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(54) METHANE ACTIVATION SYSTEMS AND RELATED ELECTROCHEMICAL APPARATUSES

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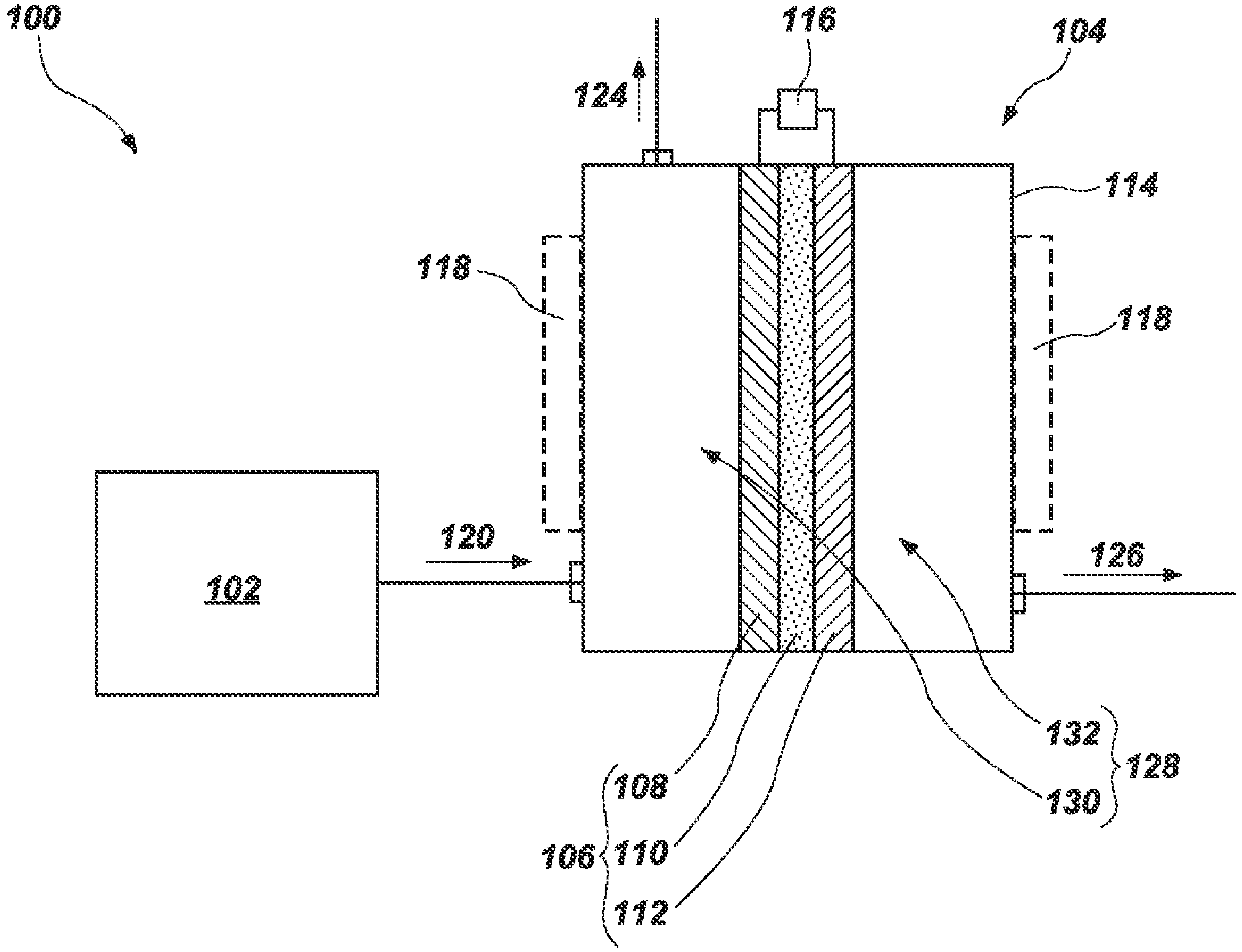
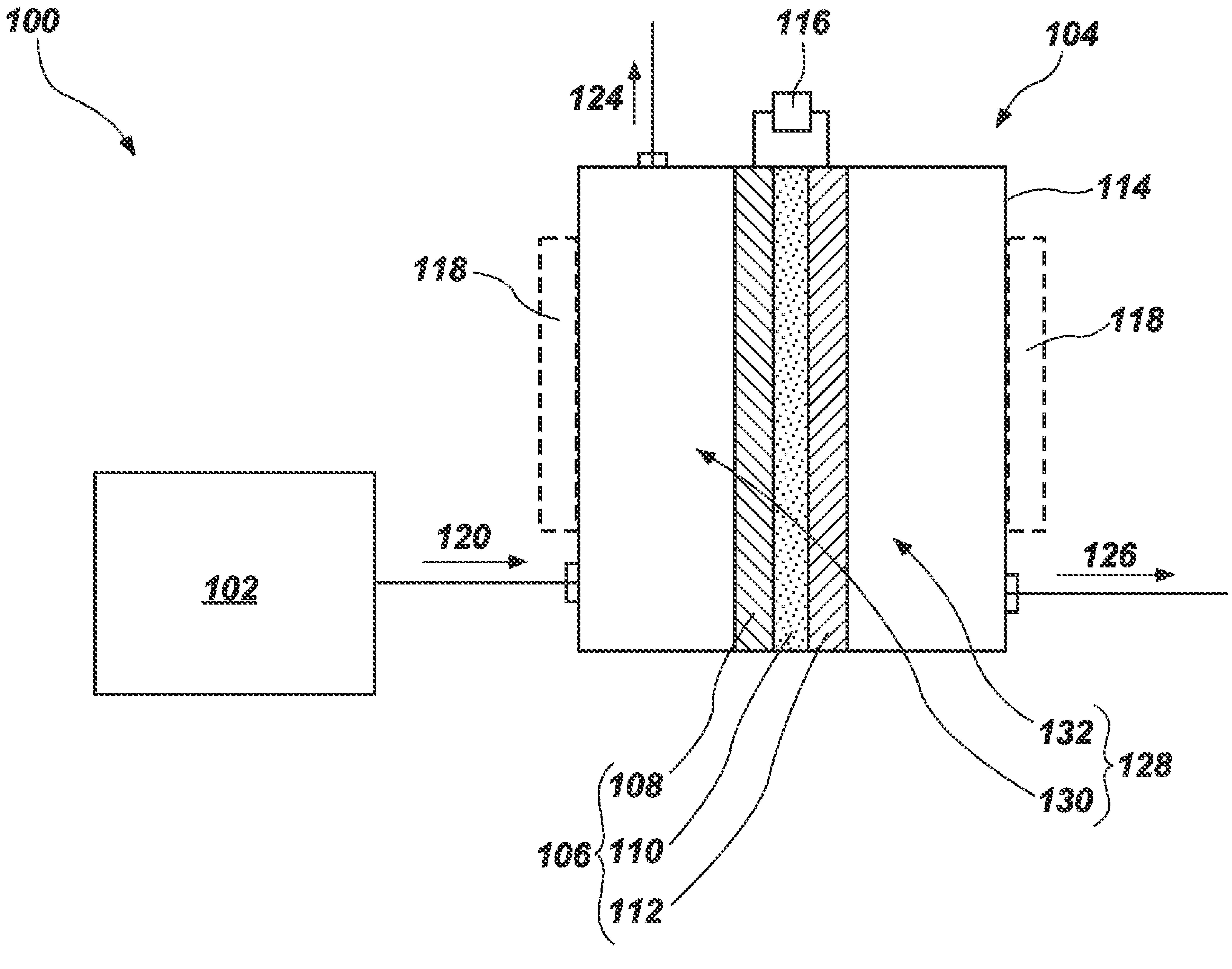
(57) ABSTRACT

A method of forming a hydrocarbon product and hydrogen gas comprises introducing CH_4 to a positive electrode of an electrochemical cell comprising the positive electrode, a negative electrode, and a proton-conducting membrane between the positive electrode and the negative electrode. The proton-conducting membrane comprises an electrolyte material having an ionic conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 600° C. A potential difference is applied between the positive electrode and the negative electrode of the electrochemical cell to produce the hydrocarbon product and the hydrogen gas. A CH_4 activation system and an electrochemical cell are also described.




