Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US2006/014496

International filing date: 18 April 2006 (18.04.2006)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/672,399
Filing date: 18 April 2005 (18.04.2005)

Date of receipt at the International Bureau: 06 July 2006 (06.07.2006)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)
June 22, 2006

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/672,399
FILING DATE: April 18, 2005
RELATED PCT APPLICATION NUMBER: PCT/US06/14496

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS US60/672,399

Certified by

[Signature]
Under Secretary of Commerce
for Intellectual Property
and Director of the United States Patent and Trademark Office
Membrane for Carbon Dioxide Separation at High Temperatures

Direct all correspondence to:

CORRESPONDENCE ADDRESS

The address corresponding to Customer Number: 28089

ENCLOSED APPLICATION PARTS (check all that apply)

Application Data Sheet. See 37 CFR 1.76
Specification Number of Pages 39
Drawing(s) Number of Sheets 6

Application Size Fee: If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(C) and 37 CFR 1.16(e).

METHOD OF PAYMENT OF FILING FEES AND APPLICATION SIZE FEE FOR THIS PROVISIONAL APPLICATION FOR PATENT

Applicant claims small entity status. See 37 CFR 1.27.
A check or money order is enclosed to cover the filing fee and application size fee (if applicable).
Payment by credit card. Form PTO-2038 is attached
The Director is hereby authorized to charge the filing fee and application size fee (if applicable) or credit any overpayment to Deposit Account Number: 08-0219. A duplicative copy of this form is enclosed for fee processing.

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. Yes, No.

Yes, the name of the U.S. Government agency and the Government contract number are:

SIGNATURE: Jane M. Love, Ph.D.

Date: April 18, 2005

REGISTRATION NO.: 42,812

Docket Number: 19240.257-US1

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9999 and select option 2.
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

U.S. PROVISIONAL PATENT APPLICATION

Title: MEMBRANE FOR CARBON DIOXIDE SEPARATION AT HIGH TEMPERATURES

Inventors: Klaus S. LACKNER
Alan C. WEST

Express Mail Label No.: EV 604919271 US
Membrane for Carbon Dioxide Separation at High Temperatures

This patent disclosure contains material that is subject to copyright protection. The copyright owner has no objection to the facsimile reproduction by anyone of the patent document or the patent disclosure, as it appears in the U.S. Patent and Trademark Office patent file or records, but otherwise reserves any and all copyright rights whatsoever.

Field of the Invention

The present invention relates to carbon management, and to apparati useful for the separation of carbon dioxide (CO\textsubscript{2}) at high temperatures.

Background of the Invention

The importance of technologies for the separation of carbon dioxide (CO\textsubscript{2}) from gaseous process streams has gained in importance, not the least because of concerns over greenhouse gas emission. In the future, power plants that generate electricity from coal, or other carbon based fuels may have to separate CO\textsubscript{2} from the gas stream. Chemical routes to hydrogen production from coal and natural gas rely on CO\textsubscript{2} separation that could be greatly simplified with the availability of high temperature CO\textsubscript{2} selective membranes. Solid oxide fuel cell designs that operate on hydrogen and carbon dioxide mixtures will have to separate CO\textsubscript{2} from the exhaust stream.

Methods conventionally used to separate carbon dioxide gas include the use of cellulose acetate or other polymer membranes, or chemical absorption using alkanolamine-based solvent. However, these methods require that the exhaust gas is at a temperature of about 200°C or lower. At elevated temperatures, solid absorbers like lime, or lithium zirconate, or lithium silicate have been proposed, but they require large material handling systems. Membrane separation techniques would be of great interest in all these cases, but so far CO\textsubscript{2} membrane separation has been limited to low temperatures. Particularly in gasification based systems it would be desirable to have CO\textsubscript{2} separation membranes that could operate in the temperature regime in
which gasification occurs. This has been recognized before, and attempts have been made to construct membranes from some of these solid sorbents, however, these efforts so far have failed to produce viable membranes.

