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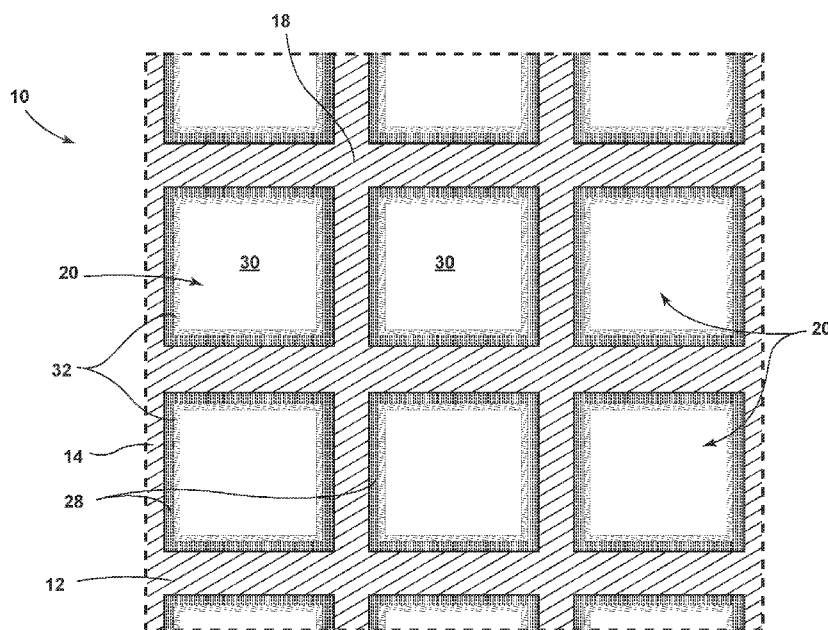


FIG. 3

(57) Abstract: A carbon capture article including: (i) a ceramic honeycomb monolith including an inlet end, an outlet end, and intersecting walls that define cells through which a fluid can flow; (ii) a zeolite coating at least partially covering the intersecting walls of the ceramic honeycomb monolith; and (iii) a silicone resin coating at least partially disposed on the zeolite coating. The zeolite coating can be a Type 13-X zeolite. The silicone resin can be a siloxane resin. A method of making the carbon capture article including a silicone coating step including coating a silicone resin at least partially onto a zeolite coating that is at least partially covering the intersecting walls of the ceramic honeycomb monolith to form a carbon capture article. A method of capturing carbon dioxide from air including a flowing step including causing a fluid comprising carbon dioxide (CO₂) molecules through a carbon capture article.



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**CARBON CAPTURE ARTICLE WITH ZEOLITE AND SILICONE RESIN,
METHOD OF MAKING SAME, AND METHOD OF USING SAME**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 of U.S. Provisional Application No. 63/599,776 filed November 16, 2023, the content of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This disclosure pertains to a carbon capture article and, more particularly, a carbon capture article with a zeolite coating and a silicone coating to impart hydrophobicity to the zeolite coating.

BACKGROUND

[0003] There are various environmental and economic incentives to capture carbon dioxide (CO₂) from waste streams generated from industrial processes (e.g., capture post-combustion of fossil fuels) before the CO₂ enters the atmosphere and to extract CO₂ directly from the atmosphere (e.g., direct air capture). Solid materials have been developed to capture the CO₂. Those solid materials typically fall within one of two categories differentiated by the mechanism of capture – physical adsorption (physisorption) or chemical adsorption (chemisorption). The former, solid materials that rely on physical adsorption, are typically highly porous to present a large surface area that adsorbs CO₂ molecules to the surface through relatively weak van der Waals forces. Activated carbon, metal-organic frameworks, and various zeolites are examples of solid adsorbents. The latter, said materials that rely on chemical mechanisms, chemically react with CO₂ molecules causing the CO₂ molecules to bond molecularly thereto (e.g., stronger than van der Waals forces). Amines and alkali metal oxides are examples. In either instance, after CO₂ molecules are captured, the solid material can be manipulated to cause release of the CO₂ molecules, which allows the solid material to be reused to capture more CO₂ molecules. For example, heating the solid material can cause the CO₂ molecules to release from the solid material. The released CO₂ molecules can be directed to a storage area, such as a retired natural gas reservoir, among other options.

[0004] Zeolites, as mentioned, are used to capture CO₂ molecules via physical adsorption. Zeolites, generally stated, are crystalline aluminosilicate materials. Zeolite coatings have been grown on porous supports, such as honeycomb ceramic monoliths, to generate gas separation articles, such as to extract CO₂ from a fluid passed therethrough.

[0005] However, there is a problem in that zeolites (and thus membranes made therefrom) naturally prefer adsorption of molecules of water (H₂O) over molecules of CO₂ and, thus, are

not utilized for direct air capture of carbon dioxide because of the presence of water within the air (e.g., humidity). Molecules of H₂O are smaller than molecules of CO₂ and thus enter adsorbing sites of the zeolite more easily than the larger CO₂ molecules. Further, oxygen within the zeolite forms hydrogen bonds with molecules of H₂O, while molecules of CO₂ lack hydrogen and thus do not engage in hydrogen bonding. Still further, the zeolite can have a surface charge that prefers polar molecules such as H₂O over non-polar molecules such as CO₂. Zeolites preferentially adsorbing molecules of H₂O over molecules of CO₂ is problematic because, when the goal is to extract CO₂, molecules of H₂O adsorbing onto the zeolite prevent molecules of CO₂ from adsorbing, defeating the goal.

SUMMARY

[0006] The present disclosure addresses that problem with a carbon capture article that includes a zeolite coating to adsorb carbon dioxide, as well as a silicone coating at least partially over the zeolite coating to impart hydrophobicity, which reduces the ability of water molecules from entering adsorbing sites of the zeolite coating, thus leaving those sites open to adsorb molecules of carbon dioxide.

[0007] According to a first aspect of the present disclosure, a carbon capture article comprises: (i) a ceramic honeycomb monolith comprising an inlet end, an outlet end, and intersecting walls that define cells through which a fluid can flow from the inlet end to the outlet end; (ii) a zeolite coating at least partially covering the intersecting walls of the ceramic honeycomb monolith; and (iii) a silicone resin coating at least partially disposed on the zeolite coating.

[0008] According to a second aspect of the present disclosure, the carbon capture article of the first aspect is presented, wherein the zeolite coating comprises zeolite with an average pore size that is greater than 3.3 Å.

[0009] According to a third aspect of the present disclosure, the carbon capture article of any one of the first through second aspects is presented, wherein the zeolite coating comprises a zeolite selected from the group consisting of an A-type zeolite, an X-type zeolite, a Y-type zeolite, mordenite, ferrierite, chabazite, clinoptilolite, and ZSM-5 zeolite.

[0010] According to a fourth aspect of the present disclosure, the carbon capture article of the third aspect is presented, wherein the zeolite coating comprises an X-type zeolite.

[0011] According to a fifth aspect of the present disclosure, the carbon capture article of the fourth aspect is presented, wherein the zeolite coating comprises Type 13-X zeolite.

[0012] According to a sixth aspect of the present disclosure, the carbon capture article of any one of the first through fifth aspects is presented, wherein the zeolite coating comprises a

density within a range of from 50 g per liter of the ceramic honeycomb monolith to 400 g per liter of ceramic honeycomb monolith.

[0013] According to a seventh aspect of the present disclosure, the carbon capture article of any one of the first through sixth aspects is presented, wherein the silicone resin comprises a density within a range of from 3.0 g per liter of the ceramic honeycomb monolith to 7.0 g per liter of the ceramic honeycomb monolith.

[0014] According to an eighth aspect of the present disclosure, the carbon capture article of any one of the first through seventh aspects is presented, wherein the silicone resin comprises a siloxane resin.

[0015] According to a ninth aspect of the present disclosure, the carbon capture article of the eighth aspect is presented, wherein the siloxane resin is alkoxy functionalized.

[0016] According to a tenth aspect of the present disclosure, the carbon capture article of the ninth aspect is presented, wherein the siloxane resin is methoxy functionalized.

[0017] According to an eleventh aspect of the present disclosure, the carbon capture article of the eighth aspect is presented, wherein the silicone resin includes one or more silsesquioxane resins.

[0018] According to a twelfth aspect of the present disclosure, the carbon capture article of any one of the first through eleventh aspects is presented, wherein the carbon capture article exhibits carbon capture per gram of zeolite coating at 0 °C, when a fluid comprising carbon dioxide (CO₂) molecules and water (H₂O) molecules is flowed through the carbon capture article, that is greater than a carbon capture per gram of zeolite coating that an otherwise identical carbon capture article without the silicone resin coating exhibits at 0 °C when the same fluid is flowed through the carbon capture article.

[0019] According to a thirteenth aspect of the present disclosure, the carbon capture article of any one of the first through twelfth aspects is presented, wherein the carbon capture article exhibits carbon capture of greater than 2.0 mmol of CO₂ per gram of zeolite coating at 0 °C when air comprising carbon dioxide (CO₂) molecules and water molecules (CO₂), as the fluid, is flowed through the carbon capture article.

[0020] According to a fourteenth aspect of the present disclosure, a method of making a carbon capture article comprises: with a ceramic honeycomb monolith comprising an inlet end, an outlet end, and intersecting walls that define cells through which a fluid can flow from the inlet end to the outlet end, a silicone coating step comprising coating a silicone resin coating at least partially onto a zeolite coating that is at least partially covering the intersecting walls of the ceramic honeycomb monolith to form a carbon capture article.

[0021] According to a fifteenth aspect of the present disclosure, the method of the fourteenth aspect is presented, wherein the silicone coating step further comprises curing the silicone resin coating to form the carbon capture article.