100
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128
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FIG. 1

METHANE ACTIVATION SYSTEMS AND RELATED ELECTROCHEMICAL APPARATUSES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional of U.S. patent application Ser. No. 16/196,283 filed Nov. 20, 2018, which claims the benefit under 35 U.S.C. § 119(e) of U.S. Provisional Patent Application Ser. No. 62/597,004, filed Dec. 11, 2017, the disclosure of each of which is hereby incorporated herein in its entirety by this reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under Contract Number DE-AC07-05ID14517 awarded by the United States Department of Energy. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The disclosure, in various embodiments, relates to methods, systems, and apparatuses for producing hydrocarbon products and hydrogen gas through electrochemical activation of methane.

BACKGROUND

[0004] Large reserves of natural gas continue to be discovered throughout the world, and have resulted in surpluses of methane (CH_4). CH_4 is predominantly formed into other hydrocarbon products such as ethylene (C_2H_4) through conventional stream cracking processes. However, conventional stream cracking of CH_4 can require high temperatures (e.g., temperatures greater than or equal to about 750° C.) to activate CH_4, resulting in undesirable energy expenditures (e.g., thermal energy expenditures) and/or environmental impacts (e.g., greenhouse gas emissions effectuated by the energy needs of the stream cracking processes). In addition, conventional stream cracking processes can require the use of complicated and costly systems and methods to purify (e.g., refine) the resulting hydrocarbon products.

[0005] It would be desirable to have new methods, systems, and apparatuses for synthesizing hydrocarbon products from CH_4. It would also be desirable if new methods, systems, and apparatuses facilitated the production of a variety of hydrocarbons, and also facilitated the production (e.g., co-production) and isolation of hydrogen gas. It would further be desirable if the new methods, systems, and apparatuses facilitated increased production efficiency, increased operational life, and were relatively inexpensive and simple in operation.

BRIEF SUMMARY

[0006] Embodiments described herein include methods, systems, and apparatuses for producing hydrocarbon products and hydrogen gas through electrochemical activation of CH_4. In accordance with one embodiment described herein, a method of forming a hydrocarbon product and hydrogen gas comprises introducing CH_4 to a positive electrode of an electrochemical cell comprising the positive electrode, a negative electrode, and a proton-conducting membrane between the positive electrode and the negative electrode. The proton-conducting membrane comprises an electrolyte material having an ionic conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 600° C. A potential difference is applied between the positive electrode and the negative electrode of the electrochemical cell.

[0007] In additional embodiments, a CH_4 activation system comprises a source of CH_4 and an electrochemical apparatus in fluid communication with the source of CH_4. The electrochemical apparatus comprises a housing structure configured and positioned to receive a CH_4 stream from the source of CH_4, and an electrochemical cell within an internal chamber of the housing structure. The electrochemical cell comprises a positive electrode, a negative electrode, and a proton-conducting membrane between the positive electrode and the negative electrode. The positive electrode comprises a catalyst material formulated to accelerate reaction rates to produce CH_3^+, H^+, and e^-, from CH_4, and to accelerate reaction rates to synthesize at least one hydrocarbon product from the produced CH_3^+. The negative electrode comprises another catalyst material formulated to accelerate reaction rates to produce $H_{2(g)}$ from H^+ and e^-. The proton-conducting membrane comprises an electrolyte material having an ionic conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 600° C.

[0008] In further embodiments, an electrochemical cell comprises a positive electrode, a negative electrode, and a proton-conducting membrane between the positive electrode and the negative electrode. The positive electrode comprises a first catalyst material formulated to accelerate to CH_4 deprotonation reaction rates to produce CH_3^+, H^+, and e^-, from CH_4, and to accelerate coupling reaction rates to synthesize at least one hydrocarbon product from the produced CH_3^+. The negative electrode comprises a second catalyst material formulated to accelerate hydrogen evolution reaction rates to produce $H_{2(g)}$ from H^+ and e^-. The proton-conducting membrane comprises an electrolyte material having an ionic conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 600° C.

BRIEF DESCRIPTION OF THE DRAWING

[0009] FIG. **1** is a simplified schematic view of a hydrogen gas production system, in accordance with an embodiment of the disclosure.

DETAILED DESCRIPTION

[0010] Methods, systems, and apparatuses for producing (e.g., co-producing) hydrocarbon products and hydrogen gas ($H_{2(g)}$) through electrochemical activation of CH_4 are disclosed. In some embodiments, a method of producing hydrocarbon products and $H_{2(g)}$ includes directing CH_4 into an electrochemical apparatus including an electrochemical cell therein. The electrochemical cell comprises a positive electrode (anode), a negative electrode (cathode), and a proton-conducting membrane between the positive electrode and the negative electrode. The proton-conducting membrane includes an electrolyte material having an ionic conductivity greater than or equal to about 10^{-2} Siemens per centimeter (S/cm) at one or more temperatures within a range of from about 150° C. to about 600° C. The positive electrode includes a catalyst material formulated to accelerate CH_4

deprotonation reaction rates to produce CH_3^+, H^+, and e^- from CH_4, and also formulated to accelerate coupling reaction rates (e.g., at least methyl coupling reaction rates) to synthesize one or more hydrocarbon products from the produced CH_3^+. The negative electrode comprises another catalyst material formulated to accelerate hydrogen evolution reaction rates to produce $H_{2(g)}$ from H^+ and e^-. Electrical current is applied to the CH_4 across the positive electrode and the negative electrode of the electrochemical cell at a temperature within the range of from about 150° C. to about 600° C. to produce at least one hydrocarbon product at the positive electrode and $H_{2(g)}$ at the negative electrode. The methods, systems, and apparatuses of the disclosure may be more efficient (e.g., increasing higher hydrocarbon and $H_{2(g)}$ production efficiency; reducing equipment, material, and/or energy requirements; etc.), more durable, and/or less complicated as compared to conventional methods, conventional systems, and conventional apparatuses for producing one or more of higher hydrocarbons and $H_{2(g)}$ from CH_4.

[0011] The following description provides specific details, such as material compositions and processing conditions (e.g., temperatures, pressures, flow rates, etc.) in order to provide a thorough description of embodiments of the disclosure. However, a person of ordinary skill in the art will understand that the embodiments of the disclosure may be practiced without necessarily employing these specific details. Indeed, the embodiments of the disclosure may be practiced in conjunction with conventional systems and methods employed in the industry. In addition, only those process components and acts necessary to understand the embodiments of the present disclosure are described in detail below. A person of ordinary skill in the art will understand that some process components (e.g., pipelines, line filters, valves, temperature detectors, flow detectors, pressure detectors, and the like) are inherently disclosed herein and that adding various conventional process components and acts would be in accord with the disclosure. In addition, the drawings accompanying the application are for illustrative purposes only, and are not meant to be actual views of any particular material, device, or system.

[0012] As used herein, the term "lower hydrocarbon" means and includes an aliphatic hydrocarbon having from one carbon atom to four carbon atoms (e.g., methane, ethane, ethylene, acetylene, propane, propylene, n-butane, isobutene, butane, isobutene, etc.).

[0013] As used herein, the terms "higher hydrocarbon" and "hydrocarbon product" mean and include an aliphatic or cyclic hydrocarbon having at least one more carbon atom than a lower hydrocarbon used to form the higher hydrocarbon.

