

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
17 December 2009 (17.12.2009)(10) International Publication Number
WO 2009/152255 A2(51) International Patent Classification:
B01D 71/00 (2006.01) **B01D 69/10** (2006.01)(21) International Application Number:
PCT/US2009/046924(22) International Filing Date:
10 June 2009 (10.06.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) Title: PROTON CONDUCTING MEMBRANES FOR HYDROGEN PRODUCTION AND SEPARATION

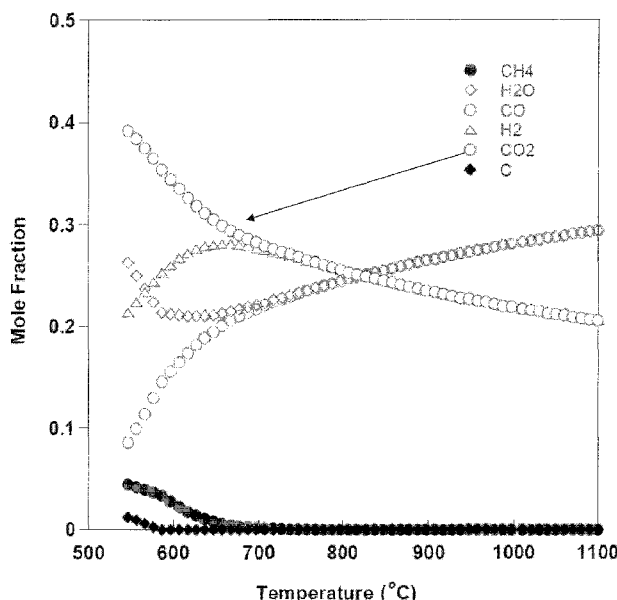


Figure 1

(57) Abstract: In one embodiment, a membrane of proton-electron conducting ceramics that is useful for the conversion of a hydrocarbon and steam to hydrogen has a porous support of $M'-Sr_{1-x}M''_xCe_{1-y}Zr_yM'''_yO_{3-\delta}$, Al_2O_3 , mullite, ZrO_2 , CeO_2 or any mixtures thereof where: M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is O to about 0.5; x' is O to about 0.5; y' is O to about 0.5; and $x' + y' > 0$; for example, $Ni-SrCe_{1-x}Zr_yO_{3-\delta}$, where x' is about 0.1 to about 0.3. The porous support is coated with a film of a Perovskite-type oxide of the formula $SrCe_{1-x-y}Zr_yMO_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.15 and y is about 0.1 to about 0.3. By including the Zr and M in the oxide in place of Ce, the stability can be improved while maintaining sufficient hydrogen flux for efficient generation of hydrogen. In this manner, the conversion can be carried out by performing steam methane reforming (SMR) and/or water-gas shift reactions (WGS) at high temperature, where the conversion of CO to CO_2 and H_2 is driven by the removal of H_2 to give high conversions. Methods of preparing the membrane cells and a system for use of the membrane cells to prepare hydrogen are presented. A method for sequestering CO_2 by reaction with methane or other hydrocarbon catalyzed by the novel membrane to form a syngas is also presented.

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- *without international search report and to be republished
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DESCRIPTIONPROTON CONDUCTING MEMBRANES
FOR HYDROGEN PRODUCTION AND SEPARATION

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GOVERNMENT SUPPORT

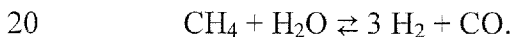
The subject matter of this application has been supported in part by a research grant from the National Aeronautic and Space Administration under Grant No. NAG3-2930. Accordingly, the government has certain rights in this invention.

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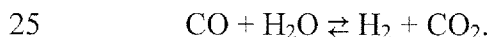
BACKGROUND

Presently, about 95% of the 9 million tons of hydrogen produced in the United States uses a thermal process with natural gas as the feedstock. The most common process involves steam methane reforming (SMR) and water-gas shift reactions (WGS) at high temperature. Hydrogen gas must then be separated from the resultant mixed gas stream.

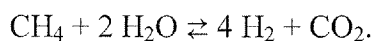
SMR is an endothermic process where methane and water are converted into hydrogen and carbon monoxide by the equation:



WGS is an exothermic process that converts carbon monoxide and water to hydrogen and carbon dioxide:

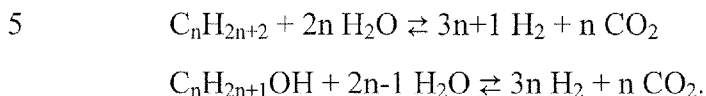


Coupling the SMR to the WGS reaction yields a net reaction of:



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In addition to or in place of the methane, higher hydrocarbons or alcohols can be used to generate H₂ by SMR and WGS, as illustrated for alkanes and mono hydroxy substituted alcohols:



Membrane reactor technology allows economic production of high purity hydrogen from natural gas, gasified coal, biomass, and other hydrocarbon feedstocks by coupling steam reforming and hydrogen transport in one step. Removal of product hydrogen continuously through the membrane shifts the equilibrium toward increased hydrogen production. Palladium metal alloy membranes have been available for hydrogen production for several decades, but these membranes are expensive and require large areas for adequate fluxes in commercial applications. In addition to industrial hydrogen production, efforts have been made to use SMR and WGS reactors and hydrocarbon fuels with hydrogen fuel cells in automotive applications to exploit the efficiencies of hydrogen fuel cell, which are generally more than twice that of internal combustion engines.

SMR is typically run at steam concentrations higher than the reaction stoichiometry to improve conversion. When the molar water-to-carbon ratio is large, WGS takes place in the same reactor allowing conversion of the hydrocarbons to H₂ and CO₂. Additionally, reactors that promote SMR and WGS must be robust as a number of secondary reactions, such as carbon formation, can occur that are detrimental to the performance of the reactor. The use of higher stoichiometry of water-to-carbon can significantly diminish the formation of undesired byproducts of these reactions. Higher temperatures also diminish the observance of these byproducts. As the SMR reaction is endothermic, high temperatures are favorable for the promotion of the reaction. On the other hand, WGS is mildly exothermic and reversible and the equilibrium constant for the formation of hydrogen is greater at lower temperatures, where the reaction rate is low. Hence, reaction is best carried out at higher temperatures in a manner that hydrogen is readily and rapidly removed from the reactor by having a high flux rate through the membrane to drive the equilibrium reaction to high conversion.

Perovskite-type oxides (e.g. $\text{BaCe}_{1-x}\text{M}_x\text{O}_3$, where M is a metal dopant) have been shown to have high proton conductivities at elevated temperature, with protonic conductivities on the order of $10^{-2} \Omega^{-1}\text{cm}^{-1}$ at 600 °C. As the hydrogen permeates through the membrane as a proton, separation selectivity for hydrogen is nearly absolute, allowing the collection of extremely pure hydrogen. The potential permeation flux rate of these materials is also extremely high if sufficient electronic conductivity can be achieved.

$\text{BaCe}_{1-x}\text{M}_x\text{O}_3$ -type protonic conductors have insufficient electronic conductivity to balance the transport of charge through the material. To address these problem similar type protonic conductors, particularly $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_3$, have been used to form a two phase proton and electric conductor where Pd acts as the electron conductor phase, as disclosed in Wachsman et al., U.S. Patent No. 6,235,417. A subsequent patent to Wachsman et al., U.S. Patent No. 6,296,687 discloses a mixed protonic-electronic conducting material useful as a H_2 permeable membrane or electrode that comprises $\text{BaCe}_{1-x}\text{M}_x\text{O}_3$ -type conductors when M is a multivalent dopant metal.

Unfortunately, these systems have not demonstrated sufficient chemical stability for many commercial applications involving hydrogen production. There remains the need for improved stable membranes where high flux is achieved. Additionally, it is desirable to use such membranes in a reactor where a single high temperature is employed for hydrogen production and separation. It is also desirable to readily fabricate such a ceramic membrane reactor.

SUMMARY OF THE INVENTION

Embodiments of the invention are directed to a membrane of proton conducting ceramics where a porous support comprising $\text{M}'\text{-Sr}_{1-z'}\text{M}''_{z'}\text{Ce}_{1-x'-y'}\text{Zr}_x\text{M}'''_{y'}\text{O}_{3-\delta}$, Al_2O_3 , mullite, ZrO_2 , CeO_2 or any mixtures thereof where: M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is 0 to about 0.5; x' is 0 to about 0.5; y' is 0 to about 0.5; and $x' + y' > 0$, for example, $\text{Ni-SrCe}_{1-x'}\text{Zr}_x\text{O}_{3-\delta}$, where x' is about 0.1 to about 0.3, has a surface covered by a film comprising a Perovskite-type oxide of the formula $\text{SrCe}_{1-x-y}\text{Zr}_x\text{M}_y\text{O}_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.15 and y is about 0.1 to about 0.3. In some embodiments of the invention it is

advantageous that at least two of x' , y' and z' are greater than 0, for example greater than 0.01. In some embodiments of the invention it is advantageous that x' is greater than 1. The film can be about 1 to about 50 μm in thickness. In an embodiment of the invention, superior stability is achieved with a Perovskite-type oxide of the formula $\text{SrCe}_{1-x-y}\text{Zr}_x\text{M}_y\text{O}_{3-\delta}$ where x is 0.1 to 0.2. The hydrogen permeation is improved because of the inclusion of M, and in one effective embodiment M is Eu.

Another embodiment of the invention is a method for construction of membranes of proton conducting ceramics described above. The method involves providing a porous support comprising $\text{M}'\text{-Sr}_{1-z}\text{M}''\text{Ce}_{1-x-y}\text{Zr}_x\text{M}'''\text{O}_{3-\delta}$, Al_2O_3 , mullite, ZrO_2 , CeO_2 or any mixtures thereof where: M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is 0 to about 0.5; x' is 0 to about 0.5; y' is 0 to about 0.5; and $x' + y' > 0$, for example, $\text{Ni-SrCe}_{1-x}\text{Zr}_x\text{O}_{3-\delta}$, where x' is about 0.1 to about 0.3, and a slurry of $\text{SrCe}_{1-x-y}\text{Zr}_x\text{M}_y\text{O}_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.15 and y is about 0.1 to about 0.3, where the slurry is deposited as a film coating a surface of the porous support. In one embodiment a precursor $\text{M}'\text{O-Sr}_{1-z}\text{M}''\text{Ce}_{1-x-y}\text{Zr}_x\text{M}'''\text{O}_{3-\delta}$ can be used and reduced to the $\text{M}'\text{-Sr}_{1-z}\text{M}''\text{Ce}_{1-x-y}\text{Zr}_x\text{M}'''\text{O}_{3-\delta}$ porous support upon reduction that is carried out either before or after the film deposition. Upon sintering the coated support and reducing the NiO of the support to $\text{Ni-SrCe}_{1-x}\text{Zr}_x\text{O}_{3-\delta}$, where x' is about 0.1 to about 0.3, a membrane of proton conducting ceramic results. In one embodiment of the inventive method, the porous support is provided by making a mixture of NiO, $\text{SrCe}_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ and a fluid which is then ball-milled and degassed and then formed into a desired shape, for example a tube which can be extruded, or tape cast into a green body tape which is then formed into a tube, and sintered to form the tubular shaped porous support. The mixture can also include a dispersant, plasticizer and/or binder. The slurry can be provided by combining SrCO_3 , CeO_2 , ZrO_2 , and Eu_2O_3 , which is ball milled, calcined, ground to a powder and combined with a fluid.

Another embodiment of the invention is directed to a membrane reactor for the production of hydrogen from a hydrocarbon feedstock. The reactor has a high temperature stable housing, at least one membrane of proton conducting ceramics as described above, one or more inlets for hydrocarbons and separate outlets where at least

one outlet is an exhaust for water and carbon dioxide and at least one outlet is for the produced hydrogen. The housing is any material that can withstand the heat from the reaction, such as quartz, metal, metal alloy, or ceramic. The hydrocarbon and water are introduced through an inlet to an isolated volume of the reactor in contact with the support side of the membrane free of the $\text{SrCe}_{1-x-y}\text{Zr}_x\text{M}_y\text{O}_{3-\delta}$ film. This volume also includes at least one outlet to exhaust water and carbon dioxide. The hydrogen is withdrawn from an isolated volume on the coated side of the membrane.

Another embodiment of the invention is method of using the membrane in a reactor for the formation of a syngas mixture with variable H_2/CO ratios necessary for subsequent catalytic conversion to chemical feedstocks and liquid fuels.

Another embodiment of the invention is a method of using the membrane in a reactor that utilizes CO_2 , from other chemical and combustion processes, as a reactant in the formation of hydrogen and syngas mixtures, for subsequent catalytic conversion to chemical feedstocks and liquid fuels, as a method to sequester CO_2 and address global climate change.

BRIEF DESCRIPTION OF THE DRAWINGS

There are shown in the drawings, embodiments, which are presently preferred, it being understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown.

Figure 1 is a plot of the equilibrium concentrations of reactants and products of the WGS process with a $\text{H}_2\text{O}/\text{CO}$ ratio of 1 as a function of temperature.

Figure 2 is a plot of the equilibrium concentrations of reactants and products of the WGS process with a $\text{H}_2\text{O}/\text{CO}$ ratio of 2 as a function of temperature.

Figure 3 is a schematic diagram of a hydrogen permeation reactor system according to an embodiment of the invention.

Figure 4 shows powder X-ray patterns for calcined $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and calcined $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$, according to an embodiment of the invention, before and after exposure to dry hydrogen at 900 °C for 24 hour.

Figure 5 is a plot of total conductivity for $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.6}\text{Zr}_{0.3}\text{Eu}_{0.1}\text{O}_{3-\delta}$, according to an embodiment of the invention, under pure H_2 atmosphere as a function of temperature.

Figure 6 is a plot of conductivity of $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and $\text{SrZr}_{0.2}\text{Ce}_{0.7}\text{Eu}_{0.1}\text{O}_{3-\delta}$, according to an embodiment of the invention, under a dry hydrogen atmosphere at 900 °C over 5 days.

Figure 7 is a photograph of a comparative $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCeO₃ hydrogen membrane cell and a photograph of a $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCe_{0.8}Zr_{0.2}O₃ hydrogen membrane cell, according to an embodiment of the invention, after exposure to methane with 8 % steam, and correlated to a plot of the temperature profile of the temperature of the membrane cell.

Figure 8 is a plot of hydrogen flux for 50 μm thick $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCe_{0.8}Zr_{0.2}O_{3-δ} membrane cells, according to an embodiment of the invention, at various hydrogen partial pressures as a function of temperature.

Figure 9 is a plot of the hydrogen flux for a comparative $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCeO₃ hydrogen membrane cell and $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCe_{0.8}Zr_{0.2}O₃ hydrogen membrane cell, according to an embodiment of the invention, with 5 volume % CO and 3 volume % H₂O at 900 °C as a function of time.

Figure 10 is (a) an SEM image and (B) the hydrogen permeation flux for various hydrogen partial pressures for 50 μm thick $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCe_{0.8}Zr_{0.2}O₃ membrane cells, according to an embodiment of the invention, at various temperatures.

Figure 11 is a plot of the hydrogen permeation flux for $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCe_{0.8}Zr_{0.2}O₃ coatings of various thicknesses, according to an embodiment of the invention, at various hydrogen contents with 3% humidity.

Figure 12 are SEM images of (a) 42.5μm, (b) 30μm and (c) 20μm thick $\text{SrCe}_{0.65}\text{Zr}_{0.2}\text{Eu}_{0.15}\text{O}_{3-\delta}$ hydrogen membrane coatings according to an embodiment of the invention on a porous support.

Figure 13 are plots of the permeation flux for (a) 42.5μm, (b) 30μm and (c) 20μm thick $\text{SrCe}_{0.65}\text{Zr}_{0.2}\text{Eu}_{0.15}\text{O}_{3-\delta}$ membranes as a function of hydrogen partial pressure at various temperatures.

Figure 14 are plots of the hydrogen permeation flux of $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.65}\text{Zr}_{0.2}\text{Eu}_{0.15}\text{O}_{3-\delta}$ membranes according to an embodiment of the invention as a function of membrane coating thickness at 900 °C for various hydrogen partial pressures.

Figure 15 is a plot of CO conversion as a function of temperature for 3 % H₂O + 3% CO (H₂O/CO = 1:1) and 6% H₂O + 3% CO (H₂O/CO = 2:1); in the absence of a proton conductive membrane, ○ (1:1) and ● (2:1); with a $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCeO₃

proton conductive membrane, $\square$ (1:1), $\blacksquare$ (2:1) and $\blacklozenge$ (2:1) with *in situ* H₂ removal; and the calculated thermodynamic equilibria conversion values, — (1:1) and -- (2:1);.

Figure 16 is a plot of the H₂ flux as a function of temperature for 3% CO + 6% H₂O using a SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCeO₃ proton conductive membrane for: $\bullet$ H₂ production without a He sweep of permeated H₂; $\blacktriangledown$ membrane permeated H₂; $\blacksquare$ H₂ production in the feed side effluent with *in situ* H₂ removal; $\blacklozenge$ total catalytic H₂ production with *in situ* H₂ removal; and — calculated thermodynamic equilibrium H₂ conversion values.

Figure 17 is a plot of H₂ yield (left scale) and H₂/CO ratio (right scale) as a function of temperature using a SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCeO₃ proton conductive membrane with 3% CO + 6% H₂O and *in situ* H₂ removal where: $\blacksquare$ permeated H₂; $\bullet$ H₂ in the feed effluent; $\blacklozenge$ total H₂ yeild; and $\blacktriangle$ the H₂/CO ratio.

