fe_{1-x} Co_x)_{\alpha+\beta} O_\delta,$$

5 where x is a number in a range from 0.01 to 1, α is a number in a range from about 1 to 4, β is a number in a range upward from 0 to about 20, and δ is a number which renders the compound charge neutral.

Oxygen is transported across the ceramic material or membrane 12 in the form of oxygen anion and not oxygen molecule. The purity of separated oxygen is

10 determined by the selectivity of ceramic material for oxygen ions. Such materials can be shaped into a hollow-tube reactor, with air passed over the shell side of the membrane and methane through the inside, as shown in Figure 1. The membrane 12 is permeable to oxygen at high temperatures, but not to nitrogen or any other gas. Thus, only oxygen from air can be transported through the membrane to the inside of

15 the reactor surface 16, where it reacts with methane to generate partial oxidation products CO, H_2, C_2, but not N_2. This consequently precludes the need for an oxygen plant and allows the integration of suitable reactors.

EXPERIMENTAL

Ceramic powders of LSFC with varying stoichiometry are made by solid-state

20 reaction of the constituent carbonates and nitrates. Appropriate amounts of $La(NO_3)_3$, $SrCO_3$, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ are mixed and milled in methanol using ZrO_2 media for ≈ 15 h. After drying, the mixtures are calcined in air

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at ≈850°C for ≈16h with an intermittent grinding. After the final calcination, the powder is ground in an agate mortar and pestle. The average particle size is ≈7 mm. The calcined powders are characterized by XRD, SEM, thermal and particle size/distribution analysis. The morphology and particle size distribution play a

5   significant role during the fabrication of membrane tubes.

The membrane tubes are fabricated by plastic extrusion. To prepare for extrusion, ceramic powder is mixed with several organic additives to make a formulation with enough plasticity to be easily formed into various shapes while retaining satisfactory strength in the green state. This formulation, known as a slip,

10   consists in general of a solvent, a dispersant, a binder, a plasticizer, and ceramic powder. The role of each additive is described in *Balachandran et al., Proceedings International Gas Research Conference*, Orlando, Florida (H.A. Thompson editor, Government Institutes, Rockville, MD), pp. 565-573 (1992). Ratios of the various constituents of a slip vary, depending on the forming process and such characteristics

15   of the ceramic powder as particle size and specific surface area. After the slip is prepared, some of the solvent is allowed to evaporate; this yields a plastic mass that is forced through a die at high pressure (≈20 MPa) to produce hollow tubes. Tubes have been extruded with outside diameter ≈6.5 mm and lengths up to ≈30 cm. The wall thicknesses are in the range 0.25-1.20 mm. In the green state (i.e., before

20   firing), extruded tubes exhibit great flexibility.

Extruded tubes are heated at a slow heating rate (≈5°C/h) in the temperature range 150-400°C to facilitate removal of gaseous species formed during

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decomposition of organic additives. After the organics are removed at low

temperatures, the heating rate is increased to $\approx 60°C/h$ and the tubes are sintered at

$\approx 1200°C$ for 5-10 h. All the heatings are done in stagnant air. Figure 2 is a

photograph of an extruded hollow tube. The sintered LSFC tubes are characterized

5   by SEM and XRD. These tubes are then used in partial oxidation studies to

transport oxygen for syngas generation in conjunction with a precious metal

reforming catalyst. Experimental results supported the oxygen transport concept

with successful utilization toward preferred oxidation. The performance

characteristics of the membranes depend on the stoichiometry of the compound. The

10   integrity of tubes fabricated using certain range of stoichiometry of cations in the

LSFC family diminished rapidly with time on stream eventually leading to

catastrophic failure. Detailed in-situ XRD experiments were done at high

temperatures and in different atmospheres on materials with varying stoichiometry to

probe the chemical phase behavior. A stable membrane was fabricated that lasted for

15   over 350 h of operation.