[0022] According to a sixteenth aspect of the present disclosure, the method of any one of the fourteenth through fifteenth aspects is presented, wherein the silicone resin coating comprises a siloxane resin.

[0023] According to a seventeenth aspect of the present disclosure, the method of the sixteenth aspect is presented, wherein the siloxane resin is alkoxy functionalized.

[0024] According to an eighteenth aspect of the present disclosure, the method of the seventeenth aspect is presented, wherein the siloxane resin is methoxy functionalized.

[0025] According to a nineteenth aspect of the present disclosure, the method of any one of the fourteenth through fifteenth aspects is presented, wherein the silicone resin comprises a silsesquioxane resin.

[0026] According to a twentieth aspect of the present disclosure, the method of any one of the fourteenth through nineteenth aspects are presented, wherein coating the silicone resin coating at least partially onto the zeolite coating comprises immersing the zeolite coating disposed on the ceramic honeycomb monolith into a solution of a solvent and the silicone resin.

[0027] According to a twenty-first aspect of the present disclosure, the method of any one of the fourteenth through twentieth aspects further comprises: a zeolite coating forming step comprising (i) coating zeolite particles onto at least part of the intersecting walls of the ceramic honeycomb monolith and (ii) calcining the zeolite particles.

[0028] According to a twenty-second aspect of the present disclosure, the method of the twenty-first aspect is presented, wherein coating the zeolite particles onto at least part of the intersecting walls of the ceramic honeycomb monolith comprises immersing at least a portion of the ceramic honeycomb monolith into a solution of water and the zeolite particles.

[0029] According to a twenty-third aspect of the present disclosure, a method of capturing carbon dioxide from air comprises: a flowing step comprising causing a fluid comprising molecules of carbon dioxide (CO₂) to flow through a carbon capture article comprising (i) a ceramic honeycomb monolith comprising an inlet end, an outlet end, and intersecting walls that define cells through which a fluid can flow from the inlet end to the outlet end; (ii) a zeolite coating at least partially covering the intersecting walls of the ceramic honeycomb monolith; and (iii) a silicone resin coating at least partially disposed on the zeolite coating, wherein at least a portion of the molecules of carbon dioxide (CO₂) are captured by the carbon capture article.

[0030] According to a twenty-fourth aspect of the present disclosure, the method of the twenty-third aspect is presented, wherein the fluid further comprises molecules of water (H_2O).

[0031] According to a twenty-fifth aspect of the present disclosure, the method of any one of the twenty-third through twenty-fourth aspects is presented, wherein the fluid is air.

[0032] According to a twenty-sixth aspect of the present disclosure, the method of any one of the twenty-third through twenty-fifth aspects further comprises: a regenerating step comprising applying thermal energy to the carbon capture article with the molecules of carbon dioxide (CO_2) captured therein until at least a portion of molecules of carbon dioxide (CO_2) are released from the carbon capture article.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] In the Drawings:

[0034] FIG. 1 is a perspective view of a carbon capture article of the present disclosure, illustrating a ceramic honeycomb monolith with intersecting walls forming cells that extend from an inlet end to an outlet end;

[0035] FIG. 2 is a plan view of the carbon capture article of FIG. 1, illustrating sides that are connected, via leads, to an electrical power supply that, when activated, increases the temperature of the carbon capture article for a regeneration step to desorb carbon dioxide from the carbon capture article;

[0036] FIG. 3 is a magnified view of area III of FIG. 2, illustrating a zeolite coating at least partially covering the intersecting walls within each cell and a silicone resin coating at least partially covering the zeolite coating within each cell;

[0037] FIG. 4 is a schematic diagram of various zeolites;

[0038] FIG. 5 is a schematic diagram of a method of making the carbon capture article of FIG. 1, illustrating a zeolite coating forming step and a silicone coating step;

[0039] FIG. 6 is a schematic diagram of a method of capturing carbon dioxide (CO_2) from a fluid, illustrating a flowing step where the fluid is flowed through the carbon capture article of FIG. 1 and a regenerating step where captured carbon dioxide is caused to desorb from the zeolite coating;

[0040] FIG. 7A, pertaining to Comparative Examples 1A-1C, is a graph plotting the mmol of carbon dioxide per gram of zeolite coating adsorbed onto the zeolite coating as a function of fluid pressure and temperature for different weights of the zeolite coating;

[0041] FIG. 7B, pertaining to Examples 1A-1C, is the same kind of graph as FIG. 7A, but illustrating that the silicone coating causes a minor decrease in carbon monoxide adsorption compared to FIG. 7A where no silicone coating is included;

[0042] FIG. 8A, pertaining to Comparative Examples 1A-1C where no silicone coating was added, is a photograph showing the zeolite coating soaking in water droplets that have been applied thereupon; and

[0043] FIG. 8B, pertaining to Examples 1A-C, where silicone coating was added over the zeolite coating, is a photograph showing the silicone coating causing water droplets to bead, illustrating the hydrophobicity that the silicone coating imparts to the zeolite coating, which reduces the number of molecules of water that compete against molecules of carbon dioxide for adsorption onto the zeolite coating, which compensates for the reduced adsorptive capacity that the silicone coating causes as shown in FIG. 7B.

DETAILED DESCRIPTION

[0044] Referring to FIGS. 1-3, a carbon capture article 10 includes a ceramic honeycomb monolith 12. In embodiments, the ceramic honeycomb monolith 12 includes an inlet end 14, an outlet end 16, and intersecting walls 18. The intersecting walls 18 define cells 20 (e.g., passages, channels, etc.) through which a fluid can flow from the inlet end 14 to the outlet end 16. In the illustrated embodiment, the cells 20 are not plugged at either the inlet end 14 or the outlet end 16, and a fluid that is caused to flow into the inlet end 14 then flows through the cells 20 and out of the outlet end 16 without being forced through the intersecting walls 18. In embodiments, the intersecting walls 18 are porous. “Fluid” in this disclosure includes both liquids and gases.

[0045] In other embodiments, although not illustrated, a portion of the cells 20 at the inlet end 14 can be plugged with plugs having same or similar composition to that of the intersecting walls 18. A portion of the cells 20 on the outlet end 16 but not corresponding to those on the inlet end 14 may also be plugged with plugs in a similar pattern. Therefore, in those embodiments, each cell 20 is plugged only at either the inlet end 14 or the outlet end 16. The result can be a checkerboard pattern of plugs. That configuration of plugs allows for more intimate contact between the fluid forced to flow through the carbon capture article 10 and the intersecting walls 18 of the ceramic honeycomb monolith 12. The fluid is forced to flow into cells 20 (not plugged) at the inlet end 14, then through the intersecting walls 18, and out through the cells 20 (not plugged) at the outlet end 16.

[0046] The ceramic honeycomb monolith 12 can be formed of any suitable ceramic. Examples include cordierite, mullite, spinel ceramics, or combinations thereof. In general, the ceramic honeycomb monolith 12 can be formed from a plasticized ceramic precursor batch composition with inorganic ceramic forming batch component(s), a pore former (e.g., a potato starch), a liquid vehicle, and a binder. A green body of a desired shape is then formed from the

plasticized ceramic precursor batch composition. The green body is then fired under conditions effective to convert the green body into the ceramic honeycomb monolith 12.

[0047] In embodiments, the inorganic batch components can be selected to provide a ceramic honeycomb monolith 12 that includes at least about 93% by weight cordierite. The cordierite consists essentially of, as characterized in an oxide weight percent basis, from about 49 to about 53 percent by weight SiO_2 , from about 33 to about 38 percent by weight Al_2O_3 , and from about 12 to about 16 percent by weight MgO . The precursor powder batch composition can include about 33 to about 41 weight percent aluminum oxide source, about 46 to about 53 weight percent of a silica source, and about 11 to about 17 weight percent of a magnesium oxide source.

[0048] Example alumina forming sources can include aluminum oxides or a compound containing aluminum which when heated to a sufficiently high temperature yields essentially 100% aluminum oxide. Non-limiting examples of alumina forming sources include corundum or alpha-alumina, gamma-alumina, transitional aluminas, aluminum hydroxide such as gibbsite and bayerite, boehmite, diaspore, aluminum isopropoxide and the like. Suitable silica forming sources can in one aspect comprise clay or mixtures, such as for example, raw kaolin, calcined kaolin, and/or mixtures thereof. An example magnesium oxide source can comprise talc.

[0049] The inorganic batch components and the pore former agent can be intimately blended with a liquid vehicle and forming aids which impart plastic formability and green strength to the raw materials when they are shaped into the green body. Forming may be done by, for example, molding or extrusion. When forming is done by extrusion, a cellulose ether binder such as methylcellulose, hydroxypropyl methylcellulose, methylcellulose derivatives, and/or any combinations thereof, can serve as a binder, and sodium stearate or oleic acid serves as a lubricant. The liquid vehicle content can be in the range of from 20% to 50% by weight of the plasticized composition. The liquid vehicle component can be water.

[0050] Referring additionally to FIG. 3, the carbon capture article 10 further includes a zeolite coating 28. The zeolite coating 28 at least partially covers the intersecting walls 18 of the ceramic honeycomb monolith 12 (e.g., the zeolite coating 28 is disposed within the cells 20). The zeolite coating 28 can extend into pores of the intersecting walls 18 but separate, at least in part, the intersecting walls 18 from a passageway 30 within the cells 20 that the intersecting walls 18 form. For any given cell 20, the zeolite coating 28 can separate completely the passageway 30 from the intersecting walls 18 that form the cell 20 within which the passageway 30 is disposed. How the zeolite coating 28 can be applied to the ceramic honeycomb monolith 12 is discussed further below.

