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(54) Title: MICROPOROUS PARTICLES TO ENHANCE GAS TRANSPORT IN MEMBRANES

(57) Abstract: This invention provides membranes including a polymer having dispersed therein a plurality of microporous particles. The membranes improve mass transport in polymer electrolyte fuel cells.



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MICROPOROUS PARTICLES TO ENHANCE GAS TRANSPORT IN MEMBRANES**Statement Regarding Federally Sponsored Research or Development**

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5 Background

Low-temperature fuel cells that produce electricity by direct electrochemical conversion of H₂ and O₂ into water represent a promising clean energy conversion technology for automotive and stationary applications.

10 There are, however, major limitations of the present technology that need to be surmounted to make low-temperature fuel cells more economically attractive. One severe limitation originates from poor gas transport, which gives rise to mass transport limitations at the electrodes.

Accordingly, there is a need for compositions and methods to facilitate efficient gas transport.

Summary of Invention

15 This invention provides a new means of addressing mass transport issues in polymer electrolyte fuel cells, which are critical to overcome in order to realize the full potential of fuel cells as a green energy producer. In particular, porous framework materials (e.g., high-silica zeolites), are powerful building blocks to create unique opportunities for facilitating gas transport in polymer electrolyte fuel cells when incorporated into a polymer matrix (e.g., a Nafion matrix) – or immobilized at a polymer/catalyst interface—owing to their high internal surface areas and high density of micropores that remain dry even
20 when surrounded by liquid water.

In one aspect the invention features a membrane including a polymer having dispersed therein a plurality of microporous particles having pores with an internal surface and having an external surface, wherein the pores are sized to allow entry of a gas. In some embodiments, the internal surface is hydrophobic, and the external surface is hydrophobic. In some embodiments, the internal surface is hydrophobic, and
25 the external surface is hydrophilic. In some embodiments, the membrane is a polymer membrane-electrolyte. In some embodiments, the membrane further includes a catalyst dispersed in the polymer. In some embodiments, the catalyst is a redox catalyst. In some embodiments, the polymer is a charged, acidic, basic, or ionic polymer. In some embodiments, the polymer is a Nafion material. In some embodiments, the microporous particles comprise a zeolite a metal-organic framework, or a covalent
30 organic framework. In some embodiments, the zeolite or metal-organic framework further comprises a hydrophilic, hydrophobic, or amphiphilic coating. In some embodiments, the microporous particles are nanoparticles or microparticles. In some embodiments, the microporous particles are covalently bound to the polymer. In some embodiments, the microporous particles are non-covalently bound to the polymer. In some embodiments, the membrane further includes the gas located in the pores of the microporous
35 particles. In some embodiments, the gas is O₂, H₂, CO₂, or CH₄.

In another aspect, the invention provides a fuel cell including a membrane as described herein adjacent an electrode. In some embodiments, the fuel cell further includes a second electrode, a second

membrane as described herein, and a polymer membrane-electrolyte, wherein the membrane is between the electrode and the polymer membrane-electrolyte, and the second membrane is between the polymer membrane-electrolyte and the second electrode.

In another aspect, the invention provides a fuel cell including a first electrode, a first catalyst layer, a first layer of microporous particles having pores with an internal surface and having an external surface, a polymer membrane-electrolyte, a second layer of a microporous particles having pores with an internal surface and having an external surface, a second catalyst layer, and a second electrode, arranged in the order listed.

Definitions

By “about” is meant $\pm 10\%$ of the specific value.

By “microporous” is meant have an average pore diameter in the range of 3 Å to 20 Å.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a schematic of an electrolyte in a fuel cell. Gas molecules from a gas diffusion electrode (top) migrate through the electrode layer (second from top) into a catalyst/Nafion matrix (middle) composed of a mixture of catalyst particles, water droplets, and porous amphiphilic silicalite-1 particles embedded in Nafion. Due to the hydrophobic pores of silicalite-1, water is thermodynamically repelled from the interior, allowing high concentrations of gas to be stored and reversibly released to the gas-reactive catalyst nanoparticles.