Power plant designs that rely on the recirculation of only partially combusted or oxidized flue gases would benefit greatly from the availability of membranes that could perform the separation at the process temperature which often would be in excess of 400°C and which could easily reach temperatures as high as 1000°C. The efficiency of recirculating the remaining gas is greatly increased if the gas can retain its sensible heat and does not have to be subjected to a cooling and heating cycle in order to allow for the removal of CO₂. For examples of such gas recirculation and gasification see (Lackner and Ziock, The US Zero Emission Coal Alliance Technology, ZECA, VGB Power Tech, (12/2001) (attached)) and (Lackner and Yegulalp, The Thermodynamic Foundation of the Zero Emission Concept, attached). Solid oxide fuel cells that use either pure carbon monoxide (CO) or a mixture of CO and hydrogen as a fuel could benefit greatly from the availability of high temperature CO₂ separation membranes, as it would make it possible to run these cells in what amounts to a steady state operation.

Materials such as selective membranes for gas absorption, including CO₂ absorption, typically operate at low temperatures, for example, about 500°C or below. Attempts to separate gases, such as mixtures of hydrogen and carbon dioxide, by use of membrane technology at high temperature have not been successful. The reasons for this lack of success include the failure of the membranes due to mechanical defects (e.g. cracking) or the attainment of undesirably low separation factors and/or flux.

The disadvantages in the art are addressed and overcome by the carbon dioxide separation membranes and methods of use thereof as embraced by the present invention.

**Summary of the Invention**

High temperature ceramic membranes that selectively pass carbon dioxide would solve the problems of carbon management. The present invention is useful for use in a number of
technologies ranging from coal-based electric power plants to ultra-efficient solid oxide fuel cells that oxidize a mixture of CO₂ and CO, which is held at an optimal concentration ratio.

While there are carbon dioxide membranes for low temperatures [1, 2], it is difficult to construct CO₂ membranes for operation at high temperatures. A membrane that could selectively pass carbon dioxide at temperatures between 500 and 1000°C would enable many new technologies. The present invention provides a novel membrane for use at high temperatures, e.g., above about 300°C or higher, which allows the selective passage of carbon dioxide (CO₂). Carbon dioxide can selectively permeate the membrane encompassed by this invention at temperatures of about 500°C to about 1200°C, or about 600°C to about 1000°C, thus affording many new technologies employing the membrane.

It is an aspect of this invention to provide a bi-continuous ceramic membrane conducive to the mobility of ions therein. In one phase, such a bi-continuous membrane conducts oxygen ions, while a second phase conducts carbonate ions. In an aspect, alkali zirconates, e.g., lithium zirconates, which can form CO₂ selective layers, can serve as precursor materials for these types of membranes. The membrane according to this invention is highly permeable and selective for CO₂ relative to other components, such as nitrogen and oxygen, at high temperatures, for example, above about 500°C. In an aspect, lithium zirconate is used to produce the ceramic membrane for CO₂ separation according to this invention.

Additional aspects, features and advantages afforded by the present invention will be apparent from the detailed description and exemplification hereinbelow.

Description of the Figures

**Figure 1** is a schematic and design of a bi-continuous membrane according to the present invention. In the membrane, regions or layers of molten carbonate alternate with regions or layers of oxygen conductive solid oxides. The concentration gradient of CO₂ drives a flux of CO₂ across the membrane. The CO₂ travels across as carbonate ion (CO₃⁻) in the molten carbonate, and the oxygen ion (O²⁻) returns without its CO₂ load through the solid oxide.

**Figure 2** is a schematic of a CO₂ membrane for a solid oxide fuel cell (SOFC).
**Figure 3** is a diagram showing the Boudouard Reaction.