Perovskites as a class (ABO_3 type oxides) are based on the structure of the

mineral perovskite, $CaTiO_3$, which has a cubic lattice with one metal ion in the

body-center, the other metal ions at the corners and the anions in the face centers. A

variety of substitutions of the A and B cations can occur. Replacing part of a

20   divalent cation by a trivalent cation or a pentavalent ion for a tetravalent ion, i.e.,

donor dopant, results in two types of charge compensation, namely, electronic and

ionic, depending on the partial pressure of oxygen in equilibrium with the oxides.

The charge compensation in acceptor-doped oxides, i.e., substituting a divalent

cation for a trivalent cation is by electronic holes at high oxygen pressures but at low

pressures it is by oxygen ion vacancies. Ion vacancies are the pathway for oxide

ions. Therefore, the oxygen flux can be increased by increasing the amount of

5   substitution of lower valence element for a higher valence metal ion. The reported

oxygen flux values in perovskites tend to follow the trends suggested by the charge

compensation theory. While the primary property of high oxygen flux appears to be

feasible in a few combination of dopants in ABO_3 type oxides, many other questions

need to be answered about the ideal material for constructing a novel membrane

10   reactor. For example, the mechanical properties of the chosen membrane must have

the strength to maintain integrity at the conditions of reaction. It must also maintain

chemical stability for long periods of time at the reaction conditions. The oxygen

flux, chemical stability, and mechanical properties depend on the stoichiometry of

the ceramic membrane.

15   Two membranes have been prepared, and are identified as LSFC-1 and

LSFC-2. The LSFC-1 membrane has the formula $SrFe_{0.2}Co_{0.8}O_x$, and the LSFC-2

membrane has the formula $SrFeCoO_x$. The characteristics and the performance in an

actual conversion reactor using these membranes were studied, and the results are

described in the following text.

20   The LSFC-1 tube sintered at $\approx 1200°C$ exhibited grain size ≈ 10 μm and

density ≈ 5 g/cm3. This tube disintegrated into several pieces within a few minutes in

the conversion reactor operated at $\approx 850°C$. In-situ XRD experiments were carried

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out using a Scintag PAD X vertical goniometer powder diffractometer equipped with

a high temperature furnace. XRD patterns were recorded at 850°C in Ar-O_2 gas

mixtures. The phase behavior of LSFC-1 at 20% O_2 and 1% O_2 is shown in Figure 3.

The material is a cubic perovskite in an oxygen-rich (20% O_2) atmosphere. Once the

5   oxygen partial pressure is lowered below 5% O_2 level, however, the cubic phase

transforms to an oxygen-vacancy-ordered phase. New peaks appear in the XRD as

seen in Fig. 3 (1% O_2). It is important to note that the material expands substantially

after the phase transition. This can be seen from the change in the position of the

Bragg peak near 32 degrees. Evidently, this peak in the oxygen-vacancy-ordered

10   phase (in 1% O_2) is shifted to the low angle (larger d-spacing) side of the

corresponding peak in the cubic perovskite phase (in 20% O_2). A detailed TGA

analysis showed that the oxygen content, x, of the sample in 1% O_2 is about 0.1

lower than that in a sample in 20% O_2. The dependence of the unit cell volume on

the oxygen content of the sample has been established by comparing the lattice

15   parameters. For example, the volume of the primitive perovskite cell, V_p, is 57.51 Å^3

for x = 2.67 and it is 59.70Å^3 for x = 2.48. These results show that this material

expands as oxygen is removed. Such behavior suggests that an electronic effect is

predominant in influencing the specific volume of this material; otherwise a simple

size effect would cause the lattice to shrink. By linear interpolation of the above

20   results, we predict that a decrease in x by 0.1 will result in an increase in V_p by ≈2%.

