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(54) **METHODS FOR ASSOCIATING OR DISSOCIATING GUEST MATERIALS WITH A METAL ORGANIC FRAMEWORK, SYSTEMS FOR ASSOCIATING OR DISSOCIATING GUEST MATERIALS WITHIN A SERIES OF METAL ORGANIC FRAMEWORKS, AND GAS SEPARATION ASSEMBLIES**

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(51) **Int. Cl.**
B01D 53/04 (2006.01)
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CPC ***C25B 15/00*** (2013.01); ***B01D 53/02*** (2013.01); ***B01D 53/04*** (2013.01); ***B01D 53/1475*** (2013.01); ***B01D 53/32*** (2013.01); ***B01D 53/326*** (2013.01); ***F23J 15/02*** (2013.01);
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(58) **Field of Classification Search**
USPC 96/121, 143; 95/139, 148; 502/526; 423/230; 204/267; 205/763
See application file for complete search history.

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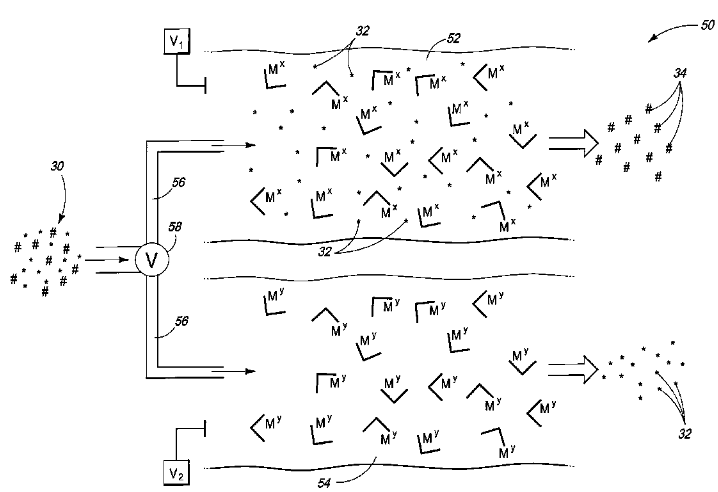
(57) **ABSTRACT**

Methods for releasing associated guest materials from a metal organic framework are provided. Methods for associating guest materials with a metal organic framework are also provided. Methods are provided for selectively associating or dissociating guest materials with a metal organic framework. Systems for associating or dissociating guest materials within a series of metal organic frameworks are provided. Gas separation assemblies are provided.

16 Claims, 9 Drawing Sheets



(51) **Int. Cl.**
C25B 15/00 (2006.01)
B01D 53/02 (2006.01)
B01D 53/14 (2006.01)
B01D 53/32 (2006.01)
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(52) **U.S. Cl.**
CPC *B01D2253/204* (2013.01); *B01D 2257/504* (2013.01); *B01D 2259/40083* (2013.01); *F23J 2215/50* (2013.01); *F23J 2219/60* (2013.01); *Y02C 10/06* (2013.01); *Y02C 10/08* (2013.01)

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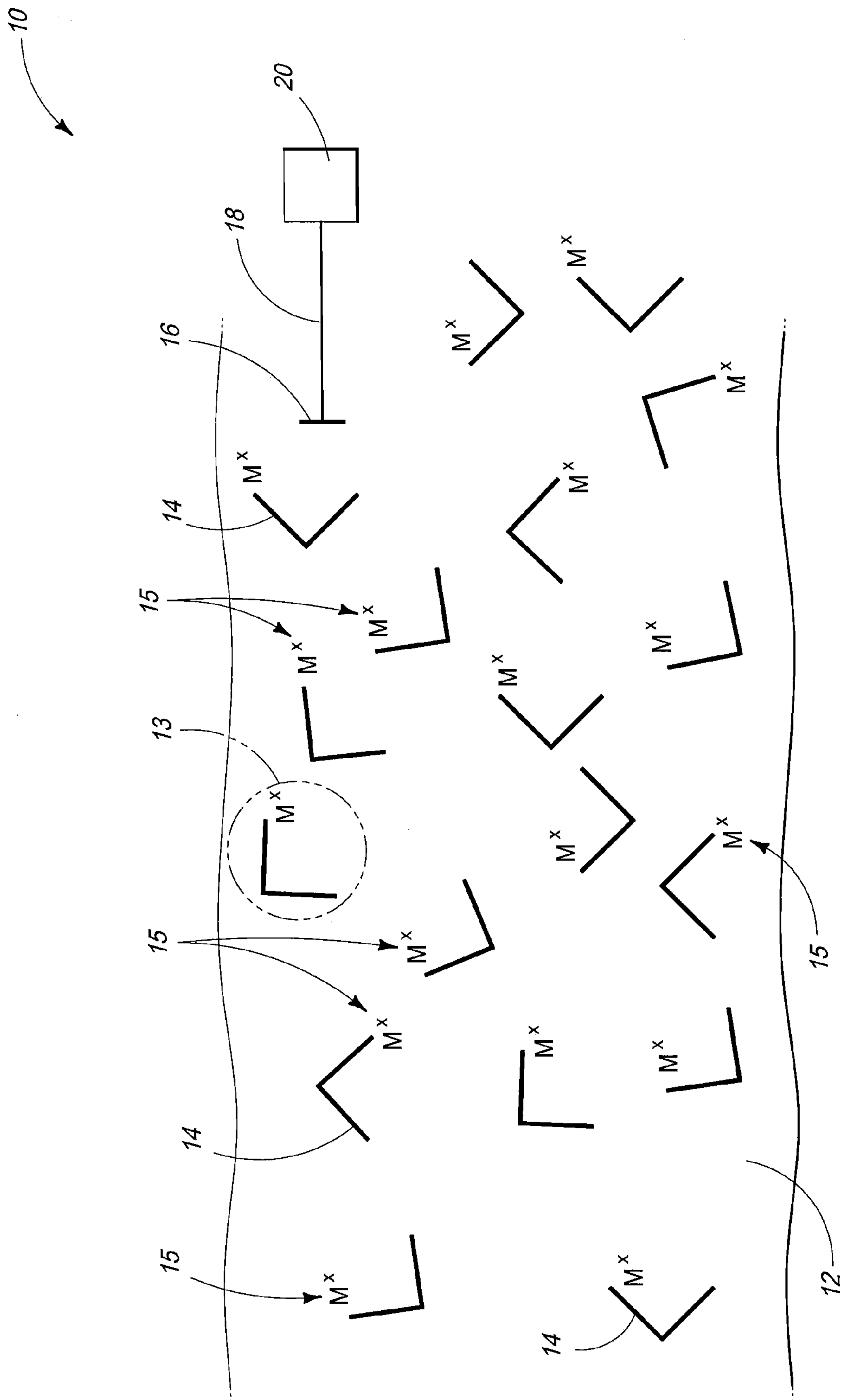


