

MEMBRANE ELECTROLYSIS CELL AND METHOD OF USE

FIELD OF INVENTION

[0001] The present invention relates to the field of electro-chemistry, particularly electrolysis.

[0002] In one form, the invention relates to an electrolytic method for gas production.

[0003] In another form there is provided an electrolytic device for use in gas synthesis.

[0004] In one particular aspect the present invention is suitable for use in water splitting.

[0005] It will be convenient to hereinafter describe the invention in relation to splitting to produce hydrogen and oxygen, however it should be appreciated that the present invention is not limited to that use only and may be used for production of other compounds such as, but not limited to, ammonia (from water and atmospheric nitrogen) or methane, methanol and ethanol from water and carbon dioxide.

BACKGROUND ART

[0006] Traditionally, electrolysis processes for water splitting have relied on electrochemical phenomena. The overall reaction of water splitting, $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ produces oxygen and hydrogen gases as end products. These gases need to be kept separate for later individual use and to avoid production of an explosive gas mixture.

[0007] The electrolyser used for water splitting electrolysis is well known in the prior art and typically comprises two electrodes separated by a membrane and immersed in water. Salts may be added to the water to increase electrical conductivity. Passage

of an electric current across the electrodes causes water to be reduced by the supply of electrons from the cathode and hydrogen gas is formed. A corresponding oxidation reaction occurs at the anode to generate gaseous oxygen.

[0008] Two main types of water splitting electrolyzers used in the past are (i) alkaline electrolyzers, typically including an electrolyte in the form of a gel, and (ii) proton exchange membrane (PEM) electrolyzers. Membrane electrode assemblies (MEAs) typically have a multi-layered structure comprising the PEM, a current collecting electrode and an electro-catalyst layer on each side.

[0009] In recent years a third type of electrolyser has been developed and includes a membrane based on oxide materials such as ceramics. Solid oxide electrolyzers allow for high-temperature operation increasing the electrolysis reaction kinetics and reaction rate.

[0010] More recently, new types of gas-to-gas reactors have been developed as described in International patent publication WO 2016/148637. The concept relies on evaporating water and subsequent separation of hydrogen and oxygen. This concept overcomes a number of limitations associated with traditional water-based electrolyzers. In particular, the concept has the advantage that no gas bubbles are formed on the electrode, a phenomenon which over time reduces the active surface of the electrode and effectively decreases the conversion efficiency.

[0011] Liquid polymers have been used as electrolytes in batteries for many decades, but hydrogels are far less utilised. In the past, some efforts have been made to use hydrogels in batteries and fuel cells as electrolytes. For example, alkaline hydrogel electrolytes have been produced by physical cross-linking using poly(vinyl alcohol) and potassium hydroxide and used in a dual role – as electrolyte and barrier in Ni-MH cells. (Osinska-Broniarz et al., Chemik 2015, 69, 12, 852-861).

[0012] Hydrogels have also been used as membrane electrolytes in application such as fuel cells. For example, direct borohydride fuel cells have been constructed

with polymer electrolyte membranes consisting of ionically cross-linked chitosan hydrogel. (Choudhury et al, J. Power Sources, 210, 2012, 358-365) However, such membranes have not previously been suitable for applications such as batteries or water splitting by electrolysis.

[0013] The prior art typically teaches carrying out water electrolysis reactions in the vapour phase using liquid electrolyte or solid-oxide electrolyte cells. The technology of vapour electrolysis cells is at an advanced stage. (Donitz, W. and Erdle, E., Int. J. of Hydrogen Energy, 10(5), 1985, p. 291-295; Salzano et al., Int. J. of Hydrogen energy, 10(12) 1985, 801-809) By contrast, hydrogel electrolyte or hydrogel cells are not taught by the prior art as being suitable for water electrolysis.

[0014] Hydrogel materials have instead been of interest for supercapacitor and rechargeable battery applications because their structures consist of a cross-linked network of polymer chains having interstitial spaces filled with solvent water. Hydrogels are thus both wet and soft, making them ideal candidates for electrolyte materials in flexible energy storage devices, and rechargeable batteries. These uses are reviewed for example in prior art document, *Hydrogel Electrolytes for Flexible Aqueous Energy Storage Devices* (Wang et al., Adv. Functional Materials 2018, 28, 1804560).