[0051] Referring additionally to FIG. 4, the zeolite coating 28 includes a zeolite. A zeolite is a hydrated aluminosilicate having symmetrically stacked alumina and silica tetrahedra that form an open, stable, three-dimensional honeycomb structure having a negative charge. The three-dimensional honeycomb structure provides open cavities in the form of channels and cages. The channels and cages (collectively “pores”) are large enough to allow the passage of desired molecules – here molecules of CO₂ – allowing the zeolite to adsorb the molecules. In short, the zeolite can be a molecular sieve configured to adsorb molecules of CO₂. In embodiments, the pores of the zeolite are characterized by an average pore size of less than 2.0 nm (20 Å). The average pore size is greater than the critical diameter of a molecule of CO₂, which is about 3.3 Å.

[0052] More particularly, the chemical composition of a zeolite can be represented by a formula of the type $A_{y/m}^{m+}[(SiO_2)_x \cdot (AlO_2^-)_y] \cdot zH_2O$, where A is a cation with charge m , $(x+y)$ is the number of tetrahedra per crystallographic unit cell, and x/y is the so-called framework silicon/aluminum ratio. Silicon and aluminum in aluminosilicate zeolites are referred to as T-atoms. The cation A can be Na⁺, K⁺, Ca²⁺ and/or Mg²⁺.

[0053] The structures of four selected zeolites are shown in FIG. 4 together with their respective void systems and pore dimensions. In the representations of FIG. 4, the T-atoms are located at the vertices, and the lines connecting them represent T-O-T bonds. If 24 tetrahedra are linked together as shown in the top line of FIG. 4, the cubo-octahedron, also referred to as a sodalite unit or β-cage, results. If sodalite units are connected via their hexagonal faces, the structure of the mineral faujasite is formed.

[0054] In embodiments, the zeolite of the zeolite coating 28 is one or more of an A-type zeolite, an X-type zeolite, a Y-type zeolite, ZSM-5 zeolite, mordenite, ferrierite, chabazite, and clinoptilolite. That list is not meant to be exhaustive. A-type zeolites may have an average formula of $(Na_2O)_m \cdot Al_2O_3 \cdot (SiO_2)_n \cdot (H_2O)_t$, wherein m has a value of from 0.9 to 1.3, n a value of from 1.3 to 4.0 and t a value of from 1 to 6. Synthesis thereof produces precisely duplicated sodalite units. A 4A-zeolite (an example A-type zeolite, e.g., $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 9/2H_2O$) can absorb molecules whose critical diameter are less than 4 Å, while a 3A-zeolite (another example A-type zeolite) cannot.

[0055] X-type and Y-type zeolites are both faujasites. X-type and Y-type zeolites have different molar ratios of constituents, with X-type having a higher molar ratio of Al₂O₃ relative to SiO₂ than Y-type. In general, Y-type zeolites have larger pores than X-type zeolites. A particular X-type zeolite, Type 13-X, has an average pore size of about 0.9 nm to 1.0 nm (9 Å

to 10 Å). ZSM-5 zeolite has more silica and less alumina than the faujasites and has pentasil units. As a consequence, ZSM-5 zeolites present a smaller average pore size (e.g., about 5 Å) than X-type and Y-type zeolites. In embodiments, the zeolite coating 28 includes an X-type zeolite.

[0056] Mordenite is found naturally and can be made synthetically, and can have a formula of $(\text{Ca}, \text{Na}_2, \text{K}_2)\text{Al}_2\text{Si}_{10}\text{O}_{24} \cdot 7\text{H}_2\text{O}$. Ferrierite and chabazite are likewise found naturally and can be made synthetically. Clinoptilolite is likewise found naturally.

[0057] In embodiments, the zeolite coating 28 has a density within a range of from 50 g of zeolite coating 28 per liter of the ceramic honeycomb monolith to 400 g per liter of ceramic honeycomb monolith 12. In embodiments, the weight of the zeolite coating 28 is 50 g/L, 100 g/L, 150 g/L, 200 g/L, 250 g/L, 300 g/L, 350 g/L, or 400 g/L, or within any range bound by any two of those values (e.g., from 50 g/L to 150 g/L, from 200 g/L to 300 g/L, and so on). The unit “g/L” here again refers to grams of zeolite coating 28 per liter of the ceramic honeycomb monolith 12. The unit of volume, here liter, is determined using the dimensions of the ceramic honeycomb monolith 12. For example, if the ceramic honeycomb monolith 12 is cube, then the volume is the length x width x height of the cube.

[0058] Referring back to FIG. 3, the carbon capture article 10 further includes a silicone resin coating 32 at least partially covering the zeolite coating 28. The silicone resin coating 32 need not entirely cover the zeolite coating 28 or otherwise totally separate the passageway 30 of the cell 20 from the zeolite coating 28. In embodiments, the silicone resin coating 32 only partially covers the zeolite coating 28 and some of the zeolite coating 28 is exposed within the cell 20 to the passageway 30. It is believed that the silicone resin coating 32 entirely covering the zeolite coating 28 would substantially degrade the ability of the zeolite coating 28 to capture CO_2 molecules. The silicone resin coating 32 increases the hydrophobicity of the zeolite coating 28 compared to if the silicone resin coating 32 were not present. The silicone resin coating 32 can be in a cured state but need not be. How the silicone resin coating 32 can be applied to the ceramic honeycomb monolith 12 is discussed further below.

[0059] In embodiments, the silicone resin coating 32 has a density within a range of from 3.0 g of silicone resin coating 32 per liter of the ceramic honeycomb monolith 12 to 7.0 g per liter of the ceramic honeycomb monolith 12. In embodiments, the density of the silicone resin coating 32 is 3.0 g/L, 3.5 g/L, 4.0 g/L, 4.5 g/L, 5.0 g/L, 5.5 g/L, 6.0 g/L, 6.5 g/L, or 7.0 g/L, or within any range bound by any two of those values (e.g., from 3.5 g/L to 6.0 g/L, from 6.0 g/L to 6.5 g/L, and so on). Again, the unit of volume, here liter, is determined using the dimensions

of the ceramic honeycomb monolith 12, as with the density of the zeolite coating 28 described above.

[0060] In embodiments, the silicone resin coating 32 includes a siloxane resin. The siloxane resin can be alkoxy (e.g., methoxy) functionalized. For example, the silicone resin coating 32 can include a single organopolysiloxane or a mixture of various organopolysiloxanes. The organopolysiloxanes may have any combination of $(R_3SiO_{0.5})$, (R_2SiO) , $(RSiO_{1.5})$, or (SiO_2) units, commonly referred to as M, D, T, and Q units respectively, where R may be any monovalent organic group, such as methyl. The organopolysiloxanes may have cyclic, linear, or branched structures.

[0061] In embodiments, the siloxane resin is a DT resin, for example a resin consisting essentially of $(CH_3)_2SiO_{2/2}$ units and $(CH_3)SiO_{3/2}$ units in the D:T ratio of from 1:20 to 20:1 (e.g., 0.5:2 to 2:0.5). An example DT resin is DOWSIL™ 2405 Resin, a methoxy functional siloxane resin available from Dow Corning (Midland, Michigan, USA). In embodiments, the siloxane resin is substantially free of (or free of) hydroxyl groups. The siloxane resins described are not meant to be exhaustive.

[0062] In embodiments, some or all of the alkyl groups in the T units of the formula $(RSiO_{3/2})$ are alkyl groups having 1 to 30 carbon atoms, for example alkyl groups having 6 to 18 carbon atoms such as octyl groups. The siloxane resin can for example be an n-octyl silsesquioxane resin or an n-octyl methyl silsesquioxane resin.

[0063] In embodiments, the carbon capture article 10 exhibits characteristic carbon capture per gram of zeolite coating 28 disposed on and within the ceramic honeycomb monolith 12 when a fluid that includes carbon dioxide (CO_2) molecules and water (H_2O) molecules is flowed through the carbon capture article 10. In embodiments, the carbon capture article 10 can exhibit carbon capture per gram of zeolite coating 28 at 0 °C from the fluid that is greater than a carbon capture that an otherwise identical carbon capture article 10, but without the silicone resin coating 32 disposed on the zeolite coating 28, exhibits when the same fluid is flowed therethrough. For example, the carbon capture article 10 can exhibit carbon capture of greater than 2.0 mmol of CO_2 per gram of zeolite coating 28 at 0 °C, such as carbon capture within a range of from 2.0 mmol CO_2 to 6.8 mmol of CO_2 per gram of zeolite coating 28 at 0 °C.

[0064] Referring now to FIG. 5, a method 100 of making the carbon capture article 10 is herein described. At a silicone coating step 102, the method 100 includes coating the silicone resin coating 32 at least partially onto the zeolite coating 28 that is at least partially covering the intersecting walls 18 of the ceramic honeycomb monolith 12 to form the carbon capture article 10. In embodiments, the silicone coating step 102 further includes curing the silicone resin

coating 32 to form the carbon capture article 10. To coat the silicone resin coating 32 onto the zeolite coating 28, the zeolite coating 28 at least partially disposed on the ceramic honeycomb monolith 12 can be immersed into a solution of solvent and the silicone resin. The solvent, for example, can be ethanol. The concentration of the silicone resin coating 32 in the solution can be any concentration that causes the carbon capture article 10 to exhibit greater capture of CO₂ per gram of the zeolite coating 28 than if the silicone resin coating 32 was not applied onto the zeolite coating 28.

[0065] In embodiments, the method 100 further includes a zeolite coating forming step 104. The zeolite coating forming step 104 occurs before the silicone coating step 102. The zeolite coating forming step 104 includes coating zeolite particles onto at least part of the intersecting walls 18 of the ceramic honeycomb monolith 12 and then calcining the zeolite particles. The ceramic honeycomb monolith 12 can be immersed into a solution of water and the zeolite seed particles to coat the zeolite seed particles onto the ceramic honeycomb monolith 12. Alternatively, the solution can be sprayed onto the ceramic honeycomb monolith 12. Calcining the zeolite particles forms the zeolite coating 28. Adding the silicone resin coating 32 after the ceramic honeycomb monolith 12 has been fired and the zeolite particles have been calcined prevents the calcining from burning out the silicone resin coating 32.