Figure 18 is a plot of the methane and carbon dioxide conversions (XCH₄ and XCO₂) as a function of temperature for reforming CH₄ and CO₂ according to an embodiment of the invention using a SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O_{3-δ} proton conductive membrane with CH₄/CO₂ ratios of : 1/2 $\blacklozenge$ (CH₄) $\blacklozenge$ (CO₂); 1/1.5 $\blacksquare$ (CH₄) $\square$ (CO₂); and 1/1 $\bullet$ (CH₄) $\circ$ (CO₂).

Figure 19 is a plot of H₂ production as a function of temperatures for reforming CH₄ and CO₂ according to an embodiment of the invention using a SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O_{3-δ} proton conductive membrane for CH₄/CO₂ ratios of : 1/1 $\blacklozenge$ (total H₂) $\blacklozenge$ (H₂ permeated (lower) and in the feed effluent (top)); 1/1.5 $\bullet$ (total H₂) $\circ$ (H₂ permeated (lower) and in the feed effluent (top)); and 1/2 $\blacksquare$ (total H₂) $\square$ (H₂ permeated (lower) and in feed effluent (top)).

Figure 20 is a plot of the H₂/CO ratio of the feed effluent as a function of temperature using a SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O_{3-δ} proton conductive membrane according to an embodiment of the invention where the CH₄/CO₂ feed ratio was $\bullet$ 1/1, $\blacksquare$ 1/1.5 and $\blacklozenge$ 1/2.

Figure 21 is a plot of CH₄ and CO₂ conversions (left scale) and the H₂/CO ratio (right scale) at 850 °C and 900 °C measured in the feed effluent from a 1/1.5 CH₄/CO₂ feed as a function of total flow rate using a SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O_{3-δ} proton conductive membrane according to an embodiment of the invention where: $\circ$ XCH₄, $\square$ CO₂ and $\blacklozenge$ H₂/CO at 850 °C; and $\bullet$ XCH₄, $\blacksquare$ CO₂ and $\blacklozenge$ H₂/CO at 900 °C.

Figure 22 is a plot of H_2 productions and its distribution between the feed effluent and that permeating through a $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ on $Ni-SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ proton conductive membrane from a 1/1.5 CH_4/CO_2 feed using a $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ on $Ni-SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ proton conductive membrane according to an embodiment of the invention, where: $\bullet$ H_2 (permeated), $\blacksquare$ H_2 (feed effluent) and $\blacklozenge$ (total H_2) at 850 °C; and ∇ H_2 (permeated), $\triangle$ H_2 (feed effluent) and $\circ$ (total H_2) at 850 °C.

Figure 23 is a plot of CH_4 (diamonds) and CO_2 (squares) conversions for $CH_4/CO_2/H_2O$ feed ratios of 2/1/1 (hollow symbols) and 2/1/1.5 (filled symbols) using a $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ on $Ni-SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ proton conductive membrane according to an embodiment of the invention.

Figure 24 is a plot of H_2 productions (circles (permeated), squares (feed effluent), and total (diamonds)) (left scale) and the H_2/CO ratio (triangles) (right scale) as a function of temperature for $CH_4/CO_2/H_2O$ feed ratios of 2/1/1 (filled symbols) and 2/1/1.5 (hollow symbols) using a $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ on $Ni-SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ proton conductive membrane according to an embodiment of the invention.

DETAILED DESCRIPTION

Embodiments of the invention are directed to Perovskite-type oxide proton conductors that are stable and can be readily fabricated as part of membranes in a form that can be used in a thermally integrated reactor where hydrogen production and separation can be carried out simultaneously at a high temperature. The novel reactor can be used to carry out hydrogen production from hydrocarbon or hydrocarbon mixture, such as CNG, or other hydrocarbons, including natural gas, coal based syngas and gasified biomass, by SMR and/or WGS reactions carried out simultaneously. In another embodiment of the invention, the membrane reactor can be used to sequester CO_2 by conversion to chemical feedstocks and fuels. The novel Perovskite-type oxide is one of an $ABO_{3-\delta}$ type where: A is Sr, Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or combinations thereof, for example Sr, Ba, Ca, Mg or combinations thereof; and B is $Ce_{1-x-y}Zr_xM_y$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb; x is 0 to about 0.2; and y is about 0.1 to about 0.3. The inclusion of Eu, for example, provides a high H_2 permeation. Although examples and description, below, are directed to the inventive composition where M is

Eu, it should be understood that any of the other metals or combination of these metals can be substituted for or included with Eu for the inventive oxide proton-electron conductor membranes. The inclusion of Zr stabilizes the oxide toward reaction of the oxide with CO and CO₂ and allows extended high temperature use of the membrane. A preferred embodiment for the novel Perovskite-type oxide is one of an ABO_{3-δ} type where A is Sr and B is Ce_{1-x-y}Zr_xM_y where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0.1 to about 0.2 and y is about 0.1 to about 0.3.

SMR and/or WGS processes are possible where sufficient water is employed and where the equilibrium can be shifted to higher yield by the removal of hydrogen. The inventive proton conductor enables a reactor based on a highly hydrogen selective membrane that employs a membrane material that is stable to high temperatures in the presence of the chemical species possible during the performance of these reactions. The thermodynamic considerations to establish appropriate conditions to carry out the reactions that avoid the formation of side products, such as carbon, in addition to the reagents, intermediates, and products of the net conversion of hydrocarbon and water to H₂ and CO₂.

Using Thermocalc® software, the theoretical composition resulting from these equilibria was calculated at H₂O/CO ratios of 1 and 2, which are plotted in Figure 1 and Figure 2, respectively. As can be seen in these plots, high temperatures and H₂O/CO ratios are conducive to the inhibition of carbon formation and having minimal residual methane. As illustrated in Figure 1, temperatures in excess of 590 °C are required to assure no carbon fowling when the H₂O/CO ratio would drop to as low as 1, although increasing the ratio to 2 allows the avoidance of carbon fowling at temperatures below 550 °C. As indicated in Figure 1, equilibrium methane concentrations are not effectively eliminated until a temperature of about 700 °C at a H₂O/CO ratio of 1. As SMR is endothermic, but entropically favorable, temperatures in excess of about 750 °C to about 1,000 °C are used.

The Perovskite-type oxide conductors for the membranes according to the invention have the structure SrCe_{1-x-y}Zr_xM_yO_{3-δ} where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.2 and y is about 0.1 to about 0.3, and provide the needed hydrogen flux and catalyst stability to achieve high conversions as a stable membrane when on a Ni-SrCe₁₋

$z\text{Zr}_z\text{O}_3$, where $z = 0.1$ to 0.3 porous support for use at temperatures of about 850°C to about 950°C or more. This novel composition was found to be stable to the presence of CO_2 at high temperatures compositions. Compositions with insufficient quantities of Zr were observed to be unstable at temperatures below 900°C . Furthermore, compositions without Zr in the porous support resulted in membrane cells that crack at elevated temperatures. The perovskite-type oxide can be deposited on the support at thicknesses of about 1 to about $50\text{ }\mu\text{m}$.

The inventive membrane uses a support that can be $\text{M}'\text{-Sr}_{1-z}\text{M}''_z\text{Ce}_{1-x-y}\text{Zr}_x\text{M}'''_y\text{O}_{3-\delta}$, Al_2O_3 , mullite, ZrO_2 , CeO_2 or any mixtures thereof where: M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is 0 to about 0.5 ; x' is 0 to about 0.5 ; y' is 0 to about 0.5 ; and $x' + y' > 0$, where the support is stable under the temperatures and reaction mixtures employed with the membrane reactor.

In one embodiment of the invention the support is $\text{Ni-SrCe}_{1-x'}\text{Zr}_{x'}\text{O}_{3-\delta}$ support, where x' is about 0.1 to about 0.3 , which acts as the catalyst for the SMR and/or WGS process. Under the required conditions for performance of these processes, the presence of the Zr was found to be critical for the resistance of the membrane to deterioration and cracking. To maintain its stability, the proton-electron conductive film also requires Zr such that the loss of Zr from the support does not occur during use.

According to an embodiment of the invention, the membrane cells can be $\text{SrCe}_{1-x-y}\text{Zr}_x\text{M}_y\text{O}_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.2 and y is about 0.1 to about 0.3 , supported on $\text{Ni-SrCe}_{1-x'}\text{Zr}_{x'}\text{O}_{3-\delta}$, where x' is about 0.1 to about 0.3 and can be prepared by a method where the membrane coating is prepared by any method where a desired stoichiometric mixture of perovskite oxide precursors are combined. For example, a mixture of SrCO_3 , CeO_2 , ZrO_2 , and Eu_2O_3 , as uniformly dispersed fine particles, for example by ball-milling, are heated at a sufficiently high temperatures so that the oxide precursors are calcined to form the Perovskite structure. The Perovskite oxide can be ground and dispersed in a fluid, such as ethanol, to form a slurry that can then be used to coat a porous support, which can be subsequently sintered to form a dense coating on the porous support.

According to an embodiment of the invention, a porous support can be prepared by combining a mixture of NiO , $\text{SrCe}_{1-x'}\text{Zr}_{x'}\text{O}_{3-\delta}$, where x' is about 0.1 to about 0.3, with a fluid, which includes an aqueous or non-aqueous liquid to suspend the particles and, as needed, appropriate dispersants, plasticizers and binders. Ball-milling the mixture achieves a dispersed finely divided solid in the fluid which can then be degassed. The mixture can then be cast, for example by tape casting or other common casting methods, molded, or extruded to form a particulate ceramic green body. In one embodiment of the invention, the green body as a tape can be form into a green body tube and sintered to form the porous support.

In an embodiment of the invention, the porous support can be coated on one surface with the Perovskite-type oxide proton conductor and the coated support sintered to form the desired membrane cell. The membrane cell can be a plate, a tube, or any geometry where a surface with the coating can be segregated from sides without the coating such that the gas volume on the two sides of the membrane cell can be segregated. A tubular support can be coated on the inside or outside surface in various embodiments of the invention. The tube can be open at both ends in some embodiments of the invention, and can be closed at one end in other embodiments of the invention.

Many different configurations of membrane cells can be used to design hydrogen permeation reactor systems according to embodiments of the invention. An embodiment of the invention where the membrane cell is in the form of an internally proton conductor coated closed end tube is illustrated in Figure 3. The reactor systems require a housing **101** to contain and direct gases and allowing the separation of the produced hydrogen comprising gas from the reactant gas stream comprising a SMR and/or WGS reaction mixture, such that the methane and/or other hydrocarbon and water vapor mixture is introduced to the porous $\text{Ni-SrCe}_{1-x'}\text{Zr}_{x'}\text{O}_{3-\delta}$, where x' is about 0.1 to about 0.3, side of the membrane cell **103** and isolated from the hydrogen comprising gas on the Perovskite-type oxides proton conductor coating side of the membrane cell. The reactor system has an inlet **102** for the reacting gas mixture and an outlet for the hydrogen comprising product gas **104** and an outlet for the other reactor product comprising gas **105**. A means to heat the membrane cell **106** can be provided if desired, although, in general, sufficient heat is generated in the process such that such a heater is not required. In this embodiment, illustrated as configured for experimental purposes, a means of heating **106** is provided within a furnace **107** and the housing **101** is quartz and essentially tubular in structure.

An inlet **108** for a sweeping carrier gas, such as helium, can be used to promote the removal of the hydrogen that crosses the tubular membrane cell. In this embodiment the tube extends through the housing **101** in a manner where the volume on the outside of the tube **103**, on the film free surface of the membrane, is where an inlet **102** allows the intake of hydrocarbon and water and CO₂ comprising gases to be isolated from the hydrogen comprising gas removed from the inside of the membrane tube **103**. Although illustrated as a tubular reactor, those skilled in the art can appreciate that the reactor can have other shapes, forms and designs. The housing need not be quartz but can be any material that has sufficient properties at the temperature where the reactor is employed. For example, the housing can be a metal or metal alloy, such as steel or can be a ceramic. To control the reaction, generally the reactor system also, but not necessarily, includes valves, temperature controlling means, and other devices to monitor and/or control the variables of gas input, output, pressure and temperature to optimize or otherwise control the rate of hydrogen formation.

In another embodiment of the invention, the proton conducting membranes can be employed to reform CO₂ with hydrogen rich hydrocarbon gases, such as CH₄, to produce CO and H₂. The product CO and H₂ can be converted through a Fischer-Tropsch process to chemical feedstocks and liquid fuels. In this manner CO₂ can be sequestered along with CH₄, a more potent green house gas, at point sources that generate large quantities of CO₂ and/or CH₄.

MATERIALS AND METHODS

Stability of Zr Containing Perovskite Oxides

SrCe_{0.9}Eu_{0.1}O_{3-δ} and SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} samples were prepared by a solid-state reaction where SrCO₃, CeO₂, ZrO₂ and Eu₂O₃ in the desired stoichiometric ratio were ball-milled for at least 24h and calcined for 10 hours at 1300 °C in air. The powders were ground and Perovskite structures were confirmed by X-ray diffraction. All samples were exposed to dry and wet hydrogen atmospheres for 24 hours and their X-ray diffraction patterns were determined after each exposure. Conductivity was measured under wet and dry H₂ atmospheres and multiple temperatures for each sample. Pellets were coated with Pt-paste (Englehard 6926) and heated to 1,000 °C for 1 hour. Conductivity measurements were performed using a Solartron 1260 Impedance Analyzer in the frequency range of 0.1 Hz to 1 MHz.

Figure 4 displays powder X-ray patterns of calcined $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and calcined $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ before and after exposure to dry hydrogen at 900 °C for 24 hour. The higher angle peak positions of calcined $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$, in comparison to the calcined $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ peaks, reflect a decreased perovskite unit cell volume with Zr substitution. After heating in dry hydrogen, the X-ray pattern of $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ does not change, indicating no secondary phase formation, and stability under these conditions.

Total conductivity was measured for $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$, $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.6}\text{Zr}_{0.3}\text{Eu}_{0.1}\text{O}_{3-\delta}$ under pure H_2 atmospheres, as shown in Figure 5. $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ shows higher conductivity than Zr substituted samples and the conductivity decreases with Zr content. The conductivity of $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and $\text{SrZr}_{0.2}\text{Ce}_{0.7}\text{Eu}_{0.1}\text{O}_{3-\delta}$ under a dry hydrogen atmosphere at 900 °C was measured for 5 days, as shown in Figure 6. The $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ conductivity increases with time due to phase decomposition. Although the total conductivity of $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ is less than that of $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$, a greater stability under dry hydrogen atmosphere was observed for $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$.

Comparative Stability of Zr Containing Supports

Ni- SrCeO_3 tubular type supports containing and free of Zr with $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ hydrogen membrane thin films were prepared by tape casting and rolling techniques. SrCeO_3 was prepared by a conventional solid state reaction method from SrCO_3 (99.9%) and CeO_2 powder (99.9%) as starting materials. $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ powder was synthesized by a citrate process, using 1 to 2 molar ratios of the total metal nitrates to citric acid, which displayed no secondary phase formation at a relatively low calcining temperature of 1300 °C in air. After presintering the support at 1100 °C for 10 hours, $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ was coated inside the support by a dip coating method. Membrane thickness was varied by depositing different numbers of coatings. The membrane tube was sintered at 1450 °C for 5 hours.

The hydrogen permeation measurement was conducted by installing the tubular hydrogen membrane cell in a high temperature reactor apparatus, as shown in Figure 3. The feed side of the membrane cell was exposed to H_2 (99.999%) diluted to a desired concentration with Ar (99.999%) at a 20 cm^3/min total flow rate. To achieve a wet gas flow, the feed gas was passed through a water bubbler at 25 °C resulting in a feed gas with 3 volume percent water vapor. The opposite (sweep) side of the membrane was

swept with He at 20 cm³/min. SMR conditions were achieved combining a CH₄ gas with 8 % water vapor in Ar. The compositions of permeated gases on the sweep side were measured using a mass spectrometer (Dycor QuadLink IPS Quadrupole Gas Analyzer).

The phase stability in a CO/CO₂ atmosphere of Ni-SrCe_{0.8}Zr_{0.2}O₃ supports was compared with Ni-SrCeO₃ supports. Figure 7 shows the SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCeO₃ and SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O₃ hydrogen membrane cells after exposure to methane with 8 % steam. No physical cracking of the membrane cells occurred to the SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O₃ hydrogen membrane cell, unlike SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCeO₃ which cracks under these conditions.

Figure 9 shows the hydrogen flux through the tubular-type SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCeO₃ hydrogen membrane cell with a SrCe_{0.9}Eu_{0.1}O_{3-δ} thickness of 50 μm and the hydrogen flux through the tubular-type SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O₃ hydrogen membrane cell with a SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} thickness of 50 μm. As shown in Figure 9, no flux degradation was observed for the SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O₃ hydrogen membrane cell. In contrast, the SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCeO₃ hydrogen membrane cell exhibited a significant decrease in flux with time. Degradation of the hydrogen permeation flux ultimately limits the use of such membrane cells.

Stability of membrane Cells with Zr in the Substrate and Coating

A Ni-SrCe_{0.8}Zr_{0.2}O_{3-δ} tubular substrate was fabricated by tape casting method followed by a rolling process. SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} powder was synthesized by a solid state reaction method and coated to the inner side of the substrate. The membrane cell's hydrogen permeability was measured with the feed side of membrane exposed to various proportions of H₂ with Ar and 3% H₂O at a total flow rate of 20 cm³/min where the sweep side of the membrane was exposed to 20 cm³/min He. The permeated gases were analyzed using a mass spectrometer (Q100MS Dycor Quadlink).