[0015] It is to be appreciated that any discussion of documents, devices, acts or knowledge in this specification is included to explain the context of the present invention. Further, the discussion throughout this specification comes about due to the realisation of the inventor and/or the identification of certain related art problems by the inventor. Moreover, any discussion of material such as documents, devices, acts or knowledge in this specification is included to explain the context of the invention in terms of the inventor's knowledge and experience and, accordingly, any such discussion should not be taken as an admission that any of the material forms part of the prior art base or the common general knowledge in the relevant art in Australia, or elsewhere, on or before the priority date of the disclosure and claims herein.

SUMMARY OF INVENTION

[0016] An object of the present invention is to provide a membrane electrolyser and method of electrolysis for gas synthesis.

[0017] A further object of the present invention is to improve the efficiency of electrolytic reactions used for synthesis.

[0018] A further object of the present invention is to alleviate at least one disadvantage associated with the related art.

[0019] It is an object of the embodiments described herein to overcome or alleviate at least one of the above noted drawbacks of related art systems or to provide a useful alternative to related art systems.

[0020] In a first aspect of embodiments described herein there is provided an electrolytic cell having an electric circuit comprising an anode and a cathode separated by a hydrogel membrane,

wherein the hydrogel membrane comprises a hydrophilic polymer and acts as an electrolyte.

[0021] Preferably, water absorbed by the polymer is electrolysed when an electric current passes through the electric circuit.

[0022] In another aspect of embodiments described herein there is provided a method of electrolysis, the method comprising the steps of;

locating a hydrogel membrane comprising a hydrophilic polymer between an anode and a cathode of an electric circuit,

absorbing liquid into the hydrogel membrane,

passing an electric current through the electric circuit.

[0023] In another aspect of embodiments described herein there is provided a method of electrolysis of water, the method comprising the steps of;

locating a hydrogel membrane comprising a hydrophilic polymer between an anode and a cathode of an electric circuit,

absorbing water into the hydrogel membrane,

passing an electric current through the electric circuit such that the water in the hydrogel membrane is reduced to hydrogen at the cathode and oxygen forms at the anode.

[0024] Preferably the gas produced at the electrodes diffuses out of the cell via the polymer membrane, separating the gas from the reaction at the electrode. Preferably the gas is separated without significant bubble formation on the electrode. Avoiding bubble formation permits reactions such as water splitting to be achieved with a low over-potential, thereby contributing to the efficiency of the electrolytic cell.

Hydrogel Membrane

[0025] The hydrogel membrane preferably comprises a hydrophilic polymer which can absorb a large proportion of water very rapidly and has a robust physical structure. A hydrogel is a macromolecular polymer gel which can hydrogen-bond molecules of water within interstices located throughout a network of crosslinked polymer chains.

[0026] Preferably, the water content in the polymer membrane can be as high as 98 wt% of the polymer, but typically the water content is at least 80 wt%, preferably at least 90 wt%. The electrolytic splitting is effectively carried out in a hydrogel environment.

[0027] It is also preferred that the membrane has sufficient mechanical strength to withstand compression pressure of up to 50 bar, preferably more, without substantial alteration in performance.

[0028] Hydrophilic polymers typically include charged functional groups. In a preferred embodiment the hydrophilic polymer of the present invention is chosen from

the group comprising acrylic acid, acrylamide, maleic anhydride, polyacrylic acid, polyacrylamide, polyvinyl alcohol polymers and copolymers thereof. The membrane may comprise one or more polymers. The main composition of the membrane is preferably the product of a copolymer of poly(sodium acrylate-co-acrylamide) with some other ingredients to reinforce the mechanical strength or tune the hydrophilicity.

[0029] In a particularly preferred embodiment the membrane is formed from reaction of a copolymer of poly(sodium acrylate-co-acrylamide) with N,N'-methylenebisacrylamide crosslinker.

[0030] During electrolysis water in the polymer membrane is converted to hydrogen and oxygen and it will be necessary to compensate for the water loss. The polymer membrane must be adequately hydrated at all times during electrolysis because dehydration can adversely affect the chemical and mechanical properties of the membrane, potentially causing the membrane to break or wear off. As such, water influx into the membrane preferably balances the amount of water converted to hydrogen and oxygen.