[0066] Referring additionally to FIG. 6, a method 200 of capturing carbon dioxide (CO₂) from a fluid is herein disclosed. The method 200 includes a flowing step 202. The flowing step 202 includes causing a fluid including carbon dioxide (CO₂) molecules to flow through the carbon capture article 10. For example, the fluid can be flowed into the passageways 30 at the inlet end 14 of the carbon capture article 10. The zeolite coating 28 absorbs (and thus captures) at least a portion of the molecules of carbon dioxide (CO₂) in the fluid before the fluid exits the passageways 30 out of the outlet end 16. In embodiments, the fluid, in addition to the carbon dioxide (CO₂) molecules, further includes molecules of water (H₂O). For example, the fluid can be air, which has a non-zero humidity.

[0067] In embodiments, the method 200 further includes a regenerating step 204. The regenerating step 204 occurs after the flowing step 202. The regenerating step 204 includes applying thermal energy to the carbon capture article 10, which has the molecules of carbon dioxide (CO₂) adsorbed (e.g., captured) therein. The thermal energy is applied until at least a portion (e.g., substantially all) of the molecules of carbon dioxide (CO₂) adsorbed therein are released (e.g., desorbed) from the carbon capture article 10. The molecules of carbon dioxide (CO₂) that are so released can be directed to a storage chamber.

[0068] To apply the thermal energy to the carbon capture article 10, the carbon capture article 10 can be subjected to thermal energy produced from an external source. For example, a heater can heat the carbon capture article 10, or a fluid having sufficient temperature and not adsorbing onto the carbon capture article 10 can be flowed through the passageways 30. In other embodiments, when the ceramic honeycomb monolith 12 is sufficiently conductive (e.g., includes graphite), a power supply can be used to pass electrical current through leads disposed at opposite sides of the carbon capture article 10. The sides resist the electrical current and thus generate heat. The electrical resistance can be within a range of from 5 ohms to 500 ohms. The electrical current can be controlled as a function of time to achieve the desired temperature of the carbon capture article 10. To cause the zeolite coating 28 to desorb the carbon dioxide, the temperature of the carbon capture article 10 (and thus the zeolite coating 28) can be increased up to about 350 °C, such as within a range of from 200 °C to 350 °C. The temperature should not be so high as to damage the silicone resin coating 32 disposed on the zeolite coating 28.

[0069] The storage chamber to which the carbon dioxide (CO₂) desorbed from the zeolite coating 28 is directed can be underground caverns and the like. Instead of a storage chamber, the carbon dioxide (CO₂) desorbed from the zeolite coating 28 can be used for other manufacturing processes, such as carbonation of beverages. After the regenerating step 204, the method 200 can be repeated to perform again the flowing step 202 and the regenerating step 204 in sequence.

[0070] The carbon capture article 10 and the method 100 of the present disclosure address the problem identified in the Background, at least in part because the silicone resin coating 32 is hydrophobic and prevents or reduces the number of molecules of water (H₂O) that can interact with the zeolite coating 28. Reducing the number of molecules of water that interact with the zeolite coating 28 reduces the number of molecules of water that the zeolite coating 28 adsorbs, which increases the capability of the zeolite coating 28 to adsorb molecules of carbon dioxide (CO₂) from the fluid when the fluid has water present (e.g., is humid). The increased capability of the zeolite coating 28 to adsorb molecules of carbon dioxide (CO₂) from the fluid means, among other things, that Type 13-X zeolites can be incorporated into the carbon capture article 10 and used for direct air capture of carbon dioxide. Although Type 13-X zeolites have been used for capture of carbon dioxide under no humidity conditions, they have heretofore not been used for direct air capture of carbon dioxide because of the selective adsorption of water molecules over carbon dioxide. The induced hydrophobicity via the silicone resin coating 32 of the present disclosure overcomes that issue and makes Type 13-X zeolites (and zeolites more

generally) usable for direct air capture of carbon dioxide. Making Type 13-X zeolites usable for direct air capture of carbon dioxide is beneficial because Type-X zeolites are relatively inexpensive compared to other sorbents.

[0071] The approach of the present disclosure is advantageous over other attempted solutions. There have been efforts to modify the composition of zeolite coatings to increase hydrophobicity, such as by optimizing the ratio of aluminum to silicon or by impregnating the pores of the zeolite particles with polyethyleneimine, among other ways. However, those other attempted solutions are impractical to scale up because of relatively high cost and relatively low reaction yield.

[0072] **EXAMPLES**

[0073] **Examples 1A-1C and Comparative Examples 1A-1C** – Ceramic honeycomb monoliths with intersecting porous walls were obtained. Each of the ceramic honeycomb monoliths were made predominately of cordierite. Each of the ceramic honeycomb monoliths were coated by immersion coating with Type 13-X zeolite particles to form a zeolite coating over the intersecting porous walls with the zeolite coating facing the passageways that the intersecting porous walls form. The zeolite coating was then calcined. After being calcined, the zeolite coating of some of the ceramic honeycomb monoliths, identified here as Example 1A and Comparative Example 1A, weighed 0.039 grams. The zeolite coating of other of the ceramic honeycomb monoliths, identified here as Example 1B and Comparative Example 1B, weighed 0.109 grams. Finally, the zeolite coating of other of the ceramic honeycomb monoliths, identified here as Example 1C and Comparative Example 1C, weighed 0.146 grams. Comparative Examples 1A-1C were then set aside.

[0074] Each of the zeolite coated ceramic honeycomb monoliths of Examples 1A-1C were then coated with a silicone resin (in particular, a siloxane resin). The siloxane resin of each was then cured at 200 °C to form carbon capture articles of the present disclosure. After curing, the siloxane resin had a density of 5 g/L of zeolite coated ceramic honeycomb monolith.

[0075] Carbon dioxide (CO₂) adsorption isotherm plots were then obtained for each of Examples 1A-1C and Comparative Examples 1A-1C at two different temperatures (0 °C and 25 °C). A Micromeritics® high pressure volumetric analyzer (“HPVA”) system was employed with a 1" sample holder to measure the CO₂ volume adsorbed (mmol/g of zeolite coating) as a function of pressure (mmHg). The isotherm plots for Comparative Examples 1A-1C are reproduced at FIG. 7A. The isotherm plots for Examples 1A-1C are reproduced at FIG. 7B. There were no water molecules intentionally added to the CO₂ gas forced to flow through any of the Examples 1A-1C or Comparative Examples 1A-1C. The adsorption isotherm plots thus

concern CO₂ adsorption only. Between each cycle, the carbon capture article of Examples 1A-1C and the zeolite coated ceramic honeycomb monoliths of Comparative Examples 1A-1C were subjected to a regeneration step to desorb the adsorbed carbon dioxide (CO₂). The regeneration temperature for the zeolite coated ceramic honeycomb monoliths of Comparative Examples 1A-1C was 350 °C. The regeneration temperature for the carbon capture articles of Examples 1A-1C were 200 °C. The lower temperature was utilized so as to not thermally disrupt the siloxane coating.

[0076] The comparison between the isotherms reproduced at FIG. 7A for Comparative Examples 1A-1C and the isotherms reproduced at FIG. 7B for Examples 1A-1C reveal that the siloxane resin applied over the zeolite coating causes a decrease in the adsorptive capacity of the zeolite coating for CO₂. However, the decrease is minor. For example, Comparative Example 1B absorbed about 6.8 mmol CO₂ per gram of zeolite coating at 0 °C, while Example 1B absorbed about 5.8 mmol per gram. The decrease is about 15%. Without being bound by theory, the decrease may be attributable to (i) the siloxane coating blocking access to sites on and within the zeolite coating to which the molecules of carbon dioxide (CO₂) could otherwise adsorb or (ii) the difference in the regeneration temperatures used for Examples 1A-1C (200 °C) compared to the Comparative Examples 1A-1C (350 °C), or some combination of (i) and (ii).

[0077] However, the siloxane coating present on Examples 1A-1C imparts hydrophobicity to the zeolite coating, and the hydrophobicity would prevent water (H₂O) molecules from occupying sites on and within the zeolite coating that molecules of CO₂ could otherwise occupy. In that regard, drops of water were placed on a zeolite (Type 13-X) coated ceramic body that was representative of Comparative Examples 1A-1C. A picture was captured. The picture is reproduced at FIG. 8A. Similarly, drops of water were placed on samples of each of the carbon capture articles Examples 1A-1C (with the siloxane coating). A picture was captured. The picture is reproduced at FIG. 8B. Comparing FIG. 8A with FIG. 8B, it is clear that the zeolite coating (without any siloxane coating thereupon) soaked in the water, while the siloxane coating of Examples 1A-1C caused the water to bead. Notably, contact angle of the water droplets increased as a function of increasing weight of the zeolite coating.