Figure 8 is a plot of the hydrogen permeation of SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} on Ni-SrCe_{0.8}Zr_{0.2}O_{3-δ} membrane cells. Hydrogen permeation flux increases with increasing temperature and hydrogen partial pressure. A hydrogen permeation flux of 0.225 ml cm⁻² min⁻¹ was achieved at 900 °C using 20 ccm H₂ as the feed gas. Figure 9 shows the hydrogen flux versus time for hydrogen with 5 volume % CO and 3 volume % H₂O at 900 °C. The hydrogen flux decreased with time for a SrCe_{0.9}Eu_{0.1}O_{3-δ} on Ni-SrCeO₃,

where an 8% drop was observed over 8 hours. In contrast the hydrogen flux was stable for the $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on $\text{Ni-SrCe}_{0.8}\text{Zr}_{0.2}\text{O}_3$ membrane cell.

Tubular Membrane Cells

5 $\text{SrCe}_{0.8-x}\text{Zr}_{0.2}\text{Eu}_x\text{O}_{3-\delta}$ ($x=0.1, 0.15$ and 0.2) on $\text{Ni-SrCe}_{0.8}\text{Zr}_{0.2}\text{O}_3$ hydrogen membrane cells were prepared by a tape casting and rolling technique. $\text{SrCe}_{0.8}\text{Zr}_{0.2}\text{O}_3$ powder was prepared by a conventional solid state reaction method from SrCO_3 (99.9%), ZrO_2 (99.9%) and CeO_2 powder (99.9%). The $\text{SrCe}_{0.8-x}\text{Zr}_{0.2}\text{Eu}_x\text{O}_{3-\delta}$ ($x=0.1, 0.15$ and 0.2) powders were synthesized by solid state reactions. After pre-sintering the support at 1100
10 $^\circ\text{C}$ for 10 hrs, $\text{SrCe}_{0.8-x}\text{Zr}_{0.2}\text{Eu}_x\text{O}_{3-\delta}$ ($x=0.1, 0.15$ and 0.2) was coated inside the support by a slurry coating method. Membrane thickness was varied by the number of coatings applied. The membrane cell was subsequently sintered at 1450 $^\circ\text{C}$ for 5 hours.

For the hydrogen permeation measurement, the tubular type hydrogen membrane cell was installed in a high temperature reactor apparatus as shown in Figure 3. The feed
15 side of the membrane cell was exposed to H_2 (99.999%) diluted to the desired concentration using Ar (99.999%) at a flow rate of 20 cm^3/min . A wet gas flow was formed by passing the feed gas through a water bubbler at 25 $^\circ\text{C}$ resulting in a 3 vol % water vapor gas mixture. The sweep side was flushed with He at 20 cm^3/min . The compositions of permeated gases on the sweep side were measured using a mass
20 spectrometer (Dycor QuadLink IPS Quadrupole Gas Analyzer).

$\text{SrCe}_{1-x}\text{Eu}_x\text{O}_{3-\delta}$ ($x=0.1, 0.15$ and 0.2) on Ni-SrCeO_3 hydrogen membrane cells were investigated for hydrogen separation under SMR conditions. During the permeation test of $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCeO_3 hydrogen membrane cells, cracking occurred at about 700 $^\circ\text{C}$ regions, as shown in Figure 7. The crack occurred under the conditions
25 where a phase change of SrCeO_3 in CO/CO_2 atmosphere and coking in SMR at a ratio exceeding 0.6 of $\text{CH}_4/\text{H}_2\text{O}$ is possible. The support materials and the fabrication process of the tubular-type hydrogen membrane cells were augmented by substitution of Zr onto Ce-site. Although permeation flux decreases by Zr substitution, continuous stable flux and chemical stability under CO/CO_2 condition was achieved.

30 Figure 10(a) shows a SEM image and Figure 10(b) is a plot of the hydrogen permeation flux as a function of the hydrogen partial pressure for 50 μm thick $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on $\text{Ni-SrCe}_{0.8}\text{Zr}_{0.2}\text{O}_3$ membrane cells at various temperatures. The hydrogen flux through the $\text{SrZr}_{0.2}\text{Ce}_{0.7}\text{Eu}_{0.1}\text{O}_{3-\delta}$ membrane was proportional to $[\text{P}_{\text{H}_2}]^{1/4}$,

agreeing well with the Norby and Larring's model. This hydrogen flux increases with temperature for all partial pressures of hydrogen. $\text{SrCe}_{0.8-x}\text{Zr}_{0.2}\text{Eu}_x\text{O}_{3-\delta}$ ($x=0.1, 0.15$ and 0.2) hydrogen membrane thickness was dependant upon the number of coating applied to the support. The permeation flux for $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on $\text{Ni-SrCe}_{0.8}\text{Zr}_{0.2}\text{O}_3$ hydrogen
 5 membrane cells is similar to that of $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on Ni-SrCeO_3 hydrogen membrane cell and, likewise, shows linearly increased hydrogen permeation flux with decreases in the membrane thicknesses, as shown in Figure 11, according to Wagner's equation:

$$J_{\text{OH}^*} = -\frac{1}{L} \left[\frac{RT}{4F^2} \int_{P_{\text{O}_2}}^{P_{\text{O}_2}'} \sigma_i t_{\text{OH}^*} t_{v_{\text{O}}} d \ln P_{\text{O}_2} + \frac{RT}{2F^2} \int_{P_{\text{H}_2}}^{P_{\text{H}_2}'} \sigma_i t_{\text{OH}^*} (t_{v_{\text{O}}} + t_{e'}) d \ln P_{\text{H}_2} \right]$$

SEM images of (a) $42.5\mu\text{m}$, (b) $30\mu\text{m}$ and (c) $20\mu\text{m}$ thick $\text{SrCe}_{0.65}\text{Zr}_{0.2}\text{Eu}_{0.15}\text{O}_{3-\delta}$
 10 hydrogen membranes are shown in Figure 12 where a clear delineation between the dense membrane coatings and the porous supports can be seen. Figure 13 shows the hydrogen permeation flux dependence on the hydrogen partial pressure and temperature for the membranes of Figure 12. It displays a similar trend of hydrogen partial pressure dependence as did $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ hydrogen membranes. The hydrogen permeation
 15 flux of $\text{SrCe}_{0.7}\text{Zr}_{0.2}\text{Eu}_{0.1}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.65}\text{Zr}_{0.2}\text{Eu}_{0.15}\text{O}_{3-\delta}$ membrane tubes for various membrane coating thicknesses at 900°C is shown in Figure 14(a) and 14(b), respectively. Hydrogen permeation shows a linear dependence with inverse membrane thickness, indicating that bulk diffusion is the rate-limiting factor for permeation.

20 *Non-equilibrium H_2 generation in a WGS reaction*

For embodiments of the invention that involve the WGS reaction, the effective removal of hydrogen to drive the equilibrium to hydrogen production can be employed to increase the conversion of CO and H_2O to CO_2 and H_2 , such that the conversion of CO is very high, particularly at higher temperatures. Although the stability of the porous
 25 support, as illustrated in Figure 9, is inferior to those of the present invention a film of $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ on a Ni-SrCeO_3 was used to demonstrate the removal of product H_2 and shift of the equilibrium to the conversion of CO, as indicated in Figure 15, and the H_2 flux, as indicated in Figure 16.

The WGS reaction was carried out in a reactor of the design shown in Figure 3,
 30 where the membrane tube **103** was prepared from polycrystalline $\text{SrCeO}_{3-\delta}$ $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ powder that was prepared by a conventional solid-state reaction on mixed stoichiometric amounts of SrCO_3 (99.9%, Alfa-Aesar), CeO_2 and Eu_2O_3 powders,

followed by ball milling and calcining at 1300 °C. The Ni-SrCeO₃ tubular support was fabricated using tape-casting (Pro-Cast) followed by a rolling process. The tubular support was sealed at one end and pre-sintered. SrCe_{0.9}Eu_{0.1}O_{3-δ} was coated on the inner side of the pre-sintered support. The tubular membranes were finally sintered at 1450 °C.

5 The membrane tube was about 17 cm long and 0.48 cm in diameter. An SEM image confirmed that the membrane is dense and ~23 μm thick on a porous support. A thermal insulator **109** was applied to one end of the membrane tube, formed an insulating region **110** to drop the temperature and allow an O-ring **111** to seal the membrane tube **101**. The area of the membrane **101** opposite insulator zone was the active area for reaction and is about 12 cm². The WGS reaction was carried out from 600 °C to 900 °C under 3% CO + 3% H₂O and 3% CO + 6% H₂O with a total flow rate of 20 sccm balanced by Ar. Gas flow rates were controlled by mass flow controllers.

A high CO conversion maximizes the H₂ production. The CO conversion is defined as follows:

$$15 \quad \text{CO conversion (\%)} = \frac{F_{CO_2}^{out}}{F_{CO}^{in}} \times 100\%$$

where $F_{CO_2}^{out}$ and F_{CO}^{in} are CO₂ output flux and CO input flux, respectively.

Figure 15 shows the CO conversion temperature dependence for different reactor configurations having H₂O/CO ratios of 1:1 and 2:1. The CO conversion decreases as the reaction temperature increases for an un-driven system, which is in line with theoretical values for a closed system, as indicated in Figure 15 where theoretical values are those of Figures 1 and 2. For a CO-H₂O mixture fed into a reactor without use of membrane separation driving reaction by H₂ removal, CO conversion was limited to thermodynamic equilibrium values. The CO conversion for system with a 2/1 H₂O/CO ratio driven by H₂ removal exceeded thermodynamic limitations, increasing with temperature and was very high at 900 °C.

In like manner H₂ flux increased with increasing temperature as shown in Figure 16 as did the CO conversion, allowing for a higher hydrogen production by actively removing the H₂ from one side of the membrane. The H₂ yield:

$$H_2 \text{ yield (\%)} = \frac{F_{H_2}^{out}}{F_{CO}^{in}} \times 100\%$$

where $F_{H_2}^{out}$ and F_{CO}^{in} are the H_2 production and CO input flux, respectively, increased with the CO conversion, as illustrated in Figure 17.

CH₄-CO₂ Reforming

5 A dense ~33 μm thick $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane coated on a $Ni-SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ support was prepared as given above. The feed side of the membrane was exposed to CH_4 and CO_2 and/or steam. The permeated H_2 was swept with He gas at 20 cm^3/min , in co-current flow to the feed gas. The flow rates of CH_4 , CO_2 and He were controlled by mass flow controllers. When steam was included to the feed, unreacted steam was
10 condensed on a cold trap before the feed side was analyzed by gas chromatography, using a Varian CP 4900 Gas Chromatograph. The concentrations of the H_2 in the sweep gas were analyzed by a mass spectrometer (Dycor QuadLink IPS Quadrupole Gas Analyzer).

The effect of the CH_4/CO_2 ratio on the composition of a syngas product was studied using a 10 cm^3/min flow of CH_4 with various flows of CO_2 . Figure 18 shows the CH_4 and CO_2 conversion and the CH_4/CO_2 ratio as a function of temperature. The CH_4 and
15 CO_2 conversions are defined by the equations:

$$XCH_4 = \frac{F_{CH_4}^{in} - F_{CH_4}^{out}}{F_{CH_4}^{in}} \times 100\%$$

$$XCO_2 = \frac{F_{CO_2}^{in} - F_{CO_2}^{out}}{F_{CO_2}^{in}} \times 100\%$$

where F_i^{in} and F_i^{out} ($i = CH_4$ or CO_2) are the input and output flux of gas i . The CH_4 and
20 CO_2 conversions increase with increasing temperature as expected due to the endothermic nature of the transformation. The CH_4 conversion was higher for all runs and increases as the CH_4/CO_2 ratio decreases.

The hydrogen production is indicated in Figure 19 where the total H_2 production is the sum of the H_2 flux on the sweep side of the membrane and the H_2 flux on the feed side effluent. For all CH_4/CO_2 ratios, the H_2 production increases with temperature due to
25 the higher ambipolar conductivity of the membrane and a higher CH_4 conversion at high temperatures. Maximum H_2 permeation through the membrane 2.2 cm^3/min (~0.2 $cm^3/cm^2 min$) occurred at 900 °C at a CH_4/CO_2 ratio of 1/1. The H_2 permeation decreases with the CH_4/CO_2 ratio. The total H_2 production using a CH_4/CO_2 ratio of 1/2 does not

vary significantly with temperature, but varies at higher CH_4/CO_2 ratios. Lower CH_4/CO_2 ratios favors the reverse of the WGS reaction, equation (1), above, that consumes H_2 . Hence, more H_2 is consumed at elevated temperature and the total H_2 does not significantly increase with temperature even though the CH_4 and CO_2 conversions
5 increase. A maximum H_2 production of $17.0 \text{ cm}^3/\text{min}$ was achieved at 900°C at a CH_4/CO_2 ratio of $1/2$.

Figure 20 shows the H_2/CO ratio in the feed side effluent. The H_2/CO ratio decreases with increasing temperature and decreasing CH_4/CO_2 ratios and can be ascribed to a combination of the higher extent of the reversed WGS reaction and higher H_2
10 permeation at elevated temperatures. When the temperature increased from 700 to 900°C , the H_2/CO ratios decreased from 1.00 to 0.91 , from 0.95 to 0.84 and from 0.92 to 0.82 for CH_4/CO_2 ratios of $1/1$, $1/1.5$ and $1/2$, respectively.

The effect of flow rate on the CH_4 and CO_2 conversions, H_2 production and H_2/CO ratio was studied using a CH_4/CO_2 ratio of $1/1.5$ and total flow rates of 25 , 37.5
15 and $50 \text{ cm}^3/\text{min}$ at 850 and 900°C . As shown in Figure 21, the CH_4 and CO_2 conversion decreases slightly with total flow rate as can be expected from shorter residence time. In contrast, the H_2/CO ratio increases with the total flow rate due to the decreased percentage of H_2 that permeates the membrane at higher flow rates. As can be determined from the data plotted in Figure 22, the percentage of H_2 permeating the membrane decreases
20 from 13.1% to 8.8% at 900°C and from 10.4% to 7.6% at 850°C as the total flow rates were increased from 20 to $50 \text{ cm}^3/\text{min}$. The H_2 production increased with total flow rates due to the increase of the mass of reactants even though the CH_4 and CO_2 conversion decreased slightly.

The H_2/CO ratio generated using the membrane reactor is a maximum of 1 , while
25 a ratio of 2 is optimal for the Fischer-Tropsch process. To increase the H_2/CO ratio, H_2O was added to the CH_4/CO_2 feed to combine CO_2 reforming of CH_4 with steam reforming of CH_4 , to increase the H_2/CO ratio. Two $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}$ compositions, with $2/1/1$ and $2/1/1.5$ proportions, were examined with respect to the resulting H_2/CO ratio and CH_4 and CO_2 conversion for a feed gas composition of $20 \text{ cm}^3/\text{min}$ CH_4 , $10 \text{ cm}^3/\text{min}$ CO_2 and
30 various amounts of steam. Figure 23 shows the CH_4 and CO_2 conversion as a function of temperature. The CH_4 conversion increases with increasing H_2O concentration. A High H_2O concentration favors steam reforming of CH_4 and enhances CH_4 conversion. Higher H_2O concentrations result in lower concentrations of CH_4 and CO_2 since the CH_4/CO_2

ratio is fixed at 2/1. As a result, the CO₂ conversion decreases. The CH₄ and CO₂ conversion are 83% and 34% at 900 °C for a CH₄/CO₂/H₂O ratio of 2/1/1, suggesting that more than half of the CH₄ conversion occurs through the SMR reaction.

Figure 24 shows H₂ production and the H₂/CO ratio as a function of temperature. The H₂ production increases with temperature. The feed effluent H₂ flux and the total H₂ production increase with increasing H₂O concentration due to the higher CH₄ conversion. In contrast, the H₂ permeation decreases with increasing H₂O since higher H₂O concentration means higher P_{O₂}. The H₂/CO ratio of the feed side effluent is 2-2.5 and 2.1-2.6 for CH₄/CO₂/H₂O ratios of 2/1/1 and 2/1/1.5, respectively, as the temperature varies from 700 °C to 900 °C. The H₂/CO decrease with temperature trends similarly as that in Figure 20 without water and is ascribed to the reverse WGS reaction. The H₂/CO ratio of nearly 2 at 900°C is well matched to that needed for a Fischer-Tropsch process that produces a liquid hydrocarbon fuel.

All patents, patent applications, provisional applications, and publications referred to or cited herein, *supra* or *infra*, are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application.