[0031] A number of water management strategies can be used to ensure constant hydration of the polymer membrane at a desired level. In a preferred embodiment, the desired level of water can be calculated by a simple mathematical model based on parameters such as temperature, voltage and current of the electric circuit, or hydrogen flow output.

[0032] In a preferred embodiment, the membrane is hydrated by circulating liquid water through the cell or by introducing water vapour to the polymer membrane. Other suitable hydration methods may also be used. For example, European patent 2 463 407 (Astrium GmbH, corresponding to US 13/991,648) describes pumping water into microchannels in a hydrophobic membrane. US patent 2014 0224668 (Jehle et al.) describes a hydrophobic membrane for electrolytic water splitting, the membrane being supplied with liquid water in a passive manner from a reservoir, without using a

pump. Water from the reservoir may pass by capillary effect via at least one cavity structure in the membrane.

[0033] As a person skilled in the art will readily realise, an electrolytic system may be formed according to the present invention, comprising a plurality of electrolytic cells according to the present invention, the electrolytic cells being connected. Each electrolytic cell may have separate or common water feeds. In particular, single electrolytic cells of the present invention can be stacked in a manner well known in the prior art to increase the power capacity or hydrogen generation.

[0034] The present invention therefore further provides an electrolytic system comprising a plurality of electrolytic cells according to the present invention, the electrolytic cells being arranged in a stack such that each electrolytic cell is in electrical connection with at least one adjacent electrolytic cell.

[0035] The polymer membrane can be made by any convenient means known in the art for constructing membranes, such as polymer moulding or phase inversion techniques. In a preferred embodiment the polymer precursor in liquid/semi-liquid form is injected into customized stainless steel or ceramic moulds. The polymer is then subjected to a predetermined process at desired temperatures, pressures and cycle times.

[0036] Alternatively, a polymeric membrane is cast onto a uniform substrate material. This is done by phase inversion – a process in which a liquid polymer dope is cast on the substrate material, then passed into a coagulation bath comprising a quenching solution where solvents are drawn out.

[0037] The catalyst may be supplied in any convenient form, such as a mesh. The electrolytic cell of the present invention may additionally comprise a catalyst associated with the hydrophilic polymer membrane. The catalyst, for example, may be deposited upon the porous membrane.

[0038] Generally, precious metals such as platinum, gold or palladium are used for water splitting. However, the electrolytic cell and method of the present invention may be used in association with less expensive and non-precious catalysts, such as nickel and manganese-based catalysts. The present invention may include incorporation of different catalysts and different chemical reactions when for production of compounds other than hydrogen and oxygen. This could include, for example ammonia (from water and atmospheric nitrogen) or methane, methanol, ethanol, formic acid, or acetic acid from water and carbon dioxide.

[0039] In a preferred embodiment the electrolytic cell and method of the present invention is used for synthesis. In another preferred embodiment the cell forms part of a fuel cell system. While the electrolytic cell of the present invention cannot be applied in the reverse reaction (that is, in a fuel cell reaction) however, it could be integrated into a fuel cell system. For example, the electrolysis cell of the present invention could be used to produce hydrogen by the water splitting reaction, and the hydrogen produced could be stored in a storage tank. Fuel cells could use the hydrogen to provide power to an appliance, such as a car.

[0040] The electrolytic cell and method of the present invention may be used for water splitting to synthesise hydrogen and oxygen, but it will be readily apparent to the person skilled in the art that other gases could be synthesised. For example, ammonia could be synthesised from nitrogen/water or methane, methanol or ethanol could be synthesised from carbon dioxide/water absorbed by the hydrogel membrane.

[0041] Other reactions may also be possible using a hydrogel membrane and various catalysts specific to the desired reaction. This potentially opens up options such as conversion of carbon dioxide to formic acid, carbon monoxide, formaldehyde or methanol gas; or halide oxidation to halide gas; or hydrogen peroxide oxidation to oxygen gas; or nitrite reduction to nitrous oxide gas or ammonia gas.