FIG. 1

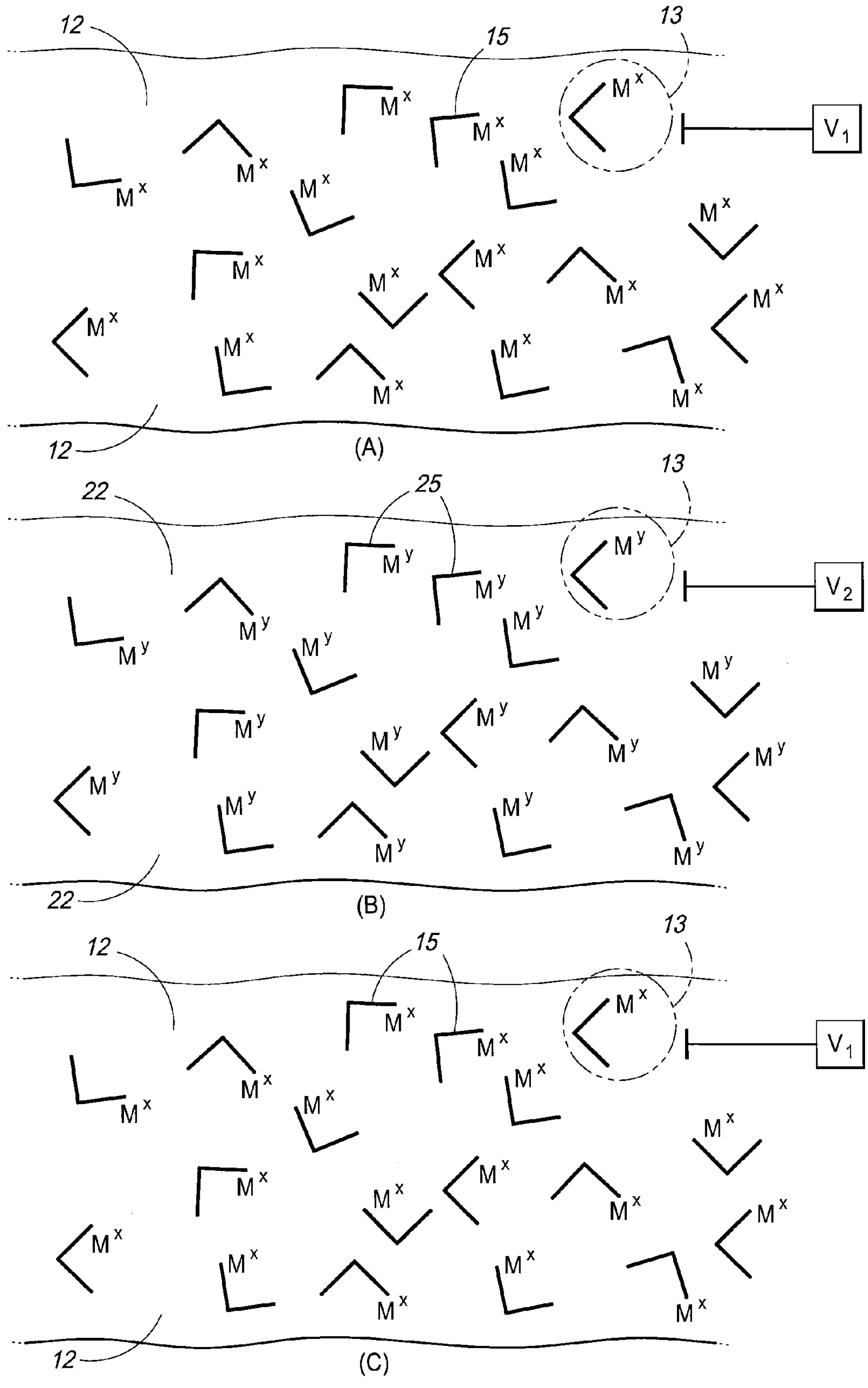
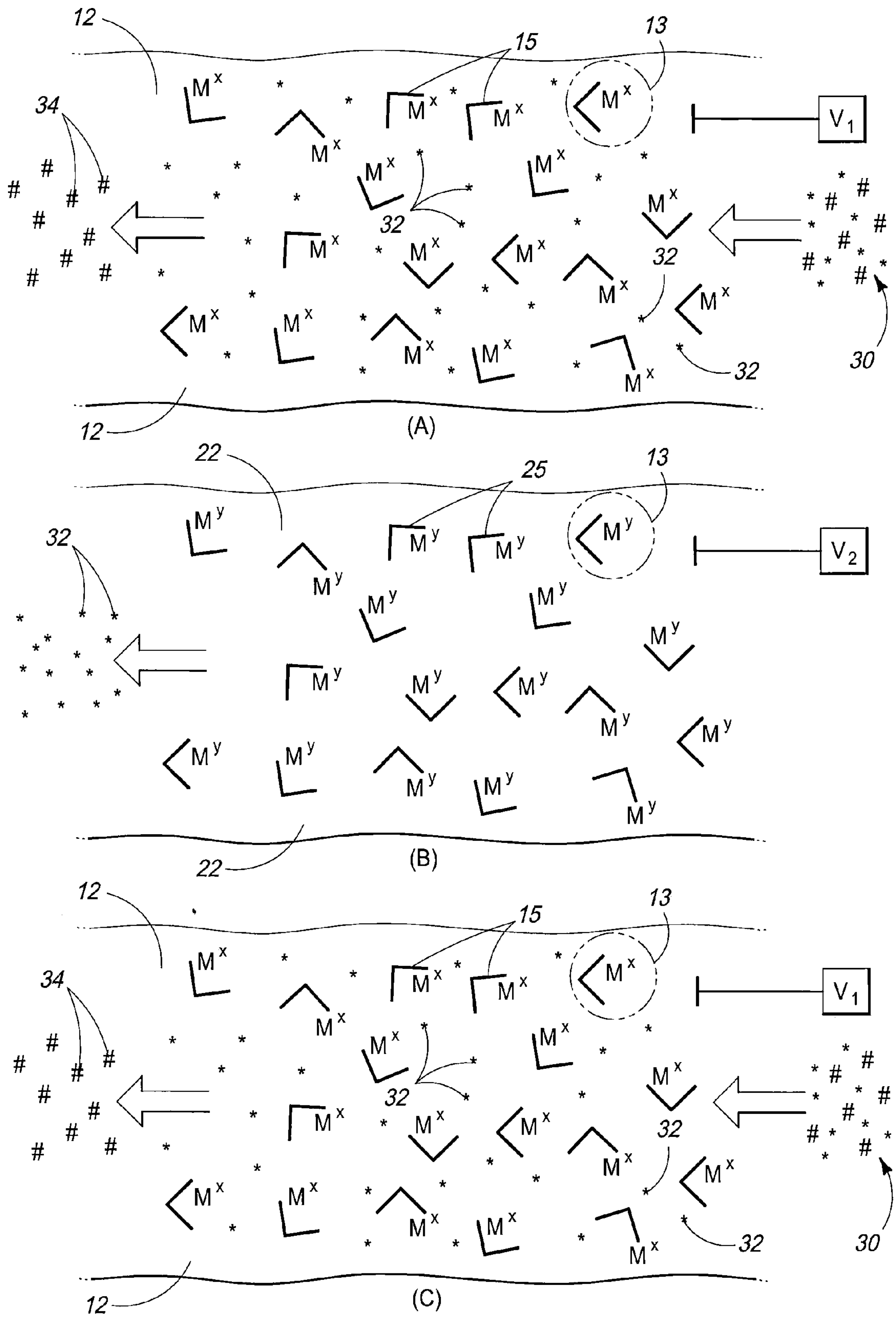


FIG. 2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(C)