CLAIM(S)

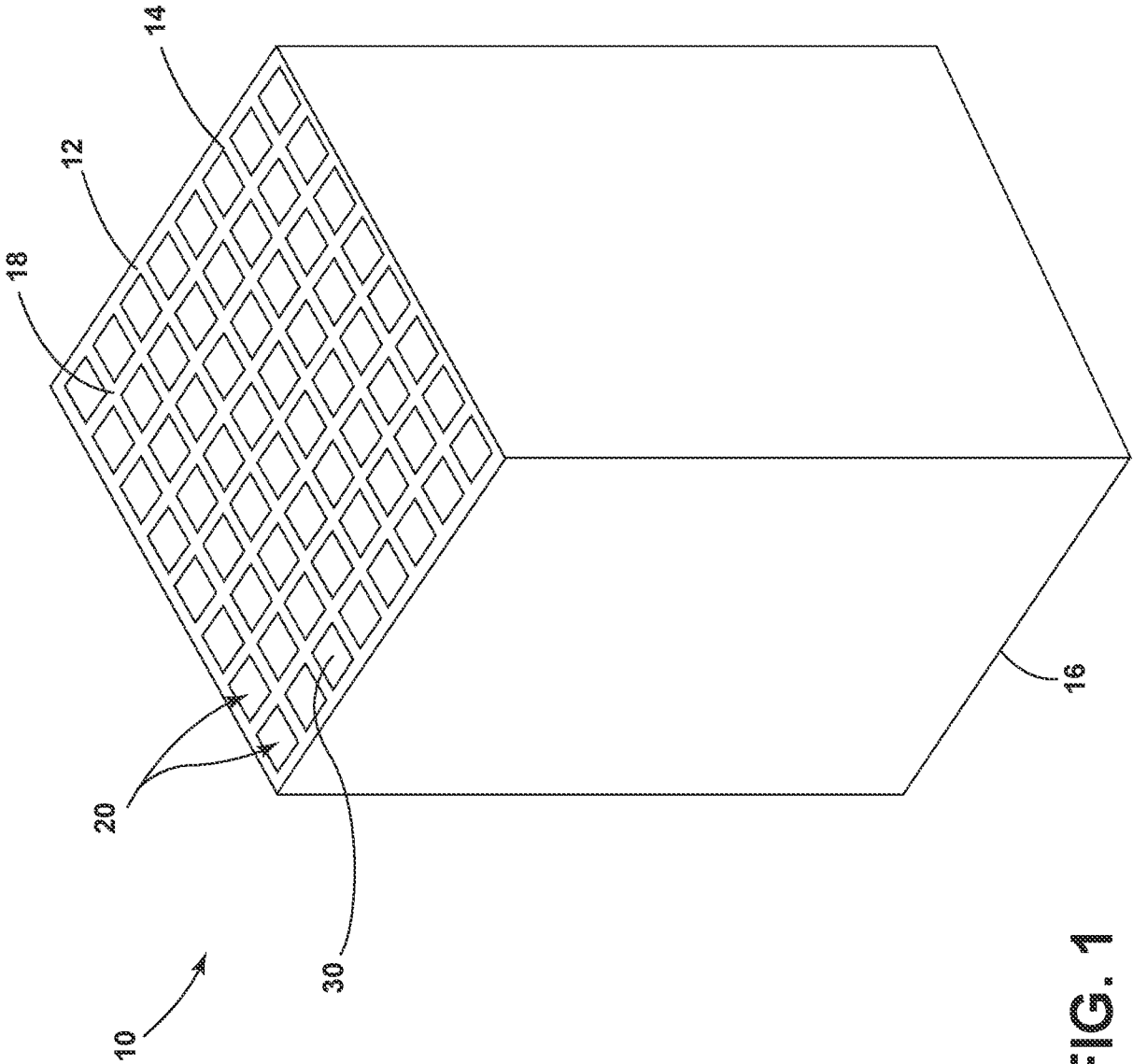
What is claimed is:

1. A carbon capture article comprising:
a ceramic honeycomb monolith comprising an inlet end, an outlet end, and intersecting walls that define cells through which a fluid can flow from the inlet end to the outlet end;
a zeolite coating at least partially covering the intersecting walls of the ceramic honeycomb monolith; and
a silicone resin coating at least partially covering the zeolite coating.
2. The carbon capture article of claim 1, wherein
the zeolite coating comprises zeolite with an average pore size that is greater than 3.3 Å.
3. The carbon capture article of any one of claims 1-2, wherein
the zeolite coating comprises a zeolite selected from the group consisting of an A-type zeolite, an X-type zeolite, a Y-type zeolite, ZSM-5 zeolite, mordenite, ferrierite, chabazite, and clinoptilolite.
4. The carbon capture article of claim 3, wherein
the zeolite coating comprises an X-type zeolite.
5. The carbon capture article of claim 4, wherein
the zeolite coating comprises Type 13-X zeolite.
6. The carbon capture article of any one of claims 1-5, wherein
the zeolite coating comprises a density within a range of from 50 g per liter of the ceramic honeycomb monolith to 300 g per liter of ceramic honeycomb monolith.
7. The carbon capture article of any one of claims 1-6, wherein
the silicone resin coating comprises a density within a range of from 3.0 g per liter of the ceramic honeycomb monolith to 7.0 g per liter of the ceramic honeycomb monolith.
8. The carbon capture article of any one of claims 1-7, wherein
the silicone resin coating comprises a siloxane resin.

9. The carbon capture article of claim 8, wherein the siloxane resin is alkoxy functionalized.
10. The carbon capture article of claim 9, wherein the siloxane resin is methoxy functionalized.
11. The carbon capture article of claim 8, wherein the silicone resin coating includes one or more silsesquioxane resins.
12. The carbon capture article of any one of claims 1-11, wherein the carbon capture article exhibits carbon capture per gram of zeolite coating at 0 °C, when a fluid comprising carbon dioxide (CO₂) molecules and water (H₂O) molecules is flowed through the carbon capture article, that is greater than a carbon capture per gram of zeolite coating that an otherwise identical carbon capture article without the silicone resin coating exhibits at 0 °C when the same fluid is flowed through the carbon capture article.
13. The carbon capture article of any one of claims 1-12, wherein the carbon capture article exhibits carbon capture of greater than 2.0 mmol of CO₂ per gram of zeolite coating at 0 °C when air comprising carbon dioxide (CO₂) molecules and water molecules (CO₂), as the fluid, is flowed through the carbon capture article.
14. A method of making a carbon capture article comprising:
 - with a ceramic honeycomb monolith comprising an inlet end, an outlet end, and intersecting walls that define cells through which a fluid can flow from the inlet end to the outlet end,
 - a silicone coating step comprising coating a silicone resin coating at least partially onto a zeolite coating that is at least partially covering the intersecting walls of the ceramic honeycomb monolith to form a carbon capture article.
15. The method of claim 14, wherein the silicone coating step further comprises curing the silicone resin coating to form the carbon capture article.

16. The method of any one of claims 14-15, wherein the silicone resin coating comprises a siloxane resin.
17. The method of claim 16, wherein the siloxane resin is alkoxy functionalized.
18. The method of claim 17, wherein the siloxane resin is methoxy functionalized.
19. The method of any one of claims 14-15, wherein the silicone resin coating comprises a silsesquioxane resin.
20. The method of any one of claims 14-19, wherein coating the silicone resin coating at least partially onto the zeolite coating comprises immersing the zeolite coating at least partially covering the ceramic honeycomb monolith into a solution of a solvent and the silicone resin.
21. The method of any one of claims 14-20 further comprising:
a zeolite coating forming step comprising (i) coating zeolite particles onto at least part of the intersecting walls of the ceramic honeycomb monolith and (ii) calcining the zeolite particles.
22. The method of claim 21, wherein coating the zeolite particles onto at least part of the intersecting walls of the ceramic honeycomb monolith comprises immersing at least a portion of the ceramic honeycomb monolith into a solution of water and the zeolite particles.

23. A method of capturing carbon dioxide from air comprising:
a flowing step comprising causing a fluid comprising molecules of carbon dioxide (CO₂) to flow through a carbon capture article comprising:
a ceramic honeycomb monolith comprising an inlet end, an outlet end, and intersecting walls that define cells through which a fluid can flow from the inlet end to the outlet end;
a zeolite coating at least partially covering the intersecting walls of the ceramic honeycomb monolith; and
a silicone resin coating at least partially disposed on the zeolite coating,
wherein at least a portion of the molecules of carbon dioxide (CO₂) are captured by the carbon capture article.
24. The method of claim 23, wherein
the fluid further comprises molecules of water (H₂O).
25. The method of any one of claims 23-24, wherein
the fluid is air.
26. The method of any one of claims 23-25 further comprising:
a regenerating step comprising applying thermal energy to the carbon capture article with the molecules of carbon dioxide (CO₂) captured therein until at least a portion of molecules of carbon dioxide (CO₂) are released from the carbon capture article.