[0014] As used herein, the term "cyclic hydrocarbon" means and includes at least one closed ring hydrocarbon, such as an alicyclic hydrocarbon, an aromatic hydrocarbon, or a combination thereof. The cyclic hydrocarbon may include only carbon and hydrogen, or may include carbon, hydrogen, and at least one heteroatom.

[0015] As used herein, the term "heteroatom" means and includes an element other than carbon and hydrogen, such as oxygen (O), nitrogen (N), or sulfur (S).

[0016] As used herein, the terms "catalyst material" and "catalyst" each mean and include a material formulated to promote one or more reactions, resulting in the formation of a product.

[0017] As used herein, the term "negative electrode" means and includes an electrode having a relatively lower electrode potential in an electrochemical cell (i.e., lower than the electrode potential in a positive electrode therein). Conversely, as used herein, the term "positive electrode" means and includes an electrode having a relatively higher electrode potential in an electrochemical cell (i.e., higher than the electrode potential in a negative electrode therein).

[0018] As used herein the term "electrolyte" means and includes an ionic conductor, which can be in a solid state, a liquid state, or a gas state (e.g., plasma).

[0019] As used herein, spatially relative terms, such as "beneath," "below," "lower," "bottom," "above," "upper," "top," "front," "rear," "left," "right," and the like, may be used for ease of description to describe one element's or feature's relationship to another element(s) or feature(s) as illustrated in the figures. Unless otherwise specified, the spatially relative terms are intended to encompass different orientations of the materials in addition to the orientation depicted in the figures. For example, if materials in the figures are inverted, elements described as "below" or "beneath" or "under" or "on bottom of" other elements or features would then be oriented "above" or "on top of" the other elements or features. Thus, the term "below" can encompass both an orientation of above and below, depending on the context in which the term is used, which will be evident to one of ordinary skill in the art. The materials may be otherwise oriented (e.g., rotated 90 degrees, inverted, flipped) and the spatially relative descriptors used herein interpreted accordingly.

[0020] As used herein, the singular forms "a," "an," and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0021] As used herein, "and/or" includes any and all combinations of one or more of the associated listed items.

[0022] As used herein, the term "configured" refers to a size, shape, material composition, material distribution, and arrangement of one or more of at least one structure and at least one apparatus facilitating operation of one or more of the structure and the apparatus in a pre-determined way.

[0023] As used herein, the term "substantially" in reference to a given parameter, property, or condition means and includes to a degree that one of ordinary skill in the art would understand that the given parameter, property, or condition is met with a degree of variance, such as within acceptable manufacturing tolerances. By way of example, depending on the particular parameter, property, or condition that is substantially met, the parameter, property, or condition may be at least 90.0% met, at least 95.0% met, at least 99.0% met, at least 99.9% met, or even 100.0% met.

[0024] As used herein, the term "about" in reference to a given parameter is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the given parameter).

[0025] As used herein, the term "compatible" means that a material does not undesirably react, decompose, or absorb another material, and also that the material does not undesirably impair the chemical and/or mechanical properties of the another material.

[0026] An embodiment of the disclosure will now be described with reference to FIG. **1**, which schematically illustrates a CH_4 activation system **100**. The CH_4 activation system **100** may be used to convert CH_4 into at least one higher hydrocarbon and $H_{2(g)}$. As shown in FIG. **1**, the CH_4 activation system **100** may include at least one CH_4 source **102** (e.g., containment vessel), and at least one electrochemical apparatus **104** in fluid communication with the CH_4 source **102**. The electrochemical apparatus **104** includes a housing structure **114**, and at least one electrochemical cell **106** contained within the housing structure **114**. The electrochemical cell **106** is electrically connected (e.g., coupled) to a power source **116**, and includes a positive electrode **108**, a negative electrode **112**, and a proton-conducting membrane **110** between the positive electrode **108** and the negative electrode **112**. As shown in FIG. **1**, optionally, the CH_4 activation system **100** may also include at least one heating apparatus **118** operatively associated with the electrochemical apparatus **104**.

[0027] During use and operation, the CH_4 activation system **100** directs a CH_4 stream **120** into the electrochemical apparatus **104** to interact with the positive electrode **108** of the electrochemical cell **106**. A potential difference (e.g., voltage) is applied between the positive electrode **108** and the negative electrode **112** of the electrochemical cell **106** by the power source **116** so that as the CH_4 interacts with the positive electrode **108**, H atoms of the CH_4 release their electrons (e^-) to produce methyl radicals (CH_3^+), hydrogen ions (H^+) (i.e., protons), and electrons (e^-) through non-oxidative deprotonation according to the following equation:

$$CH_4 \rightarrow CH_3^+ + H^+ + e^- \quad (1).$$

The generated H^+ permeate (e.g., diffuse) across the proton-conducting membrane **110** to the negative electrode **112**, and the generated e^- are directed to the power source **116** through external circuitry. At the negative electrode **112**, the generated H^+ exiting the proton-conducting membrane **110** react with e received from the power source **116** to form H atoms that the combine to form $H_{2(g)}$ through a hydrogen evolution reaction, according to the following equation:

$$4H^+ + 4e^- \rightarrow 2H_{2(g)} \quad (2).$$

The $H_{2(g)}$ then exits the electrochemical apparatus **104** as a $H_{2(g)}$ stream **126**. At the positive electrode **108**, the produced CH_3^+ undergoes at least one methyl coupling reaction in the presence of a catalyst material of the positive electrode **108** to synthesize at least one higher hydrocarbon. By way of non-limiting example, two (2) produced CH_3^+ may react with one another to produce ethane (C_2H_6), which may then react with additional produced CH_3^+ to produce ethyl radicals ($C_2H_5^+$) according to the following equations:

$$2CH_3^+ \rightarrow C_2H_6 \quad (3).$$

$$C_2H_6 \rightarrow C_2H_5^+ + CH_4 \quad (4).$$

The $C_2H_5^+$ may then be deprotonated to produce ethylene (C_2H_4) according to the following equation:

$$C_2H_5^+ \rightarrow C_2H_4 + H^+ \quad (5).$$

In addition, at least partially depending on the conditions (e.g., catalyst material(s), temperatures, pressures) at the positive electrode **108**, the produced C_2H_4 may undergo at least one ethyl coupling reaction to synthesize at least one other hydrocarbon product, according to the following equation:

$$nC_2H_4 \rightarrow C_{2n}H_{4n} \quad (6).$$

The hydrocarbon product exits the electrochemical apparatus **104** as a hydrocarbon product stream **124**.

[0028] As described in further detail below, the hydrocarbon products synthesized at the positive electrode **108** and the production of $H_{2(g)}$ at the negative electrode **112** may at least partially depend on the material composition and flow rate of the CH_4 stream **120**; the configuration (e.g., size, shape, material composition, material distribution, arrangement) of the positive electrode **108**, including the types, quantities, distribution, and properties (e.g., geometric properties, thermodynamic properties, etc.) of catalyst materials thereof promoting CH_4 deprotonation reactions and coupling reactions (e.g., methyl coupling reactions, ethyl coupling reactions (if any)); the configuration of the proton-conducting membrane **110**, and the impact thereof on the diffusivity (e.g., diffusion rate) of generated H^+ therethrough; the configuration of the negative electrode, including the types, quantities, and properties (e.g., geometric properties, thermodynamic properties, etc.) of catalyst materials thereof promoting hydrogen evolution reactions; and the operational parameters (e.g., temperatures, pressures, etc.) of the electrochemical apparatus **104**. Such operational factors may be controlled (e.g., adjusted, maintained, etc.) as desired to control the types, quantities, and rate of production of the hydrocarbon product(s) synthesized at the positive electrode **108** and to control the quantity and rate of production of the $H_{2(g)}$ produced at the negative electrode **112**. In some embodiments, the hydrocarbon product(s) exiting the electrochemical apparatus **104** in the hydrocarbon product stream **124** may be examined (e.g., through in-line gas chromatography-mass spectrometry (GS-MS)) and compared to a mathematically modeled Anderson-Schulz-Flory distribution to analyze whether or not sufficient coupling reactions are occurring at the positive electrode **108** for the synthesis of one or more desired higher hydrocarbons. One or more operational factors of the CH_4 activation system **100** (e.g., one or more of the type, quantity, and distribution of catalyst material(s) in the positive electrode **108**, the operating temperature of the electrochemical apparatus **104**, etc.) may be adjusted or maintained based on the results of the analysis. Accordingly, the operational factors of the CH_4 activation system **100** may be tailored to facilitate the production of $H_{2(g)}$ and one or more specific higher hydrocarbons from the components (e.g., CH_4) of the CH_4 stream **120**.