**Figure 4** is a diagram showing the existing high temperature separator which is a sorption technology. CO2 diffuses to the lithium zirconate surface to form zirconia and lithium carbondate. For example, the temperature for this is from about 500 to about 600 degrees C. The original lithium zirconate is doped with a Li/K carbonate mix to take advantage of a eutectic molten carbonate to increase CO2 sorption. The process becomes reversible at higher temperatures. Two units operating in parallel at different temperatures, where one in the absorption range and the other in the desorption range, are required to remove CO2 from a continuous process.

**Figure 5** is a diagram depicting an example of a membrane CO2 separator.

**Description of the Invention**

The present invention is directed to a carbon dioxide gas-selective absorbent membrane comprising a bi-continuous membrane material stable at a temperature of greater than about 200°C and comprising a porous solid oxide material that in a temperature range of interest is capable of transporting oxygen ions, and a molten carbonate phase completely filling the pores capable of conducting carbonate ions, wherein (i) a concentration gradient of carbon dioxide drives a flux of carbonate ions across the membrane and (ii) oxygen ions return the charge in the solid oxide phase.

In one embodiment, the solid oxide layer and the carbonate layer form spontaneously from a precursor in the presence of CO2 and wherein the precursor comprises an alkali metal zirconate in the presence of CO2. In another embodiment, the precursor material comprises lithium zirconate. In another embodiment, the solid oxide phase and carbonate phase are premixed and fused. In one embodiment, the solid oxide material comprises one or more of: YSZ (yttria stabilized zirconia), GCO (gadolina doped ceria), SFC (Sr-Fe-Co oxides), ABO_3-delta (general perovskite crystalline structure, exhibits oxygen ionic and electronic conductivity), or perovskite SrCO(0.8)Fe(0.2)O(3-delta), wherein the solid oxide material is capable of conducting oxygen ions. In another embodiment, the membrane is selectively permeable to
carbon dioxide relative to one or more of hydrogen, water, carbon dioxide, or oxygen. In a further embodiment, the membrane material is stable at a temperature of about 300°C to about 1200°C. In another embodiment, the membrane material is stable at a temperature of about 500°C to about 1000°C.

The invention also provides for a zero-emission coal-based electric power plant comprising the absorbent membrane described herein. The invention provides a solid oxide fuel cell comprising the absorbent membrane described herein. The invention provides for a process for carbon dioxide separation at temperatures from about 300 °C to about 1000°C, comprising subjecting a source containing carbon dioxide to the absorbent membrane described herein. In one embodiment, the source is a feed or feedstock. In another embodiment, the source is a fuel gas or an exhaust gas. In another embodiment, the temperature is greater than about 500°C.

A bi-continuous membrane is a membrane where there are passageways for two different charges to migrate through two different materials. In one embodiment of the invention, the membrane is comprised of a solid zirconate having pores that are filled with molten carbonate. The invention provides for a membrane comprising a material that absorbs CO2 on one side and desorb on the other side, and hence it becomes a membrane.

The present invention is directed to a bi-continuous membrane that in one phase conducts oxygen ions and in a second phase conducts carbonate ions. The oxygen conducting material is an oxygen ion conductive solid oxide like zirconia, the carbonate ions move freely through a carbonate melt, like lithium carbonate. By chosing the two materials appropriately, one can adjust the temperature range of the membrane. The materials comprising the membrane are fabricated into a structured membrane in accordance with this invention. In one embodiment of the invention, alkali metal zirconates, e.g., lithium zirconate (Li₂ZrO₃), are suitable precursor materials for these types of membranes and can form CO₂ selective layers. As such a single-phase membrane is exposed to CO₂ the membrane transforms itself into a two-phase mixture of zirconia and lithium carbonate. In other embodiments, one creates a porous solid oxide structure with the pores filled with a carbonate material that under operating conditions is molten. Carbonate melts include but are not limited to sodium, potassium and lithium carbonates. Other
examples include eutectics of involving calcium, barium or magnesium carbonates. The choice will depend on the pressure and temperature operating range of the membrane, as under the prevailing conditions the carbonate must be molten and retain enough carbonate ions to remain conductive.