DETAILED DESCRIPTION OF THE INVENTION

To increase the concentration of gases (H_2 and O_2) in the vicinity of the electrocatalysts, and thus increase the rate of the electrochemical reactions and power output of the fuel cell, this invention leverages hydrophobic microporous nanocrystals—including zeolites and metal–organic frameworks—to facilitate efficient gas transport from the gas diffusion layer to the electrocatalyst through the hydrated polymer electrolyte film surrounding the catalyst sites.

The invention provides systems and methods for using amphiphilic porous framework materials—with hydrophobic internal surfaces and hydrophilic external surfaces—for increasing gas concentrations in the vicinity of electrocatalysts in polymer electrolyte fuel cells.

Owing to their high internal surface areas, variable pore diameters, and well-defined sites for external surface functionalization, two classes of highly tunable microporous materials: zeolites and metal–organic frameworks may be employed in the invention. Both zeolites and metal–organic frameworks feature internal networks of angstrom-sized pores that lead to high internal surface areas, often exceeding 1,000 m^2 per g or mL of material. Even when surface interactions with gas molecules are relatively weak, these high internal surface areas concentrate gas molecules to densities that surpass those which are possible in a conventional liquid and in the bulk gas phase—even after accounting for the space occupied by the atoms framing the micropore. Due to, *inter alia*, these above factors, porous frameworks may be able to drastically increase the transport of gas through aqueous compositions.

The invention provides a polymer membrane including a microporous material that may be used in a polymer membrane electrolyte fuel cell. In addition to microporous materials, the membrane may also include a catalyst, e.g., a nanoparticle catalyst. **Fig. 1** shows the construction of an exemplary electrode of a fuel cell including the present invention.

- 5 In some embodiments, the polymer is charged. In some embodiments, the polymer may contain a charged substituent group, e.g., acidic group or a basic group (e.g., $-\text{SO}_3\text{H}$, $-\text{COOH}$, PO_3H_2 , salts of their conjugate bases, etc.), a polar functional group (e.g., CN , NO_2 , etc.), or an ionic group (e.g., pyridinium, piperidinium, ammonium (including alkyl and aryl ammoniums) etc.).

- 10 In some embodiments, the polymer membrane contains charged groups allowing it to act as an electrolyte (i.e., a “polymer membrane-electrolyte”). Exemplary charged groups include $-\text{SO}_3\text{H}$, $-\text{COOH}$, PO_3H_2 , pyridinium, piperidinium, ammonium (including alkyl and aryl ammoniums), and the conjugate bases thereof.

- 15 The polymer may be a Nafion material (i.e., a sulfonated tetrafluoroethylene based fluoropolymer) or a derivative of a Nafion material. Nafion materials are specified by a combination of their equivalent weight (the number of grams of dry Nafion material per moles of sulfonic acid functional groups, given as one hundredth of the equivalent weight) and material thickness (in thousandths of an inch). For example, Nafion 117 is a Nafion material with an equivalent weight of 1100 g/mol and a thickness of 0.007 in, and Nafion 212 is a Nafion material with an equivalent weight of 2100 g/mol and a thickness of 0.002 in.

- 20 In some embodiments, the catalyst is a redox catalyst (e.g., metals and metal alloys - e.g., Ni, Pd, Pt, Ir, Rh, Cu, Zn, Al, and ions or alloys. In some embodiments, the catalyst is a continuous material. In some embodiments, the catalyst is a nanoparticle. In some embodiments, the catalyst may account for less than 0.1 vol. % of the composition or up to 90 vol. % of the composition. In some embodiments, the catalyst is dispersed within the polymer. In some embodiments, the catalyst may be uniformly dispersed throughout the polymer. In some embodiments, the concentration of the catalyst may be variable throughout the polymer. In some embodiments, the concentration of the catalyst may increase or decrease with increasing distance from the gas layer.