10

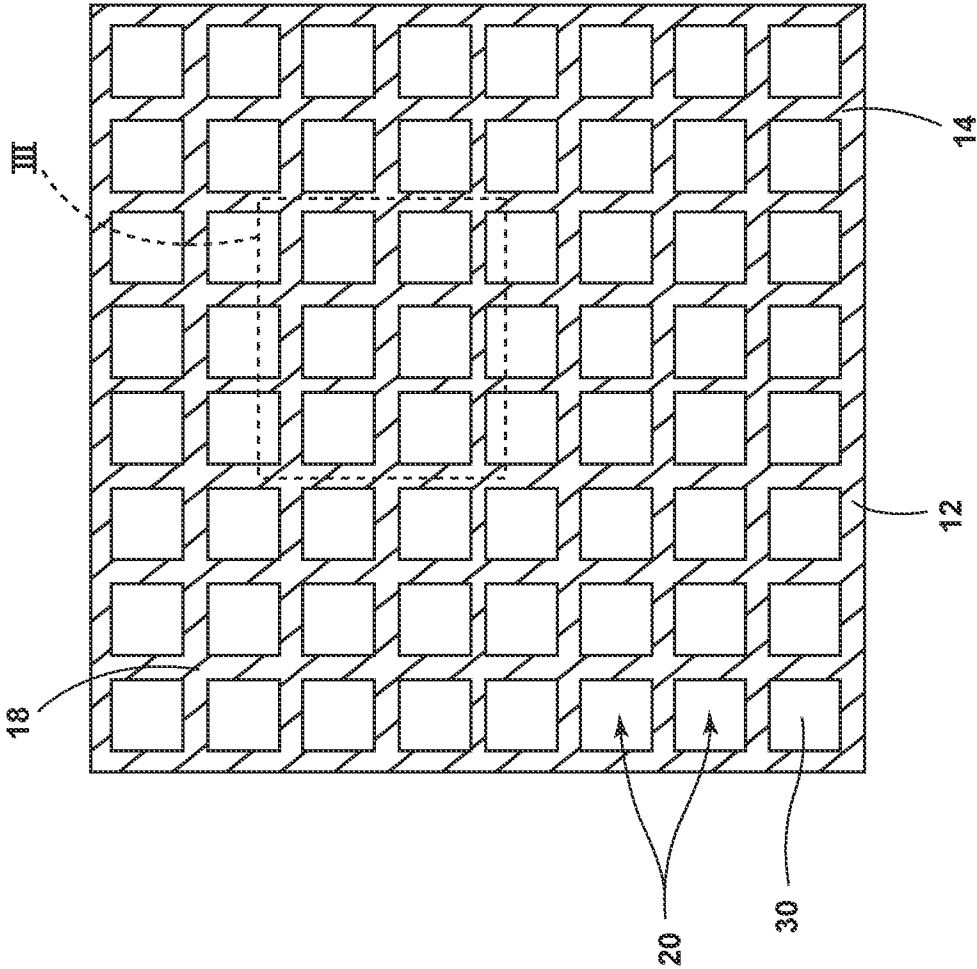


FIG. 2

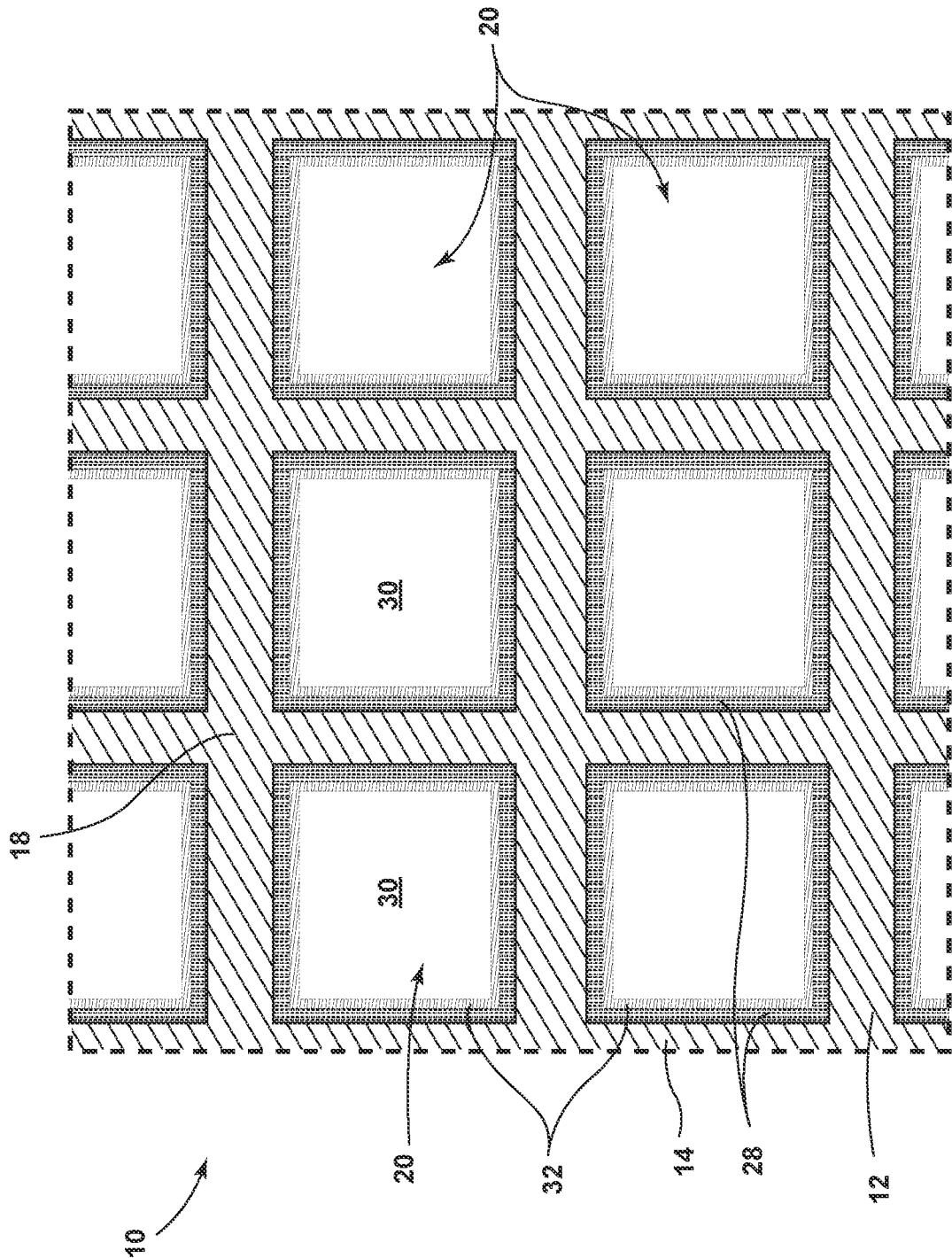


FIG. 3

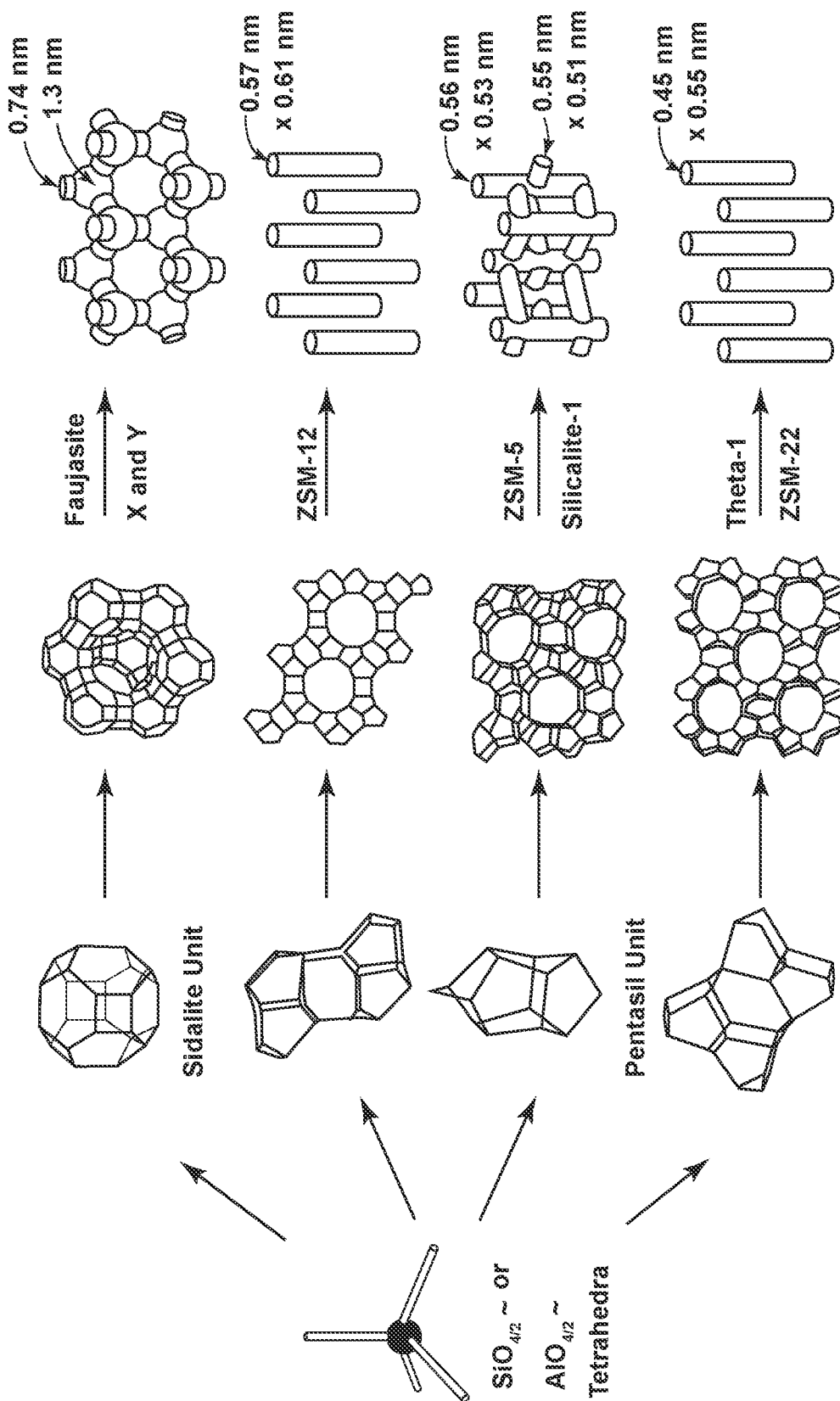


FIG. 4

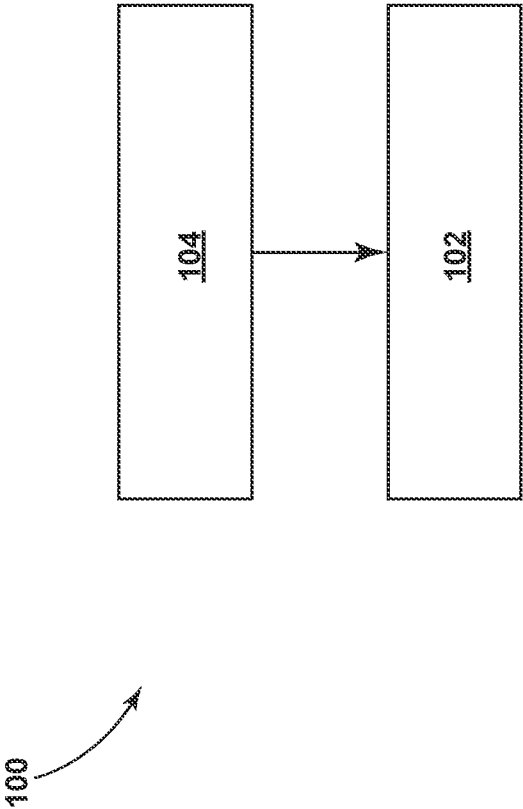


FIG. 5

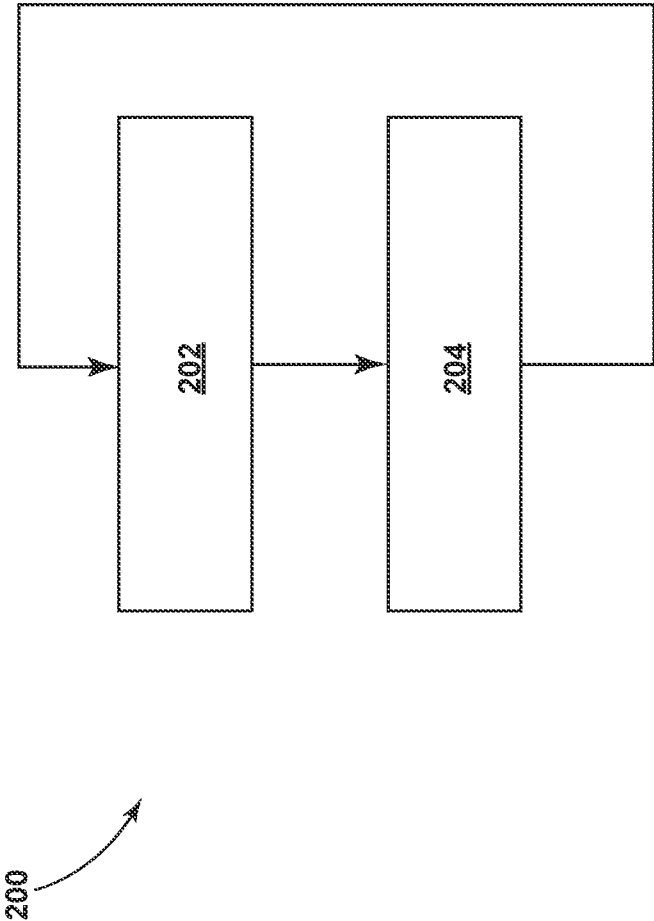


FIG. 6

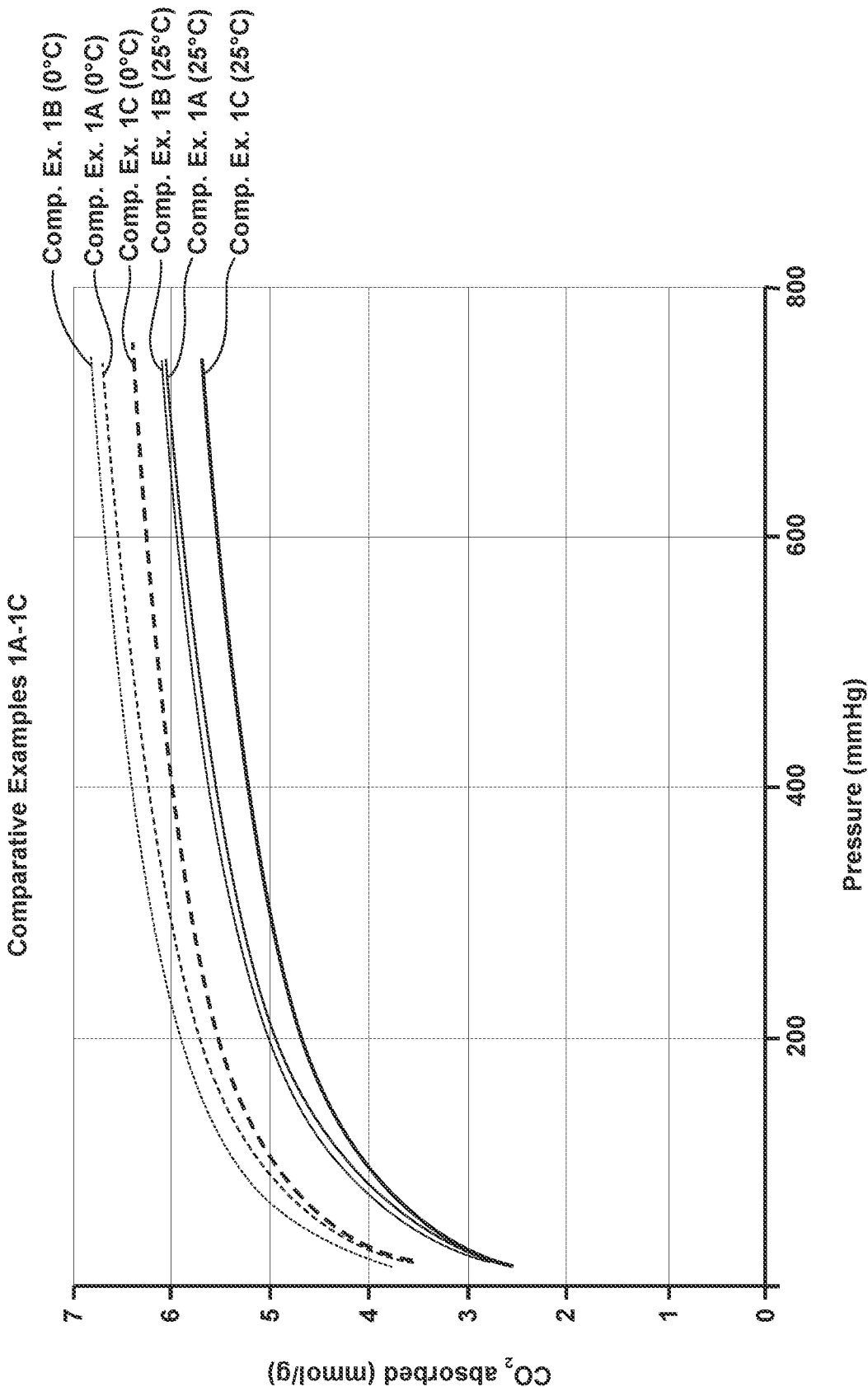


FIG. 7A

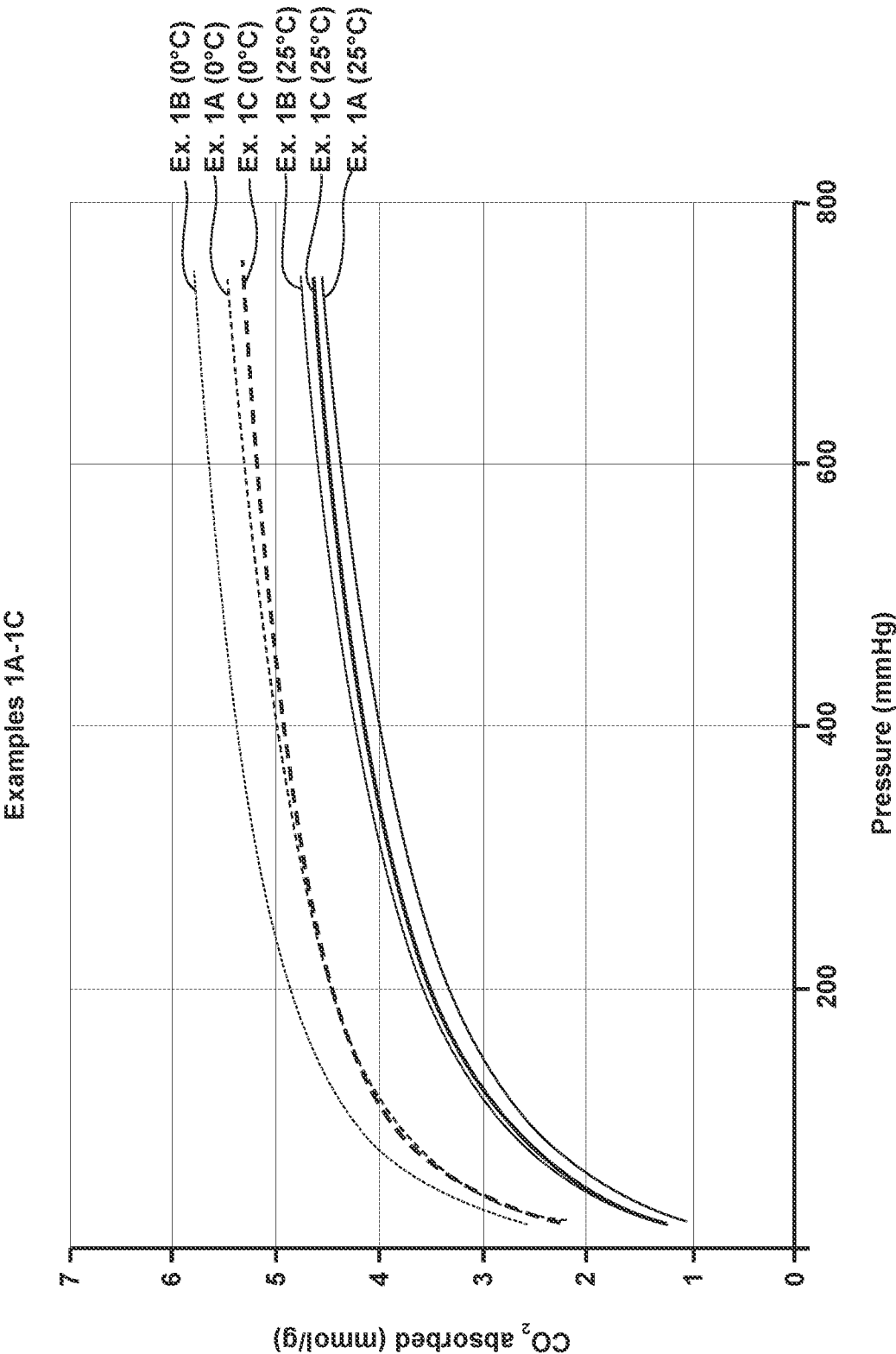


FIG. 7B

Comparative Examples 1A-1C

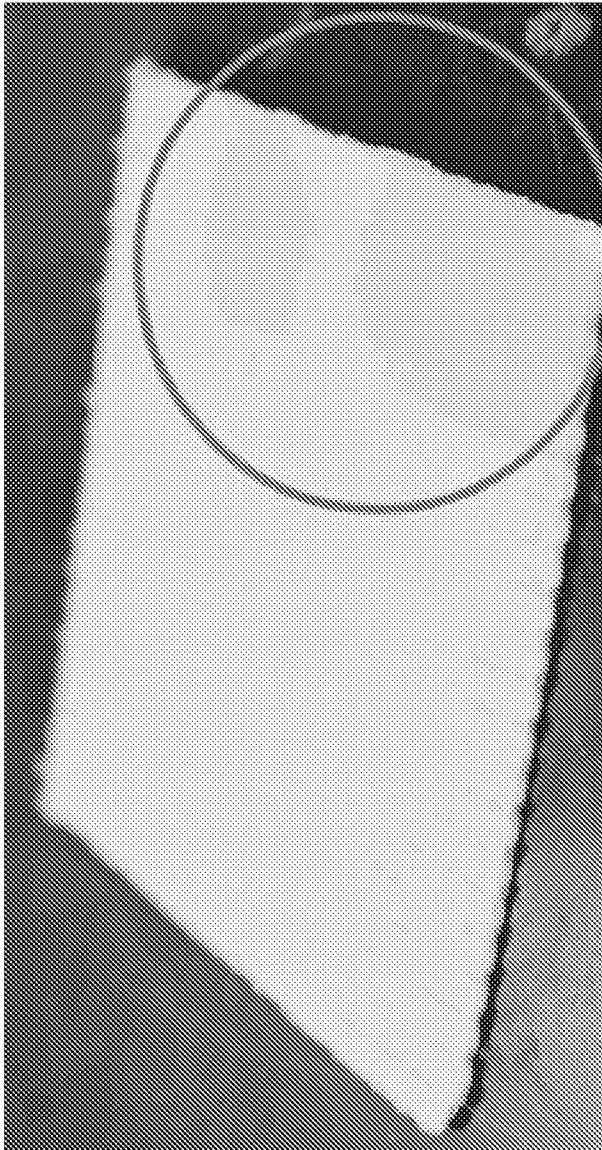


FIG. 8A

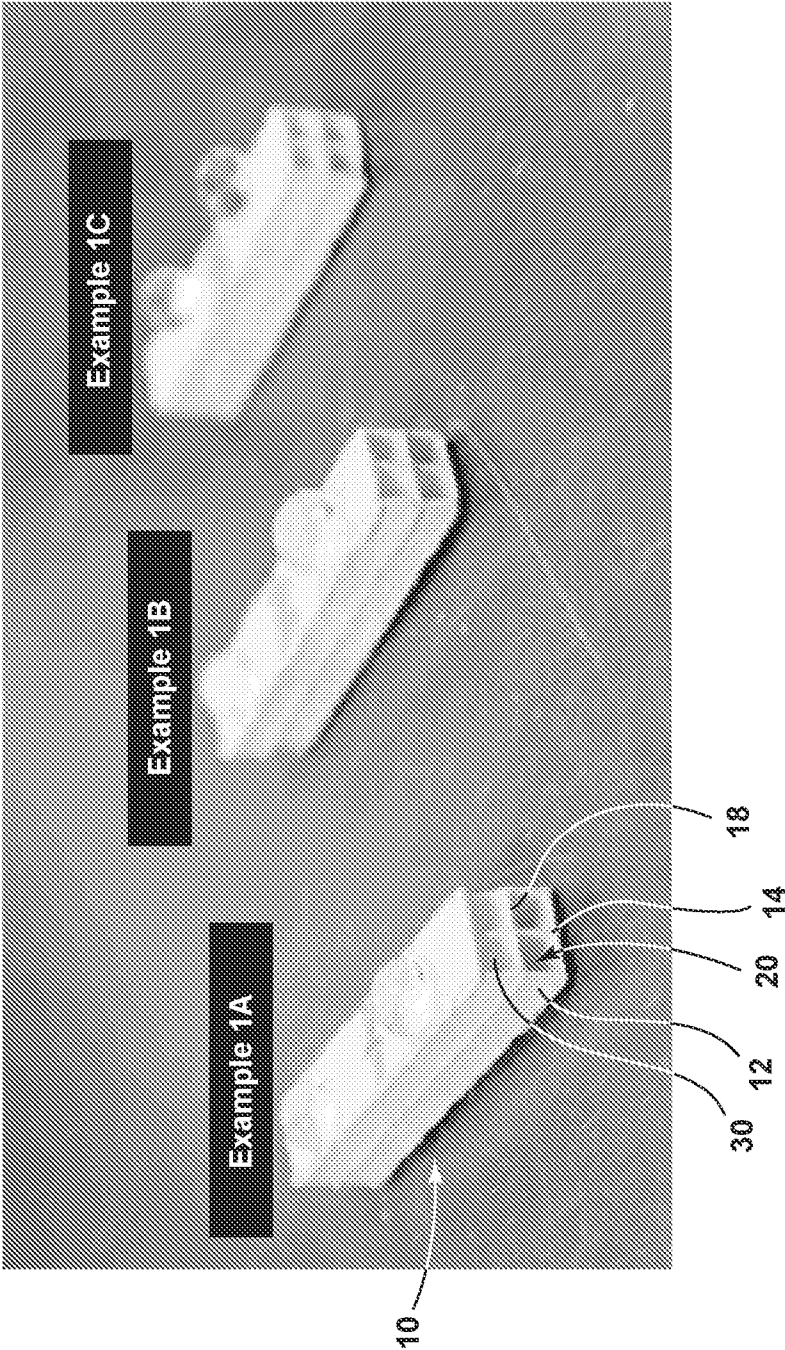


FIG. 8B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/054835

A. CLASSIFICATION OF SUBJECT MATTER**B01D 53/02(2006.01)i; B01J 20/16(2006.01)i; B01J 20/32(2006.01)i; B01J 20/28(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D 53/02(2006.01); B01D 67/00(2006.01); B01D 69/14(2006.01); B01J 21/00(2006.01); B01J 35/04(2006.01);
C04B 38/00(2006.01); F01N 3/022(2006.01); F01N 3/28(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: carbon capture, zeolite, silicon, siloxane, coating, layer, honeycomb

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014-0271394 A1 (CORNING INCORPORATED) 18 September 2014 (2014-09-18) claims 3, 9; paragraphs [0008]-[0039]; figures 3, 4	1-5,14,15,23-25