As seen in Figure 1, the invention affords one structured material in which CO$_2$ molecules are transferred across the membrane as carbonate ions. In order to avoid charge built-up in the transport the negative charge is transported back through the solid oxide. The net transport is that of a neutral CO$_2$. Charged currents flow in this membrane, but they cancel each other out. In a representative membrane of this invention, a continuous zirconia phase allows for the transport of oxide from one side of the membrane to the other; a continuous molten carbonate phase provides a pathway for the carbonate ion in the opposite direction. (See, for example, FIG. 1). The driving force for the transport is the partial pressure difference of the CO$_2$ on the two sides of the membrane. Like other membranes the system is bidirectional in that CO$_2$ can flow in either direction and the actual flow will follow the pressure gradient.

The membrane would work with any pair of materials where one phase is able to contact oxygen ions, the other phase is able to conduct carbonate ions, and where the two phases can be brought into close contact so that the charge built up on the carbonate surface can drive the current flow in the oxygen phase. Of importance is that the two phases are arranged in such a way that there are continuous paths connecting the two sides of the membrane in both, the solid oxide and the carbonate phase.

Other suitable materials for use in fabricating the membrane include, but are not limited to, a selective CO$_2$ permeable composition, which is stable and long-lasting under the conditions of preparation and operation at high temperatures. Exemplary materials may be ceramic supports or substrates formed of alumina, alpha alumina, silica, silica-alumina, zirconia, silica-zirconia, alumina-zirconia, lithium aluminate, including α-, β-, or γ-lithium aluminate, lithium zirconate, titania, silica-titania, alumina-titania, lithium titanate, etc. The membrane may be in the form of a disk or plate, a cylinder, cube, or tube, a film or sheet, etc. In an embodiment, lithium zirconate can be stabilized with MgO, Y$_2$O$_3$, or CaO. Stabilized lithium zirconate can be
prepared by reacting zirconia or zirconia stabilized with MgO, Y_2O_3, or CaO to react with a lithium carbonate, nitrate, or hydroxide. Zirconia, and various forms of stabilized zirconia can be used. Solid oxide membranes and sensor membranes can be used. The materials that can be used for the oxygen-ion conducting phase include, and are not limited to: YSZ (yttria stabilized zirconia); GCO (gadolina doped ceria; SFC (Sr-Fe-Co oxides); ABO_3-delta (general perovskite crystalline structure, exhibits oxygen ionic and electronic conductivity). In one embodiment, a more specific example of the perovskite would be SrCO(0.8)Fe(0.2)O(3-delta).

In accordance with the practice of this invention, a two phase system comprising zirconia and carbonate, e.g., an alkali metal carbonate, such as lithium, sodium, potassium, calcium, magnesium carbonate, at low partial pressures of CO_2 over the system releases CO_2 and transforms itself into a new phase of the alkali metal zirconate, e.g., lithium zirconate. Without wishing to be bound by theory and with particular regard to lithium, the ability of lithium ions to incorporate themselves into the zirconia crystal structure may aid in stabilizing the material over large ranges of CO_2 partial pressures by adjusting the carbonate volume and creating a layer of lithium zirconate along the interfaces between the carbonate and zirconia layers in the membrane. In the bi-continuous membrane, the mobilization of lithium oxide may also help in transferring the oxygen ion that just released a CO_2 from the carbonate phase into the zirconia phase, and on the other side, transfer it back into the carbonate phase. By adjusting the composition of the carbonate melt it is possible to control the miscibility of the two phases. Non-miscible carbonates would provide a greater stability to the nano-structure of the material; surface treatments may also be needed so as to effectively provide the closing of the oxygen current path. The miscible material may be limited to a thin sheet on the edge of the molten carbonate structure. Notwithstanding, the mobility of carbonate ions in molten carbonates, combined with the mobility of oxygen ions in zirconia can provide a system in which sandwich or fiber-like materials that contain parallel current paths for oxygen ions in zirconia, and for carbonate ions in the carbonate melt, may yield high conductance membranes with high selectivity for CO_2.
The materials comprising the structured solid CO₂ membranes of the invention may differ by the cation mixture in the carbonate phase and by admixtures to the zirconia and the carbonate to enhance stability, ion permeability and selectivity of the membrane. The net neutral carbon dioxide flux is established using gas chromatography. Use of other gases or an admixture of other gases can establish the selectivity of the membrane for carbon dioxide over a range of temperatures.