FIG. 3

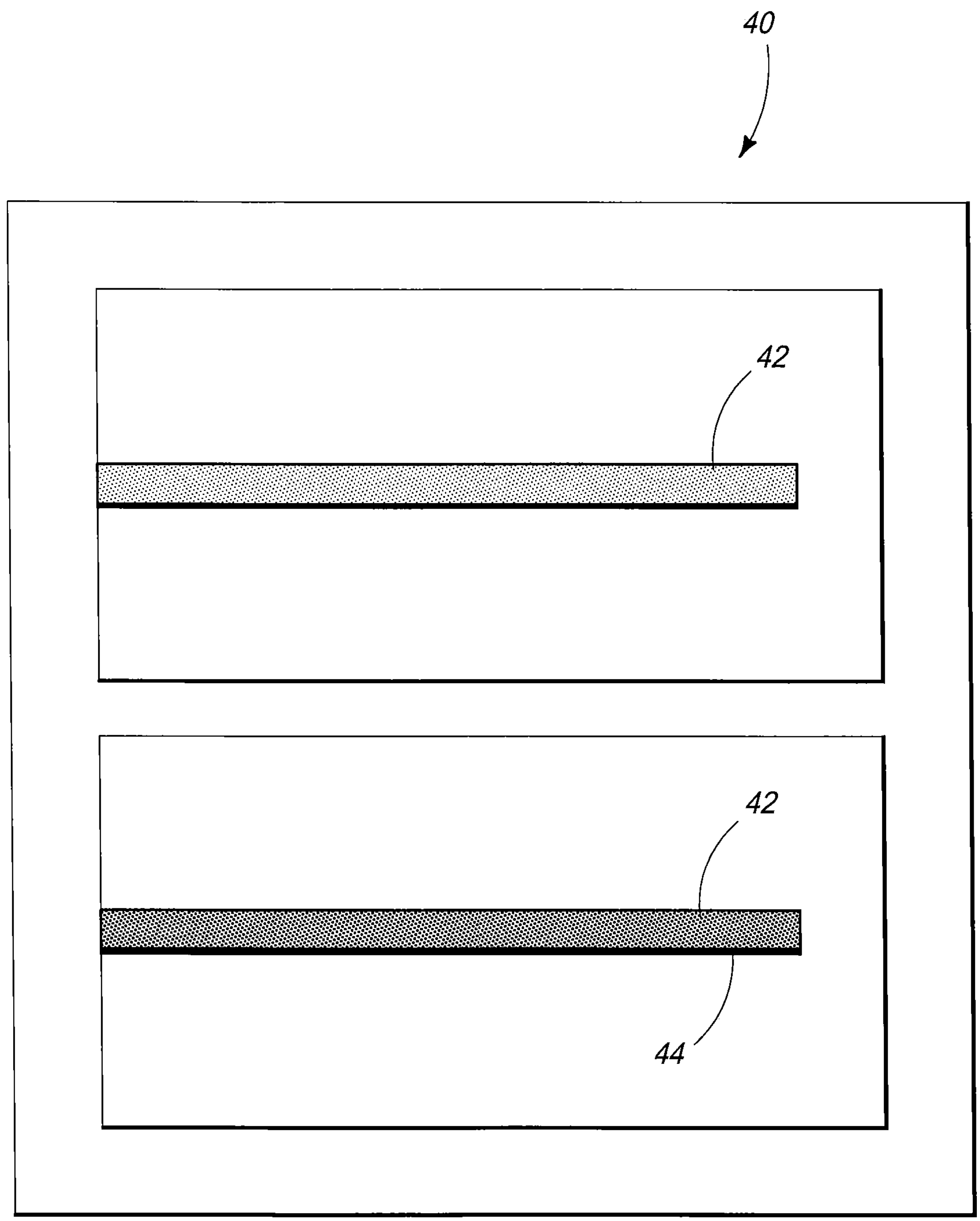

FIG. 4

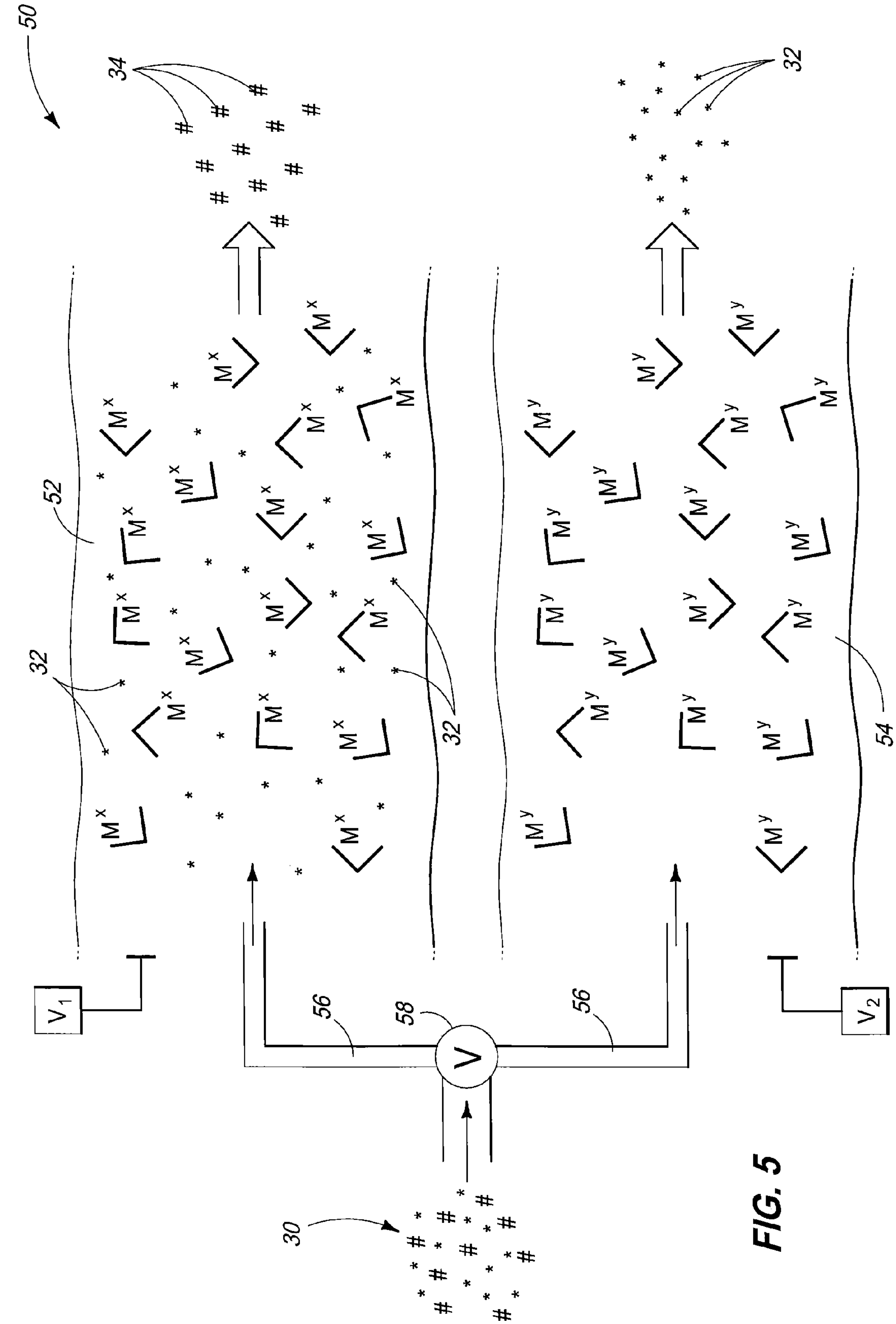

FIG. 5

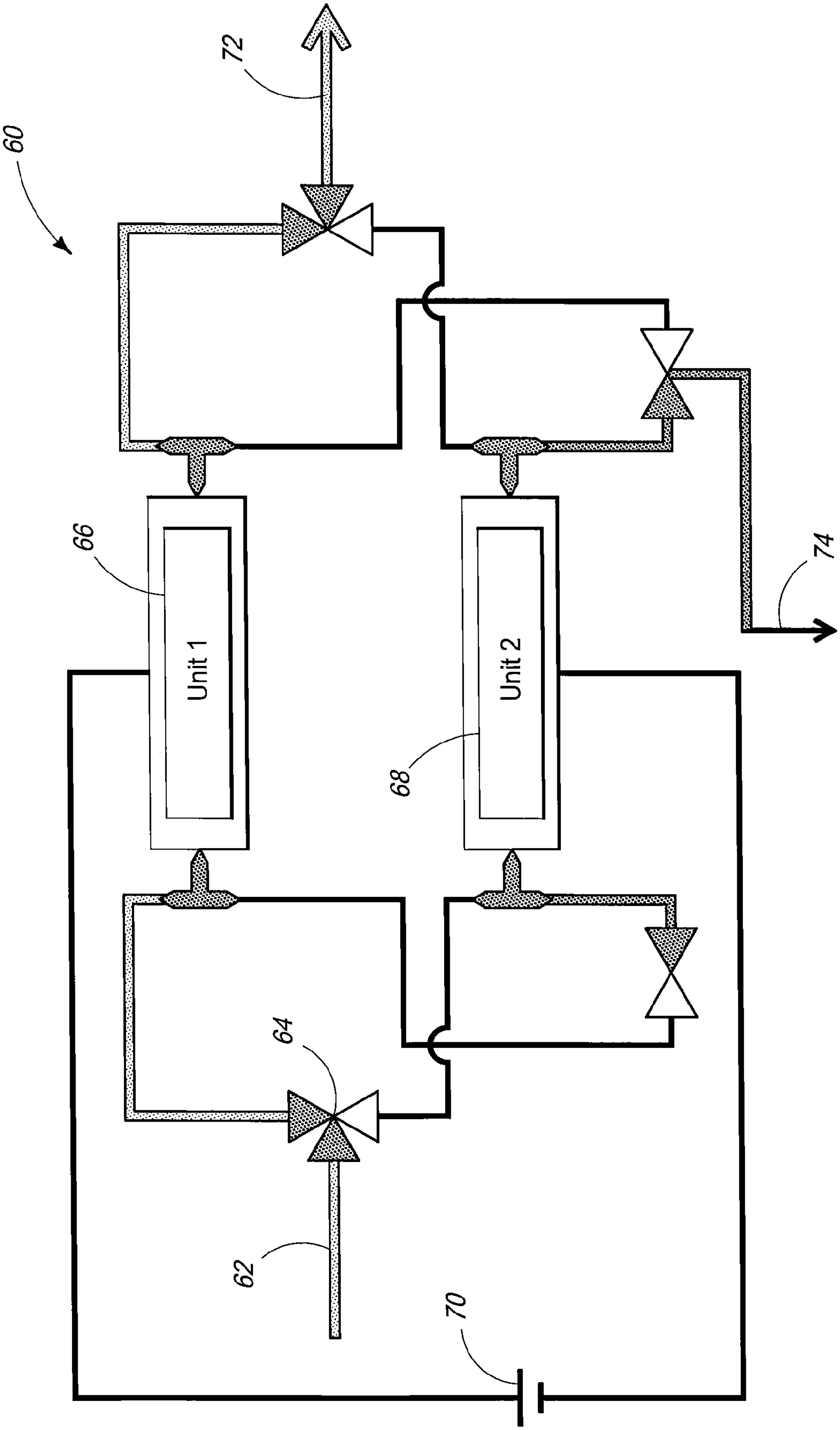

FIG. 6

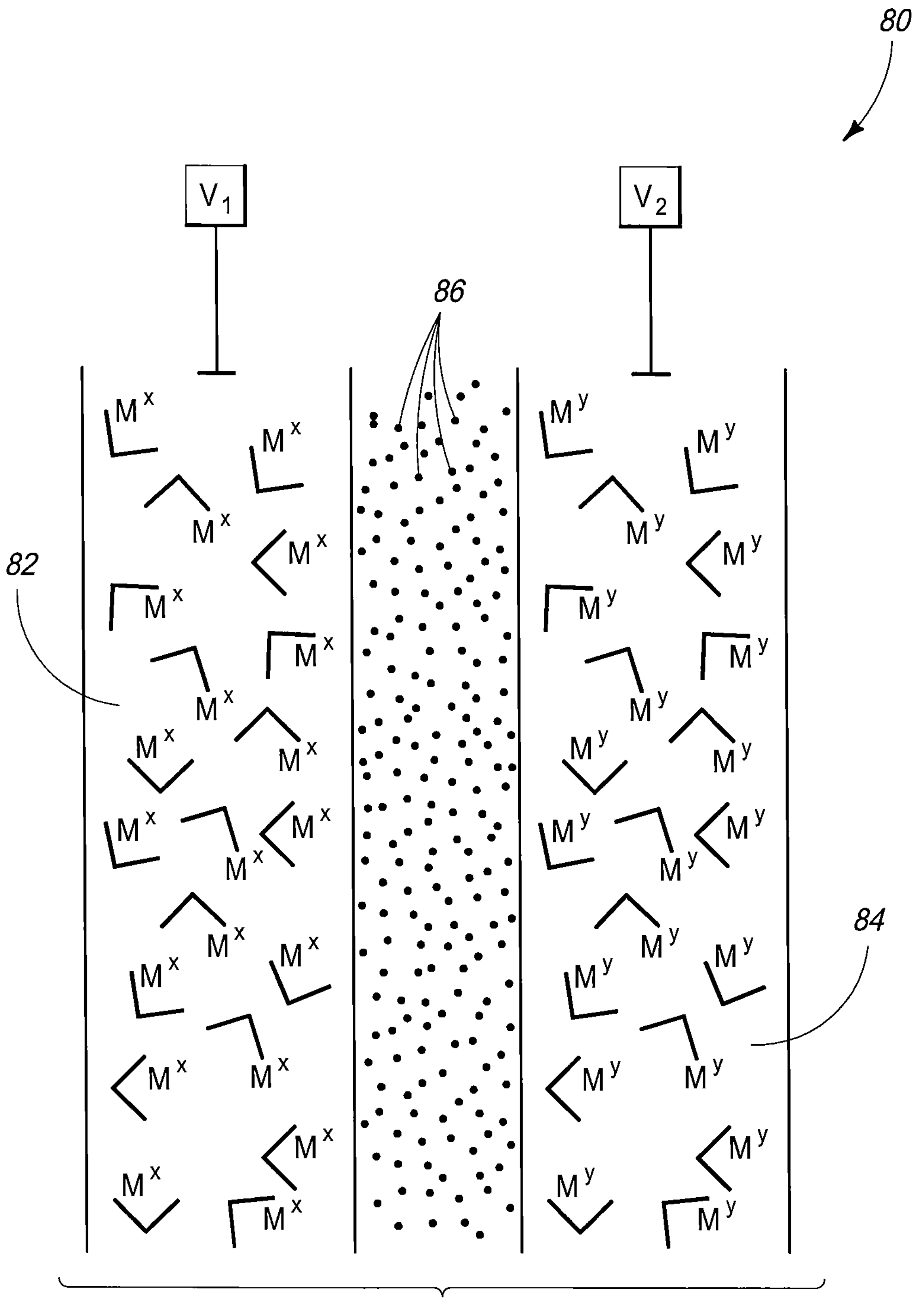

FIG. 7

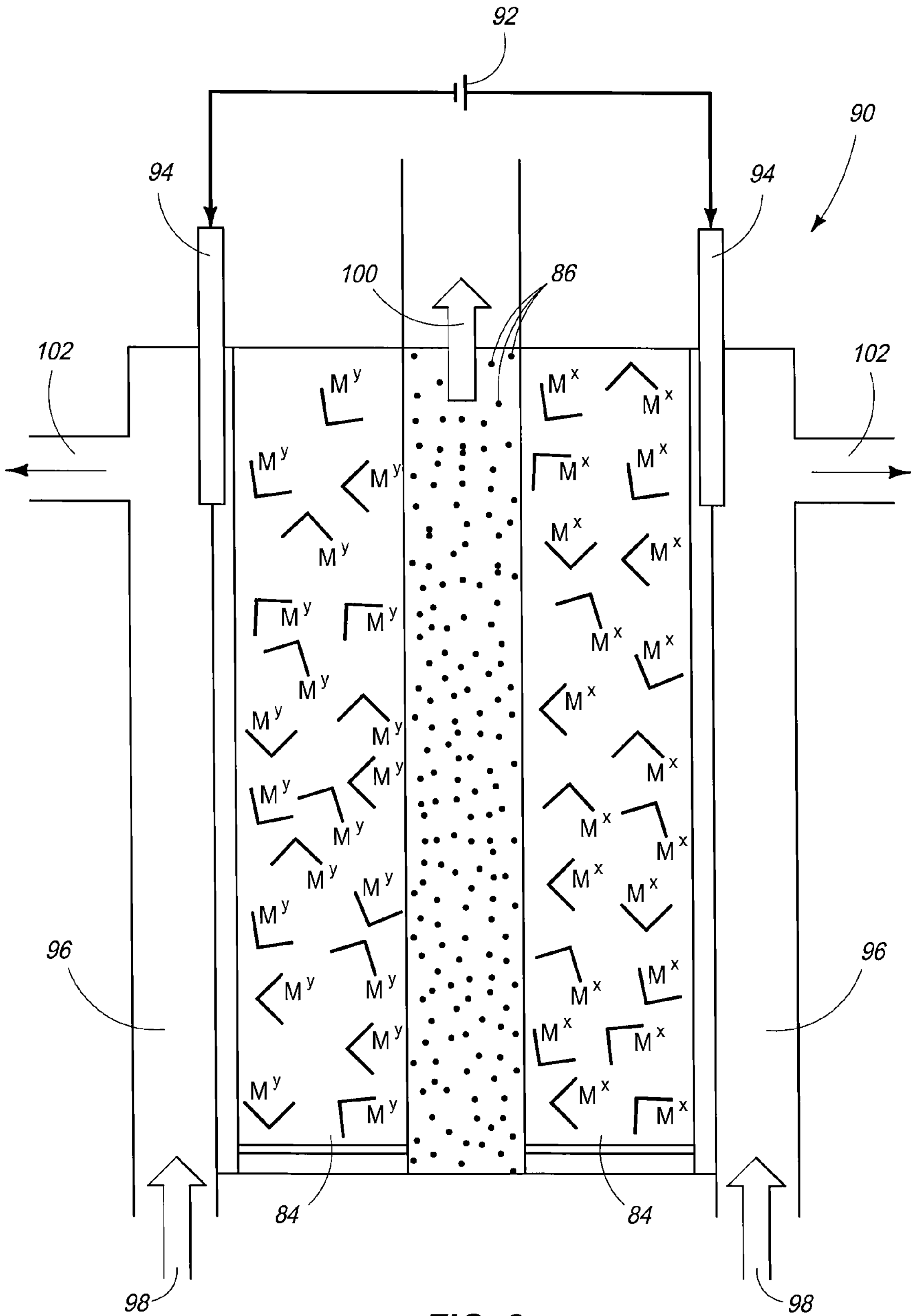

FIG. 8

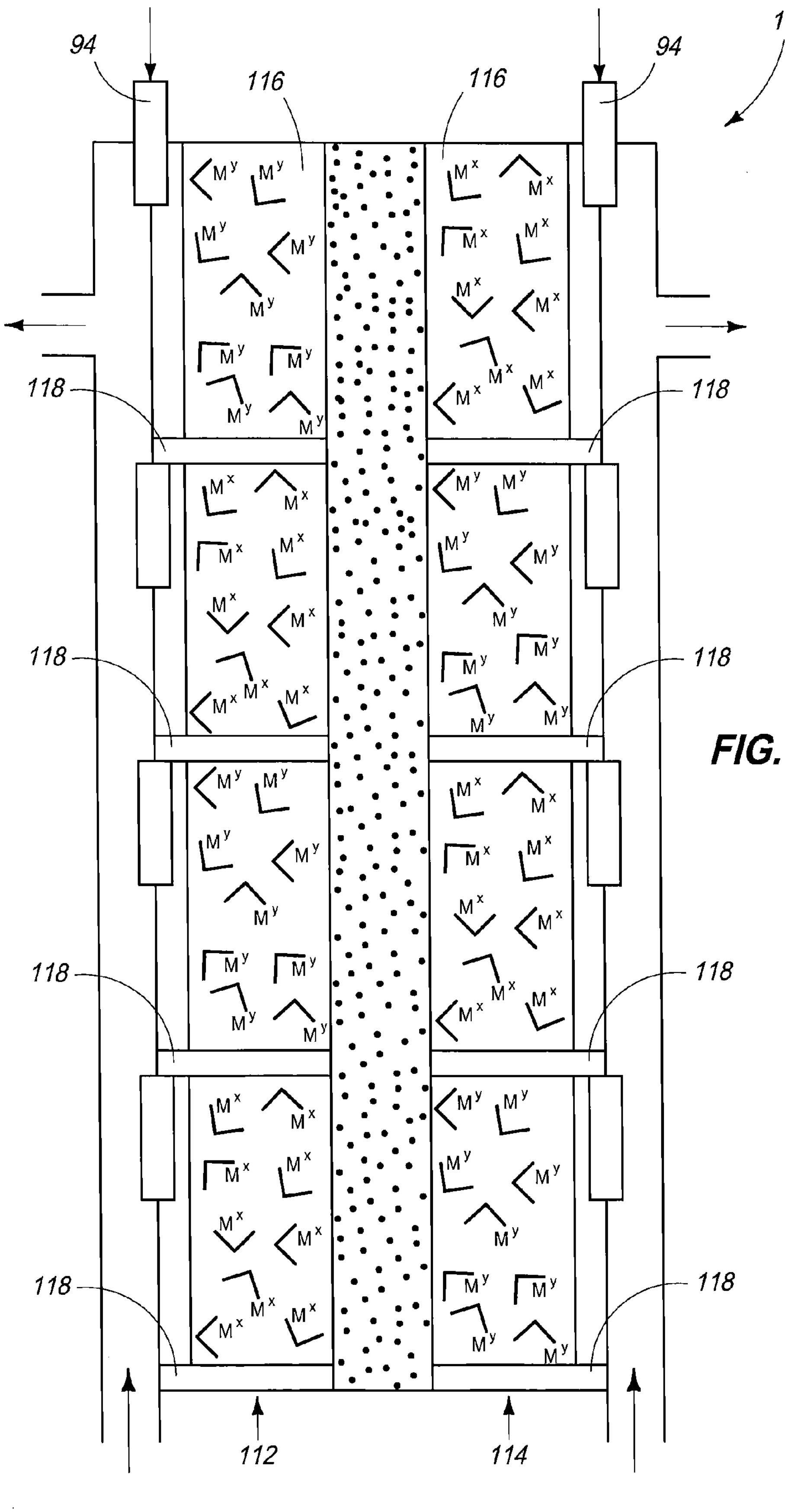

FIG. 9

METHODS FOR ASSOCIATING OR DISSOCIATING GUEST MATERIALS WITH A METAL ORGANIC FRAMEWORK, SYSTEMS FOR ASSOCIATING OR DISSOCIATING GUEST MATERIALS WITHIN A SERIES OF METAL ORGANIC FRAMEWORKS, AND GAS SEPARATION ASSEMBLIES

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation of U.S. patent application Ser. No. 13/078,548 filed Apr. 1, 2011, entitled "Methods for Associating or Dissociating Guest Materials with a Metal Organic Framework, Systems for Associating or Dissociating Guest Materials Within a Series of Metal Organic Frameworks, and Gas Separation Assemblies", now issued U.S. Pat. No. 8,425,662, which claims priority to U.S. Provisional Patent Application Ser. No. 61/320,445 which was filed on Apr. 2, 2010, the entirety of which is incorporated by reference herein.

TECHNICAL FIELD

The present disclosure relates to the use of metal organic frameworks.

BACKGROUND

Recently, metal organic frameworks have been proposed for use in various capacities. These capacities include but are not limited to the separation of molecules or materials from mixtures that include the molecules or materials. As an example, in various applications, metal organic frameworks have been proposed for use as materials that can be used to separate carbon dioxide from methane, for example.