[0029] The CH_4 stream **120** may be formed of and include CH_4. In addition, the CH_4 stream **120** may, optionally, include one or more other materials (e.g., molecules), such as one or more other lower hydrocarbons (e.g., one or more C_2 to C_4 hydrocarbons, such as one or more of C_2H_6, propane (C_3H_8), and butane (C_4H_{10})) that may undergo a chemical reaction in the presence of the positive electrode **108** of the electrochemical cell **106** to produce at least one higher hydrocarbon, and/or one or more other materials (e.g., H_2, nitrogen (N_2), etc.). In some embodiments, the CH_4 stream **120** is substantially free of materials other than CH_4. In additional embodiments, the CH_4 stream **120** includes CH_4 and C_2H_6. The CH_4 stream **120** may be substantially gaseous (e.g., may only include a single gaseous phase), may be substantially liquid (e.g., may only include a single liquid phase), or may include a combination of liquid and gaseous phases. The phase(s) of the CH_4 stream **120** (and, hence, a temperature and a pressure of the CH_4 stream **120**) may at least partially depend on the operating temperature of the electrochemical cell **106** of the electrochemical apparatus **104**. In some embodiments, the CH_4 stream **120** is substantially gaseous.

[0030] A single (e.g., only one) CH_4 stream **120** may be directed into the electrochemical apparatus **104** from the CH_4 source **102**, or multiple (e.g., more than one) CH_4 streams **120** may be directed into the electrochemical apparatus **104** from the CH_4 source **102**. If multiple CH_4 streams **120** are directed into the electrochemical apparatus **104**, each of the multiple CH_4 streams **120** may exhibit substantially the same properties (e.g., substantially the same material composition, substantially the same temperature, substantially the same pressure, substantially the same flow rate, etc.), or at least one of the multiple CH_4 streams **120** may exhibit one or more different properties (e.g., a different material composition, a different temperature, a different pressure, a different flow rate, etc.) than at least one other of the multiple CH_4 streams **120**.

[0031] The heating apparatus **118**, if present, may comprise at least one apparatus (e.g., one or more of a combustion heater, an electrical resistance heater, an inductive heater, and an electromagnetic heater) configured and operated to heat one or more of the CH_4 stream **120**, and at least a portion of the electrochemical apparatus **104** to an operating temperature of the electrochemical apparatus **104**. The operating temperature of the electrochemical apparatus **104** may at least partially depend on a material composition of the proton-conducting membrane **110** of the electrochemical cell **106** thereof, as described in further detail below. In some embodiments, the heating apparatus **118** heats one or more of the CH_4 stream **120**, and at least a portion of the electrochemical apparatus **104** to a temperature within a range of from about 150° C. to about 600° C. In additional embodiments, such as in embodiments wherein a temperature of the CH_4 stream **120** is already within the operating temperature range of the electrochemical cell **106** of the electrochemical apparatus **104**, the heating apparatus **118** may be omitted (e.g., absent) from the CH_4 activation system **100**.

[0032] With continued reference to FIG. **1**, the electrochemical apparatus **104**, including the housing structure **114** and the electrochemical cell **106** thereof, is configured and operated to form the hydrocarbon product stream **124** and the $H_{2(g)}$ stream **126** from the CH_4 stream **120**. The housing structure **114** may exhibit any shape (e.g., a tubular shape, a quadrilateral shape, a spherical shape, a semi-spherical shape, a cylindrical shape, a semi-cylindrical shape, truncated versions thereof, or an irregular shape) and size able to contain (e.g., hold) the electrochemical cell **106** therein, to receive and direct the CH_4 stream **120** to the positive electrode **108** of the electrochemical cell **106**, to direct the high hydrocarbon product(s) synthesized at the positive electrode **108** away from the electrochemical apparatus as the hydrocarbon product stream **124**, and to direct the $H_{2(g)}$ formed at the negative electrode **112** of the electrochemical cell **106** away from the electrochemical apparatus **104** as the $H_{2(g)}$ stream **126**. In addition, the housing structure **114** may be formed of and include any material (e.g., glass, metal, alloy, polymer, ceramic, composite, combination thereof, etc.) compatible with the operating conditions (e.g., temperatures, pressures, etc.) of the electrochemical apparatus **104**.

[0033] The housing structure **114** may at least partially define at least one internal chamber **128** at least partially surrounding the electrochemical cell **106**. The electrochemical cell **106** may serve as a boundary between a first region **130** (e.g., an anodic region) of the internal chamber **128** configured and positioned to receive the CH_4 stream **120** and to direct the hydrocarbon product stream **124** from the electrochemical apparatus **104**, and a second region **132** (e.g., a cathodic region) of the internal chamber **128** configured and positioned to receive the $H_{2(g)}$ produced at the positive electrode **108** of the electrochemical cell **106**. Molecules (e.g., CH_4) of the CH_4 stream **120** may be substantially limited to the first region **130** of the internal chamber **128** by the configurations and positions of the housing structure **114** and the electrochemical cell **106**. Keeping the second region **132** of the internal chamber **128** substantially free of molecules from the CH_4 stream **120** circumvents additional processing of the produced $H_{2(g)}$ (e.g., to separate the produced $H_{2(g)}$ from CH_4) that may otherwise be necessary if the components of the CH_4 stream **120** were also delivered to within the second region **132** of the internal chamber **128**.

[0034] As shown in FIG. **1**, the positive electrode **108** and the negative electrode **112** of the electrochemical cell **106** are electrically coupled to a power source **116**, and the proton-conducting membrane **110** is disposed on and between the positive electrode **108** and the negative electrode **112**. The proton-conducting membrane **110** is configured and formulated to conduct H^+ from the positive electrode **108** to the negative electrode **112**, while electrically insulating the negative electrode **112** from the positive electrode **108** and preventing the migration of molecules (e.g., CH_4, CH_3^+, higher hydrocarbons) therethrough. Electrons generated at the positive electrode **108** through the reaction of Equation (1) described above may, for example, flow from the positive electrode **108** into a negative current collector, through the power source **116** and a positive electrode current collector, and into negative electrode **112** to facilitate the production of $H_{2(g)}$ through the reaction of Equation (2) described above.

[0035] The proton-conducting membrane **110** may be formed of and include at least one electrolyte material exhibiting an ionic conductivity (e.g., H^+ conductivity) greater than or equal to about 10^{-2} S/cm (e.g., within a range of from about 10^{-2} S/cm to about 1 S/cm) at one or more temperatures within a range of from about 150° C. to about 600° C. (e.g., from about 200° C. to about 600° C.). In addition, the electrolyte material may be formulated to remain substantially adhered (e.g., laminated) to the positive electrode **108** and the negative electrode **112** at relatively high current densities, such as at current densities greater than or equal to about 0.1 amperes per square centimeter (A/cm^2) (e.g., greater than or equal to about 0.5 A/cm^2, greater than or equal to about 1.0 A/cm^2, greater than or equal to about 2.0 A/cm^2, etc.). For example, the proton-conducting membrane **110** may comprise one or more of a perovskite material, a solid acid material, and a polybenzimidazole (PBI) material. The material composition of the proton-conducting membrane **110** may provide the proton-conducting membrane **110** with enhanced ionic conductivity at a temperature within the range of from about 150° C. to about 600° C. as compared to conventional membranes (e.g., membranes employing conventional electrolyte materials, such as yttria-stabilized zirconia (YSZ)) of conventional electrochemical cells. By way of non-limiting example, the electrolyte material (e.g., perovskite material, solid acid material, PBI material) of the proton-conducting membrane **110** may have orders of magnitude higher ionic conductivity than YSZ at operational temperatures thereof within the range of from about 150° C. to about 600° C.