Illustratively, such a membrane is useful in operating a solid oxide fuel cell on carbon monoxide. Since it is inefficient for a fuel cell to drive the oxidation reaction to completion, a better strategy would be to remove continuously excess CO₂ from the reactor by letting CO₂ escape from the reaction vessel through a high temperature selective membrane that is impermeable to CO. Rather than letting the CO be depleted in the chamber, additional CO would be generated in the oxidation chamber by injecting carbon. Carbon and CO₂ would react to form additional CO (Boudouard reaction). Such a fuel cell would operate as a stirred reactor that is maintained near the equilibrium point of the Boudouard reaction. It could operate at high efficiency and entirely avoid the usually obligatory post-combustion of remnant fuel in the exhaust of the fuel cell stack. Further, such a design would naturally collect CO₂ and ready it for subsequent disposal.

Other applications for high temperature CO₂ membranes include CO₂ capture in new types of power plants that capture CO₂ from the exhaust stream at high temperatures, or promoting water gas shift reactions by removing CO₂ from the reaction zone. In other embodiments, the absorbent membrane of the invention can be used in energy producing devices, fuel synthesis, carbon chemistry, steel making processes and systems, aluminum smelter and other metallurgical processes.

In an embodiment, the membrane material comprises zirconia and molten carbonates that are mechanically stable in the range of over 200°C, or in the range of about 300°C to about 1000°C, or about 500°C to about 1000°C, and which are devoid of open cracks or pores that allow for indiscriminate gas flow. Mechanically the membrane is stable even at room temperature. The membrane will not conduct carbonate until the carbonate is molten, and that
requires some temperature. The membrane will work once the solid oxide starts to become conducting. In one embodiment, the low end for this is around 600 °C. In another embodiment, the membrane material has a substantial and selective CO₂ permeability. Comparison will be made to solid oxide fuel cells and early molten carbonate fuel cells. In another embodiment, the membrane is selectively permeable for CO₂ over other molecules such as oxygen, carbon monoxide, water, and hydrogen. In an embodiment, the invention embraces two or more of the foregoing embodiments in combination. In these embodiments, the bi-continuous membrane materials operate over a range of temperatures and CO₂ pressures.

In another embodiment, the present invention encompasses a carbon dioxide gas absorbent, comprising a bi-continuous membrane material stable at a temperature of greater than 200°C and further comprising a zirconia layer for transporting oxygen and a molten carbonate layer for conducting carbonate ions, wherein (i) a concentration gradient of carbon dioxide carries a flux of carbon dioxide across the membrane as carbonate ions and (ii) oxygen returns to the zirconia layer in the absence of carbon dioxide which transfers back to the carbonate layer. In an embodiment, the zirconia layer comprises an alkali metal zirconate. In another embodiment, the zirconia layer comprises lithium zirconate. In an embodiment, the membrane is selectively permeable to carbon dioxide relative to one or more of hydrogen, water, carbon dioxide, or oxygen. In an embodiment, the membrane material is stable at a temperature of about 300°C to about 1000°C, or at a temperature of about 500°C to about 1000°C. In an embodiment, the net carbon dioxide flux in the membrane is neutral. In another embodiment, a zero-emission coal-based electric power plant comprising the carbon dioxide absorbent of the invention is embraced. In another embodiment, a solid oxide fuel cell comprising the carbon dioxide absorbent according to the invention is embraced.