[0042] Production of ammonia may be achieved for example, by a two-step reaction process wherein a first electrolytic cell generates hydrogen from water and

supplies this hydrogen to a second cell (with a different catalyst) to combine the hydrogen electrochemically with nitrogen.

[0043] Other aspects and preferred forms are disclosed in the specification and/or defined in the appended claims, forming a part of the description of the invention.

[0044] In essence, embodiments of the present invention stem from the realization that the separation membrane of an electrolytic cell, in addition to separating gasses, may also be a source of reactant. For example, the membrane that separates oxygen and hydrogen formed during electrochemical splitting of water may also be the source of water for the electrochemical splitting.

[0045] Advantages provided by the present invention comprise the following:

- avoidance of gas bubble formation, concomitantly reduction of conversion efficiency;
- improved power conversion, in some cases, as low as 3.5 kWh Nm⁻³ of hydrogen, which translates to the conversion efficiency of about 85.6% (balance of plant);
- low system maintenance requirements;
- compact design;
- simplified structure and assembly processes to provide improved system cost and economics;
- allows the use of inexpensive and non-precious catalysts while at the same time providing superior efficiencies;
- generates hydrogen of high purity (up to 99.999%);
- can be adapted for use with various water sources, including tap water, rainwater or sea water;
- no electrolyte requirement, water is replenished in the membrane;
- provision of a simple, yet effective oxygen removal from a system by utilizing an open anode concept;
- small footprint and scalability; and

- no cooling requirement because the system may use waste heat to further reduce activation losses and increase the conversion efficiency.

[0046] Further scope of applicability of embodiments of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure herein will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0047] Further disclosure, objects, advantages and aspects of preferred and other embodiments of the present application may be better understood by those skilled in the relevant art by reference to the following description of embodiments taken in conjunction with the accompanying drawings, which are given by way of illustration only, and thus are not limitative of the disclosure herein, and in which:

FIG 1 illustrates a fully assembled electrolytic cell according to the present invention;

FIG 2 illustrates the electrolytic cell of Fig 1 expanded to show each of the components in perspective view;

FIG 3 illustrates a stack of electrolytic cells according to the present invention; and

FIG 4 illustrates the stack of electrolytic cells of Fig 3 expanded to show each of the components in perspective view;

FIG 5 is a plot of Input power (kW) against hydrogen output (Nm^3h^{-1}) for a stack of 100 electrolytic cells as depicted in FIG 1.

LIST OF PARTS

1	assembled electrolytic cell
2	Gasket
4	Ni mesh electrode (catalyst)
6	hydrogel polymer membrane
8	Ni mesh electrode (catalyst)
10	Frame
11	Gasket
12	Al corrugated plate
14	stainless steel corrugated mesh
15	tube fittings
16	Screws
17	rubber insulator
18	first stainless steel end plate
19	Cu current collectors
20	electrolytic cell
22	plastic pipe separator
24	second stainless steel end plate
26	stack of 10 electrolytic cells
30	first stack side
31	second stack side

DETAILED DESCRIPTION

[0048] The present invention provides a novel system for solid/semi-solid state water splitting, since hydrogels may be considered to be solid or semi-solid materials due to the fact that they behave more like a solid than a liquid.

[0049] In the present invention, a hydrogel membrane comprising a hydrophilic polymer is used as a solid/semi-solid membrane and electrolyte in one. The hydrogel membrane separates gasses produced by electrolytic reaction while simultaneously

providing a source of water for generation of hydrogen and oxygen. Furthermore, by contrast with the prior art, water splitting electrolysis is not performed in the vapour phase.

[0050] **FIG 1** illustrates a fully assembled electrolytic cell (1) according to the present invention.

[0051] **FIG 2** illustrates the electrolytic cell (1) of Fig 1 expanded to show each of the components. The electrolytic cell (1) comprises the following sequence of components to form a separate electrically conductive assembly: Ni mesh electrode (catalyst) (4) / hydrogel polymer membrane (6) / Ni mesh electrode (catalyst) (8) / Al corrugated plate (12) / stainless steel corrugated mesh (14).

[0052] This view also reveals structural elements such as a printed and cured gasket (2) approximately 0.1 mm thick and a polymer frame, preferably a polypropylene frame (10) serves as a support and facilitates assembly of the cell components.