[0036] In some embodiments, the proton-conducting membrane **110** is formed of and includes at least one perovskite material having an operational temperature (e.g., a temperature at which the H^+ conductivity of the perovskite material is greater than or equal to about 10^{-2} S/cm, such as within a range of from about 10^{-2} S/cm to about 10^{-1} S/cm) within a range of from about 400° C. to about 600° C. By way of non-limiting example, the proton-conducting membrane **110** may comprise one or more of a yttrium- and ytterbium-doped barium-zirconate-cerate (BZCYYb), such as $BaZr_{0.8-y}Ce_yY_{0.2-x}Yb_xO_{3-\delta}$, wherein x and y are dopant levels and δ is the oxygen deficit (e.g., $BaZr_{0.3}Ce_{0.5}Y_{0.1}Yb_{0.1}O_{3-\delta}$); a yttrium- and ytterbium-doped barium-strontium-niobate (BSNYYb), such as $Ba_3(Sr_{1-x}Nb_{2-y}Y_xYb_y)O_{9-\delta}$, wherein x and y are dopant levels and δ is the oxygen deficit; doped barium-cerate ($BaCeO_3$) (e.g., yttrium-doped $BaCeO_3$ (BCY)); doped barium-zirconate ($BaZrO_3$) (e.g., yttrium-doped $BaCeO_3$ (BZY)); barium-yttrium-stannate ($Ba_2(YSn)O_{5.5}$); and barium-calcium-niobate ($Ba_3(CaNb_2)O_9$). In some embodiments, the proton-conducting membrane **110** comprises BZCYYb.

[0037] In further embodiments, the proton-conducting membrane **110** is formed of and includes at least one solid acid material having an operational temperature (e.g., a temperature at which the H^+ conductivity of the solid acid material is greater than or equal to about 10^{-2} S/cm, such as within a range of from about 10^{-2} S/cm to about 1 S/cm) within a range of from about 200° C. to about 400° C. By way of non-limiting example, the proton-conducting membrane **110** may comprise a solid acid phosphate material, such as solid acid cesium dihydrogen phosphate (CsH_2PO_4). The solid acid material may be doped (e.g., doped CsH_2PO_4), or may be undoped (e.g., undoped CsH_2PO_4). In some embodiments, the proton-conducting membrane **110** comprises CsH_2PO_4.

[0038] In additional embodiments, the proton-conducting membrane **110** is formed of and includes at least one PBI material having an operational temperature (e.g., a temperature at which the H^+ conductivity of the PBI material is greater than or equal to about 10^{-2} S/cm, such as within a range of from about 10^{-2} S/cm to about 1 S/cm) within a range of from about 150° C. to about 250° C. By way of non-limiting example, the proton-conducting membrane **110** may comprise a doped PBI, such as phosphoric acid (H_3PO_4) doped PBI. In some embodiments, the proton-conducting membrane **110** comprises H_3PO_4-doped PBI.

[0039] The proton-conducting membrane **110** may be substantially homogeneous or may be substantially heterogeneous. As used herein, the term "homogeneous" means amounts of a material do not vary throughout different portions (e.g., different lateral and longitudinal portions) of a structure. Conversely, as used herein, the term "heterogeneous" means amounts of a material vary throughout different portions of a structure. Amounts of the material may vary stepwise (e.g., change abruptly), or may vary continuously (e.g., change progressively, such as linearly, parabolically) throughout different portions of the structure. In some embodiments, the proton-conducting membrane **110** is substantially homogeneous. In additional embodiments, the proton-conducting membrane **110** is heterogeneous. The proton-conducting membrane **110** may, for example, be formed of and include a stack of at least two (e.g., at least three, at least four, etc.) different materials. As a non-limiting example, the proton-conducting membrane **110** may comprise a stack of at least two (e.g., at least three, at least four, etc.) different perovskite materials individually having an operational temperature within a range of from about 400° C. to about 600° C. As another non-limiting example, the proton-conducting membrane **110** may comprise a stack of at least two (e.g., at least three, at least four, etc.) different solid acid materials individually having an operational temperature within a range of from about 200° C. to about 400° C. As a further non-limiting example, the proton-conducting membrane **110** may comprise a stack of at least two (e.g., at least three, at least four, etc.) different PBI materials individually having an operational temperature within a range of from about 150° C. to about 250° C.

[0040] The proton-conducting membrane **110** may exhibit any desired dimensions (e.g., length, width, thickness) and any desired shape (e.g., a cubic shape, cuboidal shape, a tubular shape, a tubular spiral shape, a spherical shape, a semi-spherical shape, a cylindrical shape, a semi-cylindrical shape, a conical shape, a triangular prismatic shape, a truncated version of one or more of the foregoing, and irregular shape). The dimensions and the shape of the proton-conducting membrane **110** may be selected such that the proton-conducting membrane **110** substantially intervenes between opposing surfaces of the positive electrode **108** and the negative electrode **112**, and exhibits an H^+ conductivity greater than or equal to about 10^{-2} S/cm (e.g., from about 10^{-2} S/cm to about 1 S/cm) at a temperature within a range of from about 150° C. to about 600° C. A thickness of the proton-conducting membrane **110** may be within a range of from about 5 micrometers (μm) to about 1000 μm, and may at least partially depend on the material composition of the proton-conducting membrane **110**. For example, a proton-conducting membrane **110** formed of and including at least one perovskite material may have a thickness with a range of from about 5 μm to about 1000 μm; a proton-conducting membrane **110** formed of and including at least one solid acid material may have a thickness with a range of from about 5 μm to about 1000 μm; and a proton-conducting membrane **110** formed of and including at least one PBI material may have a thickness with a range of from about 50 μm to about 1000 μm.

[0041] The positive electrode **108** and the negative electrode **112** may individually be formed of and include at least one catalyst-doped material compatible with the material composition of the proton-conducting membrane **110** and the operating conditions (e.g., temperature, pressure, current density, etc.) of the electrochemical cell **106**, and facilitating the formation of the hydrocarbon product stream **124** and the $H_{2(g)}$ stream **126** from the CH_4 stream **120** at an operational temperature within the range of from about 150° C. to about 600° C. Accordingly, the material compositions of the positive electrode **108** and the negative electrode **112** may be selected relative to one another, the material composition of the proton-conducting membrane **110**, the material composition of the CH_4 stream **120**, and the operating conditions of the electrochemical cell **106**.