In another embodiment, the present invention is directed to a process for carbon dioxide separation at high temperature, comprising subjecting a source containing carbon dioxide to the carbon dioxide absorbent according to the invention as described herein. In an embodiment, the source is a feed or feedstock. In an embodiment, the source is a fuel gas or an exhaust gas.
As an example of the usefulness of such a membrane, it can be used with the operation of a solid oxide fuel cell. Since it is inefficient to drive the oxidation reaction to completion, a better strategy is to remove excess CO₂ from the reactor by letting CO₂ escape from the reaction vessel through a high temperature selective membrane that is impermeable to CO. Rather than letting the CO be depleted in the chamber, additional CO can be generated in the oxidation chamber by injecting carbon. Carbon and CO₂ would react to form CO (Boudouard reaction). Such a fuel cell would operate as a stirred reactor that is maintained near the equilibrium point of the Boudouard reaction. It could operate at high efficiency and entirely avoid the usually obligatory post-combustion of remnant fuel in the exhaust of the fuel cell stack. Furthermore such a design would naturally collect CO₂ and ready it for subsequent disposal. Other applications for high temperature CO₂ membranes include CO₂ capture in novel power plants that capture CO₂ from the exhaust stream, or promoting water gas shift reactions by removing CO₂ from the reaction zone.

As shown in figure 1, the present invention provides a way to combine the oxygen ion mobility of zirconia and the carbonate ion mobility in molten carbonates into one structured material so that the net transport is that of neutral CO₂. Charged currents flow in this membrane but they cancel each other out. The invention provides for a bi-continuous membrane that in one phase conducts oxygen ions and a second phase conducts carbonate ions. The materials have been already demonstrated as effective in CO₂ absorption technologies [3-5] but have never been fabricated into a structured membrane.

The present invention also provides nano-structured solid oxide membranes with carbonate filled pore spaces that are highly permeable to CO₂ yet prevent passage of most other materials. In one embodiment, a starting material that can be used are those materials produced from the lithium zirconate materials that have been employed in CO₂ absorption technologies. The invention provides a processing of the materials that achieves a continous zirconia phase that allows for the transport of oxide from one side of the membrane to the other. A two-phase system consisting of zirconia and lithium carbonate at low partial pressures of CO₂ over the system will release CO₂ and transform itself into a new phase of lithium zirconate. The ability of
the lithium ions to incorporate themselves into the zirconia crystal structure at first sight appears appealing. One advantage of the present invention is that the incorporation can help stabilize the material over large ranges of CO₂ partial pressures by adjusting the carbonate volume and creating a layer of lithium zirconate along the interface. In an embodiment, the mobilization of lithium oxide can also help in transferring the oxygen ion that just released a CO₂ from the carbonate phase into the zirconia face and on the other side transfer it back into the carbonate phase. In another embodiment, non-miscible carbonates can be used, but surface treatments may be used also, which in effect provide the closing of the oxygen current path. In another embodiment, the miscible material can be a thin sheet on the edge of the molten carbonate structure.

In any case the mobility of carbonate ions in molten carbonates, combined with the mobility of oxygen ions in zirconia suggests that sandwich or fiber-like materials that contain parallel current paths for oxygen ions in zirconia and for carbonate ions in the carbonate melt, can provide high conductance membranes with high selectivity for CO₂.

The present invention provides a structured solid CO₂ membrane. Materials of the membrane can differ by the cation mixture in the carbonate phase and by admixtures to the zirconia and the carbonate to enhance stability, ion permeability and selectivity of the membrane.

In one embodiment of the invention, membranes are tested using various materials to optimize the net neutral carbon dioxide flux using gas chromatography.