CLAIMS

We claim:

1. A membrane of proton-electron conducting ceramics comprising:
 - 5 a porous support comprising $M'-Sr_{1-z'}M''_zCe_{1-x'-y'}Zr_xM'''_{y'}O_{3-\delta}$, Al_2O_3 , mullite, ZrO_2 , CeO_2 or any mixtures thereof where: M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is 0 to about 0.5; x' is 10 0 to about 0.5; y' is 0 to about 0.5; and $x' + y' > 0$; and
 - a film comprising a Perovskite-type oxide of the formula $SrCe_{1-x-y}Zr_xM_yO_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.2 and y is about 0.1 to about 0.3.
- 15 2. The membrane of claim 1, wherein said porous support comprises $M'-Sr_{1-z'}M''_zCe_{1-x'-y'}Zr_xM'''_{y'}O_{3-\delta}$ where at least two of x' , y' , and z' are greater than 0.
3. The membrane of claim 1, wherein said porous support comprises Ni-
 - 20 $SrCe_{1-x'}Zr_xO_{3-\delta}$ where x' is about 0.1 to about 0.3
4. The membrane of claim 1, wherein said film is about 1 to about 50 μm in thickness.
- 25 5. The membrane of claim 1, wherein x is about 0.1 to about 0.2.
6. The membrane of claim 5, wherein M is Eu.
7. A method for construction of a membrane of proton-electron conducting
 - 30 ceramics according to claim 1, comprising the steps of:
 - providing a porous support comprising: $M'-Sr_{1-z'}M''_zCe_{1-x'-y'}Zr_xM'''_{y'}O_{3-\delta}$, Al_2O_3 , mullite, ZrO_2 , CeO_2 , a precursor $M'O-Sr_{1-z'}M''_zCe_{1-x'-y'}Zr_xM'''_{y'}O_{3-\delta}$ to said $M'-Sr_{1-z'}M''_zCe_{1-x'-y'}Zr_xM'''_{y'}O_{3-\delta}$, or any mixtures thereof where:

M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is 0 to about 0.5; x' is 0 to about 0.5; y' is 0 to about 0.5; and $x' + y' > 0$; and

5 providing a slurry of $\text{SrCe}_{1-x-y}\text{Zr}_x\text{M}_y\text{O}_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.15 and y is about 0.1 to about 0.3;

depositing said slurry as a coating on a surface of said porous support;

10 sintering said coating and support; and

optionally reducing said $\text{M}'\text{O}-\text{Sr}_{1-z'}\text{M}''_{z'}\text{Ce}_{1-x'-y'}\text{Zr}_{x'}\text{M}'''_{y'}\text{O}_{3-\delta}$ to said $\text{M}'-\text{Sr}_{1-z'}\text{M}''_{z'}\text{Ce}_{1-x'-y'}\text{Zr}_{x'}\text{M}'''_{y'}\text{O}_{3-\delta}$.

8. The method of claim 7, wherein said porous support comprises $\text{Ni}-\text{SrCe}_{1-x'}\text{Zr}_{x'}\text{O}_{3-\delta}$ where x' is about 0.1 to about 0.3

9. The method of claim 8, wherein said step of providing a porous support comprises the steps of:

20 providing a mixture comprising NiO , $\text{SrCe}_{1-x'}\text{Zr}_{x'}\text{O}_{3-\delta}$ where x' is about 0.1 to about 0.3 and fluid;

ball-milling said mixture;

de-gassing said mixture;

forming a green body from said mixture; and

sintering said green body to form said porous support.

25

10. The method of claim 9, wherein said green body comprises a tube.

11. The method of claim 9, wherein said step of forming comprises tape casting, molding or extruding.

30

12. The method of claim 11, wherein said step of forming comprises tape casting followed by rolling to form a tube.

13. The method of claim 9, wherein said fluid comprises an aqueous or non-aqueous liquid.

14. The method of claim 9, wherein said mixture further comprises a dispersant.

15. The method of claim 9, wherein said mixture further comprises a plasticizer.

16. The method of claim 9, wherein said mixture further comprises a binder.

17. The method of claim 9, wherein said step of sintering comprises heating to 1150°C for 4 hours.

18. The method of claim 7 wherein said step of providing a slurry comprises the steps of:

providing a mixture of SrCO_3 , CeO_2 , ZrO_2 , and Eu_2O_3 ;

ball-milling said mixture;

calcining said milled mixture;

grinding said calcined mixture to a particulate mixture; and

combining said particulate mixture with fluid.

19. The method of claim 18, wherein said step of calcining comprises heating to 1300°C in air.

20. The method of claim 18, wherein said fluid is ethanol.

21. The method of claim 7, wherein said step of sintering comprises heating to 1450°C for about 5 hours.

22. A membrane reactor for the production of hydrogen from a hydrocarbon comprising:

a high temperature stable housing;

at least one membrane of proton-electron conducting ceramics according to claim 1, comprising a porous support comprising: $M'-Sr_{1-z'}M''_{z'}Ce_{1-x'-y'}Zr_xM'''_yO_{3-\delta}$, Al_2O_3 , mullite, ZrO_2 , CeO_2 or any mixtures thereof where: M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is 0 to about 0.5; x' is 0 to about 0.5; y' is 0 to about 0.5; and $x' + y' > 0$; with a film comprising a Perovskite-type oxide of the formula $SrCe_{1-x-y}Zr_xM_yO_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.15 and y is about 0.1 to about 0.3 on a surface of said porous support;

at least one inlet to introduce a feed gas comprising said hydrocarbon and water;

at least one first outlet to remove an exhaust gas comprising water and carbon dioxide; and

at least one second outlet to remove the hydrogen comprising gas from said reactor.

23. The membrane reactor of claim 22, wherein said porous support comprises $Ni-SrCe_{1-x'}Zr_{x'}O_{3-\delta}$ where x' is about 0.1 to about 0.3

24. The membrane reactor of claim 22, wherein said housing is quartz, metal, metal alloy or ceramic.

25. The membrane reactor of claim 22, wherein said inlet directs said feed gas to an isolated volume in contact with a surface free of said film of said membrane.

26. The membrane reactor of claim 22, wherein said first outlet removes said exhaust gas from an isolated volume in contact with a surface free of said film of said membrane.

27. The membrane reactor of claim 22, wherein said second outlet removes said hydrogen comprising gas from an isolated volume in contact with said surface having said film of said membrane.

5 28. The membrane reactor of claim 22, further comprising a second inlet to direct a carrier gas to an isolated volume in contact with said surface having said film of said membrane.

29. The membrane reactor of claim 22, wherein said membrane comprises a
10 tube, wherein the internal surface of said tube has said film.

30. A method of producing hydrogen comprising the steps of:

providing a membrane reactor comprising:

at least one membrane of proton-electron conducting
15 ceramics according to claim 1, comprising a porous support comprising $\text{Ni-SrCe}_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ where x' is about 0.1 to about 0.3, with a film comprising a Perovskite-type oxide of the formula $\text{SrCe}_{1-x-y}\text{Zr}_x\text{M}_y\text{O}_{3-\delta}$ where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.15 and y is about 0.1 to about 0.3 on a surface of said porous support;

20 at least one inlet;

at least one first outlet to remove an exhaust gas comprising water and carbon dioxide; and

at least one second outlet to remove a hydrogen comprising gas;

25 introducing a feed gas comprising a hydrocarbon and water through said inlet; and

collecting a hydrogen comprising gas.

31. The method of claim 30, wherein said hydrocarbon comprises methane,
30 ethane, propane, butane, higher alkanes, alcohols, natural gas, coal based syngas, gasified biomass, or any combination thereof.

32. The method of claim 30, wherein said water and said hydrocarbon are provided in a H₂O/C ratio of at least 1.

33. A method of producing a syngas comprising the steps of:

5 providing a membrane reactor comprising:

at least one membrane of proton-electron conducting ceramics according to claim 1, comprising a porous support comprising: $M'-Sr_{1-z}M''_zCe_{1-x'-y'}Zr_xM'''_yO_{3-\delta}$, Al₂O₃, mullite, ZrO₂, CeO₂ or any mixtures thereof where: M' is Ni, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Zn, Pt, Ru, Rh, Pd, alloys thereof or mixtures thereof; M'' is Ba, Ca, Mg, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; M''' is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb; z' is 0 to about 0.5; x' is 0 to about 0.5; y' is 0 to about 0.5; and x' + y' > 0; with a film comprising a Perovskite-type oxide of the formula SrCe_{1-x-y}Zr_xM_yO_{3-δ} where M is at least one of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, x is 0 to about 0.15 and y is about 0.1 to about 0.3 on a surface of said porous support;

at least one inlet;

at least one first outlet to remove an effluent gas; and

20 at least one second outlet to remove a hydrogen comprising gas;

introducing a feed gas comprising carbon dioxide through said inlet; and

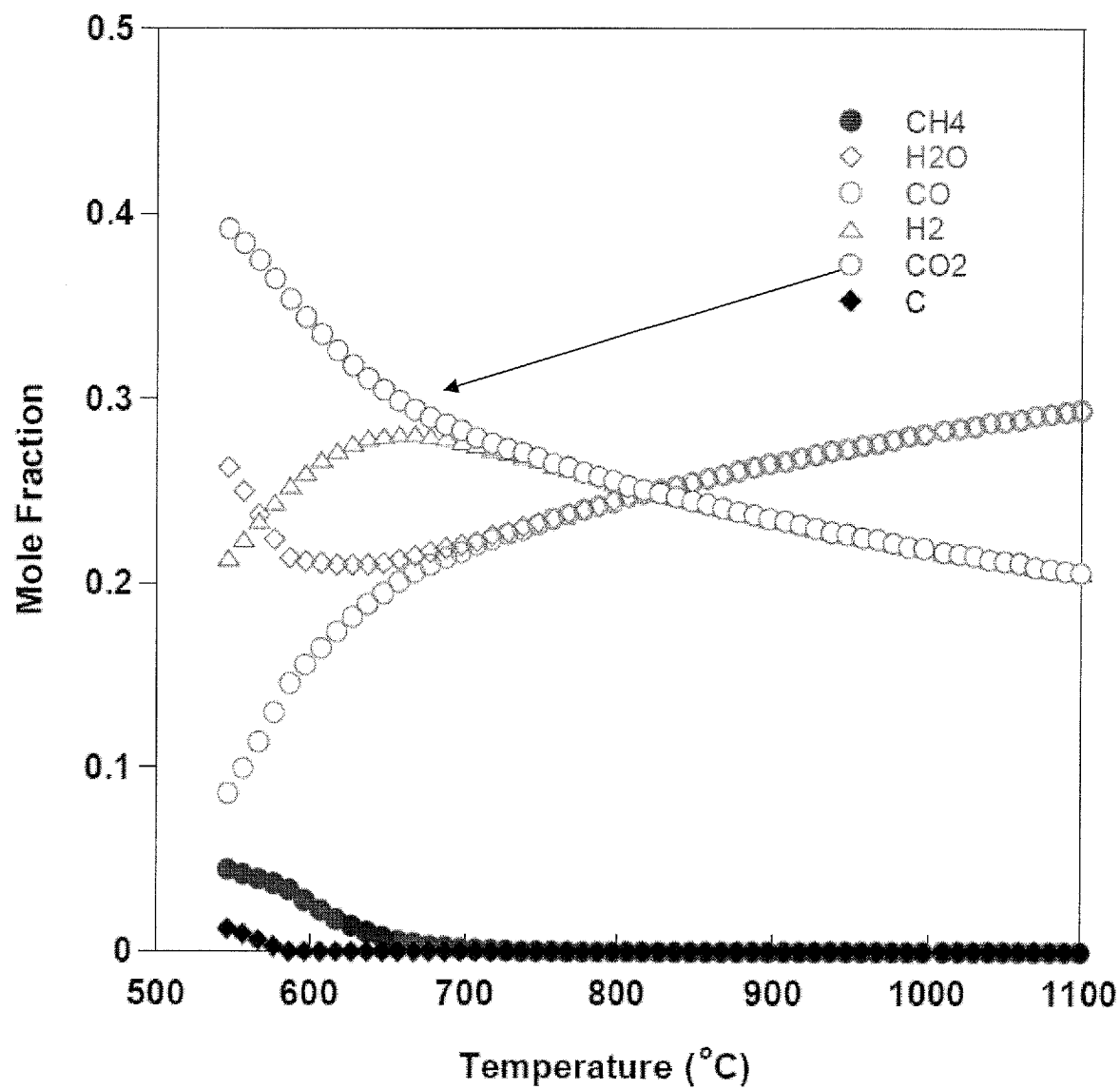
collecting a syngas comprising carbon monoxide and hydrogen.

25 34. The method of claim 33, wherein said porous support comprises Ni-SrCe_{1-x'}Zr_{x'}O_{3-δ} where x' is about 0.1 to about 0.3

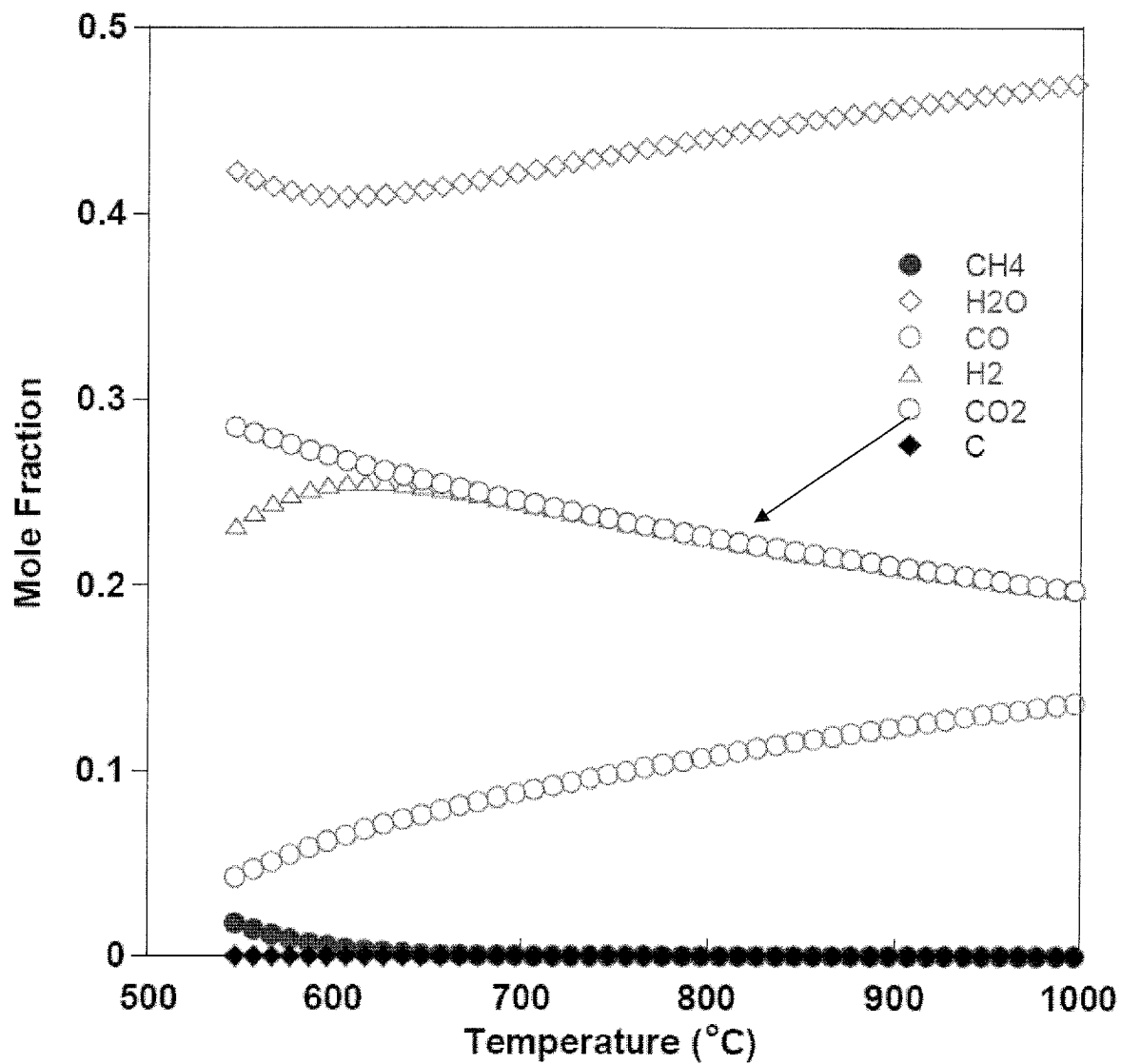
35. The method of claim 33, wherein said feed gas further comprises water.

30 36. The method of claim 33, wherein said feed gas further comprises hydrocarbon.