[0042] The catalyst-doped material of the positive electrode **108** includes at least one catalyst material thereon, thereover, and/or therein that accelerates reaction rates at the positive electrode **108** to produce CH_3^+, H^+, and e^- from

CH_4 in accordance with Equation (1) above, and that also accelerates reaction rates at the positive electrode **108** to synthesize one or more higher hydrocarbons from the produced CH_3^+ (e.g., in accordance with one or more of Equations (3) through (6) above). The catalyst material may, for example, comprise a metallic material formulated to accelerate reaction rates at the positive electrode **108** to produce CH_3^+, H^+, and e^- from CH_4, and to accelerate reaction rates for the synthesis of higher hydrocarbons from the produced CH_3^+. In some embodiments, the catalyst material comprises elemental particles of a first metal formulated to accelerate reaction rates at the positive electrode **108** to produce CH_3^+, H^+, and e^- from CH_4, and additional elemental particles of a second metal discrete from the elemental particles of the first metal and formulated to accelerate reaction rates for the synthesis of higher hydrocarbons from the produced CH_3^+. In additional embodiments, the catalyst material comprises alloy particles individually including an alloy comprising the first metal and the second metal. In further embodiments, the catalyst material comprises composite particles including one of the first metal and the second metal partially (e.g., less than completely) coating (e.g., covering, encapsulating) the other of the first metal and the second metal, such as composite particles individually including a shell of the second metal partially coating a core of the first metal, and/or composite particles individually including a shell of the first metal partially coating a core of the second metal. In yet further embodiments, the catalyst material comprises composite particles including an alloy including one of the first metal and the second metal partially coating the another alloy including the other of the first metal and the second metal, such as composite particles individually including a shell of an alloy including the second metal partially coating a core of another alloy including the first metal, and/or composite particles individually including a shell of an alloy including the first metal partially coating a core of another alloy including the second metal. In still further embodiments, the catalyst material comprises composite particles including one of the first metal and the second metal partially coating an alloy including the other of the first metal and the second metal, such as composite particles individually including a shell of the second metal partially coating a core of an alloy including the first metal, and/or composite particles individually including a shell of the first metal partially coating a core of an alloy including the second metal. In yet still further embodiments, the catalyst material comprises composite particles including an alloy including one of the first metal and the second metal partially coating the other of the first metal and the second metal, such as composite particles individually including a shell of an alloy including the second metal partially coating a core of the first metal, and/or composite particles individually including a shell of an alloy including the first metal partially coating a core of the second metal.

[0043] Particles (e.g., elemental particles, alloy particles, composite particles) of the catalyst material of the catalyst-doped material of the positive electrode **108** may be nano-sized (e.g., individually having a cross-sectional width or diameter less than about one (1) μm, such as less than or equal to about 100 nanometers (nm), less than or equal to about 20 nm, or less than or equal to about 10 nm). In addition, the catalyst-doped material of the positive electrode **108** may exhibit any amount (e.g., concentration) and distribution of the catalyst material and any ratio of components thereof (e.g., any ratio of a first metal formulated to accelerate reaction rates at the positive electrode **108** to produce CH_3^+, H^+, and e^- from CH_4 to a second metal formulated to accelerate reaction rates for the synthesis of higher hydrocarbons from the produced CH_3^+) facilitating desired CH_4 deprotonation reaction rates and desired coupling reaction rates (e.g., methyl coupling reaction rates, ethyl coupling reaction rates (if any), etc.) at the positive electrode **108**.

[0044] The catalyst-doped material of the negative electrode **112** includes at least one catalyst material thereon, thereover, and/or therein that accelerates reaction rates at the negative electrode **112** to produce $H_{2(g)}$ from H^+ and e^- in accordance with Equation (2) above. The catalyst material may, for example, comprise a metallic material including at least one metal, such as one or more of Ni and platinum (Pt), formulated to accelerate reaction rates at the negative electrode **112** to produce $H_{2(g)}$ from H^+ and e^- in accordance with Equation (2) above. The catalyst material of the catalyst-doped material of the negative electrode **112** may comprise nano-sized particles (e.g., nano-sized elemental particles, nano-sized alloy particles, and/or nano-sized composite particles). The catalyst-doped material of the negative electrode **112** may exhibit any amount (e.g., concentration) and distribution of the catalyst material any ratio of components thereof facilitating desired hydrogen evolution reaction (HER) rates at the negative electrode **112**.

[0045] By way of non-limiting example, if the proton-conducting membrane **110** comprises a perovskite material (e.g., a BZCYYb, a BSNYYb, a doped $BaCeO_3$, a doped $BaZrO_3$, $Ba_2(YSn)O_{5.5}$, $Ba_3(CaNb_2)O_9$, etc.) having an operational temperature within a range of from about 400° C. to about 600° C., the positive electrode **108** may comprise one or more of (e.g., two or more of, three or more of) ruthenium (Ru), rhodium (Rh), nickel (Ni), iridium (Ir), molybdenum (Mo), zinc (Zn), and iron (Fe); and the negative electrode **112** may comprise a catalyst-doped perovskite material. The positive electrode **108** may, for example, comprise a catalyst-doped material including elemental particles individually including Ru, Rh, Ni, Ir, Mo, Zn, or Fe; alloy particles individually including one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe; composite particles (e.g., core/shell particles) individually including silicon dioxide (SiO_2) and one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe, such as composite particles of Fe and SiO_2 (Fe@SiO_2) and/or composite particles of Mo and SiO_2 (Mo@SiO_2); composite particles individually including silicon carbide (SiC) and one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe, such as composite particles of Fe and SiC (Fe@SiC) and/or composite particles of Mo and SiC (Mo@SiC); aluminosilicate zeolite (e.g., Zeolite Socony Mobil-5 (ZSM-5), Hollow Zeolite Socony Mobil-5 (HZSM-5)) structures embedded with one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe, such as Fe/HZSM-5 and/or Mo/HZSM-5; particles individually including a carbide of one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe, such as molybdenum carbide (Mo_2C); and/or particles individually including a multi-metallic compound (e.g., a bimetallic compound, a trimetallic compound) comprising two or more (e.g., two, three, more than three) of Ru, Rh, Ni, Ir, Mo, Zn, and Fe. In addition, the negative electrode **112** may, for example, comprise a cermet material comprising at least one catalyst material including Ni, and at least one perovskite, such as a Ni/perovskite cermet (Ni-perovskite) material (e.g., Ni—BZCYYb, Ni—BSNYYb, Ni—$BaCeO_3$, Ni—$BaZrO_3$, Ni—$Ba_2(YSn)O_{5.5}$, Ni—$Ba_3(CaNb_2)O_9$). In some embodiments, the proton-conducting membrane **110** comprises BZCYYb, the positive electrode **108** comprises Fe@SiO_2, and the negative electrode **112** comprises Ni—BZCYYb. In additional embodiments, the proton-conducting membrane **110** comprises BZCYYb, the positive electrode **108** comprises Mo_2C, and the negative electrode **112** comprises Ni—BZCYYb.

[0046] As another non-limiting example, if the proton-conducting membrane **110** comprises a solid acid material (e.g., a doped CsH_2PO_4, an undoped CsH_2PO_4) having an operational temperature within a range of from about 200° C. to about 400° C., the positive electrode **108** may comprise one or more of Ni, and a metallic material (e.g., an alloy, a bimetallic compound) including Ru and cobalt (Co); and the negative electrode **112** may comprise a cermet material comprising at least one catalyst material including Pt and at least one solid acid. The positive electrode **108** may, for example, comprise Ni; and/or a Ru—Co bimetallic compound. In addition, the negative electrode **112** may, for example, comprise a cermet material comprising Pt and CsH_2PO_4 (Pt—CsH_2PO_4 cermet). In some embodiments, the positive electrode **108** comprises Ni, and the negative electrode **112** comprises Pt—CsH_2PO_4 cermet. In additional embodiments, the positive electrode **108** comprises a Ru—Co bimetallic compound, and the negative electrode **112** comprises Pt—CsH_2PO_4 cermet.