In one embodiment, the invention provides for custom materials made from zirconia and molten carbonates that are mechanically stable in the range of 500 to 1000°C (without open cracks or pores) that allow for indiscriminate gas flow. In another embodiment, the invention provides for absorbent materials that can be synthesized that have a substantial CO₂ permeability. As a yardstick to gauge permeability, current flow rates of early solid oxide fuel cells and early molten carbonate fuel cells can be used to compare with the membranes of the invention. The invention provides for membranes selective for CO₂. The membranes can operate over a range of temperatures and CO₂ pressures.
References


7. Yamaguchi, T., Development of Lithium Based Dense Membrane for High Temperature CO2 Separation and its application to Membrane Reactor, University of Tokyo, Graduate School of Engineering: Tokyo.
What is claimed is:

1. A carbon dioxide gas-selective absorbent membrane comprising a bi-continuous membrane material stable at a temperature of greater than about 200°C and comprising a porous solid oxide material that in a temperature range of interest is capable of transporting oxygen ions, and a molten carbonate phase completely filling the pores capable of conducting carbonate ions, wherein (i) a concentration gradient of carbon dioxide drives a flux of carbonate ions across the membrane and (ii) oxygen ions return the charge in the solid oxide phase.

2. The membrane of claim 1, wherein the solid oxide layer and the carbonate layer form spontaneously from a precursor in the presence of CO₂ and wherein the precursor comprises an alkali metal zirconate in the presence of CO₂.

3. The membrane of claim 2, wherein the precursor material comprises lithium zirconate.

4. The membrane of claim 1, wherein the solid oxide phase and carbonate phase are premixed and fused.

5. The membrane of claim 1, wherein the solid oxide material comprises one or more of: YSZ (yttria stabilized zirconia), GCO (gadolina doped ceria), SFC (Sr-Fe-Co oxides), ABO₃-delta (general perovskite crystalline structure, exhibits oxygen ionic and electronic conductivity), or perovskite SrCO(0.8)Fe(0.2)O(3-delta), wherein the solid oxide material is capable of conducting oxygen ions.

6. The membrane of claim 1, wherein the membrane is selectively permeable to carbon dioxide relative to one or more of hydrogen, water, carbon dioxide, or oxygen.

7. The membrane of claim 1, wherein the membrane material is stable at a temperature of about 300°C to about 1200°C.
8. The membrane of claim 1, wherein the membrane material is stable at a temperature of about 500°C to about 1000°C, from about 600°C to about 900°C, from about 650°C to about 850°C, from about 700°C to about 800°C, or from about 700 °C to about 775°C.

9. A zero-emission coal-based electric power plant comprising the absorbent according to claim 1.

10. A solid oxide fuel cell comprising the absorbent according to claim 1.

11. A process for carbon dioxide separation at temperatures from about 300 °C to about 1000°C, comprising subjecting a source containing carbon dioxide to the membrane of claim 1.

12. The process of claim 11, wherein the source is a feed or feedstock.

13. The process of claim 11, wherein the source is a fuel gas or an exhaust gas.

14. The process of claim 11, wherein the temperature is greater than about 500°C.
Abstract of the Disclosure

Carbon dioxide gas-selective bi-continuous membranes are provided in which one phase conducts oxygen ions and in a second phase conducts carbonate ions. The materials comprising the membrane are effective in CO₂ absorption technologies and are fabricated into a structured membrane in accordance with this invention. Alkali metal zirconates, e.g., lithium zirconate, are suitable materials for the preparation of these types of membranes and can form CO₂ selective and permeable layers. Molten metal carbonates also comprise the bi-continuous membrane and allow for the transport of carbonate ions.
CO₂ Membrane for SOFC

Air

SOFC

C

CO₂ Membrane

C + CO₂ → 2CO

Boudouard Gasifier

CO₂

SOFC

CO₂ Membrane
Figure 3

Boudouard Reaction
Fig. 4

\[
\text{Li}_2\text{ZrO}_3 \leftrightarrow \text{ZrO}_2 + 2\text{Li}^\text{+} + \text{O}^{2\text{-}} \\
\text{CO}_2(\text{aq}) + 2\text{Li}^\text{+} + \text{O}^{2\text{-}} \rightarrow \text{Li}_2\text{CO}_3
\]
Fig. 5