[0053] Small holes in the frame allow for a flow of water vapour as described below with reference to FIG 3. The stamped aluminium corrugated plate (12) is adjacent a stamped stainless steel corrugated mesh (14) that together facilitate oxygen and water vapour flow.

[0054] **FIG 3** illustrates ten electrolytic cells (20) of the type shown in FIG 1 and FIG 2 assembled into a stack of ten. All the electrolytic cells (20) are connected in series. There are two copper current collectors (19) at either end of the stack. The electric charge passes from one copper current collector (19) through all subsequent cells (20) in the system to the copper current collector (19) at the other end of the stack, facilitating the electrolysis reaction. The stainless steel corrugated mesh (14) in one electrochemical cell is in close contact with Ni mesh electrode (catalyst) (4) in the adjacent cell to allow electric charge to pass through the system. Both the aluminium plate (12) and stainless steel mesh (14) close the entire system electrically and allow

for a charge to flow through from one copper collector (19) to the other thus facilitating the electrolytic reaction. In another embodiment, a stainless steel plate replaces the aluminium plate.

[0055] The hydrogel membranes (6) must be kept hydrated. Water in the hydrogel is typically replenished either by supplying liquid water through the electrolyser channels or by supplying water vapour through special inlet holes on one side (30) of the electrolyser cells. The other side (31) of each of the electrolyser cells may have holes to remove the excess water vapour as well as oxygen produced by the electrolytic reaction. The water may, for example, be pumped or supplied in a passive manner from a reservoir or by any other method known in the art. The holes may also be used for removal of gas - particularly oxygen - generated during the electrolytic process

[0056] Preferably, the cell of the present invention is configured such that the anode side of the cell where oxygen is produced is a so-called open cell that allows oxygen to be easily removed. This configuration simplifies the system and associated processes, however it tends to present some difficulties with respect to oxygen collection.

[0057] The concept of an open anode cell is illustrated at FIG 3. Typically, the water vapour inlet side of the cell (30) is at the bottom and vapour flows in the direction of the arrow, excess water vapour mixed with generated hydrogen exiting from outlets on the other side (31). By putting one electrolyser stack on top of another the excess water vapour leaves one stack and enters the next stack where it is used.

[0058] **FIG 4** illustrates the stack (26) of electrolytic cells of Fig 3 expanded to show each of the components in perspective view. Fasteners (16), nominally M10 screws, pass through the edges of all elements at their edges to ensure proper sealing of the stack (26). The thick stainless steel end plates (18, 24) located at either end of the stack may be used to collect gas – particularly hydrogen gas – generated during the electrolytic process. The screws (16) are tightened to ensure that pressure evenly

distributes across the stack (26). Individual electrolytic cells (20) – ten in this example - are located between the end plates (18, 24). Plastic pipes (22) are also located at the edges of the electrolytic cells (20) to insulate the fasteners from the electrodes and other metal components of the stack (26) fasteners.

[0059] **FIG 5** is a plot of Input power (kW) against hydrogen output (Nm^3h^{-1}) for a stack of 100 electrolytic cells as depicted in FIG 1. The 12-kW system formed by the 100-cell stack has a power consumption of 3.6 to 4.4 kWh/ Nm^3 depending on the operation mode and applied power. The measurement was repeated three times to generate the three lines.

[0060] While this invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification(s). This application is intended to cover any variations uses or adaptations of the invention following in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth.

[0061] As the present invention may be embodied in several forms without departing from the spirit of the essential characteristics of the invention, it should be understood that the above described embodiments are not to limit the present invention unless otherwise specified, but rather should be construed broadly within the spirit and scope of the invention as defined in the appended claims. The described embodiments are to be considered in all respects as illustrative only and not restrictive.

[0062] Various modifications and equivalent arrangements are intended to be included within the spirit and scope of the invention and appended claims. Therefore, the specific embodiments are to be understood to be illustrative of the many ways in which the principles of the present invention may be practiced. In the following claims, means-plus-function clauses are intended to cover structures as performing the defined function and not only structural equivalents, but also equivalent structures.

[0063] “Comprises/comprising” and “includes/including” when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the words ‘comprise’, ‘comprising’, ‘includes’, ‘including’ and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.