37. The method of claim 36, wherein said hydrocarbon comprises methane.

*Figure 1*

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*Figure 2*

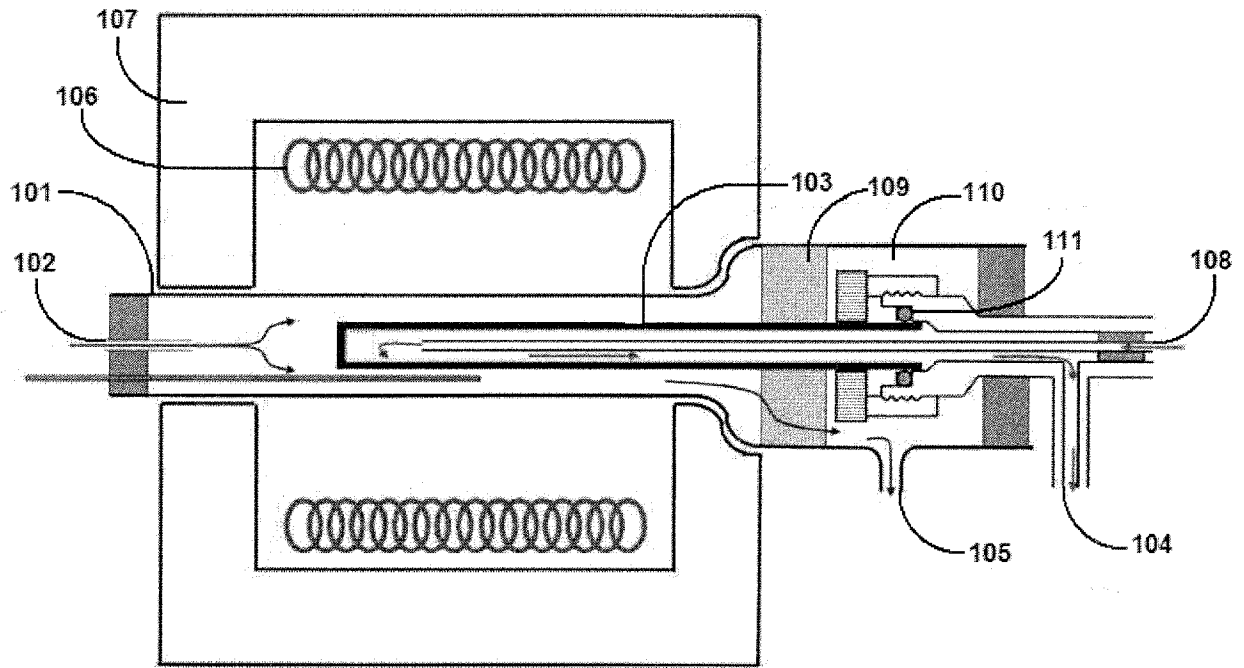
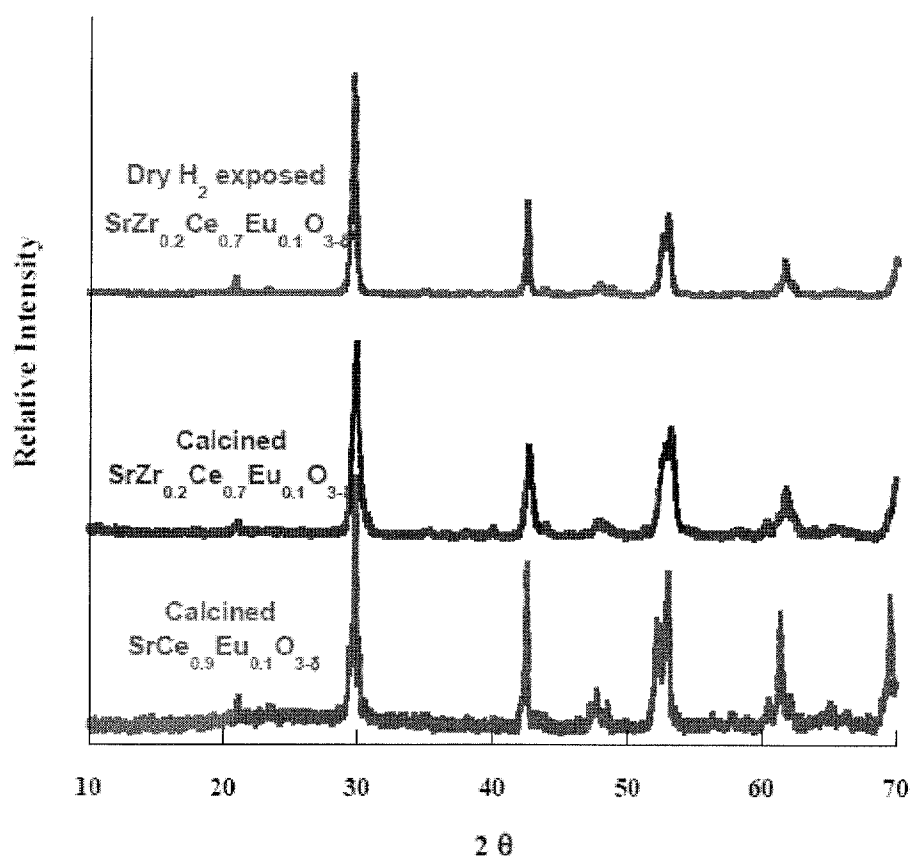
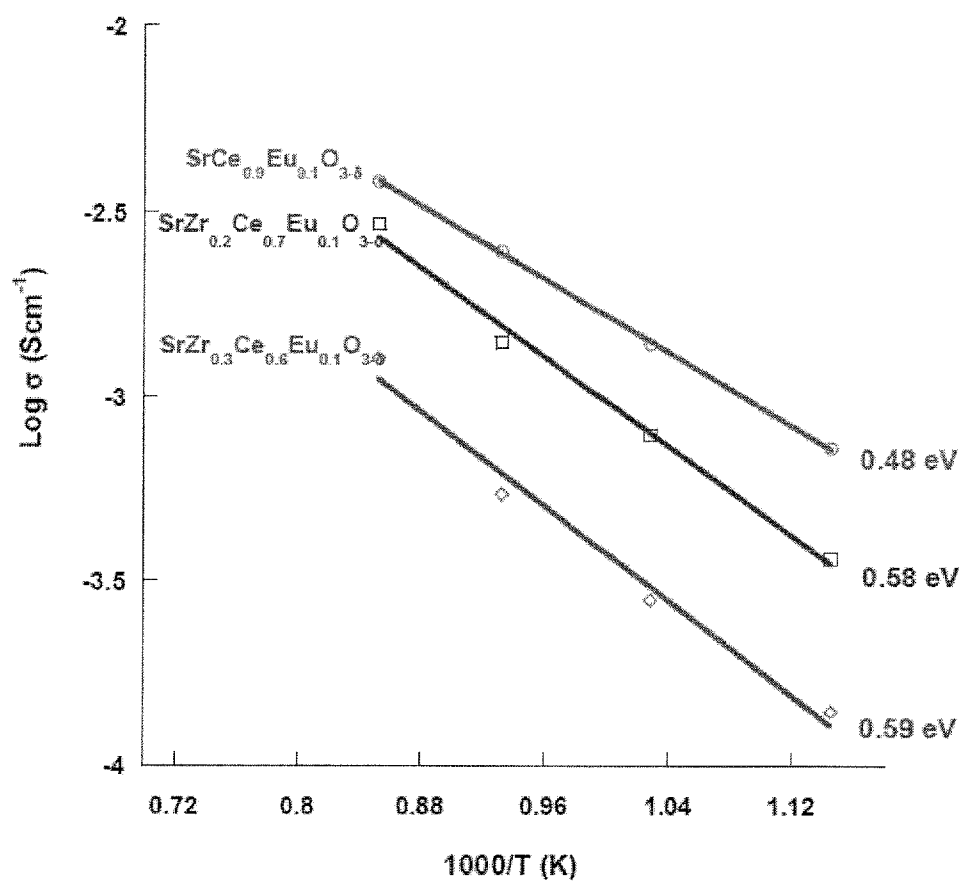


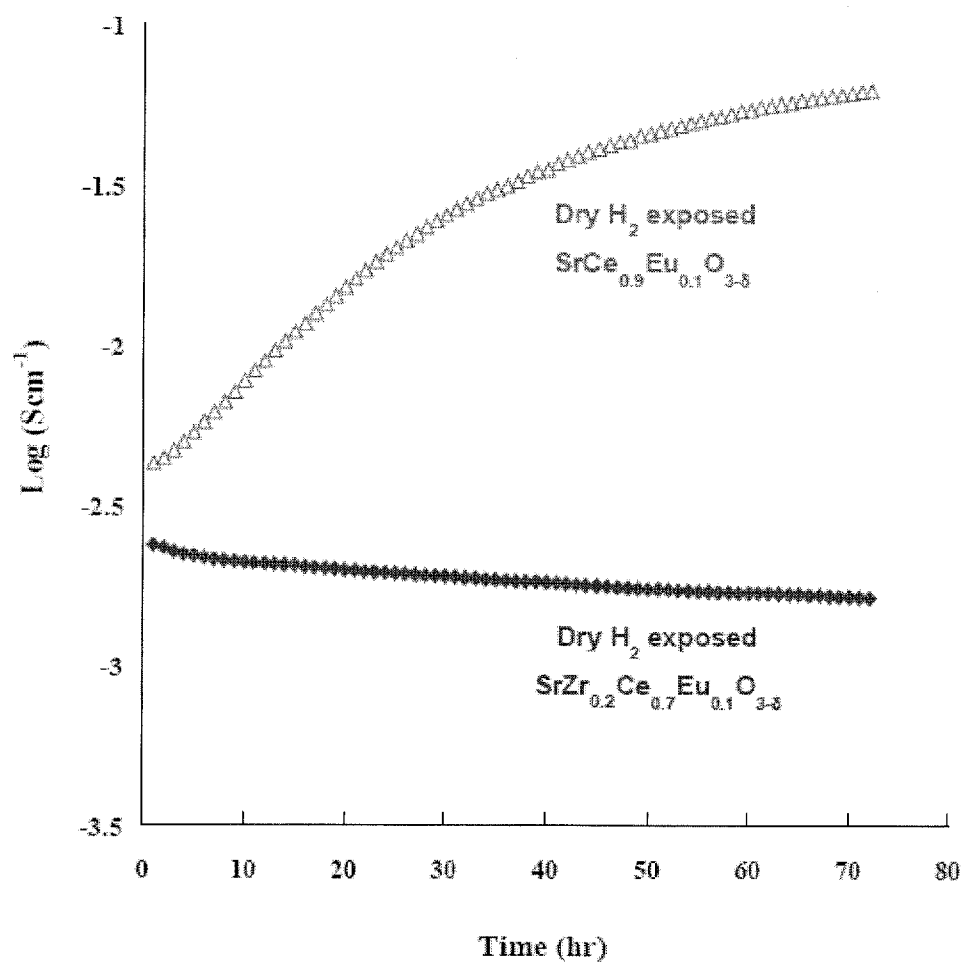
Figure 3

*Figure 4*

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*Figure 5*

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*Figure 6*

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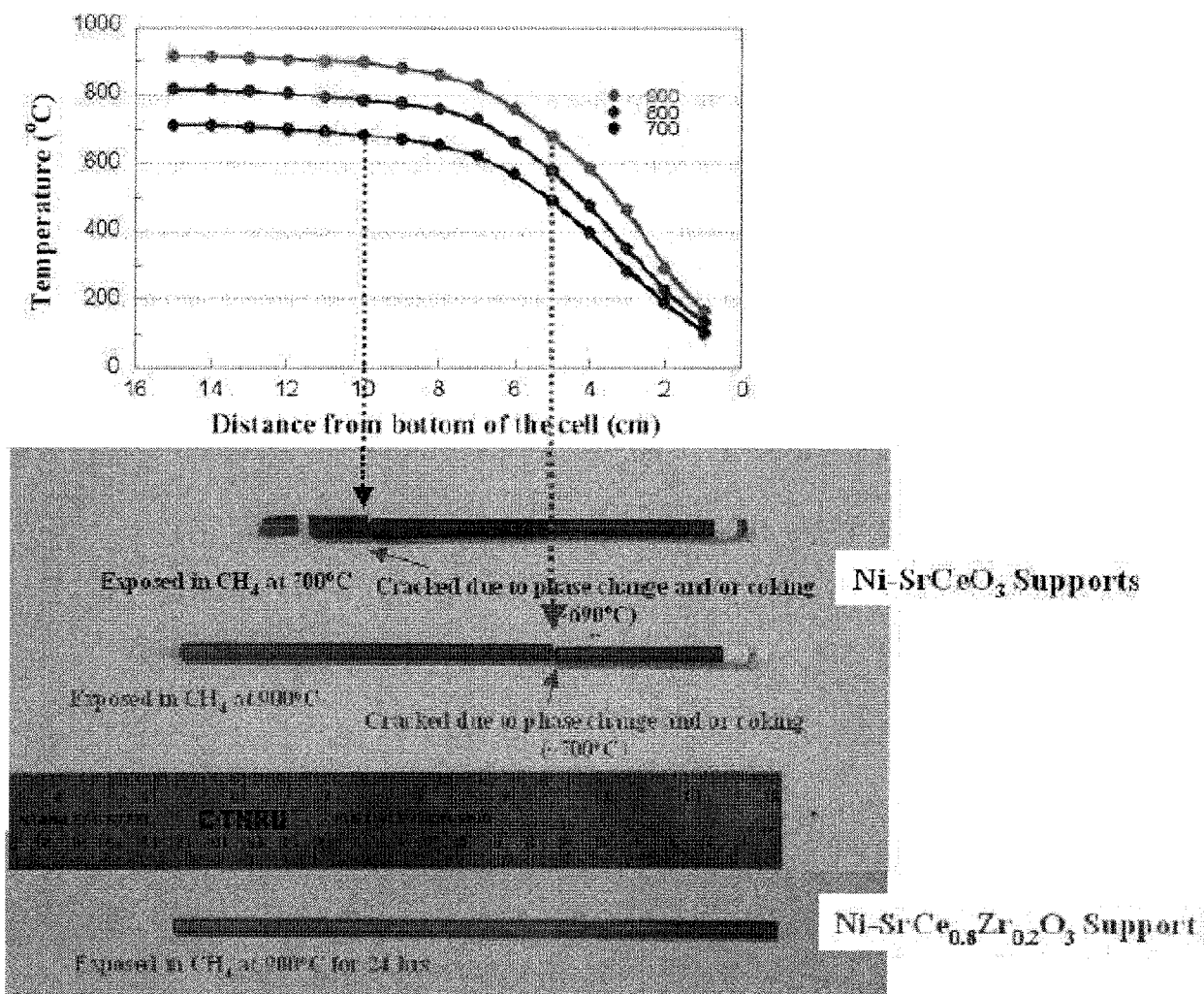
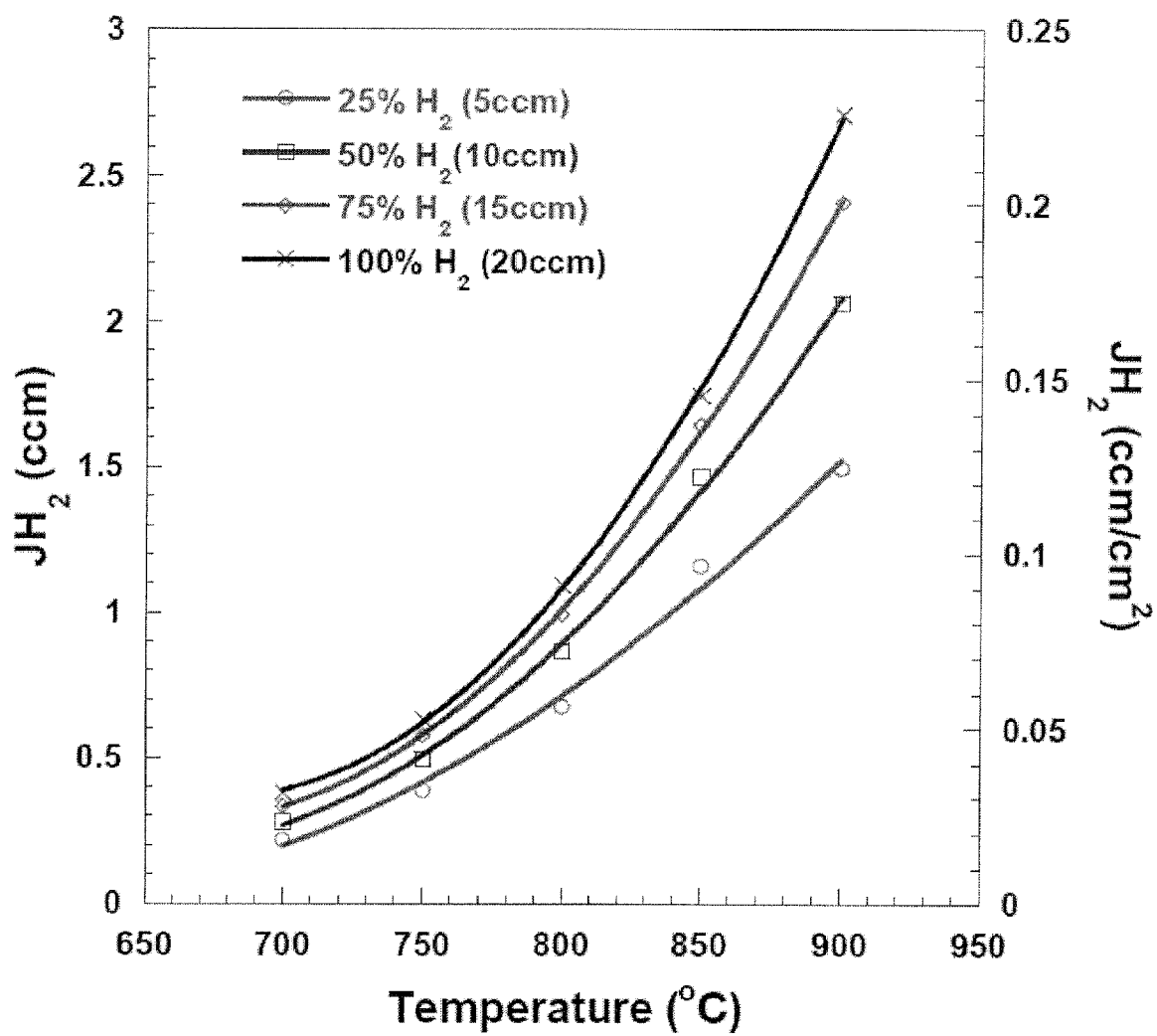
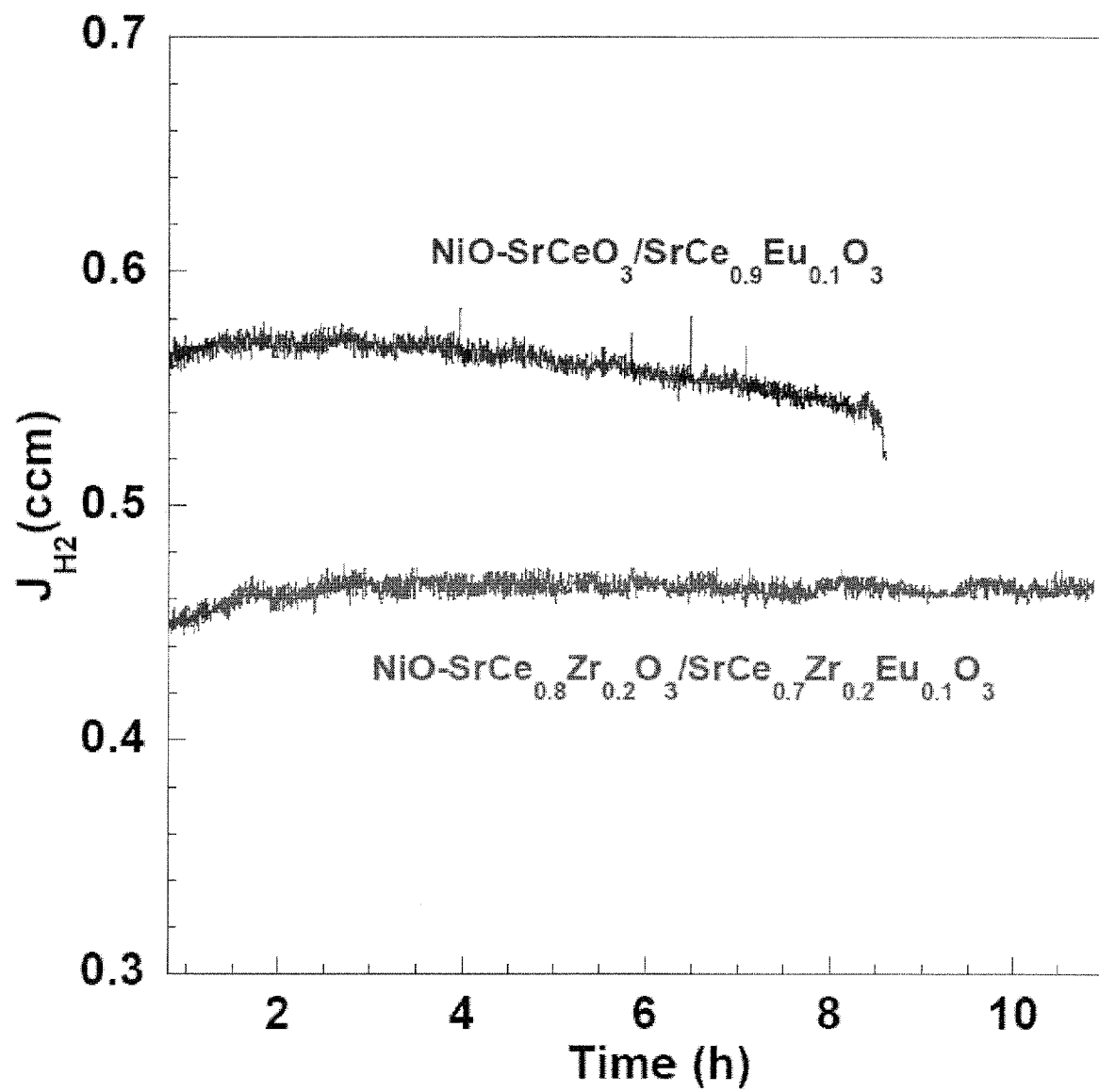