[Diagram showing layers labeled ZrO₂, Li₂ZrO₃, and Molten CO₃²⁻ with P_{CO₂} and CO₂ arrows.]
Fig. 6

Effects of Increased Carbon Dioxide

- Greenhouse Gas Causes Climate Change
- Evaporation
- Ocean Acidification Stifles Coral Growth
- Physiological Changes
- Climate Instability: Arresting the Thermohaline Circulation
- Warm, low salinity
- Cold, high salinity
- Ecosystem Changes
- Deep, cold current
Application Data Sheet

Application Information

Application Type:: Provisional
Subject Matter:: Utility
Suggested Classification:: Utility
Suggested Group Art Unit::
CD-ROM or CD-R?:: None
Number of CD disks::
Number of copies of CDs::
Sequence Submission?::
Computer Readable Form (CRF)?::
Number of copies of CRF::

Title:: Membrane for Carbon Dioxide Separation at High Temperatures

Attorney Docket Number:: 19240.257-US1
Request for Early Publication?:: No
Request for Non-Publication?:: No
Suggested Drawing Figure::
Total Drawing Sheets:: 6
Small Entity?:: Yes
Latin name::
 Variety Denomination Name::
Petition Included?:: Yes
Petition Type::
Licensed US Govt. Agency::
Contract or Grant Numbers::
Secrecy Order in Parent Appl.?:: No
Applicant Information

Applicant Authority Type:: Inventor
Primary Citizenship Country:: U.S.A.
Status:: Unknown
Given Name:: Klaus
Middle Name:: S.
Family Name:: Lackner
Name Suffix::
City of Residence:: Dobbs Ferry
State or Province of Residence:: New York
Country of Residence:: U.S.A.
Street of mailing address:: 140 Southlawn Drive

City of mailing address:: Dobbs Ferry
State or Province of mailing address:: New York
Country of mailing address:: U.S.A.
Postal or Zip Code of mailing address:: 10522

Applicant Authority Type:: Inventor
Primary Citizenship Country:: U.S.A.
Status:: Unknown
Given Name:: Alan
Middle Name:: C.
Family Name:: West
Name Suffix::
City of Residence:: Tenafly
State or Province of Residence:: New Jersey
Country of Residence:: U.S.A.
Street of mailing address:: 115 Newcomb Road

City of mailing address:: Tenafly
State or Province of mailing address:: New Jersey
Country of mailing address:: U.S.A.
Postal or Zip Code of mailing address:: 07670

Correspondence Information
Correspondence Customer
Number:: 28089
Phone number:: (212) 937-7200
Fax Number:: (212) 937-7300
E-Mail address:: jane.love@wilmerhale.com

Representative Information
Representative Customer
Number:: 28089

Domestic Priority Information

<table>
<thead>
<tr>
<th>Application ::</th>
<th>Continuity Type::</th>
<th>Parent Application::</th>
<th>Parent Filing Date::</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>/ /</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>/ /</td>
</tr>
</tbody>
</table>
Foreign Priority Information

<table>
<thead>
<tr>
<th>Country::</th>
<th>Application number::</th>
<th>Filing Date::</th>
<th>Priority Claimed::</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/ /</td>
<td>/ /</td>
<td>/ /</td>
</tr>
<tr>
<td></td>
<td>/ /</td>
<td>/ /</td>
<td>/ /</td>
</tr>
</tbody>
</table>

Assignment Information

Assignee name:: The Trustees of Columbia in the City of New York
Street of mailing address:: 110 Low Memorial Library
535 West 116th Street
City of mailing address:: New York
State or Province of mailing address:: New York
Country of mailing address:: U.S.A.
Postal or Zip Code of mailing address:: 10027