Based on the XRD results and the previous TGA data, a clear picture about

the state of the LSFC-1 membrane tube under reaction conditions can be obtained. In

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one situation, the membrane tube acts solely as an oxygen separator. In this case, high oxygen pressure is maintained outside the tube and low oxygen pressure is maintained inside the tube. Before the tube is brought up to high temperature, it has an uniform distribution of oxygen. Upon heating, the tube begins to lose oxygen that

5   was incorporated previously in the fabrication process. Moreover, the material on the inner wall will lose more oxygen than that on the outer wall. As a result, a stable oxygen gradient is generated between the outer and inner walls. It follows that the material, depending on where it is in the tube, may have different phase constituents. The likely phase representation of the tube at 850°C is shown in Figure 4. The

10   material is of single phase in the outer and inner zones but of multiphase in the middle zone. In principle, the efficiency of oxygen permeation is different from zone to zone, and the oxygen flux passing through the membrane tube is controlled by the least-permeable zone. It is believed that the inner zone is less oxygen-permeable (due to the more ordered nature of oxygen vacancies) than the outer zone. By

15   contrast, little is known about how phase separation in the middle zone would affect the rate of oxygen permeation in this material.

The most remarkable factor, which can cause tube fracture, appears to be the lattice mismatch between the materials on the two walls of the tube. As mentioned earlier, the oxygen content of the sample in 1% O_2 atmosphere is ≈ 0.1 lower than the

20   oxygen content of sample in equilibrium with 20% O_2. Therefore, the material volume on the low-oxygen-pressure side will expand an additional 2% over that on the other wall. Such compositional expansion is equivalent to a thermal expansion of

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333°C (assuming that the volumetric thermal expansion coefficient is $\approx 6 \times 10^{-5}$/°C). Considering the brittleness of oxides in this family of materials, there is no doubt that the tube will break under reaction conditions.

In comparison, sample LSFC-2 exhibits a remarkable structural stability at high temperature, as shown in Figure 5. No phase transitions were found in this material as oxygen partial pressure is changed. Furthermore, the Bragg peaks stay at the same positions regardless of the oxygen partial pressure of the atmosphere. As a result, no appreciable strain should be built up across the reactor tube. Tubes made of this material, unlike the LSFC-1, should not fracture in the reactor tests.

Figure 6 shows the conversion data obtained using a membrane tube made of LSFC-2 material and operated at 850°C for ≈ 70h. A reforming catalyst was used inside the tube. The feed gas contains 80% methane and 20% argon. Argon was used as an internal calibration standard for gas analysis. Both the feed gas and the effluents were analyzed using a gas chromatograph. Air is the source of oxygen. As seen from Fig. 6, better than 98% methane conversion efficiency is obtained. The CO selectivity is over 90%. As expected, the measured H_2 selectivity is about twice that of CO (chemical mass-balance shows that for each mole of CO there should be two moles of H_2).

Observations made by Liu et al. indicate that not only the conductivity of the membrane material but also the catalytic activity of the surface or interfaces has significant impact on the rate of oxygen permeation. The conductivity (ionic and electronic) determines the mass and charge transport rate through the membrane

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while the catalytic activity controls the rate of the interfacial electrochemical reactions. To decouple the role of catalyst in the transport of oxygen across the membrane, the LSFC-2 tube was tested without the reforming catalyst. The results for ≈350h run are shown in Figure 7. The feed gases are the same as before. In the absence of the catalyst, the oxygen transported through the membrane reacts with methane and forms CO_2 and H_2O. As seen in Fig. 7, ≈35% methane conversion efficiency was obtained and CO_2 selectivity was ≈90%. Under the experimental operating conditions, the measured oxygen flux is ≈0.3 scc/cm^2/min. As mentioned earlier, the oxygen flux depends on the temperature, oxygen potential difference between the two sides, thickness of the membrane, etc.