[0047] As a further non-limiting example, if the proton-conducting membrane **110** comprises a PBI material (e.g., a doped PBI) having an operational temperature within a range of from about 150° C. to about 250° C., the positive electrode **108** may comprise a metallic material (e.g., an alloy, a bimetallic compound, a trimetallic compound) including two or more of Pd, Co, and platinum (Pt), and the negative electrode **112** may comprise one or more of Ni and Pt. The positive electrode **108** may, for example, comprise an alloy of Pd and one of more of Pt and Co (e.g., a Pd—Co alloy, a Pd—Pt alloy, a Pd—Pt—Co alloy); a bimetallic compound comprising Pd and one of Co and Pt; and/or a trimetallic compound including Pd, Pt, and Co. In addition, the negative electrode **112** may, for example, comprise one or more of elemental (e.g., non-alloyed, non-compounded) Ni, elemental Pt, a Ni alloy, and a Pt alloy. In some embodiments, the positive electrode **108** comprises a Pd—Co bimetallic compound, and the negative electrode **112** comprises one or more of Ni and Pt. In additional embodiments, the positive electrode **108** comprises a Pd—Pt bimetallic compound, and the negative electrode **112** comprises one or more of Ni and P. In further embodiments, the positive electrode **108** comprises a Pd—Pt—Co trimetallic compound, and the negative electrode **112** comprises one or more of Ni and P.

[0048] The positive electrode **108** and the negative electrode **112** may individually exhibit any desired dimensions (e.g., length, width, thickness) and any desired shape (e.g., a cubic shape, cuboidal shape, a tubular shape, a tubular spiral shape, a spherical shape, a semi-spherical shape, a cylindrical shape, a semi-cylindrical shape, a conical shape, a triangular prismatic shape, a truncated version of one or more of the foregoing, and irregular shape). The dimensions and the shapes of the positive electrode **108** and the negative electrode **112** may be selected relative to the dimensions and the shape of the proton-conducting membrane **110** such that the proton-conducting membrane **110** substantially intervenes between opposing surfaces of the positive electrode **108** and the negative electrode **112**. Thicknesses of the positive electrode **108** and the negative electrode **112** may individually be within a range of from about 10 μm to about 1000 μm.

[0049] The electrochemical cell **106**, including the positive electrode **108**, the proton-conducting membrane **110**, and the negative electrode **112** thereof, may be formed through conventional processes (e.g., rolling process, milling processes, shaping processes, pressing processes, consolidation processes, etc.), which are not described in detail herein. The electrochemical cell **106** may be mono-faced or bi-faced and may have a prismatic, folded, wound, cylindrical, or jelly rolled configuration. The electrochemical cell **106** may be placed within the housing structure **114** to form the electrochemical apparatus **104**, and may be electrically connected to the power source **116**.

[0050] Although the electrochemical apparatus **104** is depicted as including a single (i.e., only one) electrochemical cell **106** in FIG. **1**, the electrochemical apparatus **104** may include any number of electrochemical cells **106**. Put another way, the electrochemical apparatus **104** may include a single (e.g., only one) electrochemical cell **106**, or may include multiple (e.g., more than one) electrochemical cells **106**. If the electrochemical apparatus **104** includes multiple electrochemical cells **106**, each of the electrochemical cells **106** may be substantially the same (e.g., exhibit substantially the same components, component sizes, component shapes, component material compositions, component material distributions, component positions, component orientations, etc.) and may be operated under substantially the same conditions (e.g., substantially the same temperatures, pressures, flow rates, etc.), or at least one of the electrochemical cells **106** may be different (e.g., exhibit one or more of different components, different component sizes, different component shapes, different component material compositions, different component material distributions, different component positions, different component orientations, etc.) than at least one other of the electrochemical cells **106** and/or may be operated under different conditions (e.g., different temperatures, different pressures, different flow rates, etc.) than at least one other of the electrochemical cells **106**. By way of non-limiting example, one of the electrochemical cells **106** may be configured for and operated under a different temperature (e.g., different operating temperature resulting from a different material composition of one of more components thereof, such as a different material composition of the proton-conducting membrane **110** thereof) than at least one other of the electrochemical cells **106**. In some embodiments, two of more electrochemical cells **106** are provided in parallel with one another within the housing structure **114** of the electrochemical apparatus **104**, and individually produce a portion of the hydrocarbon product(s) directed out of the electrochemical apparatus **104** as the hydrocarbon product stream **124** and a portion of the $H_{2(g)}$ directed out of the electrochemical apparatus **104** as the $H_{2(g)}$ stream **126**.

[0051] In addition, although the CH_4 activation system **100** is depicted as including a single (i.e., only one) electrochemical apparatus **104** in FIG. **1**, the CH_4 activation system **100** may include any number of electrochemical apparatuses **104**. Put another way, the CH_4 activation system **100** may include a single (e.g., only one) electrochemical apparatus **104**, or may include multiple (e.g., more than one) electrochemical apparatuses **104**. If the CH_4 activation system **100** includes multiple electrochemical apparatuses **104**, each of the electrochemical apparatuses **104** may be substantially the same (e.g., exhibit substantially the same components, component sizes, component shapes, component material compositions, component material distributions, component positions, component orientations, etc.) and may be operated under substantially the same conditions (e.g., substantially the same temperatures, pressures, flow rates, etc.), or at least one of the electrochemical apparatus **104** may be different (e.g., exhibit one or more of different components, different component sizes, different component shapes, different component material compositions, different component material distributions, different component positions, different component orientations, etc.) than at least one other of the electrochemical apparatuses **104** and/or may be operated under different conditions (e.g., different temperatures, different pressures, different flow rates, etc.) than at least one other of the electrochemical apparatuses **104**. By way of non-limiting example, one of the electrochemical apparatuses **104** may be configured for and operated under a different temperature (e.g., a different operating temperature resulting from a different material composition of one of more components of an electrochemical cell **106** thereof, such as a different material composition of the proton-conducting membrane **110** thereof) than at least one other of the electrochemical apparatuses **104**. In some embodiments, two of more electrochemical apparatuses **104** are provided in parallel with one another. Each of the two of more electrochemical apparatuses **104** may individually receive a CH_4 stream **120** and may individually form a hydrocarbon product stream **124** and a $H_{2(g)}$ stream **126**.

[0052] Still referring to FIG. **1**, the hydrocarbon product stream **124** and the $H_{2(g)}$ stream **126** exiting the electrochemical apparatus **104** may individually be utilized or disposed of as desired. In some embodiments, the hydrocarbon product stream **124** and the $H_{2(g)}$ stream **126** are individually delivered into one or more storage vessels for subsequent use, as desired. In additional embodiments, at least a portion of one or more of the hydrocarbon product stream **124** and the $H_{2(g)}$ stream **126** may be utilized (e.g., combusted) to heat one or more components (e.g., the heating apparatus **118** (if present); the electrochemical apparatus **104**; etc.) and/or streams (e.g., the CH_4 stream **120**) of the CH_4 activation system **100**. By way of non-limiting example, as shown in FIG. **1**, if the heating apparatus **118** (if present) is a combustion-based apparatus, at least a portion of one or more of the hydrocarbon product stream **124** and the $H_{2(g)}$ stream **126** may be directed into the heating apparatus **118** and undergo an combustion reaction to efficiently heat one or more of the CH_4 stream **120** entering the electrochemical apparatus **104** and at least a portion of the electrochemical apparatus **104**. Utilizing the hydrocarbon product stream **124** and/or the $H_{2(g)}$ stream **126** as described above may reduce the electrical power requirements of the CH_4 activation system **100** by enabling the utilization of direct thermal energy.

[0053] Thermal energy input into (e.g., through the heating apparatus **118** (if present)) and/or generated by the electrochemical apparatus **104** may also be used to heat one or more other components and/or streams (e.g., the CH_4 stream **120**) of the CH_4 activation system **100**. By way of non-limiting example, the hydrocarbon product stream **124** and/or the $H_2(g)$ stream **126** exiting the electrochemical apparatus **104** may be directed into a heat exchanger configured and operated to facilitate heat exchange between the hydrocarbon product stream **124** and/or the $H_{2(g)}$ stream **126** of the CH_4 activation system **100** and one or more other relatively cooler streams (e.g., the CH_4 stream **120**) of the CH_4 activation system **100** to transfer heat from the hydrocarbon product stream **124** and/or the $H_{2(g)}$ stream **126** to the relatively cooler stream(s) to facilitate the recovery of the thermal energy input into and generated within the electrochemical apparatus **104**. The recovered thermal energy may increase process efficiency and/or reduce operational costs without having to react (e.g., combust) higher hydrocarbon products of the hydrocarbon product stream **124** and/or $H_{2(g)}$ of the $H_{2(g)}$ stream **126**.