- 30 The invention includes any microporous materials, such as zeolites, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs), that can be synthesized with hydrophobic pore surfaces, e.g., in nanocrystalline form. The great range and variety of such materials makes these materials an advantageous—and highly tunable—platform to provide liquid (e.g., aqueous) solutions with permanent porosity. Exemplary microporous materials are known in the art (see, e.g., WO 2022/076883, the materials of which are incorporated herein by reference). Certain embodiments of the invention include the use of various MFI-type zeolite nanoparticles, both in pure silica form (known commonly as “silicalite-1”) and in Al-containing form (known as “ZSM-5”). In some embodiments, the zeolite is silicalite-1 or ZSM-5. In some embodiments, the metal-organic framework is ZIF-8 or ZIF-67.

Owing to their high internal surface areas, variable pore diameters, and well-defined sites for external surface functionalization, two classes of highly tunable porous materials: zeolites and metal-organic frameworks may be employed in the invention. Particles may also include activated carbon or amorphous porous silica particles. Both zeolites and metal-organic frameworks feature internal networks

of angstrom-sized pores that lead to high internal surface areas, often exceeding 1,000 m² per g or mL of material. Porous particles of the invention may have average pore diameters of between about 3 Å and about 20 Å, e.g., between about 3-5 Å, 4-6 Å, 4-10 Å, 5-10 Å, 5-15 Å, 6-8 Å, 7-9 Å, 9-11 Å, 10-12 Å, 10-15 Å, 10-20 Å, 12-15 Å, 13-18 Å, 14-18 Å, 17-19 Å, 18-20 Å, or about 19-20 Å, e.g., about 5 Å, about 10 Å, about 15 Å, or about 20 Å. Even when surface interactions with gas molecules are relatively weak, these high internal surface areas concentrate gas molecules to densities that surpass those which are possible in a conventional liquid and in the bulk gas phase—even after accounting for the space occupied by the atoms framing the pore. By preventing liquid, e.g., water molecules, from entering these pores, the invention provides porous liquids and brings the high gas capacities of porous materials to solutions, e.g., aqueous. Porous particles of the invention may range in cross-sectional dimension (e.g., diameter) from about 5 nm to about 1000 nm, e.g., between about 5-100 nm (e.g., about 5-10 nm, 5-15 nm, 5-25 nm, 10-20 nm, 25-50 nm, 20-40 nm, 30-60 nm, 50-75 nm, 60-80 nm, 75-100 nm, 70-90 nm, 80-95 nm, or 90-100 nm) or about 100-1000 nm (e.g., about 100-150 nm, 120-160 nm, 140-180 nm, 150-200 nm, 100-200 nm, 100-300 nm, 200-500 nm, 250-750 nm, 300-400 nm, 350-650 nm, 400-500 nm, 400-600 nm, 500-750 nm, 600-800 nm, 750-1000 nm, 600-950 nm, 700-900 nm, 800-1000 nm, or 900-1000 nm). The porous particles may account for less than 0.1 vol % or up to 90 vol % of the composition, for example between about 0.01 vol % to about 90 vol %, e.g., about 0.01 to about 1 vol % (e.g., about 0.01-0.05 vol %, 0.02-0.07 vol %, 0.04-0.09 vol %, 0.05-0.1 vol %, 0.06-0.12 vol %, 0.1-0.15 vol %, 0.1-0.2 vol %, 0.1-0.5 vol %, 0.2-0.6 vol %, 0.3-0.7 vol %, 0.4-0.9 vol %, 0.5-0.9 vol %, 0.5-1 vol %, or 0.9-1 vol %) or, e.g., about 1 vol % to about 10 vol % (e.g., about 1-2 vol %, 1-3 vol %, 1-4 vol %, 2-5 vol %, 2-6 vol %, 3-7 vol %, 4-8 vol %, 5-7 vol %, 5-10 vol %, 6-9 vol %, 7-10 vol %, 8-10, or 9-10 vol %), or about 10 vol % to about 90 vol % (e.g., about 10-15 vol %, 10-20 vol %, 10-50 vol %, 15-45 vol %, 25-50 vol %, 30-60 vol %, 40-80 vol %, 50-75 vol %, 50-90 vol %, 60-90 vol %, 65-85 vol %, 70-85 vol %, 75-90 vol %, or 80-90 vol %). In some embodiments, the microporous material may be uniformly dispersed throughout the polymer. In some embodiments, the concentration of the microporous material may be variable throughout the polymer. In some embodiments, the concentration of the microporous material may increase or decrease with increasing distance from the gas layer.