Due to the reaction between methane and the oxygen permeating through the membrane, H_2 and CO are generated (in the presence of a reforming catalyst). The direct contact between the tube and the H_2 gas (CO may have the same effect) may cause the perovskite phase to lose its lattice oxygen. Once much oxygen is lost, the perovskite lattice collapses, and the material decomposes and breaks into pieces. In order to apply the LSFC membrane tube in the conversion of methane to syngas, it is critical to reduce the wall thickness of the tube. Once the wall of the tube is thin (about a few microns), the oxygen lost from the perovskite phase to the reaction stream can be refilled by the oxygen permeable from the high pressure side. As a result, the material in contact with the reaction stream will not be deeply reduced and hence the chemical decomposition would not occur. Meanwhile, the difference in oxygen content between the two walls becomes smaller and consequently, the

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fracturing of the tube is less likely. Thus, a thin-wall membrane tube appears to be more promising for the application of methane conversion in the future. A thin-wall membrane will also maximize the surface area to volume ratio and thereby reduce the size of the reactor.
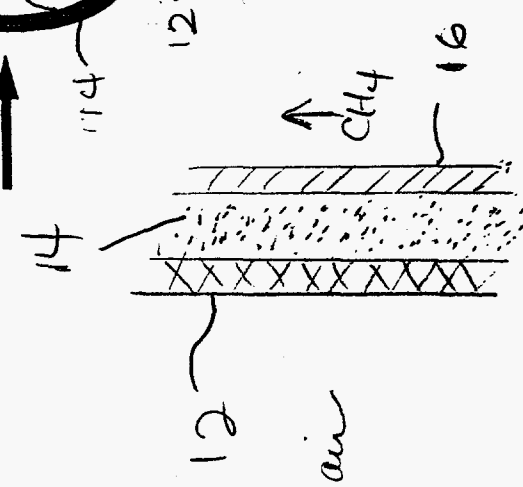
5   The foregoing description of a preferred embodiment of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiment was chosen and described to best explain the principles of the invention

10   and its practical application and thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