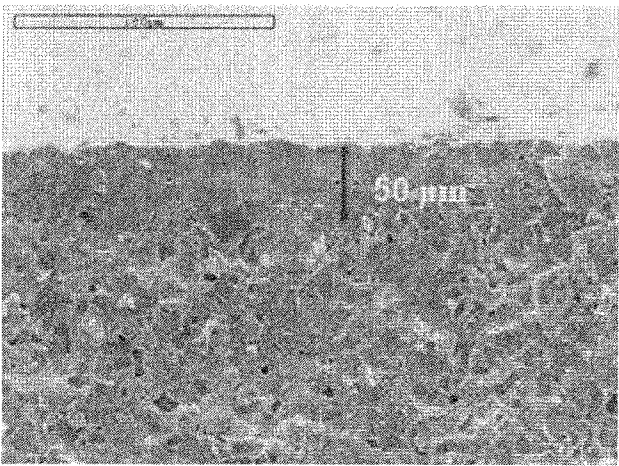
Figure 7

*Figure 8*

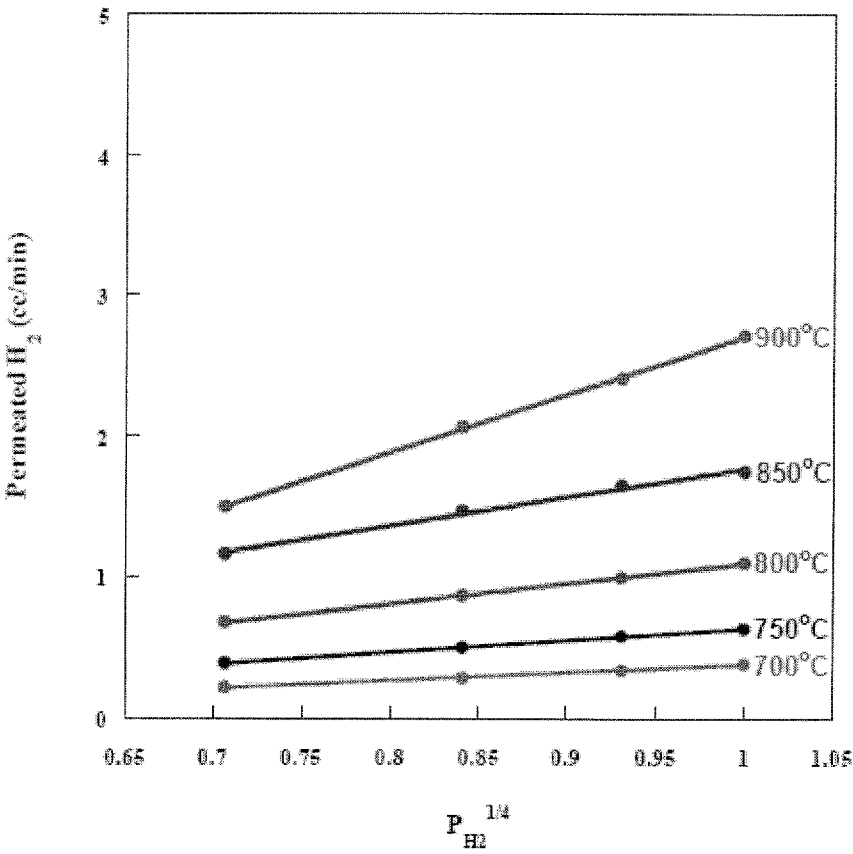
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*Figure 9*

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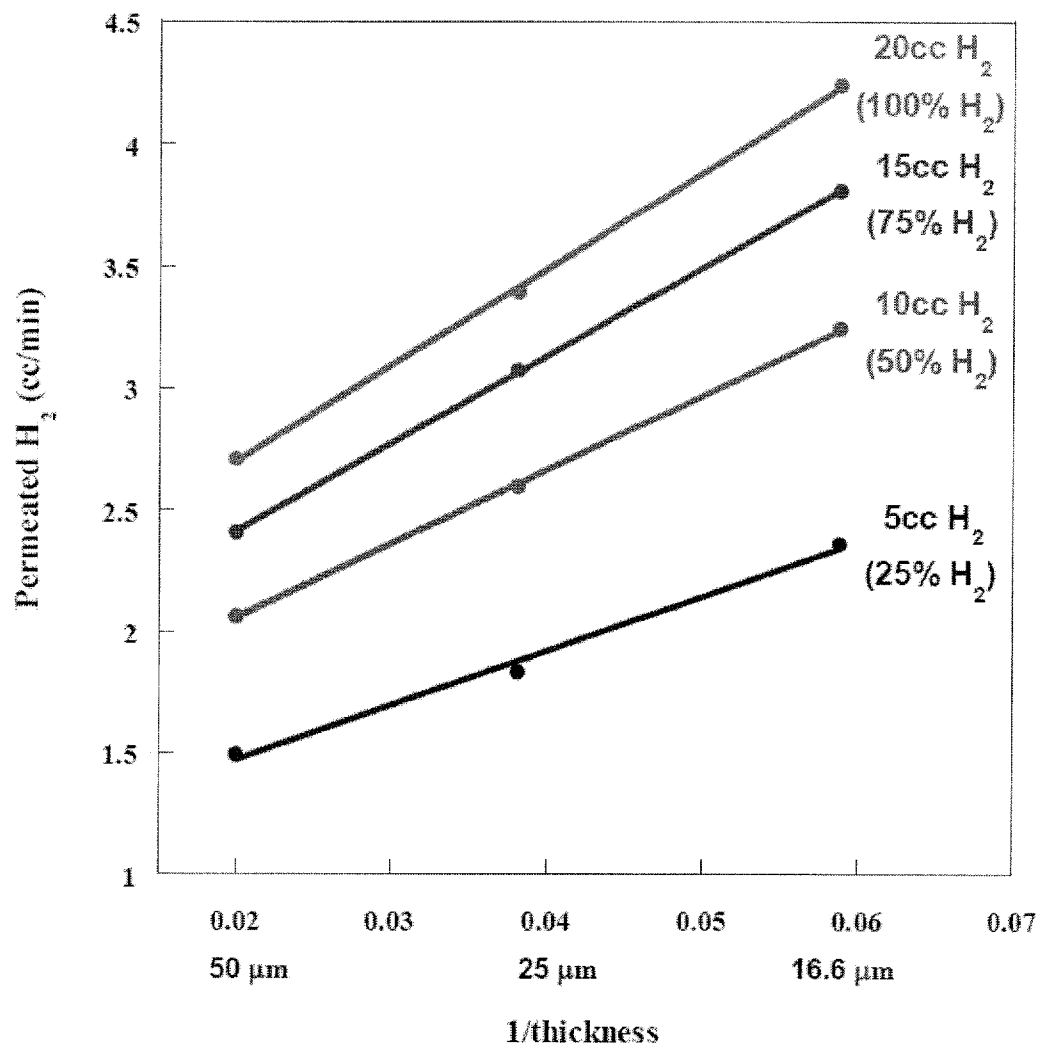
(a)



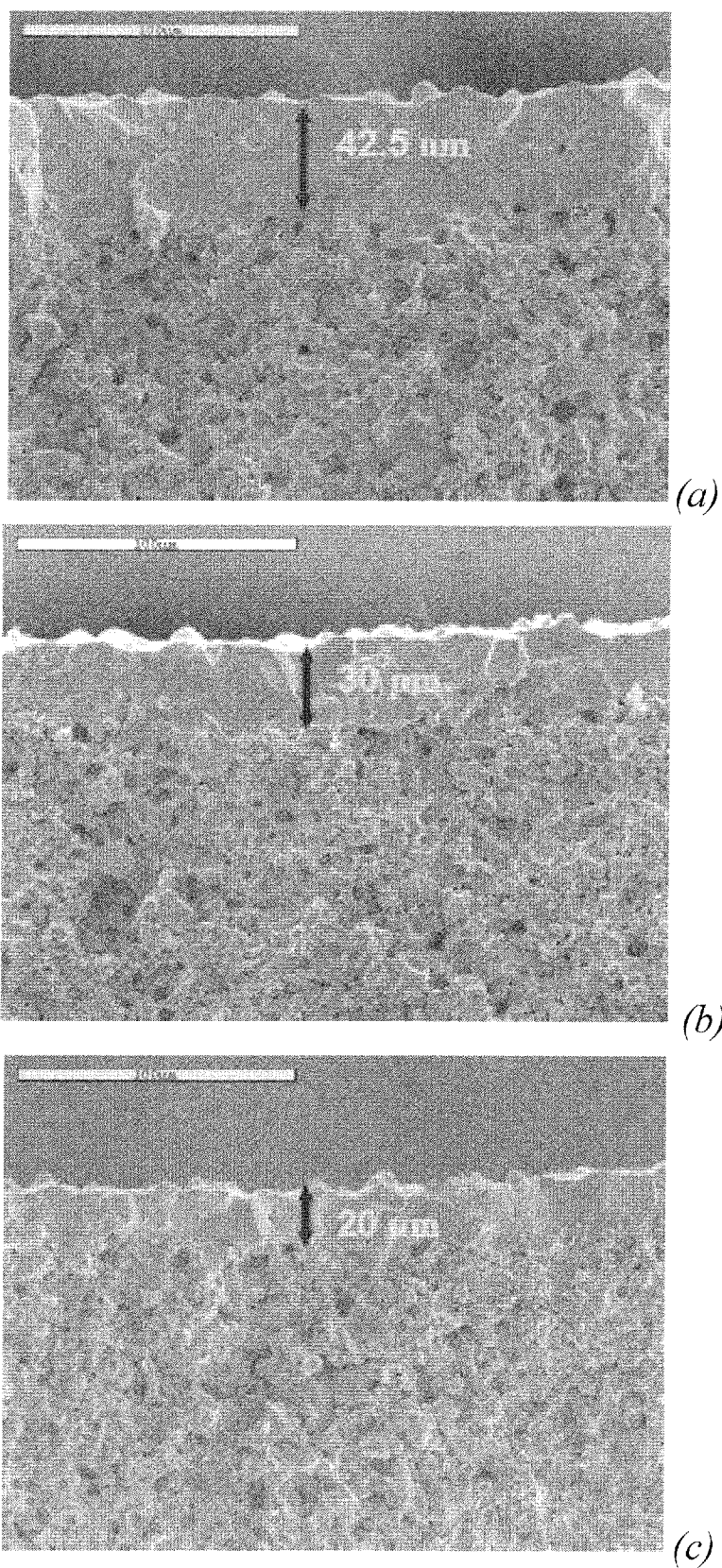
(b)

Figure 10

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*Figure 11*

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*Figure 12*

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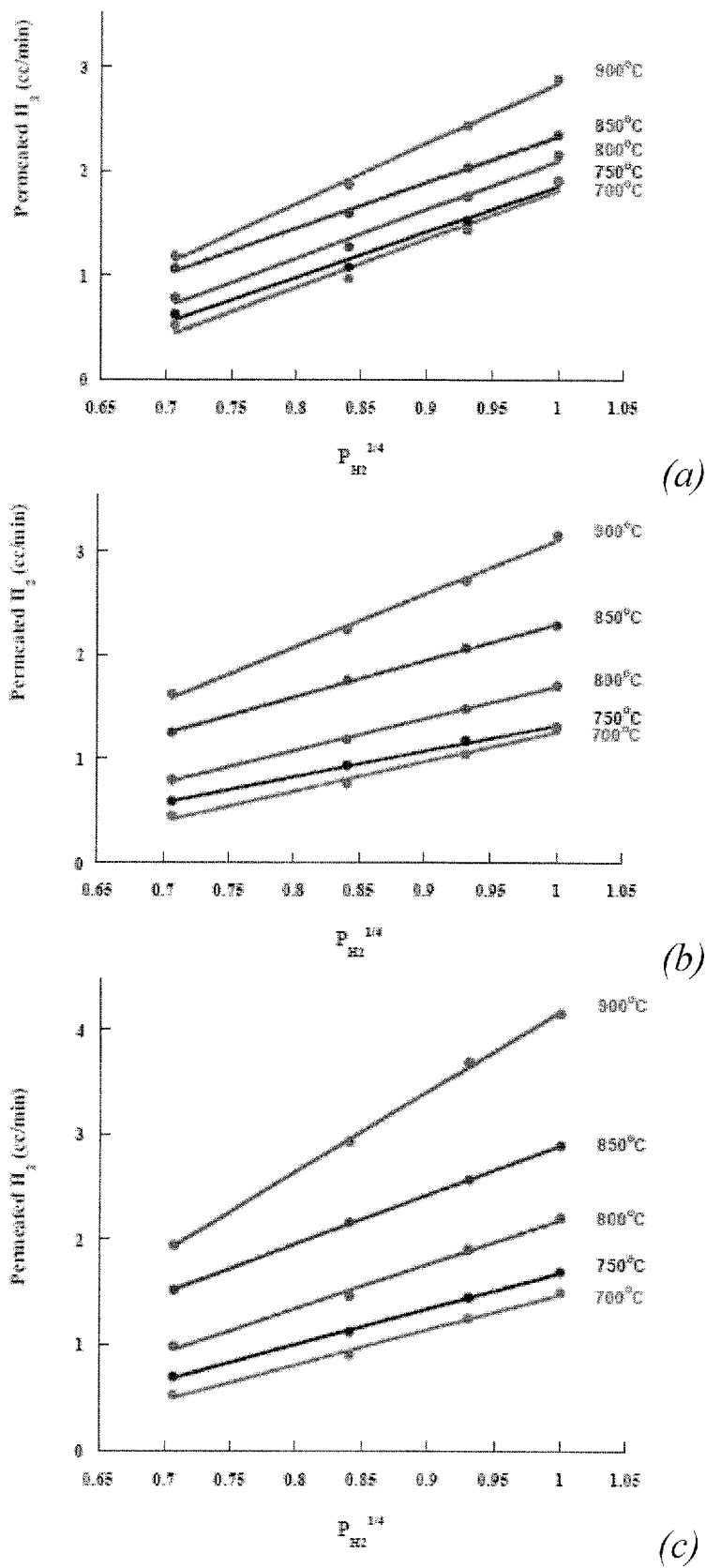
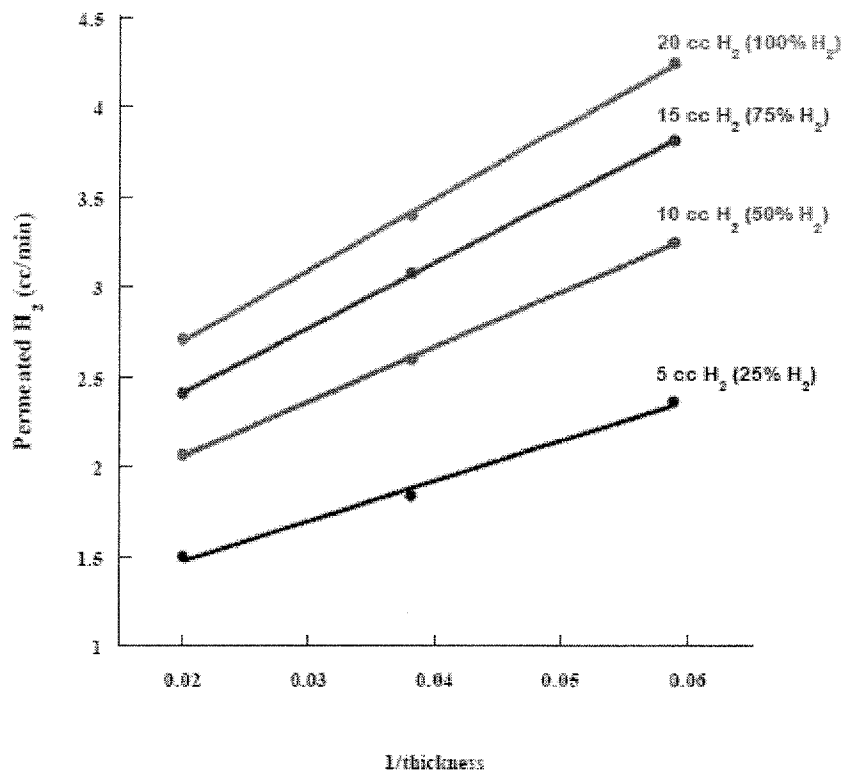
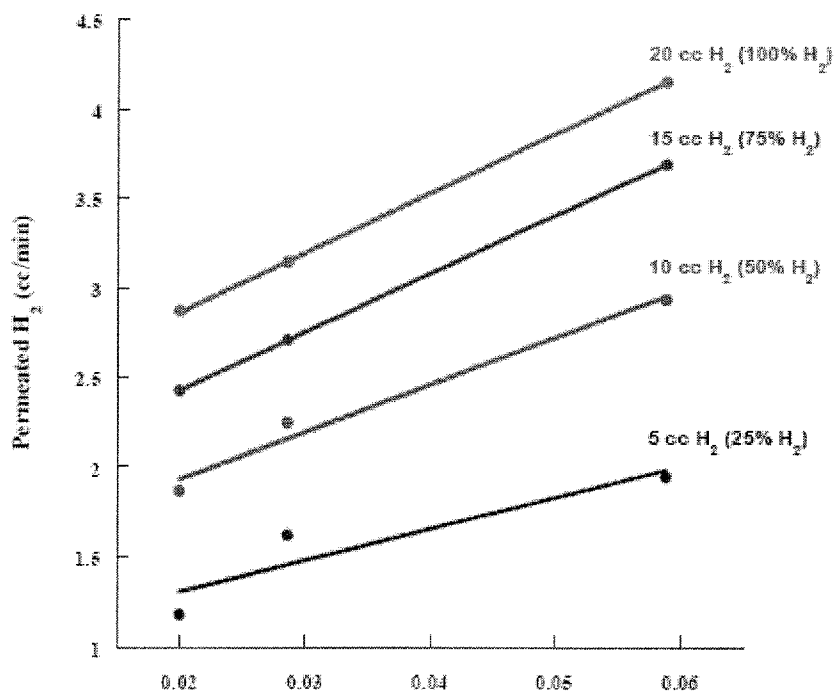