Noncovalent surface functionalization with macromolecules such as polyethylene glycol (PEG) represents one approach for dispersing nanocrystals in solvents that would otherwise induce aggregation and precipitation.

The invention also provides covalent surface functionalization approaches to producing porous particles which offer the potential for strongly bound and precisely located surface ligands that promote dispersibility and/or increased capability with a polymer membrane at lower loadings than more weakly associated surface ligands. Other surface chemistries are known in the art.

The invention may employ a redox active gas. Exemplary redox active gases include H₂, O₂, CO₂, and CH₄.

Owing to their high gas capacities, porous materials can dramatically increase the local concentration of gases. Problematically, many such candidates also uptake small molecules such as water, leading to deactivation and elimination of the accessible porosity. Herein, we propose the use of amphiphilic microporous materials—such as silicalite-1 and other high-silica zeolites—that simultaneously possess

external hydrophilicity and internal hydrophobicity. Crucially, their hydrophobic pore networks resist the intrusion of highly polar molecules (such as water and electrolytes), allowing their pores to remain vacant and accessible to gas molecules. Simultaneously, their hydrophilic exteriors make them highly compatible with polar molecules, permitting them to be easily dispersed in polar media and permitting the synthesis of composite fluids possessing dramatically increased gas capacities (see, e.g., Erdosy et al. Microporous Water with High Gas Solubilities. *Nature* **2022**, 608, 712; the entirety of which is incorporated by reference herein).

Dispersing silicalite-1 particles in a polymer matrix will introduce stable pockets capable of hosting gas throughout the polymer electrolyte, increasing the local concentration of gases in the vicinity of the catalyst and allow these molecules to “hop” between particles and the catalyst, and thus mitigate mass transport issues associated with traditional polymer electrolyte membrane fuel cells (see, e.g., Springer et al. Investigating Fuel-Cell Transport Limitations Using Hydrogen Limiting Current. *Int. J. Hydrog. Energy* **2017**, 42, 13960; and Fox et al. In Mass Transfer – Advanced Aspects; InTech, 2011; pp 305-318; the entirety of which are incorporated by reference herein).

In some embodiments, a gas layer is in contact with the polymer membrane. In some embodiments, the gas layer comprises a hydrophobic gas. In some embodiments, the gas enters the pores in the microporous material but is insoluble in the polymer membrane.

The membrane may be included in a fuel cell. In some embodiments, the fuel cell includes a first electrode and a second electrode, one or both of which may be an electrode described herein. In some embodiments, the first electrode and the second electrode may be separated by an ion exchange membrane – e.g., a polymer membrane-electrolyte such as a proton exchange membrane. In some embodiments, the fuel cell includes an electrolyte capable of transmitting ions between the first electrode and the second electrode through the ion exchange membrane. Other electrolytes may also be employed. In some embodiments, the fuel cell includes one or more gas reservoirs, each gas reservoir independently including one or more of the gases in the gas layer. In some embodiments, the fuel cell further includes one or more gas diffusion layers, e.g., one for the cathode and one for the anode. In some embodiments, the fuel cell is arranged as shown in Fig. 1, for one or both half cells, i.e., a membrane of the invention containing catalyst disposed between an electrode and a polymer membrane-electrolyte. Alternatively, the catalyst is in a separate layer between the electrode and the membrane of the invention. In some embodiments, a layer of microporous particles as described herein is disposed between a catalyst layer and a polymer membrane-electrolyte.