ABSTRACT

A functionally gradient material for a membrane reactor for converting methane gas into value-added-products includes an outer tube of perovskite, which contacts air; an inner tube which contacts methane gas, of zirconium oxide, and a bonding layer between the perovskite and zirconium oxide layers. The bonding layer has one or more layers of a mixture of perovskite and zirconium oxide, with the layers transitioning from an excess of perovskite to an excess of zirconium oxide. The transition layers match thermal expansion coefficients and other physical properties between the two different materials.
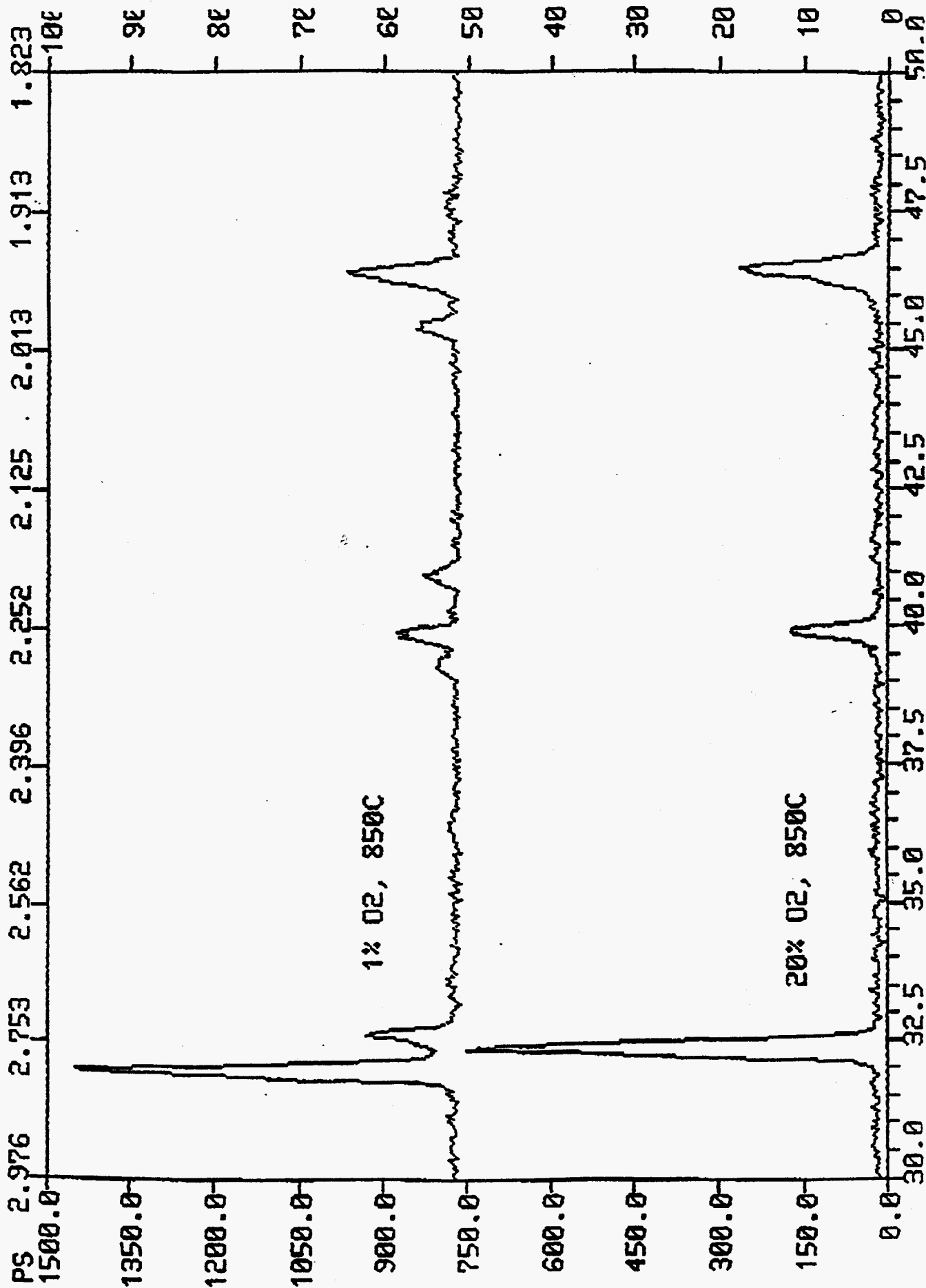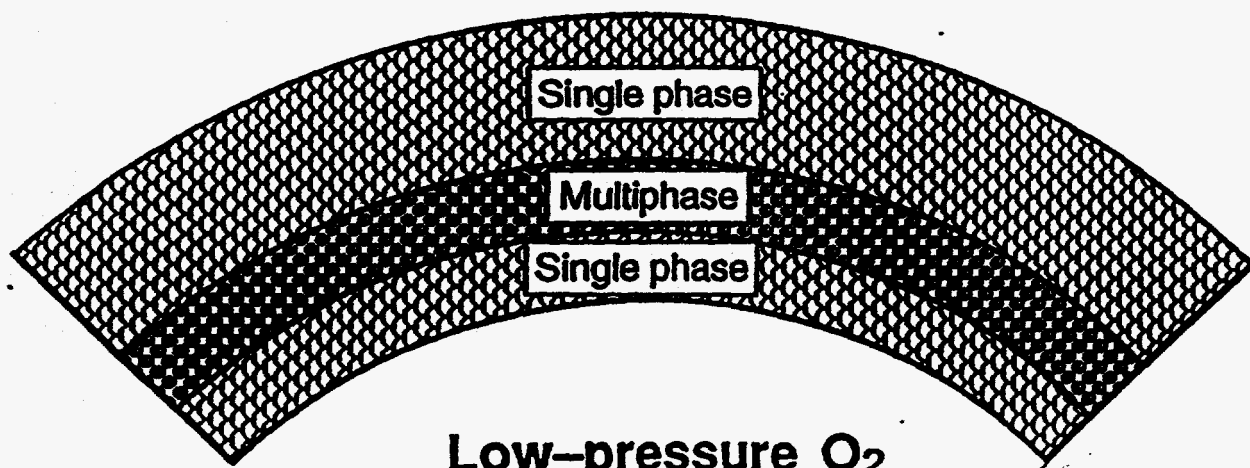
Air (O_2, N_2, ...)