Y		16-19
Y	WO 2010-138489 A1 (CORNING INCORPORATED et al.) 02 December 2010 (2010-12-02) claims 1, 12; paragraphs [0020]-[0022]	16-19
A	EP 3189020 B1 (CORNING INCORPORATED) 23 December 2020 (2020-12-23) claims 1-14	1-5,14-19,23-25
A	US 2004-0131772 A1 (YAMADA, T. et al.) 08 July 2004 (2004-07-08) claims 1-18	1-5,14-19,23-25
A	EP 1541233 A1 (NGK INSULATORS, LTD.) 15 June 2005 (2005-06-15) claims 1-6	1-5,14-19,23-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

13 February 2025

Date of mailing of the international search report

13 February 2025

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/054835

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: **9-11, 22**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Claims 9-11, 22 are regarded to be unclear because they refer to multiple dependent claims which do not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: **6-8, 12, 13, 20, 21, 26**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2024/054835

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2014-0271394	A1	18 September 2014	CN	104540584	A	22 April 2015
				CN	104540584	B	08 June 2016
				EP	2834000	A1	11 February 2015
				JP	2015-514011	A	18 May 2015
				US	9062586	B2	23 June 2015
				WO	2013-152071	A1	10 October 2013
WO	2010-138489	A1	02 December 2010	EP	2435167	A1	04 April 2012
				US	2010-0300289	A1	02 December 2010
				US	8052776	B2	08 November 2011
EP	3189020	B1	23 December 2020	CN	107073377	A	18 August 2017
				CN	107073377	B	26 February 2021
				EP	3189020	A1	12 July 2017
				JP	2017-527437	A	21 September 2017
				JP	6789927	B2	25 November 2020
				US	10898856	B2	26 January 2021
				US	2017-0282124	A1	05 October 2017
				WO	2016-036780	A1	10 March 2016
US	2004-0131772	A1	08 July 2004	EP	1418032	A2	12 May 2004
				EP	1418032	A3	14 September 2005
				EP	1418032	B1	13 February 2008
				JP	2004-168030	A	17 June 2004
				JP	4394408	B2	06 January 2010
				US	7033452	B2	25 April 2006
EP	1541233	A1	15 June 2005	EP	1541233	B1	10 September 2008
				JP	2005-169249	A	30 June 2005
				JP	4767491	B2	07 September 2011
				US	2005-0129907	A1	16 June 2005
				US	7393509	B2	01 July 2008