In some embodiments, one or more fuel cells may be combined in a single electrical circuit, forming a stack. In some embodiments, a stack may be from about 1 fuel cell to about 100 fuel cells, e.g., about 10 fuel cells, about 20 fuel cells, about 30 fuel cells, about 40 fuel cells, about 50 fuel cells, about 60 fuel cells, about 70 fuel cells, about 80 fuel cells, about 90 fuel cells, etc.

In some embodiments, the fuel cell is capable of spontaneous generation of an electrical current. In some embodiments, the fuel cell is in electronic communication with an electric circuit. In some embodiments, the fuel cell is in electronic communication with a device which stores electrical power (e.g., a battery). In some embodiments, the fuel cell is capable of providing electrical power to a circuit. In some

embodiments, the power provided is from about 0.1 V to about 10 V per fuel cell, e.g., from about 0.5 V to about 5 V per fuel cell, from about 1 V to about 3 V per fuel cell, from about 1.1 V to about 2.9 V per fuel cell, from about 1.2 V to about 2.8 V per fuel cell, from about 1.3 V to about 2.7 V per fuel cell, from about 1.4 V to about 2.6 V per fuel cell, from about 1.5 V to about 2.5 V per fuel cell, etc.

- 5 Other embodiments are in the claims.

What is claimed is:

CLAIMS

1. A membrane comprising a polymer having dispersed therein a plurality of microporous particles having pores with an internal surface and having an external surface, wherein the pores are sized to allow entry of a gas.
2. The membrane of claim 1 wherein the internal surface is hydrophilic and the external surface is hydrophobic.
3. The membrane of claim 1 wherein the internal surface is hydrophobic and the external surface is hydrophilic.
4. The membrane of claim 1, wherein the membrane is a polymer membrane-electrolyte.
5. The membrane of claim 1, further comprising a catalyst dispersed in the polymer.
6. The membrane of claim 5, wherein the catalyst is a redox catalyst.
7. The membrane of claim 1, wherein the polymer is a charged, acidic, basic, or ionic polymer.
8. The membrane of claim 1, wherein the polymer is a Nafion material.
9. The membrane of claim 1, wherein the microporous particles comprise a zeolite a metal-organic framework, or a covalent organic framework.
10. The membrane of claim 9, wherein the zeolite or metal-organic framework further comprises a hydrophilic, hydrophobic, or amphiphilic coating.
11. The membrane of claim 1, wherein the microporous particles are nanoparticles or microparticles.

12. The membrane of claim 1, wherein the microporous particles are covalently bound to the polymer.
13. The membrane of claim 1, wherein the microporous particles are non-covalently bound to the polymer.
14. The membrane of claim 1, further comprising the gas located in the pores of the microporous particles.
15. The membrane of claim 1, wherein the gas is O₂, H₂, CO₂, or CH₄.
16. A fuel cell comprising a membrane of any one of claims 1-12 adjacent an electrode.
17. The fuel cell of claim 16 further comprising a second electrode, a second membrane of any one of claims 1-12, and a polymer membrane-electrolyte, wherein the membrane is between the electrode and the polymer membrane-electrolyte, and the second membrane is between the polymer membrane-electrolyte and the second electrode.
18. A fuel cell comprising a first electrode, a first catalyst layer, a first layer of microporous particles having pores with an internal surface and having an external surface, a polymer membrane-electrolyte, a second layer of a microporous particles having pores with an internal surface and having an external surface, a second catalyst layer, and a second electrode, arranged in the order listed.

Fig. 1