CO, H_2

C_2 (no N_2)

Ceramic membrane

10

12

16

2

CH_4

14

FIG. 1

CH_4

16

14

12

air

FIG. 2

FIG. 3.

FIG. 4

1% O2, 850C

20% O2, 850C

③

Ambient–pressure O$_2$

Single phase

Multiphase

Single phase
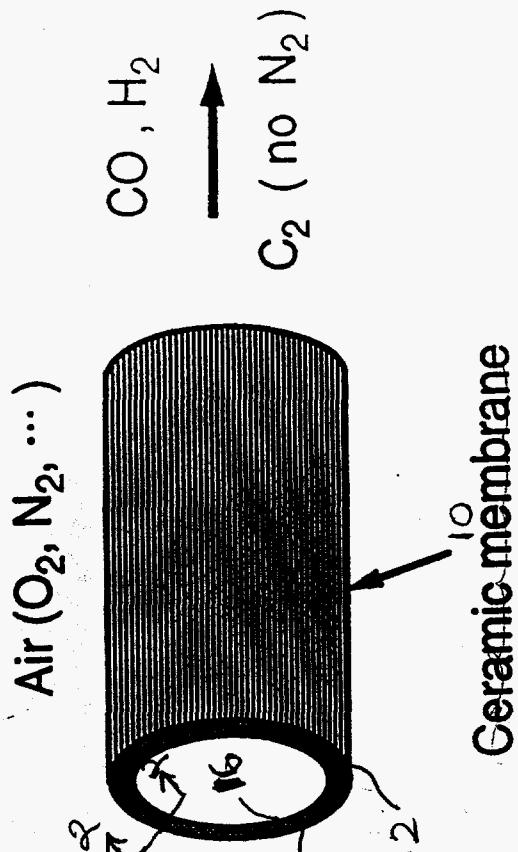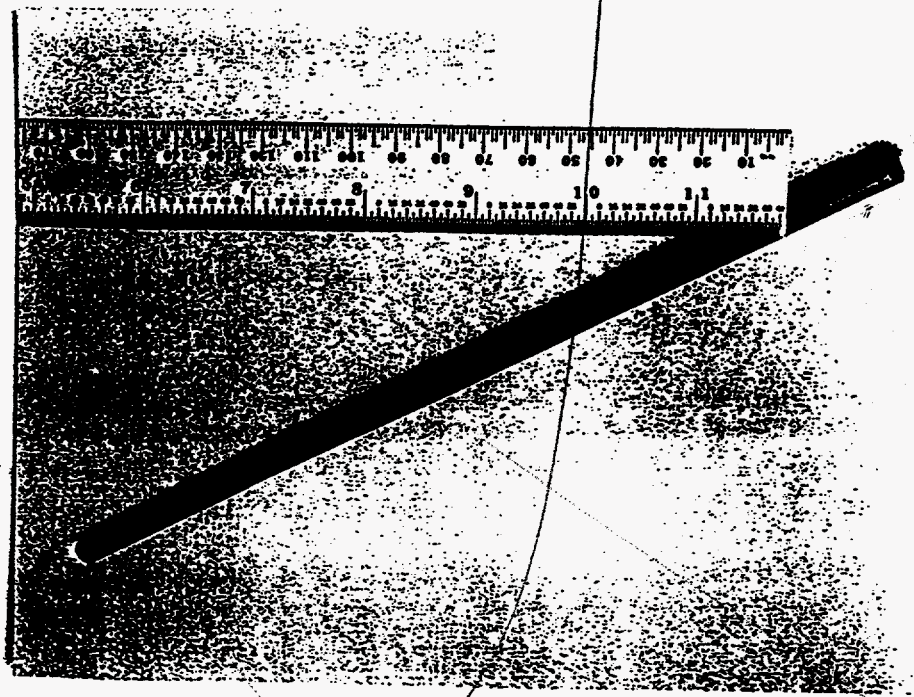
Low–pressure O$_2$

FIG. 5

FIG. 6

FIG. 7

FIG. 9