[0054] The methods, systems (e.g., the CH_4 activation system **100**), and apparatuses (e.g., the electrochemical apparatus **104**, including the electrochemical cell **106** thereof) of the disclosure facilitate the simple and efficient co-production of higher hydrocarbons (e.g., butylene, gasoline, diesel, etc.) and $H_{2(g)}$ from CH_4 at intermediate temperatures, such as temperatures within a range of from about 150° C. to about 600° C. The methods, systems, and apparatuses of the disclosure may reduce one or more of the time (e.g., processing steps), costs (e.g., material costs), and energy (e.g., thermal energy, electrical energy, etc.) required to produce higher hydrocarbons from CH_4 relative to conventional methods, systems, and apparatuses of producing higher hydrocarbons from CH_4. The methods, systems, and apparatuses of the disclosure may be more efficient, durable, and reliable that conventional methods, conventional systems, and conventional apparatuses of producing higher hydrocarbons and $H_{2(g)}$.

1. A methane (CH_4) activation system, comprising:

a source of CH_4; and

an electrochemical apparatus in fluid communication with the source of CH_4, and comprising:

a housing structure configured and positioned to receive a CH_4 stream from the source of CH_4; and

an electrochemical cell within an internal chamber of the housing structure, and comprising:

a positive electrode comprising a catalyst material formulated to accelerate reaction rates to produce CH_3^+, H^+, and e^- through non-oxidative deprotonation of CH_4, and to accelerate reaction rates to synthesize at least one hydrocarbon product from the produced CH_3^+;

a negative electrode comprising another catalyst material formulated to accelerate reaction rates to produce $H_{2(g)}$ from the produced H^+ and e^-; and

a proton-conducting membrane between the positive electrode and the negative electrode and comprising an electrolyte material having an ionic conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 600° C.

2. The CH_4 activation system of claim **1**, wherein the electrolyte material of the proton-conducting membrane is selected from the group consisting of:

a perovskite material having a H^+ conductivity greater than about 10^{-2} S/cm at one or more temperatures within a range of from about 400° C. to about 600° C.;

a solid acid material having a H^+ conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 200° C. to about 400° C.; and

a polybenzimidazole (PBI) material having a H^+ conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 200° C.

3. The CH_4 activation system of claim **2**, wherein:

the proton-conducting membrane comprises BZCYYb;

the catalyst material of the positive electrode comprises one or more of Fe@SiO_2 and Mo_2C; and

the another catalyst material of the negative electrode comprises Ni—BZCYYb.

4. The CH_4 activation system of claim **2**, wherein:

the proton-conducting membrane comprises CsH_2PO_4;

the catalyst material of the positive electrode comprises one or more of Ni and a Ru—Co bimetallic compound; and

the another catalyst material of the negative electrode comprises Pt—CsH_2PO_4.

5. The CH_4 activation system of claim **2**, wherein:

the proton-conducting membrane comprises H_3PO_4-doped PBI;

the catalyst material of the positive electrode comprises one or more of a Pd—Co bimetallic compound, a Pd—Pt bimetallic compound, and a Pd—Pt—Co trimetallic compound; and

the another catalyst material of the negative electrode comprises one or more of Ni and Pt.

6. The CH_4 activation system of claim **1**, further comprising a heating apparatus configured and positioned to heat one or more of the CH_4 stream and at least a portion of the electrochemical apparatus.

7. The CH_4 activation system of claim **1**, wherein the internal chamber comprises:

a first region configured and positioned to receive the CH_4 stream and direct a hydrocarbon product stream from the electrochemical apparatus; and

a second region configured and positioned to receive the produced $H_{2(g)}$,

the electrochemical cell separating the first region from the second region and the CH_4 substantially confined to the first region.

8. The CH_4 activation system of claim **1**, wherein the CH_4 stream comprises CH_4 and at least one C_2 to C_4 hydrocarbon compound.

9. A methane (CH_4) activation system, comprising:

a source of CH_4; and

an electrochemical apparatus in fluid communication with the source of CH_4, and comprising:

a housing structure configured and positioned to receive a CH_4 stream from the source of CH_4; and

an electrochemical cell within an internal chamber of the housing structure, and comprising:

a positive electrode comprising a catalyst-doped material including particles comprising one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe;

a negative electrode comprising a catalyst-doped perovksite material formulated to accelerate reaction rates to produce $H_{2(g)}$ from the produced H^+ and e; and

a proton-conducting membrane between the positive electrode and the negative electrode and comprising an perovskite material having an ionic conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 600° C.

10. The CH_4 activation system of claim **9**, wherein the catalyst-doped material of the positive electrode includes composite particles individually comprising:

one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe; and

one or more of silicon dioxide (SiO_2) and silicon carbide (SiC).

11. The CH_4 activation system of claim **10**, wherein the composite particles individually comprise one of:

Fe and SiO_2 (Fe@SiO_2);

Mo and SiO_2 (Mo@SiO_2);

Fe and SiC (Fe@SiC); and

Mo and SiC (Mo@SiC).

12. The CH_4 activation system of claim **9**, wherein the catalyst-doped perovskite material of the negative electrode comprises Ni.

13. The CH_4 activation system of claim **9**, wherein the catalyst-doped material of the positive electrode includes one or more of elemental Ru particles, elemental Rh particles, elemental Ni particles, elemental Ir particles, elemental Mo particles, elemental Zn particles, and elemental Fe particles.

14. The CH_4 activation system of claim **9**, wherein the catalyst-doped material of the positive electrode includes a carbide of one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe.

15. An electrochemical apparatus, comprising:

a positive electrode comprising a catalyst-doped material formulated to accelerate reaction rates to produce CH_3^+, H^+, and e^- through non-oxidative deprotonation of CH_4;

a negative electrode comprising another catalyst-doped material formulated to accelerate reaction rates to produce $H_{2(g)}$ from the produced H^+ and e^-; and

a proton-conducting membrane between the positive electrode and the negative electrode and comprising one or more of a perovskite material, a solid acid material, and a polybenzimidazole (PBI) material and exhibiting an ionic conductivity greater than or equal to about 10^{-2} S/cm at one or more temperatures within a range of from about 150° C. to about 600° C.

16. The electrochemical apparatus of claim **15**, wherein the catalyst-doped material of the positive electrode is further formulated to accelerate at least one coupling reaction to synthesize at least one hydrocarbon product from the produced CH_3^+.

17. The electrochemical apparatus of claim **15**, wherein:

the proton-conducting membrane comprises the solid acid material;

the catalyst-doped material of the positive electrode comprises one or more of Ni and a metallic material comprising Ru and Co; and

the another catalyst-doped material of the negative electrode comprises a cermet material comprising Pt and CsH_2PO_4.

18. The electrochemical apparatus of claim **15**, wherein:

the proton-conducting membrane comprises the PBI material;

the catalyst-doped material of the positive electrode comprises a metallic material comprising two or more of Pd, Co, and Pt; and the another catalyst-doped material of the negative electrode comprises one or more of Ni and Pt.

19. The electrochemical apparatus of claim **15**, wherein:

the proton-conducting membrane comprises a perovskite material;

the catalyst-doped material of the positive electrode comprises one or more of Ru, Rh, Ni, Ir, Mo, Zn, and Fe; and

the another catalyst-doped material of the negative electrode comprises a cermet material comprising Ni.

20. The electrochemical apparatus of claim **15**, wherein the proton-conducting membrane is formulated to remain substantially adhered to the positive electrode and the negative electrode at current densities greater than or equal to about 0.1 A/cm^2.

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