In accordance with other applications, metal organic frameworks have also been utilized to retain certain molecules in higher density than they would be retained at when super pressurized. As an example, metal organic frameworks have been proposed for use as hydrogen storage tanks.

In these applications, in the past, the metal organic frameworks have been configured to selectively adsorb or desorb or associate or dissociate certain materials. As an example, the temperature and/or pressure of the metal organic framework can be manipulated, as well as the chemical and/or geometric structure of the metal organic framework, to facilitate either the association or adsorption, or the dissociation or desorption of the specific materials.

The present disclosure provides methods for using metal organic frameworks as well as systems that include metal organic frameworks and assemblies that include metal organic frameworks.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the disclosure are described below with reference to the following accompanying drawings.

FIG. **1** is a configuration of a metal organic framework according to an embodiment of the disclosure.

FIG. **2** represents configurations of metal organic frameworks according to an embodiment of the disclosure.

FIG. **3** represents configurations of metal organic framework and mixtures that include guest materials depicted according to an embodiment of the disclosure.

FIG. **4** is an example metal organic framework according to an embodiment of the disclosure.

FIG. **5** represents a configuration of metal organic framework according to an embodiment of the disclosure.

FIG. **6** represents a system including metal organic frameworks according to an embodiment of the disclosure.

FIG. **7** represents a system including metal organic framework according to an embodiment of the disclosure.

FIG. **8** represents a system including metal organic framework according to an embodiment of the disclosure.

FIG. **9** represents electrolyte structures according to an embodiment of the disclosure.

DESCRIPTION

This disclosure is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

Methods for releasing associated guest materials from a metal organic framework are provided with example methods including altering the oxidation state of at least a portion of the metal of the metal organic framework to dissociate at least a portion of the guest materials from the framework. Example methods for associating guest materials with a metal organic framework are also provided with example methods including altering the oxidation state of at least a portion of the metal of the metal organic framework to associate at least a portion of the guest materials with the framework.

Methods are provided for selectively associating or dissociating guest materials with a metal organic framework. Example methods can include altering the oxidation state of at least a portion of the metal of the metal organic framework to associate or dissociate at least a portion of the guest materials with the framework.

Systems for associating or dissociating guest materials within a series of metal organic frameworks are provided. Example systems can include at least two individual metal organic frameworks, with one of the individual metal organic frameworks configured to dissociate guest materials, and the other configured to associate guest materials. One framework can include at least some metals of one oxidation state and the other framework can include the same metals of another oxidation state.