Figure 13

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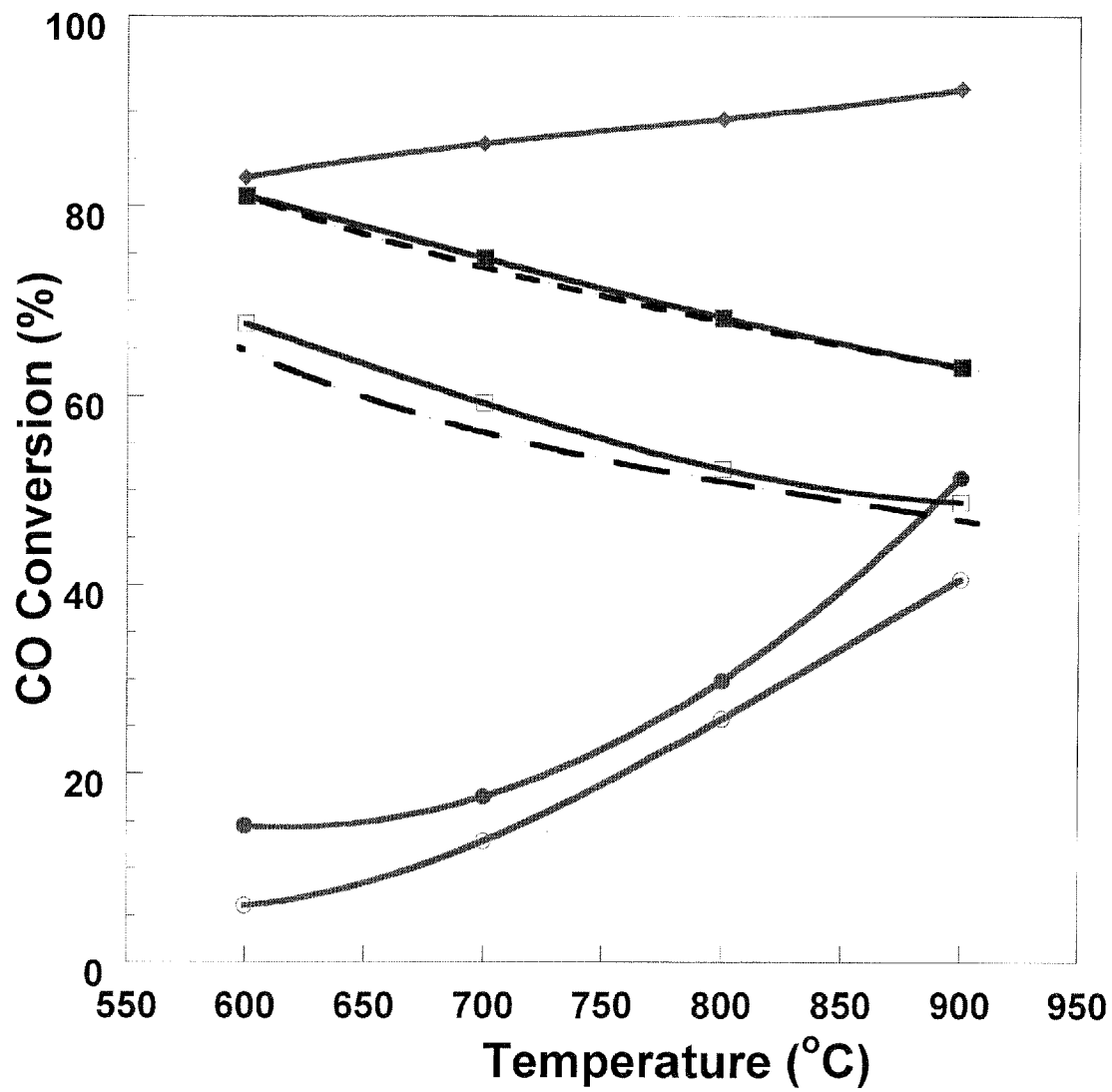


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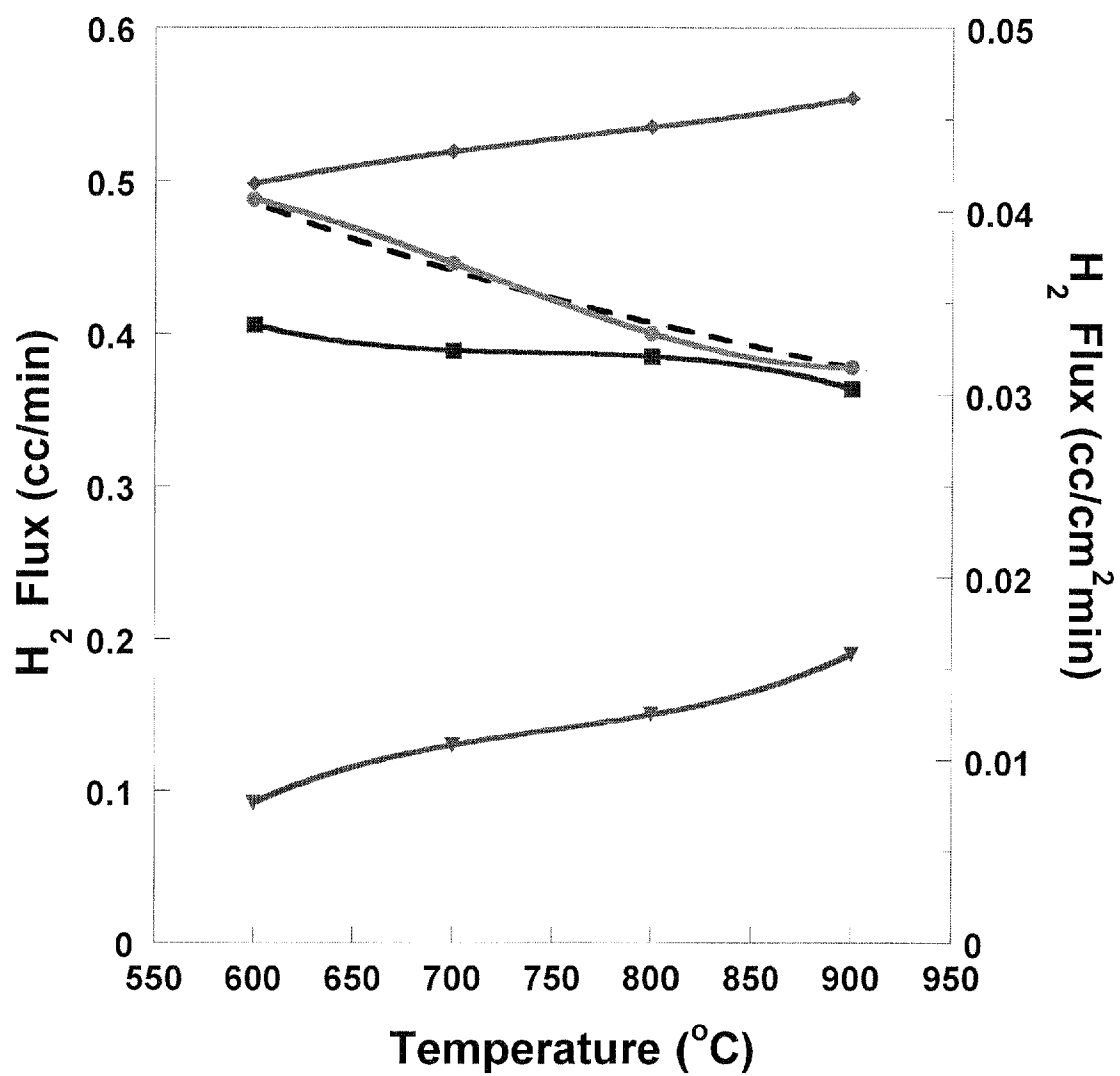


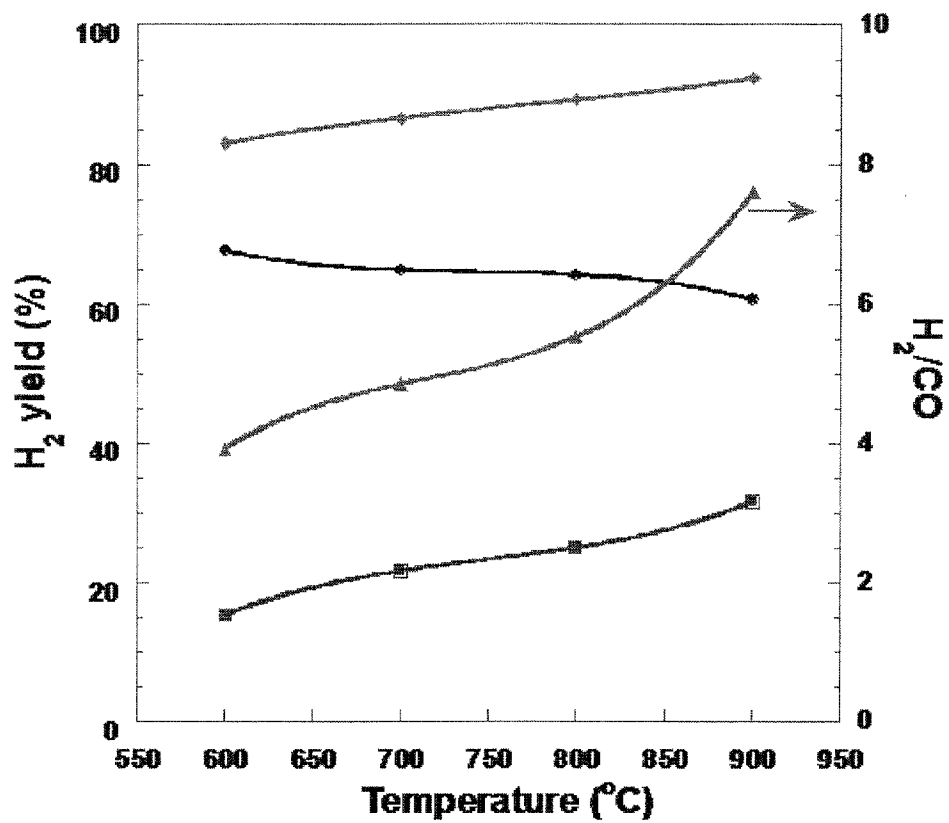
(b)