Gas separation assemblies are provided. Example assemblies can include a plurality of individual cells housing metal organic framework, with the plurality comprising at least one series of cells and another series of cells. Each series can include at least two electrically isolated individual cells. The assemblies can also include a channel between the one series of cells and the other series of cells. Power sources and a controller coupled to both the assembly and the power source can also be included in certain embodiments.

The methods, systems, and assemblies of the present disclosure will be described with reference to FIGS. **1-9**. Referring first to FIG. **1**, a metal organic framework configuration **10** is shown that includes metal organic framework **12** conductively coupled via contact **16** and conductive conduit **18** to power source **20**. Framework **12** can include metals coupled to organic components. Framework **12** may be configured to define open sites designed to receive guest materials. The open sites may be defined by more than one metal organic complex, for example. At least a portion of the metals of the metal organic framework should be electrically responsive. More than one metal may be included in metal organic complex **13** having organic portion **14** and metal portion **15**.

Metal portion **15** of complex **13** can include metals and, according to example implementations, the oxidation state of at least some of the metals will change upon application of differing voltages to the framework. The metals can include transition state metals. In accordance with example implementations, upon changing the oxidation state of some of the metals, some of the previously open sites will become closed or some of the previously closed sites will become open to receive guest materials. Example metals can include Ti, Zr, Hf, Rf, V, Nb, Ta, Db, Cr, Mo, W, Sg, Mn, Tc, Re, Bh, Fe, Ru, Os, Hs, Co, Rh, Os, Hs, Co, Rh, Ir, Mt, Ni, pd, Pt, Ds, Cu, Ag, Au, Zn, and Rg. At least a portion of framework **12** can include one or more of these metals in a charged state.

For example metal portion **15** can include mixed valence metals (M^{2+}/M^{3+}) complexed with the organic portion; M^{2+}=Fe, Cd, Co, Cu, Mn, Ni, and Zn; and M^{3+}=Fe or Co, for example. According to specific implementations, the metal portion can include (Fe^{2+}/Fe^{3+}), and this metal may be complexed as $Fe_3^{2+}[Fe^{3+}(CN)_6]_2$ or $Fe_3^{3+}[Fe^{3+}(CN)_6]$, with the former being a different oxidation state than the latter under differing electrical conditions. These mixed valence metal complexes may include tetrakis[4-(pyridyl)oxamethyl]methane as an organic component, for example. Prussian blue having the metal complex $M^{3+}[Co(CN)_6]_2$ (M=Co, Zn), may be utilized as well. The guest material can contain carbon dioxide, for example. Mixed valence forms of the framework may show a greater affinity for carbon dioxide than univalent forms.

In accordance with example implementations, the organic portion **14** may be referred to as a ligand that coordinates the metal of the framework. The ligand may be multidentate, for example. The organic portion can be a conductive organic portion. Example organic portions can include but are not limited to straight chain hydrocarbon and/or aromatic rings. These metals may be complexed with organic portions such as 2,5-dihydroxy terephthalic acid (DHTA) which can form both the tetraainionic form 2,5-dioxido-1,4-benzenedicarboxylate (COBDC), wherein both the zyloxide and carboxylate moieties may act as ligands to the metal and the dianionic form 2,5-dihydroxy-1,4-benzene-dicarboxylate (DHBDC), where only the carboxylate moieties may act as ligands to the metal and the alcohol remains protonated. The metal organic complex can include metallocenes or calixarenes for example. In accordance with example implementations, the ligand of the metal organic complex can be substantially conductive. Example organic portions of the metal organic complex can include but are not limited to tetrakis[4-(pyridyl) oxamethyl]methane or p-tert-butylcalix[4]arene.

Contact **16** can be in electrical communication with at least a portion of the metal of the metal organic framework. In accordance with example implementations, contact **16** may be in electrical communication with the organic portion of the metal organic framework and the organic portion can provide electrical communication to at least a portion of the metal of the metal organic framework. Electrical input to contact **16** from power source **20** may be controlled with a controller (not shown). The controller may be programmable and/or may be coupled to a computer operating system (not shown). In accordance with example implementations, the controller may be manipulated to provide a desired voltage to framework **12**, the voltage corresponding to the association/dissociation of guest materials. Utilizing the power source and the controller voltammetry as well as cyclic voltammetry can be applied to framework **12**.

Framework **12** of FIG. **1** is depicted without a substrate. In accordance with example implementations, framework **12** may be associated with a substrate. In specific implementations, framework **12** may be bond to a substrate and/or supported by or within a substrate. In accordance with example configurations, framework **12** may be within a housing, such as a conduit, including tubular conduits. In accordance with other configurations, framework **12** may be supported by a substrate with the substrate being a substantially open support such as a platform, or in other configurations, framework **12** may be supported by the exterior of a conduit, such as tubular conduit configured to contain framework and/or other materials therein. In accordance with example implementations, framework **12** can be applied to or within a substrate as a thin film.

Referring next to FIG. **2**, configurations of metal organic frameworks according to an embodiment of the disclosure are shown. Referring first to **2**(A), framework **12** is depicted having a metal portion **15** (M^x), representing complex **13** having an M^x oxidation state. Framework **12** has a voltage V_1 being applied thereto to maintain the M^x oxidation state. Referring next to **2**(B), framework **22** is shown having complex **13** with metal portion **25** (M^y), representing the M^y oxidation state. Framework **22** has a voltage V_2 being applied thereto to maintain the M^y oxidation state. In accordance with example implementations, the M^x oxidation state is different than the M^y oxidation state. The change in oxidation state can be facilitated by altering the voltage applied to the framework. As an example, frameworks **12** and **22** can be substantially the same, but with application of V_1 the oxidation state is M^x, and with application of V_2 the oxidation state is M^y. In accordance with example implementations, the metal of the metal organic framework can be electrochemically altered. According to example implementations the oxidation state of at least some of the metals of the metal organic framework can be changed by altering the voltage applied to the metal and/or the metal organic framework. In example implementations V_1 would be different than V_2. Referring next to **2**(C), at least a portion of the framework **12** is shown having complexes **13** including portion **15** (M^x) having voltage V_1 being applied thereto. In accordance with example implementations, framework **22** of **2**(B) can be altered to reflect framework **12** of **2**(C) by altering V_2 to V_1. According to specific implementations, by transitioning from **2**(A)-**2**(C), framework **12** can transition from having metal portions **15** through metal portions **25** to metal portions **15** again.

Referring next to FIG. **3**, configurations of metal organic framework and mixtures that include guest materials are depicted according to an embodiment of the disclosure. Referring first to **3**(A), framework **12** is shown having V_1 applied thereto to maintain M^x oxidation states of at least some of metal portions **15** of complexes **13**.

In accordance with example implementations, mixture **30** can be exposed or provided to framework **12**. Mixture **30** can include guest material **32** (*). Material **32** can be a material that is desired to be separated from mixture **30**. Example materials include but are not limited to carbon dioxide, and mixture **30** may include components of flue gas with the components other than carbon dioxide being represented as a remainder of the mixture **34** (#). Mixture **34** can further include combustion products and/or carbon dioxide and water for example. In accordance with other implementations, guest material **32** may be exposed or provided to framework **12** in substantially pure form. For example, carbon dioxide, hydrofluorocarbons (HFC's), refrigerants, N_2, He, butane, propane, pentane, ammonia, and freon may be desired as a guest material and metal organic frameworks having dynamically modifiable metal portions may be configured to associate with or adsorb same.

In accordance with **3**(A), mixture **30** is provided to framework **12** and at least some of material **32** is retained while material **34** is not. Accordingly, methods for associating guest materials with a metal organic framework are provided with the method including altering the oxidation state of at least a portion of the metal of the metal organic framework to associate at least a portion of the guest materials with the framework. Further, methods for exposing a mixture to the metal organic framework are provided with the mixture comprising the guest materials and other materials, and at least a portion of the other materials not being associated with the metal organic framework upon the exposing. Referring to **3**(B), V_2 can be applied to form framework **22** from framework **12** with framework **22** including complexes **13** having metal portions **25** (M^y). Upon changing at least some of the oxidation state of M^x to M^y, at least some of guest material **32** dissociates or desorbs from framework **22** as substantially pure guest material **32**. Accordingly, a method for releasing associated guest materials from a metal organic framework is provided with the method including altering the oxidation state of at least a portion of the metal of the metal organic framework to dissociate at least a portion of the guest materials from the framework. Referring to **3**(C), V_1 can be applied to again substantially form framework **12** from framework **22** with framework **12** including complexes **13** having metal portions **15** (M^x). Upon returning the oxidation state of M^y to M^x, mixture **30** can be exposed to framework **12** to associate or adsorb guest material **32** with or to framework **12**.

In accordance with example implementations, Prussian Blue and Prussian Green analogs of metal organic frameworks can be synthesized. Synthesis of the mixed-metal organic sorbents based on Prussian blue analogues and DHTA sorbents can be performed. Prussian blues of chemical formula $M_3^{2+}[M^{3+}(CN)_6]_2XH_2O$ can be prepared from octahedral $M^{3+}(CN)_6^{3-}$ complexes bridged unto a cubic lattice by M^{2+} ions (M^{3+}=Co; M^{2+}=Cd, Co, Cu, Mn, Ni, Zn). Prussian blue analogues with two different oxidation states in the solid state, such as $Fe_3^{2+}[Fe^{3+}(CN)_6]_2$, and univalent oxidation state $Fe_3^{3+}[Fe^{3+}(CN)_6]$, can be synthesized for basic physical property and electrochemical characterization.

Additionally, mixed valance DHTA based metal-organic sorbents can be synthesized by dissolving 2,5-dihydroxyterephthalic acid in ethanol water mixture (1:1) in a Teflon autoclave. An aqueous sodium hydroxide solution can be added to this solution while stirring. Two salts containing metals in different oxidation states may then be dissolved in water in a 1:1 ratio and added to the Teflon autoclave, upon which a precipitate may form. After allowing the mixture to react at 110° C. for several days, a mixed valence state DHTA sorbent should form. Upon production of the desired mixed valence form, templating methods may be used to enhance yields.

Sorbent materials successfully synthesized can be fully characterized using various spectroscopic techniques including single-crystal x-ray diffraction, powder x-ray diffraction, BET surface analysis, differential scanning calorimetry, and thermogravimetric analysis. Adsorption isotherm data can be collected on both the multivalent and univalent forms to determine the net working adsorption capacity using an IGA-100 gas analyzer coupled with a breakthrough reactor and mass spectrometer. The IGA-100 is designed to study the multicomponent gas and/or vapor sorption processes from vacuum to high pressure under dynamic flow-through conditions. Mixtures of up to three different gases can be introduced in the system.

In accordance with example implementations, Fe(2+) and Fe(3+) oxidation states can be synthesized by adding the saturated solution of $K_4[Fe(CN)_6]$ (1.39 g in 5 mL of DI water) to a saturated solution of $Fe(3+)Cl_3$ (3.7 g in 5 mL of DI water) at room temperature. Upon the addition of the $K_4[Fe(CN)_6]$, the color of the reaction mixture can change to blue spontaneously indicating the formation of Prussian blue. Filtration can follow with washings of water leading to the formation of pure Prussian blue ($Fe_3^{2+}[Fe^{3+}(CN)_6]_2$). Prussian green may also be synthesized by hydrothermal reaction of $K_3[Fe(CN)_6]$ and $Na_2S_2O_3$ in 10 ml of DI water followed by the autoclave heating at 130° C. for two days, which can result in the formation of a solid green product.

To evaluate the uptake of gas materials such as CO_2 at room temperature, both the green and blue samples can be activated overnight at 150° C. The blue material can show uptake of 10 wt % CO_2 selectively over N_2 at 1 bar pressure with the Prussian green not showing any CO_2 uptake. In accordance with example implementations, it has been demonstrated that the oxidized form of this metal organic framework can result in the collapse of cavities present in the mixed valence form.

Prussian blue thin films can be deposited on glassy carbon PEEK incased electrodes using prepared 0.01 M solutions of $FeCl_3$ and $K_3[Fe(CN)_6]$ using 0.01 N HCl. Repetitive potential cycling between 1.0 and −0.20 V versus Ag/AgCl of GCE in the equimolar solution of $FeCl_3$ and $K_3[Fe(CN)_6]$ can result in the formation of Prussian blue thin film as represented in FIG. **4**, wherein the glassy carbon PEEK electrode is represented as **42** and the thin film Prussian blue **44** is demonstrated as electrically deposited on electrode **42**. The electrode can be thoroughly rinsed with water and transferred to another cell containing 1 M KCl solution. The electrodes can be subjected to repetitive potential cycling between 1.0 and −0.20 V versus Ag/AgCl at 0.1 V/s. Cyclic voltammetry measurements can demonstrate the reduction and the oxidation of Fe(2+)/Fe(3+) upon cycling the potentials between 0.16 V and 0.8 V.

In accordance with **3**(A)-**3**(B) and with reference to FIG. **5**, methods for selectively associating or dissociating guest materials with a metal organic framework are provided. The methods can include altering the oxidation state of at least a portion of the metal of the metal organic framework to associate or dissociate at least a portion of the guest materials with the framework. These methods can also include exposing a mixture to the metal organic framework with the mixture including the guest materials and other materials. At least a portion of the other materials may not be associated with the metal organic framework upon the exposing, for example. In accordance with example implementations, the methods can include: ceasing the exposing; altering the oxidation state of the portion of the metal; and dissociating at least a portion of the guest materials from the metal organic framework. Further, the methods can include, after the dissociating, altering the oxidation state of the portion of the metal to return the oxidation state to an associating oxidation state; after the altering, exposing the mixture to the metal organic framework; and associating at least a portion of the guest material of the mixture with the metal organic framework. In accordance with implementations of these methods, the altering can include applying a predetermined voltage to the metal organic framework.

Referring to FIG. **5** an example system **50** including metal organic frameworks **52** and **54** is shown according to an embodiment of the disclosure. In accordance with example implementations, system **50** can be a system for associating or dissociating guest materials within a series of metal organic frameworks. System **50** can include at least two individual metal organic frameworks **52** and **54** respectively. Metal organic framework **54** can be configured to dissociate guest materials **32** and framework **52** can be configured to associate guest material **32**. In accordance with an example embodiment, framework **54** includes at least some metals of one oxidation state (M^y) and framework **52** includes the same metals of another oxidation state (M^x). While not shown, system **50** can include a power source, and a controller operatively coupled to both the power source and the metal organic frameworks (V_1 and V_2). System **50** can also include a conduit **56** extending to a valve **58** in fluid communication with both metal organic frameworks **52** and **54**. Valve **58** may be operable by a motor (not shown) and system **50** can include a controller (not shown) configured to operate the motor of valve **58** as well as the power supply to V_1 and V_2. Accordingly, system **50** may be configured to continuously adsorb and desorb guest materials from the frameworks by selectively providing and denying mixture to individual frameworks having metals of differing oxidation states. Valve **58** can be cycled consistent with V_1 and V_2 to alternatively desorb and adsorb from alternative frameworks as desired or dictated by the controller and/or computer system (not shown).

Referring next to FIG. **6**, system **60** is shown that includes frameworks **66** and **68** coupled to power source **70** and fluid communication with inlet **62**. In accordance with example implementations, system **60** may be utilized to segregate carbon dioxide from flue gas and hence flue can be provided to inlet **62** and selectively provided to one of frameworks **66** or **68** via valves/conduit assembly **64**. In accordance with example implementations, while flue gas is being provided to one of frameworks **66** and **68**, the other of the frameworks can be desorbing guest materials to outlet **74**. An example guest material is carbon dioxide. Likewise, while the one framework is being provided the flue gas, a portion of the flue gas not retained, such as nitrogen can be provided to outlet **72**. In accordance with example implementations, system **60** can be operable via a computer system as described herein.

Referring to FIG. **7**, system **80** is shown that includes at least two frameworks **82** and **84** separated by an electrolyte **86**. In the shown embodiment, V_1 can be applied to framework **82** to facilitate the formation of metals of one oxidation state (M^x), and V_2 can be applied to framework **84** to facilitate the formation of metals of another oxidation state (M^y). Electrolyte **86** can be a solid state conducting polymer that is porous. According to example implementations, electrolyte **86** can be sufficiently porous to allow guest materials to pass and/or migrate through.