Figure 14

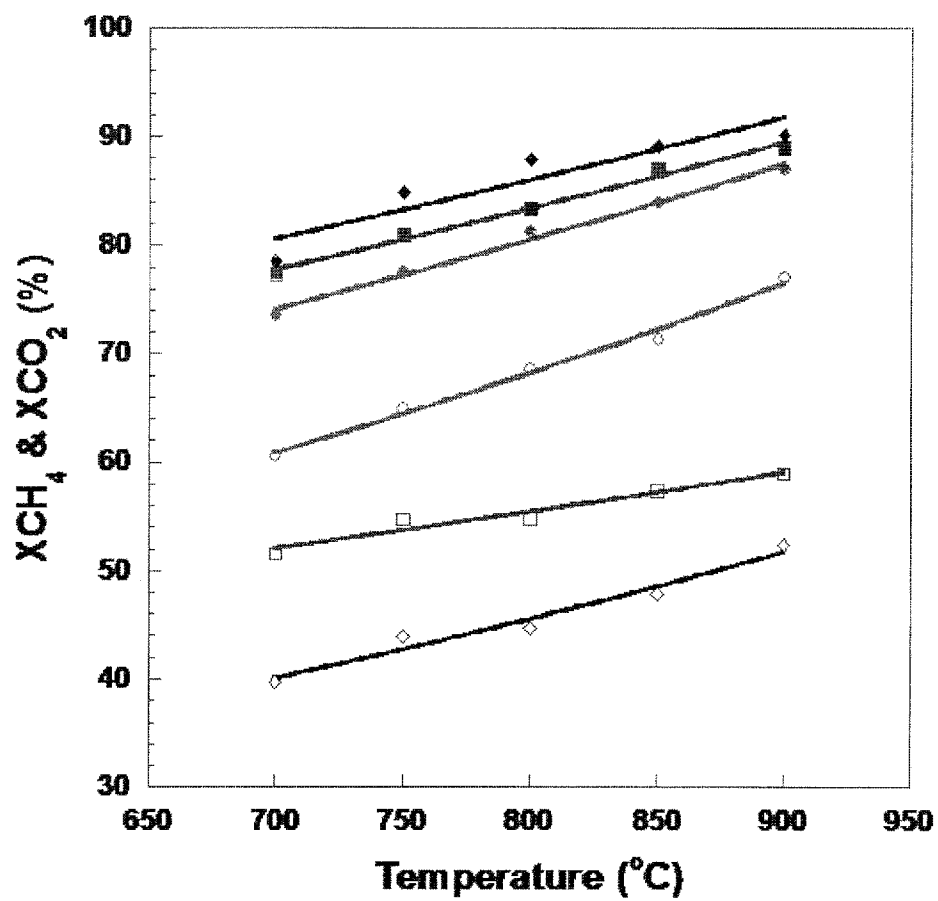
*Figure 15*

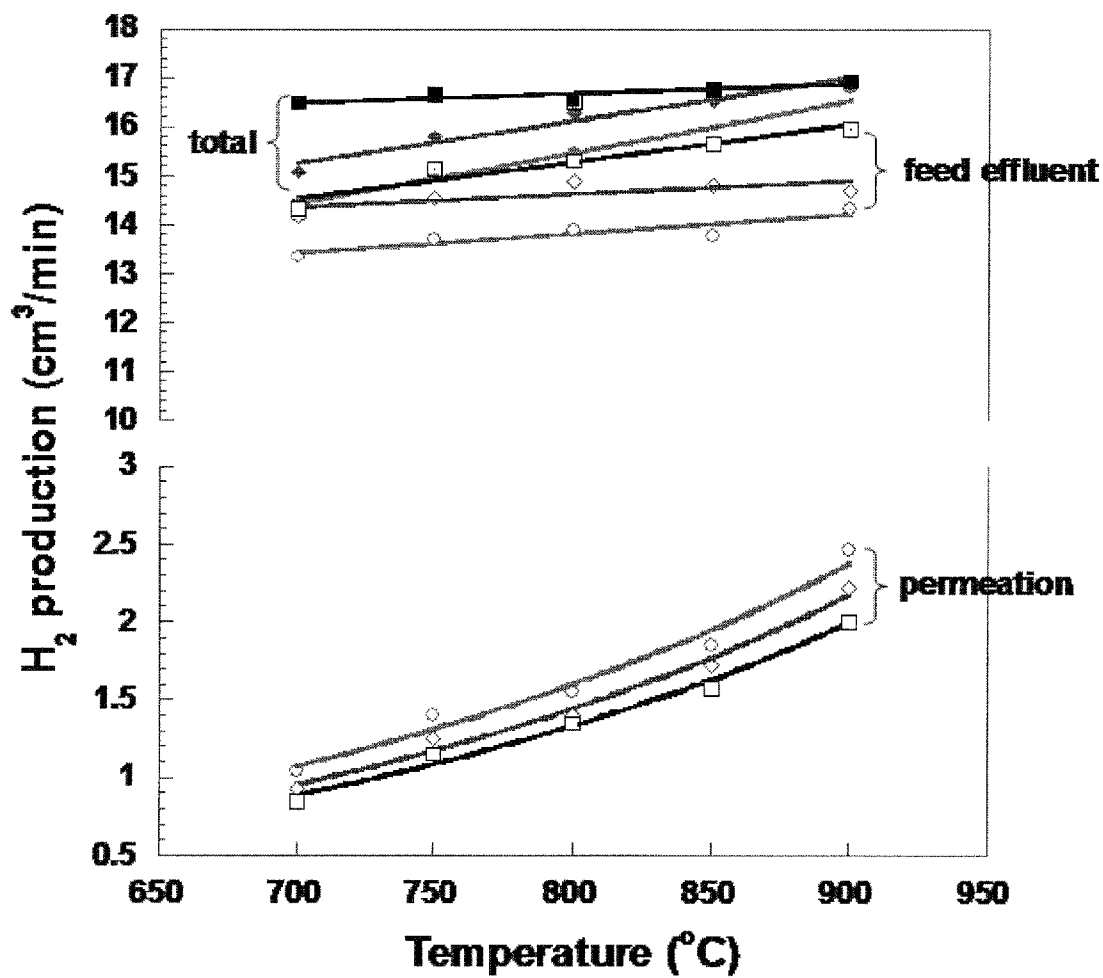
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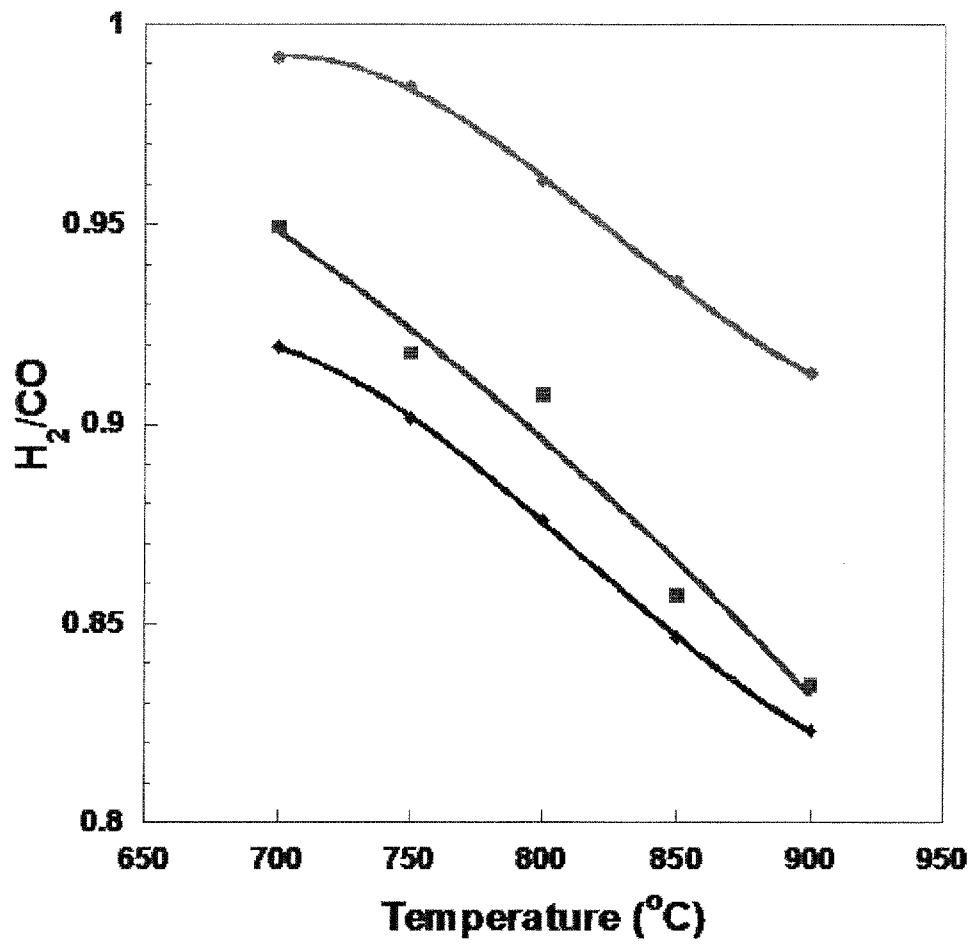
*Figure 16*

*Figure 17*

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*Figure 18*

*Figure 19*

*Figure 20*

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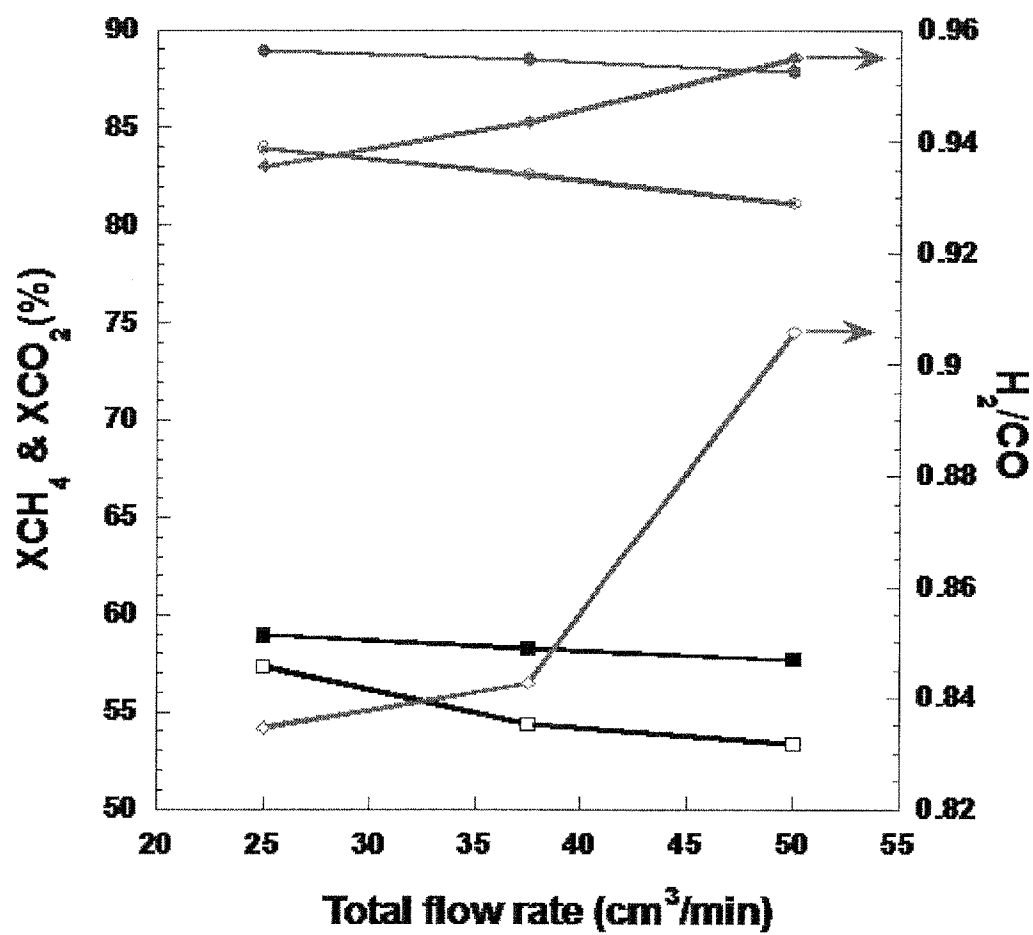
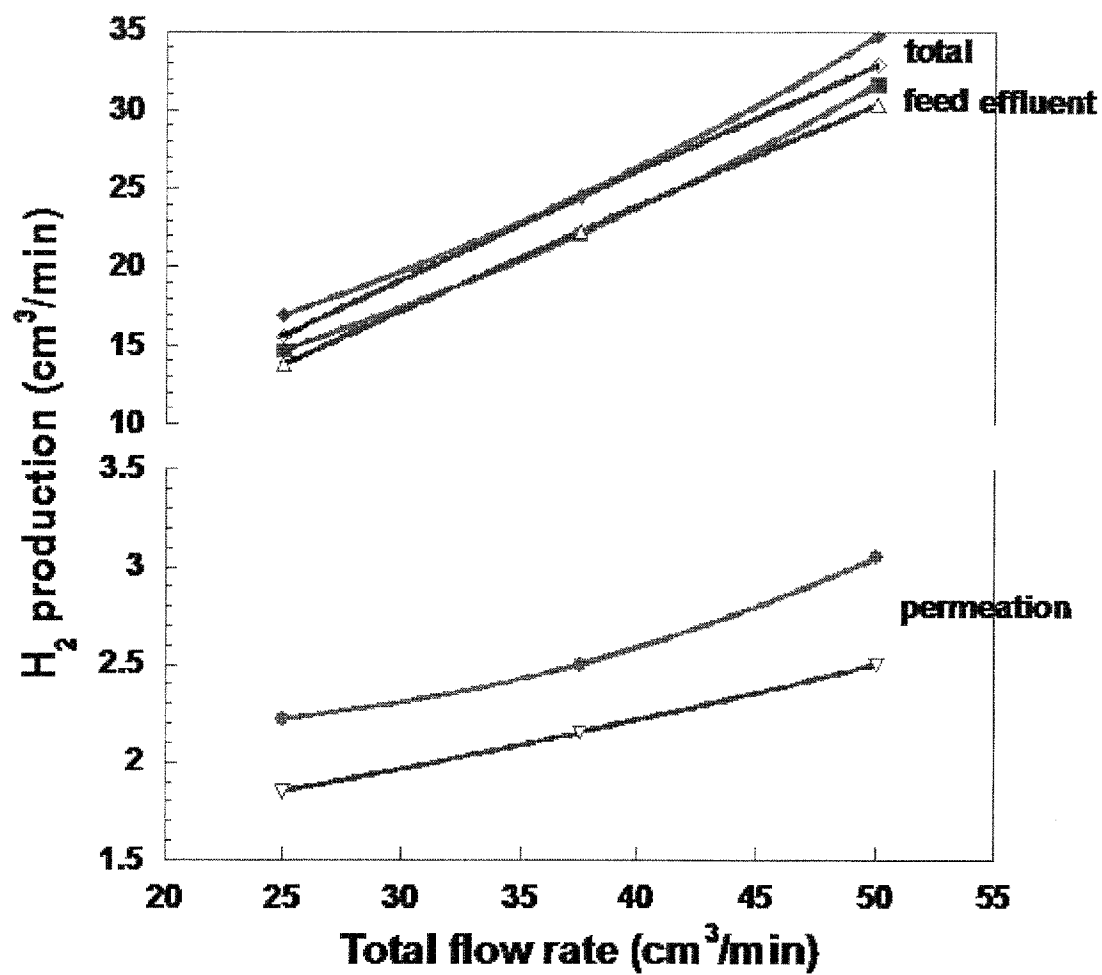
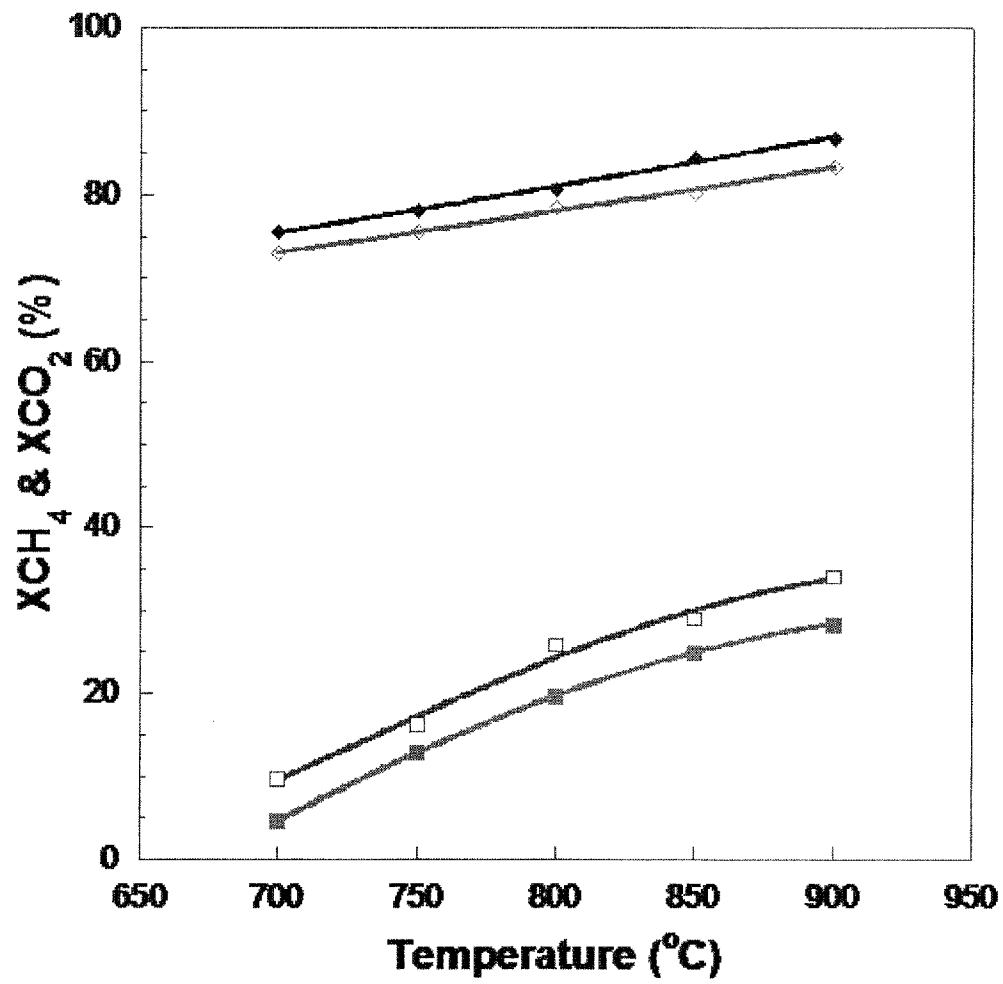
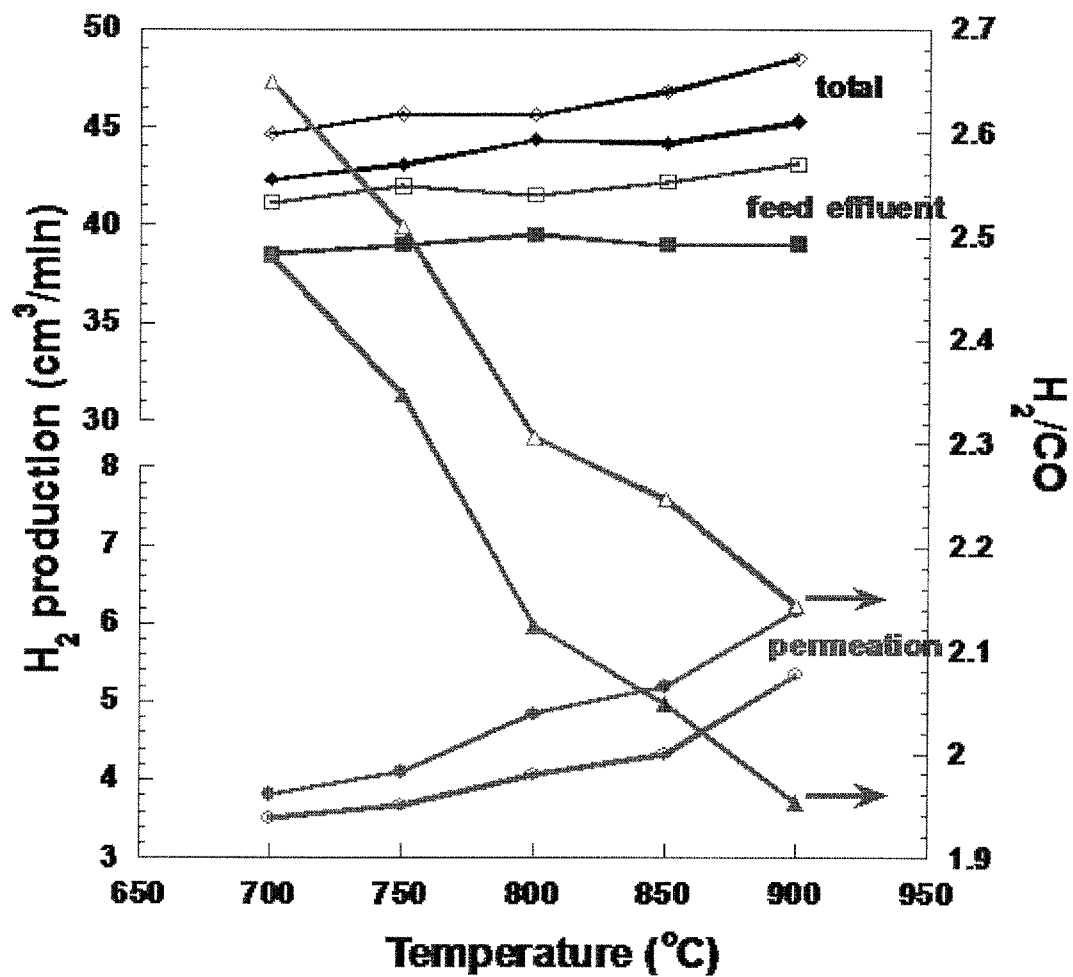


Figure 21

*Figure 22*

*Figure 23*

*Figure 24*