Electrolyte **86** can be a non-aqueous porous solid or a gel-type polymer. Electrolyte **86** can be configured to facilitate CO_2 gas transport through the electrolyte bridge in the electrochemical cell. Electrolyte **86** may take the form of a polymerized ionic liquid membrane, for example. Electrolyte **86** may also be a room-temperature ionic liquid such as those reported as promising solvents for lithium ion batteries and salts for supercapacitors. Consistent with this, electrolyte **86** can be a supported porous polymer incorporating an ionic liquid conducting medium.

The hydrophobic room temperature ionic liquids of electrolyte **86** can be those containing dialkyl imidazolium as cation and bis(trifluromethanesulfonyl)imide as anion, such as 1-ethyl-3-methylimidazolium bis(trifluromethanesulfonyl)imide (EMI-TFSI), 1-butyl-3-methylimidazolium bis (trifluromethanesulfonyl)imide (BMI-TFSI), for example. The synthesis of these ionic liquids is consistent with that which is reported in literature.

The polymerized ionic liquid of electrolyte **86** can be chosen from the side-chain poly(imidazolium) and the main-chain poly(imidazolium)s (i.e. imidazolium ionenes) with adjustable alkylene spacers-). Both types of poly(imidazolium)s can be synthesized following the procedures reported in the literature. The poly(imidazolium) polymers can be dissolved in certain organic solvents with low boiling point and then mixed with liquid electrolytes prepared by dissolving salts such as potassium bis(trifluromethanesulfonyl)imide (KTFSI) in the room temperature ionic liquids.

In accordance with an example preparation of a system, the non-woven porous polymer or fabric sheet can be immersed into the above poly(imidazolium) electrolyte solution and then taken out of the solution. After removing the low boiling point organic solvent, via evaporation for example, the porous gel polymer electrolyte separator can be formed.

The electrochemical cell can then be formed by placing the porous gel polymer electrolyte separator in between two pieces of the porous electrode sheets deposited with sorbent and coated with the polymer gel electrolyte. Once formed, the next step can involve deposition of the electrically responsive sorbent on the surface and construction of the complete electrochemical system.

Desorption of trace gases and CO_2 by the electrochemical switching may occur at different electrode potentials with some sorbents. Hence, periodic regeneration at higher applied potential may be required to maintain sorbent performance after prolonged exposure to SO_2 and other trace gases. Effluent gases from the cell can be analyzed with an in-line mass spectrometer system to enable tracking of CO_2 capture performance over the course of each test run. In addition, the system can be equipped with thermocouples and current/voltage monitoring equipment to track power consumption and electrical performance characteristics.

In accordance with example implementations system **80** can be operated as an electrical cell with cyclic voltammetry being applied to both V_1 and V_2. In this configuration, one framework may be considered an anode with the other being considered a cathode. Mixtures can be exposed to either or both of frameworks **82** and **84**, and desired guest materials retained/desorbed in accordance with the oxidation state of the metals with the metal organic framework. In accordance with example implementations, flue gas can be exposed to frameworks **82** or **84** and carbon dioxide provided to and/or through electrolyte **86** for eventual capture.

Referring next to FIG. **8**, system **90** can further include power source **92** electrically coupled to electrodes **94** and controlled by a controller (not shown). In accordance with example implementations, the controller can be configured to provide cyclic voltammetry to frameworks **82** and **84**. Conduit **96** can extend along an edge of frameworks **82** and **84**, with the conduit being configured to expose the framework to mixture **98** such as a flue gas or combustion product. Upon exposure to the framework, guest materials such as carbon dioxide can be associated or adsorbed and subsequently dissociated or desorbed into electrolyte **86** and conveyed to outlet **100** while the remaining materials of the mixture such as N_2 are conveyed to outlets **102**. To facilitate the migration of guest materials and/or remaining materials through desired outlets, the back pressure to the outlets can be manipulated.

Referring next to FIG. **9**, system **110** is shown that includes at least two series of alternating frameworks, series **112** and **114**. The series include individual frameworks electrically isolated from one another by separator **118** which can be constructed of insulative material. Series **112** and **114** can be aligned in relation to one another to facilitate pairs **116** lateral of one another. Pairs **116** can include a framework of one configuration and a framework of another configuration. As with system **90**, a mixture can be provided to the system to selectively separate a desired guest material, such as providing flue gas and separating carbon dioxide.

Accordingly, gas separation assemblies are provided that can include a plurality of individual cells housing metal organic framework. The plurality can be configured as at least one series of cells and another series of cells. Each of the series can include at least two electrically isolated individual cells. The assembly can include a channel, such as the channel of electrolyte **86** between the one series of cells and the other series of cells. In accordance with example implementations, the one series can be aligned laterally of the other series, and the individual cells of the one series are aligned lateral to the individual cells of the other series to form a pair of cells, for example. With regard to the pairs of cells, one of the pair of cells can be configured to dissociate guest materials, and the other of the pair of cells can be configured to associate guest materials. The assembly can include conduits extending along the perimeter of each of the series of cells, with the conduits configured to expose the metal organic framework of each of the cells of each of the series. One series of cells can be in fluid communication with one conduit, and the other series of cells can be in fluid communication with another conduit.

In compliance with the statute, embodiments of the invention have been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the entire invention is not limited to the specific features and/or embodiments shown and/or described, since the disclosed embodiments comprise forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

The invention claimed is:

1. An electrochemical cell comprising:

at least two individual cells;

one of the two cells comprising metal organic framework having one oxidation state;

another of the two cells comprising metal organic framework having another oxidation state, the one oxidation state being different than the other oxidation state.

2. The electrochemical cell of claim **1** wherein one or the other metal organic frameworks of the one or the other cells is configured to bind with a guest material.

3. The electrochemical cell of claim **1** wherein at least a portion of either one or the other of the metal of the metal organic framework is a transition metal.

4. The electrochemical cell of claim **1** wherein the metal of the metal organic framework is one or more of Ti, Zr, Hf, Rf, V, Nb, Ta, Db, Cr, Mo, W, Sg, Mn, Tc, Re, Bh, Fe, Ru, Os, Hs, Co, Rh, Os, Hs, Co, Rh, Ir, Mt, Ni, Pd, Pt, Ds, Cu, Ag, Au, and Rg.

5. The electrochemical cell of claim **1** wherein at least a portion of either one or the other of the metal organic framework comprises a substantially conductive organic ligand.

6. A method of separating carbon dioxide from a mixture comprising carbon dioxide, the method comprising:

providing a mixture to at least one cell and associating the carbon dioxide of the mixture with a metal organic framework of the one cell; and

altering the oxidation state of the metal organic framework to disassociate at least some of the carbon dioxide from the metal organic framework.

7. The method of claim **6** wherein the mixture comprises flue gas.

8. The method of claim **6** further comprising while providing the mixture to the cell, disassociating carbon dioxide from another cell, the metal organic framework of the one cell having a different oxidation state than the metal organic framework of the other cell.

9. The method of claim **8** further comprising alternatively associating carbon dioxide with the one cell and disassociating carbon dioxide from the other cell to separate carbon dioxide from the mixture.

10. The method of claim **8** wherein the metal organic framework of the one cell comprises (M^{2+}/M^{3+}) and the other cell comprises (M^{3+}/M^{3+}).

11. The method of claim **8** further comprising cycling the mixture between the one and another cell.

12. A method of separating one or more carbon compounds from a mixture comprising carbon compounds, the method comprising:

providing a mixture to at least one cell and associating the carbon compound of the mixture with a metal organic framework of the one cell, the carbon compound comprising carbon dioxide, hydrofluorocarbons, refrigerants, butane, propane, pentane, and/or freon; and

altering the oxidation state of the metal organic framework to disassociate at least some of the carbon compound from the metal organic framework.

13. The method of claim **12** further comprising while providing the mixture to the cell, disassociating carbon compound from another cell, the metal organic framework of the one cell having a different oxidation state than the metal organic framework of the other cell.

14. The method of claim **13** further comprising alternatively associating the carbon compound with the one cell and disassociating the carbon compound from the other cell to separate the carbon compound from the mixture.

15. The method of claim **13** wherein the metal organic framework of the one cell comprises (M^{2+}/M^{3+}) and the other cell comprises (M^{3+}/M^{3+}).

16. The method of claim **13** further comprising cycling the mixture between the one and another cell.

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